



(51) International Patent Classification:

B32B 15/04 (2006.01) C07D 235/04 (2006.01)
C23C 14/12 (2006.01)

(21) International Application Number:

PCT/US2024/056611

(22) International Filing Date:

20 November 2024 (20.11.2024)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

63/601,649 21 November 2023 (21.11.2023) US
63/682,851 14 August 2024 (14.08.2024) US

(71) Applicant: UNIVERSITY OF HOUSTON SYSTEM
[US/US]; 4800 Calhoun Rd., Houston, Texas 77004 (US).

(72) Inventors: LEE, T. Randall; 7447 Cambridge St., Apt.
100, Houston, Texas 77054 (US). TRAN, Quoc Minh;
1901 Cullen Blvd, Apt. 320C, Houston, Texas 77023 (US).

(74) Agent: LEVY, Seth D. et al.; Nixon Peabody LLP, 300
South Grand Avenue, Suite 4100, Los Angeles, California
90071 (US).

(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ,
CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM,
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG,

KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY,
MA, MD, MG, MK, MN, MU, MW, MX, MY, MZ, NA,
NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO,
RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH,
TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS,
ZA, ZM, ZW.

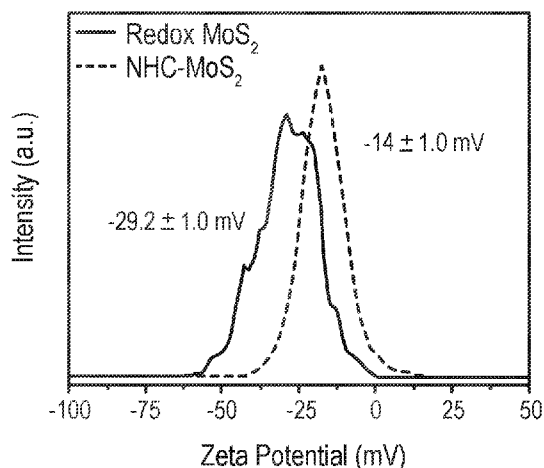
(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, CV,
GH, GM, KE, LR, LS, MW, MZ, NA, RW, SC, SD, SL, ST,
SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ,
RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ,
DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT,
LU, LV, MC, ME, MK, MT, NL, NO, PL, PT, RO, RS, SE,
SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN,
GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments (Rule 48.2(h))

(54) Title: N-HETEROCYCLIC CARBENE FUNCTIONALIZED TRANSITION METAL DICHALCOGENIDES

FIG. 20C



(57) Abstract: This invention relates to N-heterocyclic carbene functionalized transition metal dichalcogenides. This invention also relates to methods of making N-heterocyclic carbene functionalized transition metal dichalcogenides. This invention also relates to articles of manufacture comprising N-heterocyclic carbene functionalized transition metal dichalcogenides.

**N-HETEROCYCLIC CARBENE FUNCTIONALIZED
TRANSITION METAL DICHALCOGENIDES**

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of priority under 35 U.S.C. §119(e) to U.S. Provisional Patent Application No. 63/601,649 filed November 21, 2023, and U.S. Provisional Patent Application No. 63/682,851 filed August 14, 2024, both of which are incorporated herein by reference in their entirety.

**STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR
DEVELOPMENT**

[0002] This invention was made with government support under Grant Nos. FA9550-20-1-0349 and FA9550-23-1-0581 awarded by the U.S. Air Force Office of Scientific Research. The government has certain rights in the invention.

FIELD OF THE INVENTION

[0003] This invention relates to *N*-heterocyclic carbene functionalized transition metal dichalcogenides. This invention also relates to methods of making *N*-heterocyclic carbene functionalized transition metal dichalcogenides. This invention also relates to articles of manufacture comprising *N*-heterocyclic carbene functionalized transition metal dichalcogenides.

BACKGROUND

[0004] All publications herein are incorporated by reference to the same extent as if each individual publication or patent application was specifically and individually indicated to be incorporated by reference. The following description includes information that may be useful in understanding the present invention. It is not an admission that any of the information provided herein is prior art or relevant to the presently claimed invention, or that any publication specifically or implicitly referenced is prior art.

[0005] Efforts have been directed toward the functionalization of mono-to-few-layered transition metal dichalcogenides (TMDs). According to the literature, two approaches have been used to address this challenge, each employing distinctive categories of reagents: thiol-based

organic adsorbates and electron-donating molecules. However, both of these previously reported approaches currently suffer from limitations. In the thiol-based strategy, organic molecules containing thiol (-SH) or disulfide (-S-S-) groups are used to establish a sulfur-chalcogenide bridge with TMDs. This bonding interaction is, however, fragile.

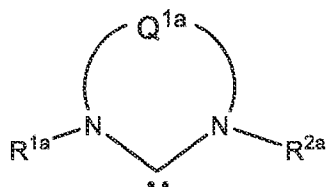
[0006] The current electron-donating strategy, while an improvement over the existing thiol-based strategy, still suffers from several limitations. Using the current electron-donating strategy, it has been observed that excessive intercalation can induce phase transformations within the TMDs. These phase transformations include a shift from the semiconducting state to the metallic state, rendering the functionalized TMDs impractical and unsuitable for use in several intended applications, specifically those where semiconducting properties and/or characteristics are needed.

[0007] Therefore, there is an ongoing need for new and improved functionalized transition metal dichalcogenides and methods of making them that overcome these limitations. The embodiments of the present invention address these needs.

SUMMARY OF THE INVENTION

[0008] In various embodiments, the present invention provides a *N*-heterocyclic carbene functionalized transition metal dichalcogenide, comprising: at least one transition metal dichalcogenide; and at least one *N*-heterocyclic carbene.

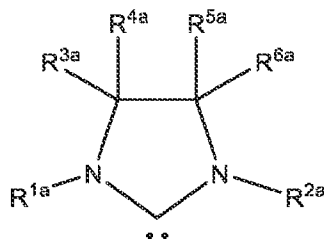
[0009] In some embodiments, the at least one *N*-heterocyclic carbene has a structure of Formula (II):



Formula (II),

wherein: R^{1a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; R^{2a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and Q^{1a} is an optionally substituted linker.

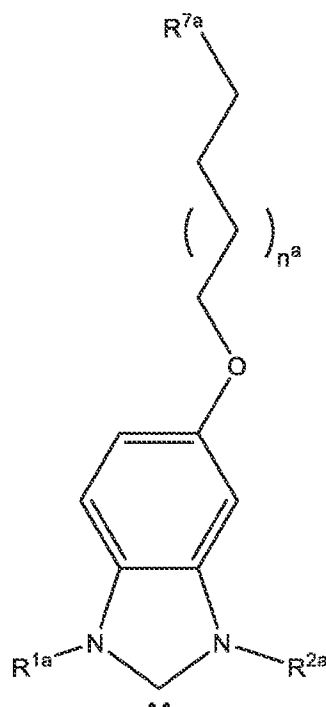
[0010] In some embodiments, the at least one *N*-heterocyclic carbene has a structure of Formula (II-A):



Formula (II-A),

wherein: R^{1a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; R^{2a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; R^{3a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; R^{4a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; R^{5a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and R^{6a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; wherein R^{3a} and R^{4a} are not both absent, and wherein R^{5a} and R^{6a} are not both absent; or R^{3a} and R^{5a} , or R^{3a} and R^{6a} , or R^{4a} and R^{5a} , or R^{4a} and R^{6a} may be taken together to form a ring, wherein the ring is optionally substituted.

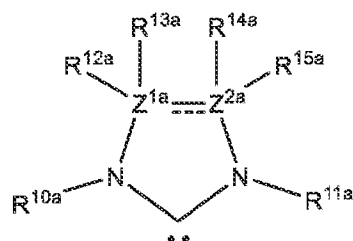
[0011] In some embodiments, the at least one *N*-heterocyclic carbene has the structure of Formula (II-B):



Formula (II-B),

wherein: n^a is 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, or 12; R^{1a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; R^{2a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and R^{7a} is H, OR^{8a} , SR^{9a} , halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl, wherein R^{8a} is H, or optionally substituted alkyl, and R^{9a} is H, or optionally substituted alkyl.

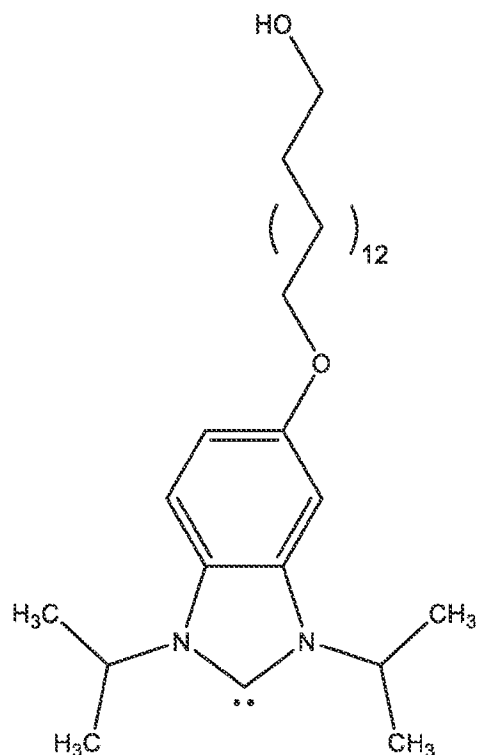
[0012] In some embodiments, the at least one *N*-heterocyclic carbene has a structure of Formula (IV):



Formula (IV)

wherein: Z^{1a} is C; Z^{2a} is C; R^{10a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; R^{11a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; R^{12a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted alkylamino, optionally substituted amino, hydroxy, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; R^{13a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted alkylamino, optionally substituted amino, hydroxy, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; R^{14a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted alkylamino, optionally substituted amino, hydroxy, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; R^{15a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted alkylamino, optionally substituted amino, hydroxy, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and wherein R^{12a} and R^{13a} are not both absent, and wherein R^{14a} and R^{15a} are not both absent; and ===== between Z^{1a} and Z^{2a} indicates a bond that may be a single bond or a double bond; or R^{12a} and R^{14a} , or R^{12a} and R^{15a} , or R^{13a} and R^{14a} , or R^{13a} and R^{15a} may be taken together to form a ring, wherein the ring is optionally substituted.

[0013] In some embodiments, the at least one *N*-heterocyclic carbene is



[0014] In some embodiments, the at least one transition metal dichalcogenide has the formula: $M^aX^a_2$, wherein: M^a is a Group 4-10 transition metal; and X^a is a chalcogen. In some embodiments, M^a is a Group 6 transition metal. In some embodiments, the chalcogen is sulfur (S), selenium (Se), or tellurium (Te). In some embodiments, the Group 6 transition metal is molybdenum (Mo) or tungsten (W). In some embodiments, the at least one transition metal dichalcogenide is MoS_2 or WS_2 .

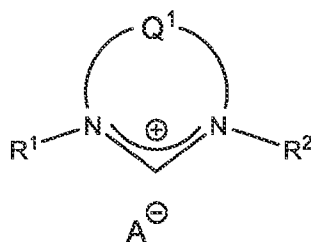
[0015] In some embodiments, the at least one transition metal dichalcogenide is an at least one exfoliated transition metal dichalcogenide, wherein the at least one exfoliated transition metal dichalcogenide comprises at least one exfoliated surface, and wherein the at least one *N*-heterocyclic carbene forms a self-assembled monolayer (SAM) or a partial self-assembled monolayer (SAM) on at least a portion of the at least one exfoliated surface of the at least one exfoliated transition metal dichalcogenide.

[0016] In some embodiments, the at least one transition metal dichalcogenide is an at least one exfoliated transition metal dichalcogenide, wherein the at least one exfoliated transition metal dichalcogenide comprises at least one exfoliated surface, wherein the at least one exfoliated

surface comprises at least one exfoliated basal plane, and wherein the at least one *N*-heterocyclic carbene forms a self-assembled monolayer (SAM) or a partial self-assembled monolayer (SAM) on at least a portion of the at least one exfoliated basal plane.

[0017] In various embodiments, the present invention provides a method of making at least one *N*-heterocyclic carbene functionalized transition metal dichalcogenide, comprising: providing at least one bulk transition metal dichalcogenide; exfoliating the at least one bulk transition metal dichalcogenide to produce at least one exfoliated transition metal dichalcogenide comprising at least one exfoliated surface; and reacting at least a portion of the at least one exfoliated surface of the at least one exfoliated transition metal dichalcogenide with at least one *N*-heterocyclic carbene precursor.

[0018] In some embodiments, the at least one *N*-heterocyclic carbene precursor has a structure of Formula (I):



Formula (I),

wherein: A⁻ is a counterion; R¹ is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; R² is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and Q¹ is an optionally substituted linker.

[0019] In various embodiments, the present invention provides an article of manufacture comprising at least one *N*-heterocyclic carbene functionalized transition metal dichalcogenide of the present invention. In some embodiments, the article of manufacture is an energy storage device, energy storage material, sensing device, sensing material, semiconductor electronic device, semiconductor electronic material, semiconductor optoelectronic device, or semiconductor optoelectronic material. In some embodiments, the article of manufacture is a semiconductor or has semiconducting properties.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020] Exemplary embodiments are illustrated in referenced figures. It is intended that the embodiments and figures disclosed herein are to be considered illustrative rather than restrictive.

[0021] FIG. 1A – FIG. 1B depicts in accordance with various embodiments of the invention, extinction spectra of redox exfoliated MoS₂ colloidal (FIG. 1A) and the corresponding 2nd derivative transformations in the A-exciton transition regions (FIG. 1B).

[0022] FIG. 2A – FIG. 2B depicts in accordance with various embodiments of the invention, the AFM image of redox exfoliated MoS₂ dispersion deposited on SiO₂/Si substrate (FIG. 2A) and the corresponding height profiles of selected nanosheets (FIG. 2B).

[0023] FIG. 3 depicts in accordance with various embodiments of the invention, XRD patterns of thin film NHC15OH[OMs]-functionalized MoS₂ where NHC = *N*-heterocyclic carbene. The functionalized samples are labeled as x-NHC-MoS₂ where x represents the NHC:MoS₂ molar ratio.

[0024] FIG. 4A – FIG. 4B depicts in accordance with various embodiments of the invention, the 2nd derivatives of exfoliated MoS₂ entire extinction spectra (FIG. 4A) and the A-exciton positions obtained by centrifuge cascade of exfoliated MoS₂ (FIG. 4B).

[0025] FIG. 5 depicts in accordance with various embodiments of the invention, AFM height distribution of redox exfoliated MoS₂, deposited onto SiO₂/Si wafer, subjected to statistical analysis. The counted population is N = 311.

[0026] FIG. 6 depicts in accordance with various embodiments of the invention, XRD patterns of bulk MoS₂ and thin film exfoliated MoS₂.

[0027] FIG. 7 depicts in accordance with various embodiments of the invention, XRD pattern of white powder NHC15OH[OMs].

[0028] FIG. 8 depicts in accordance with various embodiments of the invention, ATR-IR spectra of thin film of studied materials deposited onto optical slides.

[0029] FIG. 9 depicts in accordance with various embodiments of the invention, Zeta potential of redox exfoliated MoS₂ and anticipated NHC-functionalized MoS₂ colloidal.

[0030] FIG. 10A – FIG. 10B depicts in accordance with various embodiments of the invention, the extinction spectra of exfoliated MoS₂ suspension collected at different centrifuge rates (FIG. 10A) and the 2nd derivative transformation of the extinction spectra (FIG. 10B).

[0031] FIG. 11 depicts in accordance with various embodiments of the invention, XRD pattern of bulk, exfoliated, and functionalized MoS₂.

[0032] FIG. 12 depicts in accordance with various embodiments of the invention, Zeta potentials of redox-exfoliated MoS₂ and sonication-induced exfoliated MoS₂ colloidal.

[0033] FIG. 13 depicts various embodiments of the invention, Raman E_{12g} and A_{1g} vibrational modes of redox-exfoliated MoS₂ and NHC-functionalized MoS₂.

[0034] FIG. 14 depicts various embodiments of the invention, the hetero-superlattice structure formed by the restacking of multiple monolayers of TMDs is achieved through NHC functionalization. This approach is adaptable to different types of TMDs, with MoS₂ and WS₂ provided here as examples.

[0035] FIG. 15 depicts in accordance with various embodiments of the invention, 2D Nanolayered MoS₂ Exfoliation, redox exfoliation of 2D nanolayered MoS₂. Jawaid, A.; Che, J.; Drummy, L. F.; Bultman, J.; Waite, A.; Hsiao, M.-S.; Vaia, R. A. Redox Exfoliation of Layered Transition Metal Dichalcogenides. *ACS Nano* **2017**, 11, 635-646; Jawaid, A. M.; Ritter, A. J.; Vaia, R. A. Mechanism for Redox Exfoliation of Layered Transition Metal Dichalcogenides. *Chem. Mater.* **2020**, 32, 6550-6565.

[0036] FIG. 16 depicts in accordance with various embodiments of the invention, basal plane functionalization, proposed SAM formation and self-restacking.

[0037] FIG. 17 depicts in accordance with various embodiments of the invention, basal-plane functionalized 2D MoS₂, XRD patterns of functionalized 2D MoS₂.

[0038] FIG. 18A – FIG. 18D depicts in accordance with various embodiments of the invention, (FIG. 18A) Normalized extinction spectra of redox-exfoliated MoS₂, (FIG. 18B) the corresponding 2nd derivatives of A excitons, (FIG. 18C) the relationship between A-excitonic wavelengths and the employed centrifuge rates, and (FIG. 18D) Zeta potentials of redox-exfoliated MoS₂ and sonication-induced exfoliated MoS₂ colloidal.

[0039] FIG. 19A – FIG. 19H depicts in accordance with various embodiments of the invention, (FIG. 19A) AFM height retrace image, (FIG. 19B) the corresponding height profiles of selected nanosheets, and (FIG. 19C) AFM height distribution of redox-exfoliated MoS₂; counted population is N = 311 nanosheets. (FIG. 19D) XRD patterns and (FIG. 19E- FIG. 19H) TEM images of redox-exfoliated MoS₂.

[0040] FIG. 20A – FIG. 20D depicts in accordance with various embodiments of the invention, (FIG. 20A) XRD patterns, (FIG. 20B) ATIR spectra, (FIG. 20C) Zeta potential of NHC-functionalized MoS₂, labeled as x-NHC/MoS₂ where x represents the NHC:MoS₂ molar ratio, and (FIG. 20D) the proposed interaction scheme.

[0041] FIG. 21A – FIG. 21D depicts in accordance with various embodiments of the invention, XPS spectra of redox-exfoliated MoS₂ and 15-NHC/MoS₂.

[0042] FIG. 22A – FIG. 22B depicts in accordance with various embodiments of the invention, two intercalated structures arise from the restacking of exfoliated few- to monolayered TMDs.

[0043] FIG. 23A – FIG. 23N depicts in accordance with various embodiments of the invention, (FIG. 23A) Normalized extinction spectra, (FIG. 23B, FIG. 23D) the corresponding 2nd derivatives in the A-B-excitonic regions and A excitons in energy (eV), (FIG. 23C) A-D excitonic wavelengths, (FIG. 23E – FIG. 23H) SEM images, and (FIG. 23I – FIG. 23N) statistical size distribution of redox-exfoliated MoS₂ at four different collected fractions.

[0044] FIG. 24A – FIG. 24F depicts in accordance with various embodiments of the invention, (FIG. 24A, FIG. 24D, FIG. 24E) Raman E_{12g} and A_{1g} vibration modes of redox-exfoliated MoS₂ and 15-NHC/MoS₂; the label 15-NHC/MoS₂ Px denotes data collected at different points within the same sample. (FIG. 24B) Si transverse optical vibration mode as an internal reference, (FIG. 24C) the corresponding E_{12g} and A_{1g} peak positions, and (FIG. 24F) FMHWs of E_{12g} and A_{1g} peaks.

[0045] FIG. 25A – FIG. 25D depicts in accordance with various embodiments of the invention, (FIG. 25A) XRD patterns of 15-NHC/MoS₂ Fx, where Fx represents different redox-exfoliated MoS₂ fractions, which are categorized as: F1 at 2000-2500 rpm, F2 at 2500-3000 rpm, F3 at 3000-4000 rpm, and F4 at >4000 rpm. (FIG. 25B) XRD patterns of 15-NHC/MoS₂ Fx, which are redispersed in fresh a-ACN by sonication. (FIG. 25C) Normalized extinction spectra of redispersed 15-NHC/MoS₂ Fx in image b and (FIG. 25D) the corresponding 2nd derivatives of extinction spectra in image c.

[0046] FIG. 26A – FIG. 26B depicts in accordance with various embodiments of the invention, (FIG. 26A) Hybridization-induced by the perpendicular p_z orbitals within the aromatic π -configuration and the out-of-plane chalcogen p_z and metal d_{z2} orbitals. (FIG. 26B) Hybridization-induced by the donation of in-plane lone pair electrons from the N-heterocyclic ring

to the metal d_{z^2} orbitals. Atom color code: purple, metal; yellow, chalcogen; blue, nitrogen; grey, carbon.

[0047] FIG. 27 depicts in accordance with various embodiments of the invention, Molecular structure of NHC15OH[OMs].

[0048] FIG. 28A – FIG. 28D depicts in accordance with various embodiments of the invention, thin film fabrication by liquid-liquid thin film self-assembly technique.

[0049] FIG. 29 depicts in accordance with various embodiments of the invention, size and thickness selection of exfoliated TMD nanosheets by centrifuge cascade technique.

[0050] FIG. 30A – FIG. 30B depicts in accordance with various embodiments of the invention, The 2nd derivatives of extinction spectra of redox-exfoliated MoS₂ (FIG. 30A) and WS₂ (FIG. 30B).

[0051] FIG. 31A – FIG. 31D depicts in accordance with various embodiments of the invention, (FIG. 31A) Normalized extinction spectra, (FIG. 31B, FIG. 31D) the corresponding 2nd derivatives of A and B excitons and A-excitonic transition in energy (eV), and (FIG. 31C) A-D excitonic wavelengths of redox-exfoliated WS₂ colloidal at different centrifuge rates.

[0052] FIG. 32A – FIG. 32E depicts in accordance with various embodiments of the invention, (FIG. 32A) AFM height retrace, (FIG. 32B) the corresponding height profiles of selected nanosheets, (FIG. 32C) amplitude retrace images, (FIG. 32D) XRD patterns, and (FIG. 32E) SEM image of redox-exfoliated MoS₂ thin film rendering flat-lying nanosheets.

[0053] FIG. 33A – FIG. 33B depicts in accordance with various embodiments of the invention, AFM height retrace (FIG. 33A) and amplitude retrace images (FIG. 33B) of redox-exfoliated MoS₂.

[0054] FIG. 34A – FIG. 34E depicts in accordance with various embodiments of the invention, (FIG. 34A – FIG. 34D) AFM images and the (FIG. 34E) corresponding height profiles of selected redox-exfoliated WS₂ nanosheets.

[0055] FIG. 35A – FIG. 35D depicts in accordance with various embodiments of the invention, (FIG. 35A) AFM image, (FIG. 35B) the corresponding height profiles of selected nanosheets, and (FIG. 35C) AFM height distribution of redox-exfoliated WS₂, counted population is N = 149 nanosheets. (FIG. 35D) XRD patterns of bulk and redox-exfoliated WS₂.

[0056] FIG. 36 depicts in accordance with various embodiments of the invention, XRD patterns of powder NHC15OH[OMs].

[0057] FIG. 37A – FIG. 37D depicts in accordance with various embodiments of the invention, XPS spectra of redox-exfoliated WS₂ and 15-NHC/WS₂.

[0058] FIG. 38 depicts in accordance with various embodiments of the invention, XRD patterns of 15-NHC/MoS₂ samples at different sonicating-restacking cycles, labeled as 15-NHC-/MoS₂ xS where x represents sonicating-restacking cycles.

[0059] FIG. 39A – FIG. 39B depicts in accordance with various embodiments of the invention, XRD patterns of 15-NHC/MoS₂ and 15-NHC/WS₂, labeled as x-NHC/TMDs where x represents NHC:TMDs molar ratio (FIG. 39A), and cartoon of two intercalated structures (FIG. 39B).

[0060] FIG. 40A – FIG. 40D depicts in accordance with various embodiments of the invention, (FIG. 40A, FIG. 40B) XPS low binding energy regions, (FIG. 40C) schematic illustration of charge transfer process from NHC15OH[OMs] to MoS₂ and (FIG. 40D) energy mismatch between Fermi level (E_F) and valence band (E_{VB}) of redox-exfoliated MoS₂ and 15-NHC/MoS₂.

[0061] FIG. 41A – FIG. 41B depicts in accordance with various embodiments of the invention, XPS low binding energy regions of redox-exfoliated WS₂ and 15-NHC/WS₂.

[0062] FIG. 42A – FIG. 42F depicts in accordance with various embodiments of the invention, (FIG. 42A, FIG. 42D, FIG. 42E) Raman E_{12g} and A_{1g} vibration modes of redox-exfoliated WS₂ and 15-NHC/WS₂ samples; the label 15-NHC/WS₂ Px denotes the same deposited sample collected at different points. (FIG. 42B) Si optical transverse vibration mode as an internal reference, (FIG. 42C) the corresponding E_{12g} and A_{1g} peak positions, and (FIG. 42F) FMHWs of E_{12g} and A_{1g} peaks.

[0063] FIG. 43A – FIG. 43B depicts in accordance with various embodiments of the invention, The corresponding separation of E_{12g} – A_{1g} from FIG. 24A – FIG. 24F (FIG. 43A) and FIG. 42A – FIG. 42F (FIG. 43B).

[0064] FIG. 44A – FIG. 44B depicts in accordance with various embodiments of the invention, XRD patterns of 15-NHC/MoS₂ F4, where F4 represents for the redox-exfoliated MoS₂ fractions collected at centrifuge rate >4000 rpm, and the corresponding sonication-induced redispersed 15-NHC/MoS₂ F4 RS in a-ACN or DCM. Emerging (006*) and (008*) reflections, at 20.5 and 27.4 (2θ), respectively, are observed while trace amounts of crystallized NHC15OH[OMs] adsorbates are detected at an angle 21.3 (2θ) (see FIG. 36).

[0065] FIG. 45A – FIG. 45D depicts in accordance with various embodiments of the invention, (FIG. 45A) Absorption spectra of Mo^{6+} complexes and (FIG. 45B) extracted calibration fitting. (FIG. 45C) Extinction spectra of redox-exfoliated MoS_2 and (FIG. 45D) extracted titration fitting.

[0066] FIG. 46A – FIG. 46D depicts in accordance with various embodiments of the invention, (FIG. 46A) Absorption spectra of W^{6+} complexes and (FIG. 46B) extracted calibration fitting. (FIG. 46C) Extinction spectra of redox-exfoliated WS_2 and (FIG. 46D) extracted titration fitting.

[0067] FIG. 47 depicts in accordance with various embodiments of the invention, Image of deposited mono- to few-layered MoS_2 nanosheets on 300 nm SiO_2/Si substrate under the optical microscope equipped within AFM instrument.

[0068] FIG. 48A - FIG. 48B depicts in accordance with various embodiments of the invention, Functionalization of MoS_2 .

[0069] FIG. 49A – FIG. 49B depicts in accordance with various embodiments of the invention, (FIG. 49A) Photoluminescence of 15-NHC/ MoS_2 Fx, where Fx represents different redox-exfoliated MoS_2 fractions, which are categorized as: F1 at 2000-2500 rpm, F2 at 2500-3000 rpm, F3 at 3000-4000 rpm, and F4 at >4000 rpm. (FIG. 49B) Constructed band gap diagrams of MoS_2 and NHC-functionalized MoS_2 .

[0070] FIG. 50A – FIG. 50B depicts in accordance with various embodiments of the invention, extracted titration fitting at the local minimum ϵ_{345} of MoS_2 fraction F1 (FIG. 50A) and F4 (FIG. 50B).

[0071] FIG. 51A – FIG. 51L depicts in accordance with various embodiments of the invention, (FIG. 51A, FIG. 51D) Raman E_{2g}^1 and A_{1g} vibration modes of redox-exfoliated MoS_2 Fx and 15-NHC/ MoS_2 Fx, where Fx represents different redox-exfoliated MoS_2 fractions, which are categorized as: F1 at 2000-2500 rpm, F2 at 2500-3000 rpm, F3 at 3000-4000 rpm, and F4 at >4000 rpm. (FIG. 51B, FIG. 51C, FIG. 51E, FIG. 51F) Raman E_{2g}^1 and A_{1g} vibration modes of individual redox-exfoliated MoS_2 fraction and their corresponding 15-NHC/ MoS_2 counterpart. (FIG. 51G, FIG. 51J) The corresponding E_{2g}^1 and A_{1g} peak positions, (FIG. 51H, FIG. 51K) FMHWs of E_{2g}^1 and A_{1g} peaks, and (FIG. 51I) the intensity ratio of E_{2g}^1/A_{1g} . (FIG. 51L) Si optical transverse vibration mode as an internal reference.

[0072] FIG. 52A – FIG. 52D depicts in accordance with various embodiments of the invention, photoluminescence of individual MoS₂ Fx and their corresponding 15-NHC/MoS₂ Fx, where Fx represents different redox-exfoliated MoS₂ fractions, which are categorized as: F1 at 2000-2500 rpm (FIG. 52A), F2 at 2500-3000 rpm (FIG. 52B), F3 at 3000-4000 rpm (FIG. 52C), and F4 at >4000 rpm (FIG. 52D).

[0073] FIG. 53 depicts in accordance with various embodiments of the present invention, benzimidazolium salts as the *N*-heterocyclic carbene precursors. In various embodiments, A and B are each independently H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl. In some embodiments, A and B are each independently alkyl. In some embodiments, A and B are each independently ethyl, propyl, isopropyl, butyl, pentyl, or decyl. In various embodiments, C and D are each independently H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted alkylamino, optionally substituted amino, hydroxy, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl. In various embodiments, X⁻ is a counterion. In some embodiments, X⁻ is Cl⁻, Br⁻, I⁻, ⁻OMs, ⁻OTf, ⁻BF₄, or ⁻PF₆.

[0074] FIG. 54A – FIG. 54B depicts in accordance with various embodiments of the invention, XRD patterns of the NHC-functionalized MoS₂ (FIG. 54B), and (FIG. 54A) shows the chemical structure of the NHC precursor used to prepare the NHC-functionalized MoS₂.

DETAILED DESCRIPTION OF THE INVENTION

[0075] All references cited herein are incorporated by reference in their entirety as though fully set forth. Unless defined otherwise, technical, and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs.

[0076] One skilled in the art will recognize many methods and materials similar or equivalent to those described herein, which could be used in the practice of the present invention. Other features and advantages of the invention will become apparent from the following detailed description, taken in conjunction with the accompanying drawings, which illustrate, by way of example, various features of embodiments of the invention. Indeed, the present invention is in no

way limited to the methods and materials described. For purposes of the present invention, the following terms are defined below. For convenience, certain terms employed herein, in the specification, examples and appended claims are collected here.

[0077] Unless stated otherwise, or implicit from context, the following terms and phrases include the meanings provided below. Unless explicitly stated otherwise, or apparent from context, the terms and phrases below do not exclude the meaning that the term or phrase has acquired in the art to which it pertains. Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. It should be understood that this invention is not limited to the particular methodology, protocols, and reagents, etc., described herein and as such can vary. The definitions and terminology used herein are provided to aid in describing particular embodiments, and are not intended to limit the claimed invention, because the scope of the invention is limited only by the claims.

[0078] As used herein the term “comprising” or “comprises” is used in reference to compositions, methods, systems, articles of manufacture, apparatus, and respective component(s) thereof, that are useful to an embodiment, yet open to the inclusion of unspecified elements, whether useful or not. It will be understood by those within the art that, in general, terms used herein are generally intended as “open” terms (e.g., the term “including” should be interpreted as “including but not limited to,” the term “having” should be interpreted as “having at least,” the term “includes” should be interpreted as “includes but is not limited to,” etc.). Although the open-ended term “comprising,” as a synonym of terms such as including, containing, or having, is used herein to describe and claim the invention, the present invention, or embodiments thereof, may alternatively be described using alternative terms such as “consisting of” or “consisting essentially of.”

[0079] Unless stated otherwise, the terms “a” and “an” and “the” and similar references used in the context of describing a particular embodiment of the application (especially in the context of claims) can be construed to cover both the singular and the plural. The recitation of ranges of values herein is merely intended to serve as a shorthand method of referring individually to each separate value falling within the range. Unless otherwise indicated herein, each individual value is incorporated into the specification as if it were individually recited herein. All methods described herein can be performed in any suitable order unless otherwise indicated herein or

otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (for example, “such as”) provided with respect to certain embodiments herein is intended merely to better illuminate the application and does not pose a limitation on the scope of the application otherwise claimed. The abbreviation, “e.g.” is derived from the Latin *exempli gratia*, and is used herein to indicate a non-limiting example. Thus, the abbreviation “e.g.” is synonymous with the term “for example.” No language in the specification should be construed as indicating any non-claimed element essential to the practice of the application.

[0080] “Optional” or “optionally” means that the subsequently described circumstance may or may not occur, so that the description includes instances where the circumstance occurs and instances where it does not.

[0081] In some embodiments, the numbers expressing quantities of reagents, properties such as concentration, reaction conditions, and so forth, used to describe and claim certain embodiments of the invention are to be understood as being modified in some instances by the term “about.” Accordingly, in some embodiments, the numerical parameters set forth in the written description and attached claims are approximations that can vary depending upon the desired properties sought to be obtained by a particular embodiment. In some embodiments, the numerical parameters should be construed in light of the number of reported significant digits and by applying ordinary rounding techniques. Notwithstanding that the numerical ranges and parameters setting forth the broad scope of some embodiments of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as practicable. The numerical values presented in some embodiments of the invention may contain certain errors necessarily resulting from the standard deviation found in their respective testing measurements.

[0082] Groupings of alternative elements or embodiments of the invention disclosed herein are not to be construed as limitations. Each group member can be referred to and claimed individually or in any combination with other members of the group or other elements found herein. One or more members of a group can be included in, or deleted from, a group for reasons of convenience and/or patentability. When any such inclusion or deletion occurs, the specification is herein deemed to contain the group as modified thus fulfilling the written description of all Markush groups used in the appended claims.

[0083] As used herein the term “electron donating group” is well-known in the art and generally refers to a functional group or atom that pushes electron density away from itself, towards other portions of the molecule, e.g., through resonance and/or inductive effects. Non-limiting examples of electron-donating groups include OR^c , NR^cR^d , alkyl groups, wherein R^c and R^d are each independently H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted aryl, optionally substituted heteroaryl, optionally substituted cyclyl, or optionally substituted heterocyclyl.

[0084] As used herein the term “electron withdrawing group” is well-known in the art and generally refers to a functional group or atom that pulls electron density towards itself, away from other portions of the molecule, e.g., through resonance and/or inductive effects. Non-limiting examples of electron-withdrawing groups include NO_2 , F, Cl, Br, I, CF_3 , CN, CO_2R^a , $C(=O)NR^aR^b$, $C(=O)R^a$, SO_2R^a , SO_2OR^a , $SO_2NR^aR^b$, $PO_3R^aR^b$, or NO, wherein R^a and R^b are each independently H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted aryl, optionally substituted heteroaryl, optionally substituted cyclyl, or optionally substituted heterocyclyl.

[0085] As used herein, the term “alkyl” means a straight or branched, saturated aliphatic group having a chain of carbon atoms. C_x alkyl and C_x - C_y alkyl are typically used where X and Y indicate the number of carbon atoms in the chain. For example, C_1 - C_6 alkyl includes alkyls that have a chain of between 1 and 6 carbons (e.g., methyl, ethyl, propyl, isopropyl, butyl, sec-butyl, isobutyl, tert-butyl, pentyl, neopentyl, hexyl, and the like). Alkyl represented along with another group (e.g., as in arylalkyl) means a straight or branched, saturated alkyl divalent group having the number of atoms indicated or when no atoms are indicated means a bond, e.g., (C_6-C_{10}) aryl(C_0 - C_3)alkyl includes phenyl, benzyl, phenethyl, 1-phenylethyl 3-phenylpropyl, and the like. The backbone of the alkyl can be optionally inserted with one or more heteroatoms, such as N, O, or S.

[0086] In preferred embodiments, a straight chain or branched chain alkyl has 30 or fewer carbon atoms in its backbone (e.g., C_1 - C_{30} for straight chains, C_3 - C_{30} for branched chains), and more preferably 20 or fewer. Likewise, preferred cycloalkyls have from 3-10 carbon atoms in their ring structure, and more preferably have 5, 6 or 7 carbons in the ring structure. The term “alkyl” (or “lower alkyl”) as used throughout the specification, examples, and claims is intended to include both “unsubstituted alkyls” and “substituted alkyls”, the latter of which refers to alkyl moieties

having one or more substituents replacing a hydrogen on one or more carbons of the hydrocarbon backbone.

[0087] Unless the number of carbons is otherwise specified, “lower alkyl” as used herein means an alkyl group, as defined above, but having from one to ten carbons, more preferably from one to six carbon atoms in its backbone structure. Likewise, “lower alkenyl” and “lower alkynyl” have similar chain lengths. Throughout the application, preferred alkyl groups are lower alkyls. In preferred embodiments, a substituent designated herein as alkyl is a lower alkyl.

[0088] Non-limiting examples of substituents of a substituted alkyl can include halogen, hydroxy, nitro, thiols, amino, azido, imino, amido, phosphoryl (including phosphonate and phosphinate), sulfonyl (including sulfate, sulfonamido, sulfamoyl and sulfonate), and silyl groups, as well as ethers, alkylthios, carbonyls (including ketones, aldehydes, carboxylates, and esters), -CF₃, -CN and the like.

[0089] As used herein, the term “alkenyl” refers to unsaturated straight-chain, branched-chain or cyclic hydrocarbon group having at least one carbon-carbon double bond. C_x alkenyl and C_x-C_yalkenyl are typically used where X and Y indicate the number of carbon atoms in the chain. For example, C₂-C₆alkenyl includes alkenyls that have a chain of between 2 and 6 carbons and at least one double bond, e.g., vinyl, allyl, propenyl, isopropenyl, 1-butenyl, 2-butenyl, 3-butenyl, 2-methylallyl, 1-hexenyl, 2-hexenyl, 3-hexenyl, and the like). Alkenyl represented along with another group (e.g., as in arylalkenyl) means a straight or branched, alkenyl divalent group having the number of atoms indicated. The backbone of the alkenyl can be optionally inserted with one or more heteroatoms, such as N, O, or S.

[0090] As used herein, the term “alkynyl” refers to unsaturated hydrocarbon groups having at least one carbon-carbon triple bond. C_x alkynyl and C_x-C_yalkynyl are typically used where X and Y indicate the number of carbon atoms in the chain. For example, C₂-C₆alkynyl includes alkynyls that have a chain of between 2 and 6 carbons and at least one triple bond, e.g., ethynyl, 1-propynyl, 2-propynyl, 1-butyne, isopentyne, 1,3-hexa-diyne, *n*-hexynyl, 3-pentyne, 1-hexen-3-yne and the like. Alkynyl represented along with another group (e.g., as in arylalkynyl) means a straight or branched, alkynyl divalent group having the number of atoms indicated. The backbone of the alkynyl can be optionally inserted with one or more heteroatoms, such as N, O, or S.

[0091] The terms “alkylene,” “alkenylene,” and “alkynylene” refer to divalent alkyl, alkenyl, and alkynyl groups. Prefixes C_x and C_x-C_y are typically used where X and Y indicate the number of carbon atoms in the chain. For example, C₁-C₆alkylene includes methylene (—CH₂—), ethylene (—CH₂CH₂—), trimethylene (—CH₂CH₂CH₂—), tetramethylene (—CH₂CH₂CH₂CH₂—), 2-methyltetramethylene (—CH₂CH(CH₃)CH₂CH₂—), pentamethylene (—CH₂CH₂CH₂CH₂CH₂—) and the like).

[0092] As used herein, the term “alkylidene” means a straight or branched unsaturated, aliphatic, divalent group having a general formula =CR_aR_b. Non-limiting examples of R_a and R_b are each independently hydrogen, alkyl, substituted alkyl, alkenyl, or substituted alkenyl. C_x alkylidene and C_x-C_yalkylidene are typically used where X and Y indicate the number of carbon atoms in the chain. For example, C₂-C₆alkylidene includes methyldiene (=CH₂), ethyldiene (=CHCH₃), isopropylidene (=C(CH₃)₂), propylidene (=CHCH₂CH₃), allylidene (=CH—CH=CH₂), and the like).

[0093] The term “heteroalkyl”, as used herein, refers to straight or branched chain, or cyclic carbon-containing groups, or combinations thereof, containing at least one heteroatom. Suitable heteroatoms include, but are not limited to, O, N, Si, P, Se, B, and S, wherein the phosphorous and sulfur atoms are optionally oxidized, and the nitrogen heteroatom is optionally quaternized. Heteroalkyls can be substituted as defined above for alkyl groups.

[0094] As used herein, the term “halogen” or “halo” refers to an atom selected from fluorine (F), chlorine (Cl), bromine (Br) and iodine (I). The term “halogen radioisotope” or “halo radioisotope” refers to a radionuclide of an atom selected from fluorine (F), chlorine (Cl), bromine (Br) and iodine (I).

[0095] In some embodiments, “iodo” refers to the iodine atom (I) when it is used in the context of a halo functional group or halogen functional group or as a halo substituent or halogen substituent.

[0096] In some embodiments, “bromo” refers to the bromine atom (Br) when it is used in the context of a halo functional group or halogen functional group or as a halo substituent or halogen substituent.

[0097] In some embodiments, “chloro” refers to the chlorine atom (Cl) when it is used in the context of a halo functional group or halogen functional group or as a halo substituent or halogen substituent.

[0098] In some embodiments, “fluoro” refers to the fluorine atom (F) when it is used in the context of a halo functional group or halogen functional group or as a halo substituent or halogen substituent.

[0099] A “halogen-substituted moiety” or “halo-substituted moiety”, as an isolated group or part of a larger group, means an aliphatic, alicyclic, or aromatic moiety, as described herein, substituted by one or more “halo” atoms, as such terms are defined in this application. For example, halo-substituted alkyl includes haloalkyl, dihaloalkyl, trihaloalkyl, perhaloalkyl and the like (e.g., halosubstituted (C₁-C₃)alkyl includes chloromethyl, dichloromethyl, difluoromethyl, trifluoromethyl (-CF₃), 2,2,2-trifluoroethyl, perfluoroethyl, 2,2,2-trifluoro-1,1-dichloroethyl, and the like).

[0100] The term “aryl” refers to monocyclic, bicyclic, or tricyclic fused aromatic ring system. C_x aryl and C_x-C_yaryl are typically used where X and Y indicate the number of carbon atoms in the ring system. For example, C₆-C₁₂ aryl includes aryls that have 6 to 12 carbon atoms in the ring system. Exemplary aryl groups include, but are not limited to, pyridinyl, pyrimidinyl, furanyl, thienyl, imidazolyl, thiazolyl, pyrazolyl, pyridazinyl, pyrazinyl, triazinyl, tetrazolyl, indolyl, benzyl, phenyl, naphthyl, anthracenyl, azulenyl, fluorenyl, indanyl, indenyl, naphthyl, phenyl, tetrahydronaphthyl, benzimidazolyl, benzofuranyl, benzothiofuranyl, benzothiophenyl, benzoxazolyl, benzoxazoliny, benzthiazolyl, benztriazolyl, benztetrazolyl, benzisoxazolyl, benzisothiazolyl, benzimidazoliny, carbazolyl, 4aH carbazolyl, carbolinyl, chromanyl, chromenyl, cinnolinyl, decahydroquinolinyl, 2H,6H-1,5,2-dithiazinyl, dihydrofuro[2,3 b]tetrahydrofuran, furanyl, furazanyl, imidazolidinyl, imidazoliny, imidazolyl, 1H-indazolyl, indolenyl, indolinyl, indoliziny, indolyl, 3H-indolyl, isatinoyl, isobenzofuranyl, isochromanyl, isoindazolyl, isoindolinyl, isoindolyl, isoquinolinyl, isothiazolyl, isoxazolyl, methylenedioxyphenyl, morpholinyl, naphthyridinyl, octahydroisoquinolinyl, oxadiazolyl, 1,2,3-oxadiazolyl, 1,2,4-oxadiazolyl, 1,2,5-oxadiazolyl, 1,3,4-oxadiazolyl, oxazolidinyl, oxazolyl, oxindolyl, pyrimidinyl, phenanthridinyl, phenanthrolinyl, phenazinyl, phenothiazinyl, phenoxathinyl, phenoxazinyl, phthalazinyl, piperazinyl, piperidinyl, piperidonyl, 4-piperidonyl, piperonyl, pteridinyl, purinyl, pyranyl, pyrazinyl, pyrazolidinyl, pyrazolinyl, pyrazolyl, pyridazinyl, pyridoazole, pyridoimidazole, pyridothiazole, pyridinyl, pyridyl, pyrimidinyl, pyrrolidinyl, pyrrolinyl, 2H-pyrrolyl, pyrrolyl, quinazolinyl, quinolinyl, 4H-quinoliziny, quinoxalinyl, quinuclidinyl, tetrahydrofuranyl, tetrahydroisoquinolinyl, tetrahydroquinolinyl,

tetrazolyl, 6H-1,2,5-thiadiazinyl, 1,2,3-thiadiazolyl, 1,2,4-thiadiazolyl, 1,2,5-thiadiazolyl, 1,3,4-thiadiazolyl, thianthrenyl, thiazolyl, thienyl, thienothiazolyl, thienooxazolyl, thienoimidazolyl, thiophenyl and xanthenyl, and the like. In some embodiments, 1, 2, 3, or 4 hydrogen atoms of each ring can be substituted by a substituent.

[0101] The term “heteroaryl” refers to an aromatic 5-8 membered monocyclic, 8-12 membered fused bicyclic, or 11-14 membered fused tricyclic ring system having 1-3 heteroatoms if monocyclic, 1-6 heteroatoms if bicyclic, or 1-9 heteroatoms if tricyclic, said heteroatoms selected from O, N, or S (*e.g.*, carbon atoms and 1-3, 1-6, or 1-9 heteroatoms of N, O, or S if monocyclic, bicyclic, or tricyclic, respectively). C_x heteroaryl and C_x-C_yheteroaryl are typically used where X and Y indicate the number of carbon atoms in the ring system. For example, C₄-C₉ heteroaryl includes heteroaryls that have 4 to 9 carbon atoms in the ring system. Heteroaryls include, but are not limited to, those derived from benzo[b]furan, benzo[b] thiophene, benzimidazole, imidazo[4,5-*c*]pyridine, quinazoline, thieno[2,3-*c*]pyridine, thieno[3,2-*b*]pyridine, thieno[2, 3-*b*]pyridine, indolizine, imidazo[1,2-*a*]pyridine, quinoline, isoquinoline, phthalazine, quinoxaline, naphthyridine, quinolizine, indole, isoindole, indazole, indoline, benzoxazole, benzopyrazole, benzothiazole, imidazo[1,5-*a*]pyridine, pyrazolo[1,5-*a*]pyridine, imidazo[1,2-*a*]pyrimidine, imidazo[1,2-*c*]pyrimidine, imidazo[1,5-*a*]pyrimidine, imidazo[1,5-*c*]pyrimidine, pyrrolo[2,3-*b*]pyridine, pyrrolo[2,3-*c*]pyridine, pyrrolo[3,2-*c*]pyridine, pyrrolo[3,2-*b*]pyridine, pyrrolo[2,3-*d*]pyrimidine, pyrrolo[3,2-*d*]pyrimidine, pyrrolo [2,3-*b*]pyrazine, pyrazolo[1,5-*a*]pyridine, pyrrolo[1,2-*b*]pyridazine, pyrrolo[1,2-*c*]pyrimidine, pyrrolo[1,2-*a*]pyrimidine, pyrrolo[1,2-*a*]pyrazine, triazo[1,5-*a*]pyridine, pteridine, purine, carbazole, acridine, phenazine, phenothiazene, phenoxazine, 1,2-dihydropyrrolo[3,2,1-*hi*]indole, indolizine, pyrido[1,2-*a*]indole, 2(1H)-pyridinone, benzimidazolyl, benzofuranyl, benzothiofuranyl, benzothiophenyl, benzoxazolyl, benzoxazoliny, benzthiazolyl, benztriazolyl, benztetrazolyl, benzisoxazolyl, benzisothiazolyl, benzimidazoliny, carbazolyl, 4aH-carbazolyl, carboliny, chromanyl, chromenyl, cinnoliny, decahydroquinoliny, 2H,6H-1,5,2-dithiazinyl, dihydrofuro[2,3-*b*]tetrahydrofuran, furanyl, furazanyl, imidazolidiny, imidazoliny, imidazolyl, 1H-indazolyl, indolenyl, indoliny, indoliziny, indolyl, 3H-indolyl, isatinoyl, isobenzofuranyl, isochromanyl, isoindazolyl, isoindoliny, isoindolyl, isoquinoliny, isothiazolyl, isoxazolyl, methylenedioxyphenyl, morpholiny, naphthyridiny, octahydroisoquinoliny, oxadiazolyl, 1,2,3-oxadiazolyl, 1,2,4-oxadiazolyl, 1,2,5-oxadiazolyl, 1,3,4-oxadiazolyl, oxazolidiny, oxazolyl,

oxepanyl, oxetanyl, oxindolyl, pyrimidinyl, phenanthridinyl, phenanthrolinyl, phenazinyl, phenothiazinyl, phenoxathinyl, phenoxazinyl, phthalazinyl, piperazinyl, piperidinyl, piperidonyl, 4-piperidonyl, piperonyl, pteridinyl, purinyl, pyranyl, pyrazinyl, pyrazolidinyl, pyrazolinyl, pyrazolyl, pyridazinyl, pyridooxazole, pyridoimidazole, pyridothiazole, pyridinyl, pyridyl, pyrimidinyl, pyrrolidinyl, pyrrolinyl, 2H-pyrrolyl, pyrrolyl, quinazolinyl, quinolinyl, 4H-quinoliziny, quinoxalinyl, quinuclidinyl, tetrahydrofuranyl, tetrahydroisoquinolinyl, tetrahydropyranyl, tetrahydroquinolinyl, tetrazolyl, 6H-1,2,5-thiadiazinyl, 1,2,3-thiadiazolyl, 1,2,4-thiadiazolyl, 1,2,5-thiadiazolyl, 1,3,4-thiadiazolyl, thianthrenyl, thiazolyl, thienyl, thienothiazolyl, thienooxazolyl, thienoimidazolyl, thiophenyl and xanthenyl. Some exemplary heteroaryl groups include, but are not limited to, pyridyl, furyl or furanyl, imidazolyl, benzimidazolyl, pyrimidinyl, thiophenyl or thienyl, pyridazinyl, pyrazinyl, quinolinyl, indolyl, thiazolyl, naphthyridinyl, 2-amino-4-oxo-3,4-dihydropteridin-6-yl, tetrahydroisoquinolinyl, and the like. In some embodiments, 1, 2, 3, or 4 hydrogen atoms of each ring may be substituted by a substituent.

[0102] The term “cyclyl” or “cycloalkyl” refers to saturated and partially unsaturated cyclic hydrocarbon groups having 3 to 12 carbons, for example, 3 to 8 carbons, and, for example, 3 to 6 carbons. C_X -cyclyl and C_X - C_Y -cyclyl are typically used where X and Y indicate the number of carbon atoms in the ring system. For example, C_3 - C_8 cyclyl includes cyclyls that have 3 to 8 carbon atoms in the ring system. The cycloalkyl group additionally can be optionally substituted, e.g., with 1, 2, 3, or 4 substituents. C_3 - C_{10} cyclyl includes cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclohexenyl, 2,5-cyclohexadienyl, cycloheptyl, cyclooctyl, bicyclo[2.2.2]octyl, adamantan-1-yl, decahydronaphthyl, oxocyclohexyl, dioxocyclohexyl, thiocyclohexyl, 2-oxobicyclo [2.2.1]hept-1-yl, and the like.

[0103] Aryl and heteroaryls can be optionally substituted with one or more substituents at one or more positions, for example, halogen, alkyl, aralkyl, alkenyl, alkynyl, cycloalkyl, hydroxyl, amino, nitro, sulfhydryl, imino, amido, phosphate, phosphonate, phosphinate, carbonyl, carboxyl, silyl, ether, alkylthio, sulfonyl, ketone, aldehyde, ester, a heterocyclyl, an aromatic or heteroaromatic moiety, $-CF_3$, $-CN$, or the like.

[0104] The term “heterocyclyl” refers to a nonaromatic 4-8 membered monocyclic, 8-12 membered bicyclic, or 11-14 membered tricyclic ring system having 1-3 heteroatoms if monocyclic, 1-6 heteroatoms if bicyclic, or 1-9 heteroatoms if tricyclic, said heteroatoms selected

from O, N, or S (*e.g.*, carbon atoms and 1-3, 1-6, or 1-9 heteroatoms of N, O, or S if monocyclic, bicyclic, or tricyclic, respectively). C_x heterocyclyl and C_x-C_y heterocyclyl are typically used where X and Y indicate the number of carbon atoms in the ring system. For example, C_4-C_9 heterocyclyl includes heterocyclyls that have 4-9 carbon atoms in the ring system. In some embodiments, 1, 2 or 3 hydrogen atoms of each ring can be substituted by a substituent. Exemplary heterocyclyl groups include, but are not limited to piperazinyl, pyrrolidinyl, dioxanyl, morpholinyl, tetrahydrofuranyl, piperidyl, 4-morpholyl, 4-piperazinyl, pyrrolidinyl, perhydropyrrolizinyl, 1,4-diazaperhydroepinyl, 1,3-dioxanyl, 1,4-dioxanyl and the like.

[0105] The terms “bicyclic” and “tricyclic” refer to fused, bridged, or joined by single bond polycyclic ring assemblies.

[0106] The term “cyclylalkylene” means a divalent aryl, heteroaryl, cyclyl, or heterocyclyl.

[0107] As used herein, the term “fused ring” refers to a ring that is bonded to another ring to form a compound having a bicyclic structure when the ring atoms that are common to both rings are directly bound to each other. Non-exclusive examples of common fused rings include decalin, naphthalene, anthracene, phenanthrene, indole, furan, benzofuran, quinoline, and the like. Compounds having fused ring systems can be saturated, partially saturated, cyclyl, heterocyclyl, aromatics, heteroaromatics, and the like.

[0108] As used herein, the term “carbonyl” means the group ---C(O)--- . It is noted that the carbonyl group can be further substituted with a variety of substituents to form different carbonyl groups including acids, acid halides, amides, esters, ketones, and the like.

[0109] The term “carboxy” means the group ---C(O)O--- . It is noted that compounds described herein containing carboxy moieties can include protected derivatives thereof, *i.e.*, where the oxygen is substituted with a protecting group. Suitable protecting groups for carboxy moieties include benzyl, tert-butyl, and the like. The term “carboxyl” means ---COOH .

[0110] The term “cyano” means the group ---CN .

[0111] The term, “heteroatom” refers to an atom that is not a carbon atom. Particular examples of heteroatoms include, but are not limited to nitrogen, oxygen, sulfur and halogens. A “heteroatom moiety” includes a moiety where the atom by which the moiety is attached is not a carbon. Examples of heteroatom moieties include ---N= , $\text{---NR}^N\text{---}$, $\text{---N}^+(\text{O}^-)=$, ---O--- , ---S--- or $\text{---S(O)}_2\text{---}$, $\text{---OS(O)}_2\text{---}$, and ---SS--- , wherein R^N is H or a further substituent.

- [0112] The term “hydroxy” means the group —OH.
- [0113] The term “imine derivative” means a derivative comprising the moiety —C(NR)—, wherein R comprises a hydrogen or carbon atom alpha to the nitrogen.
- [0114] The term “nitro” means the group —NO₂.
- [0115] An “oxaaliphatic,” “oxaalicyclic”, or “oxaaromatic” mean an aliphatic, alicyclic, or aromatic, as defined herein, except where one or more oxygen atoms (—O—) are positioned between carbon atoms of the aliphatic, alicyclic, or aromatic respectively.
- [0116] An “oxoaliphatic,” “oxoalicyclic”, or “oxoaromatic” means an aliphatic, alicyclic, or aromatic, as defined herein, substituted with a carbonyl group. The carbonyl group can be an aldehyde, ketone, ester, amide, acid, or acid halide.
- [0117] As used herein, the term “aromatic” means a moiety wherein the constituent atoms make up an unsaturated ring system, all atoms in the ring system are sp² hybridized and the total number of pi electrons is equal to 4n+2. An aromatic ring can be such that the ring atoms are only carbon atoms (e.g., aryl) or can include carbon and non-carbon atoms (e.g., heteroaryl).
- [0118] As used herein, the term “substituted” refers to independent replacement of one or more (typically 1, 2, 3, 4, or 5) of the hydrogen atoms on the substituted moiety with substituents independently selected from the group of substituents listed below in the definition for “substituents” or otherwise specified. In general, a non-hydrogen substituent can be any substituent that can be bound to an atom of the given moiety that is specified to be substituted. Examples of substituents include, but are not limited to, acyl, acylamino, acyloxy, aldehyde, alicyclic, aliphatic, alkanesulfonamido, alkanesulfonyl, alkaryl, alkenyl, alkoxy, alkoxycarbonyl, alkyl, alkylamino, alkylcarbanoyl, alkylene, alkylidene, alkylthios, alkynyl, amide, amido, amino, aminoalkyl, aralkyl, aralkylsulfonamido, arenesulfonamido, arenesulfonyl, aromatic, aryl, arylamino, arylcarbanoyl, aryloxy, azido, carbamoyl, carbonyl, carbonyls including ketones, carboxy, carboxylates, CF₃, cyano (CN), cycloalkyl, cycloalkylene, ester, ether, haloalkyl, halogen, halogen, heteroaryl, heterocyclyl, hydroxy, hydroxyalkyl, imino, iminoketone, ketone, mercapto, nitro, oxaalkyl, oxo, oxoalkyl, phosphoryl (including phosphonate and phosphinate), silyl groups, sulfonamido, sulfonyl (including sulfate, sulfamoyl and sulfonate), thiols, and ureido moieties, each of which may optionally also be substituted or unsubstituted. In some cases, two substituents, together with the carbon(s) to which they are attached to, can form a ring.

[0119] Substituents may be protected as necessary and any of the protecting groups commonly used in the art may be employed. Non-limiting examples of protecting groups may be found, for example, in Greene et al., *Protective Groups in Organic Synthesis*, 3rd Ed. (New York: Wiley, 1999).

[0120] The terms “alkoxyl” or “alkoxy” as used herein refers to an alkyl group, as defined above, having an oxygen atom attached thereto. Representative alkoxyl groups include methoxy, ethoxy, propyloxy, tert-butoxy, *n*-propyloxy, iso-propyloxy, *n*-butyloxy, iso-butyloxy, and the like. An “ether” is two hydrocarbons covalently linked by an oxygen. Accordingly, the substituent of an alkyl that renders that alkyl an ether is or resembles an alkoxyl, such as can be represented by one of -O-alkyl, -O-alkenyl, and -O-alkynyl. Aroxy can be represented by -O-aryl or O-heteroaryl, wherein aryl and heteroaryl are as defined below. The alkoxy and aroxy groups can be substituted as described above for alkyl.

[0121] The term “aralkyl”, as used herein, refers to an alkyl group substituted with an aryl group (e.g., an aromatic or heteroaromatic group).

[0122] The term “alkylthio” refers to an alkyl group, as defined above, having a sulfur atom attached thereto. In preferred embodiments, the “alkylthio” moiety is represented by one of -S-alkyl, -S-alkenyl, and -S-alkynyl. Representative alkylthio groups include methylthio, ethylthio, and the like. The term “alkylthio” also encompasses cycloalkyl groups, alkene and cycloalkene groups, and alkyne groups. “Arylthio” refers to aryl or heteroaryl groups.

[0123] The term “sulfinyl” means the group —SO— . It is noted that the sulfinyl group can be further substituted with a variety of substituents to form different sulfinyl groups including sulfinic acids, sulfinamides, sulfinyl esters, sulfoxides, and the like.

[0124] The term “sulfonyl” means the group $\text{—SO}_2\text{—}$. It is noted that the sulfonyl group can be further substituted with a variety of substituents to form different sulfonyl groups including sulfonic acids ($\text{—SO}_3\text{H}$), sulfonamides, sulfonate esters, sulfones, and the like.

[0125] The term “thiocarbonyl” means the group —C(S)— . It is noted that the thiocarbonyl group can be further substituted with a variety of substituents to form different thiocarbonyl groups including thioacids, thioamides, thioesters, thioketones, and the like.

[0126] As used herein, the term “amino” means —NH_2 . The term “alkylamino” means a nitrogen moiety having at least one straight or branched unsaturated aliphatic, cyclyl, or heterocyclyl groups attached to the nitrogen. For example, representative amino groups include

---NH_2 , ---NHCH_3 , $\text{---N(CH}_3)_2$, $\text{---NH(C}_1\text{--C}_{10}\text{alkyl)}$, $\text{---N(C}_1\text{--C}_{10}\text{alkyl)}_2$, and the like. The term “alkylamino” includes “alkenylamino,” “alkynylamino,” “cyclylamino,” and “heterocyclylamino.” The term “arylamino” means a nitrogen moiety having at least one aryl group attached to the nitrogen. For example ---NHaryl , and ---N(aryl)_2 . The term “heteroarylamino” means a nitrogen moiety having at least one heteroaryl group attached to the nitrogen. For example ---NHheteroaryl , and $\text{---N(heteroaryl)}_2$. Optionally, two substituents together with the nitrogen can also form a ring. Unless indicated otherwise, the compounds described herein containing amino moieties can include protected derivatives thereof. Suitable protecting groups for amino moieties include acetyl, tert-butoxycarbonyl, benzyloxycarbonyl, and the like.

[0127] The term “aminoalkyl” means an alkyl, alkenyl, and alkynyl as defined above, except where one or more substituted or unsubstituted nitrogen atoms (---N---) are positioned between carbon atoms of the alkyl, alkenyl, or alkynyl. For example, an ($\text{C}_2\text{--C}_6$) aminoalkyl refers to a chain comprising between 2 and 6 carbons and one or more nitrogen atoms positioned between the carbon atoms.

[0128] The term “alkoxyalkoxy” means $\text{---O-(alkyl)-O-(alkyl)}$, such as $\text{---OCH}_2\text{CH}_2\text{OCH}_3$, and the like.

[0129] The term “alkoxycarbonyl” means ---C(O)O-(alkyl) , such as ---C(=O)OCH_3 , $\text{---C(=O)OCH}_2\text{CH}_3$, and the like.

[0130] The term “alkoxyalkyl” means $\text{-(alkyl)-O-(alkyl)}$, such as $\text{---CH}_2\text{OCH}_3$, $\text{---CH}_2\text{OCH}_2\text{CH}_3$, and the like.

[0131] The term “aryloxy” means ---O-(aryl) , such as ---O-phenyl , ---O-pyridinyl , and the like.

[0132] The term “arylalkyl” means -(alkyl)-(aryl) , such as benzyl (i.e., $\text{---CH}_2\text{phenyl}$), $\text{---CH}_2\text{-pyridinyl}$, and the like.

[0133] The term “arylalkyloxy” means $\text{---O-(alkyl)-(aryl)}$, such as ---O-benzyl , $\text{---O-CH}_2\text{-pyridinyl}$, and the like.

[0134] The term “cycloalkyloxy” means ---O-(cycloalkyl) , such as ---O-cyclohexyl , and the like.

[0135] The term “cycloalkylalkyloxy” means $\text{---O-(alkyl)-(cycloalkyl)}$, such as $\text{---OCH}_2\text{cyclohexyl}$, and the like.

[0136] The term "aminoalkoxy" means $-\text{O}-(\text{alkyl})-\text{NH}_2$, such as $-\text{OCH}_2\text{NH}_2$, $-\text{OCH}_2\text{CH}_2\text{NH}_2$, and the like.

[0137] The term "mono- or di-alkylamino" means $-\text{NH}(\text{alkyl})$ or $-\text{N}(\text{alkyl})(\text{alkyl})$, respectively, such as $-\text{NHCH}_3$, $-\text{N}(\text{CH}_3)_2$, and the like.

[0138] The term "mono- or di-alkylaminoalkoxy" means $-\text{O}-(\text{alkyl})-\text{NH}(\text{alkyl})$ or $-\text{O}-(\text{alkyl})-\text{N}(\text{alkyl})(\text{alkyl})$, respectively, such as $-\text{OCH}_2\text{NHCH}_3$, $-\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$, and the like.

[0139] The term "arylamino" means $-\text{NH}(\text{aryl})$, such as $-\text{NH}$ -phenyl, $-\text{NH}$ -pyridinyl, and the like.

[0140] The term "arylalkylamino" means $-\text{NH}-(\text{alkyl})-(\text{aryl})$, such as $-\text{NH}$ -benzyl, $-\text{NHCH}_2$ -pyridinyl, and the like.

[0141] The term "alkylamino" means $-\text{NH}(\text{alkyl})$, such as $-\text{NHCH}_3$, $-\text{NHCH}_2\text{CH}_3$, and the like.

[0142] The term "cycloalkylamino" means $-\text{NH}-(\text{cycloalkyl})$, such as $-\text{NH}$ -cyclohexyl, and the like.

[0143] The term "cycloalkylalkylamino" means $-\text{NH}-(\text{alkyl})-(\text{cycloalkyl})$, such as $-\text{NHCH}_2$ -cyclohexyl, and the like.

[0144] It is noted in regard to all of the definitions provided herein that the definitions should be interpreted as being open ended in the sense that further substituents beyond those specified may be included. Hence, a C_1 alkyl indicates that there is one carbon atom but does not indicate what are the substituents on the carbon atom. Hence, a C_1 alkyl comprises methyl (i.e., $-\text{CH}_3$) as well as $-\text{CR}_a\text{R}_b\text{R}_c$ where R_a , R_b , and R_c can each independently be hydrogen or any other substituent where the atom alpha to the carbon is a heteroatom or cyano. Hence, CF_3 , CH_2OH and CH_2CN are all C_1 alkyls.

[0145] Unless otherwise stated, structures depicted herein are meant to include compounds which differ only in the presence of one or more isotopically enriched atoms. For example, compounds having the present structure except for the replacement of a hydrogen atom by a deuterium or tritium, or the replacement of a carbon atom by a ^{13}C - or ^{14}C -enriched carbon are within the scope of the invention.

[0146] In various embodiments, compounds of the present invention as disclosed herein may be synthesized using any synthetic method available to one of skill in the art. Non-limiting

examples of synthetic methods used to prepare various embodiments of compounds of the present invention are disclosed in the Examples section herein.

[0147] Transition metal dichalcogenides (TMDs) adopt a general chemical formula MX_2 , where M represents a transition metal of group 4 to 10 within the periodic table and X signifies a chalcogen. TMDs exhibit diverse intrinsic properties, encompassing insulating, semiconducting, semi-metallic and metallic attributes. These materials primarily crystallize in a two-dimensional (2D) layered structure, akin to graphite. Each layer consists of a layer of hexagonally packed metal atoms sandwiched between two layers of chalcogen atoms. Based on the atomic packing order, the TMD crystal structures are divided into two main polymorphs: 1T and 2H, where the front number delineates the number of layers per unit cell and the followed letter presents for octahedral or trigonal prismatic coordination respectively. At mono- to few-layered scale, TMDs retain their bulk properties while manifesting additional characteristics and versatile chemical reactivity. Among the TMDs family, particular attention is directed towards group VI TMDs, because of their stability and semiconducting features, which demonstrate band gaps around 1–2 eV, being highly attractive for potential applications. Importantly, at few- to mono-layered architecture, these materials exhibit a gradual shift from indirect to direct band gap transition, rendering them valuable in the realm of electronic and optoelectronic applications. The change of this band structure is owing to the quantum confinement effect and the consequent change in the overlap of chalcogen p_z orbitals between the 2D TMDs layers. As a result of this special feature, exfoliated 2D TMDs are attractive for photodetectors over a wide range of wavelengths that can be selected by finely tuning the number of layers. Also, they can serve as light-absorbing materials in thin-film solar cells with a direct band gap spanning the visible region.

[0148] Consequently, scalable exfoliation methods to produce high-quality few- to mono-layered TMDs have been intensively investigated. Among these, the most efficient approach is exfoliating natural TMDs through intercalation chemistry, typically employing Li-based reagents. However, current research efforts have revealed a crucial limitation. It has been observed that excessive intercalation, beyond a certain threshold, induces phase transformation within the TMDs. In order to mitigate this issue, an alternative method - direct liquid phase exfoliation (LPE) – harnesses the intricate relation between the miss-match surface energies of TMDs and solvents, defined within the context of Hansen solubility framework. Nevertheless, this method encounters a fundamental limitation in terms of its solvent selection, primarily realizing on solvents such as

N-methyl-pyrrolidone (NMP), leading to persistence of organic residues on the TMDs' surface. Furthermore, the LPE process necessitates extended sonication periods, which tend to fragment TMDs nanosheets into relatively smaller flakes.

[0149] Hence, to avoid phase transformation, achieve high-quality mono- to few-layered nanosheets and maintain efficient exfoliation, mild redox chemistry was recently proposed in the literature and could afford large amounts of exfoliated TMDs with tunable layer thicknesses. In various embodiments, we envision exfoliating large-scale 2D nanolayered TMDs and using them as starting materials to further tune the electronic, optical, or interfacial properties for targeted goals based on the strategies discussed below.

[0150] Despite the TMDs' attractiveness at mono- to few-layered architectures, the full extent of their potential applications is limited by the inherent band gap structures of TMDs. Efforts have been directed toward engineering TMDs' band gap window. Common doping methods to modify TMDs' surface and charge density, such as ion implantation, are ineffective at mono- to few-layered scale due to local defect generation and physical damage, which are detrimental to electronic applications. Currently, two predominant approaches have been used to address this challenge, each employing distinctive categories of reagents: thiol-based organic adsorbates and electron-donating molecules. In the thiol-based strategy, organic molecules containing thiol (-SH) or disulfide (-S-S-) groups are used to establish a sulfur-chalcogenide bridge with TMDs. This bonding interaction is, however, fragile.

[0151] More recent studies have revealed that TMDs can catalyze the formation of a disulfide bridge between two thiol molecules, indicating that the organic molecules tend to be physisorbed rather than chemically bound to the surface of the TMDs. Furthermore, the affinity between transition metals and chalcogenide elements induces a pre-step modification that includes the creation of defects, such as the absence of chalcogenide atoms. These defects are poised for healing through the interaction between the transition metals and the thiol groups. Recently, a novel non-thiol-based strategy has been employed, utilizing the Michael addition reaction for the selective attack of chalcogenide nucleophiles upon the double bonds in maleimide-based adsorbates. However, this strategic approach requires the presence of maleimide ring, which severely limits the tunability of the electronic properties.

[0152] With the electron-donating strategy reported in the literature, a limited library of molecules (Lewis bases) serve as electron donors, imparting their electrons to the anti-bonding

orbitals of the transition metals of TMDs. This process leads to compression of the TMD nanosheets and intercalation of the donor molecules between the van der Waals layers of the TMDs, giving rise to an intercalated structure with an expanded interlayer spacing. This particular approach demonstrates at least two advantages over the thiol-based method. First, the electron-donating molecules form strong chemical interactions via the donating electrons, leading to more robust bond formation. Second, the degree of intercalation can be controlled by finely modulating the ratio of precursor materials, which directly influences the electronic properties of the final intercalated products. Despite these advantages, as mentioned above, excessive intercalation, using strong electron donors, induces phase transformations within the TMDs. These phase transformations include a shift from the semiconducting to the metallic state, rendering impractical and unsuitable characteristics in several intended applications, specifically those within the semiconductor realm. Hence, the need for new and improved functionalized TMDs and methods for making them.

[0153] Taking into account the limitations of previously reported work, herein in various embodiments of the present invention we successfully developed an entirely new strategy based on the use of *N*-heterocyclic carbenes (NHCs) – a gentle electron donating reagent – to intercalate and functionalize the basal plane of mono- to few-layered TMDs. Unexpectedly, the resulting NHC-functionalized TMDs did not experience any undesirable phase transformations. In particular, the *N*-heterocyclic carbene functionalized TMDs of the present invention do not undergo the undesired phase transformation from the semiconducting state to the metallic state. This is crucial for semiconducting Group VI TMDs. In various non-limiting embodiments MoS₂ was selected as a representative example for illustrating *N*-heterocyclic carbene functionalized TMDs of the present invention. The step-by-step redox exfoliation method used and the corresponding evidence of exfoliated MoS₂ are described herein. Finally, concerning basal plane functionalized TMDs, the results are demonstrated herein.

[0154] **Redox Exfoliation of Mono- to Few-layered MoS₂ Nanosheets**

[0155] The ultraviolet-visible spectroscopy (UV-vis) data, shown in FIG. 1A – FIG. 1B, depicts the extinction (ϵ) spectra of exfoliated MoS₂ colloidal obtained from the redox exfoliation process. The spectrum combines the aspects of both absorbance (α) and size-dependent scattering (σ) backgrounds; hence, pertinent information can be extracted for approximate estimation of the thicknesses and lateral sizes of exfoliated MoS₂ nanosheets. Previous literature reports observed

and reported this phenomenon, particularly as it relates to the evolving thicknesses and lateral sizes of those nanosheets. Importantly, the experimental set of data in these previous literature reports helped to interpolate the significance of a local minimum at 345 nm as an independent metric, free from the influence of scattering effects. This feature, then, can serve as a reference point for normalization in comparative analysis. Based on these previous literature reports, our data, in FIG. 1A, delineates the normalized extinction spectra of exfoliated MoS₂ nanosheets. This data was collected from exfoliated MoS₂ at different centrifuge rates subsequent to the redox exfoliation process. It is worth highlighting that increasing centrifuge rate results in thinner and smaller nanosheets, which emphasizes the discussed phenomenon in the region from 700 to 800 nm. In the spectral range from 700 to 350 nm, the exciton peaks of MoS₂ were designated as A, B, C, D from right to left respectively. Among these excitons, A presents the transition from the K-point (the highest energy point) in the valence band to the conduction band, which demonstrates the band gap of material. Consequently, the position of the A exciton can be employed to infer the thicknesses of MoS₂ nanosheets. This previously reported approach is feasible owing to 2D TMDs layer-dependent characteristics, which has been thoroughly examined and documented in the literature. Nevertheless, within the range below 700 nm, the dominance of scattering background necessitates the conversion of the original extinction spectrum into its second derivative. This mathematical transformation is recommended in the literature as an essential data processing step to reduce the peak shifts caused by the broad background. The second derivative transformation of A exciton is presented in FIG. 1B with x-axis converted to energy scale. At a high centrifuge rate of 2500 rpm (740 G), the resultant exfoliated MoS₂ nanosheets exhibit their minimum thicknesses with an approximate A-exciton transition of 1.85 eV ($\lambda_A = 671$ nm). In contrast, the thicker ones are observed when A-excitons transition energy fall below 1.85 eV at lower centrifuge rates. The full second derivate transformation (FIG. 4A – FIG. 4B) and relationship between A-exciton transition energy at different centrifuge rates are shown herein. Compared to the fitted models and corresponding reported equations, the resultant exfoliated MoS₂ nanosheets exhibit thicknesses varying from 4 – 7 layers. However, it is important to emphasize that UV-vis extinction spectrum only provide an approximate estimation about thicknesses of predominant populations of nanosheets. Furthermore, as mentioned, scattering backgrounds play a key role in understanding thicknesses-related aspects. Additionally, the inherent nature of redox exfoliation, which leads to the absorption of POMs on the surface of 2D TMDs nanosheets, might contribute

to the peak shifts. This effect might be pronounced when POMs species exhibit comparable sizes, at least 1nm in height. Hence, as a complementary data, statistical analysis based on height retrace from AFM was conducted (FIG. 5).

[0156] The height profiles of redox exfoliated MoS₂ dispersion are presented in FIG. 2A – FIG. 2B. Herein, it is important to note that the actual thickness of a single layer of TMDs is not identical to the theoretical one, owing to factors such as solvent effects and the presence of adsorbed POMs absorbed on the nanosheets' surface. To address this issue, an internal reference, known as “step height”, is employed. This solution is based on the observation that incomplete exfoliation results in staircase-like height profile. As illustrated in our data, a step height of approximate 2.0 to 2.5 nm was found and attributed to the thickness of a single layer. This observation is also in agreement with the published studies employing redox exfoliation methods. Finally, to provide further evidence of successful exfoliation of MoS₂, XRD measurements were carried out for a comparative analysis between bulk MoS₂ and thin film exfoliated materials (FIG. 6). As a consequence of mono- to few-layer architecture, the [hk0] and [h0l] reflections experience disappearance or substantial attenuation. This phenomenon is due to the loss of intralayer order within the material. Only [002] reflection, attributed to the interlayer thickness, persists after the restacking process.

[0157] **NHCs-Functionalized MoS₂ Nanosheets**

[0158] Based on our experiments we observed the interaction between NHC15OH[OMs] adsorbates (molecular structure of NHC15OH[OMs] is provided in the Examples herein) and the exfoliated MoS₂ colloidal. Following the complete dissolution of the NHC15OH[OMs] in dichloromethane (DCM), exfoliated MoS₂ in anhydrous acetonitrile (ACN) was introduced, and the system was allowed to stand undisturbed in 24 h. Typically, depending on the molar ratio between the NHCs and the exfoliated MoS₂, abrupt compression resulting precipitation could be directly observed within a matter of minutes. The resultant black powder was centrifuged and washed by DCM three times to remove unreacted NHCs. Subsequently, the washed powder was deposited as thin film on a glass slide (details provided in the Examples section herein) and subjected to X-ray powder diffraction (XRD). FIG. 3 illustrates the XRD patterns of thin film NHC15OH[OMs]-functionalized MoS₂. Interestingly, diffraction patterns of the novel material reveal two distinct and prominent peaks at 7.98 and 24.25 (2θ), which can be attributed to the molecular intercalation occurring between MoS₂ layers. Without being bound by theory, we

propose these two newly emerged peaks corresponding to the [002'] and [004'] reflections of the novel phase with an expanded thickness of 11.1 Å compared to 6.1 Å observed in bulk MoS₂. In accordance with prior published literature, intercalation chemistry of 2D TMDs within groups IV and V have been investigated. This is primarily due to their metallic characteristics, which facilitate acceptance of electrons from donating reagents, but limited studies regarding the intercalation of group VI. A common employed strategy involves the pre-step exfoliation of semiconducting group VI TMDs, accomplished by Li-based reagents, which induce a phase transition to metallic state. From another perspective, solvent or partial hydrated species intercalation have been previously documented in the literature as well. Nevertheless, recovery of initial layer thickness can be accomplished by simple drying at solvent boiling temperature. However, it is noted that our samples were washed out and dried properly (details provided in Examples section herein). Furthermore, provided powder XRD pattern of NHC15OH[OMs] (FIG. 7) shows clearly different features compared to the functionalized materials.

[0159] In various embodiments of the present invention, NHC molecules adopting longer chain length, extending up to 15 carbon atoms, led to interlayer expansion of 2.5 Å on each side of the TMDs' single layer.

[0160] In previous reports NHC15OH[OMs] shows an approximate sub-layer height of NHC molecules forming self-assembly monolayers (SAMs) at 11 ± 2 Å, even when the SAMs sub-layer was not densely packed. In another recent literature study, STM evidence was presented that revealed that the height of the carbene ring was at 235 pm, which was comparable to our calculations from our experimental data. Hence, without being bound by theory, we hypothesized that the NHC adsorbates, NHC precursors, and/or *N*-heterocyclic carbenes (NHCs) might not stand perpendicular to the plane, but rather lie nearly flat at a tilted angle. Also, as illustrated in the XRD patterns, it is evident that the intercalation process remains incomplete, even at high NHC:MoS₂ molar ratio, as indicated by the persistence of bulky MoS₂ reflection peaks. It can be potentially due to the bulky and cumbersome structure of the carbene head group. To further offer supplement about the intercalation triggered by the carbene, attenuated total reflectance infrared spectroscopy (ATR-IR) was conducted on thin film samples deposited onto optical glass slides (FIG. 8). Finally, the zeta potential of the anticipated NHC-functionalized MoS₂ was measured and compared to that of exfoliated MoS₂, providing a preliminary assessment of the surficial characteristics (FIG. 9). Since the zeta potential measurement provides surficial charge, redox

exfoliated MoS₂ shows a negative surface charge of -29.2 ± 1 mV, which is in great agreement with reported observations due to the adsorption of negative charge POMs species. Upon interaction with NHC adsorbates, NHC precursors, and/or *N*-heterocyclic carbenes (NHCs), the POMs are desorbed and replaced by *N*-heterocyclic carbenes (NHCs), which results in an increase in surface charge.

[0161] In various embodiments of the present invention described herein, the successful exfoliation of MoS₂ have been demonstrated, obtaining the recent redox exfoliation method. The interaction between the various NHC molecules (e.g., NHC adsorbates, NHC precursors, *N*-heterocyclic carbenes (NHCs)), and the representative 2D TMDs (MoS₂) are described herein in various embodiments of the present invention. Without being bound by theory, according to the experimental data provided herein molecular intercalation between the van der Waals layers of MoS₂ was illustrated.

[0162] Transition metal dichalcogenides (TMDs) adopt a general chemical formula denoted as MX₂, where M represents a transition metal of group 4 to 10 within the periodic table, and X corresponds to a chalcogen. TMDs exhibit diverse intrinsic properties that include insulating, semiconducting, semi-metallic and metallic. These materials primarily crystallize in a 2D layered structure akin to graphite. At mono- to few-layered scale, TMDs retain their inherent bulk properties while manifesting additional characteristics and versatile chemical reactivity. Among the TMD family, particular attention is directed toward group VI TMDs, because of their stability and semiconducting features. At mono-layered architectures, these materials exhibit a direct band gap transition, rendering them valuable in the realm of electronic and optoelectronic applications. Nevertheless, without being bound by theory, the full extent of their potential applications is limited by the inherent band gap structures of TMDs. Consequently, the work described herein in various embodiments of the present invention overcomes this limitation by demonstrating an entirely unique functionalization method that allows fine-tuning of the electronic properties, optical properties, band gap structures, and surficial characteristics of TMDs to broaden their applications across new and diverse technological domains.

[0163] In various embodiments of the present invention described herein we demonstrate, for the first time, the effective functionalization of the basal plane of 2D mono-to-few-layered TMDs employing NHCs (*N*-heterocyclic carbenes) and/or *N*-heterocyclic carbene precursors and/or NHC adsorbates. This pioneering and novel approach yields *N*-heterocyclic carbene

functionalized TMD superstructures with immense potential not only within the semiconductor industry, but also as nano-building blocks for electronics, optoelectronics, and semiconductor nano-micro-fabrication engineering. This transformative and novel invention marks a crucial advancement in the utilization of TMDs and their functionalized derivatives, expanding promising applications and paving the way for innovative advancements in nano-micro technology.

[0164] In various embodiments, the present invention provides an entirely new strategy based on the use of *N*-heterocyclic carbenes (NHCs) and/or *N*-heterocyclic carbene precursors and/or *N*-heterocyclic carbene adsorbates to intercalate and functionalize the basal plane of mono-to-few-layered TMDs. Unexpectedly, the resulting *N*-heterocyclic carbene functionalized TMDs do not undergo undesirable phase transformations. In particular, the *N*-heterocyclic carbene functionalized TMDs of the present invention do not undergo the undesired phase transformation from the semiconducting state to the metallic state. This is a crucial feature for semiconducting Group VI TMDs. Furthermore, in various embodiments, the electronic characteristics and band gap structures of the *N*-heterocyclic carbene functionalized TMDs of the present invention can be systematically engineered through structural variation of the *N*-heterocyclic carbene headgroups. In addition, in various embodiments the resulting superstructure of functionalized and restacked *N*-heterocyclic carbene functionalized TMDs, characterized by their expanded space, holds promise for applications in molecular encapsulation, information encoding technology, and as fundamental building blocks for nano-micro architecture engineering in the semiconductor industry and beyond.

[0165] In various embodiments the present invention provides a novel approach for the functionalization of the basal plane of two-dimensional (2D) transition metal dichalcogenides (TMDs) by employing a gentle electron-donating agent based on *N*-heterocyclic carbenes (NHCs). In various embodiments, the process of the present invention involves the exfoliation of bulk TMDs to yield mono-to-few-layered TMD nanosheets that are subsequently exposed to NHC adsorbates (i.e., NHC precursors), which interact with the TMDs. The NHC molecules (e.g., NHC adsorbates, NHC precursors, NHCs) form self-assembled monolayers (SAMs) on the TMDs, which leads to compression of the nanosheets and their subsequent self-restacking. The resulting NHC-functionalized TMDs exhibit a final superstructure comprised of NHC-intercalated layers. Surprisingly and unexpectedly, this novel and innovative functionalization method described herein in various embodiments of the present invention preserves the inherent structures and

phases of the TMDs, a critical factor for group VI TMDs that exclusively exhibit semiconducting characteristics in their natural 2H polymorph. In various embodiments, the present invention possesses the capability to fabricate advanced and unprecedented 2D assembled materials with potential applications, for example, in energy storage, sensing, and semiconductor electronics and optoelectronics.

[0166] Surface functionalization of 2D nanolayered transition metal dichalcogenides for tunable electronic and optical properties. Two-dimensional (2D) transition metal (VI) dichalcogenides (TMDs) exhibit attractive layer-dependent characteristics. Among these characteristics, direct band gap transitions spanning the visible spectrum as the thicknesses decreases to the monolayer level is a special feature that offers advantages in various device applications such as photodetectors and solar cells. In this work, 2D nanolayered TMDs were exfoliated via a facile mild redox wet chemistry method. The corresponding exfoliated products were prepared and collected as a function of the specific layer thickness and the lateral size of the 2D nanosheets. The basal planes of mono to few-layered 2D TMDs were then functionalized with organic molecules or metal complexes to form covalent bonds designed to tune the optical and electronic properties of the TMDs. Characterization by ultraviolet-visible (UV-vis) spectroscopy and photoluminescence (PL) spectroscopy revealed the layer-dependent absorption spectra of the unfunctionalized exfoliated and functionalized exfoliated materials. Surface morphology details and particle size measurements were obtained by transmission electron microscopy (TEM). Finally, X-ray photoelectron spectroscopy (XPS) was used to evaluate the covalent functionalization of the TMDs.

[0167] Two-dimensional transition metal dichalcogenides (2D TMDs) display compelling electronic and optoelectronic attributes, holding promise for microelectronic applications. Nonetheless, in contrast to their monolayer counterparts, thicker-layered TMDs manifest an indirect band gap, limiting their utility across various optoelectronic applications. This research attempts to achieve a methodology for large-scale fabrication of mono- to few-layer 2D TMDs through the process of redox exfoliation, followed by subsequent functionalization with organic adsorbates. By systematically investigating the impact of adsorbates' structures on exfoliated MoS₂, we seek to deliberately modulate the physical and chemical properties of 2D TMDs for optoelectronic devices.

[0168] A core objective of this research is to establish an effective approach for the functionalization of 2D MoS₂. Initially, the study focuses on using redox exfoliation to produce high-quality 2D nanolayered MoS₂. The exfoliation process achieves an impressive yield of up to 8% with primarily mono to few-layer MoS₂ structure (< 5 layers). Additionally, the bulk portion can be recycled for subsequent exfoliation cycles. Afterwards, the research introduces the utilization of self-assembled monolayers (SAMs) comprised of organic molecules on the basal plane of exfoliated MoS₂. This demonstrates the potential of functionalized MoS₂ as fundamental building blocks for the engineering of advanced nano-architectures within TMDs domain.

[0169] In various embodiments of the present invention, bulk MoS₂ has been effectively exfoliated using a convenient wet-chemistry method. In various embodiments of the present invention, the redox exfoliation affords substantial quantities of exfoliated materials, achieving a yield exceeding 8% per cycle. In various embodiments of the present invention, UV-vis extinction spectra validate the presence of mono to few-layered MoS₂ with prominent thicknesses ranging down to 4 layers. In various embodiments of the present invention, XRD pattern provides evidence of successful functionalization on the basal plane of MoS₂. In various embodiments of the present invention, a novel strategy to functionalize 2D TMDs is introduced.

[0170] Herein, we introduce a novel, mild electron-donating approach that enables functionalization of the basal plane of two-dimensional (2D) few- to monolayered transition metal dichalcogenides (TMDs) using *N*-Heterocyclic Carbenes (NHCs). This strategy employs benzimidazolium methanesulfonates, a representative bench stable NHC adsorbate, to functionalize semiconducting TMDs through a one-step synthesis conducted under ambient conditions at room temperature. Without being bound by theory, the functionalization is hypothesized to be driven by hybridization-induced process, which concurrently leads to restacking and entrapment of bilayer self-assembled monolayers (SAMs) of NHCs between the TMD monolayers, thereby forming superlattice structures. The resultant superlattice materials are signified by expanded van der Waals (vdW) interlayer gaps of 11.1 and 13.0 Å, which are tunable by controlling the sizes and thicknesses of TMD nanosheets. In addition to structural modifications, NHCs induce an n-doping effect, supported by alterations in both intrinsic in-plane and out-of-plane vibrations of TMDs. Finally, the experimental observations demonstrate that the bulky structures of NHCs can be incorporated into the interlayer gaps of TMDs while preserving their intrinsic semiconducting properties. Notably, the functionalized superlattice materials

preserve the semiconducting properties typical of monolayers, as evidenced by their detectable photoluminescence.

[0171] Two-dimensional transition metal dichalcogenides (2D TMDs) display compelling electronic and optoelectronic attributes at the monolayer architecture (1L). However, the ability to modulate these inherent characteristics is constrained by the electronic structures and morphological limitations inherent to 1L TMDs. To address these challenges, the work described herein aims to achieve large-scale, high-quality production of few- to monolayered 2D TMDs, followed by subsequent functionalization with custom-designed organic adsorbates.

[0172] Layered TMDs are emerging class of 2D materials with their attractive thickness-dependent optical and electrical properties (Chhowalla, M.; Shin, H. S.; Eda, G.; Li, L.-J.; Loh, K. P.; Zhang, H. The Chemistry of Two-Dimensional Layered Transition Metal Dichalcogenide Nanosheets. *Nat. Chem.* **2013**, *5*, 263–275). Akin to graphite, TMDs primarily crystallize in a 2D layered structure, wherein their composition covers transition metals from group 4 to 10 while the chalcogen atoms signify S, Se, or Te. With a vast compositional library, TMDs exhibit diverse intrinsic properties, encompassing insulating, semi-conducting, semi-metallic and metallic attributes. Notably, group VI TMDs (MoS₂, MoSe₂, WS₂, WSe₂) have garnered significant attention, thanks to their stability and semiconducting characteristics, featuring optical band gaps around 1-2 eV. These properties render this group of TMDs become highly promising for various applications. At few- to monolayered architecture, these materials undergo a gradual transition from indirect to direct band gap, thereby enhancing their utilities in the realm of electronic and optoelectronic domains, such as 2D field-effect transistors (2D FETs) (Sebastian, A.; Pendurthi, R.; Choudhury, T. H.; Redwing, J. M.; Das, S. Benchmarking Monolayer MoS₂ and WS₂ Field-Effect Transistors. *Nat. Commun.* **2021**, *12*, 693), memristors (Xu, R.; Jang, H.; Lee, M.-H.; Amanov, D.; Cho, Y.; Kim, H.; Park, S.; Shin, H.; Ham, D. Vertical MoS₂ Double-Layer Memristor with Electrochemical Metallization as an Atomic-Scale Synapse with Switching Thresholds Approaching 100 Mv. *Nano Lett.* **2019**, *19*, 2411–2417), photodetectors (Lopez-Sanchez, O.; Lembke, D.; Kayci, M.; Radenovic, A.; Kis, A. Ultrasensitive Photodetectors Based on Monolayer MoS₂. *Nat. Nanotechnol.* **2013**, *8*, 497–501), solar cell (Tsai, M.-L.; Su, S.-H.; Chang, J.-K.; Tsai, D.-S.; Chen, C.-H.; Wu, C.-I.; Li, L.-J.; Chen, L.-J.; He, J.-H. Monolayer MoS₂ Heterojunction Solar Cells. *ACS Nano* **2014**, *8*, 8317–8322). However, beyond the proof of concept from laboratory to device, several challenges have been addressed, concerning the

limitations of exfoliation methods (Velický, M.; Donnelly, G. E.; Hendren, W. R.; McFarland, S.; Scullion, D.; DeBenedetti, W. J. I.; Correa, G. C.; Han, Y.; Wain, A. J.; Hines, M. A.; Muller, D. A.; Novoselov, K. S.; Abruña, H. D.; Bowman, R. M.; Santos, E. J. G.; Huang, F. Mechanism of Gold-Assisted Exfoliation of Centimeter-Sized Transition-Metal Dichalcogenide Monolayers. *ACS Nano* **2018**, *12*, 10463–10472; Rangnekar, S. V.; Sangwan, V. K.; Jin, M.; Khalaj, M.; Szydłowska, B. M.; Dasgupta, A.; Kuo, L.; Kurtz, H. E.; Marks, T. J.; Hersam, M. C. Electroluminescence from Megasonically Solution-Processed MoS₂ Nanosheet Films. *ACS Nano* **2023**, *17*, 17516–17526; Yang, R.; Mei, L.; Zhang, Q.; Fan, Y.; Shin, H. S.; Voiry, D.; Zeng, Z. High-Yield Production of Mono- or Few-Layer Transition Metal Dichalcogenide Nanosheets by an Electrochemical Lithium Ion Intercalation-Based Exfoliation Method. *Nat. Protoc.* **2022**, *17*, 358–377 and technical fabrication issues such as metal/semiconductor contact, and resistance (Chhowalla, M.; Jena, D.; Zhang, H. Two-Dimensional Semiconductors for Transistors. *Nat. Rev. Mater.* **2016**, *1*, 1–15). Other echoing challenges are the inherent TMDs' electronic properties and band gap windows, which are primarily tunable through custom-designed thicknesses or elemental doping (Splendiani, A.; Sun, L.; Zhang, Y.; Li, T.; Kim, J.; Chim, C.-Y.; Galli, G.; Wang, F. Emerging Photoluminescence in Monolayer MoS₂. *Nano Lett.* **2010**, *10*, 1271–1275; Robertson, A. W.; Lin, Y.-C.; Wang, S.; Sawada, H.; Allen, C. S.; Chen, Q.; Lee, S.; Lee, G.-D.; Lee, J.; Han, S.; Yoon, E.; Kirkland, A. I.; Kim, H.; Suenaga, K.; Warner, J. H. Atomic Structure and Spectroscopy of Single Metal (Cr, V) Substitutional Dopants in Monolayer MoS₂. *ACS Nano* **2016**, *10*, 10227–10236). The two strategies have their own limitations; specifically, defects formation resulting from conventional doping methods at the atomically thin structure introduces additional energy levels and sites for electron-hole trapping. As a matter of fact, great efforts have been made to modify the electronic and optical properties of these group VI monolayered TMDs without causing significant damage to the crystal structure while preserving their inherent semiconducting features. A feasible approach that promotes simplicity and scalability is "chemical doping" or "chemical functionalization", achieved by regulating the properties of introduced chemical species. It should be noted that these terms encompass not only robust covalent bond formation but also physisorbed interactions, leading to unparallel outcomes.

[0173] From the covalent approach, the impact is straightforward. Despite that, natural semiconducting group VI TMDs (denoted as 2H or 1H at monolayer) exhibit chemical inertness due to the orientation of chalcogen p_z orbitals and metals d_{z^2} orbitals. These orbitals construct the

antibonding orbitals and contribute to the minimum conduction band, effectively passivating the basal plane of TMD monolayers (Chang, C.-H.; Fan, X.; Lin, S.-H.; Kuo, J.-L. Orbital Analysis of Electronic Structure and Phonon Dispersion in MoS₂, MoSe₂, WS₂, and WSe₂ Monolayers under Strain. *Phys. Rev. B* **2013**, *88*, 195420). Consequently, the range of available strategies is limited. Most studies have demonstrated the effectiveness of defects-healing approach using thiol-organic molecules; however, this strategy is constrained by the concentration of defects (Makarova, M.; Okawa, Y.; Aono, M. Selective Adsorption of Thiol Molecules at Sulfur Vacancies on MoS₂(0001), Followed by Vacancy Repair via S–C Dissociation. *J. Phys. Chem. C* **2012**, *116*, 22411–22416; Bertolazzi, S.; Bonacchi, S.; Nan, G.; Pershin, A.; Beljonne, D.; Samori, P. Engineering Chemically Active Defects in Monolayer MoS₂ Transistors via Ion-Beam Irradiation and Their Healing via Vapor Deposition of Alkanethiols. *Adv. Mater.* **2017**, *29*, 1606760; Ippolito, S.; Urban, F.; Zheng, W.; Mazzarisi, O.; Valentini, C.; Kelly, A. G.; Gali, S. M.; Bonn, M.; Beljonne, D.; Corberi, F.; Coleman, J. N.; Wang, H. I.; Samori, P. Unveiling Charge-Transport Mechanisms in Electronic Devices Based on Defect-Engineered MoS₂ Covalent Networks. *Adv. Mater.* **2023**, *35*, 2211157). A minor branch, employing the thiol-functional groups to directly interact with the basal plane of TMDs, showed negligible effects owing to the weak S–S bonds, giving to the formation of physisorbed dithiol molecules (Chen, X.; Berner, N. C.; Backes, C.; Duesberg, G. S.; McDonald, A. R. Functionalization of Two-Dimensional MoS₂: On the Reaction Between MoS₂ and Organic Thiols. *Angew. Chem. Int. Ed.* **2016**, *55*, 5803–5808). Recently, a mild covalent functionalization approach based on electrophilic maleimides through Michael addition reaction has been proposed (Vera-Hidalgo, M.; Giovanelli, E.; Navío, C.; Pérez, E. M. Mild Covalent Functionalization of Transition Metal Dichalcogenides with Maleimides: A “Click” Reaction for 2H-MoS₂ and WS₂. *J. Am. Chem. Soc.* **2019**, *141*, 3767–3771). The method offers a direct covalent toolbox; however, the extent of functionalization achieved was overestimated due to subsequent polymerization (Quirós-Ovies, R.; Vázquez Sulleiro, M.; Vera-Hidalgo, M.; Prieto, J.; Gómez, I. J.; Sebastián, V.; Santamaría, J.; Pérez, E. M. Controlled Covalent Functionalization of 2 H-MoS₂ with Molecular or Polymeric Adlayers. *Chem. – Eur. J.* **2020**, *26*, 6629–6634; Vázquez Sulleiro, M.; Quirós-Ovies, R.; Vera-Hidalgo, M.; Gómez, I. J.; Sebastián, V.; Santamaría, J.; Pérez, E. M. Covalent Cross-Linking of 2H-MoS₂ Nanosheets. *Chem. – Eur. J.* **2021**, *27*, 2993–2996). To overcome the inertness of semiconducting TMDs, a pre-activation step was proposed that converts the thermodynamically favorable 1H phase to

metastable 1T phase (Eda, G.; Fujita, T.; Yamaguchi, H.; Voiry, D.; Chen, M.; Chhowalla, M. Coherent Atomic and Electronic Heterostructures of Single-Layer MoS₂. *ACS Nano* **2012**, *6*, 7311–7317; Fan, X.; Xu, P.; Zhou, D.; Sun, Y.; Li, Y. C.; Nguyen, M. A. T.; Terrones, M.; Mallouk, T. E. Fast and Efficient Preparation of Exfoliated 2H MoS₂ Nanosheets by Sonication-Assisted Lithium Intercalation and Infrared Laser-Induced 1T to 2H Phase Reversion. *Nano Lett.* **2015**, *15*, 5956–5960). The metastable 1T phase, characterized by its high electron density, is metallic and acts as a nucleophile, enabling it to react with electrophilic species such as organohalides (Voiry, D.; Goswami, A.; Kappera, R.; Silva, C. de C. C. e; Kaplan, D.; Fujita, T.; Chen, M.; Asefa, T.; Chhowalla, M. Covalent Functionalization of Monolayered Transition Metal Dichalcogenides by Phase Engineering. *Nat. Chem.* **2015**, *7*, 45–49; Ries, L.; Petit, E.; Michel, T.; Diogo, C. C.; Gervais, C.; Salameh, C.; Bechelany, M.; Balme, S.; Miele, P.; Onofrio, N.; Voiry, D. Enhanced Sieving from Exfoliated MoS₂ Membranes via Covalent Functionalization. *Nat. Mater.* **2019**, *18*, 1112–1117) or radical-initiated species such as diazonium salts (Knirsch, K. C.; Berner, N. C.; Nerl, H. C.; Cucinotta, C. S.; Gholamvand, Z.; McEvoy, N.; Wang, Z.; Abramovic, I.; Vecera, P.; Halik, M.; Sanvito, S.; Duesberg, G. S.; Nicolosi, V.; Hauke, F.; Hirsch, A.; Coleman, J. N.; Backes, C. Basal-Plane Functionalization of Chemically Exfoliated Molybdenum Disulfide by Diazonium Salts. *ACS Nano* **2015**, *9*, 6018–6030), and alkyl azide (Tuci, G.; Mosconi, D.; Rossin, A.; Luconi, L.; Agnoli, S.; Righetto, M.; Pham-Huu, C.; Ba, H.; Cicchi, S.; Granozzi, G.; Giambastiani, G. Surface Engineering of Chemically Exfoliated MoS₂ in a “Click”: How To Generate Versatile Multifunctional Transition Metal Dichalcogenides-Based Platforms. *Chem. Mater.* **2018**, *30*, 8257–8269). Though, phase transformation diminishes the semiconducting characteristics, while an additional phase reversion, typically involving heat, generates defects and chemical transformation.

[0174] Without being bound by theory, we hypothesize that instead of complete conversion to metallic phase, a milder reductant could donate a sufficient number of electrons into the antibonding orbitals of semiconducting TMDs without inducing phase transformation. This approach would potentially allow for subsequent covalent functionalization. To test our hypothesis, we chose NHCs, owing to their mild electron donating feature (Hopkinson, M. N.; Richter, C.; Schedler, M.; Glorius, F. An Overview of *N*-Heterocyclic Carbenes. *Nature* **2014**, *510*, 485–496). Surprisingly, experimental observations exceeded our initial hypotheses. Upon interaction with group VI TMDs, NHCs possess the capability to remain on the basal plane of 2D

monolayered TMD nanosheets and subsequently drive a restacking phenomenon, giving to the entrapment of NHCs between the single layers of TMDs. This interaction is surprising since the bulky NHCs head groups are not expected to achieve an intercalation state within group VI TMD hosts. Moreover, the inertness of group VI TMDs limits the intercalation possibilities, which was previously believed to be exclusively driven by dual-charged host-guest systems (Heising, J.; Kanatzidis, M. G. Exfoliated and Restacked MoS₂ and WS₂: Ionic or Neutral Species? Encapsulation and Ordering of Hard Electropositive Cations. *J. Am. Chem. Soc.* **1999**, *121*, 11720–11732). As such, the previously reported strategies involved the use of small metallic cations or dual process of restacking and guest entrapment in chemically exfoliated few- to monolayered TMDs (Divigalpitiya, W. M. R.; Frindt, R. F.; Morrison, S. R. Inclusion Systems of Organic Molecules in Restacked Single-Layer Molybdenum Disulfide. *Science* **1989**, *246*, 369–371; Tagaya, H.; Hashimoto, T.; Karasu, M.; Izumi, T.; Chiba, K. Inclusion of Substituted Ferrocenes and Aromatic Compounds into MoS₂ Layers as New Intercalation Compounds. *Chem. Lett.* **1991**, *20*, 2113–2116. *Chem. Lett.* **1991**, *20*, 2113–2116; Bissessur, R.; Heising, J.; Hirpo, W. Toward Pillared Layered Metal Sulfides. Intercalation of the Chalcogenide Clusters Co₆Q₈(PR₃)₆ (Q = S, Se, and Te and R = Alkyl) into MoS₂. *Chem. Mater.* **1996**, *8*, 318–320; Brenner, J.; Marshall, C. L.; Ellis, L.; Tomczyk, N.; Heising, J.; Kanatzidis, M. Microstructural Characterization of Highly HDS-Active Co₆S₈-Pillared Molybdenum Sulfides. *Chem. Mater.* **1998**, *10*, 1244–1257; Kosidowski, L.; Powell, A. V. Naphthalene Intercalation into Molybdenum Disulfide. *Chem. Commun.* **1998**, 2201–2202). In either case, excessive electrons were injected into the host framework, inducing a metallic phase transformation. In our work described herein, the original exfoliated TMDs, and the resultant intercalated materials preserve the semiconducting characteristics. To our knowledge, such an observation has not been reported.

[0175] Herein, we present the first experimental functionalization of 2D few-to-monolayered MoS₂ and WS₂ using NHCs, in the form of benzimidazolium salts. The adopted molecule, labeled as NHC15OH[OMs] is shown in FIG. 27). The bulk MoS₂ and WS₂ were initially exfoliated to obtain few- to monolayered nanosheets using the redox exfoliation methods (Jawaid, A.; Che, J.; Drummy, L. F.; Bultman, J.; Waite, A.; Hsiao, M.-S.; Vaia, R. A. Redox Exfoliation of Layered Transition Metal Dichalcogenides. *ACS Nano* **2017**, *11*, 635–646; Jawaid, A. M.; Ritter, A. J.; Vaia, R. A. Mechanism for Redox Exfoliation of Layered Transition Metal Dichalcogenides. *Chem. Mater.* **2020**, *32*, 6550–6565). Herein, we demonstrate that the NHCs

interact with the basal plane of exfoliated 2D MoS₂ and WS₂ nanosheets, replacing the surface-adsorbed redox products and consequently altering the surface Zeta potential. Without being bound by theory, the interaction nature between NHCs and exfoliated TMDs is hypothesized to involve orbital hybridization, leading to a restacking phenomenon. As a result, the NHC molecules become entrapped within the interlayer gaps of the TMDs, thereby forming superlattice structures signified by interlayer expansion. The molecular entrapment and interlayer expansion are characterized by X-ray powder diffraction (XRD), attenuated total reflectance infrared spectroscopy (ATR), and X-ray photoelectron spectroscopy (XPS). The implications of intercalated NHCs are further elaborated upon using Raman spectroscopy, with complementary insights drawn from observations made via photoluminescence (PL), XPS, atomic force microscopy (AFM), scanning electron microscopy (SEM), in conjunction with centrifuge cascade and thin film fabrication methodologies.

[0176] Redox Exfoliation of Few- to Monolayered TMD Nanosheets

[0177] Exfoliation of pre-treated bulk MoS₂ and WS₂ was carried out, following the reported procedures, with minor adjustments (Jawaid, A.; Che, J.; Drummy, L. F.; Bultman, J.; Waite, A.; Hsiao, M.-S.; Vaia, R. A. Redox Exfoliation of Layered Transition Metal Dichalcogenides. *ACS Nano* **2017**, *11*, 635–646; Jawaid, A. M.; Ritter, A. J.; Vaia, R. A. Mechanism for Redox Exfoliation of Layered Transition Metal Dichalcogenides. *Chem. Mater.* **2020**, *32*, 6550–6565). (see Experimental section herein). After thorough removal of the adsorbed polyoxometalates macroanions (POMs), a centrifuge screening process was employed to isolate thin-layered nanosheets. The ultraviolet-visible spectroscopy (UV-vis) data, shown in FIG. 18A, depicts the extinction (ϵ) spectra of exfoliated MoS₂ colloidal fractions at four different centrifuge rates. The spectra combine the aspects of both absorbance (α) and size-dependent scattering (σ) background; hence, pertinent information can be extracted for approximate estimation of the thicknesses and lateral sizes of exfoliated MoS₂ nanosheets. A comprehensive study was conducted, highlighting the significance of evolving thicknesses and lateral sizes of liquid-phase-exfoliated nanosheets (Backes, C.; Smith, R. J.; McEvoy, N.; Berner, N. C.; McCloskey, D.; Nerl, H. C.; O'Neill, A.; King, P. J.; Higgins, T.; Hanlon, D.; Scheuschner, N.; Maultzsch, J.; Houben, L.; Duesberg, G. S.; Donegan, J. F.; Nicolosi, V.; Coleman, J. N. Edge and Confinement Effects Allow in Situ Measurement of Size and Thickness of Liquid-Exfoliated Nanosheets. *Nat. Commun.* **2014**, *5*, 4576; Backes, C.; Higgins, T. M.; Kelly, A.; Boland, C.; Harvey, A.; Hanlon,

D.; Coleman, J. N. Guidelines for Exfoliation, Characterization and Processing of Layered Materials Produced by Liquid Exfoliation. *Chem. Mater.* **2017**, *29*, 243–255). An important feature is the local minimum at 345 nm, extrapolated from statistical data set as an independent metric, free from the influence of scattering effects. This feature serves as a reference point for normalization in comparative analysis. Based on these aforementioned reports, our data, in FIG. 18A, delineates the normalized extinction spectra of exfoliated MoS₂. It is worth highlighting that increasing centrifuge rate results in thinner and smaller nanosheets, (Backes, C.; Smith, R. J.; McEvoy, N.; Berner, N. C.; McCloskey, D.; Nerl, H. C.; O'Neill, A.; King, P. J.; Higgins, T.; Hanlon, D.; Scheuschner, N.; Maultzsch, J.; Houben, L.; Duesberg, G. S.; Donegan, J. F.; Nicolosi, V.; Coleman, J. N. Edge and Confinement Effects Allow in Situ Measurement of Size and Thickness of Liquid-Exfoliated Nanosheets. *Nat. Commun.* **2014**, *5*, 4576; Backes, C.; Higgins, T. M.; Kelly, A.; Boland, C.; Harvey, A.; Hanlon, D.; Coleman, J. N. Guidelines for Exfoliation, Characterization and Processing of Layered Materials Produced by Liquid Exfoliation. *Chem. Mater.* **2017**, *29*, 243–255) which emphasizes the discussed phenomenon in the region from 700 to 800 nm. In the spectral range from 700 to 350 nm, the excitonic peaks of MoS₂ were designated as A, B, C, D from right to left, respectively. Among these excitons, A presents the K-point transition from valence band to conduction band, which demonstrates the band gap of material. Consequently, A-excitonic wavelength can be employed to infer the thicknesses of MoS₂ nanosheets, owing to the layer-dependent characteristics. Nevertheless, within the range below 700 nm, the dominance of scattering background necessitates the conversion of the original extinction spectrum into its second derivatives. This mathematical transformation was recommended as an essential data processing step to reduce the peak shift caused by the broad background (Backes, C.; Smith, R. J.; McEvoy, N.; Berner, N. C.; McCloskey, D.; Nerl, H. C.; O'Neill, A.; King, P. J.; Higgins, T.; Hanlon, D.; Scheuschner, N.; Maultzsch, J.; Houben, L.; Duesberg, G. S.; Donegan, J. F.; Nicolosi, V.; Coleman, J. N. Edge and Confinement Effects Allow in Situ Measurement of Size and Thickness of Liquid-Exfoliated Nanosheets. *Nat. Commun.* **2014**, *5*, 4576; Backes, C.; Higgins, T. M.; Kelly, A.; Boland, C.; Harvey, A.; Hanlon, D.; Coleman, J. N. Guidelines for Exfoliation, Characterization and Processing of Layered Materials Produced by Liquid Exfoliation. *Chem. Mater.* **2017**, *29*, 243–255). The second derivative transformation of A exciton is presented in FIG. 18B with the x-axis unit in energy (eV). As expected, at a high centrifuge rate of 2500 rpm, the resultant exfoliated MoS₂ nanosheets exhibit their minimum

thicknesses with an approximate A-excitonic transition of 1.85 eV ($\lambda_A = 671$ nm). In contrast, the thicker ones are observed when A-excitonic transition energy falls below 1.85 eV at lower centrifuge rates. The full second derivative transformation and A-excitonic wavelengths at different centrifuge rates are shown in FIG. 30A – FIG. 30B and FIG. 18C. Compared to the fitted models and corresponding reported equations, (Jawaid, A. M.; Ritter, A. J.; Vaia, R. A. Mechanism for Redox Exfoliation of Layered Transition Metal Dichalcogenides. *Chem. Mater.* **2020**, *32*, 6550–6565; Backes, C.; Smith, R. J.; McEvoy, N.; Berner, N. C.; McCloskey, D.; Nerl, H. C.; O'Neill, A.; King, P. J.; Higgins, T.; Hanlon, D.; Scheuschner, N.; Maultzsch, J.; Houben, L.; Duesberg, G. S.; Donegan, J. F.; Nicolosi, V.; Coleman, J. N. Edge and Confinement Effects Allow in Situ Measurement of Size and Thickness of Liquid-Exfoliated Nanosheets. *Nat. Commun.* **2014**, *5*, 4576; Backes, C.; Higgins, T. M.; Kelly, A.; Boland, C.; Harvey, A.; Hanlon, D.; Coleman, J. N. Guidelines for Exfoliation, Characterization and Processing of Layered Materials Produced by Liquid Exfoliation. *Chem. Mater.* **2017**, *29*, 243–255) the resultant exfoliated MoS₂ nanosheets exhibit thicknesses varying from 4–7 layers. However, it is imperative to emphasize that UV-vis extinction spectrum only provides an approximate estimation about thicknesses of predominant population of nanosheets. As mentioned, scattering background plays a key role in understanding thickness-related aspects. In addition, the inherent nature of redox exfoliation, which leads to the absorption of POMs on the surface of 2D TMD nanosheets, might contribute to the peak shifts. This effect might be pronounced when POMs species exhibit comparable sizes, at least 1 nm in height (Jawaid, A. M.; Ritter, A. J.; Vaia, R. A. Mechanism for Redox Exfoliation of Layered Transition Metal Dichalcogenides. *Chem. Mater.* **2020**, *32*, 6550–6565). The surface absorption of negatively charged POMs is supported by comparing the Zeta potentials of redox-exfoliated MoS₂ and sonication-induced exfoliated MoS₂, shown in FIG. 18D. A similar observation was recorded, shown in FIG. 31A – FIG. 31D, with redox-exfoliated WS₂ (ϵ_{235} as normalization metric).

[0178] As complementary data, statistical analysis based on height retrace from AFM was conducted. The height profiles of redox-exfoliated MoS₂ dispersion are presented in FIG. 19A – FIG. 19H. It is crucial to note that the actual thickness of a single layer is not identical to the theoretical one, owing to factors such as solvent effects and the presence of POMs absorbed on the nanosheets' surface. To address this issue, an internal reference, known as “step height”, is employed (Jawaid, A. M.; Ritter, A. J.; Vaia, R. A. Mechanism for Redox Exfoliation of Layered

Transition Metal Dichalcogenides. *Chem. Mater.* **2020**, *32*, 6550–6565; Backes, C.; Smith, R. J.; McEvoy, N.; Berner, N. C.; McCloskey, D.; Nerl, H. C.; O'Neill, A.; King, P. J.; Higgins, T.; Hanlon, D.; Scheuschner, N.; Maultzsch, J.; Houben, L.; Duesberg, G. S.; Donegan, J. F.; Nicolosi, V.; Coleman, J. N. Edge and Confinement Effects Allow in Situ Measurement of Size and Thickness of Liquid-Exfoliated Nanosheets. *Nat. Commun.* **2014**, *5*, 4576; Backes, C.; Higgins, T. M.; Kelly, A.; Boland, C.; Harvey, A.; Hanlon, D.; Coleman, J. N. Guidelines for Exfoliation, Characterization and Processing of Layered Materials Produced by Liquid Exfoliation. *Chem. Mater.* **2017**, *29*, 243–255). The solution is based on the observation that incomplete exfoliation results in staircase-like height profile. As illustrated in our data, a step height of approximate 2.0 to 3.0 nm was found and attributed to the thickness of a single layer, which is consistent with previous reports (Jawaid, A. M.; Ritter, A. J.; Vaia, R. A. Mechanism for Redox Exfoliation of Layered Transition Metal Dichalcogenides. *Chem. Mater.* **2020**, *32*, 6550–6565). Herein, we emphasize that statistical analysis is a time-intensive process and susceptible to misinterpretation of data due to the intricacies involved in samples preparation, given that the standard sample preparation method for AFM analysis typically involves extensive dilution and drop-casting. This results in random orientation of nanosheets and their tendency to self-aggregate. Fortunately, the issue can be effectively overcome by the recent self-assembled thin film formation technique (FIG. 28A – FIG. 28D) (Yu, X.; Prévot, M. S.; Guijarro, N.; Sivula, K. Self-Assembled 2D WSe₂ Thin Films for Photoelectrochemical Hydrogen Production. *Nat. Commun.* **2015**, *6*, 7596; Yun, T.; Kim, J.-S.; Shim, J.; Choi, D. S.; Lee, K. E.; Koo, S. H.; Kim, I.; Jung, H. J.; Yoo, H.-W.; Jung, H.-T.; Kim, S. O. Ultrafast Interfacial Self-Assembly of 2D Transition Metal Dichalcogenides Monolayer Films and Their Vertical and In-Plane Heterostructures. *ACS Appl. Mater. Interfaces* **2017**, *9*, 1021–1028). By leveraging this method, uniform and flat lying nanosheets can be achieved on the deposited substrates, facilitating the population height retrace analysis of 2D exfoliated TMDs (FIG. 32A – FIG. 32E). According to the height profile analysis of over 300 exfoliated MoS₂ nanosheets, we deduced the average thickness of 9.7 ± 4.2 nm, corresponding to approximately 5 layers. To further validate the probed species being indeed exfoliated materials, we compared the height and amplitude retrace profiles (FIG. 33A – FIG. 33B) with the shape images captured by transmission electron microscopy (TEM) (FIG. 19E – FIG. 19H). Finally, XRD measurements were carried out to compare bulk and thin film exfoliated MoS₂ (FIG. 19D). As a consequence of restacking, the in-plane (hk0) reflections experience disappearance or substantial attenuation.

Meanwhile, (00l) reflections, attributed to the interlayer thickness, significantly enhances. Similar analyses for redox-exfoliated WS₂ are shown in FIG. 34A – FIG. 34E and FIG. 35A – FIG. 35D.

[0179] NHC-Functionalized Few- to Monolayered TMD Nanosheets

[0180] Having successfully attained few- to monolayered MoS₂ and WS₂ nanosheets, we proceeded with functionalization experiments involving NHC15OH[OMs] adsorbate and the exfoliated TMDs. Following the complete dissolution of the molecule in dichloromethane (DCM), redox-exfoliated MoS₂ in anhydrous acetonitrile (a-ACN) was introduced, and the system was allowed to stand undisturbed for 24 h. Typically, depending on the molar ratio between the NHCs and the redox-exfoliated MoS₂, abrupt compression resulting in precipitation could be directly observed within a matter of minutes. The resultant black powder was centrifuged and washed by DCM to remove unreacted NHCs. FIG. 20A illustrates the XRD patterns of thin film NHC15OH[OMs]-functionalized MoS₂. Interestingly, diffraction patterns of the novel material reveal two distinct and prominent peaks at 7.98 and 24.25 (2 θ), which can be attributed to the molecular intercalation occurring between MoS₂ layers. We assign these new peaks corresponding to the (002') and (006') reflections of the novel phase with an expanded interlayer gap of 11.1 Å compared to 6.1 Å observed in bulk MoS₂. FIG. 36 presents a comparative analysis of the XRD pattern between powder NHC15OH[OMs] and the magnified XRD pattern of NHC15OH[OMs]-functionalized MoS₂. Within the magnified XRD pattern, the appearance of small peaks, which are negligible and similar to those observed in powder NHC15OH[OMs], indicates molecular crystallization within the structure of intercalated host. To further offer complementary evidence of interlayer entrapped NHCs, ATIR measurements were conducted on thin film samples (FIG. 20B). XPS spectra also validate the presence of NHC molecules within the NHC-functionalized samples. Only NHC-functionalized MoS₂ and NHC-functionalized WS₂ exhibit the emergence of N 1s peaks at 401.5 eV and the additional S 2p peaks at 170 eV (FIG. 21A – FIG. 21D and FIG. 37A – FIG. 37D). These peaks are attributed to the N atoms constituting the *N*-heterocyclic ring and S⁶⁺ atoms within the methanesulfonate groups, respectively. Subsequently, the zeta potential of the anticipated NHC-functionalized MoS₂ was collected, providing a preliminary assessment of the surface characteristics (FIG. 20C). Upon interaction with NHCs, the resultant material demonstrates a positive surface potential shift, compared to that of redox-exfoliated MoS₂. Without being bound by theory, we hypothesize that POMs are desorbed from TMDs surface, and replaced by NHCs, which remain strongly bound, thereby destabilizing the system. This is

followed by a self-restacking process, forming a superlattice, characterized by the expanded vdW interlayer gaps of 2D layered materials (FIG. 20D).

[0181] In pursuit of achieving a complete intercalation state, a series of samples was prepared by increasing the reacted molar ratio of NHCs to TMDs. The concentration of redox-exfoliated MoS₂ (and WS₂) within the as-prepared colloidal solution was systematically extrapolated, followed by a titration procedure (details in Experimental section herein). Surprisingly, at a high molar ratio of 15, trace amounts of multilayered MoS₂ are still detected on the XRD patterns, as evidenced at pronouncing (00l) and (h0l) reflections. Based on reported works, it was established that at the stage of complete intercalation, intercalated 2D layered TMDs typically illustrate a complete set of (00l) reflections (Pereira, J. M.; Tezze, D.; Niehues, I.; Asensio, Y.; Yang, H.; Mester, L.; Chen, S.; Casanova, F.; Bittner, A. M.; Ormaza, M.; Schiller, F.; Martín-García, B.; Hillenbrand, R.; Hueso, L. E.; Gobbi, M. Percolating Superconductivity in Air-Stable Organic-Ion Intercalated MoS₂. *Adv. Funct. Mater.* **2022**, 32, 2208761). In contrast, our data set consistently reveals only two reflections, namely (002') and (006'). Without being bound by theory, we reason that there might be three plausible explanations for this experimental observation. First, most prior works reported the intercalation of 2D layered TMDs followed by Li intercalation-induced exfoliation, which caused a phase transformation from the inherent 1H to 1T at the monolayered architecture. These two phases demonstrate fundamental structural difference, leading to variation in the stacking sequence of Mo and two S layers (Chhowalla, M.; Shin, H. S.; Eda, G.; Li, L.-J.; Loh, K. P.; Zhang, H. The Chemistry of Two-Dimensional Layered Transition Metal Dichalcogenide Nanosheets. *Nat. Chem.* **2013**, 5, 263–275). Given that 1T phase stacks in an AbC AbC order while 2H stacks in an AbA BaB order, the restacked materials after intercalation promote ordered symmetry along the direction perpendicular to the basal plane of TMDs. In our case, the exfoliated TMDs retained their initial semiconducting 2H (or 1H at monolayer) phase after redox exfoliation, as evidenced in XPS spectra (FIG. 21A – FIG. 21D). The transformation to 1T phase could be distinctly observed through the shift of both Mo 3d and S 2p peaks to lower binding energies (Fan, X.; Xu, P.; Li, Y. C.; Zhou, D.; Sun, Y.; Nguyen, M. A. T.; Terrones, M.; Mallouk, T. E. Controlled Exfoliation of MoS₂ Crystals into Trilayer Nanosheets. *J. Am. Chem. Soc.* **2016**, 138, 5143–5149). Secondly, we suspect that the introduction of NHCs abruptly alters the surface properties of redox-exfoliated TMDs, destabilizing the entire system and leading to rapid agglomeration. To address this hypothesis, a control experiment was

set up, detailed in the Experimental section herein. Shortly, following complete intercalation and restacking process, the resultant mixture was sonicated to redisperse agglomerate materials. The system was allowed to stand undisturbed, which gives to a second re-stacking process. This procedure was optionally repeated several times to achieve a set of 5 samples, then subjected to XRD measurements. FIG. 38 depicts the XRD patterns of 15-NHC/MoS₂ samples, which remain negligible change across different sonicating-restacking cycles. The data suggests the system achieving an equilibrium state no matter how aggressive disturbance was introduced. On the other hand, a minor peak emerges at a lower angle of 6.77 (2 θ), suggesting an expansion of the MoS₂ interlayer space by 13.0 Å. The novel reflection indicates a slight disruption of molecular orientation after successive dispersing and restacking processes, while the (002') reflection remains prominent. We then comprehend that additional superlattice structures might exist. Considering the elongated alkyl chain of the NHCs tail group and a comparison with the thickness of SAMs on a planar flat Au substrate (Choi, Y.; Park, C. S.; Tran, H.-V.; Li, C.-H.; Crudden, C. M.; Lee, T. R. Functionalized *N*-Heterocyclic Carbene Monolayers on Gold for Surface-Initiated Polymerizations. *ACS Appl. Mater. Interfaces* **2022**, *14*, 44969–44980) a broadened interlayer gap of only 5 Å renders the formation of NHCs arranged in a potentially flat bilayer-manner between two TMD monolayers. This geometric understanding is supported by prior observations employing aromatic ring systems such as metallocene, naphthalene, etc. (Divigalpitiya, W. M. R.; Frindt, R. F.; Morrison, S. R. Inclusion Systems of Organic Molecules in Restacked Single-Layer Molybdenum Disulfide. *Science* **1989**, *246*, 369–371; Tagaya, H.; Hashimoto, T.; Karasu, M.; Izumi, T.; Chiba, K. Inclusion of Substituted Ferrocenes and Aromatic Compounds into MoS₂ Layers as New Intercalation Compounds. *Chem. Lett.* **1991**, *20*, 2113–2116; Kuo, D.-Y.; Rice, P. S.; Raugei, S.; Cossairt, B. M. Charge Transfer in Metallocene Intercalated Transition Metal Dichalcogenides. *J. Phys. Chem. C* **2022**, *126*, 13994–14002). In addition, it has been reported that the intercalation of alkylamines with shorter alkyl chain length was able to expand the interlayer space to a greater extent (Jeong, S.; Yoo, D.; Ahn, M.; Miró, P.; Heine, T.; Cheon, J. Tandem Intercalation Strategy for Single-Layer Nanosheets as an Effective Alternative to Conventional Exfoliation Processes. *Nat. Commun.* **2015**, *6*, 5763). This might arise from the bulky carbene head groups that hinder the formation of densely packed SAMs in a standing-up configuration or from the preferential geometric hybridizations with π -electron organic molecules, which will be discussed in detail later. As a result, we come up with the third hypothesis that the

functionalization is indeed limited owing to the incomplete exfoliation of TMDs, presented in the next section.

[0182] Limitation of NHC Functionalization due to Incomplete Exfoliation of TMDs

[0183] As previously stated, the redox exfoliation method yields an average thickness distribution of 4-7 layers. Considering the bulkiness of NHC15OH[OMs], it is conceivable that the functionalization process occurs primarily at the exposed basal plane of TMDs, rather than being capable of penetrating into the intrinsic vdW gap (6.1 Å) of few-layered TMDs. Consequently, the subsequent restacking leads to the formation of two distinct structures (FIG. 22A – FIG. 22B). Herein, it is crucial to note that XRD peaks arise strictly from a periodic arrangement within the crystal lattice. Therefore, the second structure (outer right), depicted in FIG. 22A – FIG. 22B, solely contributes to the (002) reflections, resembling the behavior observed in multilayered TMDs. Despite that, the additional presence of NHC layers, effectively separate exfoliated few-layered TMDs nanosheets, giving to the broadened full half width maximum (FMHW) of (002) peak. Akin to the observation in 15-NHC/MoS₂, 15-NHC/WS₂, shown in FIG. 39A – FIG. 39B, demonstrates analogous finding.

[0184] To furnish visual evidence of the incomplete exfoliation, we set up the centrifuge cascade experiment (FIG. 29) to collect exfoliated nanosheets at distinct fractions. Each fraction underwent screening via two different centrifuge rates enabling the custom selection of nanosheet thicknesses and sizes (Backes, C.; Higgins, T. M.; Kelly, A.; Boland, C.; Harvey, A.; Hanlon, D.; Coleman, J. N. Guidelines for Exfoliation, Characterization and Processing of Layered Materials Produced by Liquid Exfoliation. *Chem. Mater.* **2017**, *29*, 243–255). Next, we prepared thin-film redox-exfoliated TMDs on Si substrates and subjected them to SEM imaging for statistical size analysis (FIG. 23A – FIG. 23H). It is observed that fractions collected at higher screening centrifuge rates exhibit nanosheets with smaller lengths and widths. This observation aligns with the concurrent shift in both A and D excitonic transitions, which can be attributed to variations in thickness and size respectively (FIG. 23A – FIG. 23D). Ultimately, the flat lying nanosheets reveal clear evidence of incomplete exfoliation, as indicated by the edge effects (FIG. 32A – FIG. 32E). FIG. 23I – FIG. 23N depicts the size distribution of 2D exfoliated few- to monolayered TMD nanosheets. Two metrics, maximum width and length, are employed for this statistical analysis, which reveals an evident shift to smaller sizes among four separated fractions.

[0185] Doping Effects of NHC15OH[OMs] Adsorbates

[0186] Chemical structures, core energy levels and electronic properties of NHC-functionalized TMDs were extracted under XPS investigations. All spectra were initially calibrated by C 1s peak at 284.8 eV. In FIG. 21A – FIG. 21D, no trace of 1T-metallic phase presents, the redox-exfoliated MoS₂ remain semiconducting 2H (1H at monolayer) after exfoliation. Typically, variation in spectra shape of Mo 3d and S 2p energy levels is negligible. Without being bound by theory, this indication suggests that the interactions between NHC15OH[OMs] and MoS₂ involve other mechanisms rather than covalent bonds. Indeed, both Mo 3d and S 2p spectra exhibit a slight shift of 0.3 eV to the lower binding energy. We then exploited the XPS low binding energy region (0-20 eV), to analyze the disparity between the material's Fermi level (E_F) and valence band (E_{VB}). By extrapolating the slopes of the low energy spectra, we deduced the energy difference $E_F - E_{VB}$ to be 0.9 and 1.2 eV for 15-NHC/MoS₂ and redox-exfoliated MoS₂, respectively (FIG. 40A – FIG. 40D). It illustrates that the adopted NHC15OH[OMs] slightly elevates the valence band by donating a gentle number of electrons into MoS₂ framework. A similar analysis was performed with redox-exfoliated WS₂ and 15-NHC/WS₂, shown in FIG. 37A – FIG. 37D and FIG. 41A – FIG. 41B, which achieved an identical observation. In this context, it is crucial to highlight that at the monolayered architecture, signified by a sub-nanometer thickness, the ultra-thin atomic resolution enhances the multifaced effects of physisorbed heterojunctions. These effects are governed by mechanisms such as simple charge transfer model, dielectric screening effect, vectorial dipole-dipole interactions, among others (Zhao, Y.; Gobbi, M.; Hueso, L. E.; Samori, P. Molecular Approach to Engineer Two-Dimensional Devices for CMOS and beyond-CMOS Applications. *Chem. Rev.* **2022**, *122*, 50–131). Consequently, a simple adsorbed molecular system could significantly perturb the energy alignments, giving to alteration of electron-phonon scattering throughout the entire 2D crystal lattice. Given the periodic nature of electron-phonon scattering, slight changes provide indication of structural alterations. In the case of 2D monolayered TMDs, electron-phonon characteristics can be elucidated through two significant vibration modes in the Raman spectra: the E'_{2g} phonon mode, representing an in-plane vibration involving both transition metal and chalcogen atoms, and the A_{1g} mode, depicting an out-of-plane vibration, solely involving chalcogen atoms. Depending on the directional shift of these two modes, deduction regarding n- or p-type doping effects can be determined. This phenomenon has been extensively studied and reported in systems involving molecular SAMs on monolayered TMDs (Kang, D.-H.; Kim, M.-S.; Shim, J.; Jeon, J.; Park, H.-

Y.; Jung, W.-S.; Yu, H.-Y.; Pang, C.-H.; Lee, S.; Park, J.-H. High-Performance Transition Metal Dichalcogenide Photodetectors Enhanced by Self-Assembled Monolayer Doping. *Adv. Funct. Mater.* **2015**, *25*, 4219–4227; Tarasov, A.; Zhang, S.; Tsai, M.-Y.; Campbell, P. M.; Graham, S.; Barlow, S.; Marder, S. R.; Vogel, E. M. Controlled Doping of Large-Area Trilayer MoS₂ with Molecular Reductants and Oxidants. *Adv. Mater.* **2015**, *27*, 1175–1181; Zhang, S.; Hill, H. M.; Moudgil, K.; Richter, C. A.; Hight Walker, A. R.; Barlow, S.; Marder, S. R.; Hacker, C. A.; Pookpanratana, S. J. Controllable, Wide-Ranging n-Doping and p-Doping of Monolayer Group 6 Transition-Metal Disulfides and Diselenides. *Adv. Mater.* **2018**, *30*, 1802991). Therefore, we performed Raman spectroscopic studies to explore the doping effects of NHC15OH[OMs] on the phonons of TMDs. Additionally, for systematic and comprehensive data collection, all samples were deposited onto 300 nm SiO₂/Si substrates, taking advantage of the Si optical transverse vibration mode as an internal reference. To avoid ambient moisture adsorption, which has been reported to partially dope TMDs, (Tongay, S.; Zhou, J.; Ataca, C.; Liu, J.; Kang, J. S.; Matthews, T. S.; You, L.; Li, J.; Grossman, J. C.; Wu, J. Broad-Range Modulation of Light Emission in Two-Dimensional Semiconductors by Molecular Physisorption Gating. *Nano Lett.* **2013**, *13*, 2831–2836) after complete solvent evaporation, the samples were stored in an environment enriched with CaSO₄ desiccant under vacuum prior to any measurements.

[0187] FIG. 24A – FIG. 24F summarizes the Raman spectra and the corresponding characteristics of the E_{12g} and A_{1g} vibration modes of redox-exfoliated MoS₂ before and after exposure to NHCs. We note that Raman spectra of all three points of 15-NHC/MoS₂ were acquired within the same day. Hence, even though the Si optical transverse mode completely diminishes in 15-NHC/MoS₂ P3 due to the thick layer of deposited materials, peak shift compared to the remaining two points is avoided. Based on the collected data, both E_{12g} and A_{1g} modes within 15-NHC/MoS₂ P1 and P2 exhibit a red shift, which is indicative of softening effect attributed to n-doping (Kang, D.-H.; Kim, M.-S.; Shim, J.; Jeon, J.; Park, H.-Y.; Jung, W.-S.; Yu, H.-Y.; Pang, C.-H.; Lee, S.; Park, J.-H. High-Performance Transition Metal Dichalcogenide Photodetectors Enhanced by Self-Assembled Monolayer Doping. *Adv. Funct. Mater.* **2015**, *25*, 4219–4227; Tarasov, A.; Zhang, S.; Tsai, M.-Y.; Campbell, P. M.; Graham, S.; Barlow, S.; Marder, S. R.; Vogel, E. M. Controlled Doping of Large-Area Trilayer MoS₂ with Molecular Reductants and Oxidants. *Adv. Mater.* **2015**, *27*, 1175–1181; Zhang, S.; Hill, H. M.; Moudgil, K.; Richter, C. A.; Hight Walker, A. R.; Barlow, S.; Marder, S. R.; Hacker, C. A.; Pookpanratana, S. J. Controllable,

Wide-Ranging n-Doping and p-Doping of Monolayer Group 6 Transition-Metal Disulfides and Diselenides. *Adv. Mater.* **2018**, *30*, 1802991). Another notable feature is the broadening and the evolving asymmetry of both E_{12g} and A_{1g} peaks at P1 and P2 points. To elucidate this phenomenon, we extracted the FMHWs of both peaks and their Raman shifts for comparison, depicted in FIG. 24C, FIG. 24F. It is observed that as the E_{12g} and A_{1g} modes undergo further red shift, their FMHWs broaden accordingly. This leads us to understand that NHC15OH[OMs] adsorbates transfer their electrons, which dissipate and delocalize over the finite 2D plane of TMD monolayers. Interestingly, the extent of the shift differs between two points while 15-NHC/MoS₂ P3 shows no changes compared to redox-exfoliated MoS₂. This can be explained by the different restacked structures, as evidenced earlier. In the case of restacked few-layered structures (P3), a small amount of intercalated NHCs exhibits negligible impact. In contrast, a rich intercalation of NHCs in restacked monolayered structure demonstrates a prominent impact, which varies as a function of the entrapped NHC content. We also address that the E_{12g} mode was reported to remain intact or undergo insignificant changes in both peak position and the FMHW, either in monolayered MoS₂ or in hybrid SAMs and monolayered MoS₂ systems (Lee, C.; Yan, H.; Brus, L. E.; Heinz, T. F.; Hone, J.; Ryu, S. Anomalous Lattice Vibrations of Single- and Few-Layer MoS₂. *ACS Nano* **2010**, *4*, 2695–2700; Li, H.; Zhang, Q.; Yap, C. C. R.; Tay, B. K.; Edwin, T. H. T.; Olivier, A.; Baillargeat, D. From Bulk to Monolayer MoS₂: Evolution of Raman Scattering. *Adv. Funct. Mater.* **2012**, *22*, 1385–1390; Wang, C.; He, Q.; Halim, U.; Liu, Y.; Zhu, E.; Lin, Z.; Xiao, H.; Duan, X.; Feng, Z.; Cheng, R.; Weiss, N. O.; Ye, G.; Huang, Y.-C.; Wu, H.; Cheng, H.-C.; Shakir, I.; Liao, L.; Chen, X.; Goddard III, W. A.; Huang, Y.; Duan, X. Monolayer Atomic Crystal Molecular Superlattices. *Nature* **2018**, *555*, 231–236; He, Q.; Lin, Z.; Ding, M.; Yin, A.; Halim, U.; Wang, C.; Liu, Y.; Cheng, H.-C.; Huang, Y.; Duan, X. In Situ Probing Molecular Intercalation in Two-Dimensional Layered Semiconductors. *Nano Lett.* **2019**, *19*, 6819–6826; Zhou, B.; Zhou, J.; Wang, L.; Kang, J. H.; Zhang, A.; Zhou, J.; Zhang, D.; Xu, D.; Hu, B.; Deng, S.; Huang, L.; Wong, C. W.; Huang, Y.; Duan, X. A Chemical-Dedoping Strategy to Tailor Electron Density in Molecular-Intercalated Bulk Monolayer MoS₂. *Nat. Synth.* **2024**, *3*, 67–75). However, in our case, pronounced shift and broadened FMHW were recorded (~ 3.5 cm⁻¹ in P1). In the case of 15-NHC/WS₂, red shift and broadened peaks were also recorded in FIG. 42A – FIG. 42F. We reason that the effect is not as prominent as that of MoS₂ due to the ineffective functionalization, shown in FIG. 39A – FIG. 39B. Finally, the A_{1g} - E_{12g} peak separation was

extracted in FIG. 43A – FIG. 43B. As previously documented, the A_{1g} - E'_{2g} - A_{1g} peak separation is approximately 19 cm^{-1} for MoS_2 monolayers. At four layers and thicker, it is consistently 25 cm^{-1} (Lee, C.; Yan, H.; Brus, L. E.; Heinz, T. F.; Hone, J.; Ryu, S. Anomalous Lattice Vibrations of Single- and Few-Layer MoS_2 . *ACS Nano* **2010**, *4*, 2695–2700; Li, H.; Zhang, Q.; Yap, C. C. R.; Tay, B. K.; Edwin, T. H. T.; Olivier, A.; Baillargeat, D. From Bulk to Monolayer MoS_2 : Evolution of Raman Scattering. *Adv. Funct. Mater.* **2012**, *22*, 1385–1390). Instead, we observed a consistent separation around 25 cm^{-1} for all 15-NHC/ MoS_2 taken points, including the restacked redox-exfoliated MoS_2 . This phenomenon will be examined in detail in the coming section, which discusses the NHC functionalization of individual redox-exfoliated MoS_2 fractions.

[0188] Tailoring Superlattice Structures

[0189] Since the behavior of NHC-functionalized TMDs are hindered by incomplete exfoliation, we employed isolated MoS_2 fractions, achieved through centrifuge cascade, and subjected them to exposure with NHC15OH[OMs] adsorbates. As depicted in FIG. 23A – FIG. 23N, in addition to reduced nanosheet sizes, fractions collected at higher centrifuge rates will result in thinner thicknesses and a richer population of monolayers. Hence, complete functionalization is presumable, characterized by the exclusive appearance of $(002')$ and $(006')$ reflections (FIG. 20A - FIG. 20D). However, experimental data reveal an unexpected phenomenon. We designate fractions collected at 2000-2500 rpm, 2500-3000 rpm, 3000-4000 rpm, and >4000 rpm as F1, F2, F3, and F4 respectively. FIG. 25A shows the XRD patterns of 15-NHC/ MoS_2 using these four fractions. These patterns consistently display trace amount of multilayered MoS_2 nanosheets, even in the final fraction F4. This suggests that the centrifuge cascade effectively collects not only thinner nanosheets but also smaller few-layered nanosheets. Remarkably, two superlattice structures are clearly identified as the sizes and thicknesses of MoS_2 nanosheets reduce. In the case of 15-NHC/ MoS_2 F1, the predominant superlattice structure is indicated by the $(002')$ reflection at $7.98 (2\theta)$; we refer to this phase as $(002')$. Conversely, the remaining three fractions showcase a different favored phase at the lower angle $6.77 (2\theta)$, which corresponds to an interlayer expansion of $13.0\text{ \AA}$, in contrast to interlayer space of $11.1\text{ \AA}$ observed at $7.98 (2\theta)$. We refer to both this newly observed reflection and the corresponding phase as (002^*) .

[0190] To investigate the excitonic characteristics of NHC-functionalized TMDs, the resultant materials of each fraction were redispersed in a-ACN by a brief bath sonication (approximately 30 seconds), following complete agglomeration and removal of unreacted

NHC15OH[OMs] species. We denote the sonication-induced redispersed samples as 15-NHC/MoS₂ RS F_x, where F_x represents for the labeled fractions. The normalized extinction spectrum and the corresponding 2nd derivatives are shown in FIG. 25C and FIG. 25D, respectively. The data reveals that the A-B excitonic transitions in all 15-NHC/MoS₂ RS F_x fractions illustrate ambiguous alterations compared to those of the in-use redox-exfoliated MoS₂ fractions in a-ACN. In contrast, the extinction intensity and spectra shape, particularly in the low wavelength range of 200-300 nm, change significantly. It is noteworthy that the spectra shape and extinction intensity in this lower wavelength region are influenced by the scattering background of light, indirectly indicating an overall modification in morphology of the NHC-functionalized MoS₂ nanosheets. Herein, we double-checked the local minimum ϵ_{345} to ensure that the normalization metric remained consistent across individual fractions, confirming the reliability of the normalization for comparing alterations in spectra shape. The first fraction, F1, and the last fraction, F4 - utilized as the boundary condition - show negligible variation in ϵ_{345} , remaining within acceptable experimental error margins (FIG. 50A – FIG. 50B). To further confirm that these observations originate from the configuration where NHC15OH[OMs] molecules remain on the basal plane of MoS₂ nanosheets and are undetached by sonication, we directly dropped 15-NHC/MoS₂ RS F_x fractions onto glasses and subjected to XRD measurement (FIG. 25B). On the other hand, we realize that NHC15OH[OMs] is poorly soluble in a-ACN, likely due to its superior polarity compared to DCM while the long carbon alkyl chain of NHC15OH[OMs] exhibits nonpolar characteristics. Then, we performed an additional control experiment using DCM instead of a-ACN for the sonication-induced redispersion step (FIG. 44A – FIG. 44B). In both cases, the (002*) phase of 15-NHC/MoS₂ RS F4 in a-ACN or DCM remains, suggesting that NHCs are strongly bound onto the basal plane of the TMD nanosheets. The transition between (002') to (002*) is obviously spotted as the sizes and thicknesses of MoS₂ nanosheets reduce. A single (002*) phase is attained when employing the thinnest and smallest nanosheets, regardless of sonication. Nevertheless, the primary factor influencing the phase transition warrants further study, as the centrifuge cascade produces fractions containing both smaller and thinner nanosheets.

[0191] Nature of NHC-TMD Interaction

[0192] Seeking a comprehensive explanation of the fundamental interactions between NHCs and group VI TMDs (MoS₂ and WS₂ in this work), we have reviewed literature that claims the formation of covalent bonds. Reported evidence includes a significant change in XPS spectra

shape of the studied TMDs (Vera-Hidalgo, M.; Giovanelli, E.; Navío, C.; Pérez, E. M. Mild Covalent Functionalization of Transition Metal Dichalcogenides with Maleimides: A “Click” Reaction for 2H-MoS₂ and WS₂. *J. Am. Chem. Soc.* **2019**, *141*, 3767–3771; Kerwin, B.; Liu, S. E.; Sadhukhan, T.; Dasgupta, A.; Jones, L. O.; López-Arteaga, R.; Zeng, T. T.; Facchetti, A.; Schatz, G. C.; Hersam, M. C.; Marks, T. J. Trifluoromethylation of 2D Transition Metal Dichalcogenides: A Mild Functionalization and Tunable p-Type Doping Method. *Angew. Chem. Int. Ed.* **2024**, *63*, e202403494). In case of a dual-phase metallic 1T and semiconducting 1H, solid-state C¹³ NMR provides strong support if peak shift of the molecular carbon components is observed (Voiry, D.; Goswami, A.; Kappera, R.; Silva, C. de C. C. e; Kaplan, D.; Fujita, T.; Chen, M.; Asefa, T.; Chhowalla, M. Covalent Functionalization of Monolayered Transition Metal Dichalcogenides by Phase Engineering. *Nat. Chem.* **2015**, *7*, 45–49; Ries, L.; Petit, E.; Michel, T.; Diogo, C. C.; Gervais, C.; Salameh, C.; Bechelany, M.; Balme, S.; Miele, P.; Onofrio, N.; Voiry, D. Enhanced Sieving from Exfoliated MoS₂ Membranes via Covalent Functionalization. *Nat. Mater.* **2019**, *18*, 1112–1117). However, our current observations potentially suggest the presence of interactions beyond merely strongly covalent bonding or physisorbed heterojunctions. Without being bound by theory, we hypothesize that there are two potential scenarios for the interaction between NHCs and group VI TMDs. The first one might involve the orbital hybridization between the conjugated electron density of perpendicular π -orbitals of NHC aromatic rings and the out-of-plane orbitals of TMDs (FIG. 26A). The hybridization results in additional mixed electronic states, contributed from both NHCs and TMDs (Amsterdam, S. H.; Marks, T. J.; Hersam, M. C. Leveraging Molecular Properties to Tailor Mixed-Dimensional Heterostructures beyond Energy Level Alignment. *J. Phys. Chem. Lett.* **2021**, *12*, 4543–4557). As a consequence, it leads to a net change in electron density distribution, and an electron donation flows from one material to another. In our work described herein, a fraction of electrons flows from NHC15OH[OMs] adsorbates to MoS₂ or WS₂. Among prior works reporting heterojunctions between adsorbed π -organic molecules and monolayered group VI TMDs, we address comparable references studying perylene-derivatives. In case of 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA), its molecular structure renders a flat lying geometry on the MoS₂ monolayer (Habib, M. R.; Li, H.; Kong, Y.; Liang, T.; Obaidulla, S. M.; Xie, S.; Wang, S.; Ma, X.; Su, H.; Xu, M. Tunable Photoluminescence in a van Der Waals Heterojunction Built from a MoS₂ Monolayer and a PTCDA Organic Semiconductor. *Nanoscale* **2018**, *10*, 16107–16115). Density of states

calculation showed that S p_z and Mo d_{z^2} orbitals, which compose the conduction band minimum of MoS₂, can hybridize with the conjugated C p_z orbitals of PTCDA. In contrast to PTCDA, N,N'-diphenyl-3,4,9,10-perylenedicarboximide (PTCDI-Ph) renders a non-planar geometry on MoS₂ monolayer, resulting in reduced overlap of the π -orbitals with the out-of-plane MoS₂ orbitals. The isotropic and anisotropic geometries then affect the electronic and photoelectronic performance of the hybrid system (Obaidulla, S. M.; Habib, M. R.; Khan, Y.; Kong, Y.; Liang, T.; Xu, M. MoS₂ and Perylene Derivative Based Type-II Heterostructure: Bandgap Engineering and Giant Photoluminescence Enhancement. *Adv. Mater. Interfaces* **2020**, *7*, 1901197). Recently, in addition to studies involving large well-defined grown monolayers, a solution-based approach employing exfoliated 2H-WS₂ nanosheets and a perylene diimide derivative has been reported (Scharl, T.; Binder, G.; Chen, X.; Yokosawa, T.; Cadranet, A.; Knirsch, K. C.; Spiecker, E.; Hirsch, A.; Guldi, D. M. Noncovalent Liquid Phase Functionalization of 2H-WS₂ with PDI: An Energy Conversion Platform with Long-Lived Charge Separation. *J. Am. Chem. Soc.* **2022**, *144*, 5834–5840). The work demonstrated that the semiconducting phase was well preserved while additional characteristics emerged from the adsorbed species. Unfortunately, the final hybrid structure has not been fully characterized.

[0193] In the second scenario, hybridization might originate from electron donation from the in-plane carbon orbital of the *N*-heterocyclic ring to the transition metal d_{z^2} orbitals (FIG. 26B). To elucidate this idea, we revisit the intercalation chemistry of 2D layered TMDs (Jacobson, A. J. 7 - Organic and Organometallic Intercalation Compounds of the Transition Metal Dichalcogenides. In *Intercalation Chemistry*; Whittingham, M. S., Jacobson, A. J., Eds.; Academic Press, 1982; pp 229–265). In case of metallic 2D layered group IV and V TMDs, direct intercalation can be achieved in the bulk powder form. Due to their half-filled orbitals, intercalation can be explained by the Lewis acid-base model. The metallic TMDs act as electron donors, implying the possibility of saturation of the frontier metal d-orbitals and collapsing a metallic structure to a semiconducting manifold (Jawaid, A.; Pike, N. A.; Pachter, R.; Vaia, R. Basal Surface Hybridization of Group V Layered Transition Metal Dichalcogenides. *ACS Mater. Au* **2023**, *3*, 55–65). In the case of 2D layered group VI TMDs, direct intercalation of large species has not been observed in their inherent semiconducting state. The intercalation must be preceded by a pre-intercalation step, followed by an ion-exchange process. Common pre-intercalation methods involve strong reductants such as Butyllithium or direct insertion of alkali cations via

electrochemistry, which induces a phase transformation from 2H to 1T. Consequently, the resulting metallic group VI TMDs act as Lewis bases towards exchangeable cations or, in some cases, neutral molecules (Divigalpitiya, W. M. R.; Frindt, R. F.; Morrison, S. R. Inclusion Systems of Organic Molecules in Restacked Single-Layer Molybdenum Disulfide. *Science* **1989**, *246*, 369–371; Tagaya, H.; Hashimoto, T.; Karasu, M.; Izumi, T.; Chiba, K. Inclusion of Substituted Ferrocenes and Aromatic Compounds into MoS₂ Layers as New Intercalation Compounds. *Chem. Lett.* **1991**, *20*, 2113–2116; Bissessur, R.; Heising, J.; Hirpo, W. Toward Pillared Layered Metal Sulfides. Intercalation of the Chalcogenide Clusters Co₆Q₈(PR₃)₆ (Q = S, Se, and Te and R = Alkyl) into MoS₂. *Chem. Mater.* **1996**, *8*, 318–320; Brenner, J.; Marshall, C. L.; Ellis, L.; Tomczyk, N.; Heising, J.; Kanatzidis, M. Microstructural Characterization of Highly HDS-Active Co₆S₈-Pillared Molybdenum Sulfides. *Chem. Mater.* **1998**, *10*, 1244–1257; Kosidowski, L.; Powell, A. V. Naphthalene Intercalation into Molybdenum Disulfide. *Chem. Commun.* **1998**, 2201–2202). Recently, the strategy has been progressively innovated by Xiangfeng Duan's group (Wang, C.; He, Q.; Halim, U.; Liu, Y.; Zhu, E.; Lin, Z.; Xiao, H.; Duan, X.; Feng, Z.; Cheng, R.; Weiss, N. O.; Ye, G.; Huang, Y.-C.; Wu, H.; Cheng, H.-C.; Shakir, I.; Liao, L.; Chen, X.; Goddard III, W. A.; Huang, Y.; Duan, X. Monolayer Atomic Crystal Molecular Superlattices. *Nature* **2018**, *555*, 231–236; He, Q.; Lin, Z.; Ding, M.; Yin, A.; Halim, U.; Wang, C.; Liu, Y.; Cheng, H.-C.; Huang, Y.; Duan, X. In Situ Probing Molecular Intercalation in Two-Dimensional Layered Semiconductors. *Nano Lett.* **2019**, *19*, 6819–6826; Zhou, B.; Zhou, J.; Wang, L.; Kang, J. H.; Zhang, A.; Zhou, J.; Zhang, D.; Xu, D.; Hu, B.; Deng, S.; Huang, L.; Wong, C. W.; Huang, Y.; Duan, X. A Chemical-Dedoping Strategy to Tailor Electron Density in Molecular-Intercalated Bulk Monolayer MoS₂. *Nat. Synth.* **2024**, *3*, 67–75). Apart from traditional pre-intercalation methods, positively charged alkylammonium salts were directly inserted into the interlayer gaps of a single crystal MoS₂ via electrochemistry. This process gave an injection of electrons into the MoS₂ host framework. The adopted alkylammonium salts, with various molecular structures, limited the extent of intercalation, thereby determining the number of injected electrons. Hence, a phase transformation from 2H to 1T could be controlled by custom-designed molecular structures, achieving an intercalation state through dual-charged host-guest system. From those mentioned above, the mild reducing capability of the lone pair electrons residing in the in-plane *N*-heterocyclic ring has the potential to generate comparable interactions without driving a phase transformation (Jones, L. O.; Mosquera, M. A.; Ratner, M. A.; Schatz, G. C. Control of Charge

Carriers and Band Structure in 2D Monolayer Molybdenum Disulfide via Covalent Functionalization. *ACS Appl. Mater. Interfaces* **2020**, *12*, 4607–4615; Sadhukhan, T.; Schatz, G. C. Generating Bright Emissive States by Modulating the Bandgap of Monolayer Tungsten Diselenide. *J. Phys. Chem. C* **2022**, *126*, 5598–5606; Jones, L. O.; Sadhukhan, T.; Schatz, G. C. Localized π Surface States on 2D Molybdenum Disulfide from Carbene-Functionalization as a Qubit Design Strategy. *ACS Phys. Chem. Au* **2022**, *2*, 277–281).

[0194] We have demonstrated the first experimental functionalization of 2D nanolayered TMDs, utilizing *N*-Heterocyclic Carbenes. Following the desorption of POMs, a restacking process was witnessed that entrapped NHC molecules between the van der Waal layers of 2D TMDs. Remarkably, this intercalation process can occur despite the semiconducting nature of exfoliated TMDs and the cumbersome structure of NHC15OH[OMs]. Without being bound by theory, the intercalated species are hypothesized to hybridize with the basal plane of TMDs, leading to interlayer expansion and formation of superlattice structures. These structural changes are further influenced by the collective effects of both sizes and thicknesses of the nanosheet population. The NHC functionalization induces an n-doping effect, injecting and redistributing the electron density across the entire 2D plane of the TMDs. Given the extent of exfoliation as well as the complex molecular structure of NHC15OH[OMs], further investigation is warranted. In summary, our findings present a novel strategic approach to functionalize 2D layered TMDs and introduce an entirely new intercalated families built on the framework of 2D layered TMD hosts and the NHC family. Notably, the NHC-functionalized superlattice structures retain the semiconducting monolayer characteristics, even at the restacked multilayer configuration.

[0195] Monolayer Behavior of Tailored Superlattice Structures

[0196] Recently, it has been reported that a semiconducting multilayered superlattice structures also demonstrate monolayer-like behavior, evidenced by strong photoluminescent intensity characteristic of monolayer architecture, attributed to the direct excitonic transitions (Wang, C.; He, Q.; Halim, U.; Liu, Y.; Zhu, E.; Lin, Z.; Xiao, H.; Duan, X.; Feng, Z.; Cheng, R.; Weiss, N. O.; Ye, G.; Huang, Y.-C.; Wu, H.; Cheng, H.-C.; Shakir, I.; Liao, L.; Chen, X.; Goddard III, W. A.; Huang, Y.; Duan, X. Monolayer Atomic Crystal Molecular Superlattices. *Nature* **2018**, *555*, 231–236; He, Q.; Lin, Z.; Ding, M.; Yin, A.; Halim, U.; Wang, C.; Liu, Y.; Cheng, H.-C.; Huang, Y.; Duan, X. In Situ Probing Molecular Intercalation in Two-Dimensional Layered Semiconductors. *Nano Lett.* **2019**, *19*, 6819–6826; Zhou, B.; Zhou, J.; Wang, L.; Kang, J. H.;

Zhang, A.; Zhou, J.; Zhang, D.; Xu, D.; Hu, B.; Deng, S.; Huang, L.; Wong, C. W.; Huang, Y.; Duan, X. A Chemical-Dedoping Strategy to Tailor Electron Density in Molecular-Intercalated Bulk Monolayer MoS₂. *Nat. Synth.* **2024**, *3*, 67–75). Building on these concepts, we further investigated the E_{12g} and A_{1g} vibration modes, along with the photoluminescent properties, of individual MoS₂ fractions and their respective NHC-functionalized derivatives. FIG. 51A – FIG. 51L presents the Raman spectra, highlighting the characteristics of the E_{12g} and A_{1g} vibration modes for MoS₂ F1–4 and their respective NHC-functionalized counterparts. From the fractional data set, all redox-exfoliated MoS₂ fractional thin films illustrate similar vibrational characteristics, with a slight shift of the A_{1g} mode position to a lower Raman shift and a slight reduction in the FMHWs across samples F1 to F4. It suggests that MoS₂ F4 does contain a richer proportion of thinner nanosheets. Despite that, the FMHWs are still larger than the reported one for monolayers (19.0 cm⁻¹) (Lee, C.; Yan, H.; Brus, L. E.; Heinz, T. F.; Hone, J.; Ryu, S. Anomalous Lattice Vibrations of Single- and Few-Layer MoS₂. *ACS Nano* **2010**, *4*, 2695–2700; Li, H.; Zhang, Q.; Yap, C. C. R.; Tay, B. K.; Edwin, T. H. T.; Olivier, A.; Baillargeat, D. From Bulk to Monolayer MoS₂: Evolution of Raman Scattering. *Adv. Funct. Mater.* **2012**, *22*, 1385–1390). This can be attributed to the high concentration of redox-exfoliated MoS₂ Fx (0.1 mM, compared to 0.0125 mM used for AFM analysis) during the thin-film fabrication process, leading to the formation of a restacked multilayered thin film. In contrast, the corresponding 15-NHC/MoS₂ Fx samples display vibrational variations across samples F1 to F4 in both peak positions and FMHWs. In all four functionalized fractions, a softening effect, characterized by a red shift to lower Raman shift in both E_{12g} and A_{1g} modes, accompanied by the broadened FMHWs of their respective peaks. The observation is consistent with our previous Raman data set for functionalized, fractional-combined, redox-exfoliated MoS₂. The effect is most pronounced in 15-NHC/MoS₂ F4, which is rich in restacked monolayers, further supporting the influence of incomplete exfoliation on functionalization. As a result, despite the separation introduced by the NHCs, the overall restacked multilayered superlattice structures do not exhibit the vibrational characteristics typical of monolayered MoS₂, as indicated by an A_{1g} – E_{12g} peak separation similar to that of bulk MoS₂. We attribute this phenomenon to lattice disorder, as well as the applied strain and doping carriers induced by the NHC functionalization (Busch, R. T.; Sun, L.; Austin, D.; Jiang, J.; Miesle, P.; Susner, M. A.; Conner, B. S.; Jawaide, A.; Becks, S. T.; Mahalingam, K.; Velez, M. A.; Torsi, R.; Robinson, J. A.; Rao, R.; Glavin, N. R.; Vaia, R. A.; Pachter, R.; Joshua Kennedy, W.; Vernon, J.

P.; Stevenson, P. R. Exfoliation Procedure-Dependent Optical Properties of Solution Deposited MoS₂ Films. *Npj 2D Mater. Appl.* **2023**, *7*, 1–13). The related calculations and discussions will be detailed in the experimental section herein.

[0197] FIG. 49A – FIG. 49B provide an overview of the photoluminescent behavior observed in all four 15-NHC/MoS₂ Fx samples. Additional photoluminescent data for individual MoS₂ Fx and their respective 15-NHC/MoS₂ Fx is shown in FIG. 52A – FIG. 52D. The high photoluminescent intensity supports our hypothesis that when TMD (MoS₂ in this case) monolayers are extensively spaced by foreign species (NHCs), even if they are restacked in superlattice configurations, they retain the characteristics typical of individual monolayers. The data shows an increase in photoluminescent intensity across four fractions, indicating an enhanced periodicity in the arrangement of the restacked monolayers. It is important to note that the lower energy region (1.6-1.8 eV) corresponds to the A-excitonic transition, representing the optical band gap and encompassing contributions from both excitons and trions. Unlike conventional undoped MoS₂ monolayers, where the spectral profile of the direct A-excitonic transition is sharp and primarily dominated by excitons, the spectra observed in all four functionalized fractions exhibit a broader profile, suggesting an increased trion content. Additionally, the optical band gaps illustrate a slight shift from F1 to F4 with the highest energy reaching 1.74 eV in 15-NHC/MoS₂ F4. However, this optical band gap remains smaller than that reported for undoped MoS₂ monolayers (1.85 eV) (Splendiani, A.; Sun, L.; Zhang, Y.; Li, T.; Kim, J.; Chim, C.-Y.; Galli, G.; Wang, F. Emerging Photoluminescence in Monolayer MoS₂. *Nano Lett.* **2010**, *10*, 1271–1275). We hypothesized that this phenomenon is due to the quantity of injected electrons by the doping species (NHCs), which not only increase the trion content but also progressively modifies the overall band gap structure of MoS₂. Moreover, the photoluminescent behavior confirm that our electron injection approach via using NHC functionalization, does not cause a phase transition, thereby preserving TMDs' semiconducting properties. Based on the photoluminescent data and the deduced valence band edge at low energy region in XPS, a band gap structure of MoS₂ and NHC-functionalized MoS₂ is constructed in FIG. 49B.

[0198] **Various Embodiments of the Invention**

[0199] Embodiments include those listed below.

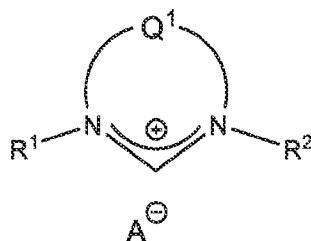
[0200] Embodiment 1. A method of making at least one *N*-heterocyclic carbene functionalized transition metal dichalcogenide, comprising: providing at least one bulk transition

metal dichalcogenide; exfoliating the at least one bulk transition metal dichalcogenide to produce at least one exfoliated transition metal dichalcogenide comprising at least one exfoliated surface; and reacting at least a portion of the at least one exfoliated surface of the at least one exfoliated transition metal dichalcogenide with at least one *N*-heterocyclic carbene precursor.

[0201] Embodiment 2. The method of embodiment 1, wherein the at least one exfoliated surface of the at least one exfoliated transition metal dichalcogenide comprises at least one exfoliated basal plane.

[0202] Embodiment 3. The method of embodiment 1 or embodiment 2, wherein the exfoliating is conducted by a redox exfoliation process.

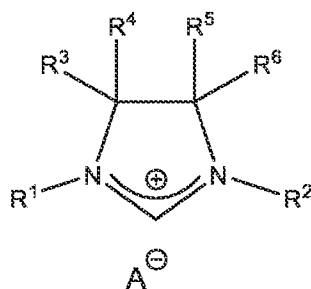
[0203] Embodiment 4. The method of any one of embodiments 1-3, wherein the *N*-heterocyclic carbene precursor has a structure of Formula (I):



Formula (I),

wherein: A⁻ is a counterion; R¹ is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; R² is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and Q¹ is an optionally substituted linker.

[0204] Embodiment 5. The method of any one of embodiments 1-4, wherein the *N*-heterocyclic carbene precursor has a structure of Formula (I-A):



Formula (I-A),

wherein:

A⁻ is a counterion;

R¹ is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R² is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R³ is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

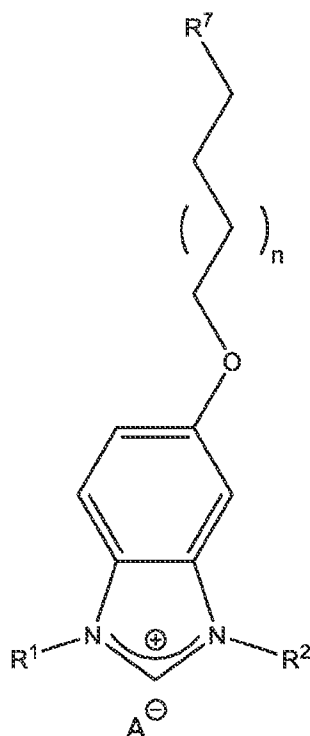
R⁴ is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R⁵ is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and

R⁶ is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; or

R³ and R⁵, or R³ and R⁶, or R⁴ and R⁵, or R⁴ and R⁶ may be taken together to form a ring, wherein the ring is optionally substituted.

[0205] Embodiment 6. The method of any one of embodiments 1-5, wherein the *N*-heterocyclic carbene precursor has the structure of Formula (I-B):



Formula (I-B),

wherein:

A^- is a counterion;

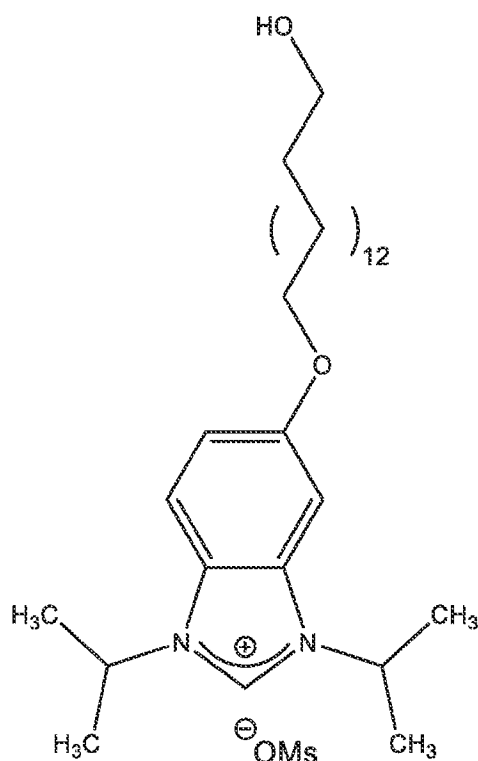
n is 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, or 12;

R^1 is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^2 is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and

R^7 is H, OR^8 , SR^9 , halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl, wherein R^8 is H, or optionally substituted alkyl, and R^9 is H, or optionally substituted alkyl.

[0206] Embodiment 7. The method of any one of embodiments 1-6, wherein the *N*-heterocyclic carbene precursor is

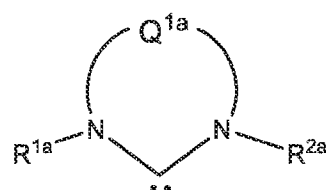


[0207] Embodiment 8. The method of any one of embodiments 1-7, wherein the at least one *N*-heterocyclic carbene precursor forms a self-assembled monolayer (SAM) on the at least one exfoliated surface of the at least one exfoliated transition metal dichalcogenide.

[0208] Embodiment 9. The method of any one of embodiments 1-8, wherein the self-assembled monolayer (SAM) is a homogenous self-assembled monolayer, or heterogenous self-assembled monolayer.

[0209] Embodiment 10. The method of any one of embodiments 1-9, wherein the self-assembled monolayer (SAM) comprises at least one *N*-heterocyclic carbene.

[0210] Embodiment 11. The method of embodiment 10, wherein the at least one *N*-heterocyclic carbene has a structure of Formula (II):



Formula (II),

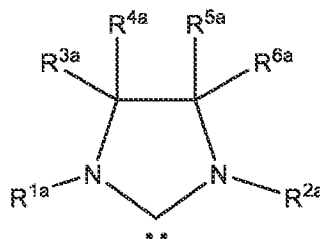
wherein:

R^{1a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{2a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and

Q^{1a} is an optionally substituted linker.

[0211] Embodiment 12. The method of embodiment 10 or embodiment 11, wherein the at least one *N*-heterocyclic carbene has a structure of Formula (II-A):



Formula (II-A),

wherein:

R^{1a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{2a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{3a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

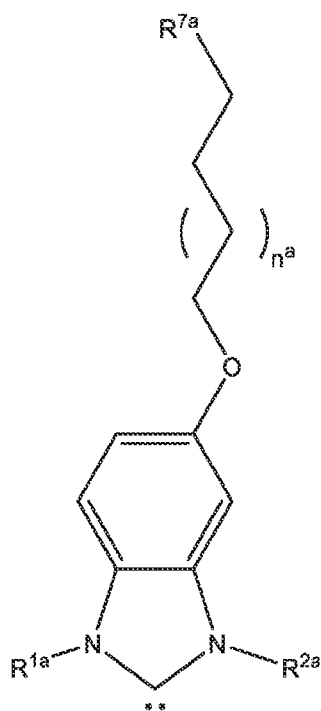
R^{4a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{5a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and

R^{6a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; or

R^{3a} and R^{5a} , or R^{3a} and R^{6a} , or R^{4a} and R^{5a} , or R^{4a} and R^{6a} may be taken together to form a ring, wherein the ring is optionally substituted.

[0212] Embodiment 13. The method of any one of embodiments 10-12, wherein the at least one *N*-heterocyclic carbene has the structure of Formula (II-B):



Formula (II-B),

wherein:

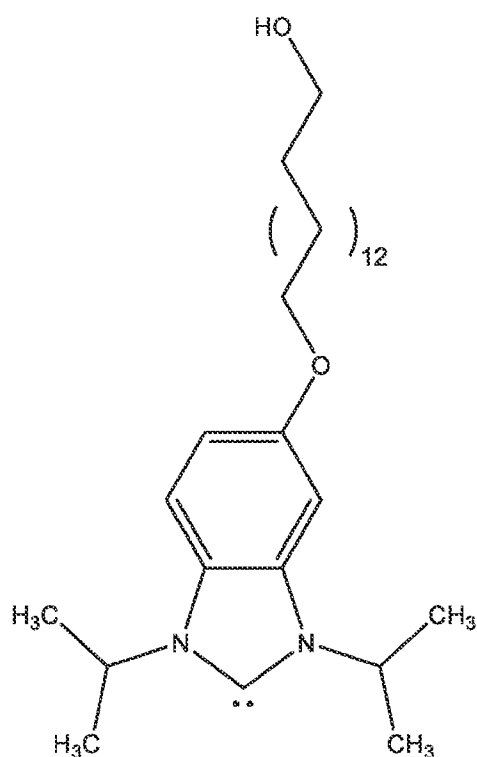
n^a is 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, or 12;

R^{1a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{2a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and

R^{7a} is H, OR^{8a} , SR^{9a} , halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl, wherein R^{8a} is H, or optionally substituted alkyl, and R^{9a} is H, or optionally substituted alkyl.

[0213] Embodiment 14. The method of any one of embodiments 10-13, wherein the at least one *N*-heterocyclic carbene is

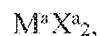


[0214] Embodiment 15. The method of any one of embodiments 10-13, wherein the at least one *N*-heterocyclic carbene is the same or different.

[0215] Embodiment 16. The method of any one of embodiments 1-15, wherein the at least one bulk transition metal dichalcogenide comprises a two-dimensional (2D) structure.

[0216] Embodiment 17. The method of embodiment 16, wherein the 2D structure comprises one layer, or a plurality of layers.

[0217] Embodiment 18. The method of any one of embodiments 1-17, wherein the at least one bulk transition metal dichalcogenide has the formula:



wherein:

M^a is a Group 4-10 transition metal; and

X^a is a chalcogen.

[0218] Embodiment 19. The method of embodiment 18, wherein M^a is a Group 6 transition metal.

[0219] Embodiment 20. The method of embodiment 18 or embodiment 19, wherein the chalcogen is sulfur (S), selenium (Se), or tellurium (Te).

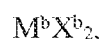
[0220] Embodiment 21. The method of any one of embodiments 18-20, wherein the Group 6 transition metal is molybdenum (Mo).

[0221] Embodiment 22. The method of any one of embodiments 1-21, wherein the at least one bulk transition metal dichalcogenide is MoS_2 .

[0222] Embodiment 23. The method of any one of embodiments 1-22, wherein the at least one exfoliated transition metal dichalcogenide comprises a two-dimensional (2D) structure.

[0223] Embodiment 24. The method of embodiment 23, wherein the 2D structure comprises one layer, or a plurality of layers.

[0224] Embodiment 25. The method of any one of embodiments 1-24, wherein the at least one exfoliated transition metal dichalcogenide has the formula:



wherein:

M^b is a Group 4-10 transition metal; and

X^b is a chalcogen.

[0225] Embodiment 26. The method of embodiment 25, wherein M^b is a Group 6 transition metal.

[0226] Embodiment 27. The method of embodiment 25 or embodiment 26, wherein the chalcogen is sulfur (S), selenium (Se), or tellurium (Te).

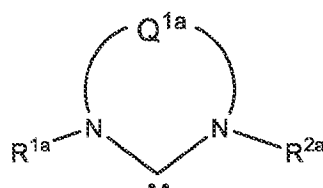
[0227] Embodiment 28. The method of any one of embodiments 25-27, wherein the Group 6 transition metal is molybdenum (Mo).

[0228] Embodiment 29. The method of any one of embodiments 1-28, wherein the at least one exfoliated transition metal dichalcogenide is MoS₂.

[0229] Embodiment 30. The method of any one of embodiments 1-29, wherein the reaction of the at least a portion of the at least one exfoliated surface of the at least one exfoliated transition metal dichalcogenide with at least one *N*-heterocyclic carbene precursor to make the at least one *N*-heterocyclic carbene functionalized transition metal dichalcogenide.

[0230] Embodiment 31. The method of any one of embodiments 1-30, wherein the at least one *N*-heterocyclic carbene functionalized transition metal dichalcogenide comprises at least one *N*-heterocyclic carbene.

[0231] Embodiment 32. The method of embodiment 31, wherein the at least one *N*-heterocyclic carbene has a structure of Formula (II):



Formula (II),

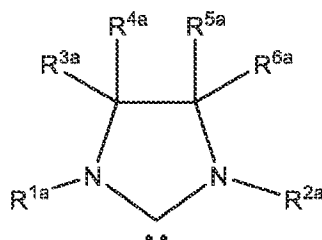
wherein:

R^{1a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{2a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and

Q^{1a} is an optionally substituted linker.

[0232] Embodiment 33. The method of embodiment 31 or embodiment 32, wherein the at least one *N*-heterocyclic carbene has a structure of Formula (II-A):



Formula (II-A),

wherein:

R^{1a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{2a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{3a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

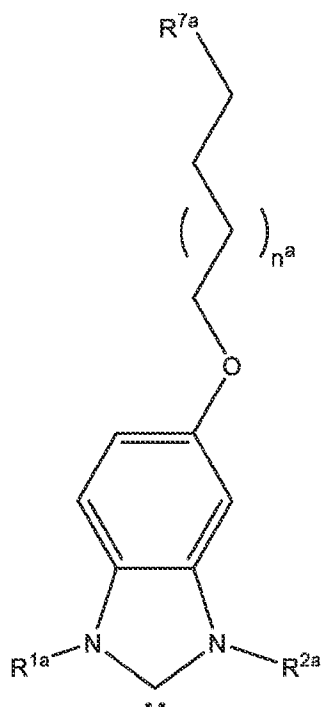
R^{4a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{5a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and

R^{6a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; or

R^{3a} and R^{5a} , or R^{3a} and R^{6a} , or R^{4a} and R^{5a} , or R^{4a} and R^{6a} may be taken together to form a ring, wherein the ring is optionally substituted.

[0233] Embodiment 34. The method of any one of embodiments 31-33, wherein the at least one *N*-heterocyclic carbene has the structure of Formula (II-B):



Formula (II-B),

wherein:

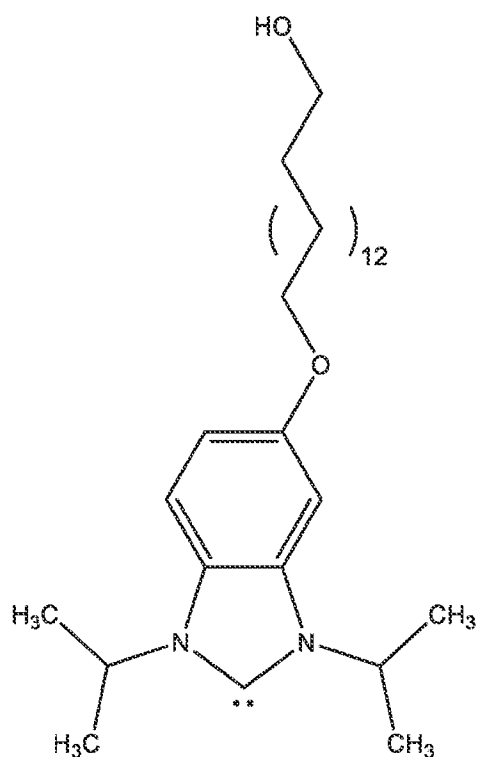
n^a is 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, or 12;

R^{1a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{2a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and

R^{7a} is H, OR^{8a} , SR^{9a} , halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl, wherein R^{8a} is H, or optionally substituted alkyl, and R^{9a} is H, or optionally substituted alkyl.

[0234] Embodiment 35. The method of any one of embodiments 31-34, wherein the at least one *N*-heterocyclic carbene is



[0235] Embodiment 36. A *N*-heterocyclic carbene functionalized transition metal dichalcogenide made by the method of any one of embodiments 1-35.

[0236] Embodiment 37. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 36, wherein the *N*-heterocyclic carbene functionalized transition metal dichalcogenide is insulating, semiconducting, conducting, semi-metallic, metallic, or any combination thereof.

[0237] Embodiment 38. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 36, wherein the *N*-heterocyclic carbene functionalized transition metal dichalcogenide is semiconducting.

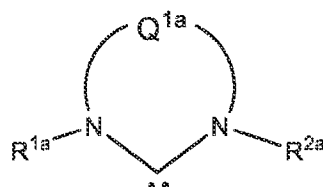
[0238] Embodiment 39. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 36, wherein the *N*-heterocyclic carbene functionalized transition metal dichalcogenide is a semiconductor.

[0239] Embodiment 40. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of any one of embodiments 36-39, wherein the *N*-heterocyclic carbene functionalized transition metal dichalcogenide comprises a self-assembled monolayer (SAM).

[0240] Embodiment 41. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 40, wherein the self-assembled monolayer (SAM) is a homogenous self-assembled monolayer, or heterogenous self-assembled monolayer.

[0241] Embodiment 42. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 40 or embodiment 41, wherein the self-assembled monolayer (SAM) comprises at least one *N*-heterocyclic carbene.

[0242] Embodiment 43. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 42, wherein the at least one *N*-heterocyclic carbene has a structure of Formula (II):



Formula (II),

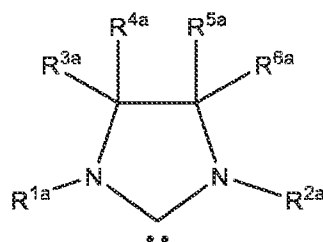
wherein:

R^{1a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{2a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and

Q^{1a} is an optionally substituted linker.

[0243] Embodiment 44. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 42 or embodiment 43, wherein the at least one *N*-heterocyclic carbene has a structure of Formula (II-A):



Formula (II-A),

wherein:

R^{1a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{2a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{3a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

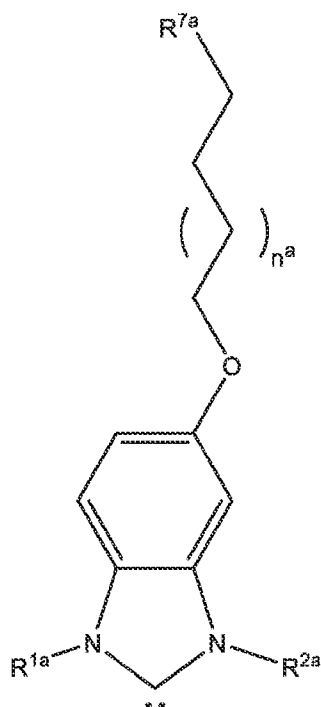
R^{4a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{5a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and

R^{6a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; or

R^{3a} and R^{5a}, or R^{3a} and R^{6a}, or R^{4a} and R^{5a}, or R^{4a} and R^{6a} may be taken together to form a ring, wherein the ring is optionally substituted.

[0244] Embodiment 45. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of any one of embodiments 42-44, wherein the at least one *N*-heterocyclic carbene has the structure of Formula (II-B):



Formula (II-B),

wherein:

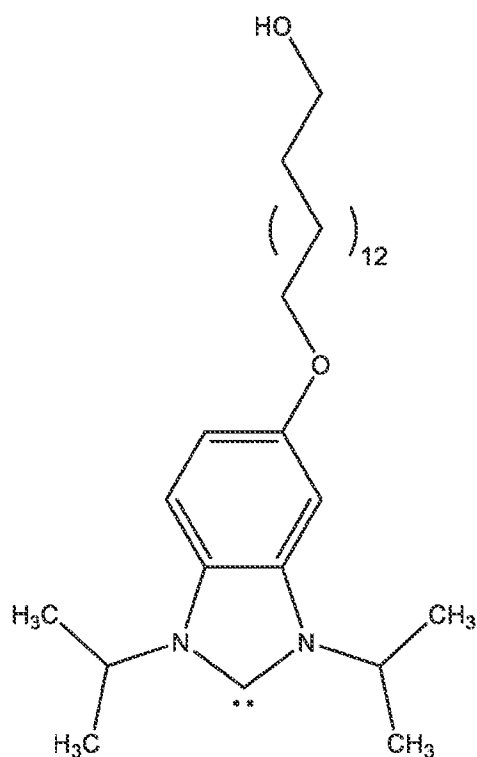
n^a is 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, or 12;

R^{1a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{2a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and

R^{7a} is H, OR^{8a} , SR^{9a} , halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl, wherein R^{8a} is H, or optionally substituted alkyl, and R^{9a} is H, or optionally substituted alkyl.

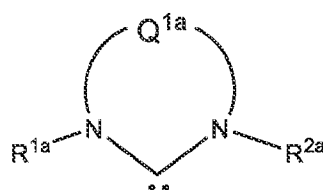
[0245] Embodiment 46. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of any one of embodiments 42-45, wherein the at least one *N*-heterocyclic carbene is



[0246] Embodiment 47. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of any one of embodiments 42-45, wherein the at least one *N*-heterocyclic carbene is the same or different.

[0247] Embodiment 48. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of any one of embodiments 36-47, wherein the *N*-heterocyclic carbene functionalized transition metal dichalcogenide comprises a superstructure comprising intercalated layers, wherein the intercalated layers comprise at least one *N*-heterocyclic carbene.

[0248] Embodiment 49. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 48, wherein the at least one *N*-heterocyclic carbene has a structure of Formula (II):



Formula (II),

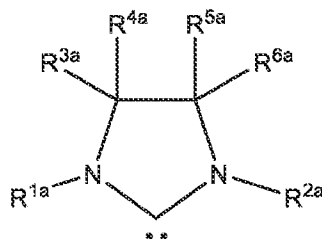
wherein:

R^{1a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{2a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and

Q^{1a} is an optionally substituted linker.

[0249] Embodiment 50. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 48 or embodiment 49, wherein the at least one *N*-heterocyclic carbene has a structure of Formula (II-A):



Formula (II-A),

wherein:

R^{1a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{2a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{3a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

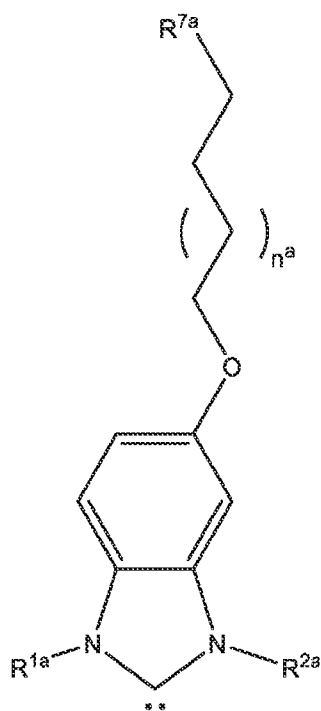
R^{4a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{5a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and

R^{6a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; or

R^{3a} and R^{5a} , or R^{3a} and R^{6a} , or R^{4a} and R^{5a} , or R^{4a} and R^{6a} may be taken together to form a ring, wherein the ring is optionally substituted.

[0250] Embodiment 51. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of any one of embodiments 48-50, wherein the at least one *N*-heterocyclic carbene has the structure of Formula (II-B):



Formula (II-B),

wherein:

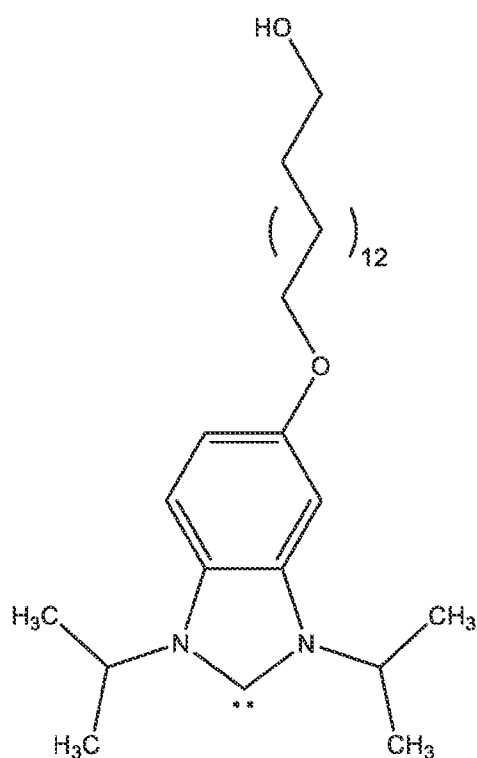
n^a is 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, or 12;

R^{1a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and

R^{2a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and

R^{7a} is H, OR^{8a}, SR^{9a}, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl, wherein R^{8a} is H, or optionally substituted alkyl, and R^{9a} is H, or optionally substituted alkyl.

[0251] Embodiment 52. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of any one of embodiments 48-51, wherein the at least one *N*-heterocyclic carbene is



[0252] Embodiment 53. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of any one of embodiments 48-51, wherein the at least one *N*-heterocyclic carbene is the same or different.

[0253] Embodiment 54. An article of manufacture comprising a *N*-heterocyclic carbene functionalized transition metal dichalcogenide of any one of embodiments 36-53.

[0254] Embodiment 55. The article of manufacture of embodiment 54, wherein the article of manufacture is an energy storage device, energy storage material, sensing device, sensing material, semiconductor electronic device, semiconductor electronic material, semiconductor optoelectronic device, or semiconductor optoelectronic material.

[0255] Embodiment 56. The article of manufacture of embodiment 54, wherein the article of manufacture is a semiconductor.

[0256] Embodiment 57. An article of manufacture comprising a *N*-heterocyclic carbene functionalized transition metal dichalcogenide made by the method of any one of embodiments 1-35.

[0257] Embodiment 58. The article of manufacture of embodiment 57, wherein the article of manufacture is an energy storage device, energy storage material, sensing device, sensing material, semiconductor electronic device, semiconductor electronic material, semiconductor optoelectronic device, or semiconductor optoelectronic material.

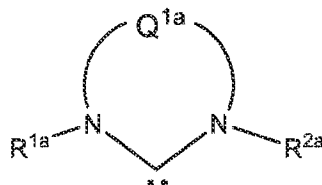
[0258] Embodiment 59. The article of manufacture of embodiment 57, wherein the article of manufacture is a semiconductor.

[0259] Embodiment 60. Use of the *N*-heterocyclic carbene functionalized transition metal dichalcogenide of any one of embodiments 36-53.

[0260] Embodiment 61. Use of the *N*-heterocyclic carbene functionalized transition metal dichalcogenide made by the method of any one of embodiments 1-35.

[0261] Embodiment 62. A *N*-heterocyclic carbene functionalized transition metal dichalcogenide, comprising: at least one transition metal dichalcogenide; and at least one *N*-heterocyclic carbene.

[0262] Embodiment 63. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 62, wherein the at least one *N*-heterocyclic carbene has a structure of Formula (II):



Formula (II),

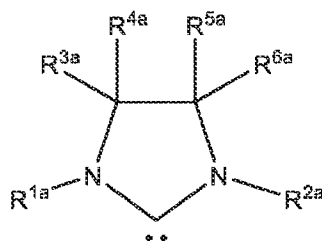
wherein:

R^{1a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{2a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and

Q^{1a} is an optionally substituted linker.

[0263] Embodiment 64. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 62 or embodiment 63, wherein the at least one *N*-heterocyclic carbene has a structure of Formula (II-A):



Formula (II-A),

wherein:

R^{1a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{2a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{3a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

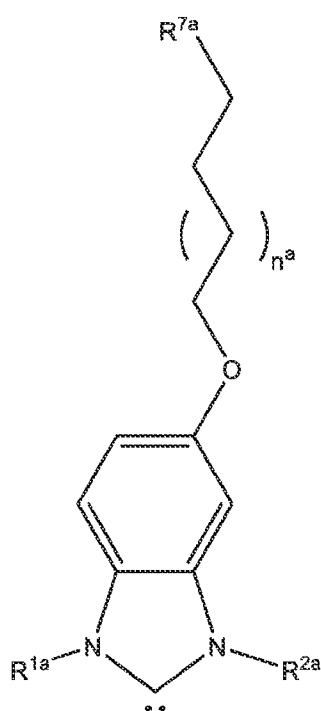
R^{4a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{5a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and

R^{6a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; or

R^{3a} and R^{5a} , or R^{3a} and R^{6a} , or R^{4a} and R^{5a} , or R^{4a} and R^{6a} may be taken together to form a ring, wherein the ring is optionally substituted.

[0264] Embodiment 65. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of any one of embodiments 62-64, wherein the at least one *N*-heterocyclic carbene has the structure of Formula (II-B):



Formula (II-B),

wherein:

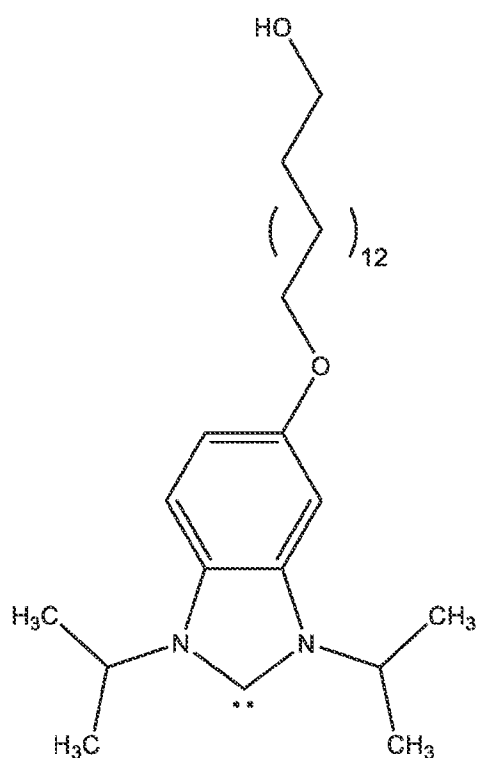
n is 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, or 12;

R^{1a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{2a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and

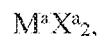
R^{7a} is H, OR^{8a}, SR^{9a}, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl, wherein R^{8a} is H, or optionally substituted alkyl, and R^{9a} is H, or optionally substituted alkyl.

[0265] Embodiment 66. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of any one of embodiments 62-65, wherein the at least one *N*-heterocyclic carbene is



[0266] Embodiment 67. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of any one of embodiments 62-64, wherein the at least one *N*-heterocyclic carbene is the same or different.

[0267] Embodiment 68. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of any one of embodiments 62-67, wherein the at least one transition metal dichalcogenide has the formula:



wherein:

M^a is a Group 4-10 transition metal; and

X^a is a chalcogen.

[0268] Embodiment 69. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 68, wherein M^a is a Group 6 transition metal.

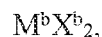
[0269] Embodiment 70. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 68 or embodiment 69, wherein the chalcogen is sulfur (S), selenium (Se), or tellurium (Te).

[0270] Embodiment 71. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of any one of embodiments 68-70, wherein the Group 6 transition metal is molybdenum (Mo).

[0271] Embodiment 72. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of any one of embodiments 62-71, wherein the at least one transition metal dichalcogenide is MoS_2 .

[0272] Embodiment 73. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of any one of embodiments 62-72, wherein the at least one transition metal dichalcogenide is an at least one exfoliated transition metal dichalcogenide.

[0273] Embodiment 74. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 73, wherein the at least one exfoliated transition metal dichalcogenide has the formula:



wherein:

M^b is a Group 4-10 transition metal; and

X^b is a chalcogen.

[0274] Embodiment 75. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 74, wherein M^b is a Group 6 transition metal.

[0275] Embodiment 76. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 74 or embodiment 75, wherein the chalcogen is sulfur (S), selenium (Se), or tellurium (Te).

[0276] Embodiment 77. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of any one of embodiments 74-76, wherein the Group 6 transition metal is molybdenum (Mo).

[0277] Embodiment 78. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of any one of embodiments 73-77, wherein the at least one exfoliated transition metal dichalcogenide is MoS_2 .

[0278] Embodiment 79. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of any one of embodiments 73-78, wherein the at least one exfoliated transition metal dichalcogenide comprises at least one exfoliated surface.

[0279] Embodiment 80. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of any one of embodiments 62-79, wherein the at least one *N*-heterocyclic carbene forms a self-assembled monolayer (SAM) on the at least one exfoliated surface of the at least one exfoliated transition metal dichalcogenide.

[0280] Embodiment 81. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 80, wherein the self-assembled monolayer (SAM) is a homogenous self-assembled monolayer, or heterogenous self-assembled monolayer.

[0281] Embodiment 82. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of any one of embodiments 73-78, wherein the at least one exfoliated transition metal dichalcogenide comprises at least one exfoliated basal plane.

[0282] Embodiment 83. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 82, wherein the at least one exfoliated basal plane is functionalized with the at least one *N*-heterocyclic carbene.

[0283] Embodiment 84. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of any one of embodiments 73-78, wherein the at least one exfoliated transition metal dichalcogenide comprises a two-dimensional (2D) structure.

[0284] Embodiment 85. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 84, wherein the 2D structure comprises one layer, or a plurality of layers.

[0285] Embodiment 86. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of any one of embodiments 62-84, wherein the *N*-heterocyclic carbene functionalized transition metal dichalcogenide comprises a superstructure comprising intercalated layers.

[0286] Embodiment 87. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 86, wherein the intercalated layers comprise the at least one *N*-heterocyclic carbene.

[0287] Embodiment 88. An article of manufacture comprising a *N*-heterocyclic carbene functionalized transition metal dichalcogenide of any one of embodiments 62-87.

[0288] Embodiment 89. The article of manufacture of embodiment 88, wherein the article of manufacture is an energy storage device, energy storage material, sensing device, sensing material, semiconductor electronic device, semiconductor electronic material, semiconductor optoelectronic device, or semiconductor optoelectronic material.

[0289] Embodiment 90. The article of manufacture of embodiment 88, wherein the article of manufacture is a semiconductor.

[0290] Embodiment 91. Use of the *N*-heterocyclic carbene functionalized transition metal dichalcogenide of any one of embodiments 62-87.

[0291] Embodiments include those listed below.

[0292] In various embodiments of the present invention, *N*-heterocyclic carbene is represented as N-heterocyclic carbene. In various embodiments of the present invention, *N*-heterocyclic carbene precursor is represented as N-heterocyclic carbene precursor. In various embodiments of the present invention, *N*-heterocyclic carbene adsorbate is represented as N-heterocyclic carbene adsorbate. In various embodiments of the present invention, *N*-heterocyclic carbene functionalized transition metal dichalcogenide is represented as N-heterocyclic carbene functionalized transition metal dichalcogenide.

[0293] In various embodiments, the present invention provides a method of making at least one *N*-heterocyclic carbene functionalized transition metal dichalcogenide, comprising: providing at least one bulk transition metal dichalcogenide; exfoliating the at least one bulk transition metal

dichalcogenide to produce at least one exfoliated transition metal dichalcogenide; and reacting the at least one exfoliated transition metal dichalcogenide with at least one *N*-heterocyclic carbene precursor.

[0294] In various embodiments, the present invention provides a method of making at least one *N*-heterocyclic carbene functionalized transition metal dichalcogenide, comprising: providing at least one bulk transition metal dichalcogenide; exfoliating the at least one bulk transition metal dichalcogenide to produce at least one exfoliated transition metal dichalcogenide; and reacting at least a portion of the at least one exfoliated transition metal dichalcogenide with at least one *N*-heterocyclic carbene precursor.

[0295] In some embodiments, the *N*-heterocyclic carbene adsorbate is a *N*-heterocyclic carbene precursor.

[0296] In some embodiments, the *N*-heterocyclic carbene precursor has a structure of Formula (I). In some embodiments, the *N*-heterocyclic carbene precursor has a structure of Formula (I-A). In some embodiments, the *N*-heterocyclic carbene precursor has a structure of Formula (I-B). In some embodiments, the *N*-heterocyclic carbene precursor of Formula (I) is a *N*-heterocyclic carbene precursor of Formula (I-A). In some embodiments, the *N*-heterocyclic carbene precursor of Formula (I) is a *N*-heterocyclic carbene precursor of Formula (I-B). In some embodiments, the *N*-heterocyclic carbene precursor of Formula (I-A) is a *N*-heterocyclic carbene precursor of Formula (I-B).

[0297] In some embodiments, the *N*-heterocyclic carbene has a structure of Formula (II). In some embodiments, the *N*-heterocyclic carbene has a structure of Formula (II-A). In some embodiments, the *N*-heterocyclic carbene has a structure of Formula (II-B). In some embodiments, the *N*-heterocyclic carbene of Formula (II) is a *N*-heterocyclic carbene of Formula (II-A). In some embodiments, the *N*-heterocyclic carbene of Formula (II) is a *N*-heterocyclic carbene of Formula (II-B). In some embodiments, the *N*-heterocyclic carbene of Formula (II-A) is a *N*-heterocyclic carbene of Formula (II-B).

[0298] Additional embodiments include those listed below.

[0299] In various embodiments, the present invention aims to establish an effective method for functionalizing 2D TMDs. The work described herein focuses on using redox exfoliation to produce 2D nanolayered MoS₂, thereby affording few- to monolayered nanosheets. Additionally, nanosheets with varied sizes and thicknesses were collected for characterization and evaluation.

Subsequently, exposure of the exfoliated materials to selected organic ligands induced functionalization, leading to the formation of self-assembled monolayers (SAMs) of organic molecules on the basal plane of exfoliated MoS₂ nanosheets. Consequently, a new family of 2D materials was created with custom-designed interlayer expansions.

[0300] In various embodiments of the present invention, the work described herein demonstrates the successful exfoliation of 2D nanolayered MoS₂, primarily achieving nanosheets with fewer than 5 layers. Crucially, the exfoliated materials retained their semiconducting properties without any indication of phase transformation. Subsequent exposure to organic adsorbates led to functionalization of the basal plane of the MoS₂ nanosheets, leading to the formation of new structures with entrapped molecules between the interlayer gaps of the 2D materials. These novel 2D structures exhibited interlayer expansion, which could be modulated for targeted applications.

[0301] Additional embodiments include those listed below.

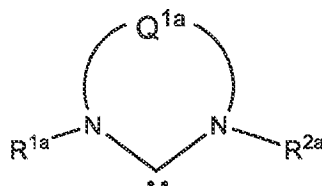
[0302] In various embodiments, the present invention provides a method of making at least one *N*-heterocyclic carbene functionalized transition metal dichalcogenide, comprising: providing at least one bulk transition metal dichalcogenide; exfoliating the at least one bulk transition metal dichalcogenide to produce at least one exfoliated transition metal dichalcogenide comprising at least one exfoliated surface; and reacting at least a portion of the at least one exfoliated surface of the at least one exfoliated transition metal dichalcogenide with at least one *N*-heterocyclic carbene precursor. In various embodiments, the present invention provides a *N*-heterocyclic carbene functionalized transition metal dichalcogenide made by a method of the present invention. In various embodiments, the present invention provides an article of manufacture comprising a *N*-heterocyclic carbene functionalized transition metal dichalcogenide made by a method of the present invention.

[0303] In various embodiments, the present invention provides a *N*-heterocyclic carbene functionalized transition metal dichalcogenide, comprising: at least one transition metal dichalcogenide; and at least one *N*-heterocyclic carbene. In various embodiments, the present invention provides an article of manufacture comprising a *N*-heterocyclic carbene functionalized transition metal dichalcogenide.

[0304] Additional embodiments include those listed below.

[0305] Embodiment 92. A *N*-heterocyclic carbene functionalized transition metal dichalcogenide, comprising: at least one transition metal dichalcogenide; and at least one *N*-heterocyclic carbene.

[0306] Embodiment 93. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 92, wherein the at least one *N*-heterocyclic carbene has a structure of Formula (II):



Formula (II),

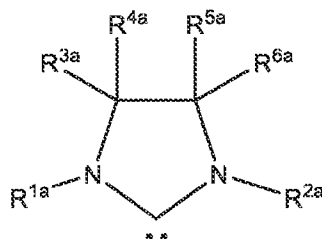
wherein:

R^{1a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{2a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and

Q^{1a} is an optionally substituted linker.

[0307] Embodiment 94. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 92, wherein the at least one *N*-heterocyclic carbene has a structure of Formula (II-A):



Formula (II-A),

wherein:

R^{1a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{2a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{3a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

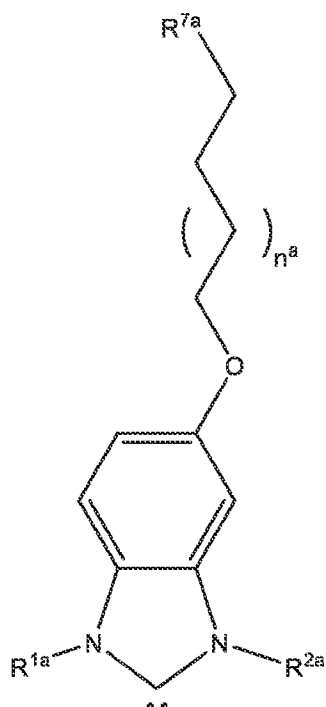
R^{4a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{5a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and

R^{6a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; wherein R^{3a} and R^{4a} are not both absent, and wherein R^{5a} and R^{6a} are not both absent; or

R^{3a} and R^{5a}, or R^{3a} and R^{6a}, or R^{4a} and R^{5a}, or R^{4a} and R^{6a} may be taken together to form a ring, wherein the ring is optionally substituted.

[0308] Embodiment 95. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 92, wherein the at least one *N*-heterocyclic carbene has the structure of Formula (II-B):



Formula (II-B),

wherein:

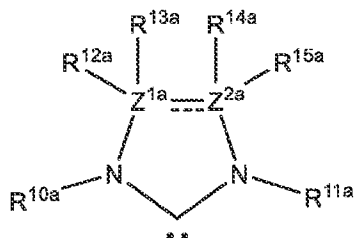
n^a is 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, or 12;

R^{1a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{2a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and

R^{7a} is H, OR^{8a} , SR^{9a} , halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl, wherein R^{8a} is H, or optionally substituted alkyl, and R^{9a} is H, or optionally substituted alkyl.

[0309] Embodiment 96. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 92, wherein the at least one *N*-heterocyclic carbene has a structure of Formula (IV).



Formula (IV)

wherein:

Z^{1a} is C;

Z^{2a} is C;

R^{10a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{11a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{12a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted alkylamino, optionally substituted amino, hydroxy, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{13a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted alkylamino, optionally substituted amino, hydroxy, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

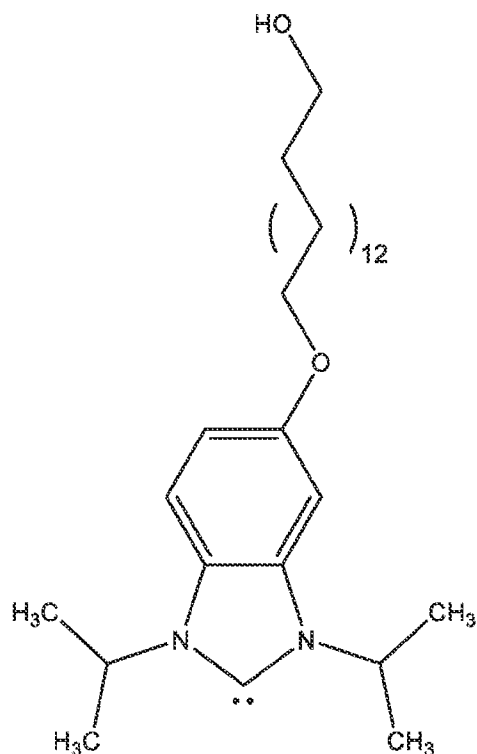
R^{14a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted alkylamino, optionally substituted amino, hydroxy, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{15a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted alkylamino, optionally substituted amino, hydroxy, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and

wherein R^{12a} and R^{13a} are not both absent, and wherein R^{14a} and R^{15a} are not both absent; and

===== between Z^{1a} and Z^{2a} indicates a bond that may be a single bond or a double bond; or R^{12a} and R^{14a} , or R^{12a} and R^{15a} , or R^{13a} and R^{14a} , or R^{13a} and R^{15a} may be taken together to form a ring, wherein the ring is optionally substituted.

[0310] Embodiment 97. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 92, wherein the at least one *N*-heterocyclic carbene is



[0311] Embodiment 98. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 92, wherein the at least one transition metal dichalcogenide has the formula: $M^aX^a_2$, wherein: M^a is a Group 4-10 transition metal; and X^a is a chalcogen.

[0312] Embodiment 99. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 98, wherein M^a is a Group 6 transition metal.

[0313] Embodiment 100. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 98, wherein the chalcogen is sulfur (S), selenium (Se), or tellurium (Te).

[0314] Embodiment 101. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 99, wherein the Group 6 transition metal is molybdenum (Mo) or tungsten (W).

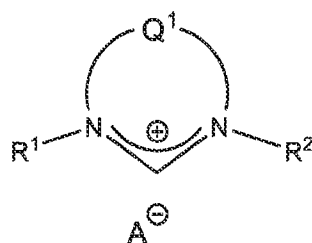
[0315] Embodiment 102. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 92, wherein the at least one transition metal dichalcogenide is MoS₂ or WS₂.

[0316] Embodiment 103. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 92, wherein the at least one transition metal dichalcogenide is an at least one exfoliated transition metal dichalcogenide, wherein the at least one exfoliated transition metal dichalcogenide comprises at least one exfoliated surface, and wherein the at least one *N*-heterocyclic carbene forms a self-assembled monolayer (SAM) or a partial self-assembled monolayer (SAM) on at least a portion of the at least one exfoliated surface of the at least one exfoliated transition metal dichalcogenide.

[0317] Embodiment 104. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 92, wherein the at least one transition metal dichalcogenide is an at least one exfoliated transition metal dichalcogenide, wherein the at least one exfoliated transition metal dichalcogenide comprises at least one exfoliated surface, wherein the at least one exfoliated surface comprises at least one exfoliated basal plane, and wherein the at least one *N*-heterocyclic carbene forms a self-assembled monolayer (SAM) or a partial self-assembled monolayer (SAM) on at least a portion of the at least one exfoliated basal plane.

[0318] Embodiment 105. A method of making at least one *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 92, comprising: providing at least one bulk transition metal dichalcogenide; exfoliating the at least one bulk transition metal dichalcogenide to produce at least one exfoliated transition metal dichalcogenide comprising at least one exfoliated surface; and reacting at least a portion of the at least one exfoliated surface of the at least one exfoliated transition metal dichalcogenide with at least one *N*-heterocyclic carbene precursor.

[0319] Embodiment 106. The method of embodiment 105, wherein the at least one *N*-heterocyclic carbene precursor has a structure of Formula (I):



Formula (I),

wherein:

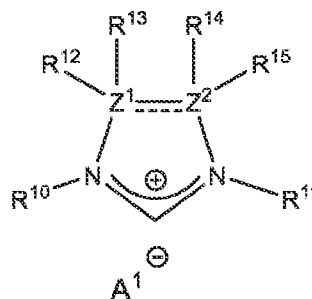
A⁻ is a counterion;

R¹ is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R² is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and

Q¹ is an optionally substituted linker.

[0320] Embodiment 107. The method of embodiment 105, wherein the at least one *N*-heterocyclic carbene precursor has a structure of Formula (III):



Formula (III)

wherein:

A¹⁻ is a counterion;

Z¹ is C;

Z² is C;

R¹⁰ is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R¹¹ is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R¹² is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted alkylamino, optionally substituted amino, hydroxy, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R¹³ is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted alkylamino, optionally substituted amino, hydroxy, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

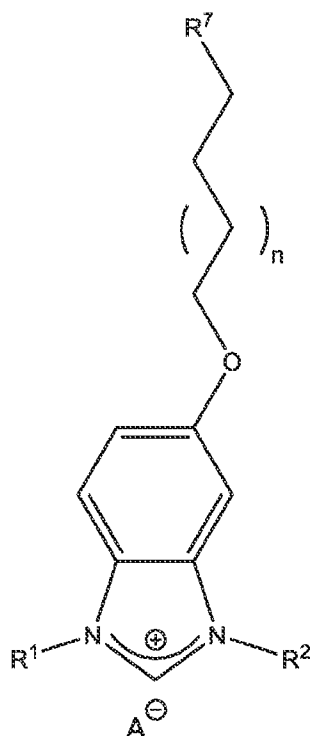
R¹⁴ is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted alkylamino, optionally substituted amino, hydroxy, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R¹⁵ is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted alkylamino, optionally substituted amino, hydroxy, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and

wherein R¹² and R¹³ are not both absent, and wherein R¹⁴ and R¹⁵ are not both absent; and

===== between Z¹ and Z² indicates a bond that may be a single bond or a double bond; or R¹² and R¹⁴, or R¹² and R¹⁵, or R¹³ and R¹⁴, or R¹³ and R¹⁵ may be taken together to form a ring, wherein the ring is optionally substituted.

[0321] Embodiment 108. The method of embodiment 105, wherein the *N*-heterocyclic carbene precursor has the structure of Formula (I-B):



Formula (I-B),

wherein:

A^- is a counterion;

n is 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, or 12;

R^1 is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^2 is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and

R^7 is H, OR^8 , SR^9 , halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl, wherein R^8 is H, or optionally substituted alkyl, and R^9 is H, or optionally substituted alkyl.

[0322] Embodiment 109. An article of manufacture comprising at least one *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 92.

[0323] Embodiment 110. The article of manufacture of embodiment 109, wherein the article of manufacture is an energy storage device, energy storage material, sensing device, sensing material, semiconductor electronic device, semiconductor electronic material, semiconductor optoelectronic device, or semiconductor optoelectronic material.

[0324] Embodiment 111. The article of manufacture of embodiment 109, wherein the article of manufacture is a semiconductor or has semiconducting properties.

[0325] Additional embodiments include those listed below.

[0326] In various embodiments, the present invention provides a *N*-heterocyclic carbene functionalized transition metal dichalcogenide, comprising: at least one transition metal dichalcogenide; and at least one *N*-heterocyclic carbene.

[0327] In some embodiments, the at least one *N*-heterocyclic carbene is chemically bonded to the at least one transition metal dichalcogenide. In some embodiments, the at least one *N*-heterocyclic carbene is chemically bonded to an at least one transition metal of the at least one transition metal dichalcogenide. In some embodiments, the chemical bond is a covalent bond, ionic bond, or combination thereof. In some embodiments, the at least one *N*-heterocyclic carbene is chemically bonded to the at least one exfoliated transition metal dichalcogenide. In some embodiments, the at least one *N*-heterocyclic carbene is chemically bonded to the at least one exfoliated surface of the at least one exfoliated transition metal dichalcogenide. In some embodiments, the at least one *N*-heterocyclic carbene is chemically bonded to the at least one exfoliated basal plane of the at least one exfoliated transition metal dichalcogenide.

[0328] In some embodiments, the at least one *N*-heterocyclic carbene is physisorbed to the at least one transition metal dichalcogenide. In some embodiments, the at least one *N*-heterocyclic carbene is physisorbed to the at least one exfoliated transition metal dichalcogenide. In some embodiments, the at least one *N*-heterocyclic carbene is physisorbed to the at least one exfoliated surface of the at least one exfoliated transition metal dichalcogenide. In some embodiments, the at least one *N*-heterocyclic carbene is physisorbed to the at least one exfoliated basal plane of the at least one exfoliated transition metal dichalcogenide.

[0329] In some embodiments, the at least one *N*-heterocyclic carbene is chemisorbed to the at least one transition metal dichalcogenide. In some embodiments, the at least one *N*-heterocyclic carbene is chemisorbed to the at least one exfoliated transition metal dichalcogenide. In some embodiments, the at least one *N*-heterocyclic carbene is chemisorbed to the at least one

exfoliated surface of the at least one exfoliated transition metal dichalcogenide. In some embodiments, the at least one *N*-heterocyclic carbene is chemisorbed to the at least one exfoliated basal plane of the at least one exfoliated transition metal dichalcogenide.

[0330] In various embodiments, the present invention provides at least one transition metal dichalcogenide, wherein the at least one transition metal dichalcogenide has the formula: $M^aX^a_2$, wherein: M^a is a Group 4-10 transition metal; and X^a is a chalcogen.

[0331] In some embodiments, M^a is a Group 4 transition metal, or Group 5 transition metal, or Group 6 transition metal, or Group 7 transition metal, or Group 8 transition metal, or Group 9 transition metal, or Group 10 transition metal.

[0332] In some embodiments, M^a is a Group 6 transition metal.

[0333] In some embodiments, the chalcogen is sulfur (S), selenium (Se), or tellurium (Te). In some embodiments the chalcogen is sulfur (S). In some embodiments, the chalcogen is selenium (Se). In some embodiments, the chalcogen is tellurium (Te).

[0334] In some embodiments, the Group 6 transition metal is molybdenum (Mo). In some embodiments, the Group 6 transition metal is molybdenum (Mo) or tungsten (W). In some embodiments, the Group 6 transition metal is tungsten (W).

[0335] In some embodiments, the at least one transition metal dichalcogenide is MoS_2 . In some embodiments, the at least one transition metal dichalcogenide is MoS_2 or WS_2 . In some embodiments, the at least one transition metal dichalcogenide is WS_2 .

[0336] In some embodiments, the at least one transition metal dichalcogenide is an at least one exfoliated transition metal dichalcogenide.

[0337] In some embodiments, the at least one transition metal dichalcogenide is an at least one exfoliated transition metal dichalcogenide, wherein the at least one exfoliated transition metal dichalcogenide comprises at least one exfoliated surface, and wherein the at least one *N*-heterocyclic carbene forms a self-assembled monolayer (SAM) on at least a portion of the at least one exfoliated surface of the at least one exfoliated transition metal dichalcogenide.

[0338] In some embodiments, the at least one transition metal dichalcogenide is an at least one exfoliated transition metal dichalcogenide, wherein the at least one exfoliated transition metal dichalcogenide comprises at least one exfoliated surface, and wherein the at least one *N*-heterocyclic carbene forms a self-assembled monolayer (SAM) or partial self-assembled

monolayer (SAM) on at least a portion of the at least one exfoliated surface of the at least one exfoliated transition metal dichalcogenide.

[0339] In some embodiments, the at least one transition metal dichalcogenide is an at least one exfoliated transition metal dichalcogenide, wherein the at least one exfoliated transition metal dichalcogenide comprises at least one exfoliated surface, wherein the at least one exfoliated surface comprises at least one exfoliated basal plane, and wherein the at least one *N*-heterocyclic carbene forms a self-assembled monolayer (SAM) on at least a portion of the at least one exfoliated basal plane.

[0340] In some embodiments, the at least one transition metal dichalcogenide is an at least one exfoliated transition metal dichalcogenide, wherein the at least one exfoliated transition metal dichalcogenide comprises at least one exfoliated surface, wherein the at least one exfoliated surface comprises at least one exfoliated basal plane, and wherein the at least one *N*-heterocyclic carbene forms a self-assembled monolayer (SAM) or partial self-assembled monolayer (SAM) on at least a portion of the at least one exfoliated basal plane.

[0341] In some embodiments, the self-assembled monolayer (SAM) is a homogenous self-assembled monolayer, or heterogenous self-assembled monolayer. In some embodiments, the partial self-assembled monolayer (SAM) is a homogenous self-assembled monolayer, or heterogenous self-assembled monolayer.

[0342] In some embodiments, the self-assembled monolayer (SAM) comprises at least one *N*-heterocyclic carbene. In some embodiments, the partial self-assembled monolayer (SAM) comprises at least one *N*-heterocyclic carbene.

[0343] In some embodiments, the at least one *N*-heterocyclic carbene is the same or different. In some embodiments, the at least one *N*-heterocyclic carbene precursor is the same or different.

[0344] In various embodiments, the present invention provides a method of making at least one *N*-heterocyclic carbene functionalized transition metal dichalcogenide, comprising: providing at least one bulk transition metal dichalcogenide; exfoliating the at least one bulk transition metal dichalcogenide to produce at least one exfoliated transition metal dichalcogenide comprising at least one exfoliated surface; and reacting at least a portion of the at least one exfoliated surface of the at least one exfoliated transition metal dichalcogenide with at least one *N*-heterocyclic carbene precursor.

[0345] In various embodiments, the present invention provides a method of making at least one *N*-heterocyclic carbene functionalized transition metal dichalcogenide, comprising: providing at least one bulk transition metal dichalcogenide; exfoliating the at least one bulk transition metal dichalcogenide to produce at least one exfoliated transition metal dichalcogenide; and reacting the at least one exfoliated transition metal dichalcogenide with at least one *N*-heterocyclic carbene precursor.

[0346] In various embodiments, the present invention provides a method of making at least one *N*-heterocyclic carbene functionalized transition metal dichalcogenide, comprising: providing at least one bulk transition metal dichalcogenide; exfoliating the at least one bulk transition metal dichalcogenide to produce at least one exfoliated transition metal dichalcogenide comprising at least one exfoliated surface; and reacting at least a portion of the at least one exfoliated surface of the at least one exfoliated transition metal dichalcogenide with at least one *N*-heterocyclic carbene precursor.

[0347] In some embodiments, reacting the at least one exfoliated transition metal dichalcogenide with at least one *N*-heterocyclic carbene precursor is performed under conditions sufficient to make the at least one *N*-heterocyclic carbene functionalized transition metal dichalcogenide.

[0348] In some embodiments, reacting at least a portion of the at least one exfoliated surface of the at least one exfoliated transition metal dichalcogenide with at least one *N*-heterocyclic carbene precursor is performed under conditions sufficient to make the at least one *N*-heterocyclic carbene functionalized transition metal dichalcogenide.

[0349] In some embodiments, reacting the at least one exfoliated transition metal dichalcogenide with at least one *N*-heterocyclic carbene precursor is performed under conditions effective to make the at least one *N*-heterocyclic carbene functionalized transition metal dichalcogenide.

[0350] In some embodiments, reacting at least a portion of the at least one exfoliated surface of the at least one exfoliated transition metal dichalcogenide with at least one *N*-heterocyclic carbene precursor is performed under conditions effective to make the at least one *N*-heterocyclic carbene functionalized transition metal dichalcogenide.

[0351] In some embodiments, the at least one exfoliated surface of the at least one exfoliated transition metal dichalcogenide comprises at least one exfoliated basal plane.

[0352] In some embodiments, the at least one exfoliated transition metal dichalcogenide comprises at least one exfoliated basal plane.

[0353] In some embodiments, the exfoliating is conducted by a redox exfoliation process.

[0354] In some embodiments, the at least one *N*-heterocyclic carbene precursor forms a self-assembled monolayer (SAM) on the at least one exfoliated surface of the at least one exfoliated transition metal dichalcogenide.

[0355] In some embodiments, the at least one *N*-heterocyclic carbene precursor forms a partial self-assembled monolayer (SAM) on the at least one exfoliated surface of the at least one exfoliated transition metal dichalcogenide.

[0356] In some embodiments, the self-assembled monolayer (SAM) is a homogenous self-assembled monolayer, or heterogenous self-assembled monolayer.

[0357] In some embodiments, the partial self-assembled monolayer (SAM) is a homogenous self-assembled monolayer, or heterogenous self-assembled monolayer.

[0358] In some embodiments, the self-assembled monolayer (SAM) comprises at least one *N*-heterocyclic carbene.

[0359] In some embodiments, the partial self-assembled monolayer (SAM) comprises at least one *N*-heterocyclic carbene.

[0360] In some embodiments, the at least one bulk transition metal dichalcogenide comprises a two-dimensional (2D) structure. In some embodiments, the 2D structure comprises one layer, or a plurality of layers.

[0361] In some embodiments, the at least one bulk transition metal dichalcogenide has the formula: $M^cX^c_2$, wherein: M^c is a Group 4-10 transition metal; and X^c is a chalcogen.

[0362] In some embodiments, M^c is a Group 4 transition metal, or Group 5 transition metal, or Group 6 transition metal, or Group 7 transition metal, or Group 8 transition metal, or Group 9 transition metal, or Group 10 transition metal.

[0363] In some embodiments, M^c is a Group 6 transition metal.

[0364] In some embodiments, the chalcogen is sulfur (S), selenium (Se), or tellurium (Te). In some embodiments the chalcogen is sulfur (S). In some embodiments, the chalcogen is selenium (Se). In some embodiments, the chalcogen is tellurium (Te).

[0365] In some embodiments, the Group 6 transition metal is molybdenum (Mo). In some embodiments, the Group 6 transition metal is molybdenum (Mo) or tungsten (W). In some embodiments, the Group 6 transition metal is tungsten (W).

[0366] In some embodiments, the at least one bulk transition metal dichalcogenide is MoS₂. In some embodiments, the at least one bulk transition metal dichalcogenide is MoS₂ or WS₂. In some embodiments, the at least one transition metal dichalcogenide is WS₂.

[0367] In some embodiments, the at least one exfoliated transition metal dichalcogenide has the formula: M^bX^b₂, wherein: M^b is a Group 4-10 transition metal; and X^b is a chalcogen.

[0368] In some embodiments, M^b is a Group 4 transition metal, or Group 5 transition metal, or Group 6 transition metal, or Group 7 transition metal, or Group 8 transition metal, or Group 9 transition metal, or Group 10 transition metal.

[0369] In some embodiments, M^b is a Group 6 transition metal.

[0370] In some embodiments, the chalcogen is sulfur (S), selenium (Se), or tellurium (Te). In some embodiments the chalcogen is sulfur (S). In some embodiments, the chalcogen is selenium (Se). In some embodiments, the chalcogen is tellurium (Te).

[0371] In some embodiments, the Group 6 transition metal is molybdenum (Mo). In some embodiments, the Group 6 transition metal is molybdenum (Mo) or tungsten (W). In some embodiments, the Group 6 transition metal is tungsten (W).

[0372] In some embodiments, the at least one exfoliated transition metal dichalcogenide is MoS₂. In some embodiments, the at least one exfoliated transition metal dichalcogenide is MoS₂ or WS₂. In some embodiments, the at least one exfoliated transition metal dichalcogenide is WS₂.

[0373] In some embodiments, the at least one exfoliated transition metal dichalcogenide comprises a two-dimensional (2D) structure. In some embodiments, the 2D structure comprises one layer, or a plurality of layers.

[0374] In some embodiments, the at least one exfoliated transition metal dichalcogenide comprises at least one exfoliated surface.

[0375] In some embodiments, the reaction of the at least a portion of the at least one exfoliated surface of the at least one exfoliated transition metal dichalcogenide with at least one *N*-heterocyclic carbene precursor to make the at least one *N*-heterocyclic carbene functionalized transition metal dichalcogenide.

[0376] In some embodiments, the at least one *N*-heterocyclic carbene functionalized transition metal dichalcogenide comprises at least one *N*-heterocyclic carbene.

[0377] In some embodiments, the *N*-heterocyclic carbene functionalized transition metal dichalcogenide is insulating, semiconducting, conducting, semi-metallic, metallic, or any combination thereof.

[0378] In some embodiments, the *N*-heterocyclic carbene functionalized transition metal dichalcogenide is semiconducting.

[0379] In some embodiments, the *N*-heterocyclic carbene functionalized transition metal dichalcogenide is a semiconductor.

[0380] In some embodiments, the *N*-heterocyclic carbene functionalized transition metal dichalcogenide comprises a self-assembled monolayer (SAM). In some embodiments, the self-assembled monolayer (SAM) is a homogenous self-assembled monolayer, or heterogenous self-assembled monolayer. In some embodiments, the self-assembled monolayer (SAM) comprises at least one *N*-heterocyclic carbene.

[0381] In some embodiments, the *N*-heterocyclic carbene functionalized transition metal dichalcogenide comprises a partial self-assembled monolayer (SAM). In some embodiments, the partial self-assembled monolayer (SAM) is a homogenous self-assembled monolayer, or heterogenous self-assembled monolayer. In some embodiments, the partial self-assembled monolayer (SAM) comprises at least one *N*-heterocyclic carbene.

[0382] In some embodiments, the *N*-heterocyclic carbene functionalized transition metal dichalcogenide comprises a superstructure comprising intercalated layers. In some embodiments, the intercalated layers comprise the at least one *N*-heterocyclic carbene.

[0383] In some embodiments, the *N*-heterocyclic carbene functionalized transition metal dichalcogenide comprises a superstructure comprising intercalated layers, wherein the intercalated layers comprise at least one *N*-heterocyclic carbene.

[0384] In some embodiments, the at least one *N*-heterocyclic carbene forms a self-assembled monolayer (SAM) or partial self-assembled monolayer (SAM) on the at least one exfoliated surface of the at least one exfoliated transition metal dichalcogenide.

[0385] In some embodiments, the self-assembled monolayer (SAM) is a homogenous self-assembled monolayer, or heterogenous self-assembled monolayer. In some embodiments, the

partial self-assembled monolayer (SAM) is a homogenous self-assembled monolayer, or heterogenous self-assembled monolayer.

[0386] In some embodiments, the at least one exfoliated transition metal dichalcogenide comprises at least one exfoliated basal plane. In some embodiments, the at least one exfoliated basal plane is functionalized with the at least one *N*-heterocyclic carbene. In some embodiments, the at least one exfoliated transition metal dichalcogenide comprises a two-dimensional (2D) structure. In some embodiments, the 2D structure comprises one layer, or a plurality of layers.

[0387] In various embodiments, the present invention provides an article of manufacture comprising at least one *N*-heterocyclic carbene functionalized transition metal dichalcogenide of the present invention.

[0388] In some embodiments, the article of manufacture is an energy storage device, energy storage material, sensing device, sensing material, semiconductor electronic device, semiconductor electronic material, semiconductor optoelectronic device, or semiconductor optoelectronic material.

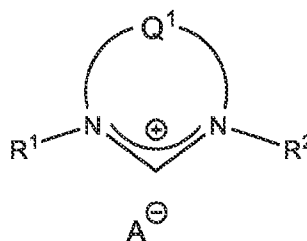
[0389] In some embodiments, the article of manufacture is a semiconductor. In some embodiments, the article of manufacture is a semiconductor, or has semiconducting properties.

[0390] In various embodiments, the present invention provides for use of the *N*-heterocyclic carbene functionalized transition metal dichalcogenide of the present invention.

[0391] In various embodiments, the present invention provides for use of the *N*-heterocyclic carbene functionalized transition metal dichalcogenide made by the method of the present invention.

[0392] Additional embodiments include those listed below.

[0393] In various embodiments, the present invention provides at least one *N*-heterocyclic carbene precursor, wherein the at least one *N*-heterocyclic carbene precursor has a structure of Formula (I):



Formula (I),

wherein:

A^- is a counterion;

R^1 is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

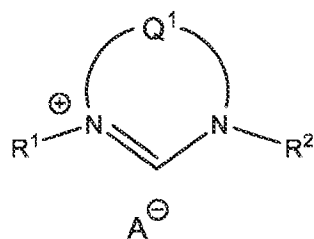
R^2 is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and Q^1 is an optionally substituted linker.

[0394] In some embodiments, the optionally substituted linker comprises at least one carbon-carbon double bond. In some embodiments, the optionally substituted linker is an optionally substituted alkylene, or optionally substituted alkenylene.

[0395] In some embodiments, R^1 is ethyl, propyl, isopropyl, butyl, pentyl, or decyl. In some embodiments, R^2 is ethyl, propyl, isopropyl, butyl, pentyl, or decyl.

[0396] In some embodiments, A^- is Cl^- , Br^- , I^- , OMs^- , OTf^- , BF_4^- , or PF_6^- . In some embodiments, OMs^- is represented by $CH_3SO_3^-$. In some embodiments, OTf^- is represented by $CF_3SO_3^-$.

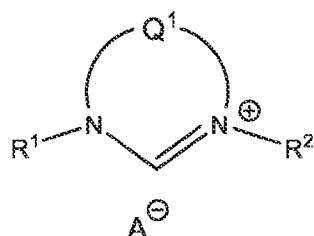
[0397] In some embodiments, the *N*-heterocyclic carbene precursor of Formula (I) may be represented by the *N*-heterocyclic carbene precursor of Formula (I-1), wherein the *N*-heterocyclic carbene precursor of Formula (I-1) has the following structure:



Formula (I-1),

wherein A^- , R^1 , R^2 , and Q^1 are as defined for the *N*-heterocyclic carbene precursor of Formula (I).

[0398] In some embodiments, the *N*-heterocyclic carbene precursor of Formula (I) may be represented by the *N*-heterocyclic carbene precursor of Formula (I-2), wherein the *N*-heterocyclic carbene precursor of Formula (I-2) has the following structure:

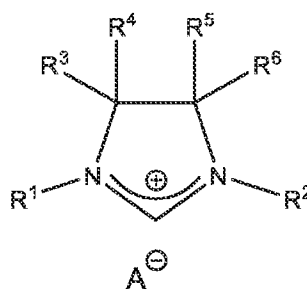


Formula (I-2),

wherein A^- , R^1 , R^2 , and Q^1 are as defined for the *N*-heterocyclic carbene precursor of Formula (I).

[0399] Additional embodiments include those listed below.

[0400] In various embodiments, the present invention provides a *N*-heterocyclic carbene precursor, wherein the *N*-heterocyclic carbene precursor has a structure of Formula (I-A):



Formula (I-A),

wherein:

A^- is a counterion;

R^1 is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^2 is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^3 is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R⁴ is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R⁵ is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and

R⁶ is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; or R³ and R⁵, or R³ and R⁶, or R⁴ and R⁵, or R⁴ and R⁶ may be taken together to form a ring, wherein the ring is optionally substituted.

[0401] In some embodiments, R³ and R⁴ are not both absent, and R⁵ and R⁶ are not both absent. In some embodiments, R³ and R⁴ are not both absent. In some embodiments, R⁵ and R⁶ are not both absent.

[0402] In some embodiments, the ring comprises at least one carbon-carbon double bond. In some embodiments, the ring is an optionally substituted aromatic ring. In some embodiments, the ring is an optionally substituted benzene ring. In some embodiments, the ring is an aromatic ring. In some embodiments, the ring is a benzene ring.

[0403] In some embodiments, A⁻ is Cl⁻, Br⁻, I⁻, ⁻OMs, ⁻OTf, ⁻BF₄, or ⁻PF₆. In some embodiments, ⁻OMs is represented by CH₃SO₃⁻. In some embodiments, ⁻OTf is represented by CF₃SO₃⁻.

[0404] In some embodiments, R¹ is ethyl, propyl, isopropyl, butyl, pentyl, or decyl. In some embodiments, R² is ethyl, propyl, isopropyl, butyl, pentyl, or decyl.

[0405] In some embodiments, R³ is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted alkylamino, optionally substituted amino, hydroxy, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl.

[0406] In some embodiments, R⁴ is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted alkylamino, optionally substituted amino, hydroxy, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl.

[0407] In some embodiments, R⁵ is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted alkylamino, optionally substituted amino, hydroxy, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl.

[0408] In some embodiments, R⁶ is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted alkylamino, optionally substituted amino, hydroxy, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl.

[0409] In some embodiments, R³ is absent, H, halo, OR⁵⁰, SR⁵¹, or NR⁵²R⁵³, wherein R⁵⁰ is H, or optionally substituted alkyl; wherein R⁵¹ is H, or optionally substituted alkyl; wherein R⁵² is H, or optionally substituted alkyl; and wherein R⁵³ is H, or optionally substituted alkyl.

[0410] In some embodiments, R⁴ is absent, H, halo, OR⁵⁴, SR⁵⁵, or NR⁵⁶R⁵⁷, wherein R⁵⁴ is H, or optionally substituted alkyl; wherein R⁵⁵ is H, or optionally substituted alkyl; wherein R⁵⁶ is H, or optionally substituted alkyl; and wherein R⁵⁷ is H, or optionally substituted alkyl.

[0411] In some embodiments, R⁵ is absent, H, halo, OR⁵⁸, SR⁵⁹, or NR⁶⁰R⁶¹, wherein R⁵⁸ is H, or optionally substituted alkyl; wherein R⁵⁹ is H, or optionally substituted alkyl; wherein R⁶⁰ is H, or optionally substituted alkyl; and wherein R⁶¹ is H, or optionally substituted alkyl.

[0412] In some embodiments, R⁶ is absent, H, halo, OR⁶², SR⁶³, or NR⁶⁴R⁶⁵, wherein R⁶² is H, or optionally substituted alkyl; wherein R⁶³ is H, or optionally substituted alkyl; wherein R⁶⁴ is H, or optionally substituted alkyl; and wherein R⁶⁵ is H, or optionally substituted alkyl.

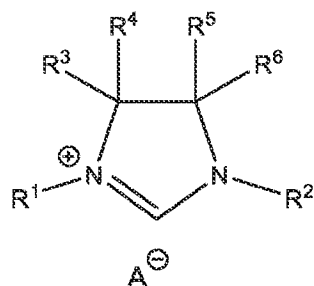
[0413] In some embodiments, if R⁴ and R⁵ are absent, then the bond between the carbon attached to R³ and the carbon attached to R⁶ is a carbon-carbon double bond.

[0414] In some embodiments, if R⁴ and R⁶ are absent, then the bond between the carbon attached to R³ and the carbon attached to R⁵ is a carbon-carbon double bond.

[0415] In some embodiments, if R³ and R⁵ are absent, then the bond between the carbon attached to R⁴ and the carbon attached to R⁶ is a carbon-carbon double bond.

[0416] In some embodiments, if R³ and R⁶ are absent, then the bond between the carbon attached to R⁴ and the carbon attached to R⁵ is a carbon-carbon double bond.

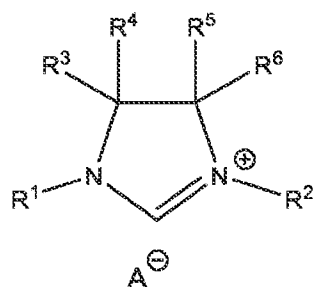
[0417] In some embodiments, the *N*-heterocyclic carbene precursor of Formula (I-A) may be represented by the *N*-heterocyclic carbene precursor of Formula (I-A-1), wherein the *N*-heterocyclic carbene precursor of Formula (I-A-1) has the following structure:



Formula (I-A-1),

wherein A^- , R^1 , R^2 , R^3 , R^4 , R^5 , and R^6 are as defined for the *N*-heterocyclic carbene precursor of Formula (I-A).

[0418] In some embodiments, the *N*-heterocyclic carbene precursor of Formula (I-A) may be represented by the *N*-heterocyclic carbene precursor of Formula (I-A-2), wherein the *N*-heterocyclic carbene precursor of Formula (I-A-2) has the following structure:

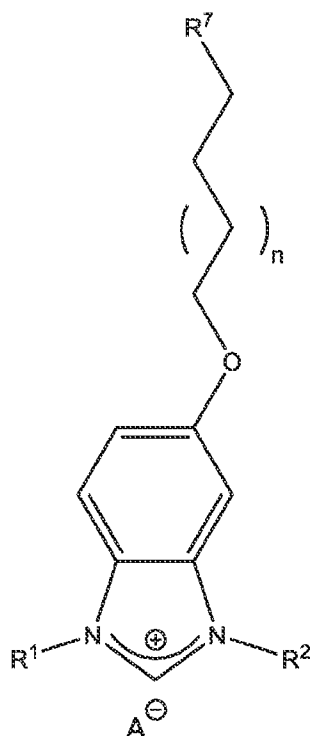


Formula (I-A-2),

wherein A^- , R^1 , R^2 , R^3 , R^4 , R^5 , and R^6 are as defined for the *N*-heterocyclic carbene precursor of Formula (I-A).

[0419] Additional embodiments include those listed below.

[0420] In some embodiments, the present invention provides a *N*-heterocyclic carbene precursor, wherein the *N*-heterocyclic carbene precursor has the structure of Formula (I-B):



Formula (I-B),

wherein:

A⁻ is a counterion;

n is 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, or 12;

R¹ is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

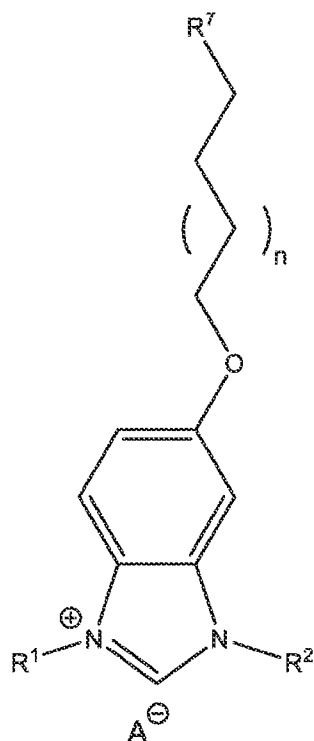
R² is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and

R⁷ is H, OR⁸, SR⁹, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl, wherein R⁸ is H, or optionally substituted alkyl, and R⁹ is H, or optionally substituted alkyl.

[0421] In some embodiments, R¹ is ethyl, propyl, isopropyl, butyl, pentyl, or decyl. In some embodiments, R² is ethyl, propyl, isopropyl, butyl, pentyl, or decyl.

[0422] In some embodiments, A^- is Cl^- , Br^- , I^- , ^-OMs , ^-OTf , $^-BF_4$, or $^-PF_6$. In some embodiments, ^-OMs is represented by $CH_3SO_3^-$. In some embodiments, ^-OTf is represented by $CF_3SO_3^-$.

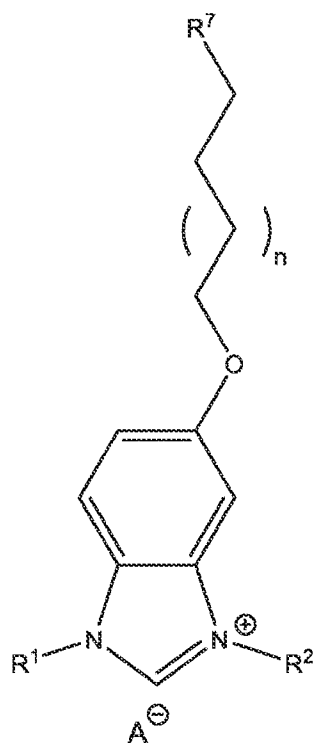
[0423] In some embodiments, the *N*-heterocyclic carbene precursor of Formula (I-B) may be represented by the *N*-heterocyclic carbene precursor of Formula (I-B-1), wherein the *N*-heterocyclic carbene precursor of Formula (I-B-1) has the following structure:



Formula (I-B-1),

wherein A^- , R^1 , R^2 , n , and R^7 are as defined for the *N*-heterocyclic carbene precursor of Formula (I-B).

[0424] In some embodiments, the *N*-heterocyclic carbene precursor of Formula (I-B) may be represented by the *N*-heterocyclic carbene precursor of Formula (I-B-2), wherein the *N*-heterocyclic carbene precursor of Formula (I-B-2) has the following structure:

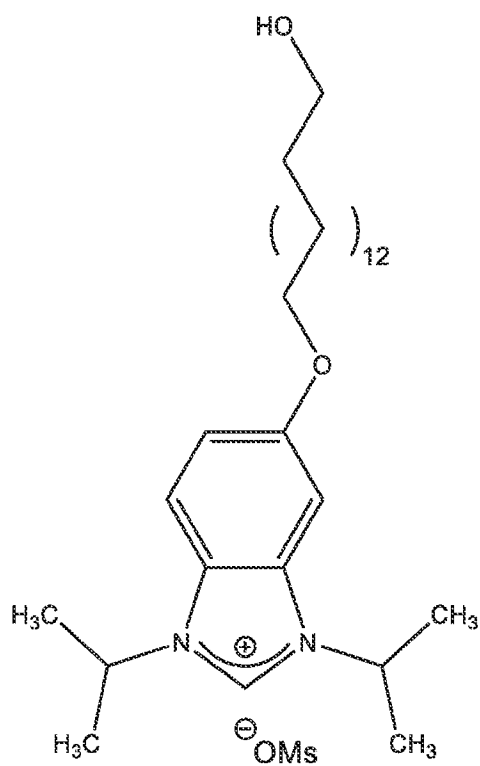


Formula (I-B-2),

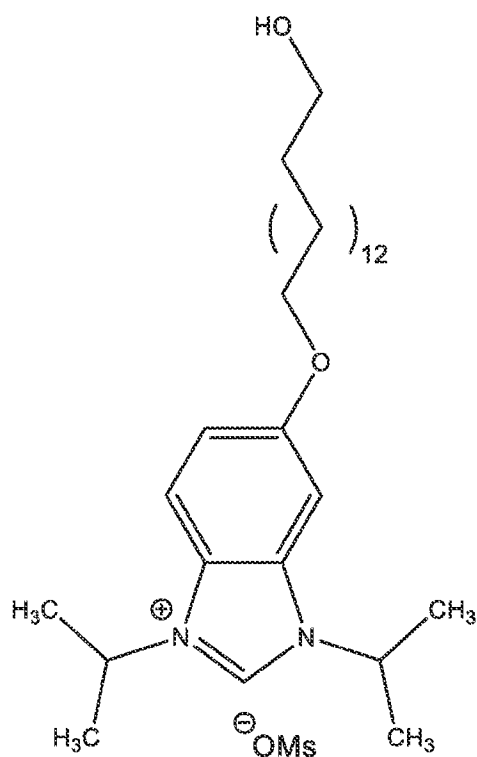
wherein A[⊖], R¹, R², n, and R⁷ are as defined for the *N*-heterocyclic carbene precursor of Formula (I-B).

[0425] Additional embodiments include those listed below.

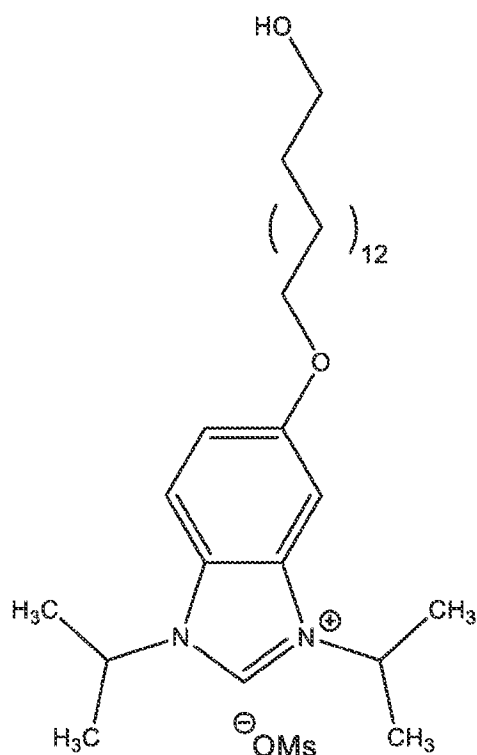
[0426] In various embodiments, the present invention provides at least one *N*-heterocyclic carbene precursor, wherein the at least one *N*-heterocyclic carbene precursor is



[0427] In various embodiments, the present invention provides at least one *N*-heterocyclic carbene precursor, wherein the at least one *N*-heterocyclic carbene precursor is

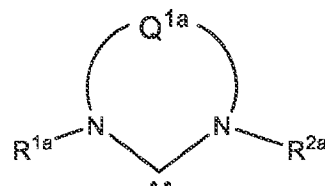


[0428] In various embodiments, the present invention provides at least one *N*-heterocyclic carbene precursor, wherein the at least one *N*-heterocyclic carbene precursor is



[0429] Additional embodiments include those listed below.

[0430] In various embodiments, the present invention provides at least one *N*-heterocyclic carbene, wherein the at least one *N*-heterocyclic carbene has a structure of Formula (II):



Formula (II),

wherein:

R^{1a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

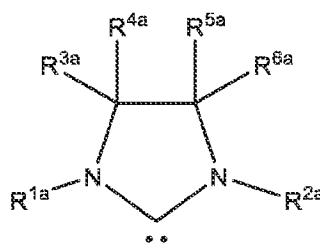
R^{2a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and Q^{1a} is an optionally substituted linker.

[0431] In some embodiments, the optionally substituted linker comprises at least one carbon-carbon double bond. In some embodiments, the optionally substituted linker is an optionally substituted alkylene, or optionally substituted alkenylene.

[0432] In some embodiments, R^{1a} is ethyl, propyl, isopropyl, butyl, pentyl, or decyl. In some embodiments, R^{2a} is ethyl, propyl, isopropyl, butyl, pentyl, or decyl.

[0433] Additional embodiments include those listed below.

[0434] In various embodiments, the present invention provides at least one *N*-heterocyclic carbene, wherein the at least one *N*-heterocyclic carbene has a structure of Formula (II-A).



Formula (II-A),

wherein:

R^{1a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{2a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{3a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{4a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{5a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and

R^{6a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; or

R^{3a} and R^{5a}, or R^{3a} and R^{6a}, or R^{4a} and R^{5a}, or R^{4a} and R^{6a} may be taken together to form a ring, wherein the ring is optionally substituted.

[0435] In some embodiments, wherein R^{3a} and R^{4a} are not both absent, and wherein R^{5a} and R^{6a} are not both absent. In some embodiments, wherein R^{3a} and R^{4a} are not both absent. In some embodiments, wherein R^{5a} and R^{6a} are not both absent.

[0436] In some embodiments, the ring comprises at least one carbon-carbon double bond. In some embodiments, the ring is an optionally substituted aromatic ring. In some embodiments, the ring is an optionally substituted benzene ring. In some embodiments, the ring is an aromatic ring. In some embodiments, the ring is a benzene ring.

[0437] In some embodiments, R^{1a} is ethyl, propyl, isopropyl, butyl, pentyl, or decyl. In some embodiments, R^{2a} is ethyl, propyl, isopropyl, butyl, pentyl, or decyl.

[0438] In some embodiments, R^{3a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted alkylamino, optionally substituted amino, hydroxy, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl.

[0439] In some embodiments, R^{4a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted alkylamino, optionally substituted amino, hydroxy, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl.

[0440] In some embodiments, R^{5a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted alkylamino, optionally substituted amino, hydroxy, optionally substituted

cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl.

[0441] In some embodiments, R^{6a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted alkylamino, optionally substituted amino, hydroxy, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl.

[0442] In some embodiments, R^{3a} is absent, H, halo, OR^{50a} , SR^{51a} , or $NR^{52a}R^{53a}$, wherein R^{50a} is H, or optionally substituted alkyl; wherein R^{51a} is H, or optionally substituted alkyl; wherein R^{52a} is H, or optionally substituted alkyl; and wherein R^{53a} is H, or optionally substituted alkyl.

[0443] In some embodiments, R^{4a} is absent, H, halo, OR^{54a} , SR^{55a} , or $NR^{56a}R^{57a}$, wherein R^{54a} is H, or optionally substituted alkyl; wherein R^{55a} is H, or optionally substituted alkyl; wherein R^{56a} is H, or optionally substituted alkyl; and wherein R^{57a} is H, or optionally substituted alkyl.

[0444] In some embodiments, R^{5a} is absent, H, halo, OR^{58a} , SR^{59a} , or $NR^{60a}R^{61a}$, wherein R^{58a} is H, or optionally substituted alkyl; wherein R^{59a} is H, or optionally substituted alkyl; wherein R^{60a} is H, or optionally substituted alkyl; and wherein R^{61a} is H, or optionally substituted alkyl.

[0445] In some embodiments, R^{6a} is absent, H, halo, OR^{62a} , SR^{63a} , or $NR^{64a}R^{65a}$, wherein R^{62a} is H, or optionally substituted alkyl; wherein R^{63a} is H, or optionally substituted alkyl; wherein R^{64a} is H, or optionally substituted alkyl; and wherein R^{65a} is H, or optionally substituted alkyl.

[0446] In some embodiments, if R^{4a} and R^{5a} are absent, then the bond between the carbon attached to R^{3a} and the carbon attached to R^{6a} is a carbon-carbon double bond.

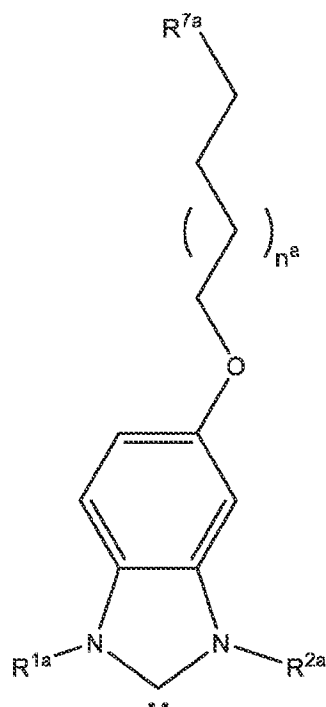
[0447] In some embodiments, if R^{4a} and R^{6a} are absent, then the bond between the carbon attached to R^{3a} and the carbon attached to R^{5a} is a carbon-carbon double bond.

[0448] In some embodiments, if R^{3a} and R^{5a} are absent, then the bond between the carbon attached to R^{4a} and the carbon attached to R^{6a} is a carbon-carbon double bond.

[0449] In some embodiments, if R^{3a} and R^{6a} are absent, then the bond between the carbon attached to R^{4a} and the carbon attached to R^{5a} is a carbon-carbon double bond.

[0450] Additional embodiments include those listed below.

[0451] In some embodiments, the at least one *N*-heterocyclic carbene has the structure of Formula (II-B):



Formula (II-B),

wherein:

n^a is 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, or 12;

R^{1a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

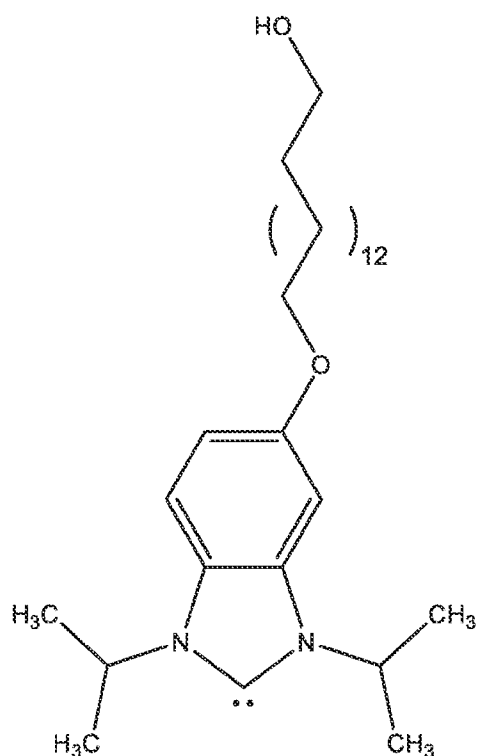
R^{2a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and

R^{7a} is H, OR^{8a} , SR^{9a} , halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl, wherein R^{8a} is H, or optionally substituted alkyl, and R^{9a} is H, or optionally substituted alkyl.

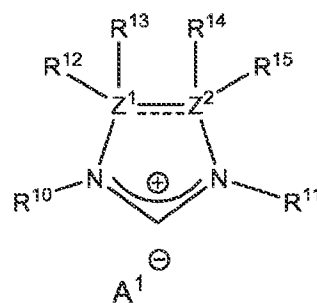
[0452] In some embodiments, R^{1a} is ethyl, propyl, isopropyl, butyl, pentyl, or decyl. In some embodiments, R^{2a} is ethyl, propyl, isopropyl, butyl, pentyl, or decyl.

[0453] Additional embodiments include those listed below.

[0454] In various embodiments, the present invention provides at least one *N*-heterocyclic carbene, wherein the at least one *N*-heterocyclic carbene is



[0455] In various embodiments, the present invention provides at least one *N*-heterocyclic carbene precursor, wherein the at least one *N*-heterocyclic carbene precursor has a structure of Formula (III):



Formula (III)

wherein:

A^{1-} is a counterion,

Z^1 is C;

Z^2 is C;

R^{10} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{11} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{12} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted alkylamino, optionally substituted amino, hydroxy, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{13} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted alkylamino, optionally substituted amino, hydroxy, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

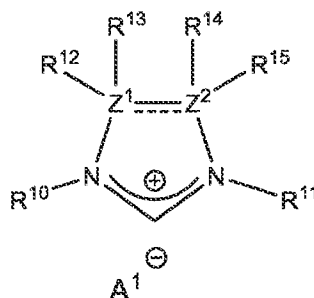
R^{14} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted alkylamino, optionally substituted amino, hydroxy, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{15} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted alkylamino, optionally substituted amino, hydroxy, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and

===== between Z^1 and Z^2 indicates a bond that may be a single bond or a double bond; or R^{12} and R^{14} , or R^{12} and R^{15} , or R^{13} and R^{14} , or R^{13} and R^{15} may be taken together to form a ring, wherein the ring is optionally substituted.

[0456] In some embodiments, R^{12} and R^{13} are not both absent, and wherein R^{14} and R^{15} are not both absent. In some embodiments, R^{12} and R^{13} are not both absent. In some embodiments, R^{14} and R^{15} are not both absent.

[0457] In various embodiments, the present invention provides at least one *N*-heterocyclic carbene precursor, wherein the at least one *N*-heterocyclic carbene precursor has a structure of Formula (III):



Formula (III)

wherein:

A¹ is a counterion;

Z¹ is C;

Z² is C;

R¹⁰ is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R¹¹ is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R¹² is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted alkylamino, optionally substituted amino, hydroxy, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R¹³ is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted alkylamino, optionally substituted amino, hydroxy, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R¹⁴ is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted alkylamino, optionally

substituted amino, hydroxy, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R¹⁵ is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted alkylamino, optionally substituted amino, hydroxy, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and

wherein R¹² and R¹³ are not both absent, and wherein R¹⁴ and R¹⁵ are not both absent; and

===== between Z¹ and Z² indicates a bond that may be a single bond or a double bond; or R¹² and R¹⁴, or R¹² and R¹⁵, or R¹³ and R¹⁴, or R¹³ and R¹⁵ may be taken together to form a ring, wherein the ring is optionally substituted.

[0458] In some embodiments, if R¹² is absent and R¹⁴ is absent, then the bond between Z¹ and Z² is a double bond. In some embodiments, if R¹² is absent and R¹⁵ is absent, then the bond between Z¹ and Z² is a double bond.

[0459] In some embodiments, if R¹³ is absent and R¹⁴ is absent, then the bond between Z¹ and Z² is a double bond. In some embodiments, if R¹³ is absent and R¹⁵ is absent, then the bond between Z¹ and Z² is a double bond.

[0460] In some embodiments, the ring comprises at least one carbon-carbon double bond. In some embodiments, the ring is an optionally substituted aromatic ring. In some embodiments, the ring is an optionally substituted benzene ring. In some embodiments, the ring is an aromatic ring. In some embodiments, the ring is a benzene ring.

[0461] In some embodiments, A¹⁻ is Cl⁻, Br⁻, I⁻, ⁻OMs, ⁻OTf, ⁻BF₄, or ⁻PF₆. In some embodiments, ⁻OMs is represented by CH₃SO₃⁻. In some embodiments, ⁻OTf is represented by CF₃SO₃⁻.

[0462] In some embodiments, R¹⁰ is ethyl, propyl, isopropyl, butyl, pentyl, or decyl. In some embodiments, R¹¹ is ethyl, propyl, isopropyl, butyl, pentyl, or decyl.

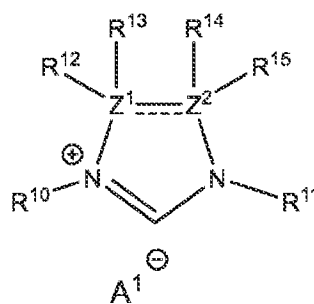
[0463] In some embodiments, R¹² is absent, H, halo, OR¹⁶, SR¹⁷, or NR¹⁸R¹⁹, wherein R¹⁶ is H, or optionally substituted alkyl; wherein R¹⁷ is H, or optionally substituted alkyl; wherein R¹⁸ is H, or optionally substituted alkyl; and wherein R¹⁹ is H, or optionally substituted alkyl.

[0464] In some embodiments, R¹³ is absent, H, halo, OR²⁰, SR²¹, or NR²²R²³, wherein R²⁰ is H, or optionally substituted alkyl; wherein R²¹ is H, or optionally substituted alkyl; wherein R²² is H, or optionally substituted alkyl; and wherein R²³ is H, or optionally substituted alkyl.

[0465] In some embodiments, R^{14} is absent, H, halo, OR^{24} , SR^{25} , or $NR^{26}R^{27}$, wherein R^{24} is H, or optionally substituted alkyl; wherein R^{25} is H, or optionally substituted alkyl; wherein R^{26} is H, or optionally substituted alkyl; and wherein R^{27} is H, or optionally substituted alkyl.

[0466] In some embodiments, R^{15} is absent, H, halo, OR^{28} , SR^{29} , or $NR^{30}R^{31}$, wherein R^{28} is H, or optionally substituted alkyl; wherein R^{29} is H, or optionally substituted alkyl; wherein R^{30} is H, or optionally substituted alkyl; and wherein R^{31} is H, or optionally substituted alkyl.

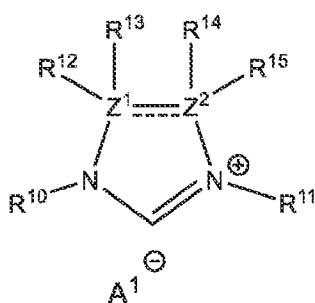
[0467] In some embodiments, the *N*-heterocyclic carbene precursor of Formula (III) may be represented by the *N*-heterocyclic carbene precursor of Formula (III-1), wherein the *N*-heterocyclic carbene precursor of Formula (III-1) has the following structure:



Formula (III-1),

wherein A¹, R¹⁰, R¹¹, R¹², R¹³, R¹⁴, R¹⁵, Z¹ and Z² are as defined for the *N*-heterocyclic carbene precursor of Formula (III).

[0468] In some embodiments, the *N*-heterocyclic carbene precursor of Formula (III) may be represented by the *N*-heterocyclic carbene precursor of Formula (III-2), wherein the *N*-heterocyclic carbene precursor of Formula (III-2) has the following structure:

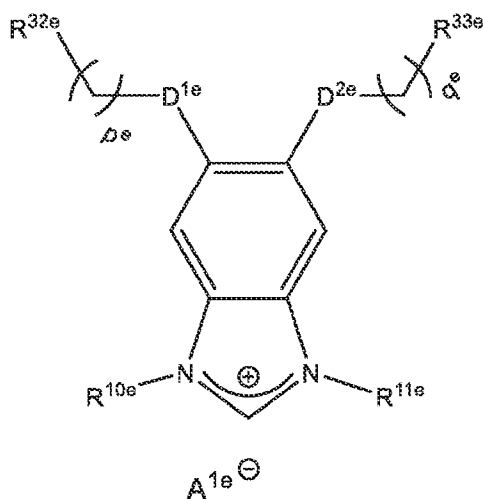


Formula (III-2),

wherein A¹, R¹⁰, R¹¹, R¹², R¹³, R¹⁴, R¹⁵, Z¹ and Z² are as defined for the *N*-heterocyclic carbene precursor of Formula (III).

[0469] Additional embodiments include those listed below.

[0470] In various embodiments, the present invention provides at least one *N*-heterocyclic carbene precursor, wherein the at least one *N*-heterocyclic carbene precursor has the structure of Formula (III-A):



Formula (III-A),

wherein:

A^{1e-} is a counterion;

p^e is 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, or 16;

q^e is 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, or 16;

D^{1e} is CH_2 , O, S, or NR^{34e} , where R^{34e} is H, or optionally substituted alkyl;

D^{2e} is CH_2 , O, S, or NR^{35e} , where R^{35e} is H, or optionally substituted alkyl;

R^{10e} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{11e} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

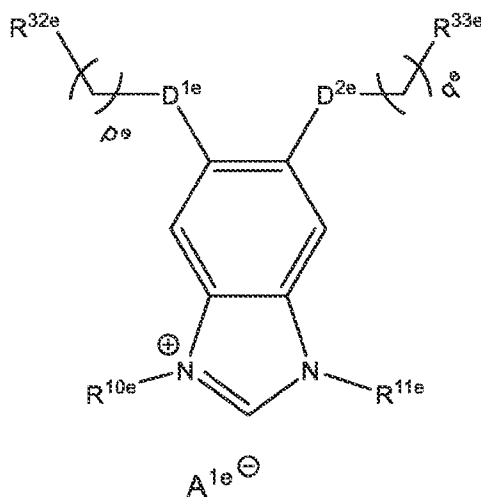
R^{32e} is H, OR^{12e} , SR^{13e} , $NR^{14e}R^{15e}$, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; wherein R^{12e} is H, or optionally substituted alkyl; and R^{13e} is H, or optionally substituted alkyl; wherein R^{14e} is H, or optionally substituted alkyl; and wherein R^{15e} is H, or optionally substituted alkyl; and

R^{33e} is H, OR^{16e} , SR^{17e} , $NR^{18e}R^{19e}$, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; wherein R^{16e} is H, or optionally substituted alkyl; R^{17e} is H, or optionally substituted alkyl; R^{18e} is H, or optionally substituted alkyl; and R^{19e} is H, or optionally substituted alkyl.

[0471] In some embodiments, A^{1e-} is Cl^- , Br^- , I^- , ^-OMs , ^-OTf , $^-BF_4$, or $^-PF_6$. In some embodiments, ^-OMs is represented by $CH_3SO_3^-$. In some embodiments, ^-OTf is represented by $CF_3SO_3^-$.

[0472] In some embodiments, R^{10e} is ethyl, propyl, isopropyl, butyl, pentyl, or decyl. In some embodiments, R^{11e} is ethyl, propyl, isopropyl, butyl, pentyl, or decyl.

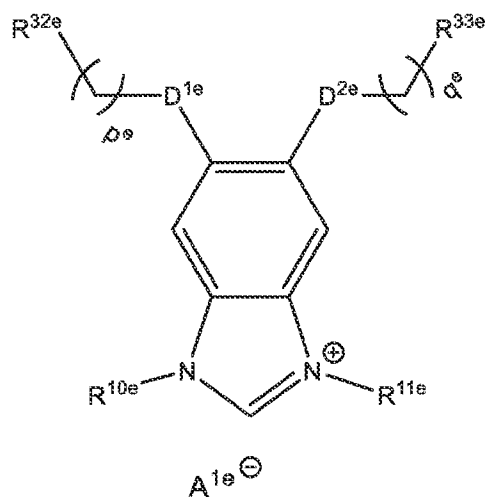
[0473] In some embodiments, the *N*-heterocyclic carbene precursor of Formula (III-A) may be represented by the *N*-heterocyclic carbene precursor of Formula (III-A-1), wherein the *N*-heterocyclic carbene precursor of Formula (III-A-1) has the following structure:



Formula (III-A-1),

where A^{1e-} , R^{10e} , R^{11e} , R^{32e} , R^{33e} , D^{1e} , D^{2e} , p^e and q^e are as defined for the *N*-heterocyclic carbene precursor of Formula (III-A).

[0474] In some embodiments, the *N*-heterocyclic carbene precursor of Formula (III-A) may be represented by the *N*-heterocyclic carbene precursor of Formula (III-A-2), wherein the *N*-heterocyclic carbene precursor of Formula (III-A-2) has the following structure:

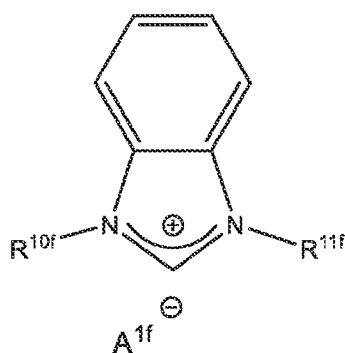


Formula (III-A-2),

where A^{1e}, R^{10e}, R^{11e}, R^{32e}, R^{33e}, D^{1e}, D^{2e}, p^e and q^e are as defined for the *N*-heterocyclic carbene precursor of Formula (III-A).

[0475] Additional embodiments include those listed below.

[0476] In various embodiments, the present invention provides at least one *N*-heterocyclic carbene precursor, wherein the at least one *N*-heterocyclic carbene precursor has a structure of Formula (III-B):



Formula (III-B),

wherein:

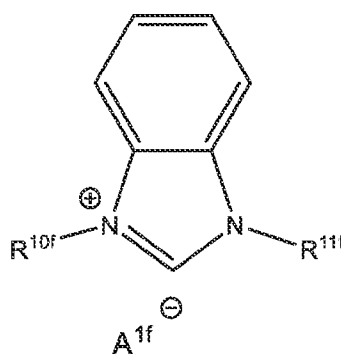
A^{1f} is a counterion;

R^{10f} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and

R^{11f} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl.

[0477] In some embodiments, A^{1f} is Cl^- , Br^- , I^- , ^-OMs , ^-OTf , $^-BF_4$, or $^-PF_6$. In some embodiments, ^-OMs is represented by $CH_3SO_3^-$. In some embodiments, ^-OTf is represented by $CF_3SO_3^-$.

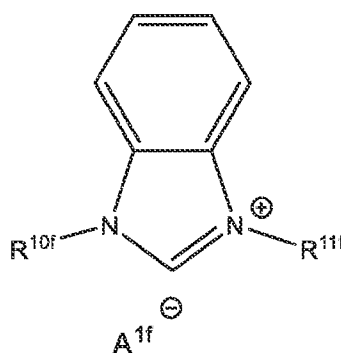
[0478] In some embodiments, the *N*-heterocyclic carbene precursor of Formula (III-B) may be represented by the *N*-heterocyclic carbene precursor of Formula (III-B-1), wherein the *N*-heterocyclic carbene precursor of Formula (III-B-1) has the following structure:



Formula (III-B-1),

where A^{1f} , R^{10f} , and R^{11f} are as defined for the *N*-heterocyclic carbene precursor of Formula (III-B).

[0479] In some embodiments, the *N*-heterocyclic carbene precursor of Formula (III-B) may be represented by the *N*-heterocyclic carbene precursor of Formula (III-B-2), wherein the *N*-heterocyclic carbene precursor of Formula (III-B-2) has the following structure:



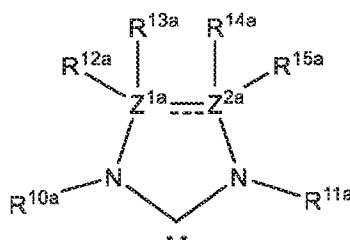
substituted amino, hydroxy, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{15a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted alkylamino, optionally substituted amino, hydroxy, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and

==== between Z^{1a} and Z^{2a} indicates a bond that may be a single bond or a double bond; or R^{12a} and R^{14a}, or R^{12a} and R^{15a}, or R^{13a} and R^{14a}, or R^{13a} and R^{15a} may be taken together to form a ring, wherein the ring is optionally substituted.

[0482] In some embodiments, wherein R^{12a} and R^{13a} are not both absent, and wherein R^{14a} and R^{15a} are not both absent. In some embodiments, wherein R^{12a} and R^{13a} are not both absent. In some embodiments, wherein R^{14a} and R^{15a} are not both absent.

[0483] In various embodiments, the present invention provides at least one *N*-heterocyclic carbene, wherein the at least one *N*-heterocyclic carbene has a structure of Formula (IV):



Formula (IV)

wherein:

Z^{1a} is C;

Z^{2a} is C;

R^{10a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{11a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{12a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted alkylamino, optionally

substituted amino, hydroxy, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{13a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted alkylamino, optionally substituted amino, hydroxy, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{14a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted alkylamino, optionally substituted amino, hydroxy, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{15a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted alkylamino, optionally substituted amino, hydroxy, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and

wherein R^{12a} and R^{13a} are not both absent, and wherein R^{14a} and R^{15a} are not both absent; and ===== between Z^{1a} and Z^{2a} indicates a bond that may be a single bond or a double bond; or R^{12a} and R^{14a}, or R^{12a} and R^{15a}, or R^{13a} and R^{14a}, or R^{13a} and R^{15a} may be taken together to form a ring, wherein the ring is optionally substituted.

[0484] In some embodiments, if R^{12a} is absent and R^{14a} is absent, then the bond between Z^{1a} and Z^{2a} is a double bond. In some embodiments, if R^{12a} is absent and R^{15a} is absent, then the bond between Z^{1a} and Z^{2a} is a double bond.

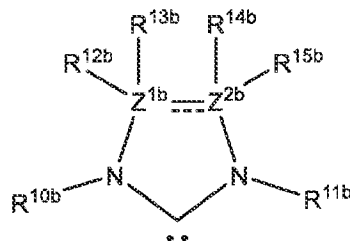
[0485] In some embodiments, if R^{13a} is absent and R^{14a} is absent, then the bond between Z^{1a} and Z^{2a} is a double bond. In some embodiments, if R^{13a} is absent and R^{15a} is absent, then the bond between Z^{1a} and Z^{2a} is a double bond.

[0486] In some embodiments, the ring comprises at least one carbon-carbon double bond. In some embodiments, the ring is an optionally substituted aromatic ring. In some embodiments, the ring is an optionally substituted benzene ring. In some embodiments, the ring is an aromatic ring. In some embodiments, the ring is a benzene ring.

[0487] In some embodiments, R^{16a} is ethyl, propyl, isopropyl, butyl, pentyl, or decyl. In some embodiments, R^{11a} is ethyl, propyl, isopropyl, butyl, pentyl, or decyl.

[0488] Additional embodiments include those listed below.

[0489] In various embodiments, the present invention provides at least one *N*-heterocyclic carbene, wherein the at least one *N*-heterocyclic carbene has a structure of Formula (IV-A):



Formula (IV-A)

wherein:

Z^{1b} is C;

Z^{2b} is C;

R^{10b} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{11b} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{12b} is absent, H, halo, OR^{16b}, SR^{17b}, or NR^{18b}R^{19b}, wherein R^{16b} is H, or optionally substituted alkyl; wherein R^{17b} is H, or optionally substituted alkyl; wherein R^{18b} is H, or optionally substituted alkyl; and wherein R^{19b} is H, or optionally substituted alkyl;

R^{13b} is absent, H, halo, OR^{20b}, SR^{21b}, or NR^{22b}R^{23b}, wherein R^{20b} is H, or optionally substituted alkyl; wherein R^{21b} is H, or optionally substituted alkyl; wherein R^{22b} is H, or optionally substituted alkyl; and wherein R^{23b} is H, or optionally substituted alkyl;

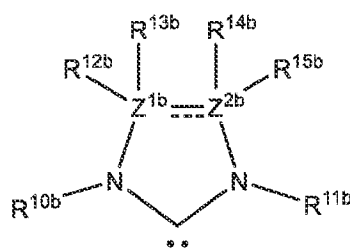
R^{14b} is absent, H, halo, OR^{24b}, SR^{25b}, or NR^{26b}R^{27b}, wherein R^{24b} is H, or optionally substituted alkyl; wherein R^{25b} is H, or optionally substituted alkyl; wherein R^{26b} is H, or optionally substituted alkyl; and wherein R^{27b} is H, or optionally substituted alkyl.

R^{15b} is absent, H, halo, OR^{28b}, SR^{29b}, or NR^{30b}R^{31b}, wherein R^{28b} is H, or optionally substituted alkyl; wherein R^{29b} is H, or optionally substituted alkyl; wherein R^{30b} is H, or optionally substituted alkyl; and wherein R^{31b} is H, or optionally substituted alkyl; and

===== between Z^{1b} and Z^{2b} indicates a bond that may be a single bond or a double bond; or R^{12b} and R^{14b} , or R^{12b} and R^{15b} , or R^{13b} and R^{14b} , or R^{13b} and R^{15b} may be taken together to form a ring, wherein the ring is optionally substituted.

[0490] In some embodiments, wherein R^{12b} and R^{13b} are not both absent, and wherein R^{14b} and R^{15b} are not both absent. In some embodiments, wherein R^{12b} and R^{13b} are not both absent. In some embodiments, wherein R^{14b} and R^{15b} are not both absent.

[0491] In various embodiments, the present invention provides at least one *N*-heterocyclic carbene, wherein the at least one *N*-heterocyclic carbene has a structure of Formula (IV-A):



Formula (IV-A)

wherein:

Z^{1b} is C;

Z^{2b} is C;

R^{10b} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{11b} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{12b} is absent, H, halo, OR^{16b} , SR^{17b} , or $NR^{18b}R^{19b}$, wherein R^{16b} is H, or optionally substituted alkyl; wherein R^{17b} is H, or optionally substituted alkyl; wherein R^{18b} is H, or optionally substituted alkyl; and wherein R^{19b} is H, or optionally substituted alkyl;

R^{13b} is absent, H, halo, OR^{20b} , SR^{21b} , or $NR^{22b}R^{23b}$, wherein R^{20b} is H, or optionally substituted alkyl; wherein R^{21b} is H, or optionally substituted alkyl; wherein R^{22b} is H, or optionally substituted alkyl; and wherein R^{23b} is H, or optionally substituted alkyl;

R^{14b} is absent, H, halo, OR^{24b} , SR^{25b} , or $NR^{26b}R^{27b}$, wherein R^{24b} is H, or optionally substituted alkyl; wherein R^{25b} is H, or optionally substituted alkyl; wherein R^{26b} is H, or optionally substituted alkyl; and wherein R^{27b} is H, or optionally substituted alkyl.

R^{15b} is absent, H, halo, OR^{28b} , SR^{29b} , or $NR^{30b}R^{31b}$, wherein R^{28b} is H, or optionally substituted alkyl; wherein R^{29b} is H, or optionally substituted alkyl; wherein R^{30b} is H, or optionally substituted alkyl; and wherein R^{31b} is H, or optionally substituted alkyl; and

wherein R^{12b} and R^{13b} are not both absent, and wherein R^{14b} and R^{15b} are not both absent; and

===== between Z^{1b} and Z^{2b} indicates a bond that may be a single bond or a double bond; or R^{12b} and R^{14b} , or R^{12b} and R^{15b} , or R^{13b} and R^{14b} , or R^{13b} and R^{15b} may be taken together to form a ring, wherein the ring is optionally substituted.

[0492] In some embodiments, if R^{12b} is absent and R^{14b} is absent, then the bond between Z^{1b} and Z^{2b} is a double bond. In some embodiments, if R^{12b} is absent and R^{15b} is absent, then the bond between Z^{1b} and Z^{2b} is a double bond.

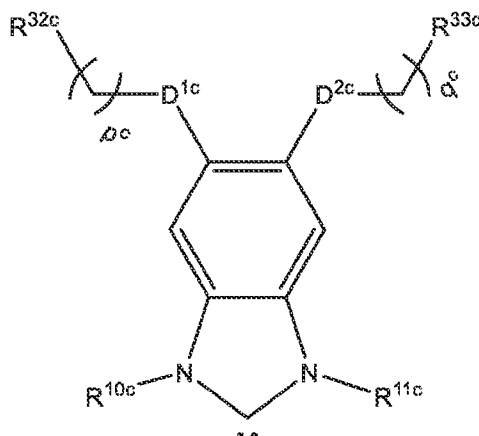
[0493] In some embodiments, if R^{13b} is absent and R^{14b} is absent, then the bond between Z^{1b} and Z^{2b} is a double bond. In some embodiments, if R^{13b} is absent and R^{15b} is absent, then the bond between Z^{1b} and Z^{2b} is a double bond.

[0494] In some embodiments, the ring comprises at least one carbon-carbon double bond. In some embodiments, the ring is an optionally substituted aromatic ring. In some embodiments, the ring is an optionally substituted benzene ring. In some embodiments, the ring is an aromatic ring. In some embodiments, the ring is a benzene ring.

[0495] In some embodiments, R^{10b} is ethyl, propyl, isopropyl, butyl, pentyl, or decyl. In some embodiments, R^{11b} is ethyl, propyl, isopropyl, butyl, pentyl, or decyl.

[0496] Additional embodiments include those listed below.

[0497] In various embodiments, the present invention provides a *N*-heterocyclic carbene, wherein the *N*-heterocyclic carbene has the structure of Formula (IV-B):



Formula (IV-B),

wherein:

p^c is 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, or 16;

q^c is 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, or 16;

D^{1c} is CH_2 , O, S, or NR^{34c} , where R^{34c} is H, or optionally substituted alkyl;

D^{2c} is CH_2 , O, S, or NR^{35c} , where R^{35c} is H, or optionally substituted alkyl;

R^{10c} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{11c} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

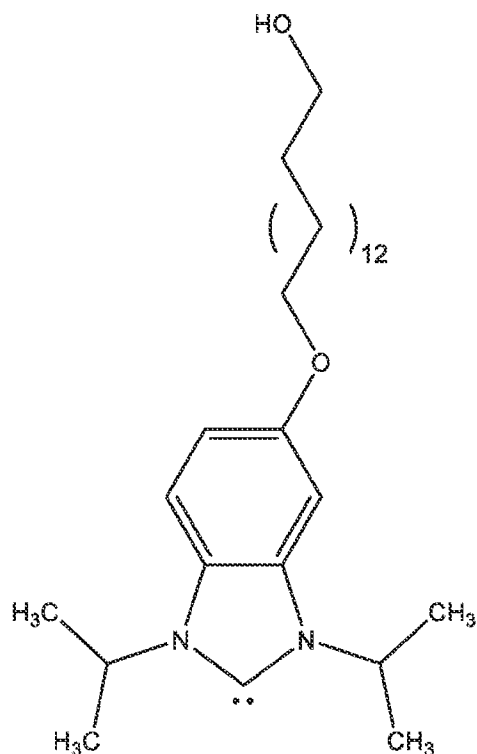
R^{32c} is H, OR^{12c} , SR^{13c} , $\text{NR}^{14c}\text{R}^{15c}$, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; wherein R^{12c} is H, or optionally substituted alkyl; and R^{13c} is H, or optionally substituted alkyl; wherein R^{14c} is H, or optionally substituted alkyl; and wherein R^{15c} is H, or optionally substituted alkyl; and

R^{33c} is H, OR^{16c} , SR^{17c} , $\text{NR}^{18c}\text{R}^{19c}$, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; wherein R^{16c} is H, or optionally substituted alkyl; R^{17c} is H, or optionally substituted alkyl; R^{18c} is H, or optionally substituted alkyl; and R^{19c} is H, or optionally substituted alkyl.

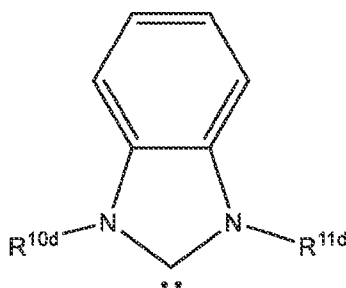
[0498] In some embodiments, R^{10c} is ethyl, propyl, isopropyl, butyl, pentyl, or decyl. In some embodiments, R^{11c} is ethyl, propyl, isopropyl, butyl, pentyl, or decyl.

[0499] Additional embodiments include those listed below.

[0500] In various embodiments, the present invention provides at least one *N*-heterocyclic carbene, wherein the at least one *N*-heterocyclic carbene is



[0501] In various embodiments, the present invention provides at least one *N*-heterocyclic carbene, wherein the at least one *N*-heterocyclic carbene has a structure of Formula (IV-C):



Formula (IV-C),

wherein:

R^{10d} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and

R^{11d} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl.

[0502] In some embodiments, R^{10d} is ethyl, propyl, isopropyl, butyl, pentyl, or decyl. In some embodiments, R^{11d} is ethyl, propyl, isopropyl, butyl, pentyl, or decyl.

[0503] Additional embodiments include those listed below.

[0504] In various embodiments, the present invention provides a carbene functionalized transition metal dichalcogenide, comprising: at least one transition metal dichalcogenide; and at least one carbene.

[0505] In some embodiments, the at least one carbene is chemically bonded to the at least one transition metal dichalcogenide. In some embodiments, the at least one carbene is chemically bonded to an at least one transition metal of the at least one transition metal dichalcogenide. In some embodiments, the chemical bond is a covalent bond, ionic bond, or combination thereof. In some embodiments, the at least one carbene is chemically bonded to the at least one exfoliated transition metal dichalcogenide. In some embodiments, the at least one carbene is chemically bonded to the at least one exfoliated surface of the at least one exfoliated transition metal dichalcogenide. In some embodiments, the at least one carbene is chemically bonded to the at least one exfoliated basal plane of the at least one exfoliated transition metal dichalcogenide.

[0506] In some embodiments, the at least one carbene is physisorbed to the at least one transition metal dichalcogenide. In some embodiments, the at least one carbene is physisorbed to the at least one exfoliated transition metal dichalcogenide. In some embodiments, the at least one carbene is physisorbed to the at least one exfoliated surface of the at least one exfoliated transition metal dichalcogenide. In some embodiments, the at least one carbene is physisorbed to the at least one exfoliated basal plane of the at least one exfoliated transition metal dichalcogenide.

[0507] In some embodiments, the at least one carbene is chemisorbed to the at least one transition metal dichalcogenide. In some embodiments, the at least one carbene is chemisorbed to the at least one exfoliated transition metal dichalcogenide. In some embodiments, the at least one carbene is chemisorbed to the at least one exfoliated surface of the at least one exfoliated transition

metal dichalcogenide. In some embodiments, the at least one carbene is chemisorbed to the at least one exfoliated basal plane of the at least one exfoliated transition metal dichalcogenide.

[0508] In various embodiments, the present invention provides at least one transition metal dichalcogenide, wherein the at least one transition metal dichalcogenide has the formula: $M^aX^a_2$, wherein: M^a is a Group 4-10 transition metal; and X^a is a chalcogen.

[0509] In some embodiments, M^a is a Group 4 transition metal, or Group 5 transition metal, or Group 6 transition metal, or Group 7 transition metal, or Group 8 transition metal, or Group 9 transition metal, or Group 10 transition metal.

[0510] In some embodiments, M^a is a Group 6 transition metal.

[0511] In some embodiments, the chalcogen is sulfur (S), selenium (Se), or tellurium (Te). In some embodiments the chalcogen is sulfur (S). In some embodiments, the chalcogen is selenium (Se). In some embodiments, the chalcogen is tellurium (Te).

[0512] In some embodiments, the Group 6 transition metal is molybdenum (Mo). In some embodiments, the Group 6 transition metal is molybdenum (Mo) or tungsten (W). In some embodiments, the Group 6 transition metal is tungsten (W).

[0513] In some embodiments, the at least one transition metal dichalcogenide is MoS_2 . In some embodiments, the at least one transition metal dichalcogenide is MoS_2 or WS_2 . In some embodiments, the at least one transition metal dichalcogenide is WS_2 .

[0514] In some embodiments, the at least one transition metal dichalcogenide is an at least one exfoliated transition metal dichalcogenide.

[0515] In some embodiments, the at least one transition metal dichalcogenide is an at least one exfoliated transition metal dichalcogenide, wherein the at least one exfoliated transition metal dichalcogenide comprises at least one exfoliated surface, and wherein the at least one carbene forms a self-assembled monolayer (SAM) on at least a portion of the at least one exfoliated surface of the at least one exfoliated transition metal dichalcogenide.

[0516] In some embodiments, the at least one transition metal dichalcogenide is an at least one exfoliated transition metal dichalcogenide, wherein the at least one exfoliated transition metal dichalcogenide comprises at least one exfoliated surface, and wherein the at least one carbene forms a self-assembled monolayer (SAM) or partial self-assembled monolayer (SAM) on at least a portion of the at least one exfoliated surface of the at least one exfoliated transition metal dichalcogenide.

[0517] In some embodiments, the at least one transition metal dichalcogenide is an at least one exfoliated transition metal dichalcogenide, wherein the at least one exfoliated transition metal dichalcogenide comprises at least one exfoliated surface, wherein the at least one exfoliated surface comprises at least one exfoliated basal plane, and wherein the at least one carbene forms a self-assembled monolayer (SAM) on at least a portion of the at least one exfoliated basal plane.

[0518] In some embodiments, the at least one transition metal dichalcogenide is an at least one exfoliated transition metal dichalcogenide, wherein the at least one exfoliated transition metal dichalcogenide comprises at least one exfoliated surface, wherein the at least one exfoliated surface comprises at least one exfoliated basal plane, and wherein the at least one carbene forms a self-assembled monolayer (SAM) or partial self-assembled monolayer (SAM) on at least a portion of the at least one exfoliated basal plane.

[0519] In some embodiments, the self-assembled monolayer (SAM) is a homogenous self-assembled monolayer, or heterogenous self-assembled monolayer. In some embodiments, the partial self-assembled monolayer (SAM) is a homogenous self-assembled monolayer, or heterogenous self-assembled monolayer.

[0520] In some embodiments, the self-assembled monolayer (SAM) comprises at least one carbene. In some embodiments, the partial self-assembled monolayer (SAM) comprises at least one carbene.

[0521] In some embodiments, the at least one carbene is the same or different. In some embodiments, the at least one carbene precursor is the same or different.

[0522] In various embodiments, the present invention provides a method of making at least one carbene functionalized transition metal dichalcogenide, comprising: providing at least one bulk transition metal dichalcogenide; exfoliating the at least one bulk transition metal dichalcogenide to produce at least one exfoliated transition metal dichalcogenide comprising at least one exfoliated surface; and reacting at least a portion of the at least one exfoliated surface of the at least one exfoliated transition metal dichalcogenide with at least one carbene precursor.

[0523] In various embodiments, the present invention provides a method of making at least one carbene functionalized transition metal dichalcogenide, comprising: providing at least one bulk transition metal dichalcogenide; exfoliating the at least one bulk transition metal dichalcogenide to produce at least one exfoliated transition metal dichalcogenide; and reacting the at least one exfoliated transition metal dichalcogenide with at least one carbene precursor.

[0524] In various embodiments, the present invention provides a method of making at least one carbene functionalized transition metal dichalcogenide, comprising: providing at least one bulk transition metal dichalcogenide; exfoliating the at least one bulk transition metal dichalcogenide to produce at least one exfoliated transition metal dichalcogenide comprising at least one exfoliated surface; and reacting at least a portion of the at least one exfoliated surface of the at least one exfoliated transition metal dichalcogenide with at least one carbene precursor.

[0525] In some embodiments, reacting the at least one exfoliated transition metal dichalcogenide with at least one carbene precursor is performed under conditions sufficient to make the at least one carbene functionalized transition metal dichalcogenide.

[0526] In some embodiments, reacting at least a portion of the at least one exfoliated surface of the at least one exfoliated transition metal dichalcogenide with at least one carbene precursor is performed under conditions sufficient to make the at least one carbene functionalized transition metal dichalcogenide.

[0527] In some embodiments, reacting the at least one exfoliated transition metal dichalcogenide with at least one carbene precursor is performed under conditions effective to make the at least one carbene functionalized transition metal dichalcogenide.

[0528] In some embodiments, reacting at least a portion of the at least one exfoliated surface of the at least one exfoliated transition metal dichalcogenide with at least one carbene precursor is performed under conditions effective to make the at least one carbene functionalized transition metal dichalcogenide.

[0529] In some embodiments, the at least one exfoliated surface of the at least one exfoliated transition metal dichalcogenide comprises at least one exfoliated basal plane.

[0530] In some embodiments, the at least one exfoliated transition metal dichalcogenide comprises at least one exfoliated basal plane.

[0531] In some embodiments, the exfoliating is conducted by a redox exfoliation process.

[0532] In some embodiments, the at least one carbene precursor forms a self-assembled monolayer (SAM) on the at least one exfoliated surface of the at least one exfoliated transition metal dichalcogenide.

[0533] In some embodiments, the at least one *N*-heterocyclic carbene precursor forms a partial self-assembled monolayer (SAM) on the at least one exfoliated surface of the at least one exfoliated transition metal dichalcogenide.

[0534] In some embodiments, the self-assembled monolayer (SAM) is a homogenous self-assembled monolayer, or heterogenous self-assembled monolayer.

[0535] In some embodiments, the partial self-assembled monolayer (SAM) is a homogenous self-assembled monolayer, or heterogenous self-assembled monolayer.

[0536] In some embodiments, the self-assembled monolayer (SAM) comprises at least one carbene.

[0537] In some embodiments, the partial self-assembled monolayer (SAM) comprises at least one *N*-heterocyclic carbene.

[0538] In some embodiments, the at least one bulk transition metal dichalcogenide comprises a two-dimensional (2D) structure. In some embodiments, the 2D structure comprises one layer, or a plurality of layers.

[0539] In some embodiments, the at least one bulk transition metal dichalcogenide has the formula: $M^cX^c_2$, wherein: M^c is a Group 4-10 transition metal; and X^c is a chalcogen.

[0540] In some embodiments, M^c is a Group 4 transition metal, or Group 5 transition metal, or Group 6 transition metal, or Group 7 transition metal, or Group 8 transition metal, or Group 9 transition metal, or Group 10 transition metal.

[0541] In some embodiments, M^c is a Group 6 transition metal.

[0542] In some embodiments, the chalcogen is sulfur (S), selenium (Se), or tellurium (Te). In some embodiments the chalcogen is sulfur (S). In some embodiments, the chalcogen is selenium (Se). In some embodiments, the chalcogen is tellurium (Te).

[0543] In some embodiments, the Group 6 transition metal is molybdenum (Mo). In some embodiments, the Group 6 transition metal is molybdenum (Mo) or tungsten (W). In some embodiments, the Group 6 transition metal is tungsten (W).

[0544] In some embodiments, the at least one bulk transition metal dichalcogenide is MoS_2 . In some embodiments, the at least one bulk transition metal dichalcogenide is MoS_2 or WS_2 . In some embodiments, the at least one transition metal dichalcogenide is WS_2 .

[0545] In some embodiments, the at least one exfoliated transition metal dichalcogenide has the formula: $M^bX^b_2$, wherein: M^b is a Group 4-10 transition metal; and X^b is a chalcogen.

[0546] In some embodiments, M^b is a Group 4 transition metal, or Group 5 transition metal, or Group 6 transition metal, or Group 7 transition metal, or Group 8 transition metal, or Group 9 transition metal, or Group 10 transition metal.

[0547] In some embodiments, M^b is a Group 6 transition metal.

[0548] In some embodiments, the chalcogen is sulfur (S), selenium (Se), or tellurium (Te). In some embodiments the chalcogen is sulfur (S). In some embodiments, the chalcogen is selenium (Se). In some embodiments, the chalcogen is tellurium (Te).

[0549] In some embodiments, the Group 6 transition metal is molybdenum (Mo). In some embodiments, the Group 6 transition metal is molybdenum (Mo) or tungsten (W). In some embodiments, the Group 6 transition metal is tungsten (W).

[0550] In some embodiments, the at least one exfoliated transition metal dichalcogenide is MoS_2 . In some embodiments, the at least one exfoliated transition metal dichalcogenide is MoS_2 or WS_2 . In some embodiments, the at least one exfoliated transition metal dichalcogenide is WS_2 .

[0551] In some embodiments, the at least one exfoliated transition metal dichalcogenide comprises a two-dimensional (2D) structure. In some embodiments, the 2D structure comprises one layer, or a plurality of layers.

[0552] In some embodiments, the at least one exfoliated transition metal dichalcogenide comprises at least one exfoliated surface.

[0553] In some embodiments, the reaction of the at least a portion of the at least one exfoliated surface of the at least one exfoliated transition metal dichalcogenide with at least one carbene precursor to make the at least one carbene functionalized transition metal dichalcogenide.

[0554] In some embodiments, the at least one carbene functionalized transition metal dichalcogenide comprises at least one carbene.

[0555] In some embodiments, the carbene functionalized transition metal dichalcogenide is insulating, semiconducting, conducting, semi-metallic, metallic, or any combination thereof.

[0556] In some embodiments, the carbene functionalized transition metal dichalcogenide is semiconducting.

[0557] In some embodiments, the carbene functionalized transition metal dichalcogenide is a semiconductor.

[0558] In some embodiments, the carbene functionalized transition metal dichalcogenide comprises a self-assembled monolayer (SAM). In some embodiments, the self-assembled monolayer (SAM) is a homogenous self-assembled monolayer, or heterogenous self-assembled monolayer. In some embodiments, the self-assembled monolayer (SAM) comprises at least one carbene.

[0559] In some embodiments, the carbene functionalized transition metal dichalcogenide comprises a partial self-assembled monolayer (SAM). In some embodiments, the partial self-assembled monolayer (SAM) is a homogenous self-assembled monolayer, or heterogenous self-assembled monolayer. In some embodiments, the partial self-assembled monolayer (SAM) comprises at least one carbene.

[0560] In some embodiments, the carbene functionalized transition metal dichalcogenide comprises a superstructure comprising intercalated layers. In some embodiments, the intercalated layers comprise the at least one carbene.

[0561] In some embodiments, the carbene functionalized transition metal dichalcogenide comprises a superstructure comprising intercalated layers, wherein the intercalated layers comprise at least one carbene.

[0562] In some embodiments, the at least one carbene forms a self-assembled monolayer (SAM) or partial self-assembled monolayer (SAM) on the at least one exfoliated surface of the at least one exfoliated transition metal dichalcogenide.

[0563] In some embodiments, the self-assembled monolayer (SAM) is a homogenous self-assembled monolayer, or heterogenous self-assembled monolayer. In some embodiments, the partial self-assembled monolayer (SAM) is a homogenous self-assembled monolayer, or heterogenous self-assembled monolayer.

[0564] In some embodiments, the at least one exfoliated transition metal dichalcogenide comprises at least one exfoliated basal plane. In some embodiments, the at least one exfoliated basal plane is functionalized with the at least one carbene. In some embodiments, the at least one exfoliated transition metal dichalcogenide comprises a two-dimensional (2D) structure. In some embodiments, the 2D structure comprises one layer, or a plurality of layers.

[0565] In various embodiments, the present invention provides an article of manufacture comprising at least one carbene functionalized transition metal dichalcogenide of the present invention.

[0566] In some embodiments, the article of manufacture is an energy storage device, energy storage material, sensing device, sensing material, semiconductor electronic device, semiconductor electronic material, semiconductor optoelectronic device, or semiconductor optoelectronic material.

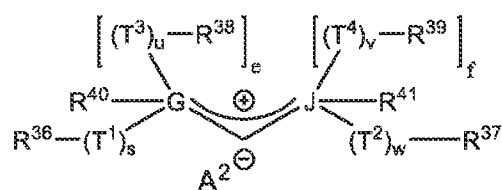
[0567] In some embodiments, the article of manufacture is a semiconductor. In some embodiments, the article of manufacture is a semiconductor, or has semiconducting properties.

[0568] In various embodiments, the present invention provides for use of the carbene functionalized transition metal dichalcogenide of the present invention.

[0569] In various embodiments, the present invention provides for use of the carbene functionalized transition metal dichalcogenide made by the method of the present invention.

[0570] Additional embodiments include those listed below.

[0571] In various embodiments, the present invention provides at least one carbene precursor, wherein the at least one carbene precursor has a structure of Formula (V):



Formula (V)

wherein:

A^{2-} is a counterion;

R^{36} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{37} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{38} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{39} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{40} is absent, H, or optionally substituted alkyl;

R^{41} is absent, H or optionally substituted alkyl;

G is C, N, P, O, or S;

J is C, N, P, O, or S;

T¹ is a linker;

T² is a linker;

T³ is a linker;

T⁴ is a linker;

e is zero or 1;

f is zero or 1;

s is zero or 1;

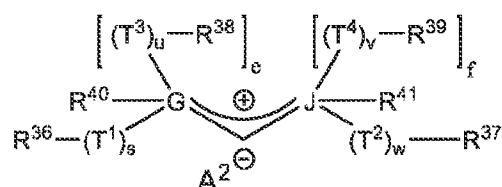
u is zero or 1;

v is zero or 1; and

w is zero or 1; or wherein any two or more of R³⁶, R³⁷, R³⁸, R³⁹, R⁴⁰, R⁴¹, T¹, T², T³, and T⁴ can be taken together to form a cyclic group.

[0572] In some embodiments, wherein G and J are not both C.

[0573] In various embodiments, the present invention provides at least one carbene precursor, wherein the at least one carbene precursor has a structure of Formula (V):



Formula (V)

wherein:

A²⁻ is a counterion;

R³⁶ is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R³⁷ is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R³⁸ is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R³⁹ is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R⁴⁰ is absent, H, or optionally substituted alkyl;

R⁴¹ is absent, H or optionally substituted alkyl;

G is C, N, P, O, or S;

J is C, N, P, O, or S;

T¹ is a linker;

T² is a linker;

T³ is a linker;

T⁴ is a linker;

e is zero or 1;

f is zero or 1;

s is zero or 1;

u is zero or 1;

v is zero or 1; and

w is zero or 1; and wherein G and J are not both C; or wherein any two or more of R³⁶, R³⁷, R³⁸, R³⁹, R⁴⁰, R⁴¹, T¹, T², T³, and T⁴ can be taken together to form a cyclic group..

[0574] In some embodiments, wherein when G is N or P, then R⁴⁰ is absent, or e is zero.

In some embodiments, wherein when J is N or P, then R⁴¹ is absent, or f is zero.

[0575] In some embodiments, wherein when G is O or S, then R⁴⁰ is absent, and e is zero.

In some embodiments, when J is O or S, then R⁴¹ is absent, and f is zero.

[0576] In some embodiments, the cyclic group comprises at least one carbon-carbon double bond.

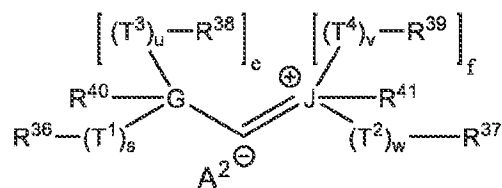
[0577] In some embodiments, T¹ is a linker, wherein the linker is optionally substituted alkyl, optionally substituted alkylene, or optionally substituted alkenylene. In some embodiments, T² is a linker, wherein the linker is optionally substituted alkyl, optionally substituted alkylene, or optionally substituted alkenylene. In some embodiments, T³ is a linker, wherein the linker is

optionally substituted alkyl, optionally substituted alkylene, or optionally substituted alkenylene. In some embodiments, T⁴ is a linker, wherein the linker is optionally substituted alkyl, optionally substituted alkylene, or optionally substituted alkenylene.

[0578] In some embodiments, A²⁻ is Cl⁻, Br⁻, I⁻, ⁻OMs, ⁻OTf, ⁻BF₄, or ⁻PF₆. In some embodiments, A²⁻ is Cl, Br, I, OMs, OTf, BF₄, or PF₆. In some embodiments, ⁻OMs is represented by CH₃SO₃⁻. In some embodiments, ⁻OTf is represented by CF₃SO₃⁻.

[0579] In some embodiments, w is zero and R³⁷ is ethyl, propyl, isopropyl, butyl, pentyl, or decyl. In some embodiments, s is zero and R³⁶ is ethyl, propyl, isopropyl, butyl, pentyl, or decyl.

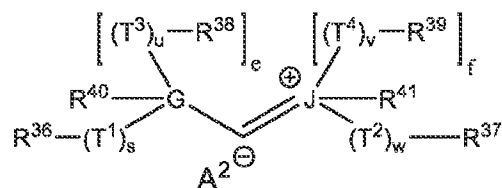
[0580] In some embodiments, the carbene precursor of Formula (V) may be represented by the carbene precursor of Formula (V-A), wherein the carbene of Formula (V-A) has the following structure:



Formula (V-A),

where A²⁻, R³⁶, R³⁷, R³⁸, R³⁹, R⁴⁰, R⁴¹, G, J, T¹, T², T³, T⁴, s, u, v, w, e and f are as defined for the carbene precursor of Formula (V). In some embodiments, it is provided that J is not C. In some embodiments, wherein G and J are not both C.

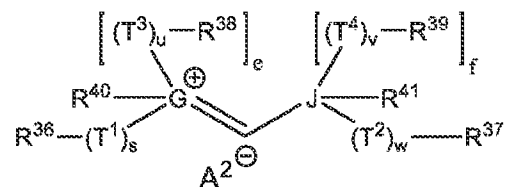
[0581] In some embodiments, the carbene precursor of Formula (V) may be represented by the carbene precursor of Formula (V-A), wherein the carbene of Formula (V-A) has the following structure:



Formula (V-A),

where A^{2-} , R^{36} , R^{37} , R^{38} , R^{39} , R^{40} , R^{41} , G , J , T^1 , T^2 , T^3 , T^4 , s , u , v , w , e and f are as defined for the carbene precursor of Formula (V), provided that J is not C . In some embodiments, wherein G and J are not both C .

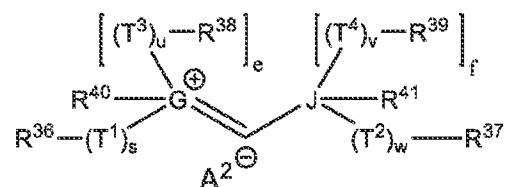
[0582] In some embodiments, the carbene precursor of Formula (V) may be represented by the carbene precursor of Formula (V-B), wherein the carbene precursor of Formula (V-B) has the following structure:



Formula (V-B),

where A^{2-} , R^{36} , R^{37} , R^{38} , R^{39} , R^{40} , R^{41} , G , J , T^1 , T^2 , T^3 , T^4 , s , u , v , w , e and f are as defined for the carbene precursor of Formula (V). In some embodiments, it is provided that G is not C . In some embodiments, wherein G and J are not both C .

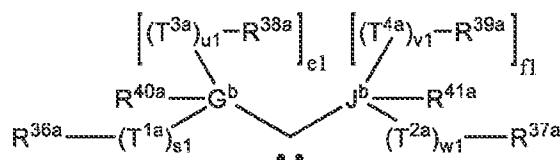
[0583] In some embodiments, the carbene precursor of Formula (V) may be represented by the carbene precursor of Formula (V-B), wherein the carbene precursor of Formula (V-B) has the following structure:



Formula (V-B),

where A^{2-} , R^{36} , R^{37} , R^{38} , R^{39} , R^{40} , R^{41} , G , J , T^1 , T^2 , T^3 , T^4 , s , u , v , w , e and f are as defined for the carbene precursor of Formula (V), provided that G is not C . In some embodiments, wherein G and J are not both C .

[0584] In various embodiments, the present invention provides at least one carbene, wherein the at least one carbene has a structure of Formula (VI):



Formula (VI)

wherein:

R^{36a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{37a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{38a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{39a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{40a} is absent, H, or optionally substituted alkyl;

R^{41a} is absent, H, or optionally substituted alkyl;

G^b is C, N, P, O, or S;

J^b is C, N, P, O, or S;

T^{1a} is a linker;

T^{2a} is a linker;

T^{3a} is a linker;

T^{4a} is a linker;

e^1 is zero or 1;

f^1 is zero or 1;

s^1 is zero or 1;

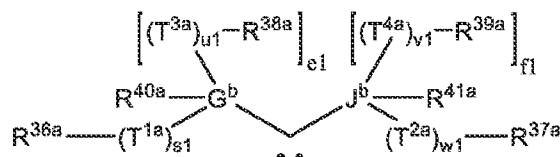
u^1 is zero or 1;

v^1 is zero or 1; and

w^l is zero or 1; or wherein any two or more of R^{36a} , R^{37a} , R^{38a} , R^{39a} , R^{40a} , R^{41a} , T^{1a} , T^{2a} , T^{3a} , and T^{4a} can be taken together to form a cyclic group.

[0585] In some embodiments, wherein G^b and J^b are not both C.

[0586] In various embodiments, the present invention provides at least one carbene, wherein the at least one carbene has a structure of Formula (VI):



Formula (VI)

wherein:

R^{36a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{37a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{38a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{39a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{40a} is absent, H, or optionally substituted alkyl;

R^{41a} is absent, H, or optionally substituted alkyl;

G^b is C, N, P, O, or S;

J^b is C, N, P, O, or S;

T^{1a} is a linker;

T^{2a} is a linker;

T^{3a} is a linker;

T^{4a} is a linker;

e^1 is zero or 1;

f^1 is zero or 1;

s^1 is zero or 1;

u^1 is zero or 1;

v^1 is zero or 1; and

w^1 is zero or 1; and wherein G^b and J^b are not both C; or wherein any two or more of R^{36a} , R^{37a} , R^{38a} , R^{39a} , R^{40a} , R^{41a} , T^{1a} , T^{2a} , T^{3a} , and T^{4a} can be taken together to form a cyclic group.

[0587] In some embodiments, wherein when G^b is N or P, then R^{40a} is absent or e^1 is zero. In some embodiments, wherein when J^b is N or P, then R^{41a} is absent or f^1 is zero.

[0588] In some embodiments, wherein when G^b is O or S, then R^{40a} is absent and e^1 is zero. In some embodiments, when J^b is O or S, then R^{41a} is absent and f^1 is zero.

[0589] In some embodiments, the cyclic group comprises at least one carbon-carbon double bond.

[0590] In some embodiments, T^{1a} is a linker, wherein the linker is optionally substituted alkyl, optionally substituted alkylene, or optionally substituted alkenylene. In some embodiments, T^{2a} is a linker, wherein the linker is optionally substituted alkyl, optionally substituted alkylene, or optionally substituted alkenylene. In some embodiments, T^{3a} is a linker, wherein the linker is optionally substituted alkyl, optionally substituted alkylene, or optionally substituted alkenylene. In some embodiments, T^{4a} is a linker, wherein the linker is optionally substituted alkyl, optionally substituted alkylene, or optionally substituted alkenylene.

[0591] In some embodiments, w^1 is zero and R^{37a} is ethyl, propyl, isopropyl, butyl, pentyl, or decyl. In some embodiments, s^1 is zero and R^{36a} is ethyl, propyl, isopropyl, butyl, pentyl, or decyl.

[0592] Additional embodiments include those listed below.

[0593] In various embodiments, the present invention provides a method of making at least one carbene functionalized transition metal dichalcogenide, comprising: providing at least one bulk transition metal dichalcogenide; exfoliating the at least one bulk transition metal dichalcogenide to produce at least one exfoliated transition metal dichalcogenide; and reacting the at least one exfoliated transition metal dichalcogenide with at least one carbene precursor.

[0594] In various embodiments, the present invention provides a method of making at least one carbene functionalized transition metal dichalcogenide, comprising: providing at least one bulk transition metal dichalcogenide; exfoliating the at least one bulk transition metal dichalcogenide to produce at least one exfoliated transition metal dichalcogenide; and reacting at least a portion of the at least one exfoliated transition metal dichalcogenide with at least one carbene precursor.

[0595] In some embodiments, the carbene adsorbate is a carbene precursor.

[0596] Additional embodiments include those listed below.

[0597] In various embodiments, the present invention provides a method of making at least one carbene functionalized transition metal dichalcogenide, comprising: providing at least one bulk transition metal dichalcogenide; exfoliating the at least one bulk transition metal dichalcogenide to produce at least one exfoliated transition metal dichalcogenide comprising at least one exfoliated surface; and reacting at least a portion of the at least one exfoliated surface of the at least one exfoliated transition metal dichalcogenide with at least one carbene precursor. In various embodiments, the present invention provides a carbene functionalized transition metal dichalcogenide made by a method of the present invention. In various embodiments, the present invention provides an article of manufacture comprising a carbene functionalized transition metal dichalcogenide made by a method of the present invention.

[0598] In various embodiments, the present invention provides a carbene functionalized transition metal dichalcogenide, comprising: at least one transition metal dichalcogenide; and at least one carbene. In various embodiments, the present invention provides an article of manufacture comprising a carbene functionalized transition metal dichalcogenide.

[0599] Additional embodiments include those listed below.

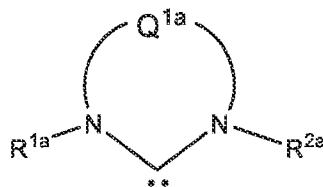
[0600] In some embodiments, the present invention provides ligand-induced functionalization of 2D nanolayered materials for properties modulation. In some embodiments, two-dimensional (2D) nanolayered materials exhibit attractive electronic and optoelectronic properties as their thickness reduces to the monolayer level. In some embodiments, these unique features offer distinctive advantages across various device applications, including photodetectors, field-effect transistors (FETs), sensors, and solar cells. In some embodiments, envisioning a material functionalization strategy capable of modulating the structures and properties of 2D materials without introducing atomic dopants or distortion in the atomic structures represents a

distinctive approach with undiscovered and potentially unparalleled outcomes. In various embodiments of the present invention provided herein a chemical method is introduced involving the interaction between 2D nanosheets and custom-designed ligands, providing evidence of self-assembled monolayers on the basal planes of the sheets. In some embodiments, this strategy offers an opportunity to generate unique 2D heterostructures with broadly tunable intrinsic properties. In some embodiments, the selected organic ligands will be designed to tailor the electronic and optoelectronic characteristics of 2D nanolayered materials such as the density of charge carriers and the electron mobility. Additionally, in some embodiments, structural alternations induced by the organic adsorbates will facilitate the design of a series of functionalized nanosheets with diverse stacking compositions and features, thus leaving ample room for in-depth studies of the properties and applications of the materials.

[0601] Additional embodiments include those listed below.

[0602] Embodiment 112. A *N*-heterocyclic carbene functionalized transition metal dichalcogenide, comprising: at least one transition metal dichalcogenide; and at least one *N*-heterocyclic carbene.

[0603] Embodiment 113. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 112, wherein the at least one *N*-heterocyclic carbene has a structure of Formula (II):



Formula (II),

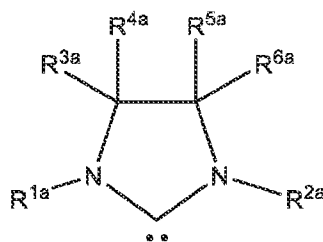
wherein:

R^{1a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{2a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and

Q^{1a} is an optionally substituted linker.

[0604] Embodiment 114. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 112, wherein the at least one *N*-heterocyclic carbene has a structure of Formula (II-A):



Formula (II-A),

wherein:

R^{1a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{2a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{3a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

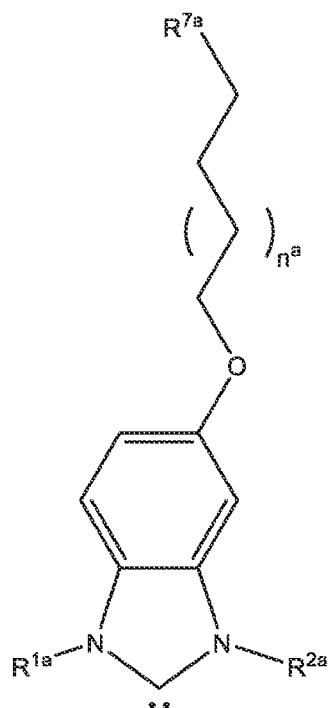
R^{4a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{5a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and

R^{6a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; wherein R^{3a} and R^{4a} are not both absent, and wherein R^{5a} and R^{6a} are not both absent; or

R^{3a} and R^{5a}, or R^{3a} and R^{6a}, or R^{4a} and R^{5a}, or R^{4a} and R^{6a} may be taken together to form a ring, wherein the ring is optionally substituted.

[0605] Embodiment 115. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 112, wherein the at least one *N*-heterocyclic carbene has the structure of Formula (II-B):



Formula (II-B),

wherein:

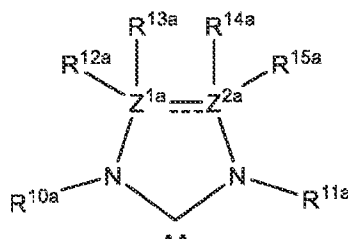
n^a is 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, or 12;

R^{1a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{2a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and

R^{7a} is H, OR^{8a} , SR^{9a} , halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl, wherein R^{8a} is H, or optionally substituted alkyl, and R^{9a} is H, or optionally substituted alkyl.

[0606] Embodiment 116. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 112, wherein the at least one *N*-heterocyclic carbene has a structure of Formula (IV):



Formula (IV)

wherein:

Z^{1a} is C;

Z^{2a} is C;

R^{10a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{11a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{12a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted alkylamino, optionally substituted amino, hydroxy, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{13a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted alkylamino, optionally substituted amino, hydroxy, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

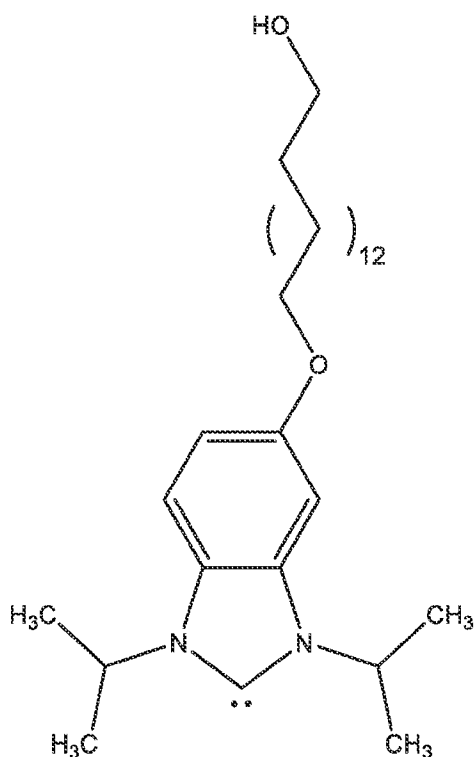
R^{14a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted alkylamino, optionally substituted amino, hydroxy, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{15a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted alkylamino, optionally substituted amino, hydroxy, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and

wherein R^{12a} and R^{13a} are not both absent, and wherein R^{14a} and R^{15a} are not both absent; and

===== between Z^{1a} and Z^{2a} indicates a bond that may be a single bond or a double bond; or R^{12a} and R^{14a} , or R^{12a} and R^{15a} , or R^{13a} and R^{14a} , or R^{13a} and R^{15a} may be taken together to form a ring, wherein the ring is optionally substituted.

[0607] Embodiment 117. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 112, wherein the at least one *N*-heterocyclic carbene is



[0608] Embodiment 118. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 112, wherein the at least one transition metal dichalcogenide has the formula: $M^aX^a_2$, wherein: M^a is a Group 4-10 transition metal; and X^a is a chalcogen.

[0609] Embodiment 119. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 118, wherein M^a is a Group 6 transition metal.

[0610] Embodiment 120. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 118, wherein the chalcogen is sulfur (S), selenium (Se), or tellurium (Te).

[0611] Embodiment 121. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 119, wherein the Group 6 transition metal is molybdenum (Mo) or tungsten (W).

[0612] Embodiment 122. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 112, wherein the at least one transition metal dichalcogenide is MoS_2 or WS_2 .

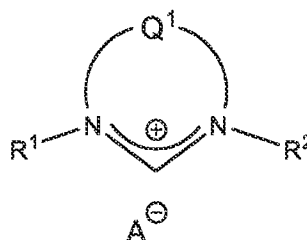
[0613] Embodiment 123. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 112, wherein the at least one transition metal dichalcogenide is an at least one exfoliated transition metal dichalcogenide, wherein the at least one exfoliated transition metal dichalcogenide comprises at least one exfoliated surface, and wherein the at least one *N*-heterocyclic carbene forms a self-assembled monolayer (SAM) or a partial self-assembled monolayer (SAM) on at least a portion of the at least one exfoliated surface of the at least one exfoliated transition metal dichalcogenide.

[0614] Embodiment 124. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 112, wherein the at least one transition metal dichalcogenide is an at least one exfoliated transition metal dichalcogenide, wherein the at least one exfoliated transition metal dichalcogenide comprises at least one exfoliated surface, wherein the at least one exfoliated surface comprises at least one exfoliated basal plane, and wherein the at least one *N*-heterocyclic carbene forms a self-assembled monolayer (SAM) or a partial self-assembled monolayer (SAM) on at least a portion of the at least one exfoliated basal plane.

[0615] Embodiment 125. A method of making at least one *N*-heterocyclic carbene functionalized transition metal dichalcogenide of embodiment 112, comprising: providing at least one bulk transition metal dichalcogenide; exfoliating the at least one bulk transition metal dichalcogenide to produce at least one exfoliated transition metal dichalcogenide comprising at least one exfoliated surface; and reacting at least a portion of the at least one exfoliated surface of

the at least one exfoliated transition metal dichalcogenide with at least one *N*-heterocyclic carbene precursor.

[0616] Embodiment 126. The method of embodiment 125, wherein the at least one *N*-heterocyclic carbene precursor has a structure of Formula (I):



Formula (I),

wherein:

A⁻ is a counterion;

R¹ is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R² is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and

Q¹ is an optionally substituted linker.

[0617] Embodiment 127. An article of manufacture comprising at least one *N*-heterocyclic carbene functionalized transition metal dichalcogenide of any one of embodiments 112-124.

[0618] Embodiment 128. The article of manufacture of embodiment 127, wherein the article of manufacture is an energy storage device, energy storage material, sensing device, sensing material, semiconductor electronic device, semiconductor electronic material, semiconductor optoelectronic device, or semiconductor optoelectronic material.

[0619] Embodiment 129. The article of manufacture of embodiment 127, wherein the article of manufacture is a semiconductor or has semiconducting properties.

[0620] Additional embodiments include those listed below.

[0621] In some embodiments, the *N*-heterocyclic carbene precursor has a structure of Formula (I). In some embodiments, the *N*-heterocyclic carbene precursor has a structure of Formula (I-1). In some embodiments, the *N*-heterocyclic carbene precursor has a structure of

Formula (I-2). In some embodiments, the *N*-heterocyclic carbene precursor has a structure of Formula (I-A). In some embodiments, the *N*-heterocyclic carbene precursor has a structure of Formula (I-A-1). In some embodiments, the *N*-heterocyclic carbene precursor has a structure of Formula (I-A-2). In some embodiments, the *N*-heterocyclic carbene precursor has a structure of Formula (I-B). In some embodiments, the *N*-heterocyclic carbene precursor has a structure of Formula (I-B-1). In some embodiments, the *N*-heterocyclic carbene precursor has a structure of Formula (I-B-2). In some embodiments, the *N*-heterocyclic carbene precursor has a structure of Formula (III). In some embodiments, the *N*-heterocyclic carbene precursor has a structure of Formula (III-1). In some embodiments, the *N*-heterocyclic carbene precursor has a structure of Formula (III-2). In some embodiments, the *N*-heterocyclic carbene precursor has a structure of Formula (III-A). In some embodiments, the *N*-heterocyclic carbene precursor has a structure of Formula (III-A-1). In some embodiments, the *N*-heterocyclic carbene precursor has a structure of Formula (III-A-2). In some embodiments, the *N*-heterocyclic carbene precursor has a structure of Formula (III-B). In some embodiments, the *N*-heterocyclic carbene precursor has a structure of Formula (III-B-1). In some embodiments, the *N*-heterocyclic carbene precursor has a structure of Formula (III-B-2).

[0622] In some embodiments, the *N*-heterocyclic carbene precursor of Formula (I) is a *N*-heterocyclic carbene precursor of Formula (I-A). In some embodiments, the *N*-heterocyclic carbene precursor of Formula (I-A) is a *N*-heterocyclic carbene precursor of Formula (I). In some embodiments, the *N*-heterocyclic carbene precursor of Formula (I) is a *N*-heterocyclic carbene precursor of Formula (I-B). In some embodiments, the *N*-heterocyclic carbene precursor of Formula (I-B) is a *N*-heterocyclic carbene precursor of Formula (I). In some embodiments, the *N*-heterocyclic carbene precursor of Formula (I-A) is a *N*-heterocyclic carbene precursor of Formula (I-B). In some embodiments, the *N*-heterocyclic carbene precursor of Formula (I-B) is a *N*-heterocyclic carbene precursor of Formula (I-A). In some embodiments, the *N*-heterocyclic carbene precursor of Formula (I) is a *N*-heterocyclic carbene precursor of Formula (III). In some embodiments, the *N*-heterocyclic carbene precursor of Formula (III) is a *N*-heterocyclic carbene precursor of Formula (I). In some embodiments, the *N*-heterocyclic carbene precursor of Formula (I) is a *N*-heterocyclic carbene precursor of Formula (III-A). In some embodiments, the *N*-heterocyclic carbene precursor of Formula (III-A) is a *N*-heterocyclic carbene precursor of Formula (I). In some embodiments, the *N*-heterocyclic carbene precursor of Formula (I) is a *N*-

heterocyclic carbene precursor of Formula (III-B). In some embodiments, the *N*-heterocyclic carbene precursor of Formula (III-B) is a *N*-heterocyclic carbene precursor of Formula (I). In some embodiments, the *N*-heterocyclic carbene precursor of Formula (III) is a *N*-heterocyclic carbene precursor of Formula (III-A). In some embodiments, the *N*-heterocyclic carbene precursor of Formula (III-A) is a *N*-heterocyclic carbene precursor of Formula (III). In some embodiments, the *N*-heterocyclic carbene precursor of Formula (III) is a *N*-heterocyclic carbene precursor of Formula (III-B). In some embodiments, the *N*-heterocyclic carbene precursor of Formula (III-B) is a *N*-heterocyclic carbene precursor of Formula (III). In some embodiments, the *N*-heterocyclic carbene precursor of Formula (III) is a *N*-heterocyclic carbene precursor of Formula (I-A). In some embodiments, the *N*-heterocyclic carbene precursor of Formula (I-A) is a *N*-heterocyclic carbene precursor of Formula (III). In some embodiments, the *N*-heterocyclic carbene precursor of Formula (III) is a *N*-heterocyclic carbene precursor of Formula (I-B). In some embodiments, the *N*-heterocyclic carbene precursor of Formula (I-B) is a *N*-heterocyclic carbene precursor of Formula (III).

[0623] In some embodiments, the *N*-heterocyclic carbene has a structure of Formula (II). In some embodiments, the *N*-heterocyclic carbene has a structure of Formula (II-A). In some embodiments, the *N*-heterocyclic carbene has a structure of Formula (II-B). In some embodiments, the *N*-heterocyclic carbene has a structure of Formula (IV). In some embodiments, the *N*-heterocyclic carbene has a structure of Formula (IV-A). In some embodiments, the *N*-heterocyclic carbene has a structure of Formula (IV-B). In some embodiments, the *N*-heterocyclic carbene has a structure of Formula (IV-C).

[0624] In some embodiments, the *N*-heterocyclic carbene of Formula (II) is a *N*-heterocyclic carbene of Formula (II-A). In some embodiments, the *N*-heterocyclic carbene of Formula (II-A) is a *N*-heterocyclic carbene of Formula (II). In some embodiments, the *N*-heterocyclic carbene of Formula (II) is a *N*-heterocyclic carbene of Formula (II-B). In some embodiments, the *N*-heterocyclic carbene of Formula (II-B) is a *N*-heterocyclic carbene of Formula (II). In some embodiments, the *N*-heterocyclic carbene of Formula (II) is a *N*-heterocyclic carbene of Formula (IV). In some embodiments, the *N*-heterocyclic carbene of Formula (IV) is a *N*-heterocyclic carbene of Formula (II). In some embodiments, the *N*-heterocyclic carbene of Formula (II) is a *N*-heterocyclic carbene of Formula (IV-A). In some embodiments, the *N*-heterocyclic carbene of Formula (IV-A) is a *N*-heterocyclic carbene of Formula (II). In some

embodiments, the *N*-heterocyclic carbene of Formula (II) is a *N*-heterocyclic carbene of Formula (IV-B). In some embodiments, the *N*-heterocyclic carbene of Formula (IV-B) is a *N*-heterocyclic carbene of Formula (II). In some embodiments, the *N*-heterocyclic carbene of Formula (II) is a *N*-heterocyclic carbene of Formula (IV-C). In some embodiments, the *N*-heterocyclic carbene of Formula (IV-C) is a *N*-heterocyclic carbene of Formula (II). In some embodiments, the *N*-heterocyclic carbene of Formula (IV) is a *N*-heterocyclic carbene of Formula (IV-A). In some embodiments, the *N*-heterocyclic carbene of Formula (IV-A) is a *N*-heterocyclic carbene of Formula (IV). In some embodiments, the *N*-heterocyclic carbene of Formula (IV) is a *N*-heterocyclic carbene of Formula (IV-B). In some embodiments, the *N*-heterocyclic carbene of Formula (IV-B) is a *N*-heterocyclic carbene of Formula (IV). In some embodiments, the *N*-heterocyclic carbene of Formula (IV) is a *N*-heterocyclic carbene of Formula (IV-C). In some embodiments, the *N*-heterocyclic carbene of Formula (IV-C) is a *N*-heterocyclic carbene of Formula (IV). In some embodiments, the *N*-heterocyclic carbene of Formula (IV) is a *N*-heterocyclic carbene of Formula (II-A). In some embodiments, the *N*-heterocyclic carbene of Formula (II-A) is a *N*-heterocyclic carbene of Formula (IV). In some embodiments, the *N*-heterocyclic carbene of Formula (IV) is a *N*-heterocyclic carbene of Formula (II-B). In some embodiments, the *N*-heterocyclic carbene of Formula (II-B) is a *N*-heterocyclic carbene of Formula (IV).

[0625] Additional embodiments include those listed below.

[0626] In some embodiments, the at least one *N*-heterocyclic carbene precursor is 1,3-Diethylbenzimidazolium iodide; 1,3-Dipropylbenzimidazolium iodide; 1,3-Diisopropylbenzimidazolium iodide; 1,3-Dibutylbenzimidazolium iodide; 1,3-Dipentylbenzimidazolium iodide; 1,3-Didecylbenzimidazolium iodide; 1,3-Diethylbenzimidazolium bromide; 1,3-Dipropylbenzimidazolium bromide; 1,3-Diisopropylbenzimidazolium bromide; 1,3-Dibutylbenzimidazolium bromide; 1,3-Dipentylbenzimidazolium bromide; 1,3-Didecylbenzimidazolium bromide; 1,3-Diethylbenzimidazolium chloride; 1,3-Dipropylbenzimidazolium chloride; 1,3-Diisopropylbenzimidazolium chloride; 1,3-Dibutylbenzimidazolium chloride; 1,3-Dipentylbenzimidazolium chloride; 1,3-Didecylbenzimidazolium chloride; 1,3-Diethylbenzimidazolium methanesulfonate; 1,3-Dipropylbenzimidazolium methanesulfonate; 1,3-Diisopropylbenzimidazolium methanesulfonate; 1,3-Dibutylbenzimidazolium

methanesulfonate; 1,3-Dipentylbenzimidazolium methanesulfonate; 1,3-Didecylbenzimidazolium methanesulfonate; 1,3-Diethylbenzimidazolium trifluoromethanesulfonate; 1,3-Dipropylbenzimidazolium trifluoromethanesulfonate; 1,3-Diisopropylbenzimidazolium trifluoromethanesulfonate; 1,3-Dibutylbenzimidazolium trifluoromethanesulfonate; 1,3-Dipentylbenzimidazolium trifluoromethanesulfonate; 1,3-Didecylbenzimidazolium trifluoromethanesulfonate; 1,3-Diethylbenzimidazolium tetrafluoroborate; 1,3-Dipropylbenzimidazolium tetrafluoroborate; 1,3-Diisopropylbenzimidazolium tetrafluoroborate; 1,3-Dibutylbenzimidazolium tetrafluoroborate; 1,3-Dipentylbenzimidazolium tetrafluoroborate; 1,3-Didecylbenzimidazolium tetrafluoroborate; 1,3-Diethylbenzimidazolium hexafluorophosphate; 1,3-Dipropylbenzimidazolium hexafluorophosphate; 1,3-Diisopropylbenzimidazolium hexafluorophosphate; 1,3-Dibutylbenzimidazolium hexafluorophosphate; 1,3-Dipentylbenzimidazolium hexafluorophosphate; or 1,3-Didecylbenzimidazolium hexafluorophosphate.

[0627] In some embodiments, the at least one *N*-heterocyclic carbene precursor is 1,3-Diethylbenzimidazolium iodide; 1,3-Dipropylbenzimidazolium iodide; 1,3-Diisopropylbenzimidazolium iodide; 1,3-Dibutylbenzimidazolium iodide; 1,3-Dipentylbenzimidazolium iodide; or 1,3-Didecylbenzimidazolium iodide.

[0628] In some embodiments, the at least one *N*-heterocyclic carbene precursor is 1,3-Diethylbenzimidazolium bromide; 1,3-Dipropylbenzimidazolium bromide; 1,3-Diisopropylbenzimidazolium bromide; 1,3-Dibutylbenzimidazolium bromide; 1,3-Dipentylbenzimidazolium bromide; or 1,3-Didecylbenzimidazolium bromide.

[0629] In some embodiments, the at least one *N*-heterocyclic carbene precursor is 1,3-Diethylbenzimidazolium chloride; 1,3-Dipropylbenzimidazolium chloride; 1,3-Diisopropylbenzimidazolium chloride; 1,3-Dibutylbenzimidazolium chloride; 1,3-Dipentylbenzimidazolium chloride; or 1,3-Didecylbenzimidazolium chloride.

[0630] In some embodiments, the at least one *N*-heterocyclic carbene precursor is 1,3-Diethylbenzimidazolium methanesulfonate; 1,3-Dipropylbenzimidazolium methanesulfonate; 1,3-Diisopropylbenzimidazolium methanesulfonate; 1,3-Dibutylbenzimidazolium methanesulfonate; 1,3-Dipentylbenzimidazolium methanesulfonate; or 1,3-Didecylbenzimidazolium methanesulfonate.

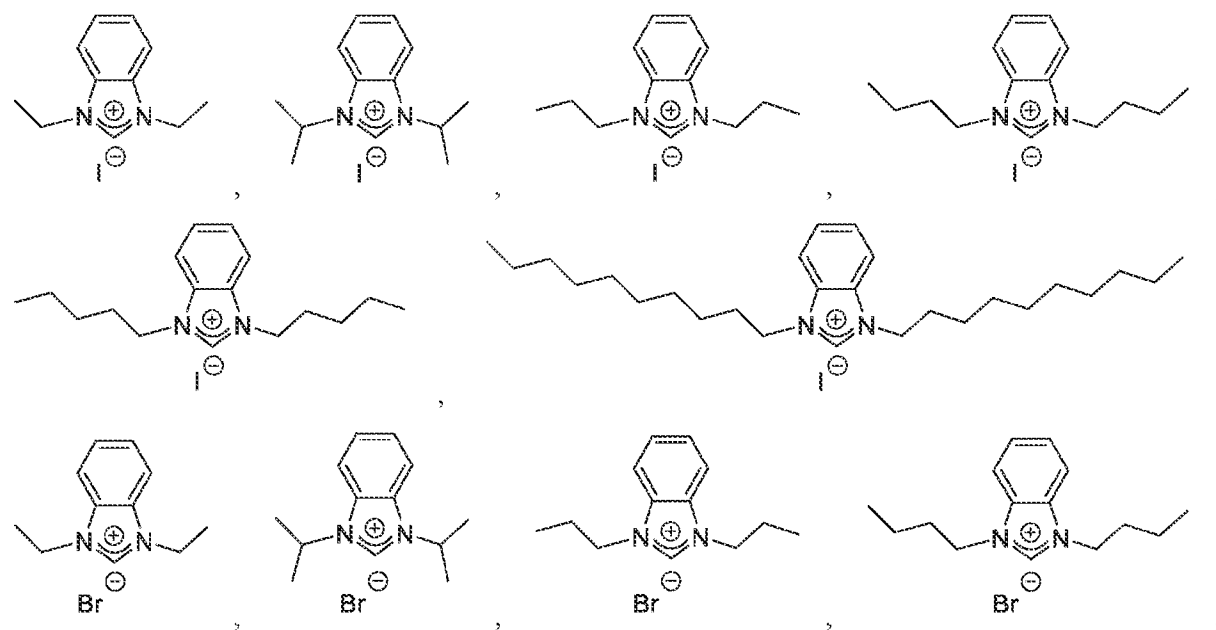
[0631] In some embodiments, the at least one *N*-heterocyclic carbene precursor is 1,3-Diethylbenzimidazolium trifluoromethanesulfonate; 1,3-Dipropylbenzimidazolium trifluoromethanesulfonate; 1,3-Diisopropylbenzimidazolium trifluoromethanesulfonate; 1,3-Dibutylbenzimidazolium trifluoromethanesulfonate; 1,3-Dipentylbenzimidazolium trifluoromethanesulfonate; or 1,3-Didecylbenzimidazolium trifluoromethanesulfonate.

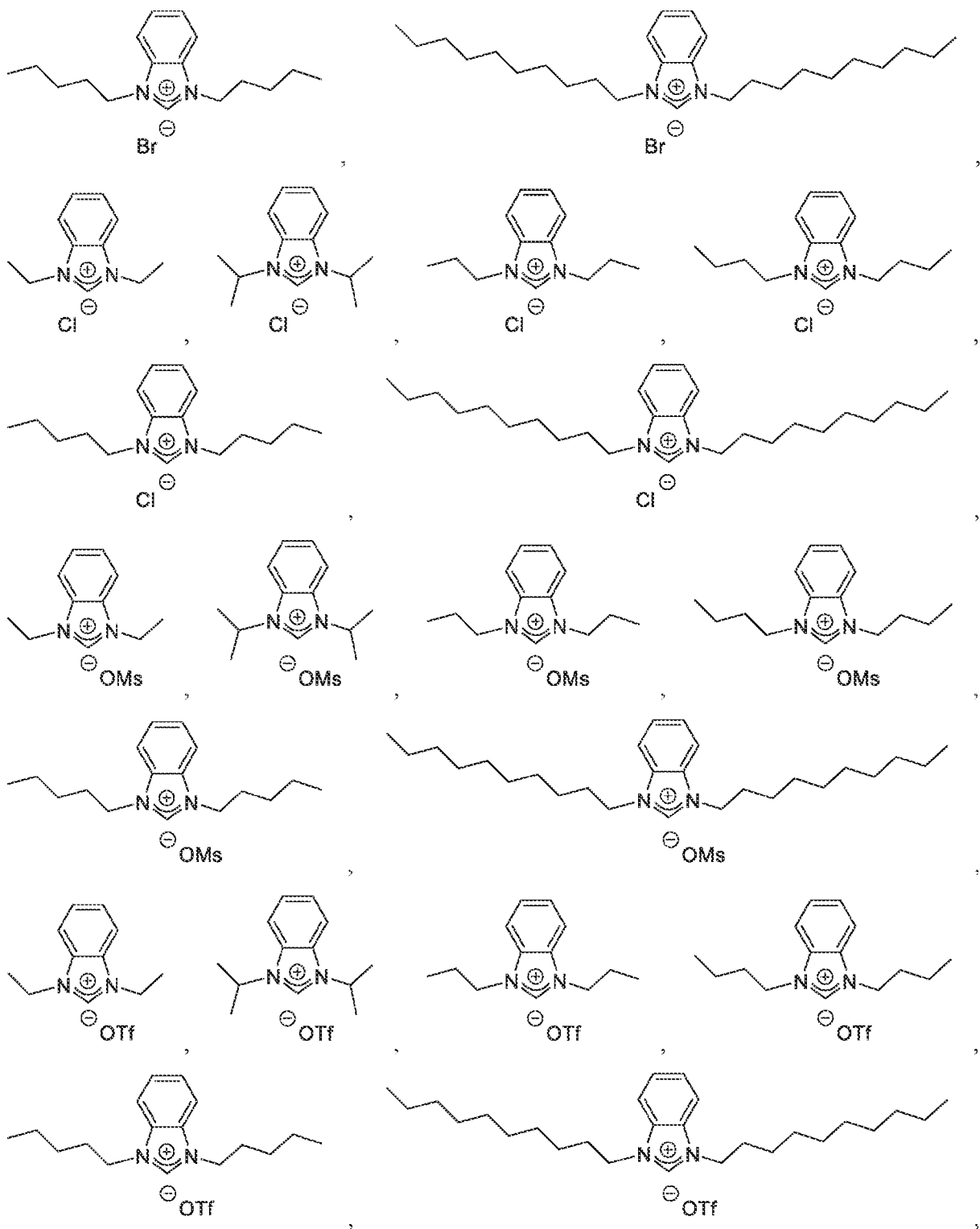
[0632] In some embodiments, the at least one *N*-heterocyclic carbene precursor is 1,3-Diethylbenzimidazolium tetrafluoroborate; 1,3-Dipropylbenzimidazolium tetrafluoroborate; 1,3-Diisopropylbenzimidazolium tetrafluoroborate; 1,3-Dibutylbenzimidazolium tetrafluoroborate; 1,3-Dipentylbenzimidazolium tetrafluoroborate; or 1,3-Didecylbenzimidazolium tetrafluoroborate.

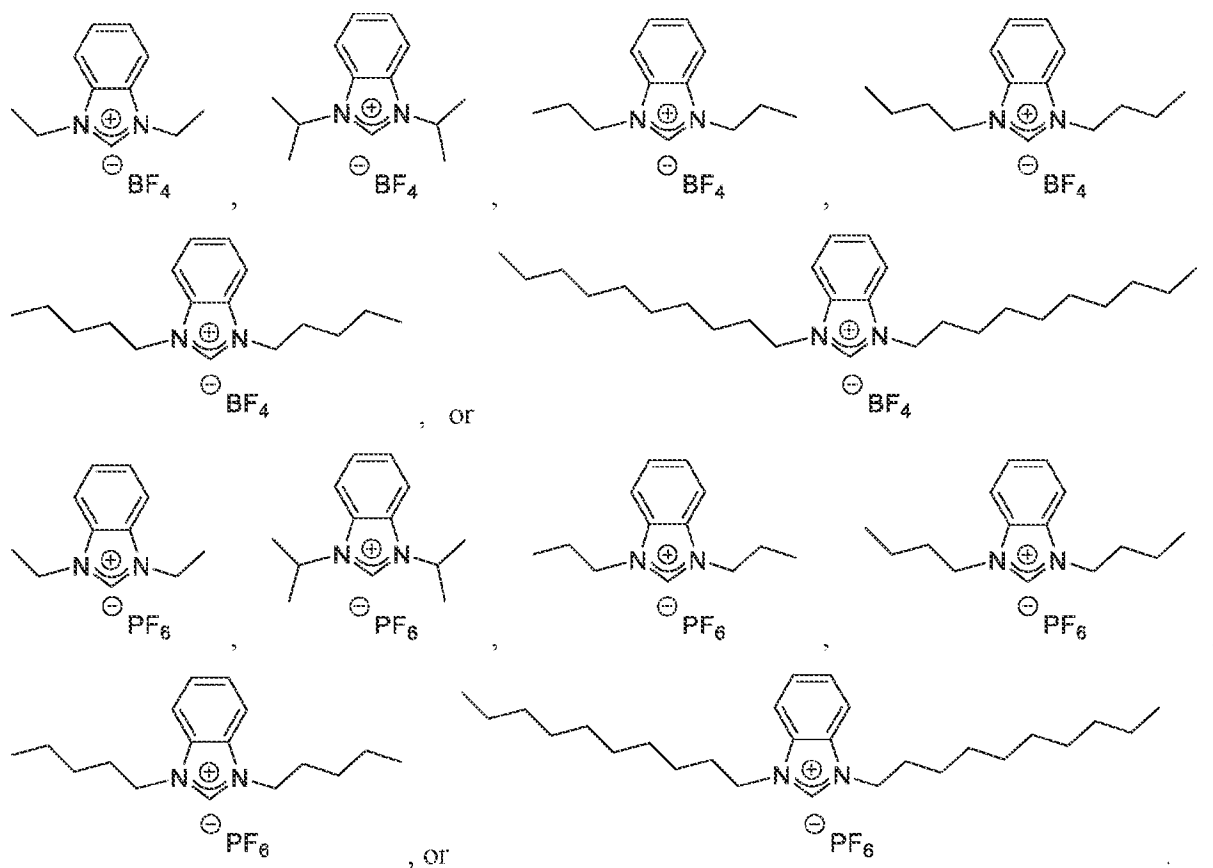
[0633] In some embodiments, the at least one *N*-heterocyclic carbene precursor is 1,3-Diethylbenzimidazolium hexafluorophosphate; 1,3-Dipropylbenzimidazolium hexafluorophosphate; 1,3-Diisopropylbenzimidazolium hexafluorophosphate; 1,3-Dibutylbenzimidazolium hexafluorophosphate; 1,3-Dipentylbenzimidazolium hexafluorophosphate; or 1,3-Didecylbenzimidazolium hexafluorophosphate.

[0634] Additional embodiments include those listed below.

[0635] In some embodiments, the at least one *N*-heterocyclic carbene precursor is

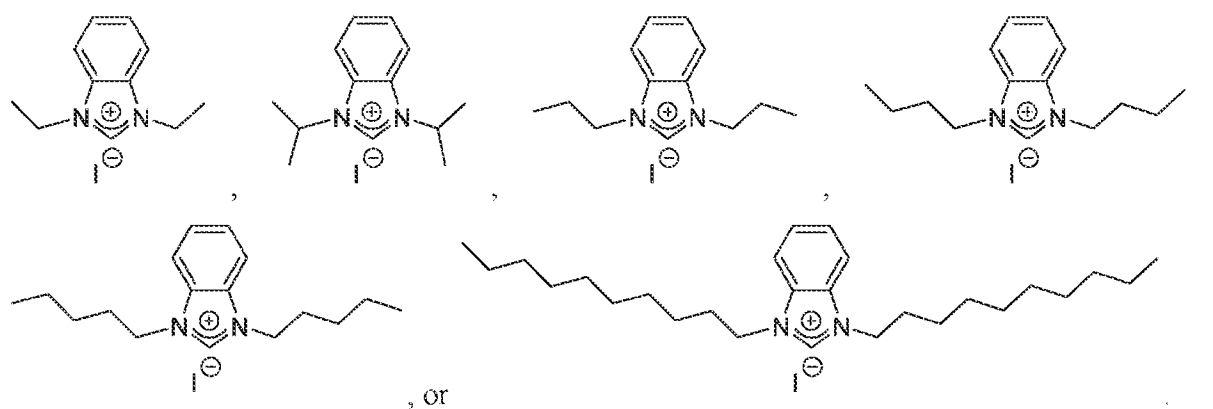




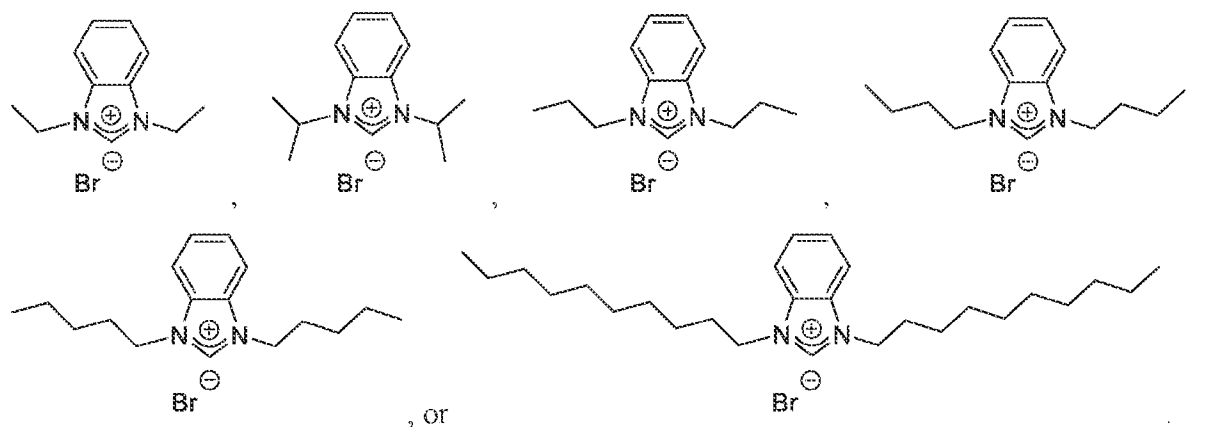


[0636] Additional embodiments include those listed below.

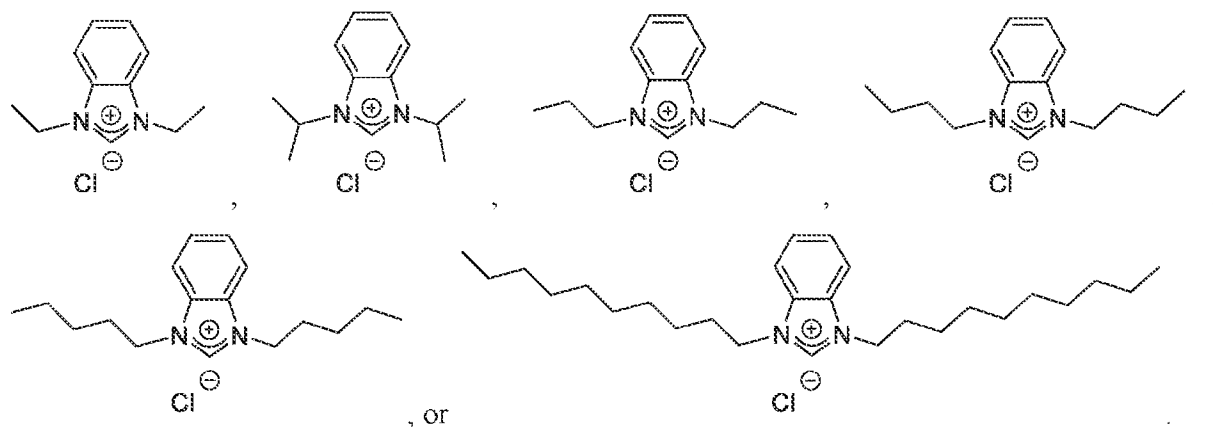
[0637] In some embodiments, the at least one *N*-heterocyclic carbene precursor is



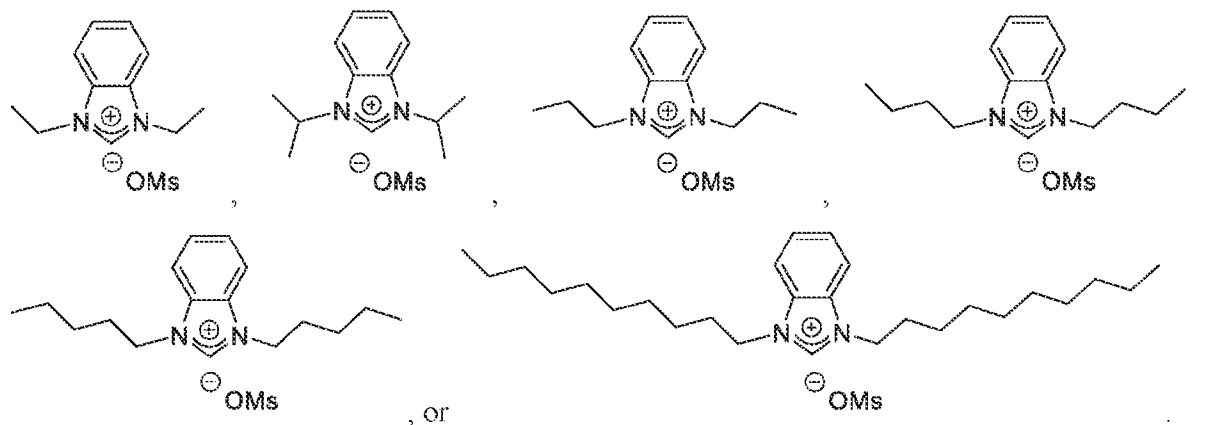
[0638] In some embodiments, the at least one *N*-heterocyclic carbene precursor is



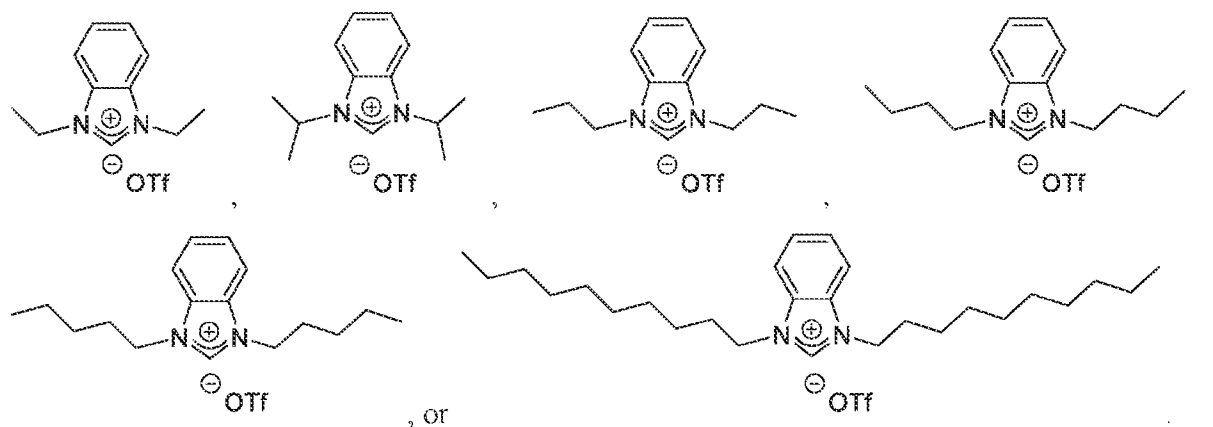
[0639] In some embodiments, the at least one *N*-heterocyclic carbene precursor is



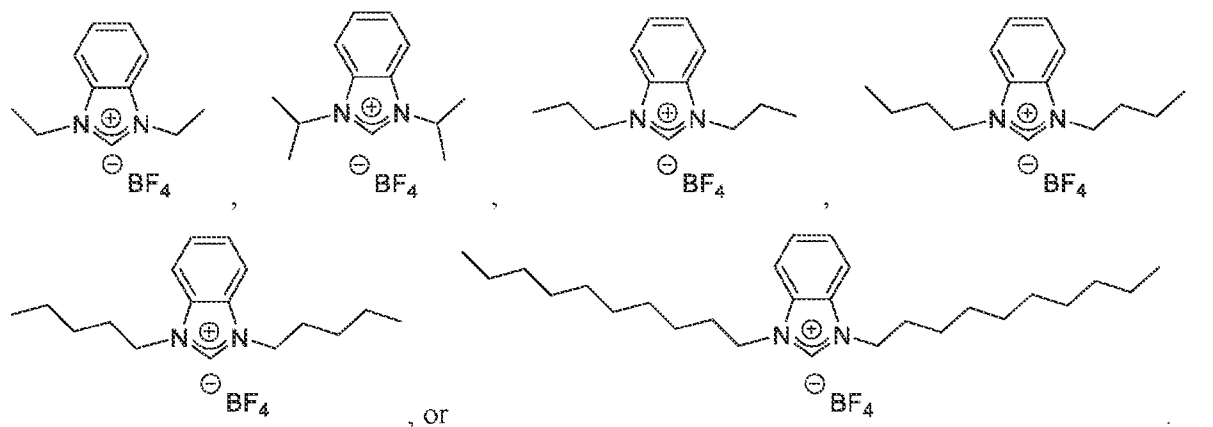
[0640] In some embodiments, the at least one *N*-heterocyclic carbene precursor is



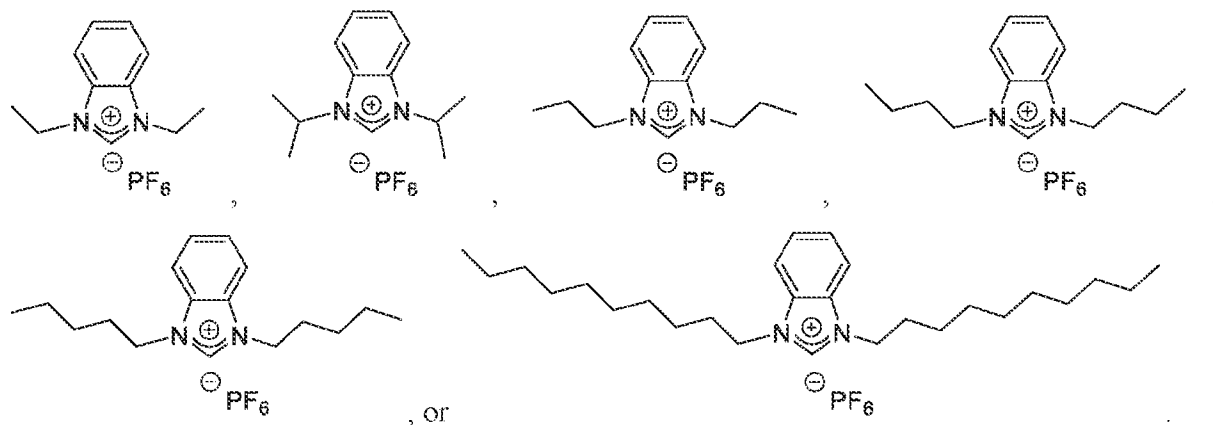
[0641] In some embodiments, the at least one *N*-heterocyclic carbene precursor is



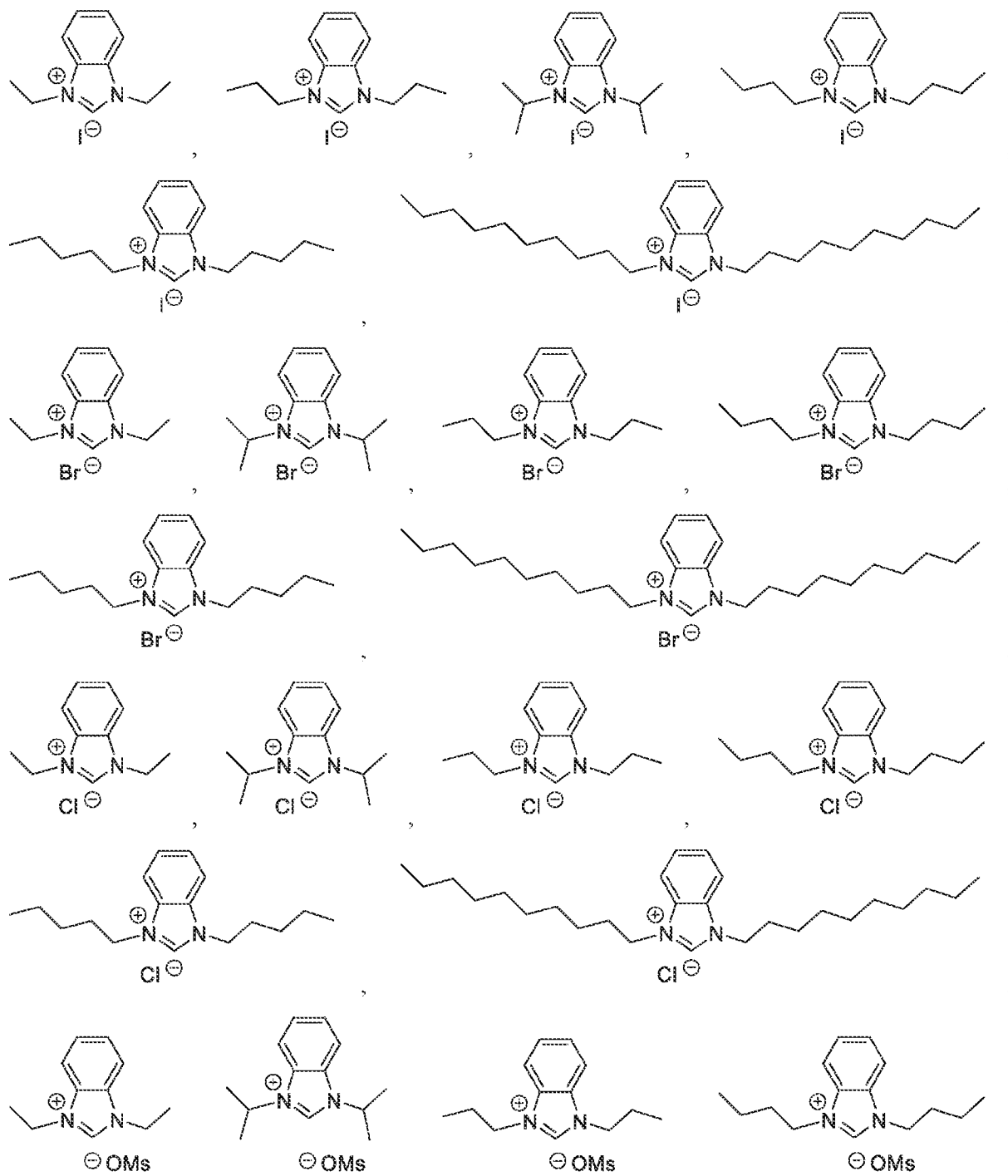
[0642] In some embodiments, the at least one *N*-heterocyclic carbene precursor is

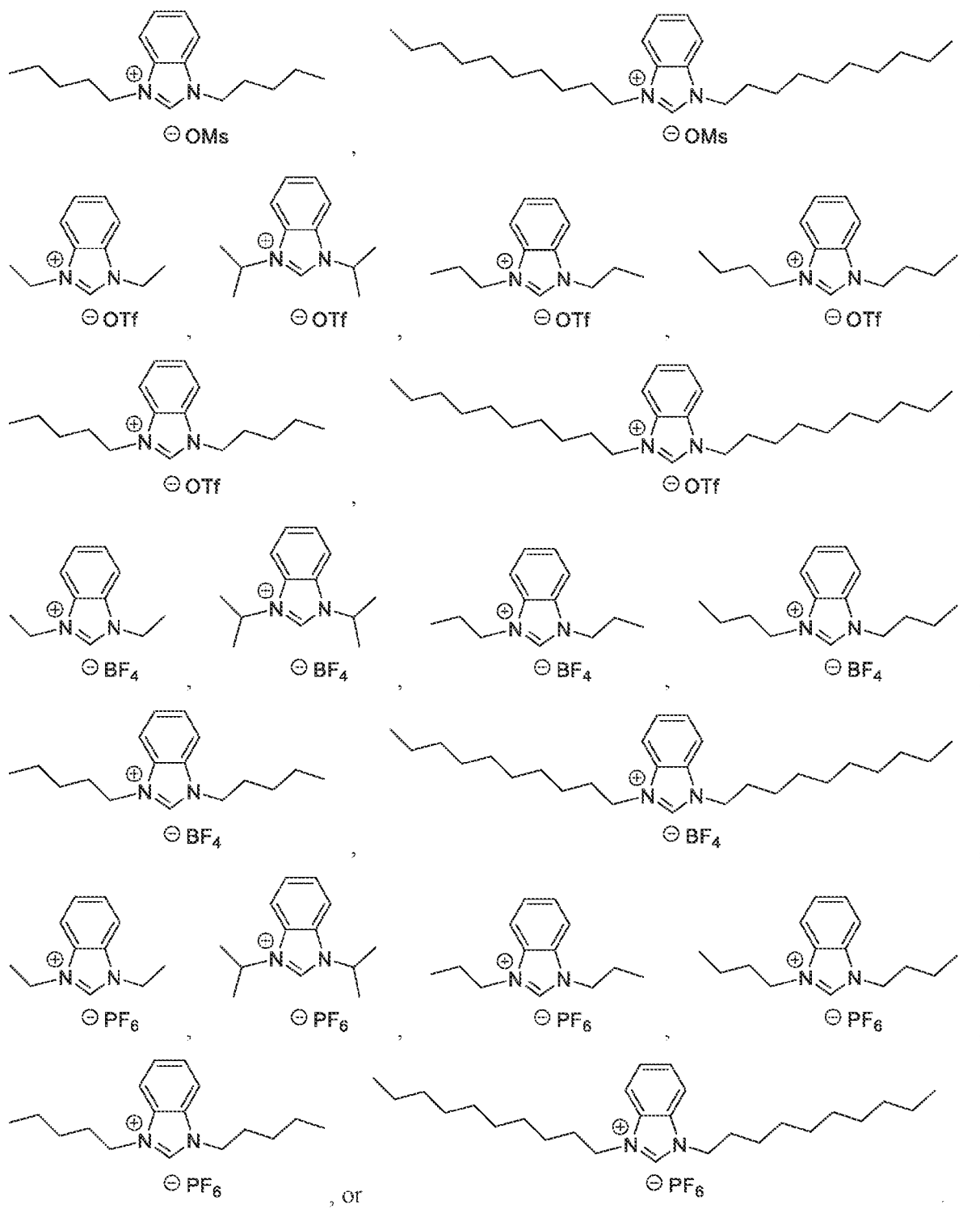


[0643] In some embodiments, the at least one *N*-heterocyclic carbene precursor is

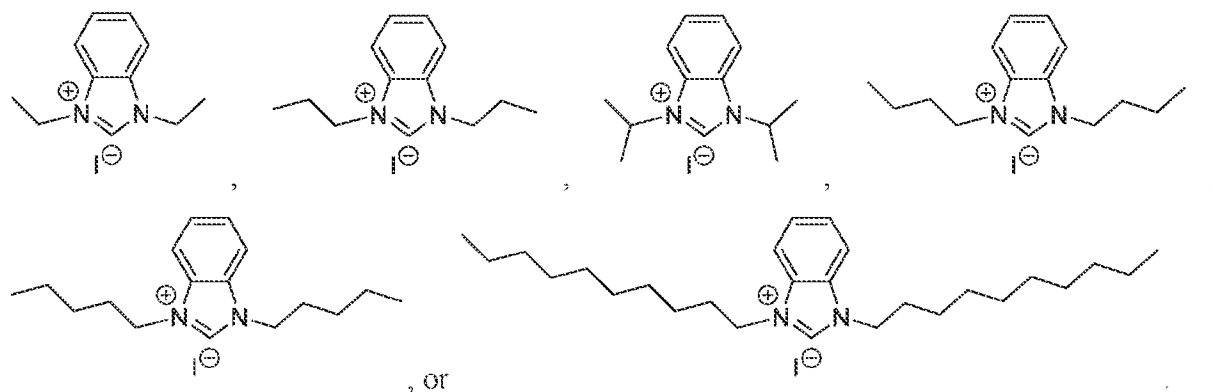


[0644] In some embodiments, the at least one *N*-heterocyclic carbene precursor is

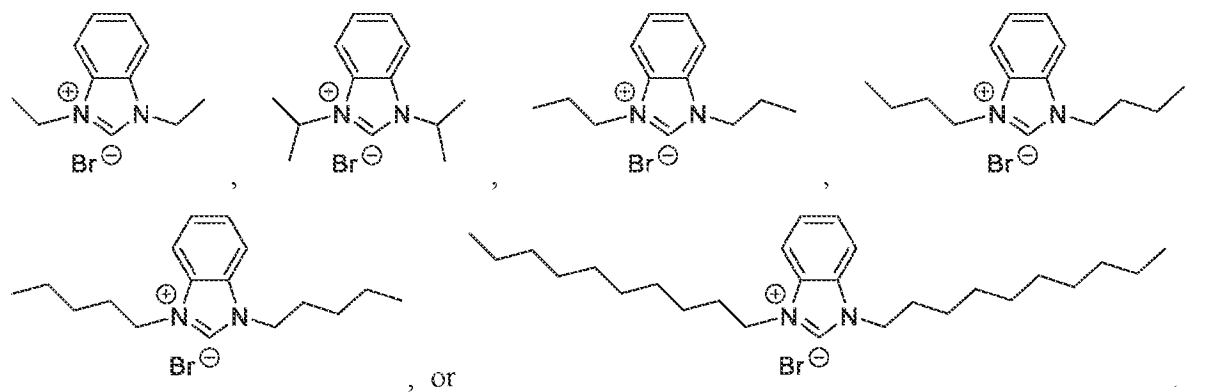




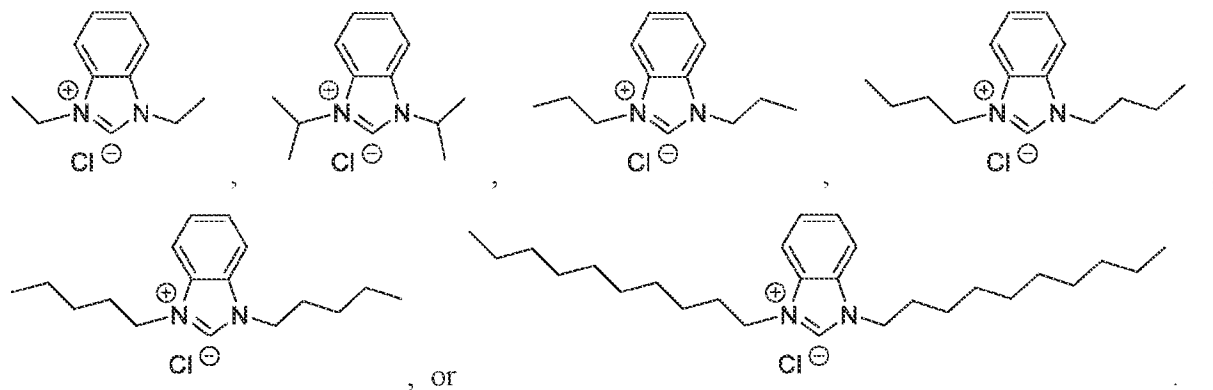
[0645] In some embodiments, the at least one *N*-heterocyclic carbene precursor is



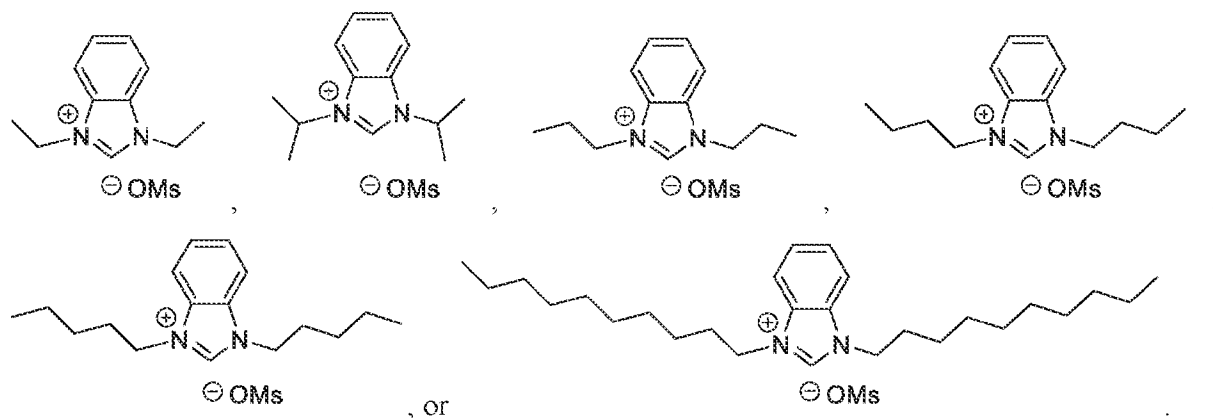
[0646] In some embodiments, the at least one *N*-heterocyclic carbene precursor is



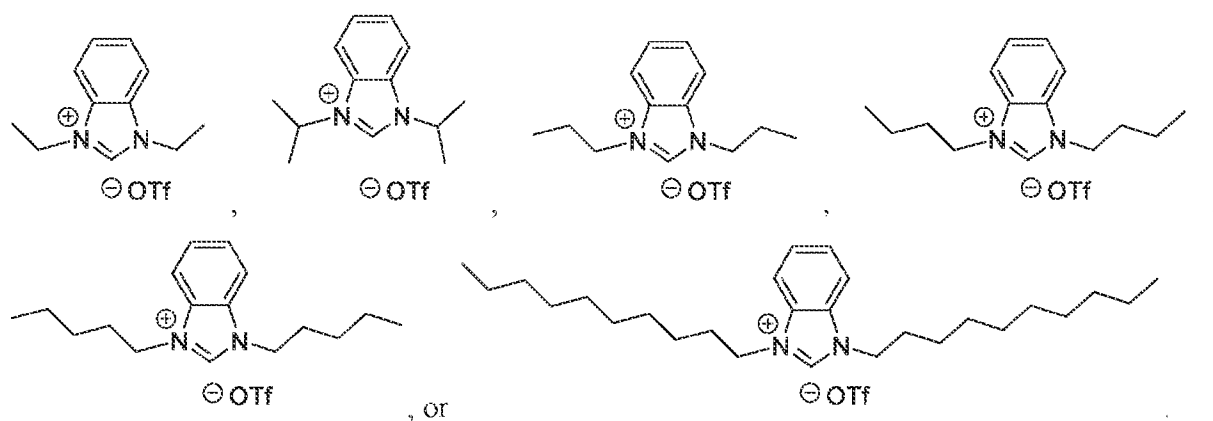
[0647] In some embodiments, the at least one *N*-heterocyclic carbene precursor is



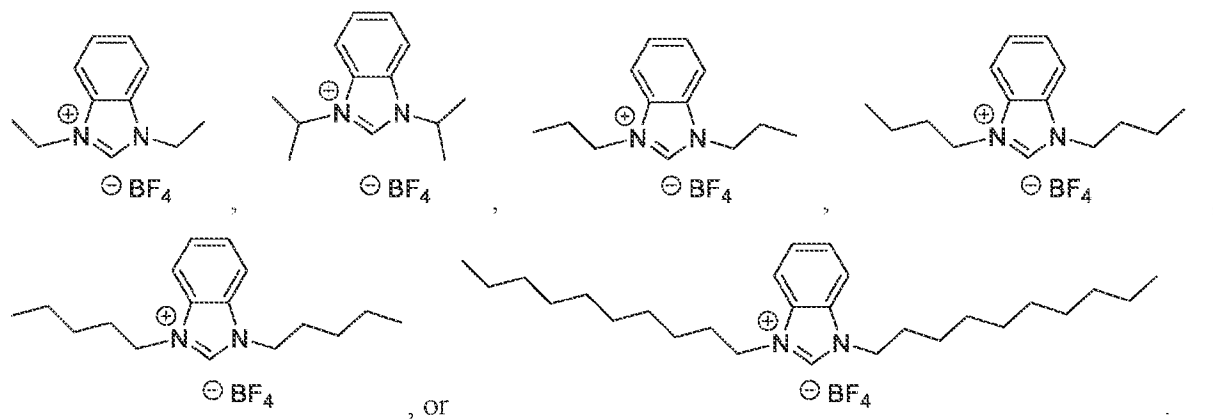
[0648] In some embodiments, the at least one *N*-heterocyclic carbene precursor is



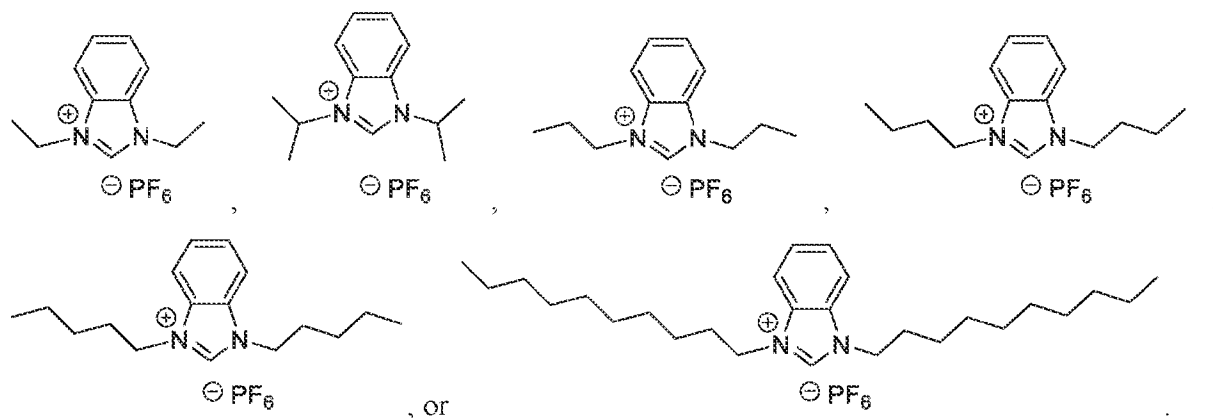
[0649] In some embodiments, the at least one *N*-heterocyclic carbene precursor is



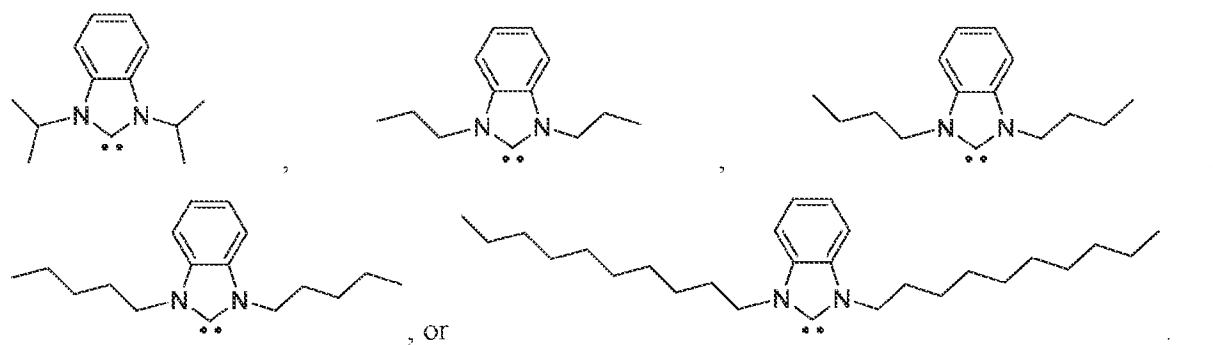
[0650] In some embodiments, the at least one *N*-heterocyclic carbene precursor is



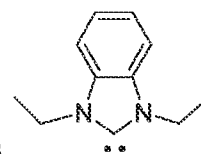
[0651] In some embodiments, the at least one *N*-heterocyclic carbene precursor is



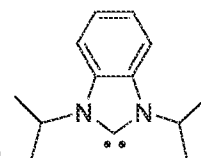
[0652] In some embodiments, the at least one *N*-heterocyclic carbene is



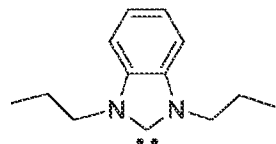
[0653] In some embodiments, the at least one *N*-heterocyclic carbene is



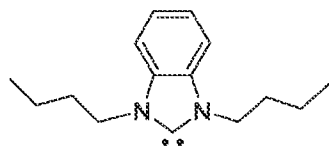
[0654] In some embodiments, the at least one *N*-heterocyclic carbene is



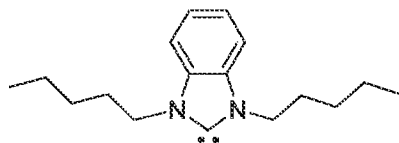
[0655] In some embodiments, the at least one *N*-heterocyclic carbene is



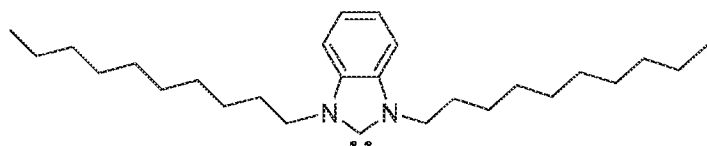
[0656] In some embodiments, the at least one *N*-heterocyclic carbene is



[0657] In some embodiments, the at least one *N*-heterocyclic carbene is



[0658] In some embodiments, the at least one *N*-heterocyclic carbene is



[0659] In various embodiments, the present invention provides a composition comprising at least one *N*-heterocyclic carbene functionalized transition metal dichalcogenide, wherein the at least one *N*-heterocyclic carbene functionalized transition metal dichalcogenide comprises at least one transition metal dichalcogenide; and at least one *N*-heterocyclic carbene.

[0660] In various embodiments, present invention provides an article of manufacture comprising at least one *N*-heterocyclic carbene functionalized transition metal dichalcogenide, wherein the at least one *N*-heterocyclic carbene functionalized transition metal dichalcogenide comprises at least one transition metal dichalcogenide; and at least one *N*-heterocyclic carbene.

EXAMPLES

[0661] The following examples are provided to better illustrate the claimed invention and are not to be interpreted as limiting the scope of the invention. To the extent that specific materials are mentioned, it is merely for purposes of illustration and is not intended to limit the invention. One skilled in the art may develop equivalent means or reactants without the exercise of inventive capacity and without departing from the scope of the invention.

[0662] **Example 1 - Example 4**

[0663] **Materials**

[0664] Molybdenum disulfide (MoS_2 , $< 2 \mu\text{m}$), hydroquinone (HQ), cumene hydroperoxide (CHP), anhydrous acetonitrile ($\text{a-CH}_3\text{CN}$), sodium borohydride (NaBH_4), potassium thiocyanate (NaSCN), sodium molybdate (Na_2MoO_4), pentadecalactone, hydrobromic acid (48 wt%), dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridine (DMAP), 4-amino-3-nitrophenol, potassium carbonate (K_2CO_3), lithium aluminum hydride (LiAlH_4), iron powder 325 mesh (Fe), ammonium chloride (NH_4Cl), isopropyl methanesulfonate, cesium carbonate (Cs_2CO_3), acetic acid (AcOH), methanol (MeOH), dichloromethane (DCM), acetonitrile (CH_3CN), formic acid (HCOOH), isopropyl alcohol (iPrOH), and tetrahydrofuran (THF) were purchased from Sigma-Aldrich. Hydrochloric acid was purchased from Oakwood. Water was purified to a resistance of $18 \text{ M}\Omega$, employing an Academic Milli-Q Water System (Millipore Corporation) and filtered through a $0.22 \mu\text{m}$ membrane before usage. Silica gel for column chromatography was obtained from Sorbent Technologies.

[0665] **Example 1. Synthesis of the adsorbates.**

[0666] The NHC adsorbate 6-((15-hydroxypentadecyl)oxy)-1,3-diisopropyl-1H-benzo[d]imidazol-3-ium methanesulfonate ($\text{NHC15OH}[\text{OMs}]$) was synthesized following the procedure described in Choi, Y.; Park, C. S.; Tran, H.-V.; Li, C.-H.; Crudden, C. M.; Lee, T. R. Functionalized *N*-Heterocyclic Carbene Monolayers on Gold for Surface-Initiated Polymerizations. *ACS Appl. Mater. Interfaces* **2022**, *14*, 44969-44980. The synthesized NHC molecular structure is shown as:



[0667] **Example 2. Exfoliation of MoS_2 .**

[0668] The exfoliation of MoS₂ was performed following the methods described in Jawaid, A. M.; Ritter, A. J.; Vaia, R. A. Mechanism for Redox Exfoliation of Layered Transition Metal Dichalcogenides. *Chem. Mater.* **2020**, *32*, 6550-6565 with minor modifications as mentioned below:

[0669] *Pretreatment of MoS₂*

[0670] Pristine MoS₂ powder, purchased from Sigma (< 2 μm), was washed prior to use for exfoliation by gently refluxing at 50°C in ethanol/acetone (1:1) in 24 h (100 mg/mL). After refluxing, the slurry underwent filtration, employing a filter membrane with pore size of 0.22 μm, sourced from TISCH Scientific. The caked MoS₂ was subjected to additional washing step utilizing 50 mL ethanol/acetone (1:1) solvent mixture. This sequence of steps constituted one washing cycle, which was repeated two additional times to ensure the complete elimination of oxidized species on the surface of MoS₂. The final powder underwent vacuum-drying process and stored in an environment enriched with CaSO₄ desiccant under vacuum.

[0671] *MoS₂ oxidation*

[0672] In a 100 mL bottle flask, 50 mL a-CH₃CN was introduced, followed by the addition of 1500 mg washed MoS₂. The resulting mixture was briefly sonicated in 15 minutes, aiming at dispersing the aggregated MoS₂ particles. Subsequently, 150 μL CHP 80% was added to the flask. The reaction system was heated up to 55°C and gently stirred in 24 h.

[0673] *Mo⁶⁺ titration analysis*

[0674] After oxidation process, the bottle flask was let cool down to room temperature and undisturbed in 2 h. Subsequently, 2 mL from the yellow supernatant was pipetted and subjected to centrifugation at 10000 rpm in 10 minutes. The centrifugation process would remove the left MoS₂ from the solution. A total volume of 500 μL supernatant was subjected to a 20 mL vial, followed by 500 μL HCl 6M. The mixture was swirled to ensure thorough homogeneity. Following this step, 500 μL NaSCN 2M and 500 μL NaBH₄ 0.01 M were added subsequently to the vial. The resulting solution was allowed to stand undisturbed for a period of 10 minutes. Subsequently, an additional volume of 4 mL distilled acetone was added to the vial to dissolve insoluble organic species. The absorption spectra were collected by a Cary 60 UV-vis spectrophotometer. Absorption peak at 460 nm, resulting from the molybdenum thiocyanate complex, was recorded; the absorbance was interpolated to Mo⁶⁺ concentration, based on the constructed Mo⁶⁺ calibration curve.

[0675] *Mo⁶⁺ titration calibration*

[0676] Na₂MoO₄ was dissolved in water to prepare a series of stock solutions with different concentrations (0, 0.01, 0.03, 0.05, 0.07, 0.1, 0.2, and 0.3 M). 500 μ L HCl 6M was added to each 20 mL vial containing the respective stock solution (500 μ L). The mixture was swirled to ensure thorough homogeneity. Following this step, 500 μ L NaSCN 2M and 500 μ L NaBH₄ 0.01 M were added subsequently to each vial. The resulting solution was allowed to stand undisturbed for a period of 10 minutes. Subsequently, an additional volume of 1.5 mL distilled H₂O was added to each vial. The absorption spectrum of each solution was collected by a Cary 60 UV-vis spectrophotometer. Absorption peak at 460 nm, resulting from the molybdenum thiocyanate complex, was recorded, and employed to construct a calibration curve, enabling the quantification of Mo⁶⁺ concentrations across the various solutions under investigation ($\alpha_{460} = 9.4 \text{ mL } \mu\text{mol}^{-1} \text{ cm}^{-1}$, $R^2 = 0.99986$).

[0677] *MoS₂ exfoliation*

[0678] Following the analysis of Mo⁶⁺ concentration, HQ was dissolved in a-CH₃CN to produce a solution with a concentration of 0.1M. Next, the oxidized slurry was treated with a stoichiometric amount of HQ (HQ/Mo⁶⁺ 50:1). Crucially, HQ 0.1M solution was added dropwise to ensure an efficient exfoliation process. The ensuing reaction was stirred at room temperature in 48 h.

[0679] Upon achieving complete exfoliation, the slurry underwent centrifugation at 10000 rpm in 10 minutes to remove all traces of inorganic polyoxometalate macro-anions (POMs), characterized by their distinct blue color. In the next step, 10 mL of a-CH₃CN was introduced; the mixture was vortexed and sonicated in 30 minutes, followed by a subsequent centrifugation at 10000 rpm in 10 minutes. This process constituted one cycle. It is imperative to emphasize the crucial significance of this purification step to obtain exfoliated MoS₂ at high quality and good dispersion. This procedure was repeated 4 – 7 additional cycles for efficient removal of POMs. Ultimately, 30 mL a-CH₃CN was added, and the mixture was vortexed and sonicated in 30 minutes. The temperature during sonication was controlled between 5°C – 20°C. The ensuing mixture was centrifuged at 2000 rpm in 30 minutes. Following, 20 mL supernatant was pipetted out and subjected to subsequent centrifugation at 10000 rpm in 10 minutes to eliminate small exfoliated MoS₂ sheets. The precipitated MoS₂ was then redispersed by addition of 30 mL a-

CH₃CN. This process was carried out several times to achieve any desired concentration of exfoliated MoS₂.

[0680] Note: The centrifuge rate in rpm (revolutions per minute) varies strongly depending on the rotor in use. Hence, for a comprehensive and consistent comparison, unit in rpm should be converted to G (relative centrifuge force) and reported accordingly. In our experimental setup, the following centrifuge rates were used with the corresponding number in G: 10000 rpm (11980 G), 2500 rpm (740 G), 2000 rpm (470 G), 1500 rpm (269 G), 1000 rpm (120 G), and 500 rpm (30 G).

[0681] *MoS₂ titration*

[0682] A concentrated exfoliated MoS₂ colloidal was diluted to make a series of stock solutions with the dilution of 6, 12, 18, 24, and 30 times. 300 µL from each stock solution was dropped carefully on a separate gold quartz crystal (QCM) plate (Novaetech S.r.l., resonance frequency 10 MHz) accordingly. The loaded QCM plates, then, were dried in 60°C oven overnight, ensuring complete solvent evaporation. Frequency analysis was carried out employing an eQCM from Camry Instruments. The mass of MoS₂ within the dropped volume was deduced accordingly and fitted with the minima extinction at 345 nm from the UV-vis extinction spectrum of exfoliated MoS₂ ($\epsilon_{345} = 42 \text{ mL mg}^{-1} \text{ cm}^{-1}$, $R^2 = 0.93887$).

[0683] **Example 3. Functionalization of Exfoliated MoS₂ by NHC Adsorbates.**

[0684] A 6.25 mL portion of exfoliated MoS₂ (1 mM; 1 mg) was introduced to a 40 mL glass vial. Subsequently, 6.25 mL NHC15OH[OMs] x mM in DCM was quickly injected into the solution. The reaction was left undisturbed at room temperature in 24 h. Then, the slurry was transferred to a centrifuge tube and subjected to centrifugation at 5000 rpm in 10 minutes to sediment all functionalized and unfunctionalized MoS₂. The resulting material was additionally washed with 10 mL DCM, stirred in 5 minutes in a 20 mL glass vial, and subjected to centrifugation at 5000 rpm in 10 minutes. This process constituted one washing cycle and was repeated two more times to eliminate all unreacted NHCs. The final product was redispersed in DCM as an ink type for later characterization.

[0685] **Example 4. Characterization**

[0686] *Ultraviolet-visible spectroscopy (UV-vis)*

[0687] UV-vis data was collected by a Cary 60 UV-vis spectrophotometer. UV-vis technical parameters, data analysis, and mathematical transformation (the 2nd derivative of

extinction spectrum and corresponding smoothing steps) were followed as the protocol in Backes, C.; Hanlon, D.; Szydłowska, B. M.; Harvey, A.; Smith, R. J.; Higgins, T. M.; Coleman, J. N. Preparation of Liquid-Exfoliated Transition Metal Dichalcogenide Nanosheets with Controlled Size and Thickness: A State of the Art Protocol. *J. Vis. Exp.* **2016**, 118, e54806.

[0688] *Atomic force microscope (AFM)*

[0689] 1 x 1 cm² 300 nm thick SiO₂ layer-covered Si substrate, sourced from MSE Supplies, was obtained and pre-dipped into piranha solution over night to wash away inorganic and organic residues contaminants. Subsequently, the substrate was washed thoroughly with DI water and dried by N₂ gas. Consequently, 20 μ L exfoliated MoS₂ colloidal ($\epsilon_{345} = 0.6$) was dropped onto the polished side of the substrate. The dropped sample was dried naturally overnight prior to AFM measurement. Surface images were obtained employing an AFM, MFP-3D Origin+, Oxford Instruments in a non-contact soft tapping mode. Certain numbers of images were collected and subsequently underwent a statistical analysis and generated a statistical height retrace histogram.

[0690] Note: Owing to the inherent self-dried aggregation tendency of exfoliated nanosheets, care must be taken to select analysis locations. Guidelines for differentiating between promising, non-aggregated regions have been demonstrated in the prior publication, Backes, C.; Higgins, T. M.; Kelly, A.; Boland, C.; Harvey, A.; Hanlon, D.; Coleman, J. N. Guidelines for Exfoliation, Characterization and Processing of Layered Materials Produced by Liquid Exfoliation. *Chem. Mater.* **2017**, 29, 1, 243-255. Typically, when situated on 300 nm thick SiO₂ layer, even the nanoscale nanosheets still manifest as distinctive green dots, even under a standard optical microscope equipped within AFM instruments. In contrast, aggregated materials results in prominent green clusters. Hence, during the scanning analysis, it is imperative to probe close, but not within the green regions to avoid thick, aggregation effects.

[0691] *X-ray powder diffraction (XRD)*

[0692] Exfoliated MoS₂ was prepared by drop-casting on a glass slide and drying in an oven at 80°C in 2h. A controlled circular area, with a radius of 0.7 cm, was fashioned on a glass slide by the application of a double-layer heat-resistant tape (2 mm thick). Subsequently, functionalized MoS₂ ink was dropped into the aperture, followed by natural evaporation of solvent at room temperature. Then, the covered tape was removed, and the sample was further dried at 100°C in 1h, followed by situated at 80°C overnight. The XRD pattern was collected employing an X-ray diffractometer (XRD, Smart Lab, Rigaku, Cu-K α radiation ($\lambda = 0.15406$ nm) operated at

40 kV and 44 mA, 5 mm beam mask, 0.5° divergence slit, step size 0.02° (2 θ), scanning rate 1.5° min⁻¹).

[0693] *Attenuated total reflectance infrared spectroscopy (ATR-IR)*

[0694] The sample was prepared the same way as mentioned protocol for XRD analysis. The IR data was collected, employing an ATR-IR, Nicolet iS10, Thermo Scientific in the range of 500–4000 cm⁻¹ with 2 cm⁻¹ resolution.

[0695] *Zeta potential*

[0696] Zeta potential measurements were conducted on a Malvern Zetasizer model ZEN3600. Exfoliated MoS₂ colloidal nanosheets or NHC-functionalized MoS₂ was briefly sonicated and diluted to achieve a concentration of 0.01 mM, prior to undergoing subsequent Zeta potential measurements.

[0697] **Example 5 – Example 10**

[0698] **Materials**

[0699] Molybdenum disulfide (MoS₂, < 2 μ m), hydroquinone (HQ), cumene hydroperoxide (CHP), anhydrous acetonitrile (a-CH₃CN), sodium borohydride (NaBH₄), potassium thiocyanate (NaSCN), sodium molybdate (Na₂MoO₄), pentadecalactone, hydrobromic acid (48 wt%), dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridine (DMAP), 4-amino-3-nitrophenol, potassium carbonate (K₂CO₃), lithium aluminum hydride (LiAlH₄), iron powder 325 mesh (Fe), ammonium chloride (NH₄Cl), isopropyl methanesulfonate, cesium carbonate (Cs₂CO₃), acetic acid (AcOH), methanol (MeOH), dichloromethane (DCM), acetonitrile (CH₃CN), formic acid (HCOOH), isopropyl alcohol (iPrOH), and tetrahydrofuran (THF) were purchased from Sigma-Aldrich. Hydrochloric acid was purchased from Oakwood. Water was purified to a resistance of 18 M Ω , employing an Academic Milli-Q Water System (Millipore Corporation) and filtered through a 0.22 μ m membrane before usage. Silica gel for column chromatography was obtained from Sorbent Technologies.

[0700] **Example 5. Synthesis of the adsorbates**

[0701] The NHC adsorbate 6-((15-hydroxypentadecyl)oxy)-1,3-diisopropyl-1H-benzo[d]imidazol-3-ium methanesulfonate (NHC15OH[OMs]) was synthesized following the procedure described in Choi, Y.; Park, C. S.; Tran, H.-V.; Li, C.-H.; Crudden, C. M.; Lee, T. R. Functionalized *N*-Heterocyclic Carbene Monolayers on Gold for Surface-Initiated Polymerizations. *ACS Appl. Mater. Interfaces* **2022**, *14*, 44969-44980.

[0702] **Example 6. Exfoliation of MoS₂**

[0703] The exfoliation of MoS₂ was performed following the methods described in Jawaid, A. M.; Ritter, A. J.; Vaia, R. A. Mechanism for Redox Exfoliation of Layered Transition Metal Dichalcogenides. *Chem. Mater.* **2020**, *32*, 6550-6565 with minor modifications as mentioned below:

[0704] *Pretreatment of MoS₂*

[0705] Pristine MoS₂ powder, purchased from Sigma (< 2μm), was washed prior to use for exfoliation by gently refluxing at 50°C in ethanol/acetone (1:1) in 24 h (100 mg/mL). After

[0710] *Mo⁶⁺ Titration Analysis*

[0711] After oxidation process, the bottle flask was let cool down to room temperature and undisturbed in 2 h. Subsequently, 2 mL from the yellow supernatant was pipetted and subjected to centrifugation at 10000 rpm in 10 minutes. The centrifugation process would remove the left MoS₂ from the solution. A total volume of 500 μ L supernatant was subjected to a 20 mL vial, followed by 500 μ L HCl 6M. The mixture was swirled to ensure thorough homogeneity. Following this step, 500 μ L NaSCN 2M and 500 μ L NaBH₄ 0.01 M were added subsequently to the vial. The resulting solution was allowed to stand undisturbed for a period of 10 minutes. Subsequently, an additional volume of 4 mL distilled acetone was added to the vial to dissolve insoluble organic species. The absorption spectra were collected by a Cary 60 UV-vis spectrophotometer. Absorption peak at 460 nm, resulting from the molybdenum thiocyanate complex, was recorded; the absorbance was interpolated to Mo⁶⁺ concentration, based on the constructed Mo⁶⁺ calibration curve.

[0712] *MoS₂ exfoliation*

[0713] Following the analysis of Mo⁶⁺ concentration, HQ was dissolved in a-CH₃CN to produce a solution with a concentration of 0.1M. Next, the oxidized slurry was treated with a stoichiometric amount of HQ (HQ/Mo⁶⁺:50:1). Crucially, HQ 0.1M solution was added dropwise to ensure an efficient exfoliation process. The ensuing reaction was stirred at room temperature in 48 hours.

[0714] Upon achieving complete exfoliation, the slurry underwent centrifugation at 10000 rpm in 10 minutes to remove all traces of inorganic polyoxometalate macro-anions (POMs), characterized by their distinct blue color. In the next step, 10 mL of a-CH₃CN was introduced; the mixture was vortexed and sonicated in 30 minutes, followed by a subsequent centrifugation at 10000 rpm in 10 minutes. It is imperative to emphasize the crucial significance of this purification step to obtain exfoliated MoS₂ at high quality and good dispersion. This procedure was repeated 4 – 7 times for efficient removal of POMs. Ultimately, 30 mL a-CH₃CN was added, and the mixture was vortexed and sonicated in 30 minutes. The temperature during sonication was controlled between 5°C – 20°C. The ensuing mixture was centrifuged at 2000 rpm in 30 minutes. Following, 20 mL supernatant was pipetted out and subjected to subsequent centrifugation at 10000 rpm in 10 minutes to eliminate small exfoliated MoS₂ sheets. The precipitated MoS₂ was then redispersed

by addition of 30 mL a-CH₃CN. This process was carried out several times to achieve any desired concentration of exfoliated MoS₂.

[0715] MoS₂ Titration

[0716] A concentrated exfoliated MoS₂ colloidal was diluted to make a series of stock solutions with the dilution of 6, 12, 18, 24, and 30 times. 300 µL from each stock solution was dropped carefully on a separate gold quartz crystal (QCM) plate (Novaetech S.r.l., resonance frequency 10 MHz) accordingly. Frequency analysis was carried out employing an eQCM from Camry Instruments. The mass of MoS₂ within the dropped volume was deduced accordingly and fitted with the minima extinction at 345 nm from the UV-vis extinction spectrum of exfoliated MoS₂ ($\epsilon_{345} = 42 \text{ mL mg}^{-1} \text{ cm}^{-1}$).

[0717] Example 7. Functionalization of Exfoliated MoS₂ by NHC Adsorbates

[0718] A 12.5 mL portion of exfoliated MoS₂ (1 mM; 2 mg) was introduced to a 50 mL round bottom flask. Subsequently, 12.5 mL NHC15OH[OMs] 5 mM in DCM was quickly injected into the solution. The reaction was stirred at room temperature in 24 h. Then, the slurry was transferred to a centrifuge tube and subjected to centrifugation at 10000 rpm in 10 minutes to sediment all functionalized and unfunctionalized MoS₂. The resulting material was additionally washed with DCM, gently swirled, and subjected to centrifugation at 10000 rpm in 10 minutes. This process constituted one washing cycle and was repeated two more times to eliminate all unreacted NHC. The final product was redispersed in DCM as an ink type for later characterization.

[0719] Example 8. UV-vis Analysis

[0720] UV-vis technical parameters, data analysis, and mathematical transformation were followed as the protocol in Backes, C.; Hanlon, D.; Szydłowska, B. M.; Harvey, A.; Smith, R. J.; Higgins, T. M.; Coleman, J. N. Preparation of Liquid-Exfoliated Transition Metal Dichalcogenide Nanosheets with Controlled Size and Thickness: A State of the Art Protocol. *J. Vis. Exp.* **2016**, 118, e54806.

[0721] Example 9. XRD Analysis

[0722] A controlled circular area, with a radius of 0.7 cm, was fashioned on an optical microscope glass by the application of a double-layer heat-resistant tape. Subsequently, either exfoliated MoS₂ or functionalized MoS₂ ink was dropped into the aperture, followed by natural evaporation of solvent at room temperature. Then, the covered tape was removed, and the sample was further dried at 100°C in 1h, followed by situated at 80°C overnight. The XRD pattern was

collected employing an X-ray diffractometer (XRD, Smart Lab, Rigaku, Cu-K α irradiation operated at 40 kV and 44 mA).

[0723] Example 10. ATR-IR Analysis

[0724] The sample was prepared the same way as mentioned protocol for XRD analysis. The IR data was collected, employing an ATR-IR, Nicolet iS10, Thermo Scientific in the range of 500–4000 cm⁻¹ with 2 cm⁻¹ resolution.

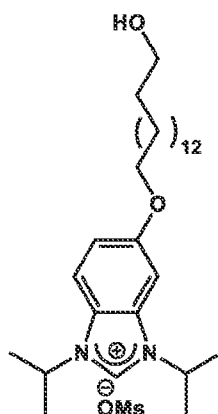
[0725] Example 11 – Example 19

[0726] Materials

[0727] Molybdenum disulfide (MoS₂, < 2 μ m), tungsten disulfide (WS₂, < 2 μ m), hydroquinone (HQ), cumene hydroperoxide (CHP), anhydrous acetonitrile (a-CH₃CN), sodium borohydride (NaBH₄), sodium thiocyanate (NaSCN), sodium molybdate (Na₂MoO₄), sodium tungstate dihydrate (Na₂WO₄·2H₂O), pentadecalactone, hydrobromic acid (48 wt%), dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridine (DMAP), 4-amino-3-nitrophenol, potassium carbonate (K₂CO₃), lithium aluminum hydride (LiAlH₄), iron powder 325 mesh (Fe), ammonium chloride (NH₄Cl), isopropyl methanesulfonate, cesium carbonate (Cs₂CO₃), acetic acid (AcOH), methanol (MeOH), dichloromethane (DCM), acetonitrile (CH₃CN), formic acid (HCOOH), isopropyl alcohol (iPrOH), and tetrahydrofuran (THF) were purchased from Sigma-Aldrich, USA. Hydrochloric acid was purchased from Oakwood Chemical, USA. Water was purified to a resistance of 18 M Ω , employing an Academic Milli-Q Water System (Millipore Corporation) and filtered through a 0.22 μ m membrane before usage. Silica gel for column chromatography was obtained from Sorbent Technologies.

[0728] Example 11. Synthesis of the Adsorbates

[0729] The NHC adsorbate 6-((15-hydroxypentadecyl)oxy)-1,3-diisopropyl-1H-benzo[d]imidazol-3-ium methanesulfonate (NHC15OH[OMs]) was synthesized following the procedure described in Choi, Y.; Park, C. S.; Tran, H.-V.; Li, C.-H.; Crudden, C. M.; Lee, T. R. Functionalized *N*-Heterocyclic Carbene Monolayers on Gold for Surface-Initiated Polymerizations. *ACS Appl. Mater. Interfaces* **2022**, *14*, 44969–44980. The synthesized NHC molecular structure is shown as:



[0730] Example 12. Redox Exfoliation of MoS₂.

[0731] The exfoliation of MoS₂ was performed following the methods described in Jawaid, A.; Che, J.; Drummy, L. F.; Bultman, J.; Waite, A.; Hsiao, M.-S.; Vaia, R. A. Redox Exfoliation of Layered Transition Metal Dichalcogenides. *ACS Nano* **2017**, *11*, 635–646 and Jawaid, A. M.; Ritter, A. J.; Vaia, R. A. Mechanism for Redox Exfoliation of Layered Transition Metal Dichalcogenides. *Chem. Mater.* **2020**, *32*, 6550–6565 with minor modifications as mentioned below:

[0732] Pretreatment of MoS₂

[0733] Pristine MoS₂ powder, purchased from Sigma, USA (< 2 μm), was washed prior to use for exfoliation by gently refluxing at 50°C in ethanol/acetone (1:1) solution for 24 h (100 mg/mL). After refluxing, the slurry underwent filtration, employing a filter membrane with pore size of 0.22 μm, purchased from TISCH Scientific. The caked MoS₂ was subjected to an additional washing step utilizing 50 mL of ethanol/acetone (1:1) solvent mixture. This sequence of steps constituted one washing cycle, which was repeated four additional times to ensure the complete elimination of oxidized species on the surface of MoS₂. The final powder underwent the vacuum-drying process and was stored in an environment enriched with CaSO₄ desiccant under vacuum.

[0734] MoS₂ oxidation

[0735] In a 100 mL bottle flask, 50 mL of a-CH₃CN was added, followed by the addition of 1500 mg washed MoS₂. The resultant mixture was briefly sonicated for 15 min, aiming at dispersing the aggregated MoS₂ particles. Subsequently, 150 μL of 80% CHP was added to the flask. The reaction system was heated up to 55°C and gently stirred for 24 h.

[0736] Mo⁶⁺ titration analysis

[0737] After the oxidation process, the bottle flask was let cool down to room temperature undisturbed for 2 h. Subsequently, 2 mL of the yellow supernatant was pipetted and subjected to centrifugation at 10000 rpm for 10 min. The centrifugation process would remove the remaining unreacted MoS_2 from the solution. A total volume of 500 μL of the supernatant was transferred to a 20-mL vial, followed by an addition of 500 μL of 6M HCl. The mixture was swirled to ensure thorough homogeneity. Following this step, 500 μL of 2M NaSCN and 500 μL of 0.01M NaBH_4 were added subsequently to the vial. The resultant solution was allowed to stand undisturbed for a period of 10 min. Subsequently, an additional volume of 4 mL of distilled acetone was added to the vial to dissolve insoluble organic species. The absorption spectra were collected by a Cary 60 UV-vis spectrophotometer. Absorption peak at 460 nm, resulting from the molybdenum thiocyanate complex, was recorded; the absorbance was extrapolated to Mo^{6+} concentration, based on the constructed Mo^{6+} calibration curve.

[0738] *Mo⁶⁺ titration calibration*

[0739] Na_2MoO_4 was dissolved in water to prepare a series of stock solutions with different concentrations (0, 0.01, 0.03, 0.05, 0.07, 0.1, 0.2, and 0.3 mM). 500 μL of 6M HCl was added to each 20-mL vial containing the respective stock solution (500 μL). The mixture was swirled to ensure thorough homogeneity. Following this step, 500 μL of 2M NaSCN and 500 μL of 0.01M NaBH_4 were added subsequently to each vial. The resultant solution was allowed to stand undisturbed for a period of 10 min. Subsequently, an additional volume of 1.5 mL of distilled water was added to each vial. The absorption spectrum of each solution was collected by a Cary 60 UV-vis spectrophotometer. Absorption peak at 460 nm, resulting from the molybdenum thiocyanate complex, was recorded, and employed to construct a calibration curve, enabling the quantification of Mo^{6+} concentrations across the various solutions under investigation ($\epsilon_{460} = 9.4 \text{ mL } \mu\text{mol}^{-1} \text{ cm}^{-1}$, $R^2 = 0.99986$) (FIG. 45A – FIG. 45D).

[0740] *MoS₂ exfoliation*

[0741] Following the analysis of Mo^{6+} concentration, HQ was dissolved in a- CH_3CN to produce a solution with a concentration of 0.1M. Next, the oxidized slurry was treated with a stoichiometric amount of HQ (HQ/ Mo^{6+} 40:1). Crucially, 0.1M HQ solution was added dropwise to ensure an efficient exfoliation process. The resultant reaction was stirred at room temperature for 48 h.

[0742] Upon achieving complete exfoliation, the slurry underwent centrifugation at 10000 rpm for 10 min to remove all traces of inorganic polyoxometalate macro-anions (POMs), characterized by their distinct blue color. In the next step, 10 mL of a-CH₃CN was added; the mixture was vortexed and sonicated for 30 min, followed by a subsequent centrifugation at 10000 rpm for 10 min. This process constituted one cycle. It is imperative to emphasize the crucial significance of this purification step to obtain exfoliated MoS₂ at high quality and good dispersion. This procedure was repeated 4–7 additional cycles for efficient removal of POMs. Ultimately, 30 mL of a-CH₃CN was added, and the mixture was vortexed and sonicated for 30 min. The temperature during sonication was controlled between 5°C–20°C. The resultant mixture was centrifuged at 2000 rpm for 30 min. Subsequently, 20 mL of the supernatant was pipetted out and subjected to subsequent centrifugation at 10000 rpm for 10 min to eliminate small exfoliated MoS₂ sheets. The precipitated MoS₂ was then redispersed by the addition of 30 mL of a-CH₃CN. This process was carried out several times to achieve any desired concentration of exfoliated MoS₂.

[0743] **Note:** Apart from employing HQ, NaBH₄ could serve as a reducing agent for the exfoliation process. NaBH₄ was dissolved in deionized water (DI H₂O). The oxidized slurry underwent treatment with a stoichiometric amount of NaBH₄ (NaBH₄/Mo⁶⁺ 12:1). Subsequently, 2 mL NaBH₄ solution was added dropwise to ensure an efficient exfoliation process. The resultant reaction was stirred at room temperature for 48 h. Next steps were carried out as previously described.

[0744] **Note:** The centrifuge rate in rpm (revolutions per minute) varies strongly depending on the rotor in use. Hence, for a comprehensive and consistent comparison, unit in rpm should be converted to G (relative centrifuge force) and reported accordingly. In our experimental setup, the following centrifuge rates were used with the corresponding number in G: 10000 rpm (11980 G), 2500 rpm (740 G), 2000 rpm (470 G), 1500 rpm (269 G), 1000 rpm (120 G), and 500 rpm (30 G).

[0745] *MoS₂ titration*

[0746] A concentrated exfoliated MoS₂ colloidal was diluted to make a series of stock solutions with the dilution of 6, 12, 18, 24, and 30 times. 300 µL from each stock solution was dropped carefully on a separate gold quartz crystal (QCM) plate (Novaetech S.r.l., resonance frequency 10 MHz) accordingly. The loaded QCM plates, then, were dried in 60°C oven overnight, ensuring complete solvent evaporation. Frequency analysis was carried out employing

an eQCM from Camry Instruments. The mass of MoS₂ within the dropped volume was deduced accordingly and fitted with the minima extinction at 345 nm from the UV-vis extinction spectrum of exfoliated MoS₂ ($\epsilon_{345} = 42 \text{ mL mg}^{-1} \text{ cm}^{-1}$, $R^2 = 0.93887$) (FIG. 45A – FIG. 45D).

[0747] **Example 13. Redox Exfoliation of WS₂**

[0748] In contrast to MoS₂, WS₂ exhibited sensitivity during the exfoliation process. We conducted W⁶⁺ calibration and W⁶⁺ titration analyses. However, the extracted absorbance attributable to W⁶⁺ complexes at 396 nm was relatively small compared to that of Mo⁶⁺. Additionally, based on the extracted absorbance, the subsequent exfoliation was inefficient, followed by the same calculated stoichiometric reductant quantity of both HQ and NaBH₄ for MoS₂ exfoliation (FIG. 46A – FIG. 46D). Hence, we modified the protocol as follows:

[0749] *Pretreatment of WS₂*

[0750] Pristine WS₂ powder, purchased from Sigma, USA (< 2 μm), was washed prior to use for exfoliation by gently refluxing at 70°C in ethanol/acetone (1:1) solution for 24 h (100 mg/mL). After refluxing, the slurry underwent filtration, employing a filter membrane with pore size of 0.22 μm , purchased from TISCH Scientific. The caked WS₂ was subjected to an additional washing step utilizing 50 mL of ethanol/acetone (1:1) solvent mixture. This sequence of steps constituted one washing cycle, which was repeated four additional times to ensure the complete elimination of oxidized species on the surface of WS₂. The final powder underwent the vacuum-drying process and was stored in an environment enriched with CaSO₄ desiccant under vacuum.

[0751] *WS₂ oxidation*

[0752] In a 100 mL bottle flask, 50 mL of a-CH₃CN was added, followed by the addition of 1500 mg washed WS₂. The resultant mixture was briefly sonicated for 15 min, aiming at dispersing the aggregated MoS₂ particles. Subsequently, 450 μL of 80% CHP was added to the flask. The reaction system was heated up to 70°C and gently stirred for 24 h.

[0753] *WS₂ exfoliation*

[0754] Following oxidation, NaBH₄ was dissolved in DI H₂O to make 0.1M NaBH₄ solution. Subsequently, 2 mL 0.1M NaBH₄ solution was added dropwise to ensure an efficient exfoliation process. The resultant reaction was stirred at room temperature for 4 days. Next steps were carried out similarly to that of WS₂.

[0755] *WS₂ titration*

[0756] A concentrated exfoliated WS₂ colloidal was diluted to make a series of stock solutions with the dilution of 6, 12, 18, 24, and 30 times. 300 μ L from each stock solution was dropped carefully on a separate gold quartz crystal (QCM) plate (Novaetech S.r.l., resonance frequency 10 MHz) accordingly. The loaded QCM plates, then, were dried in 60°C oven overnight, ensuring complete solvent evaporation. Frequency analysis was carried out employing an eQCM from Camry Instruments. The mass of WS₂ within the dropped volume was deduced accordingly and fitted with the extinction at 235 nm from the UV-vis extinction spectrum of exfoliated WS₂ ($\epsilon_{235} = 54 \text{ mL mg}^{-1} \text{ cm}^{-1}$, $R^2 = 0.99678$) (FIG. 46A – FIG. 46D).

[0757] **Example 14. Bath Sonication-induced Exfoliation**

[0758] In a 40 mL glass vial, 30 mL of a-CH₃CN was added, followed by the addition of 500 mg washed MoS₂ (or washed WS₂). The resultant mixture was briefly sonicated for 3 days, employing a Branson CPX1800H. The temperature during sonication was controlled between 5°C–20°C. The resultant mixture was centrifuged at 2000 rpm for 30 min. Subsequently, 20 mL of the supernatant was pipetted out and subjected to subsequent centrifugation at 10000 rpm for 10 min to eliminate small exfoliated MoS₂ sheets. The precipitated MoS₂ was then redispersed by the addition of 30 mL of a-CH₃CN.

[0759] **Example 15. Thin Film Fabrication**

[0760] Employing the high surface tension at the interface of two immiscible liquids (hexane-water), the exfoliated TMDs were injected near interface where TMD nanosheets tend to assemble and form a thin film. To reduce the high surface energy, TMD nanosheets, with their basal plane offering the largest surface area, lay flat at the interface. Typically, the deposited substrates were positioned at an angle of 45° to the vertical lifting pin of a custom-designed lifting tool. The entire system was then placed inside a 50 mL glass beaker, followed by the addition of 20 mL DI H₂O and subsequently 20 mL hexane. The exfoliated TMD suspension was initially diluted to a concentration of 0.0125 mM, resulting in an almost colorless solution. Next, 1 mL 0.0125 mM exfoliated TMDs was injected near the hexane-water interface. The system was left undisturbed for 30 min to allow the TMD nanosheets to spread out and stabilize the surface energy system. Finally, the assembled thin film was scooped onto the substrates by gently lifting the vertical pin (FIG. 28A – FIG. 28D). The deposited substrates were dried in an 80°C oven before any characterizations.

[0761] **Note:** Low concentration of 0.0125 mM is crucially important to prevent nanosheets from lying on top of others. The lifting process should be executed gently and slowly while the hexane layer has not been completely evaporated. If significant evaporation occurs, refilling is necessary. The high surface tension at the hexane-water interface will generate a force to pull TMD nanosheets in the opposite direction to the lifting vector, thereby maximizing flat lying orientation and minimizing the risk of the nanosheets sliding over each other.

[0762] **Example 16. Size Selection by Centrifuge Cascade**

[0763] Following centrifuge screening after exfoliation, TMD nanosheets underwent a post-centrifuge cascade for size selection. Briefly, the 2000 rpm-redispersed suspension underwent another centrifuge cycle at 2500 rpm. The supernatant was collected and subjected to the next centrifuge cycle at 3000 rpm, while the precipitant was redispersed in fresh a-ACN, labeled as the 2000-2500 rpm fraction. Subsequent steps followed as illustrated in FIG. 29. The last fraction (>4000 rpm) underwent an additional screening at 9000 rpm. The supernatant after 9000 rpm was discarded.

[0764] **Example 17. Functionalization of Exfoliated TMDs by NHC Adsorbates**

[0765] A 5 mL portion of exfoliated TMDs (1 mM) was introduced to a 40-mL glass vial. Subsequently, 5 mL of NHC15OH[OMs] (1, 5, 10, and 15 mM in DCM) was quickly injected into the solution. The reaction was left undisturbed at room temperature for 24 h. Then, the slurry was transferred to a centrifuge tube and subjected to centrifugation at 2000 rpm for 10 min to precipitate all functionalized and unfunctionalized TMDs. The resultant material was additionally washed with 10 mL of DCM, and subjected to centrifugation at 2000 rpm for 10 min. This process constituted one washing cycle and was repeated one more time to eliminate all unreacted NHCs. The final product was redispersed in DCM as an ink type for later characterization. **Note:** The redispersing step was carried out by physical shaking exclusively; no sonication was performed.

[0766] **Example 18. NHC Functionalization of Exfoliated TMDs under Sonication Impact**

[0767] A 5 mL portion of exfoliated TMDs (1 mM) was introduced to a 40-mL glass vial. Subsequently, 5 mL of NHC15OH[OMs] (15mM in DCM) was quickly injected into the solution. The reaction was left undisturbed at room temperature for 24 h. Then, the slurry was briefly sonicated in 1 min and left undisturbed until the complete restacking process occurred. This sonicating-restacking process constituted one cycle and was optionally repeated 2, 3, and 5 more

times to achieve a set of 5 samples. Subsequently, each resultant material was transferred to a centrifuge tube and subjected to centrifugation at 2000 rpm for 10 min to precipitate all functionalized and unfunctionalized TMDs. The resultant material was additionally washed with 10 mL of DCM, and subjected to centrifugation at 2000 rpm for 10 min. This process constituted one washing cycle and was repeated one more time to eliminate all unreacted NHCs. The final product was redispersed in DCM as an ink type for later characterization. **Note:** The sonicating and subsequent agglomerating steps were carried out when NHCs and redox-exfoliated TMDs coexisted within the solvent mixture.

[0768] **Example 19. Characterization**

[0769] *Ultraviolet-visible spectroscopy (UV-vis)*

[0770] UV-vis data was collected by a Cary 60 UV-vis spectrophotometer. UV-vis technical parameters, data analysis, and mathematical transformation (second derivative of extinction spectrum and corresponding smoothing steps) were followed as the protocol in previously reported (Backes, C.; Hanlon, D.; Szydlowska, B. M.; Harvey, A.; Smith, R. J.; Higgins, T. M.; Coleman, J. N. Preparation of Liquid-Exfoliated Transition Metal Dichalcogenide Nanosheets with Controlled Size and Thickness: A State of the Art Protocol. *J. Vis. Exp.* **2016**, 118, e54806).

[0771] *Atomic force microscopy (AFM)*

[0772] A 1 x 1 cm² 300 nm thick SiO₂ layer-covered Si substrate, sourced from MSE Supplies, was obtained and pre-dipped into piranha solution in 5 min to wash away inorganic and organic residues contaminants. Subsequently, the substrate was washed thoroughly with DI water and dried with N₂ gas. Consequently, 20 µL dilute exfoliated TMDs colloidal (almost colorless) was dropped onto the polished side of the substrate. The dropped sample was dried naturally overnight prior to AFM measurement. Surface images were collected employing an AFM, MFP-3D Origin+, Oxford Instruments in a non-contact soft tapping mode. The AFM tips utilized were Bruker TESPA-V2 model. Certain numbers of images were collected and subsequently underwent a statistical analysis to generate a height retrace histogram.

[0773] **Note:** Owing to the inherent self-dried aggregation tendency of exfoliated nanosheets, care must be taken to select analysis locations. Guidelines for differentiating between promising, non-aggregated regions have been demonstrated in the prior publication (Backes, C.;

Higgins, T. M.; Kelly, A.; Boland, C.; Harvey, A.; Hanlon, D.; Coleman, J. N. Guidelines for Exfoliation, Characterization and Processing of Layered Materials Produced by Liquid Exfoliation. *Chem. Mater.* **2017**, *29*, 243–255). Typically, when situated on 300 nm thick SiO₂ layer, the nanoscale nanosheets still manifest as distinctive blue dots, even under a standard optical microscope equipped within AFM instruments. In contrast, aggregated materials results in prominent blue clusters as illustrated in FIG. 47. Hence, during the scanning analysis, it is imperative to probe close, but not within the blue regions to avoid thick, aggregation effects. The aggregation effects could be overcome by TMDs thin film fabrication technique, which rendered the exfoliated nanosheets lying flat on the substrate.

[0774] *X-ray powder diffraction (XRD)*

[0775] Exfoliated TMDs were prepared by drop-casting on a glass slide and drying in an oven at 80°C for 2 h. For NHC-functionalized samples, a controlled circular area, with a radius of 0.35 cm, was fashioned on a glass slide by the application of a double-layer heat-resistant tape (2 mm thick). Subsequently, functionalized TMDs ink was dropped into the aperture, followed by natural evaporation of solvent at room temperature. Then, the covered tape was removed, and the sample was further dried at 100°C overnight. The XRD patterns were collected employing an X-ray diffractometer (XRD, Smart Lab, Rigaku, Cu-K α radiation ($\lambda = 0.15406$ nm) operated at 40 kV and 44 mA, 5 mm beam mask, 1/8° divergence slit, step size 0.02° (2 θ), scanning rate 1.5° min⁻¹).

[0776] *Attenuated total reflectance infrared spectroscopy (ATR)*

[0777] The samples were prepared similarly as mentioned in the protocol for XRD analysis. The IR data was collected, employing an ATR-IR, Nicolet iS10, Thermo Scientific in the range of 500–4000 cm⁻¹ with 2 cm⁻¹ resolution.

[0778] *Zeta potential*

[0779] Zeta potential measurements were conducted on a Malvern Zetasizer model ZEN3600. Exfoliated TMDs colloidal or NHC-functionalized TMDs was briefly sonicated and diluted to achieve a concentration of 0.01 mM, prior to subsequent Zeta potential measurements.

[0780] *Scanning electron microscopy (SEM)*

[0781] Exfoliated TMDs nanosheets were deposited onto Si substrates, employing thin film fabrication as mentioned above. All samples were characterized by a scanning electron microscope (SEM, LEO-1525) with an accelerating voltage of 15 kV.

[0782] *Transmission electron microscopy (TEM)*

[0783] Images were taken by JEOL JEM-2010 TEM operating at an accelerating voltage of 200 kV. Dilute exfoliated TMDs suspension was dropped onto 200 mesh holey carbon-coated copper grid, sourced from TED PELLA, INC (200 mesh Cu). Deposited samples were let dried overnight before analysis.

[0784] *Raman spectroscopy*

[0785] The Raman scattering spectra were measured using a Horiba JY T64000 triple spectrometer. The spectrometer was coupled with an Olympus optical microscope, which focused the 488 nm laser beam on the samples using 50x or 100x objectives, collected the scattered light, and directed it to the spectrometer. The laser power was maintained at minimum, typically below 10^3 W/cm², to prevent overheating or phase transformation of the samples. All spectra were recorded in the backscattering configuration, with incident and scattered light propagating perpendicular to the sample surfaces. All samples were dropped onto 300 nm SiO₂/Si substrates and let dried in 100°C oven overnight. Subsequently, samples were vacuumed and stored in an environment enriched with CaSO₄ desiccant under vacuum prior to any measurements.

[0786] *X-ray photoelectron spectroscopy (XPS)*

[0787] Materials were deposited by drop-casting onto Si substrates. Data was collected using a PHI 5700 X-ray photoelectron spectrometer equipped with a monochromatic Al K α source with 10 mA emission current and 15 kV emission bias. Prior to deposition, Si substrates were washed carefully with DI H₂O, ethanol, and acetone. The deposited samples were dried under vacuum overnight before analysis.

[0788] *Raman spectroscopy and photoluminescence*

[0789] The photoluminescence and Raman scattering spectra of centrifuge cascade fractions and their corresponding functionalized fractions were measured using a Renishaw inVia using a 532 nm laser with a 50x LWD objective with a numerical aperture of 0.75 and an 1800 lines/mm grating. All spectra were collected with a 60 second acquisition time at 10% laser power (606 μ W). Baselines from the spectra were corrected using asymmetrically reweighted penalized least squares smoothing before fitting with pseudo-Voigt line shapes. Redox-exfoliated MoS₂ fractional thin films were made employing the thin film fabrication technique mentioned above (2 mL 0.1 mM redox-exfoliated MoS₂). All NHC-functionalized MoS₂ fractional samples were dropped directly onto VWR microscope slides and dried in 100°C oven overnight. Subsequently,

samples were vacuumed and stored in an environment enriched with CaSO_4 desiccant under vacuum prior to any measurements.

[0790] Example 20. Additional Raman Analysis

[0791] Additional insights from the Raman dataset can be used to quantify the differences in between redox-exfoliated MoS_2 and NHC-functionalized MoS_2 . According to Peter R. Stevenson and colleagues, the intensity ratio of the LA mode corresponding to the scattering of longitudinal acoustic (LA) phonons at the M point in the Brillouin zone, with respect to either the E_{12g}^1 or A_{1g} can be related to the lattice disorder (Busch, R. T.; Sun, L.; Austin, D.; Jiang, J.; Miesle, P.; Susner, M. A.; Conner, B. S.; Jawaid, A.; Becks, S. T.; Mahalingam, K.; Velez, M. A.; Torsi, R.; Robinson, J. A.; Rao, R.; Glavin, N. R.; Vaia, R. A.; Pachter, R.; Joshua Kennedy, W.; Vernon, J. P.; Stevenson, P. R. Exfoliation Procedure-Dependent Optical Properties of Solution Deposited MoS_2 Films. *Npj 2D Mater. Appl.* **2023**, 7, 1–13). A lower ratio indicates reduced lattice disorder within the 2D crystal structure. To conduct the analysis, Raman spectra of the same sample set are collected employing two different excitation wavelengths: 633 nm (resonant) and 514.5 nm (non-resonant). The resonant 633 nm excitation wavelength, due to vibrational resonance, allows for the observable intensity of the LA mode, which will be used in subsequent calculation. On the other hand, the non-resonant 514.5 nm, free from the complexity of overlapping resonant vibration modes, simplifies the data extraction for the two signature in-plane E_{12g}^1 and out-of-plane A_{1g} . This simplification enables deduction of strain and carrier doping levels within the MoS_2 flakes.

[0792] Lattice disorder quantification

[0793] Both LA/E_{12g}^1 and LA/A_{1g} ratios are proportionally related, with reported data indicating that both exhibit comparable rates of change (Mignuzzi, S.; Pollard, A. J.; Bonini, N.; Brennan, B.; Gilmore, I. S.; Pimenta, M. A.; Richards, D.; Roy, D. Effect of Disorder on Raman Scattering of Single-Layer MoS_2 . *Phys. Rev. B* **2015**, 91, 195411). In other words, if the lattice disorder arises from the same underlying mechanism, the A_{1g}/E_{12g}^1 ratios will remain the same for both unfunctionalized and functionalized samples. FIG. 51i presents the calculated A_{1g}/E_{12g}^1 ratios for both fractionally unfunctionalized and functionalized datasets, revealing a significant increase in the ratios for NHC-functionalized samples compared to those of the corresponding redox-exfoliated MoS_2 fractions. This newly determined ratios suggest that the influence of NHCs on the 2D plane of the MoS_2 monolayer is directional, with a more pronounced effect on the out-of-plane A_{1g} modes. This enhanced impact might be attributed to the direct interaction between NHC

molecules and the basal plane of the monolayer. On the other hand, the variation in the A_{1g}/E_{12g} ratios across fractional samples might result from the combined influence of multiple complex species, including the inherent concentration of defects, the presence of absorbed POMs, and the degree of NHC functionalization.

[0794] *Strain and carrier doping levels quantification*

[0795] The strain and carrier doping levels were calculated following the methodology outlined in the referenced work (Busch, R. T.; Sun, L.; Austin, D.; Jiang, J.; Miesle, P.; Susner, M. A.; Conner, B. S.; Jawaid, A.; Becks, S. T.; Mahalingam, K.; Velez, M. A.; Torsi, R.; Robinson, J. A.; Rao, R.; Glavin, N. R.; Vaia, R. A.; Pachter, R.; Joshua Kennedy, W.; Vernon, J. P.; Stevenson, P. R. Exfoliation Procedure-Dependent Optical Properties of Solution Deposited MoS₂ Films. *Npj 2D Mater. Appl.* **2023**, 7, 1–13). As the NHC molecules introduce a certain level of strain (ϵ_s) and a doping carrier concentration (n_D , which is negative here due to electron injection from NHCs), the vibrational frequencies ω_E and ω_A of the E_{12g} and A_{1g} modes, respectively, will shift accordingly. These frequency shifts are expressed by equations (1) and (2) below:

$$\Delta\omega_E = -2\gamma_E\omega_E^0\epsilon_s + k_{n,E}n_D \quad (\text{Equation 1})$$

$$\Delta\omega_A = -2\gamma_A\omega_A^0\epsilon_s + k_{n,A}n_D \quad (\text{Equation 2})$$

[0796] The Grüneisen parameter (γ) and k_n are constants that relate to changes in the lattice volume and dopant concentration to vibrational frequencies, respectively. ω^0 is the frequency corresponding to undoped and unstrained MoS₂. For each unfunctionalized and functionalized fractional film, the ω_E^0 ($E = E_{12g}$) and ω_A^0 ($A = A_{1g}$) values were obtained from previously reported work (Lee, C.; Yan, H.; Brus, L. E.; Heinz, T. F.; Hone, J.; Ryu, S. Anomalous Lattice Vibrations of Single- and Few-Layer MoS₂. *ACS Nano* **2010**, 4, 2695–2700). The γ_E and γ_A values were set to 0.45 and 0.21, respectively, corresponding to few-layered MoS₂ (Guo, Y.; Li, B.; Huang, Y.; Du, S.; Sun, C.; Luo, H.; Liu, B.; Zhou, X.; Yang, J.; Li, J.; Gu, C. Direct Bandgap Engineering with Local Biaxial Strain in Few-Layer MoS₂ Bubbles. *Nano Res.* **2020**, 13, 2072–2078). The respective $k_{n,E}$ and $k_{n,A}$ values were set to the monolayer values of -0.33×10^{-13} and -2.22×10^{-13} . The extracted strain and carrier doping levels are shown in Table 1 and Table 2. It is important to emphasize that meticulous attention is required to determine the ω_E^0 and ω_A^0 values of these calculations. Our analysis reveals that the MoS₂ dataset calculated using reference values form

multilayered MoS₂ (Table 1) differs significantly from the dataset calculated using reference values from monolayered MoS₂ (Table 2). Given that the FMHWs for all four fractional MoS₂ films are consistent with the reported value for multilayered MoS₂ and considering the absence of a detectable PL signal (FIG. 52A – FIG. 52D), we conclude that the ω_E^o and ω_A^o values for multilayered MoS₂ are more reliable for use in calculations and comparisons. In the case of NHC-functionalized MoS₂ samples, several assumptions are made to establish the reference values. First, the doping effects of NHCs doping are assumed to have a more pronounced impact on the out-of-plane A_{1g} vibration mode compared to the in-plane E_{2g} vibration mode, as indicated by the change in A_{1g}/E_{2g} intensity ratio. Second, since MoS₂ monolayers are separated by NHCs and exhibit monolayer characteristics, evidenced by a detectable PL signal, ω_A^o value from monolayered MoS₂ is adopted. Third, considering that the adsorbed POMs species function as p-type dopants (Busch, R. T.; Sun, L.; Austin, D.; Jiang, J.; Miesle, P.; Susner, M. A.; Conner, B. S.; Jawaid, A.; Becks, S. T.; Mahalingam, K.; Velez, M. A.; Torsi, R.; Robinson, J. A.; Rao, R.; Glavin, N. R.; Vaia, R. A.; Pachter, R.; Joshua Kennedy, W.; Vernon, J. P.; Stevenson, P. R. Exfoliation Procedure-Dependent Optical Properties of Solution Deposited MoS₂ Films. *Npj 2D Mater. Appl.* **2023**, 7, 1–13) while NHCs are expected to act as n-type dopants, and acknowledging the uncertainty regarding whether the resultant superlattice structure material will exhibit properties entirely analogous to monolayered MoS₂, the ω_E^o values from both monolayered and multilayered are used for comparison of the results. Lastly, the correlation between the PL peak position shift and the associated strain will be employed to reassess the validity of the calculations (the PL peak position should shift -0.2 eV per strain percent) (Michail, A.; Delikoukos, N.; Parthenios, J.; Galiotis, C.; Papagelis, K. Optical Detection of Strain and Doping Inhomogeneities in Single Layer MoS₂. *Appl. Phys. Lett.* **2016**, 108, 173102).

[0797] Table 1 and Table 2 both illustrate a slight variation in strain across four fractional MoS₂ samples. However, in the calculations presented in Table 1, the doping carrier concentration represents a significant variation, indicating a trend towards increased p-doping. This observation can be attributed by the extent of the p-doping effect, signified by the effective charge of adsorbed POMs per unit volume of the fractional MoS₂ nanosheets. Calculations in Table 1 also indicate that the NHC-functionalized samples are highly n-doped following functionalization. In contrast, the calculations in Table 2 show a slight trend toward p-doping. Both calculations demonstrate that an increase in strain applied to the MoS₂ monolayers following functionalization; however, a

huger gap is detected in the case, where the ω_E^o value from multilayered MoS₂ is employed. As a final step to assess the validity of these two calculations, we obtain the correlation between the PL peak position shift and the associated strain. The PL peak position shift of the NHC-functionalized MoS₂ compared to monolayered MoS₂ is 1.1 eV corresponding to 0.55% increase in strain. This aligns closely with the obtained value for unfunctionalized and functionalized MoS₂ F4, which displays a 0.58% increase in strain. Herein, fraction 4 is used for comparison because it contains the richest population of monolayers, giving to a well-ordered superlattice structure, where monolayers are periodically separated by NHC molecules. This aligns with the second assumption made in the analysis. Consequently, we propose that the use of ω_A^o value from monolayered MoS₂ and ω_E^o value from multilayered MoS₂ as reference points provides a more reliable model for interpreting and comparing the changes between the initial and final functionalized samples.

[0798] **Table 1.** The amount of strain and carrier doping concentration of unfunctionalized and NHC-functionalized MoS₂ fractions; the calculations were conducted, using the vibration mode value E_{12g} and A_{1g} specific to multilayer and a monolayer of MoS₂ respectively.

	E _{12g} (cm ⁻¹)	A _{1g} (cm ⁻¹)	ε (%)	nd (10 ¹³ cm ⁻²)
MoS ₂ F1	383.5	408.7	-0.39	-0.45
MoS ₂ F2	383.5	408.6	-0.40	-0.40
MoS ₂ F3	383.4	408.4	-0.38	-0.33
MoS ₂ F4	383.5	407.9	-0.42	-0.07
15-NHC/MoS ₂ F1	382.9 ± 0.3	408.2 ± 0.2	-0.04 ± 0.10	-198.17 ± 0.02
15-NHC/MoS ₂ F2	383.1 ± 0.2	408.2 ± 0.3	-0.11 ± 0.05	-198.14 ± 0.09

15-NHC/MoS₂ F3	382.8 ± 0.2	407.8 ± 0.3	-0.01 ± 0.06	-198.03 ± 0.11
15-NHC/MoS₂ F4	382.0 ± 1.0	406.5 ± 0.8	0.16 ± 0.29	-197.58 ± 0.19

[0799] **Table 2.** The amount of strain and carrier doping concentration of unfunctionalized and NHC-functionalized MoS₂ fractions; the calculations were conducted, using the vibration mode value E_{12g} and A_{1g} specific to a monolayer of MoS₂.

	$E_{12g} (cm^{-1})$	$A_{1g} (cm^{-1})$	$\varepsilon (\%)$	$n_D (10^{13} cm^{-2})$
MoS₂ F1	383.5	408.7	0.42	-2.87
MoS₂ F2	383.5	408.6	0.41	-2.82
MoS₂ F3	383.4	408.4	0.43	-2.76
MoS₂ F4	383.5	407.9	0.39	-2.50
15-NHC/MoS₂ F1	382.9 ± 0.3	408.2 ± 0.2	0.59 ± 0.1	-2.74 ± 0.14
15-NHC/MoS₂ F2	383.1 ± 0.2	408.2 ± 0.3	0.52 ± 0.05	-2.48 ± 0.38
15-NHC/MoS₂ F3	382.8 ± 0.2	407.8 ± 0.3	0.61 ± 0.06	-2.64 ± 0.11
15-NHC/MoS₂ F4	382.0 ± 1.0	406.5 ± 0.8	0.78 ± 0.29	-2.18 ± 0.19

[0800] **Example 21 – Example 62**

[0801] **Materials**

[0802] Molybdenum disulfide (MoS_2 , $< 2 \mu\text{m}$), tungsten disulfide (WS_2 , $< 2 \mu\text{m}$), hydroquinone (HQ), cumene hydroperoxide (CHP), anhydrous acetonitrile ($\text{a-CH}_3\text{CN}$), sodium borohydride (NaBH_4), sodium thiocyanate (NaSCN), sodium molybdate (Na_2MoO_4), sodium tungstate dihydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$), pentadecalactone, hydrobromic acid (48 wt%), dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridine (DMAP), 4-amino-3-nitrophenol, potassium carbonate (K_2CO_3), lithium aluminum hydride (LiAlH_4), iron powder 325 mesh (Fe), ammonium chloride (NH_4Cl), isopropyl methanesulfonate, cesium carbonate (Cs_2CO_3), acetic acid (AcOH), methanol (MeOH), dichloromethane (DCM), chloroform (TCM), acetonitrile (CH_3CN), formic acid (HCOOH), isopropyl alcohol (iPrOH), tetrahydrofuran (THF), ethyl acetate (EtOAc), benzimidazole, iodoethane ($\text{C}_2\text{H}_5\text{I}$), 1-iodopropane ($\text{C}_3\text{H}_7\text{I}$), 2-iodopropane ($(\text{CH}_3)_2\text{CHI}$), 1-iodobutane ($\text{C}_4\text{H}_9\text{I}$), 1-iodopentane ($\text{C}_5\text{H}_{11}\text{I}$), 1-iododecane ($\text{C}_{10}\text{H}_{21}\text{I}$), bromoethane ($\text{C}_2\text{H}_5\text{Br}$), 1-bromopropane ($\text{C}_3\text{H}_7\text{Br}$), 2-bromopropane ($(\text{CH}_3)_2\text{CHBr}$), 1-bromobutane ($\text{C}_4\text{H}_9\text{Br}$), 1-bromopentane ($\text{C}_5\text{H}_{11}\text{Br}$), 1-bromodecane ($\text{C}_{10}\text{H}_{21}\text{Br}$), barium chloride dihydrate ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$), silver sulfate (Ag_2SO_4), silver tetrafluoroborate (AgBF_4), silver methanesulfonate (AgOMs), silver trifluoromethanesulfonate (AgOTf), potassium hexafluorophosphate (KPF_6) were purchased from Sigma-Aldrich, USA. Hydrochloric acid was purchased from Oakwood Chemical, USA. Water was purified to a resistance of 18 M Ω , employing an Academic Milli-Q Water System (Millipore Corporation) and filtered through a 0.22 μm membrane before usage. Silica gel for column chromatography was obtained from Sorbent Technologies.

[0803] **Synthesis of the Adsorbates**

[0804] **Example 21**

[0805] *1,3-Diethylbenzimidazolium iodide (Et-NHC[II])*. To the suspension of benzimidazole (2.36 g, 20 mmol) and K_2CO_3 (3.04 g, 22 mmol) in acetonitrile (20 mL) in a pressure vessel, to which iodoethane (4.8 mL, 60 mmol) was added. The reaction mixture was refluxed at 80°C for 2 days. After cooling to room temperature, the solvent was removed under reduced pressure, followed by addition of DCM. The resultant suspension was filtered through celite, and the filtrate was concentrated under reduced pressure to yield a solid powder. The solid residue was subsequently washed with ethyl acetate to afford product as a white powder (5.25 g,

87%). ¹H NMR (400 MHz, CDCl₃): δ 11.13 (s, 1H), 7.76 (dd, *J* = 6.3, 3.1 Hz, 2H), 7.67 (dd, *J* = 6.3, 3.1 Hz, 2H), 4.68 (q, *J* = 7.4 Hz, 4H), 1.76 (t, *J* = 7.4 Hz, 6H).

[0806] **Example 22**

[0807] *1,3-Dipropylbenzimidazolium iodide (Pr-NHC[II])*. To the suspension of benzimidazole (2.36 g, 20 mmol) and K₂CO₃ (3.04 g, 22 mmol) in acetonitrile (20 mL) in a pressure vessel, to which 1-iodopropane (5.9 mL, 60 mmol) was added. The reaction mixture was refluxed at 80°C for 2 days. After cooling to room temperature, the solvent was removed under reduced pressure, followed by addition of DCM. The resultant suspension was filtered through celite, and the filtrate was concentrated under reduced pressure to yield a solid powder. The solid residue was subsequently washed with ethyl acetate to afford product as a white powder (6.27 g, 95%). ¹H NMR (400 MHz, CDCl₃): δ 11.09 (s, 1H), 7.76 (dd, *J* = 6.3, 3.2 Hz, 2H), 7.66 (dd, *J* = 6.3, 3.2 Hz, 2H), 4.6 (t, *J* = 7.6 Hz, 4H), 2.12 (m, *J* = 7.5 Hz, 4H), 1.05 (t, *J* = 7.4 Hz, 6H).

[0808] **Example 23**

[0809] *1,3-Diisopropylbenzimidazolium iodide (iPr-NHC[II])*. To the suspension of benzimidazole (2.36 g, 20 mmol) and K₂CO₃ (3.04 g, 22 mmol) in acetonitrile (20 mL) in a pressure vessel, to which 2-iodopropane (6.0 mL, 60 mmol) was added. The reaction mixture was refluxed at 80°C for 2 days. After cooling to room temperature, the solvent was removed under reduced pressure, followed by addition of DCM. The resultant suspension was filtered through celite, and the filtrate was concentrated under reduced pressure to yield a solid powder. The solid residue was subsequently washed with ethyl acetate to afford product as a white powder (5.68 g, 86%). ¹H NMR (400 MHz, CDCl₃): δ 10.85 (s, 1H), 7.82 (dd, *J* = 6.3, 3.2 Hz, 2H), 7.65 (dd, *J* = 6.3, 3.2 Hz, 2H), 5.21 (m, *J* = 6.7 Hz, 2H), 1.85 (d, *J* = 6.8 Hz, 12H).

[0810] **Example 24**

[0811] *1,3-Dibutylbenzimidazolium iodide (But-NHC[II])*. To the suspension of benzimidazole (2.36 g, 20 mmol) and K₂CO₃ (3.04 g, 22 mmol) in acetonitrile (20 mL) in a pressure vessel, to which 1-iodobutane (6.8 mL, 60 mmol) was added. The reaction mixture was refluxed at 80°C for 2 days. After cooling to room temperature, the solvent was removed under reduced pressure, followed by addition of DCM. The resultant suspension was filtered through celite, and the filtrate was concentrated under reduced pressure to yield a solid powder. The solid residue was subsequently washed with ethyl acetate to afford product as a white powder (6.59 g, 92%). ¹H NMR (400 MHz, CDCl₃): δ 11.12 (s, 1H), 7.76 (dd, *J* = 6.3, 3.2 Hz, 2H), 7.65 (dd, *J* =

6.3, 3.2 Hz, 2H), 4.64 (t, $J = 7.4$ Hz, 4H), 2.05 (m, $J = 6.8$ Hz, 4H), 1.46 (m, $J = 7.2$ Hz, 4H), 0.99 (t, $J = 7.4$ Hz, 6H).

[0812] **Example 25**

[0813] *1,3-Dipentylbenzimidazolium iodide (Pen-NHC[II])*. To the suspension of benzimidazole (2.36 g, 20 mmol) and K_2CO_3 (3.04 g, 22 mmol) in acetonitrile (20 mL) in a pressure vessel, to which 1-iodopentane (7.8 mL, 60 mmol) was added. The reaction mixture was refluxed at 80°C for 2 days. After cooling to room temperature, the solvent was removed under reduced pressure, followed by addition of DCM. The resultant suspension was filtered through celite, and the filtrate was concentrated under reduced pressure to yield a solid powder. The solid residue was subsequently washed with ethyl acetate to afford product as a white powder (6.56 g, 85%). 1H NMR (400 MHz, $CDCl_3$): δ 11.26 (s, 1H), 7.69 (m, 4H), 4.62 (t, $J = 7.6$ Hz, 4H), 2.08 (m, $J = 7.2$ Hz, 4H), 1.46 (m, $J = 7.2$ Hz, 4H), 0.91 (t, $J = 7.2$ Hz, 6H).

[0814] **Example 26**

[0815] *1,3-Didecylbenzimidazolium iodide (Dec-NHC[II])*. To the suspension of benzimidazole (2.36 g, 20 mmol) and K_2CO_3 (3.04 g, 22 mmol) in acetonitrile (20 mL) in a pressure vessel, to which 1-iododecane (12.3 mL, 60 mmol) was added. The reaction mixture was refluxed at 80°C for 2 days. After cooling to room temperature, the solvent was removed under reduced pressure, followed by addition of DCM. The resultant suspension was filtered through celite, and the filtrate was concentrated under reduced pressure to yield a solid powder. The solid residue was subsequently washed with ethyl acetate to afford product as a white powder (8.52 g, 81%). 1H NMR (400 MHz, $CDCl_3$): δ 11.2 (s, 1H), 7.69 (m, 4H), 4.61 (t, $J = 7.6$ Hz, 4H), 2.05 (m, $J = 7.2$ Hz, 4H), 1.46-1.16 (m, 32H), 0.86 (t, $J = 7.1$ Hz, 6H).

[0816] **Example 27**

[0817] *1,3-Diethylbenzimidazolium bromide (Et-NHC[Br])*. To the suspension of benzimidazole (2.36 g, 20 mmol) and K_2CO_3 (3.04 g, 22 mmol) in acetonitrile (20 mL) in a pressure vessel, to which bromoethane (4.5 mL, 60 mmol) was added. The reaction mixture was refluxed at 80°C for 2 days. After cooling to room temperature, the solvent was removed under reduced pressure, followed by addition of DCM. The resultant suspension was filtered through celite, and the filtrate was concentrated under reduced pressure to yield a solid powder. The solid residue was subsequently washed with ethyl acetate to afford product as a white powder (4.79 g,

94%). ¹H NMR (400 MHz, CDCl₃): δ 11.36 (s, 1H), 7.74 (dd, *J* = 6.3, 3.2 Hz, 2H), 7.65 (dd, *J* = 6.3, 3.1 Hz, 2H), 4.69 (q, *J* = 7.4 Hz, 4H), 1.72 (t, *J* = 7.3 Hz, 6H).

[0818] Example 28

[0819] *1,3-Dipropylbenzimidazolium bromide (Pr-NHC[Br])*. To the suspension of benzimidazole (2.36 g, 20 mmol) and K₂CO₃ (3.04 g, 22 mmol) in acetonitrile (20 mL) in a pressure vessel, to which 1-bromopropane (5.9 mL, 60 mmol) was added. The reaction mixture was refluxed at 80°C for 2 days. After cooling to room temperature, the solvent was removed under reduced pressure, followed by addition of DCM. The resultant suspension was filtered through celite, and the filtrate was concentrated under reduced pressure to yield a solid powder. The solid residue was subsequently washed with ethyl acetate to afford product as a white powder (4.7 g, 83%). ¹H NMR (400 MHz, CDCl₃): δ 11.5 (s, 1H), 7.72 (dd, *J* = 6.3, 3.2 Hz, 2H), 7.66 (dd, *J* = 6.3, 3.2 Hz, 2H), 4.61 (t, *J* = 7.5 Hz, 4H), 2.11 (m, *J* = 7.5 Hz, 4H), 1.05 (t, *J* = 7.4 Hz, 6H).

[0820] Example 29

[0821] *1,3-Diisopropylbenzimidazolium bromide (iPr-NHC[Br])*. To the suspension of benzimidazole (2.36 g, 20 mmol) and K₂CO₃ (3.04 g, 22 mmol) in acetonitrile (20 mL) in a pressure vessel, to which 2-bromopropane (5.6 mL, 60 mmol) was added. The reaction mixture was refluxed at 80°C for 2 days. After cooling to room temperature, the solvent was removed under reduced pressure, followed by addition of DCM. The resultant suspension was filtered through celite, and the filtrate was concentrated under reduced pressure to yield a solid powder. The solid residue was subsequently washed with ethyl acetate to afford product as a white powder (4.53 g, 80%). ¹H NMR (400 MHz, CDCl₃): δ 11.44 (s, 1H), 7.78 (dd, *J* = 6.3, 3.2 Hz, 2H), 7.64 (dd, *J* = 6.3, 3.2 Hz, 2H), 5.2 (m, *J* = 6.8 Hz, 2H), 1.86 (d, *J* = 6.8 Hz, 12H).

[0822] Example 30

[0823] *1,3-Dibutylbenzimidazolium bromide (But-NHC[Br])*. To the suspension of benzimidazole (2.36 g, 20 mmol) and K₂CO₃ (3.04 g, 22 mmol) in acetonitrile (20 mL) in a pressure vessel, to which 1-bromobutane (6.5 mL, 60 mmol) was added. The reaction mixture was refluxed at 80°C for 2 days. After cooling to room temperature, the solvent was removed under reduced pressure, followed by addition of DCM. The resultant suspension was filtered through celite, and the filtrate was concentrated under reduced pressure to yield a solid powder. The solid residue was subsequently washed with ethyl acetate to afford product as a white powder

(6.03 g, 97%). ^1H NMR (400 MHz, CDCl_3): δ 11.43 (s, 1H), 7.72 (dd, $J = 6.3, 3.2$ Hz, 2H), 7.65 (dd, $J = 6.3, 3.2$ Hz, 2H), 4.63 (t, $J = 7.4$ Hz, 4H), 2.02 (m, $J = 6.8$ Hz, 4H), 1.44 (m, $J = 7.2$ Hz, 4H), 0.97 (t, $J = 7.4$ Hz, 6H).

[0824] **Example 31**

[0825] *1,3-Dipentylbenzimidazolium bromide (Pen-NHC[Br])*. To the suspension of benzimidazole (2.36 g, 20 mmol) and K_2CO_3 (3.04 g, 22 mmol) in acetonitrile (20 mL) in a pressure vessel, to which 1-bromopentane (7.4 mL, 60 mmol) was added. The reaction mixture was refluxed at 80°C for 2 days. After cooling to room temperature, the solvent was removed under reduced pressure, followed by addition of DCM. The resultant suspension was filtered through celite, and the filtrate was concentrated under reduced pressure to yield a solid powder. The solid residue was subsequently washed with ethyl acetate to afford product as a white powder (6.17 g, 91%). ^1H NMR (400 MHz, CDCl_3): δ 11.45 (s, 1H), 7.68 (m, 4H), 4.62 (t, $J = 7.6$ Hz, 4H), 2.05 (m, $J = 7.2$ Hz, 4H), 1.39 (m, $J = 7.2$ Hz, 4H), 0.88 (t, $J = 7.2$ Hz, 6H).

[0826] **Example 32**

[0827] *1,3-Didecylbenzimidazolium bromide (Dec-NHC[Br])*. To the suspension of benzimidazole (2.36 g, 20 mmol) and K_2CO_3 (3.04 g, 22 mmol) in acetonitrile (20 mL) in a pressure vessel, to which 1-bromodecane (12.4 mL, 60 mmol) was added. The reaction mixture was refluxed at 80°C for 2 days. After cooling to room temperature, the solvent was removed under reduced pressure, followed by addition of DCM. The resultant suspension was filtered through celite, and the filtrate was concentrated under reduced pressure to yield a solid powder. The solid residue was subsequently washed with ethyl acetate to afford product as a white powder (8.62 g, 90%). ^1H NMR (400 MHz, CDCl_3): δ 11.46 (s, 1H), 7.68 (m, 4H), 4.62 (t, $J = 7.6$ Hz, 4H), 2.03 (m, $J = 7.2$ Hz, 4H), 1.45-1.15 (m, 32H), 0.85 (t, $J = 7.1$ Hz, 6H).

[0828] **Example 33**

[0829] *1,3-Diethylbenzimidazolium chloride (Et-NHC[Cl])*. To the solution of **Et-NHC[I]** (0.604 g, 2 mmol) in chloroform (20 mL), Ag_2SO_4 was added (1.248 g, 4 mmol), resulting in the immediate formation of a yellow precipitate. The mixture was stirred for 2 hours at room temperature and subsequently filtered through celite. The filtrate was concentrated under reduced pressure, yielding a sticky solid, which was washed with ethyl acetate to obtain a white powder. This white powder was dissolved in methanol (20 mL), and a solution of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (0.976 g, 4 mmol) in DI water (10 mL) was added. A white precipitate formed immediately. The mixture

was stirred for an additional 2 hours at room temperature, followed by filtration through celite. The filtrate was concentrated under reduced pressure, after which chloroform was added to the residue. The mixture was filtered again through celite, and the solvent was removed from the filtrate under reduced pressure. The resultant sticky solid was washed with ethyl acetate to obtain a white powder (0.257 g, 61%). ^1H NMR (400 MHz, CDCl_3): δ 11.72 (s, 1H), 7.72 (dd, $J = 6.3$, 3.2 Hz, 2H), 7.66 (dd, $J = 6.3$, 3.1 Hz, 2H), 4.70 (q, $J = 7.3$ Hz, 4H), 1.73 (t, $J = 7.3$ Hz, 6H).

[0830] **Example 34**

[0831] *1,3-Dipropylbenzimidazolium chloride (Pr-NHC[Cl]).* To the solution of **Pr-NHC[I]** (0.66 g, 2 mmol) in chloroform (20 mL), Ag_2SO_4 was added (1.248 g, 4 mmol), resulting in the immediate formation of a yellow precipitate. The mixture was stirred for 2 hours at room temperature and subsequently filtered through celite. The filtrate was concentrated under reduced pressure, yielding a sticky solid, which was washed with ethyl acetate to obtain a white powder. This white powder was dissolved in methanol (20 mL), and a solution of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (0.976 g, 4 mmol) in DI water (10 mL) was added. A white precipitate formed immediately. The mixture was stirred for an additional 2 hours at room temperature, followed by filtration through celite. The filtrate was concentrated under reduced pressure, after which chloroform was added to the residue. The mixture was filtered again through celite, and the solvent was removed from the filtrate under reduced pressure. The resultant sticky solid was washed with ethyl acetate to obtain a white powder (0.4 g, 84%). ^1H NMR (400 MHz, CDCl_3): δ 11.72 (s, 1H), 7.71 (dd, $J = 6.3$, 3.2 Hz, 2H), 7.64 (dd, $J = 6.3$, 3.1 Hz, 2H), 4.60 (t, $J = 7.4$ Hz, 4H), 2.09 (m, $J = 7.5$ Hz, 4H), 1.04 (t, $J = 7.4$ Hz, 6H).

[0832] **Example 35**

[0833] *1,3-Diisopropylbenzimidazolium chloride (iPr-NHC[Cl]).* To the solution of **iPr-NHC[I]** (0.66 g, 2 mmol) in chloroform (20 mL), Ag_2SO_4 was added (1.248 g, 4 mmol), resulting in the immediate formation of a yellow precipitate. The mixture was stirred for 2 hours at room temperature and subsequently filtered through celite. The filtrate was concentrated under reduced pressure, yielding a sticky solid, which was washed with ethyl acetate to obtain a white powder. This white powder was dissolved in methanol (20 mL), and a solution of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (0.976 g, 4 mmol) in DI water (10 mL) was added. A white precipitate formed immediately. The mixture was stirred for an additional 2 hours at room temperature, followed by filtration through celite. The filtrate was concentrated under reduced pressure, after which chloroform was added to the

residue. The mixture was filtered again through celite, and the solvent was removed from the filtrate under reduced pressure. The resultant sticky solid was washed with ethyl acetate to obtain a white powder (0.357 g, 84%). ¹H NMR (400 MHz, CDCl₃): δ 11.78 (s, 1H), 7.77 (dd, *J* = 6.3, 3.2 Hz, 2H), 7.62 (dd, *J* = 6.3, 3.2 Hz, 2H), 5.18 (m, *J* = 6.8 Hz, 2H), 1.84 (d, *J* = 6.5 Hz, 12H).

[0834] **Example 36**

[0835] *1,3-Dibutylbenzimidazolium chloride (But-NHC[Cl]).* To the solution of **But-NHC[II]** (0.716 g, 2 mmol) in chloroform (20 mL), Ag₂SO₄ was added (1.248 g, 4 mmol), resulting in the immediate formation of a yellow precipitate. The mixture was stirred for 2 hours at room temperature and subsequently filtered through celite. The filtrate was concentrated under reduced pressure, yielding a sticky solid, which was washed with ethyl acetate to obtain a white powder. This white powder was dissolved in methanol (20 mL), and a solution of BaCl₂·2H₂O (0.976 g, 4 mmol) in DI water (10 mL) was added. A white precipitate formed immediately. The mixture was stirred for an additional 2 hours at room temperature, followed by filtration through celite. The filtrate was concentrated under reduced pressure, after which chloroform was added to the residue. The mixture was filtered again through celite, and the solvent was removed from the filtrate under reduced pressure. The resultant sticky solid was washed with ethyl acetate to obtain a white powder (0.352 g, 66%). ¹H NMR (400 MHz, CDCl₃): δ 11.8 (s, 1H), 7.7 (dd, *J* = 6.3, 3.2 Hz, 2H), 7.64 (dd, *J* = 6.3, 3.2 Hz, 2H), 4.63 (t, *J* = 7.4 Hz, 4H), 2.03 (m, *J* = 7.5 Hz, 4H), 1.45 (m, *J* = 7.4 Hz, 4H), 0.98 (t, *J* = 7.4 Hz, 6H).

[0836] **Example 37**

[0837] *1,3-Dipentylbenzimidazolium chloride (Pen-NHC[Cl]).* To the solution of **Pen-NHC[II]** (0.772 g, 2 mmol) in chloroform (20 mL), Ag₂SO₄ was added (1.248 g, 4 mmol), resulting in the immediate formation of a yellow precipitate. The mixture was stirred for 2 hours at room temperature and subsequently filtered through celite. The filtrate was concentrated under reduced pressure, yielding a sticky solid, which was washed with ethyl acetate to obtain a white powder. This white powder was dissolved in methanol (20 mL), and a solution of BaCl₂·2H₂O (0.976 g, 4 mmol) in DI water (10 mL) was added. A white precipitate formed immediately. The mixture was stirred for an additional 2 hours at room temperature, followed by filtration through celite. The filtrate was concentrated under reduced pressure, after which chloroform was added to the residue. The mixture was filtered again through celite, and the solvent was removed from the filtrate under reduced pressure. The resultant sticky solid was washed with ethyl acetate to obtain

a white powder (0.418 g, 71%). ¹H NMR (400 MHz, CDCl₃): δ 11.87 (s, 1H), 7.66 (m, 4H), 4.62 (t, *J* = 7.5 Hz, 4H), 2.04 (m, *J* = 7.2 Hz, 4H), 1.38 (m, *J* = 7.2 Hz, 4H), 0.89 (t, *J* = 7.2 Hz, 6H).

[0838] **Example 38**

[0839] *1,3-Didecylbenzimidazolium chloride (Dec-NHC[Cl])*. To the solution of **Dec-NHC[I]** (1.052 g, 2 mmol) in chloroform (20 mL), Ag₂SO₄ was added (1.248 g, 4 mmol), resulting in the immediate formation of a yellow precipitate. The mixture was stirred for 2 hours at room temperature and subsequently filtered through celite. The filtrate was concentrated under reduced pressure, yielding a sticky solid, which was washed with ethyl acetate to obtain a white powder. This white powder was dissolved in methanol (20 mL), and a solution of BaCl₂·2H₂O (0.976 g, 4 mmol) in DI water (10 mL) was added. A white precipitate formed immediately. The mixture was stirred for an additional 2 hours at room temperature, followed by filtration through celite. The filtrate was concentrated under reduced pressure, after which chloroform was added to the residue. The mixture was filtered again through celite, and the solvent was removed from the filtrate under reduced pressure. The resultant sticky solid was washed with ethyl acetate to obtain a white powder (0.634 g, 73%). ¹H NMR (400 MHz, CDCl₃): δ 11.86 (s, 1H), 7.67 (m, 4H), 4.62 (t, *J* = 7.6 Hz, 4H), 2.04 (m, *J* = 7.2 Hz, 4H), 1.45-1.17 (m, 32H), 0.86 (t, *J* = 7.1 Hz, 6H).

[0840] **Example 39**

[0841] *1,3-Diethylbenzimidazolium methanesulfonate (Et-NHC[OMs])*. To the solution of **Et-NHC[I]** (0.604 g, 2 mmol) in chloroform (20 mL), AgOMs was added (0.812 g, 4 mmol), resulting in the immediate formation of a yellow precipitate. The mixture was stirred for 2 hours at room temperature and subsequently filtered through celite. The filtrate was concentrated under reduced pressure, yielding solid powder (0.486 g, 90%). ¹H NMR (400 MHz, CDCl₃): δ 10.68 (s, 1H), 7.71 (dd, *J* = 6.3, 3.2 Hz, 2H), 7.65 (dd, *J* = 6.3, 3.1 Hz, 2H), 4.64 (q, *J* = 7.3 Hz, 4H), 2.81 (s, 3H), 1.7 (t, *J* = 7.3 Hz, 6H).

[0842] **Example 40**

[0843] *1,3-Dipropylbenzimidazolium methanesulfonate (Pr-NHC[OMs])*. To the solution of **Pr-NHC[I]** (0.66 g, 2 mmol) in chloroform (20 mL), AgOMs was added (0.812 g, 4 mmol), resulting in the immediate formation of a yellow precipitate. The mixture was stirred for 2 hours at room temperature and subsequently filtered through celite. The filtrate was concentrated under reduced pressure, yielding solid powder (0.519 g, 87%). ¹H NMR (400 MHz, CDCl₃): δ 10.77 (s,

1H), 7.71 (dd, $J = 6.3, 3.2$ Hz, 2H), 7.64 (dd, $J = 6.3, 3.1$ Hz, 2H), 4.57 (t, $J = 7.4$ Hz, 4H), 2.83 (s, 3H), 2.07 (m, $J = 7.5$ Hz, 4H), 1.04 (t, $J = 7.4$ Hz, 6H).

[0844] **Example 41**

[0845] *1,3-Diisopropylbenzimidazolium methanesulfonate (iPr-NHC[OMs])*. To the solution of **iPr-NHC[I]** (0.66 g, 2 mmol) in chloroform (20 mL), AgOMs was added (0.812 g, 4 mmol), resulting in the immediate formation of a yellow precipitate. The mixture was stirred for 2 hours at room temperature and subsequently filtered through celite. The filtrate was concentrated under reduced pressure, yielding solid powder (0.525 g, 88%). ^1H NMR (400 MHz, CDCl_3): δ 10.66 (s, 1H), 7.77 (dd, $J = 6.3, 3.2$ Hz, 2H), 7.62 (dd, $J = 6.3, 3.2$ Hz, 2H), 5.12 (m, $J = 6.8$ Hz, 2H), 2.83 (s, 3H), 1.83 (d, $J = 6.5$ Hz, 12H).

[0846] **Example 42**

[0847] *1,3-Dibutylbenzimidazolium methanesulfonate (But-NHC[OMs])*. To the solution of **But-NHC[I]** (0.716 g, 2 mmol) in chloroform (20 mL), AgOMs was added (0.812 g, 4 mmol), resulting in the immediate formation of a yellow precipitate. The mixture was stirred for 2 hours at room temperature and subsequently filtered through celite. The filtrate was concentrated under reduced pressure, yielding solid powder (0.554 g, 85%). ^1H NMR (400 MHz, CDCl_3): δ 10.74 (s, 1H), 7.7 (dd, $J = 6.3, 3.2$ Hz, 2H), 7.64 (dd, $J = 6.3, 3.2$ Hz, 2H), 4.59 (t, $J = 7.4$ Hz, 4H), 2.83 (s, 3H), 2.00 (m, $J = 7.5$ Hz, 4H), 1.43 (m, $J = 7.4$ Hz, 4H), 0.98 (t, $J = 7.4$ Hz, 6H).

[0848] **Example 43**

[0849] *1,3-Dipentylbenzimidazolium methanesulfonate (Pen-NHC[OMs])*. To the solution of **Pen-NHC[I]** (0.772 g, 2 mmol) in chloroform (20 mL), AgOMs was added (0.812 g, 4 mmol), resulting in the immediate formation of a yellow precipitate. The mixture was stirred for 2 hours at room temperature and subsequently filtered through celite. The filtrate was concentrated under reduced pressure, yielding solid powder (0.481 g, 68%). ^1H NMR (400 MHz, CDCl_3): δ 10.72 (s, 1H), 7.67 (m, 4H), 4.58 (t, $J = 7.5$ Hz, 4H), 2.83 (s, 3H), 2.02 (m, $J = 7.2$ Hz, 4H), 1.38 (m, $J = 7.2$ Hz, 4H), 0.89 (t, $J = 7.2$ Hz, 6H).

[0850] **Example 44**

[0851] *1,3-Didecylbenzimidazolium methanesulfonate (Dec-NHC[OMs])*. To the solution of **Dec-NHC[I]** (1.052 g, 2 mmol) in chloroform (20 mL), AgOMs was added (0.812 g, 4 mmol), resulting in the immediate formation of a yellow precipitate. The mixture was stirred for 2 hours at room temperature and subsequently filtered through celite. The filtrate was concentrated under

reduced pressure, yielding solid powder (0.86 g, 87%). ¹H NMR (400 MHz, CDCl₃): δ 10.76 (s, 1H), 7.66 (m, 4H), 4.58 (t, *J* = 7.6 Hz, 4H), 2.84 (s, 3H), 2.01 (m, *J* = 7.2 Hz, 4H), 1.45-1.16 (m, 32H), 0.86 (t, *J* = 7.1 Hz, 6H).

[0852] **Example 45**

[0853] *1,3-Diethylbenzimidazolium trifluoromethanesulfonate (Et-NHC[OTf])*. To the solution of **Et-NHC[I]** (0.604 g, 2 mmol) in chloroform (20 mL), AgOTf was added (1.028 g, 4 mmol), resulting in the immediate formation of a yellow precipitate. The mixture was stirred for 2 hours at room temperature and subsequently filtered through celite. The filtrate was concentrated under reduced pressure, yielding solid powder (0.46 g, 71%). ¹H NMR (400 MHz, CDCl₃): δ 9.99 (s, 1H), 7.74 (dd, *J* = 6.3, 3.2 Hz, 2H), 7.68 (dd, *J* = 6.3, 3.1 Hz, 2H), 4.59 (q, *J* = 7.3 Hz, 4H), 1.7 (t, *J* = 7.3 Hz, 6H).

[0854] **Example 46**

[0855] *1,3-Dipropylbenzimidazolium trifluoromethanesulfonate (Pr-NHC[OTf])*. To the solution of **Pr-NHC[I]** (0.66 g, 2 mmol) in chloroform (20 mL), AgOTf was added (1.028 g, 4 mmol), resulting in the immediate formation of a yellow precipitate. The mixture was stirred for 2 hours at room temperature and subsequently filtered through celite. The filtrate was concentrated under reduced pressure, yielding solid powder (0.556 g, 79%). ¹H NMR (400 MHz, CDCl₃): δ 9.97 (s, 1H), 7.75 (dd, *J* = 6.3, 3.2 Hz, 2H), 7.67 (dd, *J* = 6.3, 3.1 Hz, 2H), 4.5 (t, *J* = 7.4 Hz, 4H), 2.06 (m, *J* = 7.5 Hz, 4H), 1.03 (t, *J* = 7.4 Hz, 6H).

[0856] **Example 47**

[0857] *1,3-Diisopropylbenzimidazolium trifluoromethanesulfonate (iPr-NHC[OTf])*. To the solution of **iPr-NHC[I]** (0.66 g, 2 mmol) in chloroform (20 mL), AgOTf was added (1.028 g, 4 mmol), resulting in the immediate formation of a yellow precipitate. The mixture was stirred for 2 hours at room temperature and subsequently filtered through celite. The filtrate was concentrated under reduced pressure, yielding solid powder (0.563 g, 78%). ¹H NMR (400 MHz, CDCl₃): δ 9.88 (s, 1H), 7.8 (dd, *J* = 6.3, 3.2 Hz, 2H), 7.66 (dd, *J* = 6.3, 3.2 Hz, 2H), 5.03 (m, *J* = 6.8 Hz, 2H), 1.8 (d, *J* = 6.5 Hz, 12H).

[0858] **Example 48**

[0859] *1,3-Dibutylbenzimidazolium trifluoromethanesulfonate (But-NHC[OTf])*. To the solution of **But-NHC[I]** (0.716 g, 2 mmol) in chloroform (20 mL), AgOTf was added (1.028 g, 4 mmol), resulting in the immediate formation of a yellow precipitate. The mixture was stirred for

2 hours at room temperature and subsequently filtered through celite. The filtrate was concentrated under reduced pressure, yielding solid powder (0.676 g, 89%). ¹H NMR (400 MHz, CDCl₃): δ 9.92 (s, 1H), 7.75 (dd, *J* = 6.3, 3.2 Hz, 2H), 7.67 (dd, *J* = 6.3, 3.2 Hz, 2H), 4.52 (t, *J* = 7.4 Hz, 4H), 1.99 (m, *J* = 7.5 Hz, 4H), 1.42 (m, *J* = 7.4 Hz, 4H), 0.97 (t, *J* = 7.4 Hz, 6H).

[0860] **Example 49**

[0861] *1,3-Dipentylbenzimidazolium trifluoromethanesulfonate (Pen-NHC[OTf])*. To the solution of **Pen-NHC[I]** (0.772 g, 2 mmol) in chloroform (20 mL), AgOTf was added (1.028 g, 4 mmol), resulting in the immediate formation of a yellow precipitate. The mixture was stirred for 2 hours at room temperature and subsequently filtered through celite. The filtrate was concentrated under reduced pressure, yielding solid powder (0.693 g, 85%). ¹H NMR (400 MHz, CDCl₃): δ 10.02 (s, 1H), 7.7 (m, 4H), 4.52 (t, *J* = 7.5 Hz, 4H), 2.02 (m, *J* = 7.2 Hz, 4H), 1.38 (m, *J* = 7.2 Hz, 4H), 0.9 (t, *J* = 7.2 Hz, 6H).

[0862] **Example 50**

[0863] *1,3-Didecylbenzimidazolium trifluoromethanesulfonate (Dec-NHC[OTf])*. To the solution of **Dec-NHC[I]** (1.052 g, 2 mmol) in chloroform (20 mL), AgOTf was added (1.028 g, 4 mmol), resulting in the immediate formation of a yellow precipitate. The mixture was stirred for 2 hours at room temperature and subsequently filtered through celite. The filtrate was concentrated under reduced pressure, yielding solid powder (0.943 g, 86%). ¹H NMR (400 MHz, CDCl₃): δ 10.04 (s, 1H), 7.7 (m, 4H), 4.51 (t, *J* = 7.6 Hz, 4H), 2.01 (m, *J* = 7.3 Hz, 4H), 1.45-1.16 (m, 32H), 0.87 (t, *J* = 6.8 Hz, 6H).

[0864] **Example 51**

[0865] *1,3-Diethylbenzimidazolium tetrafluoroborate (Et-NHC[BF₄])*. To the solution of **Et-NHC[I]** (0.604 g, 2 mmol) in chloroform (20 mL), AgBF₄ was added (0.78 g, 4 mmol), resulting in the immediate formation of a yellow precipitate. The mixture was stirred for 2 hours at room temperature and subsequently filtered through celite. The filtrate was concentrated under reduced pressure, yielding solid powder (0.435 g, 83%). ¹H NMR (400 MHz, CDCl₃): δ 9.61 (s, 1H), 7.74 (dd, *J* = 6.3, 3.2 Hz, 2H), 7.68 (dd, *J* = 6.3, 3.1 Hz, 2H), 4.57 (q, *J* = 7.3 Hz, 4H), 1.71 (t, *J* = 7.3 Hz, 6H).

[0866] **Example 52**

[0867] *1,3-Dipropylbenzimidazolium tetrafluoroborate (Pr-NHC[BF₄])*. To the solution of **Pr-NHC[I]** (0.66 g, 2 mmol) in chloroform (20 mL), AgBF₄ was added (0.78 g, 4 mmol),

resulting in the immediate formation of a yellow precipitate. The mixture was stirred for 2 hours at room temperature and subsequently filtered through celite. The filtrate was concentrated under reduced pressure, yielding solid powder (0.371 g, 64%). ¹H NMR (400 MHz, CDCl₃): δ 9.57 (s, 1H), 7.75 (dd, *J* = 6.3, 3.2 Hz, 2H), 7.67 (dd, *J* = 6.3, 3.1 Hz, 2H), 4.49 (t, *J* = 7.4 Hz, 4H), 2.06 (m, *J* = 7.5 Hz, 4H), 1.03 (t, *J* = 7.4 Hz, 6H).

[0868] **Example 53**

[0869] *1,3-Diisopropylbenzimidazolium tetrafluoroborate (iPr-NHC[BF₄])*. To the solution of **iPr-NHC[I]** (0.66 g, 2 mmol) in chloroform (20 mL), AgBF₄ was added (0.78 g, 4 mmol), resulting in the immediate formation of a yellow precipitate. The mixture was stirred for 2 hours at room temperature and subsequently filtered through celite. The filtrate was concentrated under reduced pressure, yielding solid powder (0.342 g, 59%). ¹H NMR (400 MHz, CDCl₃): δ 9.5 (s, 1H), 7.8 (dd, *J* = 6.3, 3.2 Hz, 2H), 7.66 (dd, *J* = 6.3, 3.2 Hz, 2H), 5.00 (m, *J* = 6.8 Hz, 2H), 1.79 (d, *J* = 6.5 Hz, 12H).

[0870] **Example 54**

[0871] *1,3-Dibutylbenzimidazolium tetrafluoroborate (But-NHC[BF₄])*. To the solution of **But-NHC[I]** (0.716 g, 2 mmol) in chloroform (20 mL), AgBF₄ was added (0.78 g, 4 mmol), resulting in the immediate formation of a yellow precipitate. The mixture was stirred for 2 hours at room temperature and subsequently filtered through celite. The filtrate was concentrated under reduced pressure, yielding solid powder (0.42 g, 66%). ¹H NMR (400 MHz, CDCl₃): δ 9.55 (s, 1H), 7.75 (dd, *J* = 6.3, 3.2 Hz, 2H), 7.67 (dd, *J* = 6.3, 3.2 Hz, 2H), 4.51 (t, *J* = 7.4 Hz, 4H), 1.99 (m, *J* = 7.5 Hz, 4H), 1.43 (m, *J* = 7.4 Hz, 4H), 0.98 (t, *J* = 7.4 Hz, 6H).

[0872] **Example 55**

[0873] *1,3-Dipentylbenzimidazolium tetrafluoroborate (Pen-NHC[BF₄])*. To the solution of **Pen-NHC[I]** (0.772 g, 2 mmol) in chloroform (20 mL), AgBF₄ was added (0.78 g, 4 mmol), resulting in the immediate formation of a yellow precipitate. The mixture was stirred for 2 hours at room temperature and subsequently filtered through celite. The filtrate was concentrated under reduced pressure, yielding solid powder (0.381 g, 55%). ¹H NMR (400 MHz, CDCl₃): δ 9.63 (s, 1H), 7.7 (m, 4H), 4.5 (t, *J* = 7.5 Hz, 4H), 2.02 (m, *J* = 7.2 Hz, 4H), 1.38 (m, *J* = 7.2 Hz, 4H), 0.91 (t, *J* = 7.2 Hz, 6H).

[0874] **Example 56**

[0875] *1,3-Didecylbenzimidazolium tetrafluoroborate (Dec-NHC[BF₄])*. To the solution of **Dec-NHC[I]** (1.052 g, 2 mmol) in chloroform (20 mL), AgBF₄ was added (0.78 g, 4 mmol), resulting in the immediate formation of a yellow precipitate. The mixture was stirred for 2 hours at room temperature and subsequently filtered through celite. The filtrate was concentrated under reduced pressure, yielding solid powder (0.797 g, 82%). ¹H NMR (400 MHz, CDCl₃): δ 9.61 (s, 1H), 7.7 (m, 4H), 4.5 (t, *J* = 7.6 Hz, 4H), 2.00 (m, *J* = 7.3 Hz, 4H), 1.45-1.16 (m, 32H), 0.87 (t, *J* = 6.8 Hz, 6H).

[0876] **Example 57**

[0877] *1,3-Diethylbenzimidazolium hexafluorophosphate (Et-NHC[PF₆])*. To the solution of **Et-NHC[I]** (0.604 g, 2 mmol) in methanol (15 mL), a solution of KPF₆ (0.736 g, 4 mmol) in DI water (15 mL) was added, resulting in the immediate formation of a white precipitate. The mixture was stirred for 24 hours at room temperature and subsequently filtered to obtain solid powder (0.48 g, 75%). ¹H NMR (400 MHz, CDCl₃): δ 9.61 (s, 1H), 7.74 (dd, *J* = 6.3, 3.2 Hz, 2H), 7.68 (dd, *J* = 6.3, 3.1 Hz, 2H), 4.55 (q, *J* = 7.3 Hz, 4H), 1.7 (t, *J* = 7.3 Hz, 6H).

[0878] **Example 58**

[0879] *1,3-Dipropylbenzimidazolium hexafluorophosphate (Pr-NHC[PF₆])*. To the solution of **Pr-NHC[I]** (0.66 g, 2 mmol) in methanol (15 mL), a solution of KPF₆ (0.736 g, 4 mmol) in DI water (15 mL) was added, resulting in the immediate formation of a white precipitate. The mixture was stirred for 2 hours at room temperature and subsequently filtered through celite. The filtrate was concentrated under reduced pressure, yielding solid powder (0.633 g, 91%). ¹H NMR (400 MHz, CDCl₃): δ 9.30 (s, 1H), 7.75 (dd, *J* = 6.3, 3.2 Hz, 2H), 7.67 (dd, *J* = 6.3, 3.1 Hz, 2H), 4.46 (t, *J* = 7.4 Hz, 4H), 2.06 (m, *J* = 7.5 Hz, 4H), 1.04 (t, *J* = 7.4 Hz, 6H).

[0880] **Example 59**

[0881] *1,3-Diisopropylbenzimidazolium hexafluorophosphate (iPr-NHC[PF₆])*. To the solution of **iPr-NHC[I]** (0.66 g, 2 mmol) in methanol (15 mL), a solution of KPF₆ (0.736 g, 4 mmol) in DI water (15 mL) was added, resulting in the immediate formation of a white precipitate. The mixture was stirred for 2 hours at room temperature and subsequently filtered through celite. The filtrate was concentrated under reduced pressure, yielding solid powder (0.591 g, 85%). ¹H NMR (400 MHz, CDCl₃): δ 9.18 (s, 1H), 7.8 (dd, *J* = 6.3, 3.2 Hz, 2H), 7.67 (dd, *J* = 6.3, 3.2 Hz, 2H), 4.98 (m, *J* = 6.8 Hz, 2H), 1.79 (d, *J* = 6.5 Hz, 12H).

[0882] **Example 60**

[0883] *1,3-Dibutylbenzimidazolium hexafluorophosphate (But-NHC[PF₆])*. To the solution of **But-NHC[I]** (0.716 g, 2 mmol) in methanol (15 mL), a solution of KPF₆ (0.736 g, 4 mmol) in DI water (15 mL) was added, resulting in the immediate formation of a white precipitate. The mixture was stirred for 2 hours at room temperature and subsequently filtered through celite. The filtrate was concentrated under reduced pressure, yielding solid powder (0.624 g, 83%). ¹H NMR (400 MHz, CDCl₃): δ 9.26 (s, 1H), 7.75 (dd, *J* = 6.3, 3.2 Hz, 2H), 7.67 (dd, *J* = 6.3, 3.2 Hz, 2H), 4.48 (t, *J* = 7.4 Hz, 4H), 1.99 (m, *J* = 7.5 Hz, 4H), 1.43 (m, *J* = 7.4 Hz, 4H), 0.99 (t, *J* = 7.4 Hz, 6H).

[0884] **Example 61**

[0885] *1,3-Dipentylbenzimidazolium hexafluorophosphate (Pen-NHC[PF₆])*. To the solution of **Pen-NHC[I]** (0.772 g, 2 mmol) in methanol (15 mL), a solution of KPF₆ (0.736 g, 4 mmol) in DI water (15 mL) was added, resulting in the immediate formation of a white precipitate. The mixture was stirred for 2 hours at room temperature and subsequently filtered through celite. The filtrate was concentrated under reduced pressure, yielding solid powder (0.598 g, 74%). ¹H NMR (400 MHz, CDCl₃): δ 9.2 (s, 1H), 7.7 (m, 4H), 4.46 (t, *J* = 7.5 Hz, 4H), 2.01 (m, *J* = 7.2 Hz, 4H), 1.37 (m, *J* = 7.2 Hz, 4H), 0.9 (t, *J* = 7.2 Hz, 6H).

[0886] **Example 62**

[0887] *1,3-Didecylbenzimidazolium hexafluorophosphate (Dec-NHC[PF₆])*. To the solution of **Dec-NHC[I]** (1.052 g, 2 mmol) in methanol (15 mL), a solution of KPF₆ (0.736 g, 4 mmol) in DI water (15 mL) was added, resulting in the immediate formation of a white precipitate. The mixture was stirred for 2 hours at room temperature and subsequently filtered through celite. The filtrate was concentrated under reduced pressure, yielding solid powder (0.751 g, 69%). ¹H NMR (400 MHz, CDCl₃): δ 9.38 (s, 1H), 7.7 (m, 4H), 4.48 (t, *J* = 7.6 Hz, 4H), 2.00 (m, *J* = 7.3 Hz, 4H), 1.45-1.16 (m, 32H), 0.86 (t, *J* = 6.8 Hz, 6H).

[0888] **Example 63. Functionalization of Exfoliated TMDs by Pen-NHC[I]**

[0889] A 5 mL portion of exfoliated TMDs (1 mM) was introduced to a 40-mL glass vial. Subsequently, 5 mL of Pen-NHC[I] (150 mM in DCM) was quickly injected into the solution. The reaction was left undisturbed at room temperature for 24 h. Then, the slurry was transferred to a centrifuge tube and subjected to centrifugation at 2000 rpm for 10 min to precipitate all functionalized and unfunctionalized TMDs. The resultant material was additionally washed with 10 mL of DCM, and subjected to centrifugation at 2000 rpm for 10 min. This process constituted

one washing cycle and was repeated one more time to eliminate all unreacted NHCs. The final product was redispersed in DCM as an ink type for later characterization.

[0890] Various embodiments of the invention are described above in the Detailed Description. While these descriptions directly describe the above embodiments, it is understood that those skilled in the art may conceive modifications and/or variations to the specific embodiments shown and described herein. Any such modifications or variations that fall within the purview of this description are intended to be included therein as well. Unless specifically noted, it is the intention of the inventors that the words and phrases in the specification and claims be given the ordinary and accustomed meanings to those of ordinary skill in the applicable art(s).

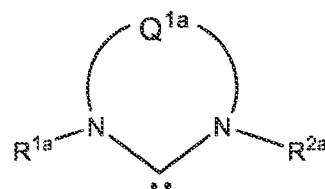
[0891] The foregoing description of various embodiments of the invention known to the applicant at this time of filing the application has been presented and is intended for the purposes of illustration and description. The present description is not intended to be exhaustive nor limit the invention to the precise form disclosed and many modifications and variations are possible in the light of the above teachings. The embodiments described serve to explain the principles of the invention and its practical application and to enable others skilled in the art to utilize the invention in various embodiments and with various modifications as are suited to the particular use contemplated. Therefore, it is intended that the invention is not limited to the particular embodiments disclosed for carrying out the invention.

[0892] While particular embodiments of the present invention have been shown and described, it will be obvious to those skilled in the art that, based upon the teachings herein, changes and modifications may be made without departing from this invention and its broader aspects and, therefore, the appended claims are to encompass within their scope all such changes and modifications as are within the true spirit and scope of this invention. It will be understood by those within the art that, in general, terms used herein are generally intended as “open” terms (*e.g.*, the term “including” should be interpreted as “including but not limited to,” the term “having” should be interpreted as “having at least,” the term “includes” should be interpreted as “includes but is not limited to,” etc.).

CLAIMS

What is claimed is:

1. A *N*-heterocyclic carbene functionalized transition metal dichalcogenide, comprising:
at least one transition metal dichalcogenide; and
at least one *N*-heterocyclic carbene.
2. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of claim 1, wherein the at least one *N*-heterocyclic carbene has a structure of Formula (II):



Formula (II),

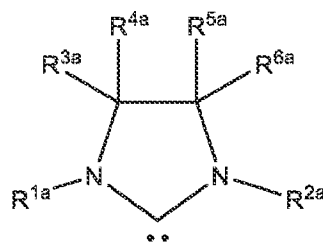
wherein:

R^{1a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{2a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and

Q^{1a} is an optionally substituted linker.

3. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of claim 1, wherein the at least one *N*-heterocyclic carbene has a structure of Formula (II-A):



Formula (II-A),

wherein:

R^{1a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{2a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{3a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

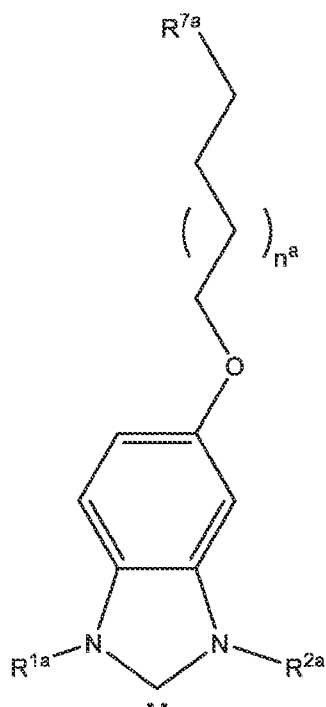
R^{4a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{5a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and

R^{6a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; wherein R^{3a} and R^{4a} are not both absent, and wherein R^{5a} and R^{6a} are not both absent; or

R^{3a} and R^{5a}, or R^{3a} and R^{6a}, or R^{4a} and R^{5a}, or R^{4a} and R^{6a} may be taken together to form a ring, wherein the ring is optionally substituted.

4. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of claim 1, wherein the at least one *N*-heterocyclic carbene has the structure of Formula (II-B):



Formula (II-B),

wherein:

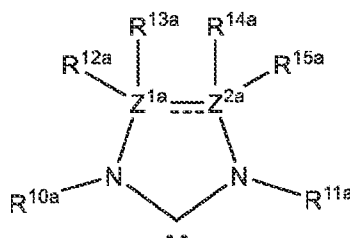
n^a is 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, or 12;

R^{1a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{2a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and

R^{7a} is H, OR^{8a} , SR^{9a} , halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl, wherein R^{8a} is H, or optionally substituted alkyl, and R^{9a} is H, or optionally substituted alkyl.

5. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of claim 1, wherein the at least one *N*-heterocyclic carbene has a structure of Formula (IV):



Formula (IV)

wherein:

Z^{1a} is C;

Z^{2a} is C;

R^{10a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{11a} is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{12a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted alkylamino, optionally substituted amino, hydroxy, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

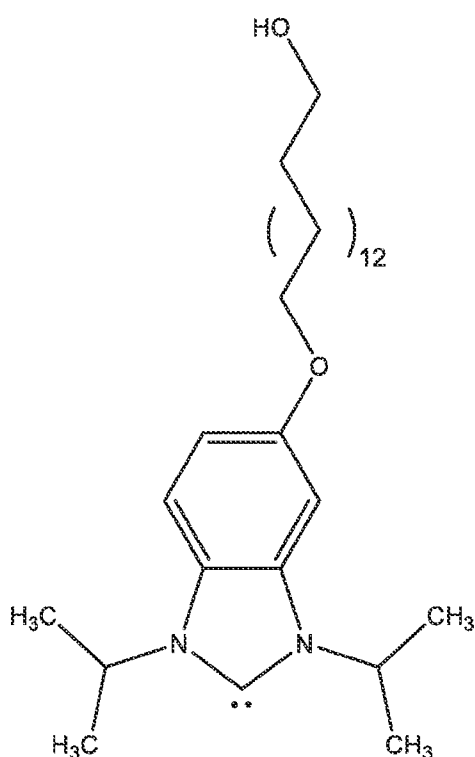
R^{13a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted alkylamino, optionally substituted amino, hydroxy, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R^{14a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted alkylamino, optionally substituted amino, hydroxy, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

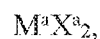
R^{15a} is absent, H, halo, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted alkylamino, optionally

substituted amino, hydroxy, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and wherein R^{12a} and R^{13a} are not both absent, and wherein R^{14a} and R^{15a} are not both absent; and ===== between Z^{1a} and Z^{2a} indicates a bond that may be a single bond or a double bond; or R^{12a} and R^{14a} , or R^{12a} and R^{15a} , or R^{13a} and R^{14a} , or R^{13a} and R^{15a} may be taken together to form a ring, wherein the ring is optionally substituted.

6. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of claim 1, wherein the at least one *N*-heterocyclic carbene is



7. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of claim 1, wherein the at least one transition metal dichalcogenide has the formula:



wherein:

M^a is a Group 4-10 transition metal; and

X^a is a chalcogen.

8. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of claim 7, wherein M^a is a Group 6 transition metal.

9. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of claim 7, wherein the chalcogen is sulfur (S), selenium (Se), or tellurium (Te).

10. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of claim 8, wherein the Group 6 transition metal is molybdenum (Mo) or tungsten (W).

11. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of claim 1, wherein the at least one transition metal dichalcogenide is MoS₂ or WS₂.

12. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of claim 1, wherein the at least one transition metal dichalcogenide is an at least one exfoliated transition metal dichalcogenide, wherein the at least one exfoliated transition metal dichalcogenide comprises at least one exfoliated surface, and wherein the at least one *N*-heterocyclic carbene forms a self-assembled monolayer (SAM) or a partial self-assembled monolayer (SAM) on at least a portion of the at least one exfoliated surface of the at least one exfoliated transition metal dichalcogenide.

13. The *N*-heterocyclic carbene functionalized transition metal dichalcogenide of claim 1, wherein the at least one transition metal dichalcogenide is an at least one exfoliated transition metal dichalcogenide, wherein the at least one exfoliated transition metal dichalcogenide comprises at least one exfoliated surface, wherein the at least one exfoliated surface comprises at least one exfoliated basal plane, and wherein the at least one *N*-heterocyclic carbene forms a self-assembled monolayer (SAM) or a partial self-assembled monolayer (SAM) on at least a portion of the at least one exfoliated basal plane.

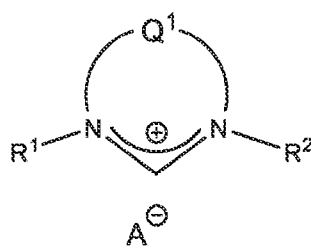
14. A method of making at least one *N*-heterocyclic carbene functionalized transition metal dichalcogenide of claim 1, comprising:

providing at least one bulk transition metal dichalcogenide;

exfoliating the at least one bulk transition metal dichalcogenide to produce at least one exfoliated transition metal dichalcogenide comprising at least one exfoliated surface; and

reacting at least a portion of the at least one exfoliated surface of the at least one exfoliated transition metal dichalcogenide with at least one *N*-heterocyclic carbene precursor.

15. The method of claim 14, wherein the at least one *N*-heterocyclic carbene precursor has a structure of Formula (I):



Formula (I),

wherein:

A[⊖] is a counterion;

R¹ is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl;

R² is H, optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted cyclyl, optionally substituted heterocyclyl, optionally substituted aryl, or optionally substituted heteroaryl; and

Q¹ is an optionally substituted linker.

16. An article of manufacture comprising at least one *N*-heterocyclic carbene functionalized transition metal dichalcogenide of any one of claims 1-13.

17. The article of manufacture of claim 16, wherein the article of manufacture is an energy storage device, energy storage material, sensing device, sensing material, semiconductor electronic device,

semiconductor electronic material, semiconductor optoelectronic device, or semiconductor optoelectronic material.

18. The article of manufacture of claim 16, wherein the article of manufacture is a semiconductor or has semiconducting properties.

FIG. 1B

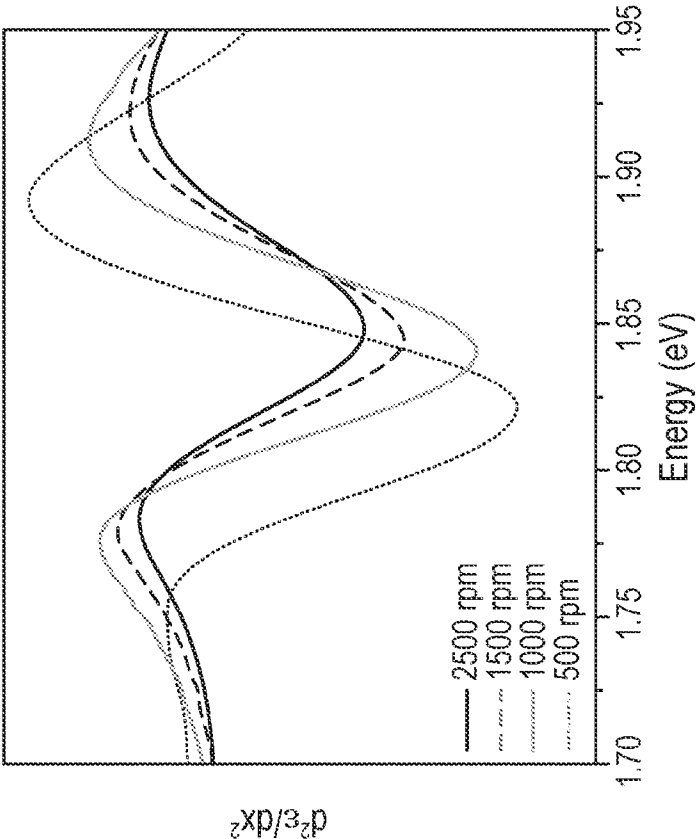


FIG. 1A

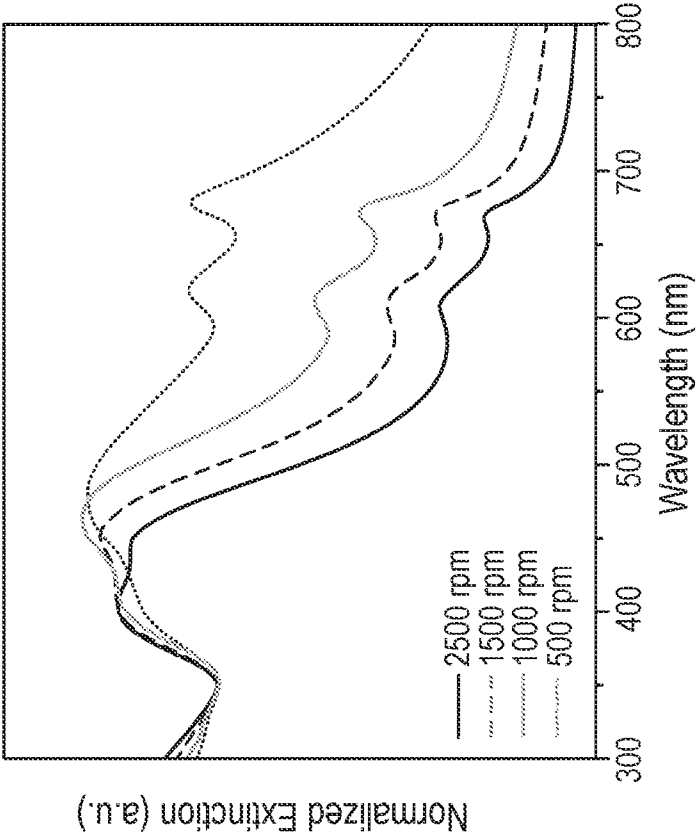


FIG. 2B

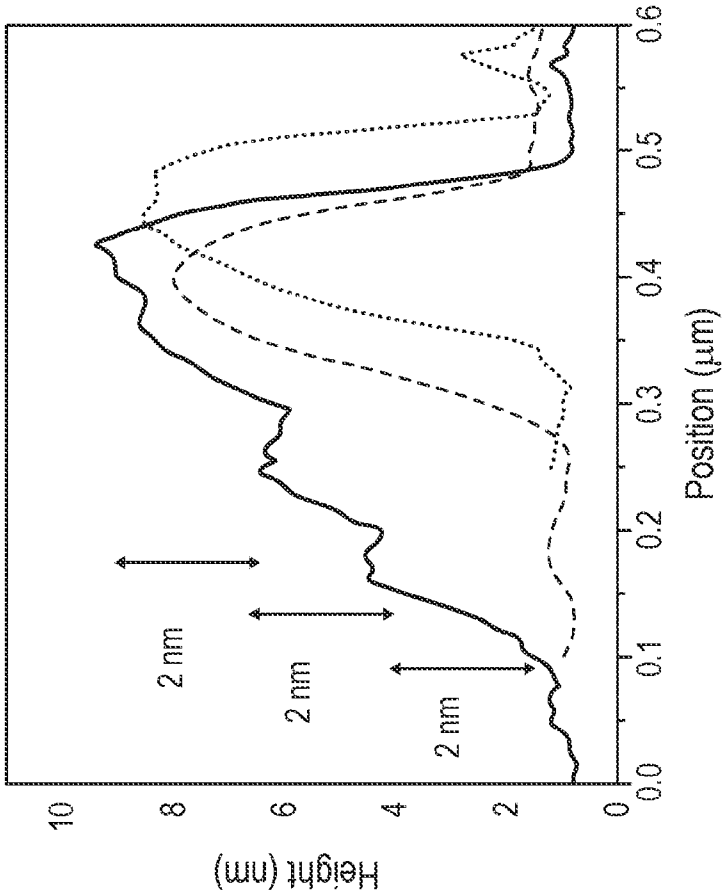


FIG. 2A

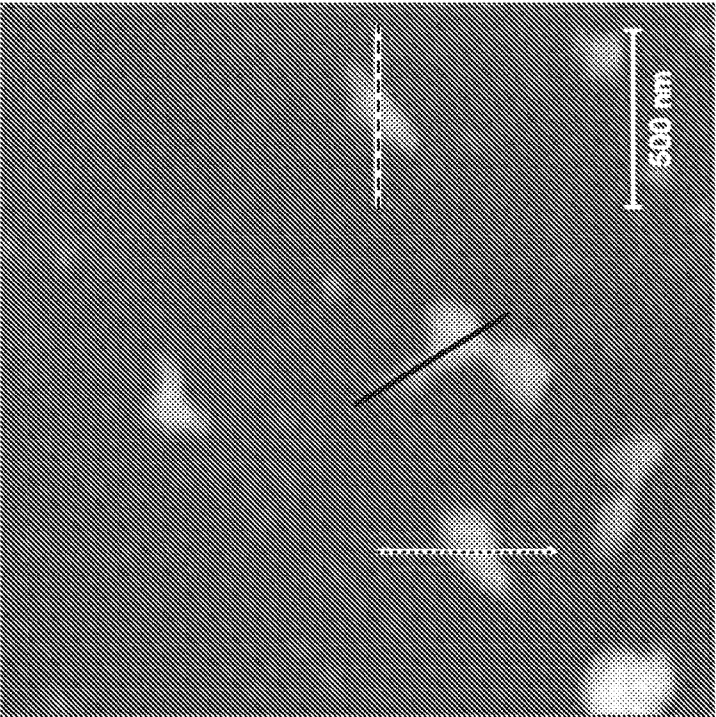


FIG. 3

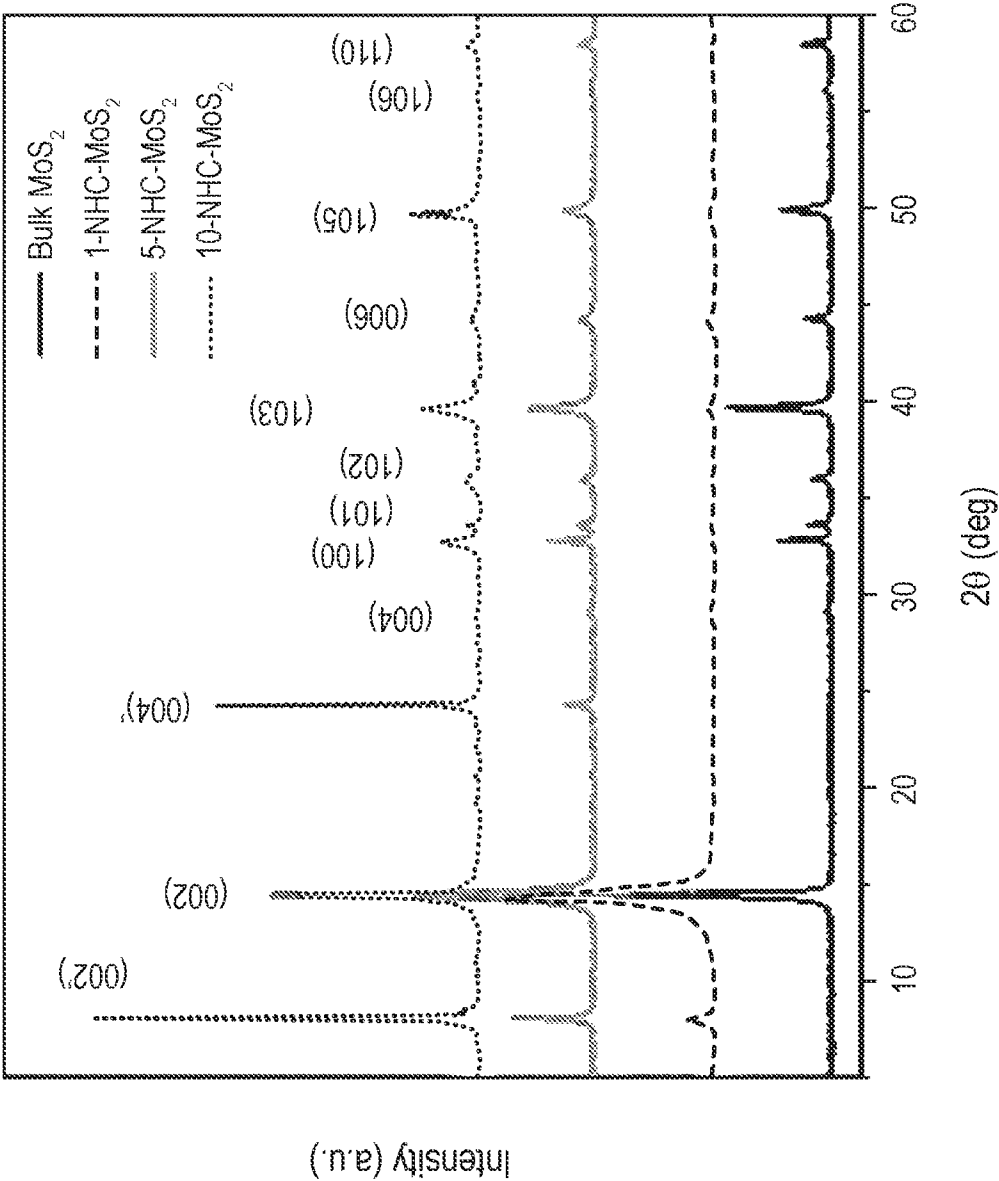


FIG. 4B

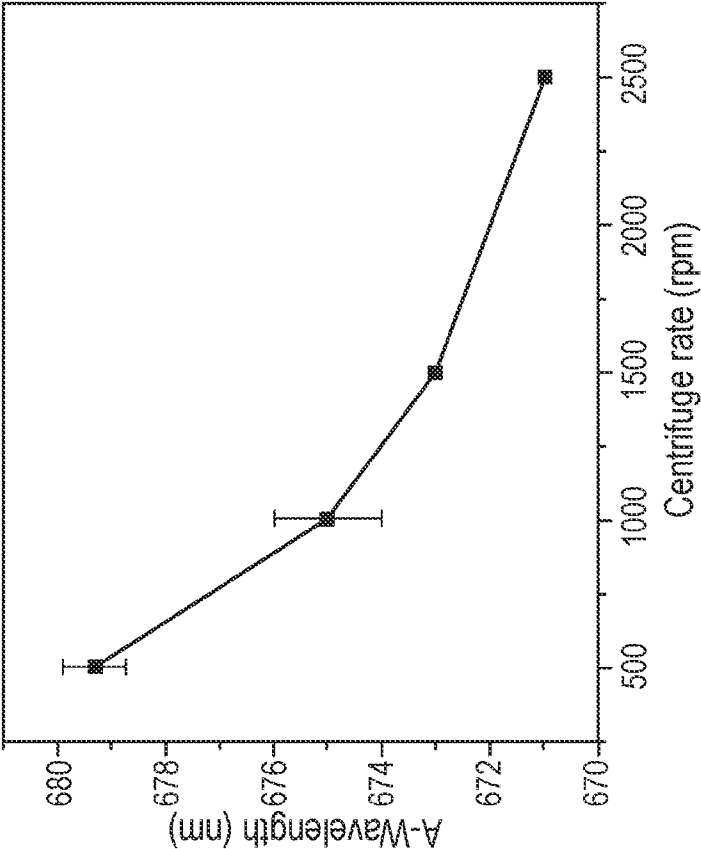


FIG. 4A

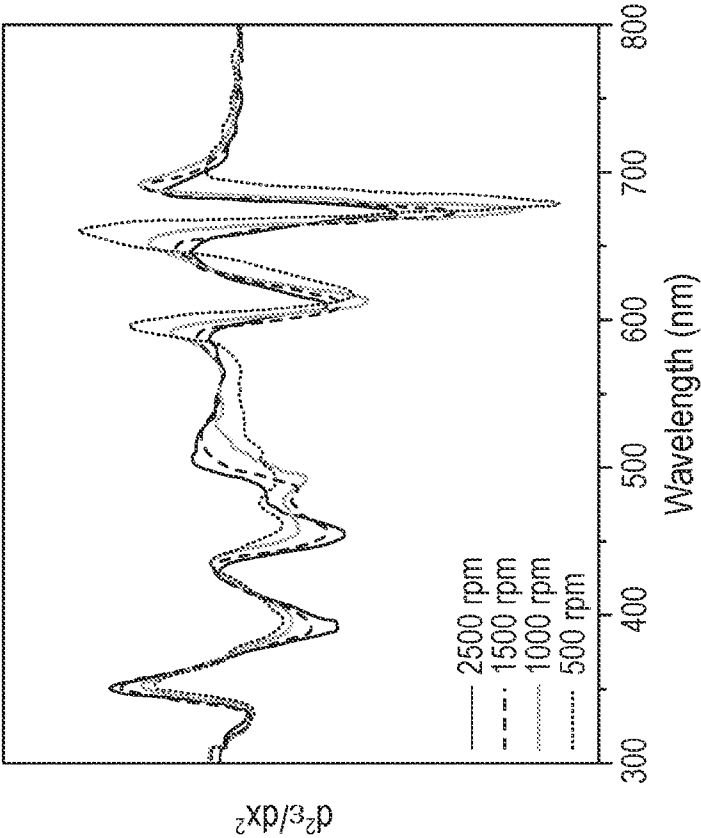


FIG. 6

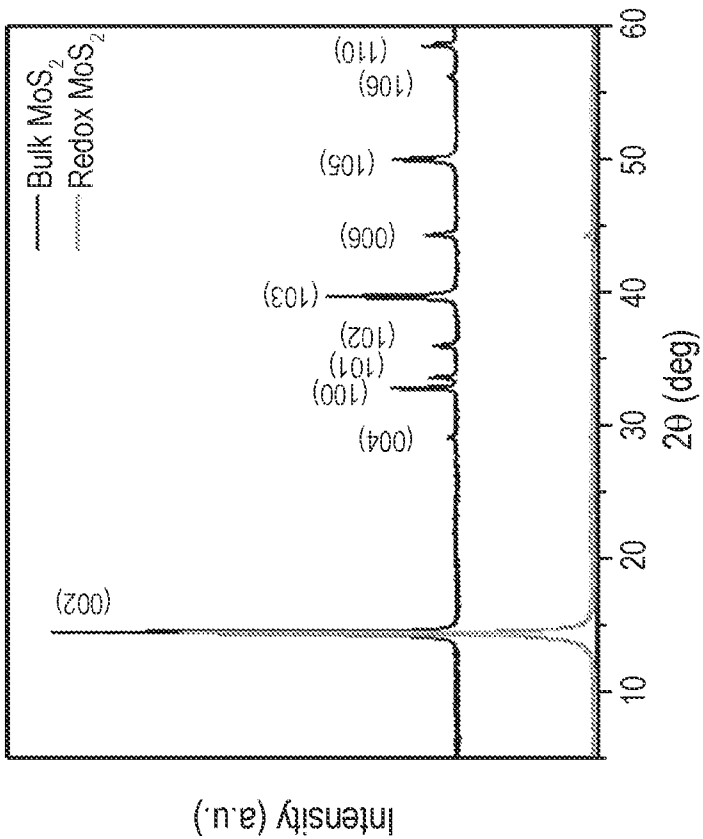


FIG. 5

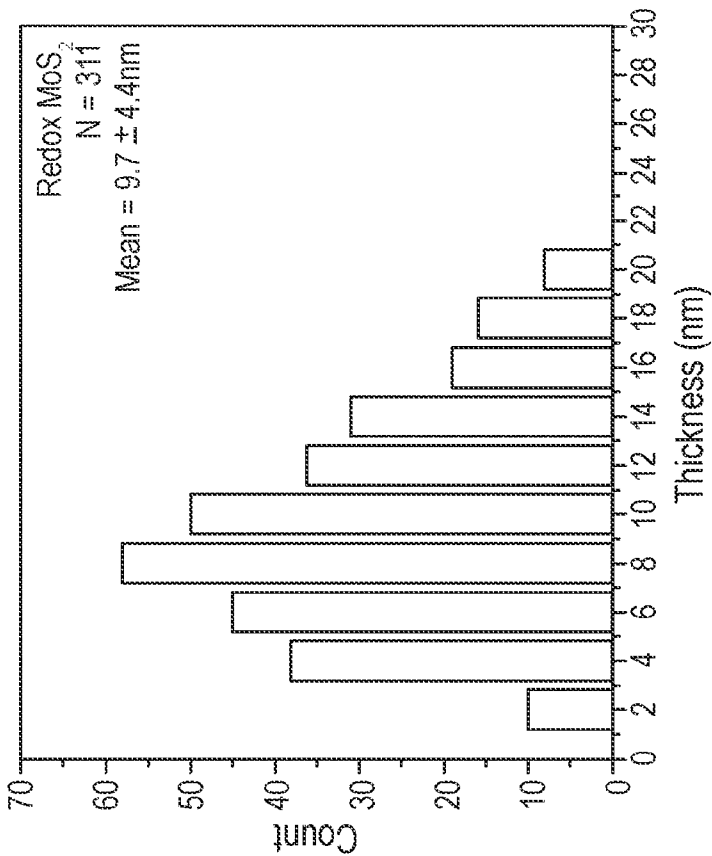


FIG. 8

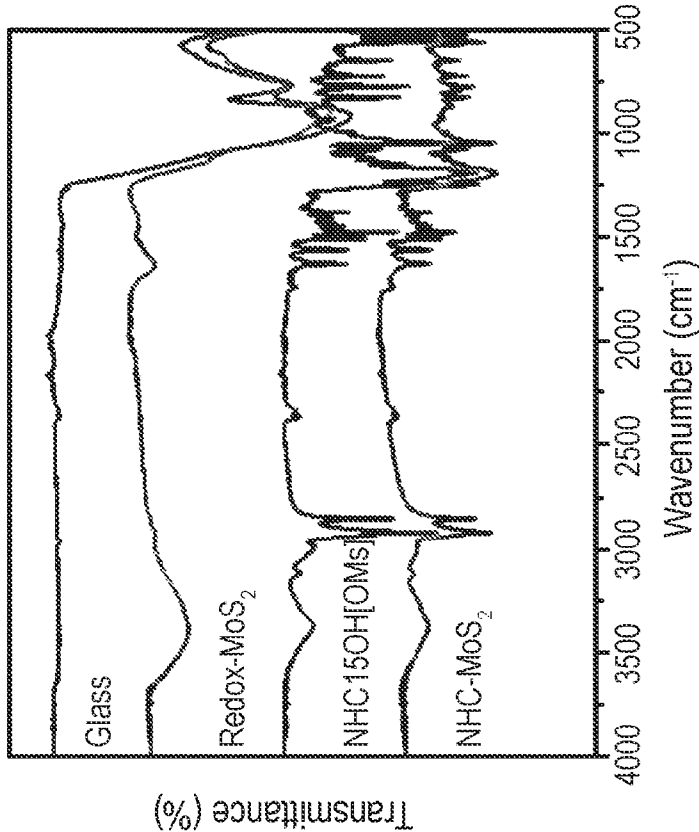


FIG. 7

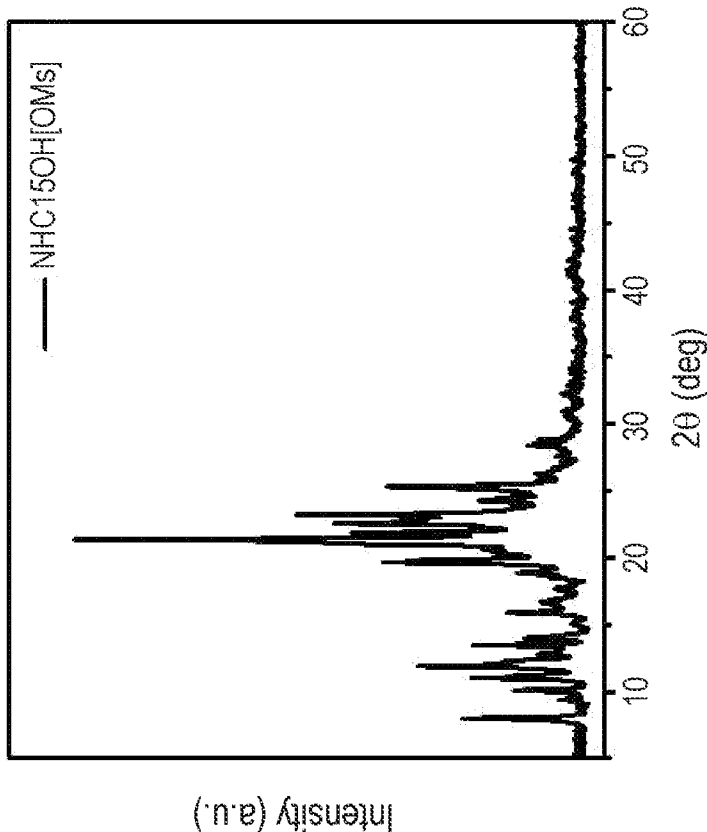


FIG. 9

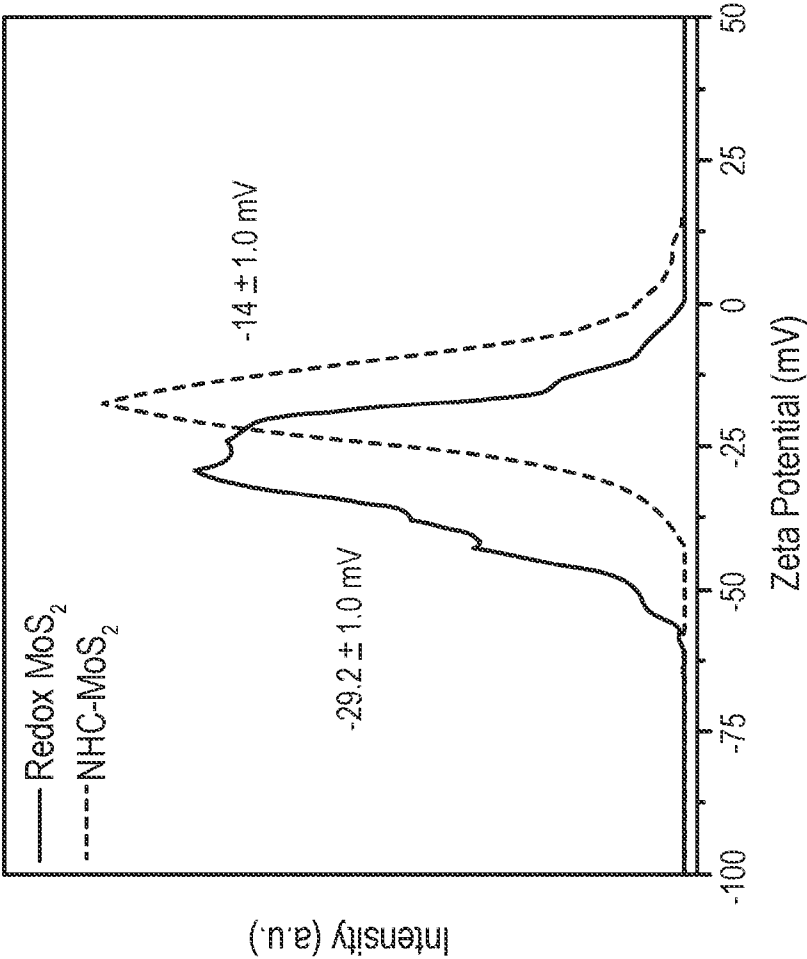


FIG. 10B

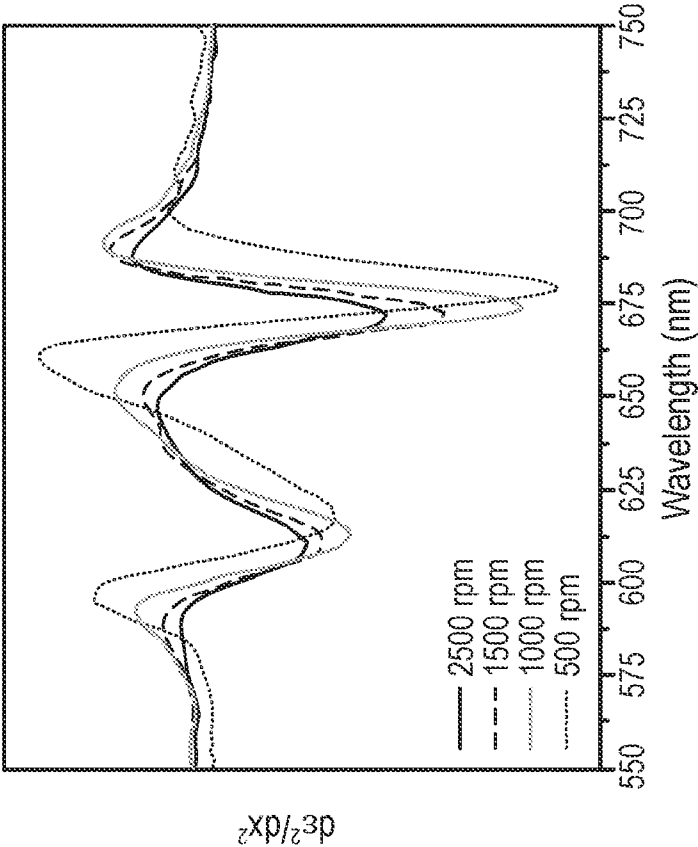
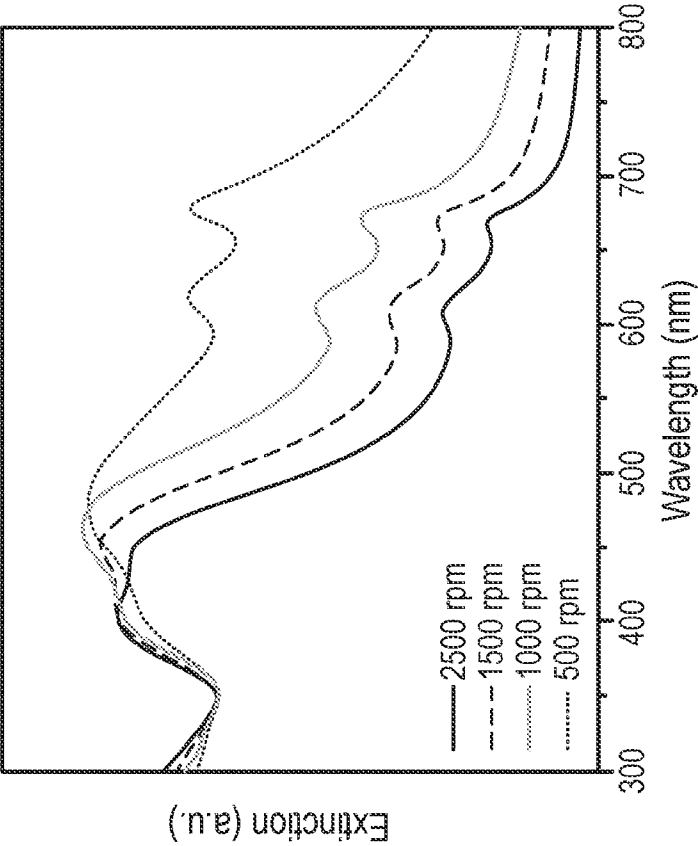


FIG. 10A



9/73

FIG. 11

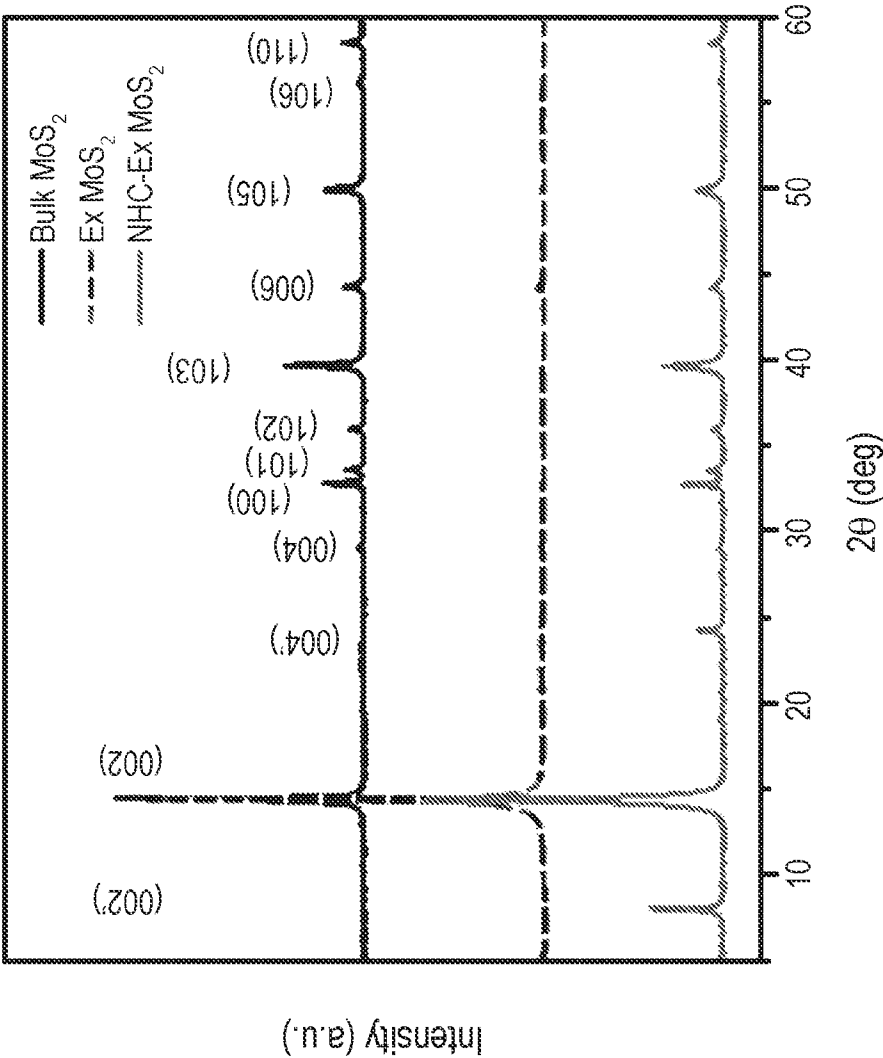


FIG. 12

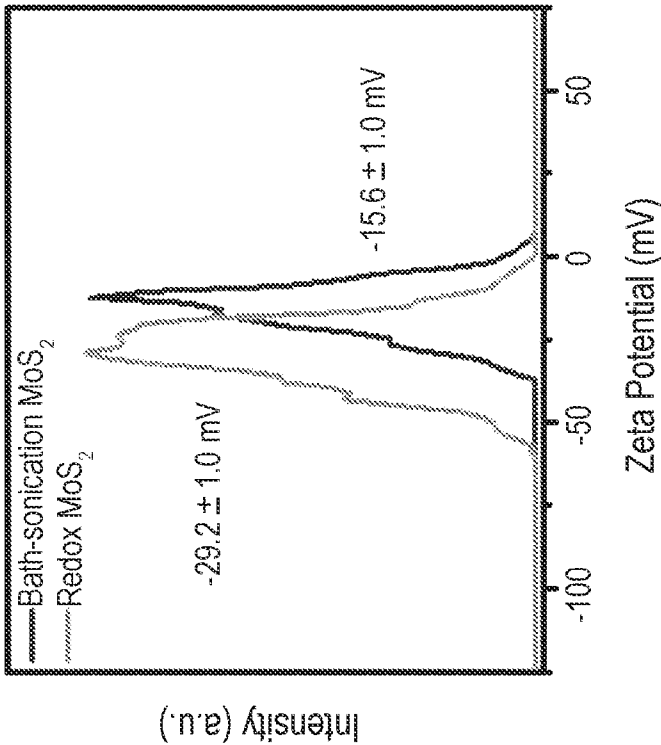


FIG. 13

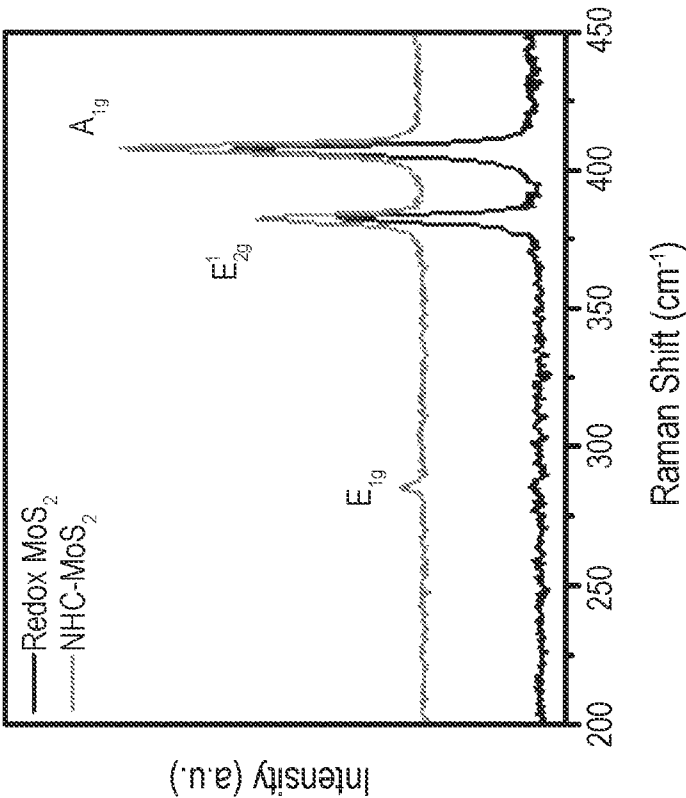


FIG. 14

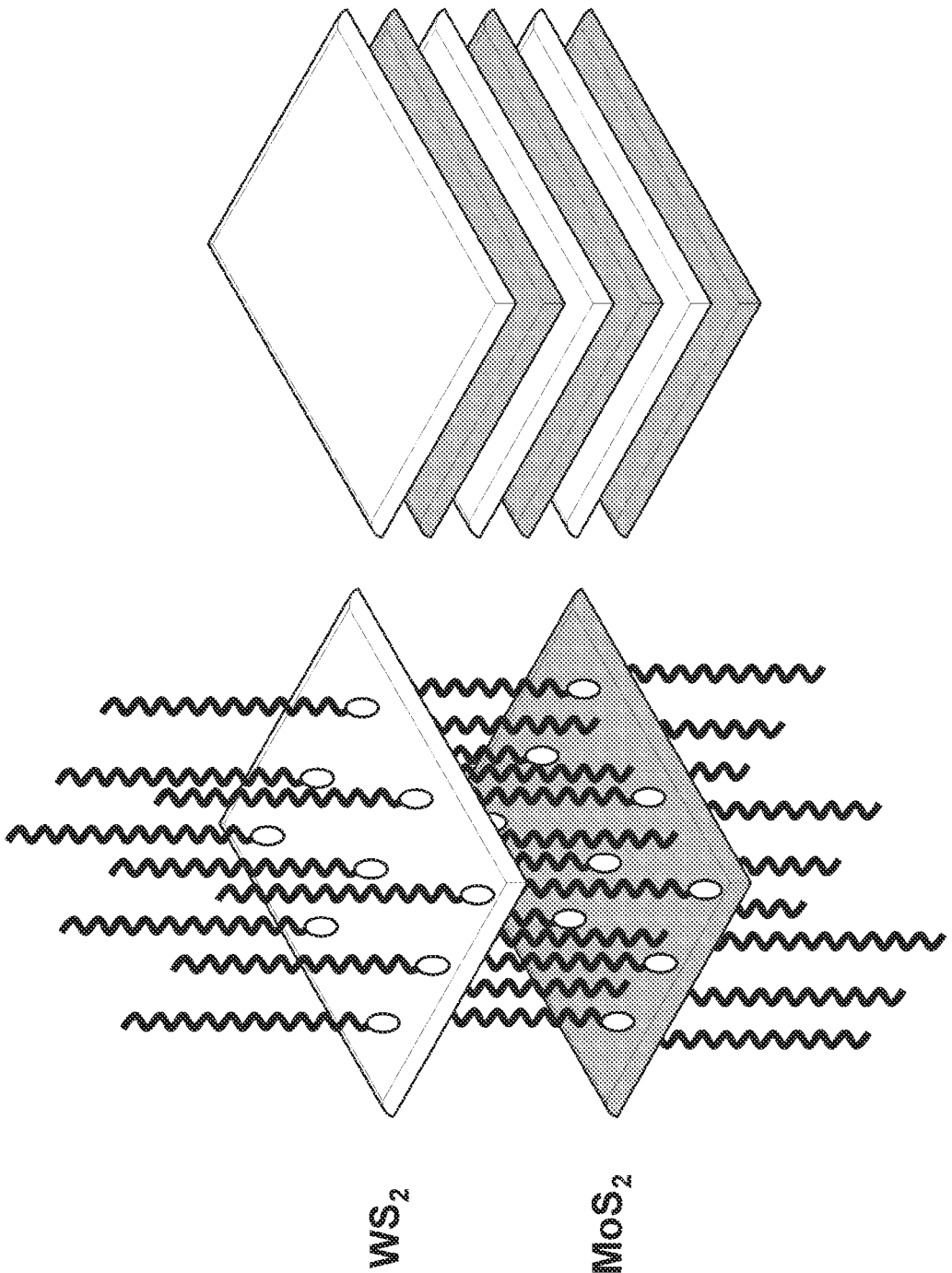
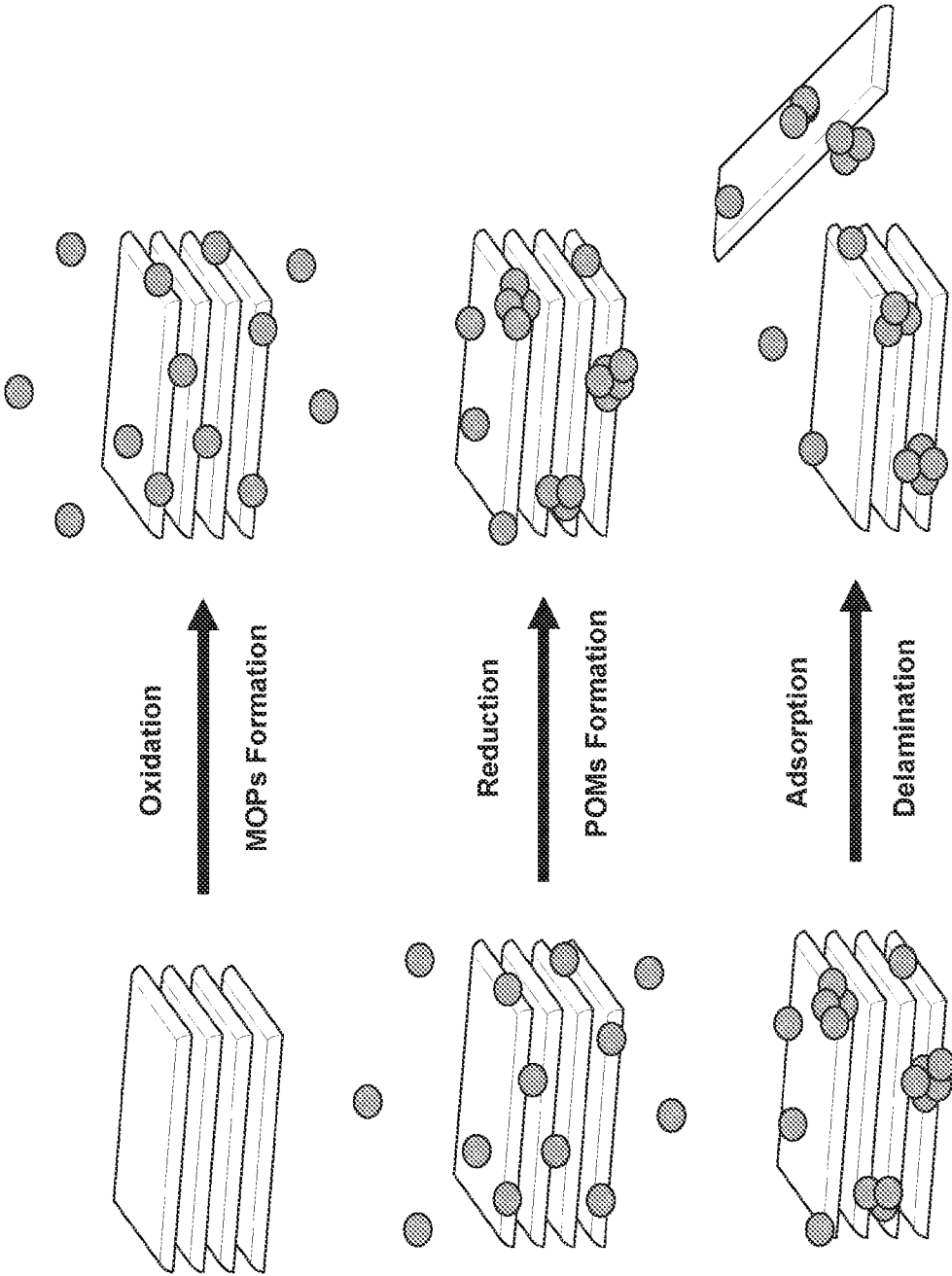


FIG. 15



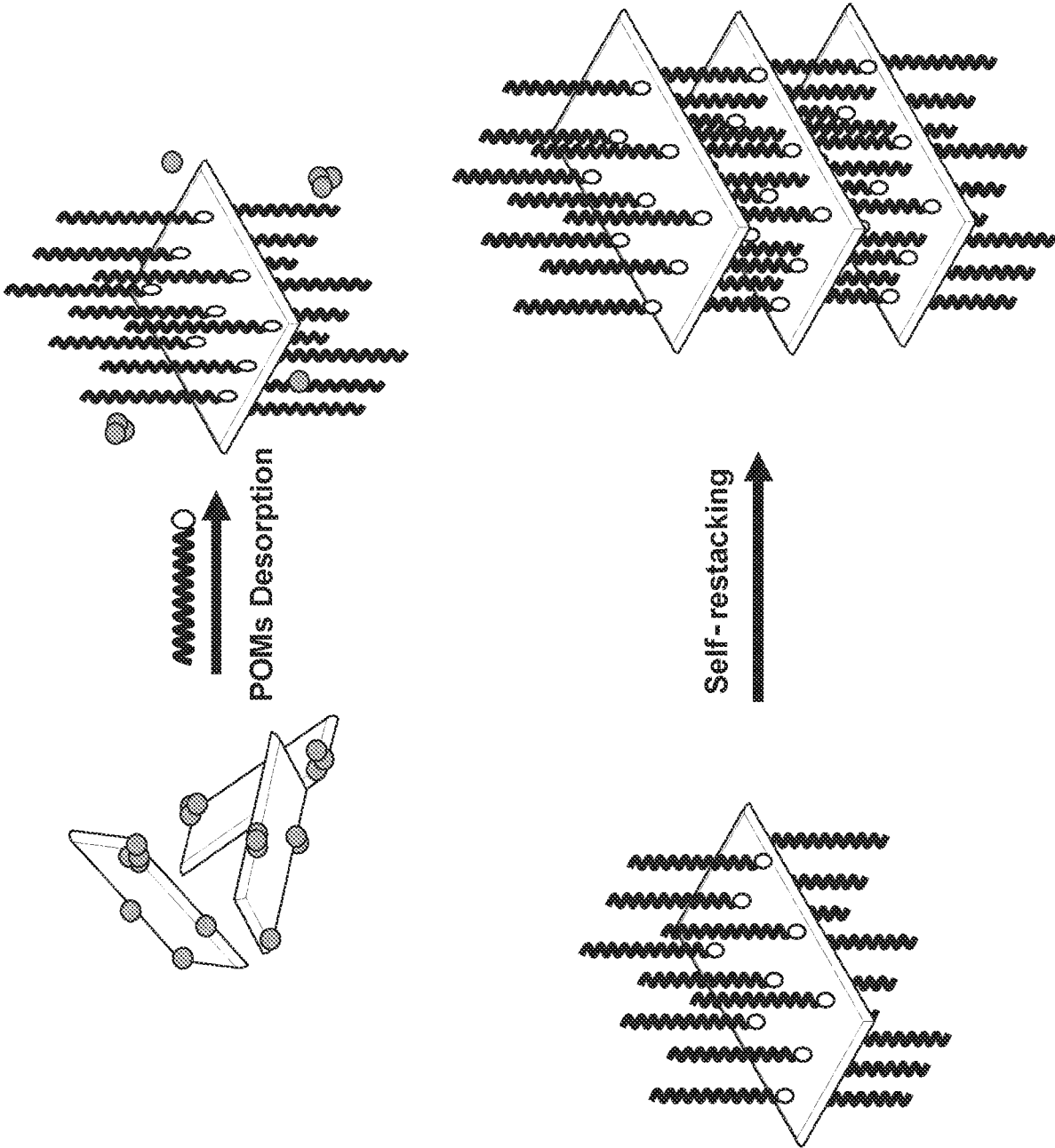


FIG. 16

FIG. 17

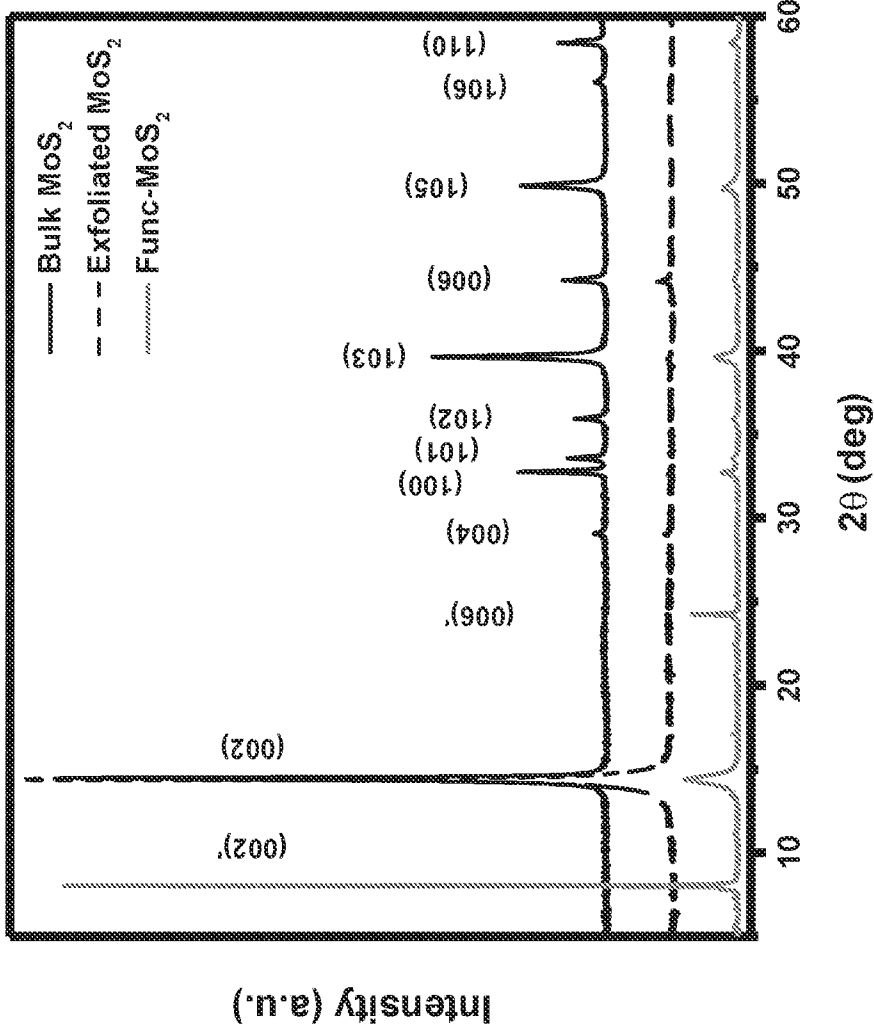


FIG. 18B

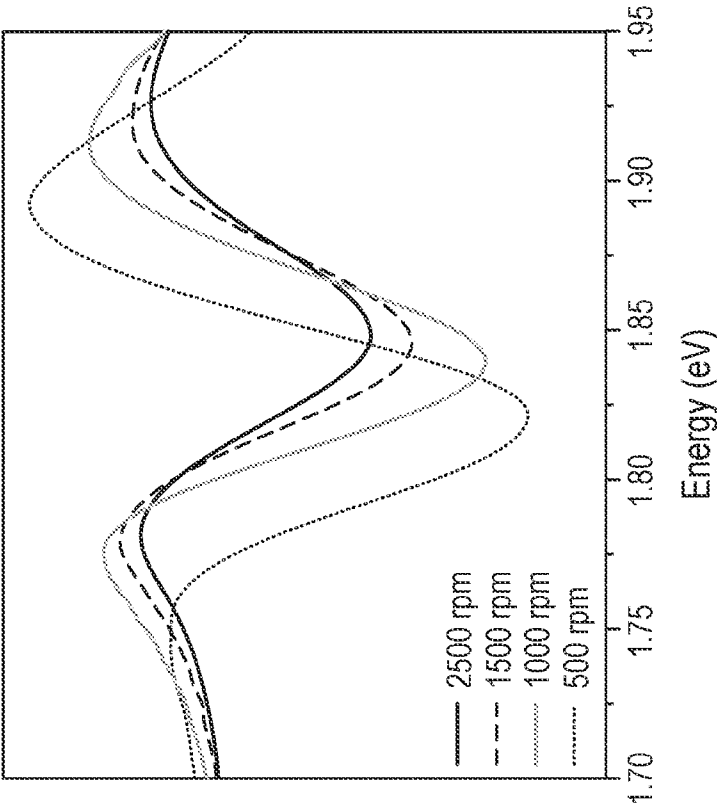


FIG. 18A

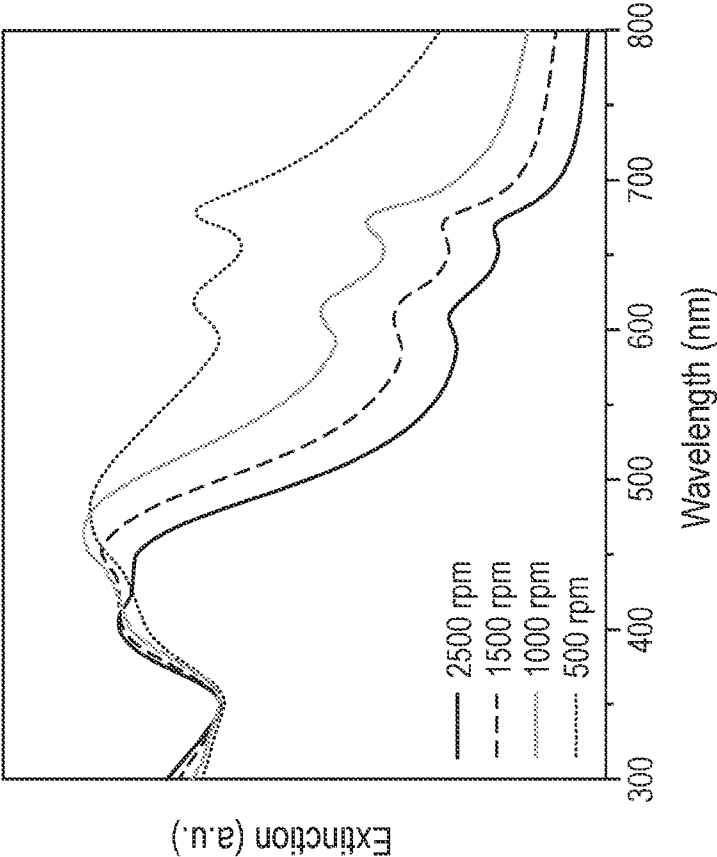


FIG. 18D

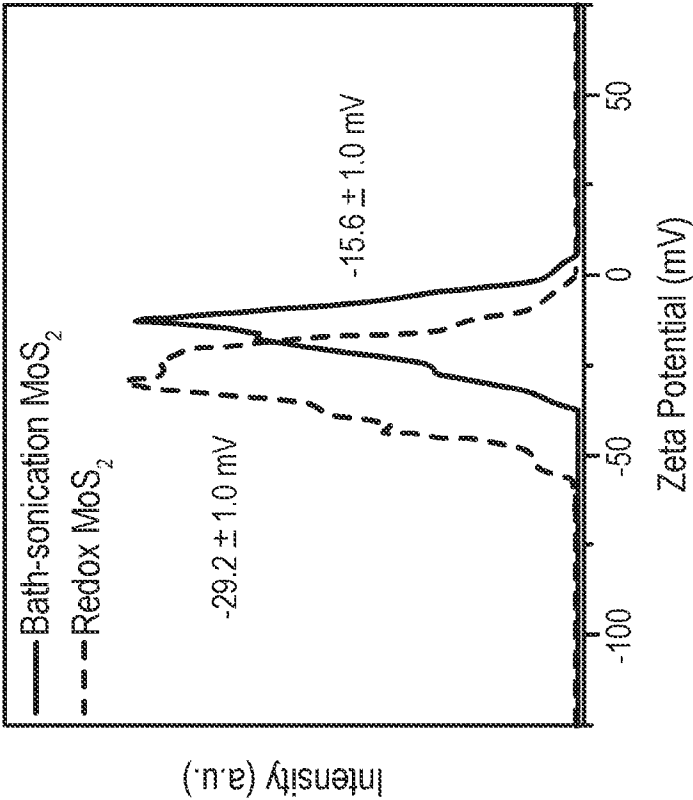


FIG. 18C

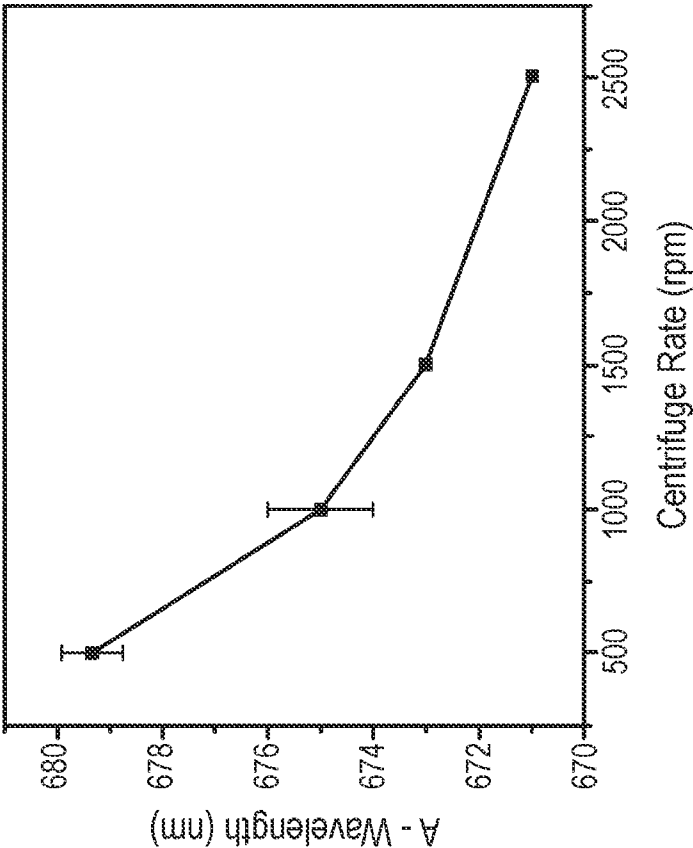


FIG. 19B

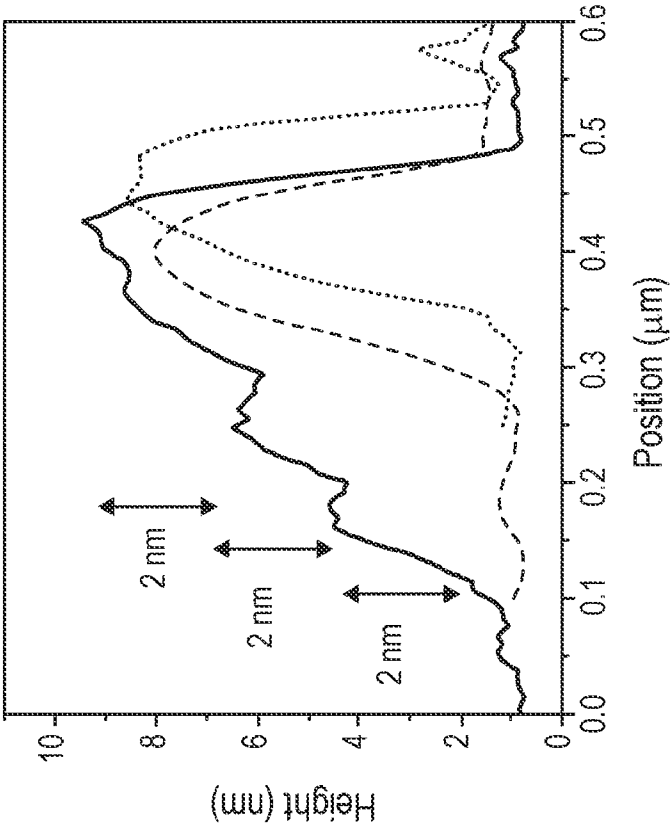


FIG. 19A

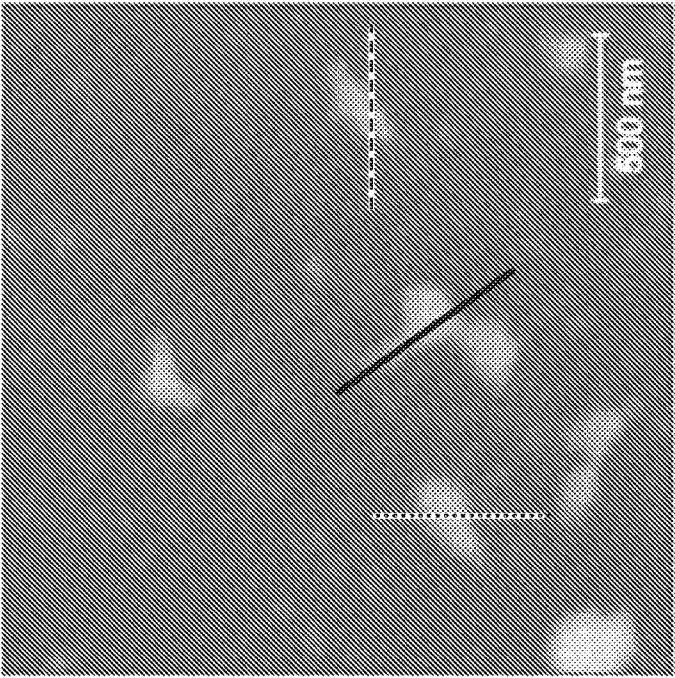


FIG. 19D

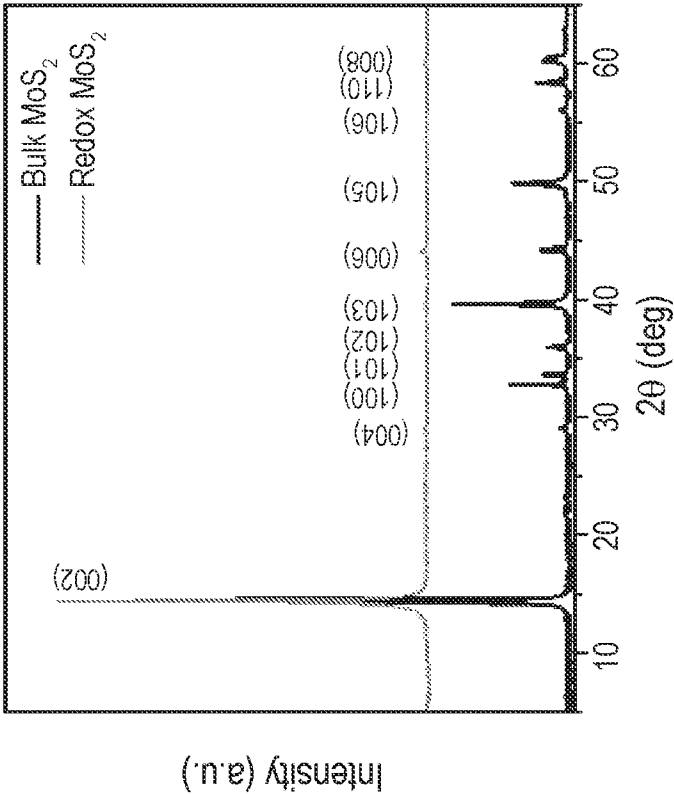


FIG. 19C

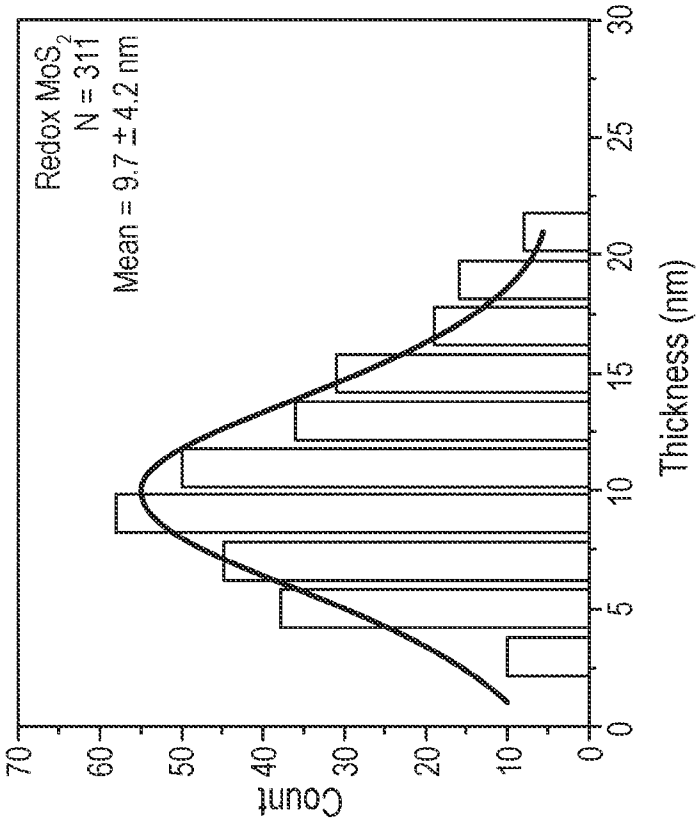


FIG.19F

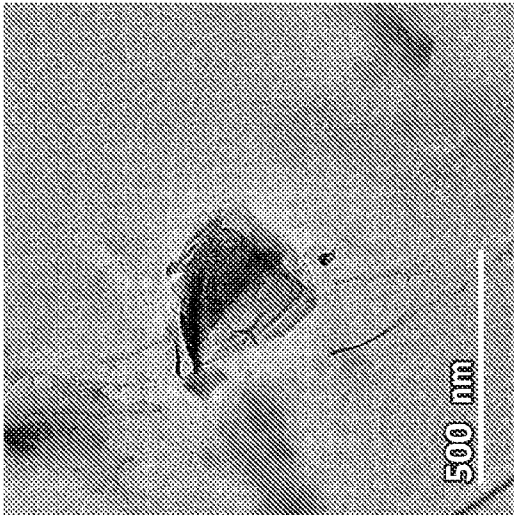


FIG.19H

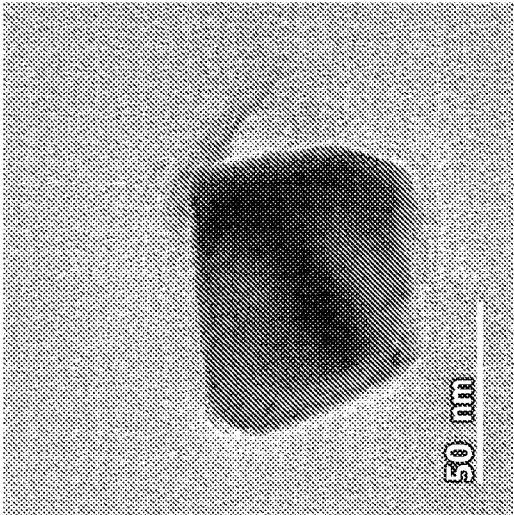


FIG.19E

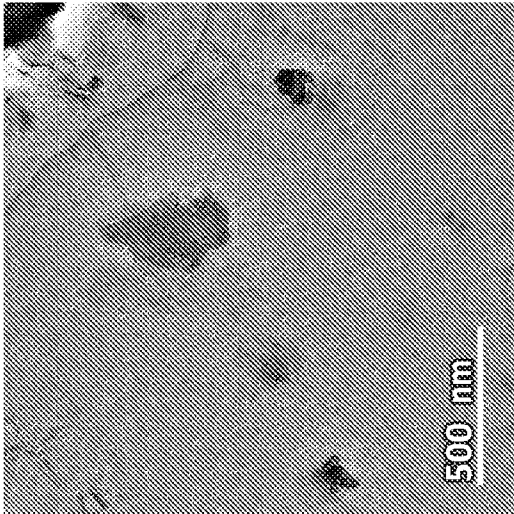


FIG.19G

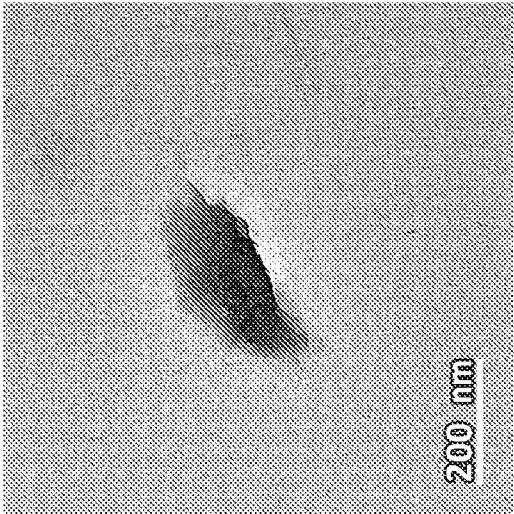


FIG. 20B

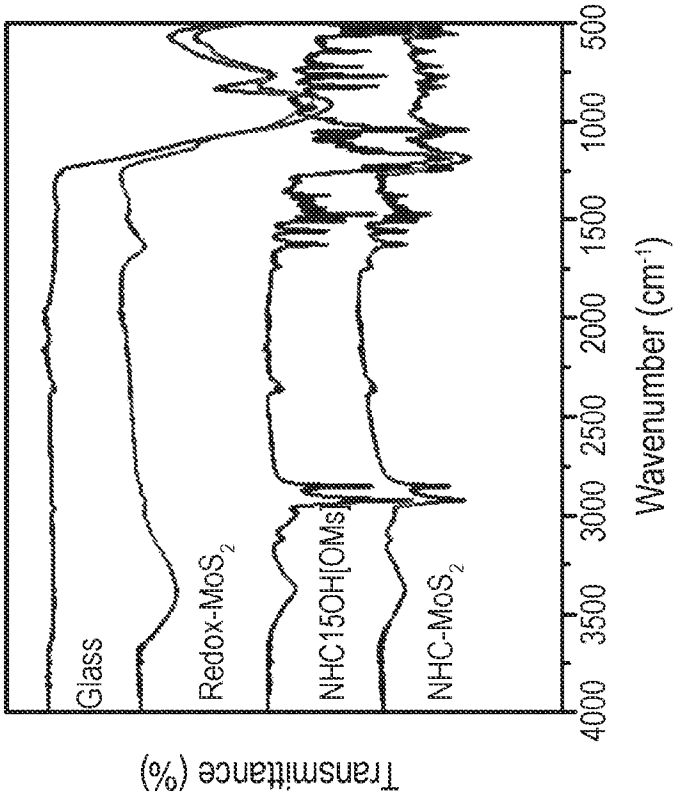


FIG. 20A

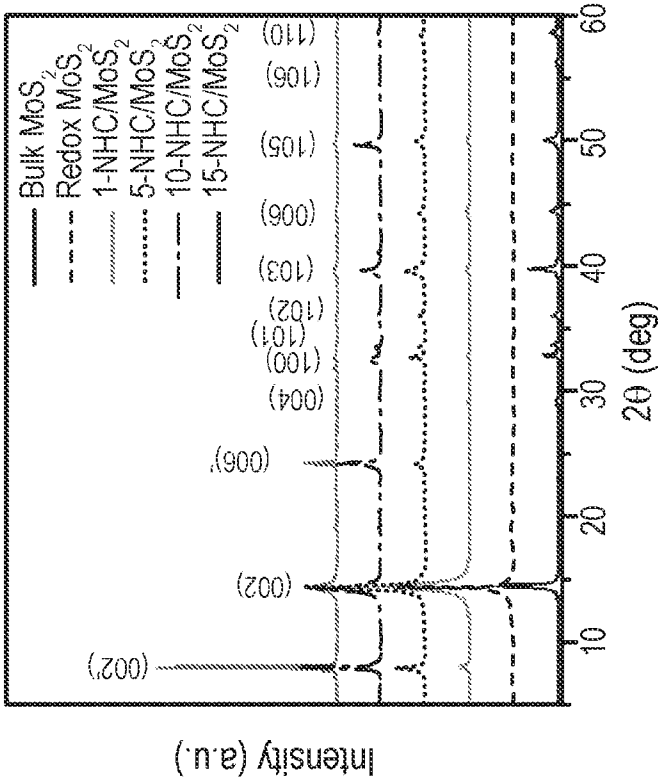


FIG. 20D

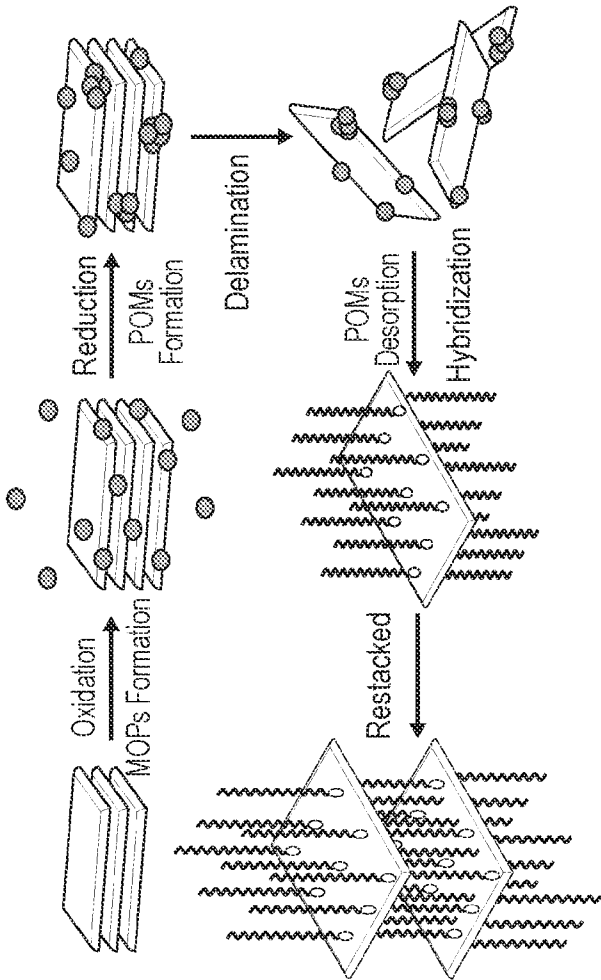
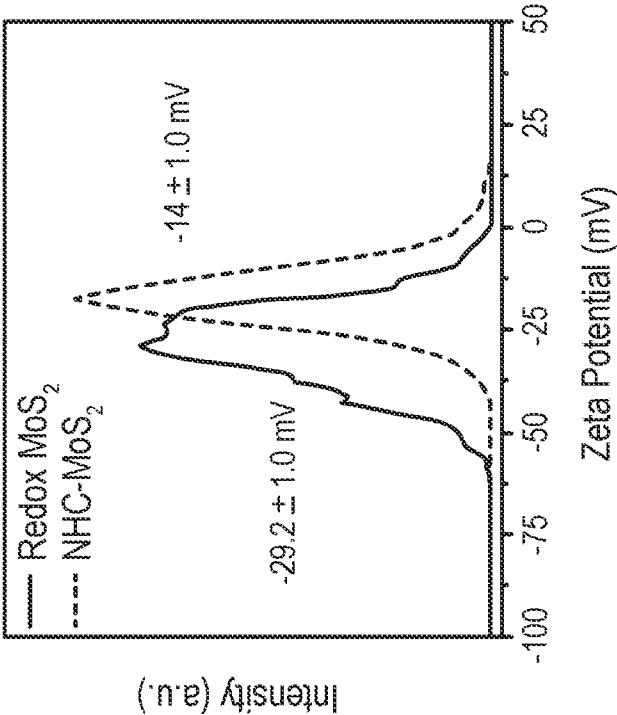


FIG. 20C



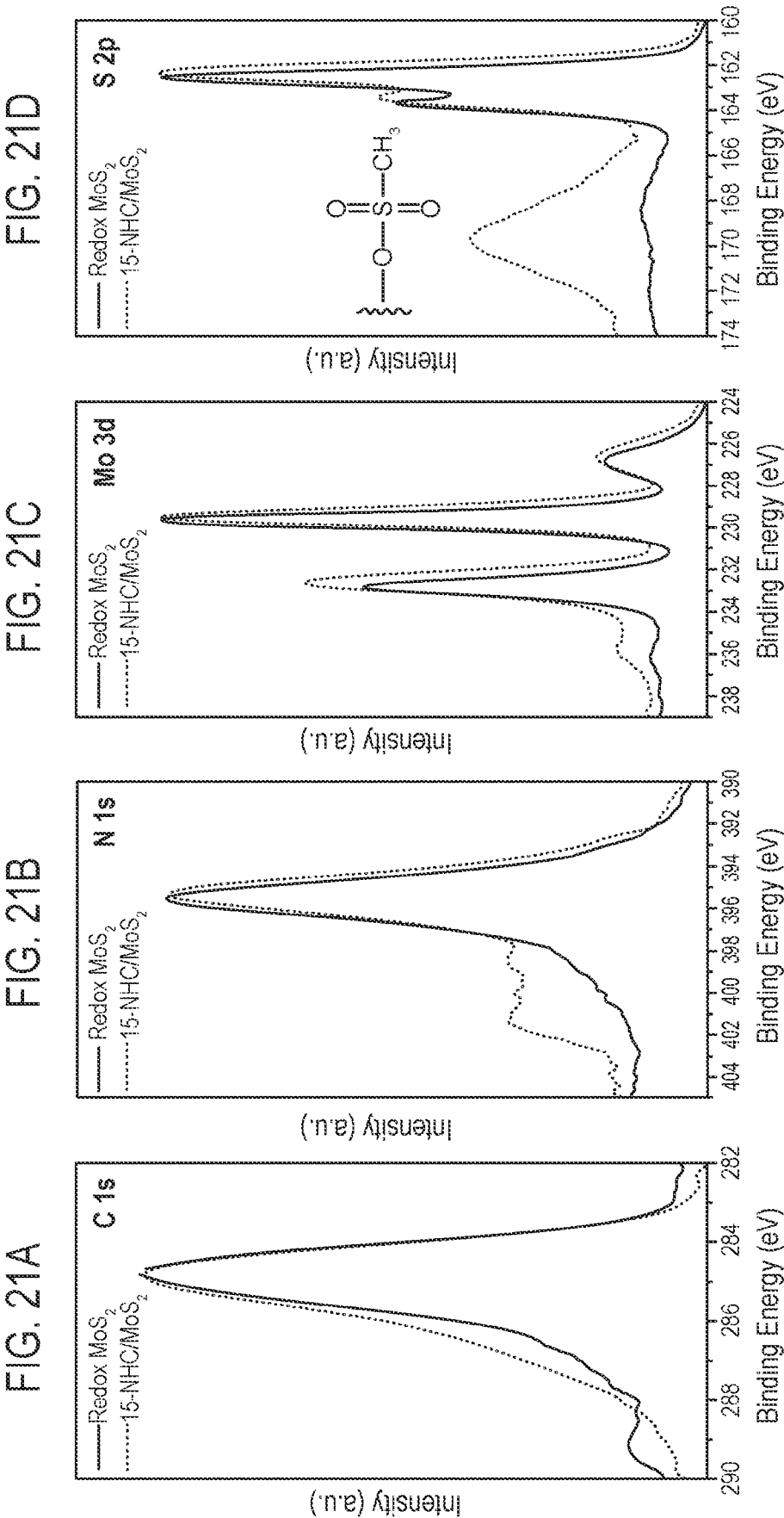


FIG. 22B

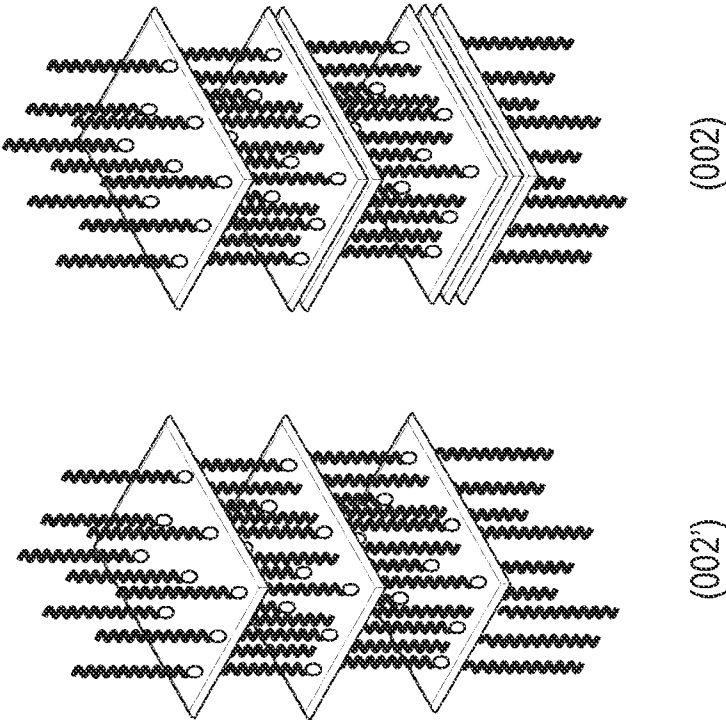


FIG. 22A

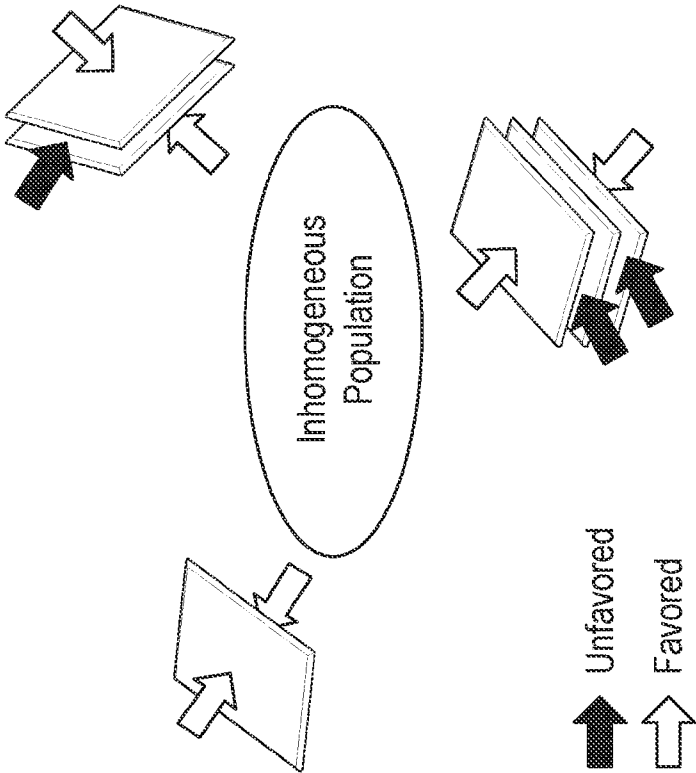


FIG. 23B

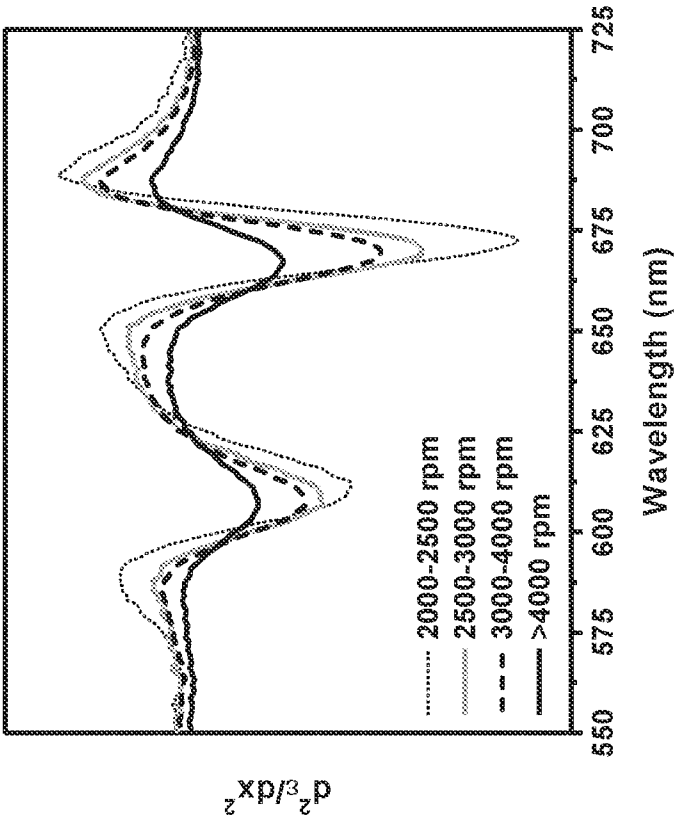


FIG. 23A

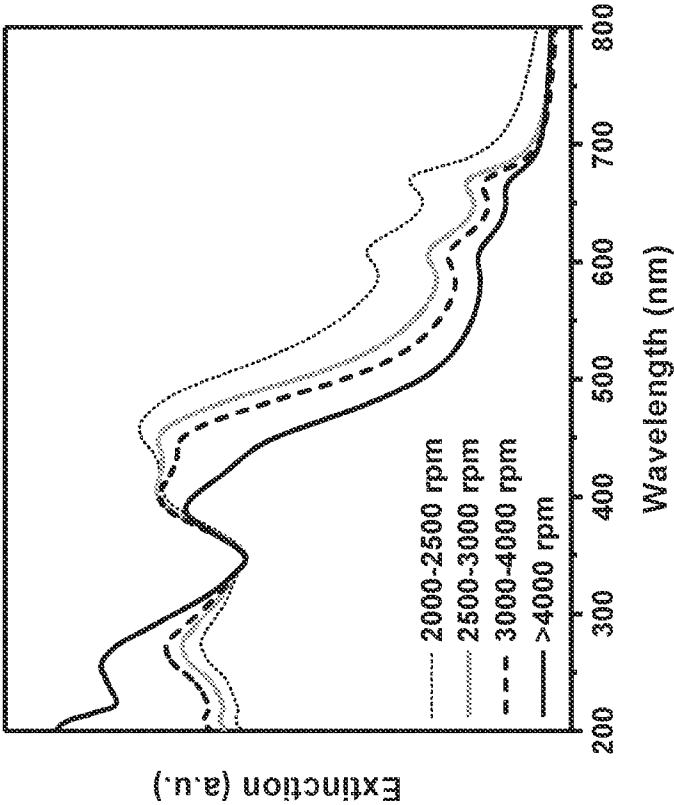


FIG. 23D

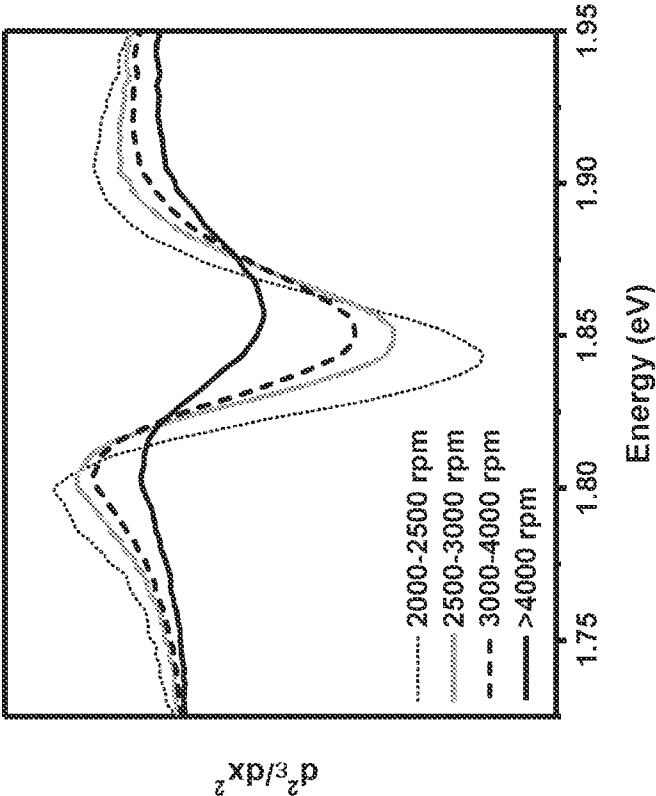


FIG. 23C

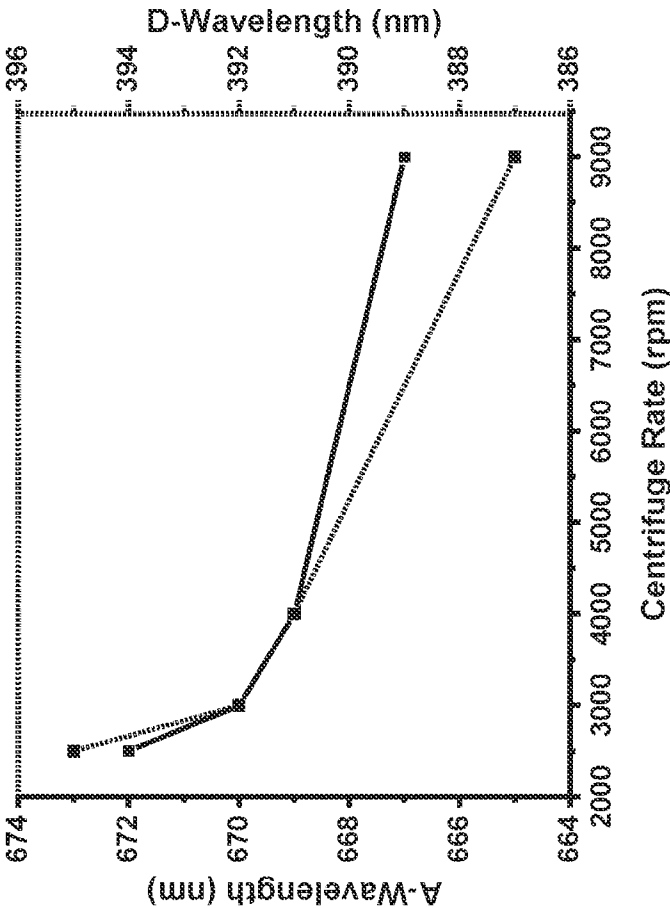


FIG. 23F

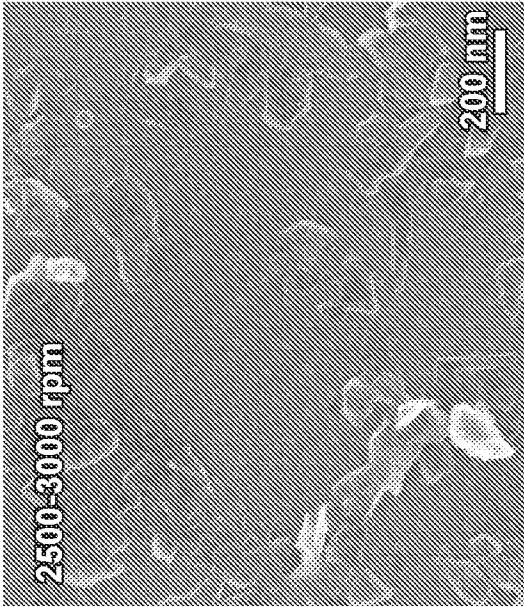


FIG. 23H

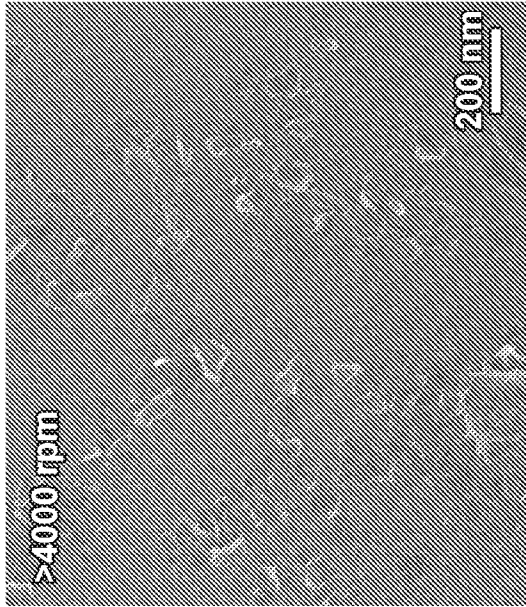


FIG. 23E

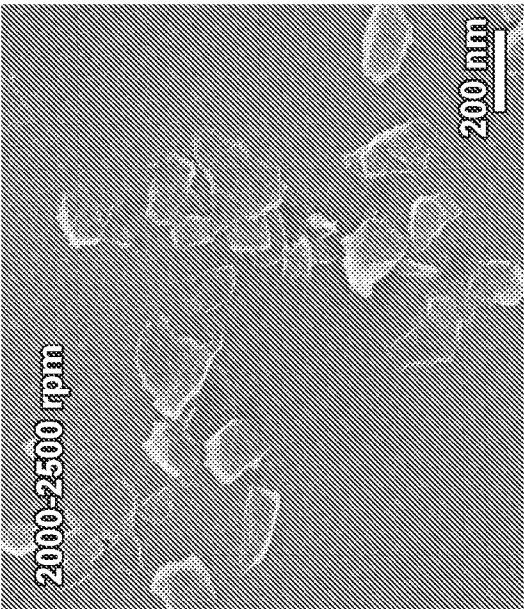


FIG. 23G

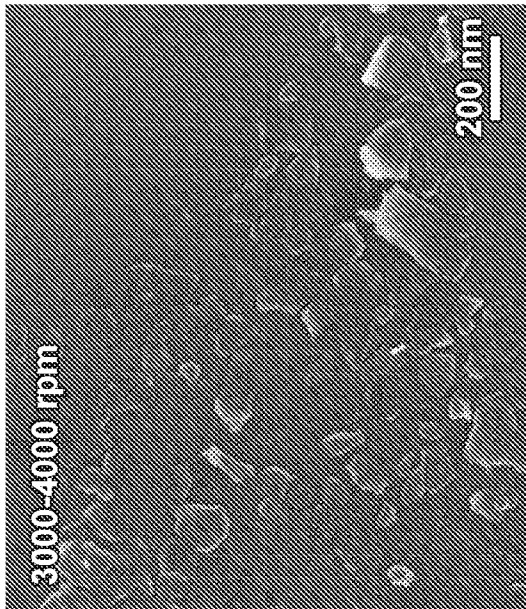


FIG. 23I

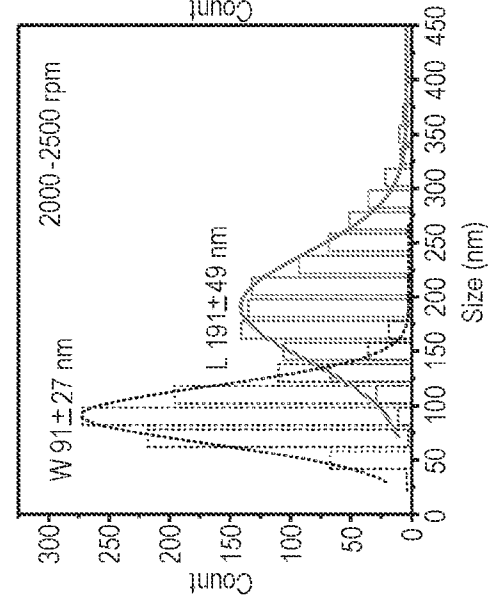


FIG. 23J

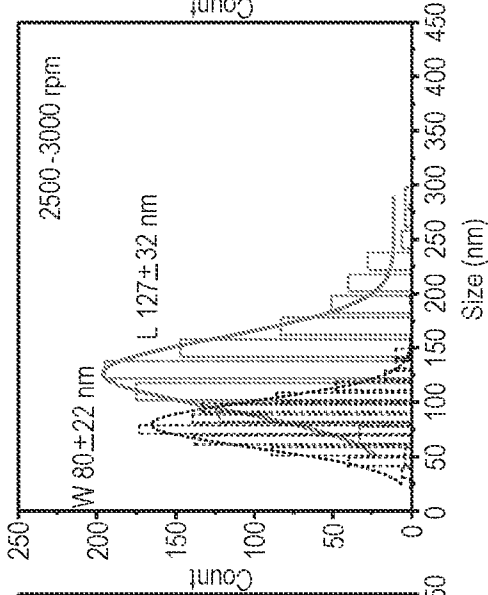


FIG. 23K

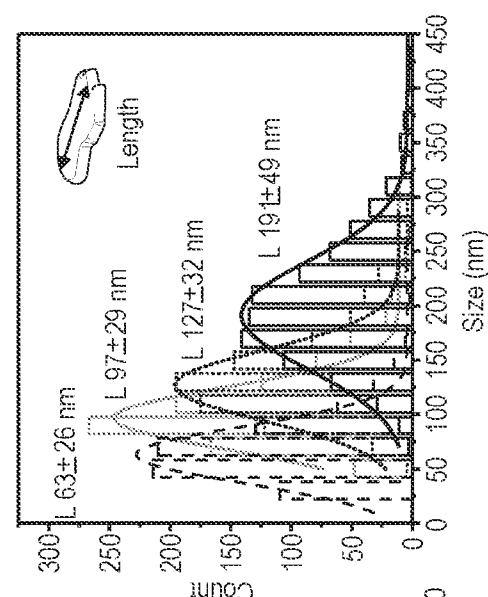


FIG. 23N

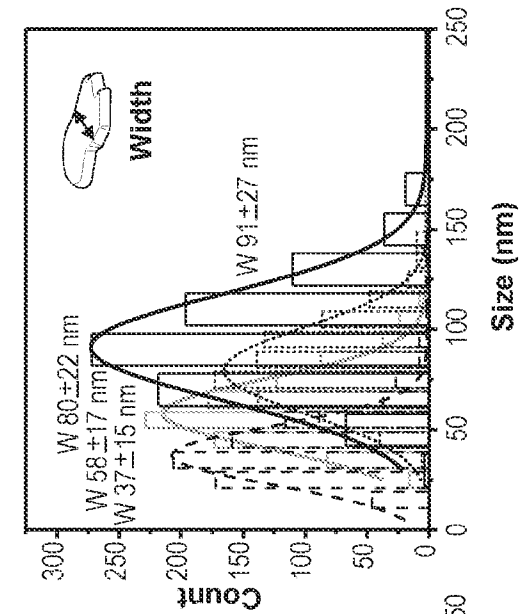


FIG. 23M

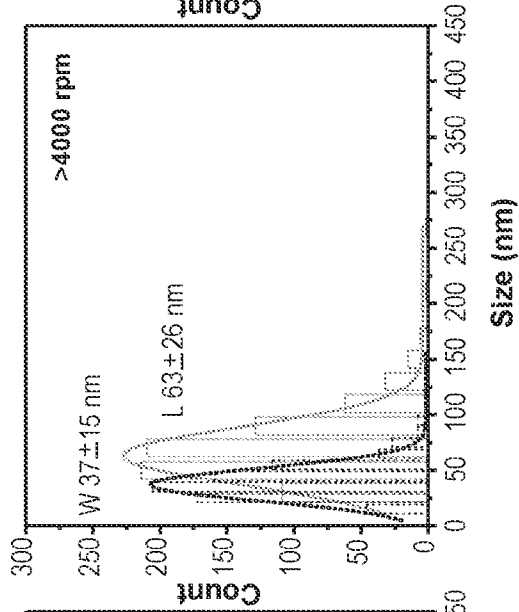
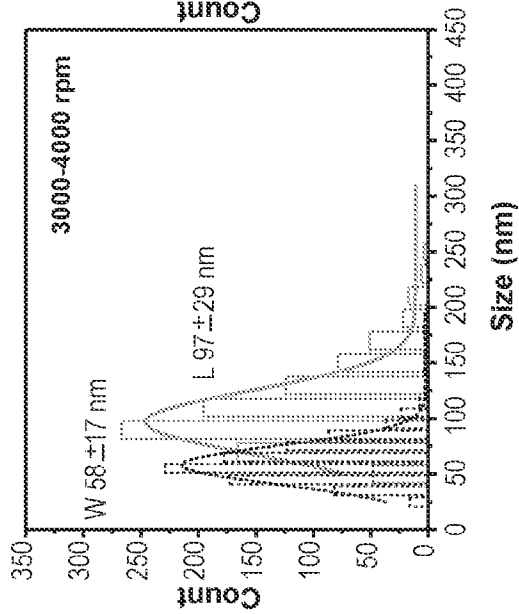


FIG. 23L



29/73

FIG. 24C

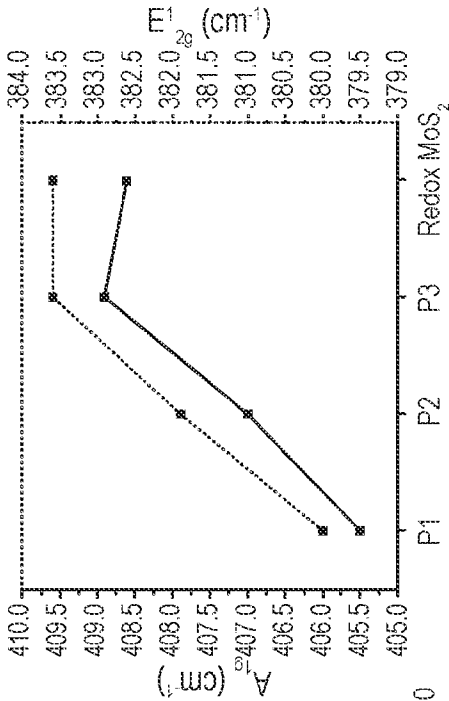


FIG. 24B

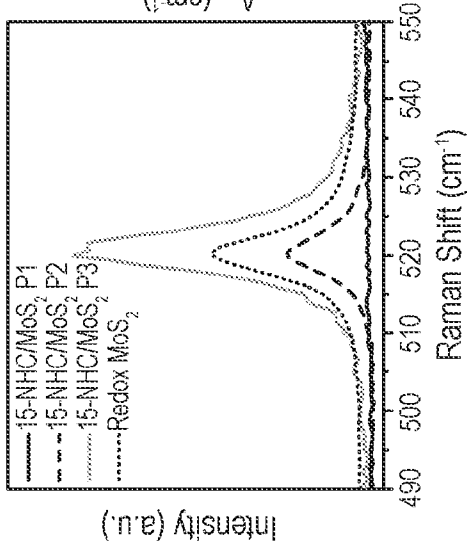


FIG. 24A

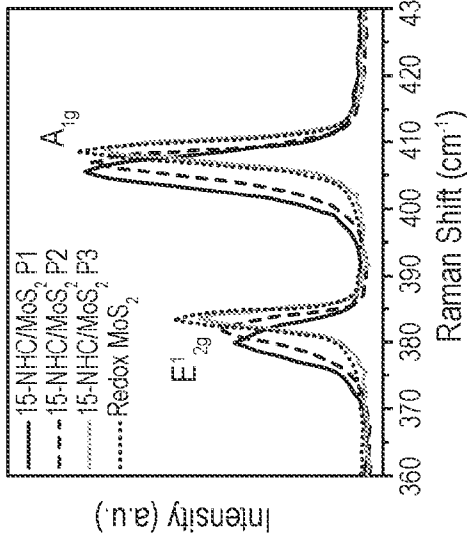


FIG. 24D

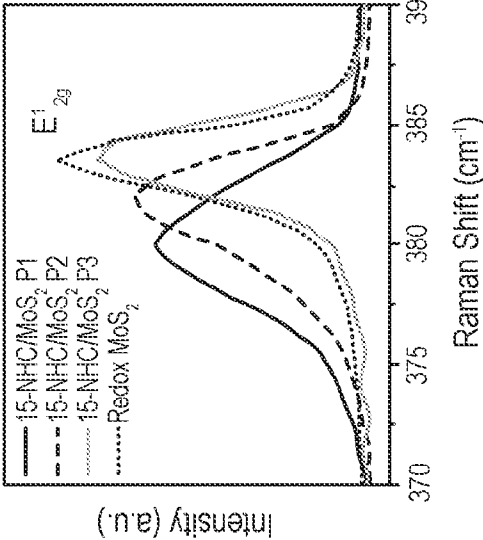


FIG. 24E

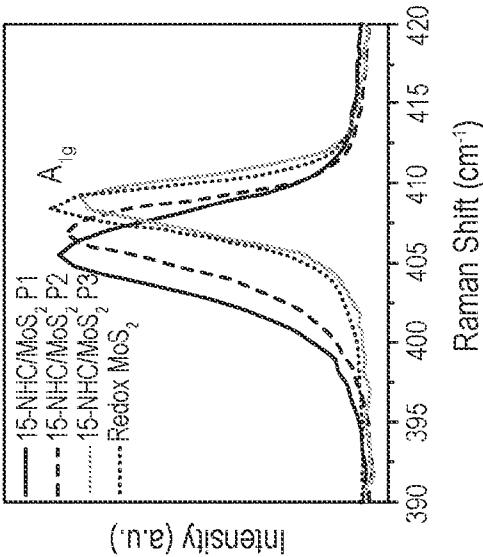


FIG. 24F

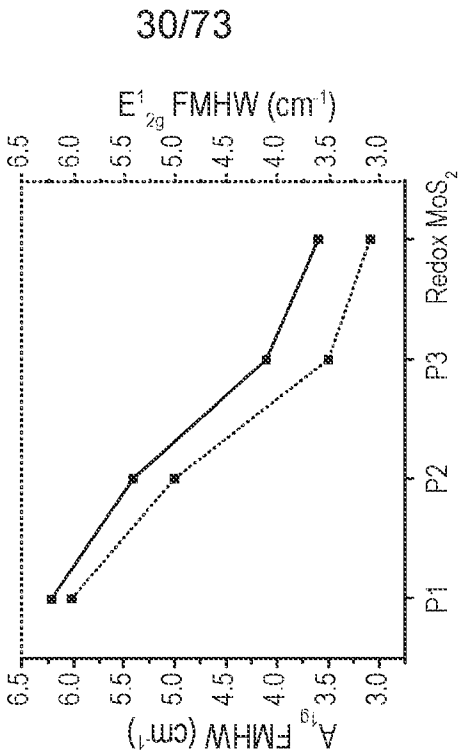


FIG. 25B

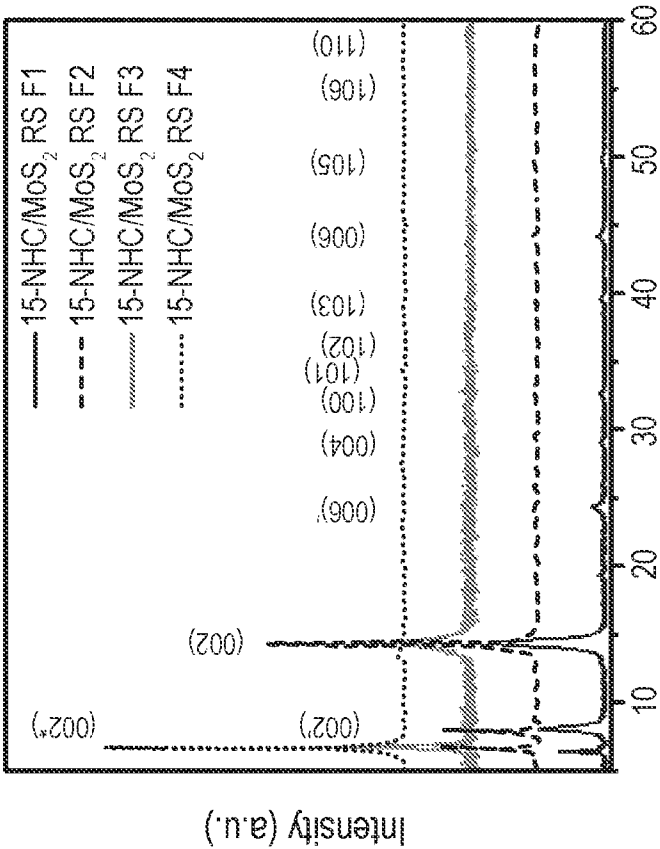


FIG. 25A

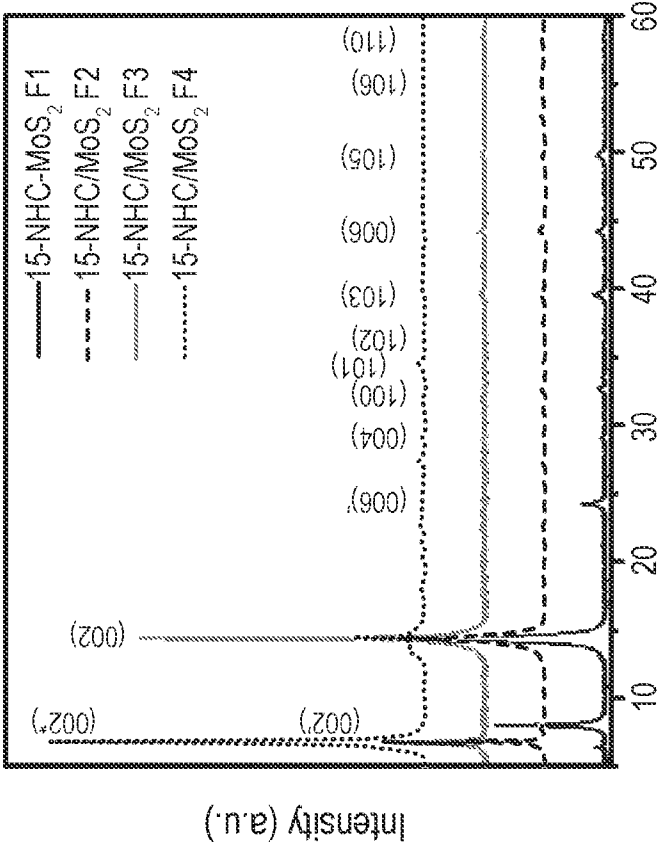


FIG. 25D

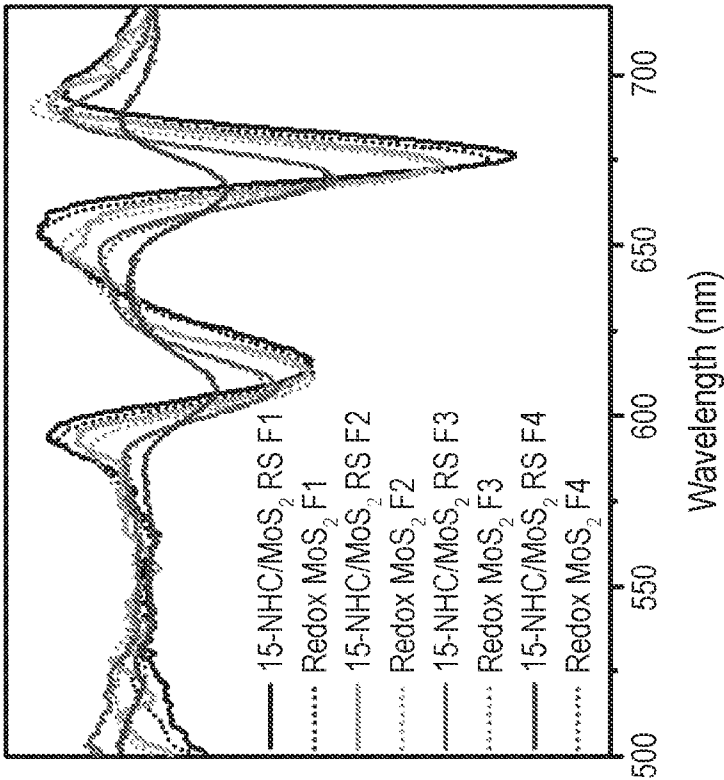


FIG. 25C

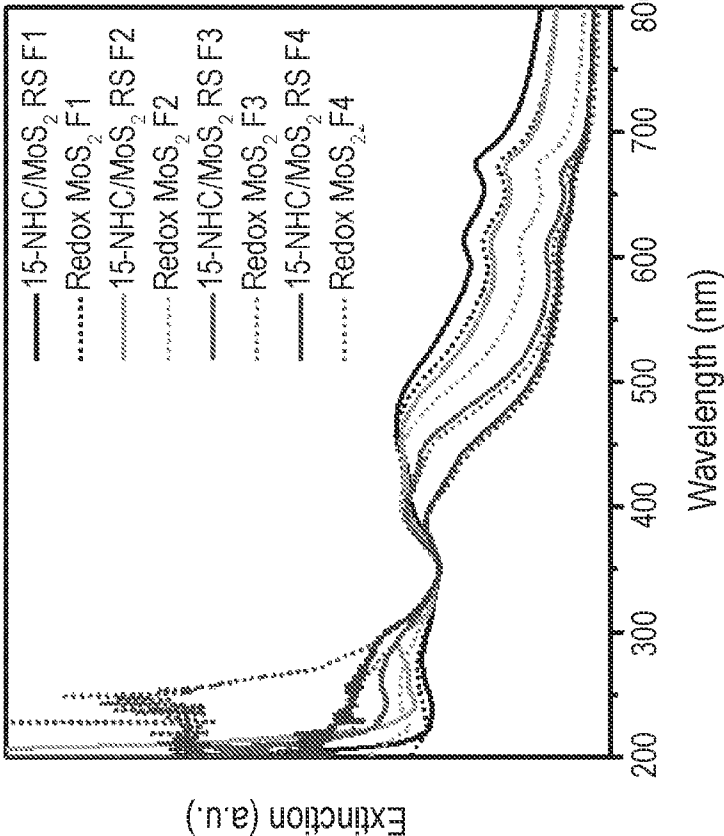


FIG. 26B

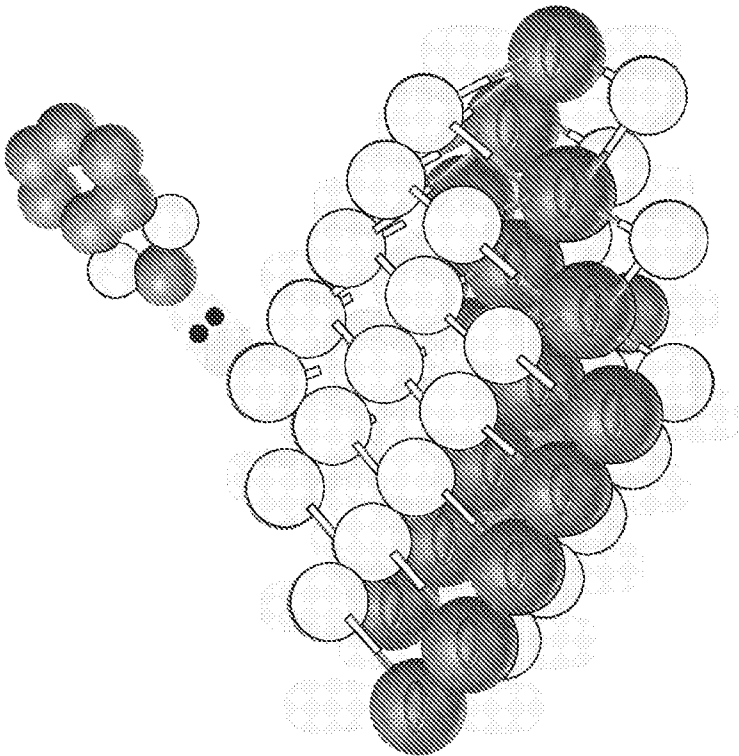


FIG. 26A

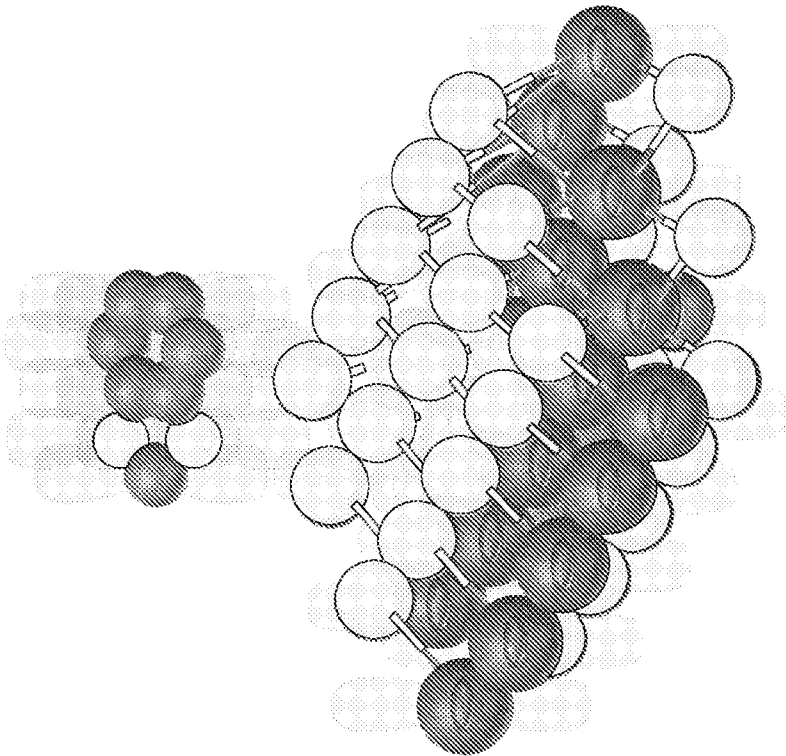


FIG. 27

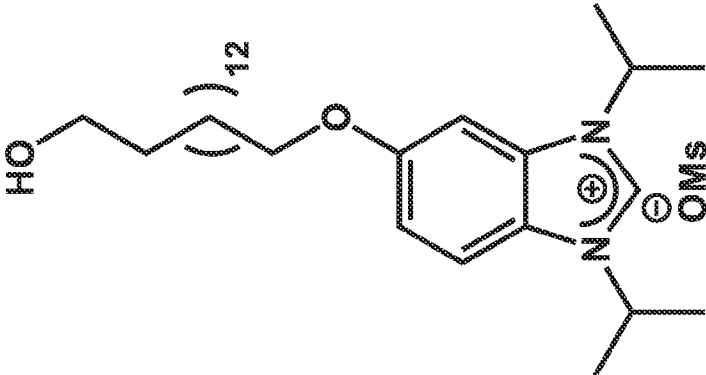


FIG. 28A

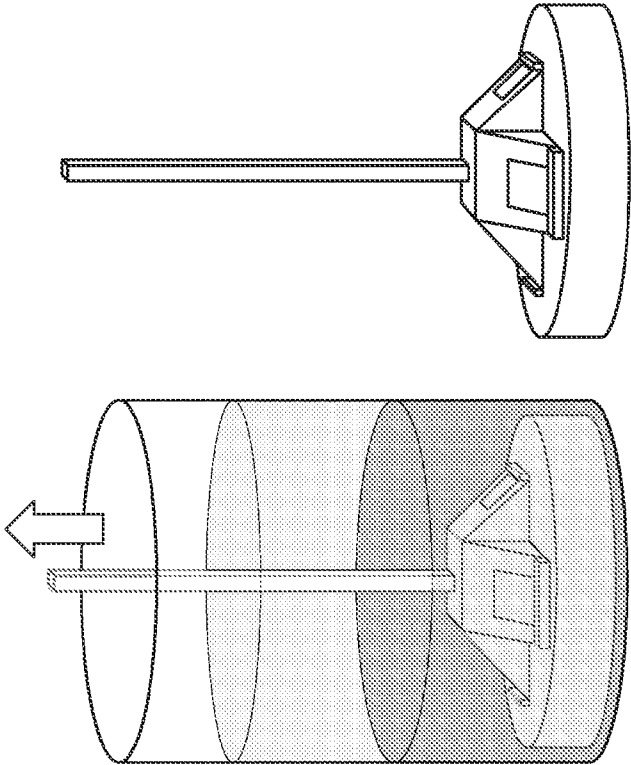


FIG. 28B

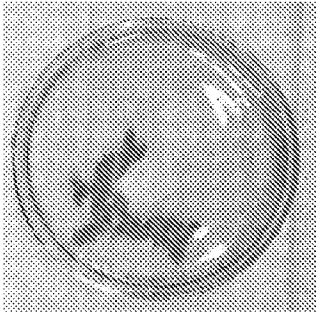


FIG. 28C

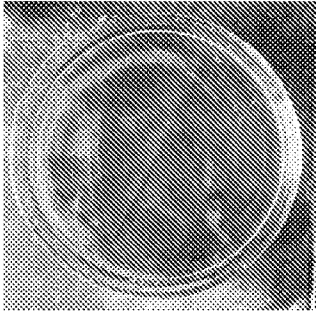


FIG. 28D

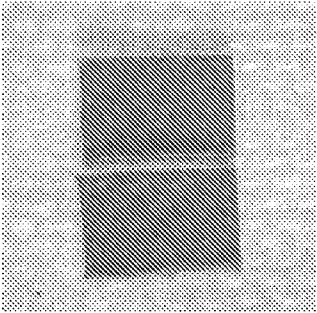


FIG. 29

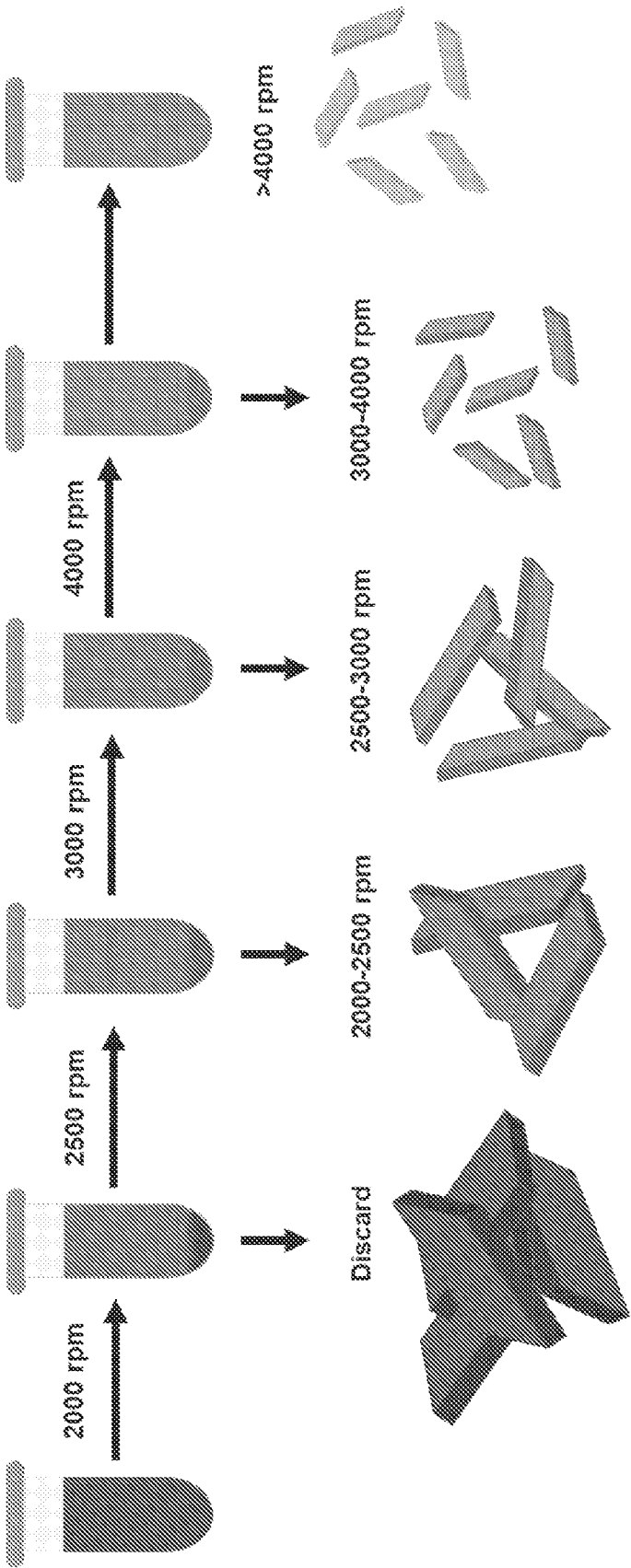


FIG. 30B

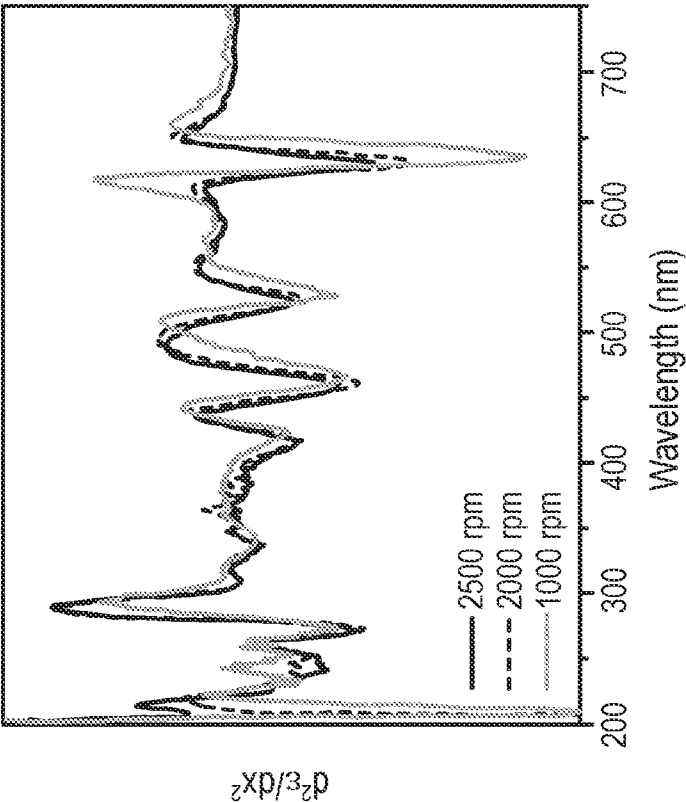


FIG. 30A

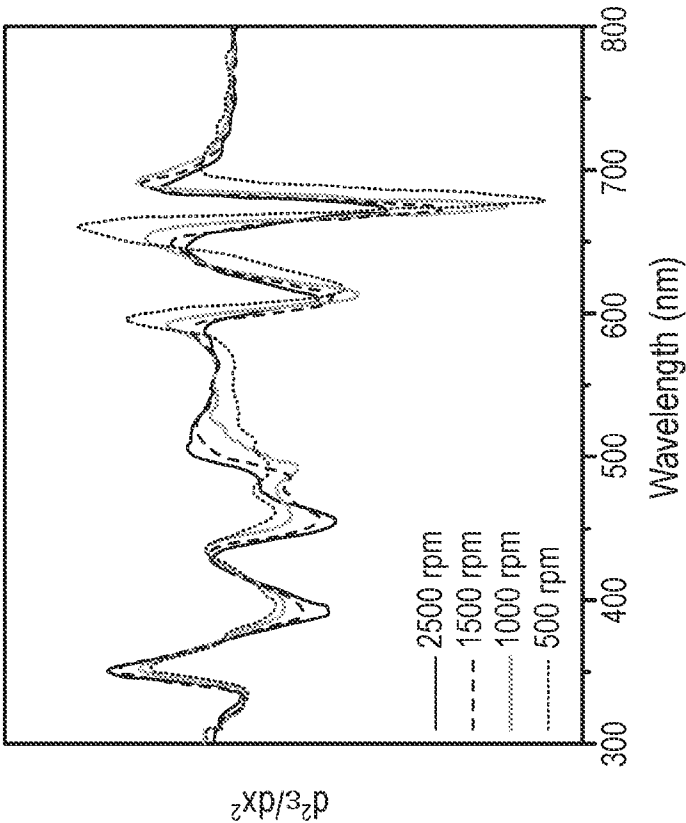


FIG. 31A

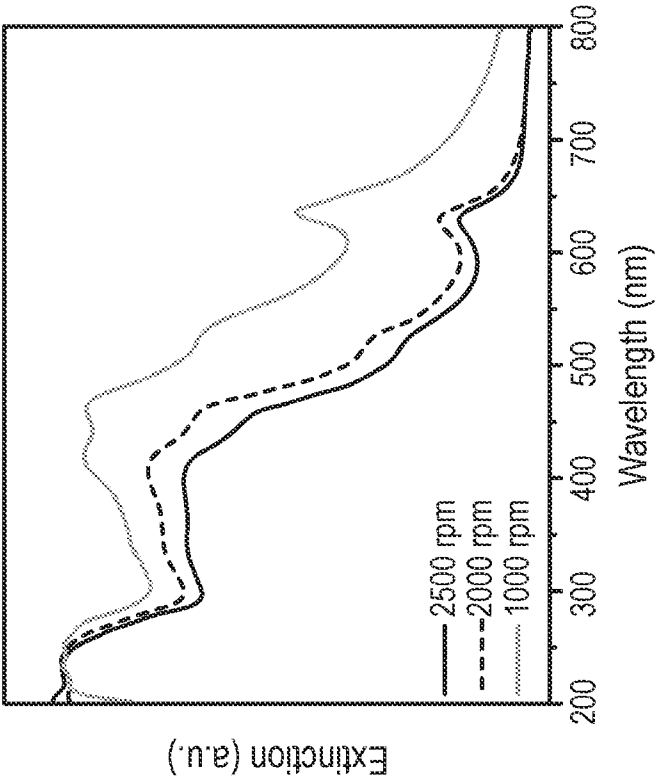


FIG. 31B

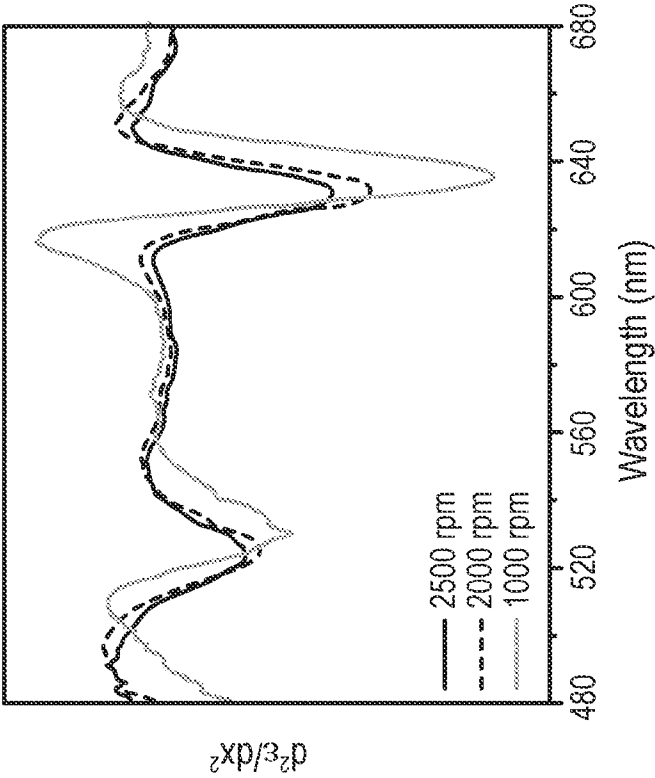


FIG. 31D

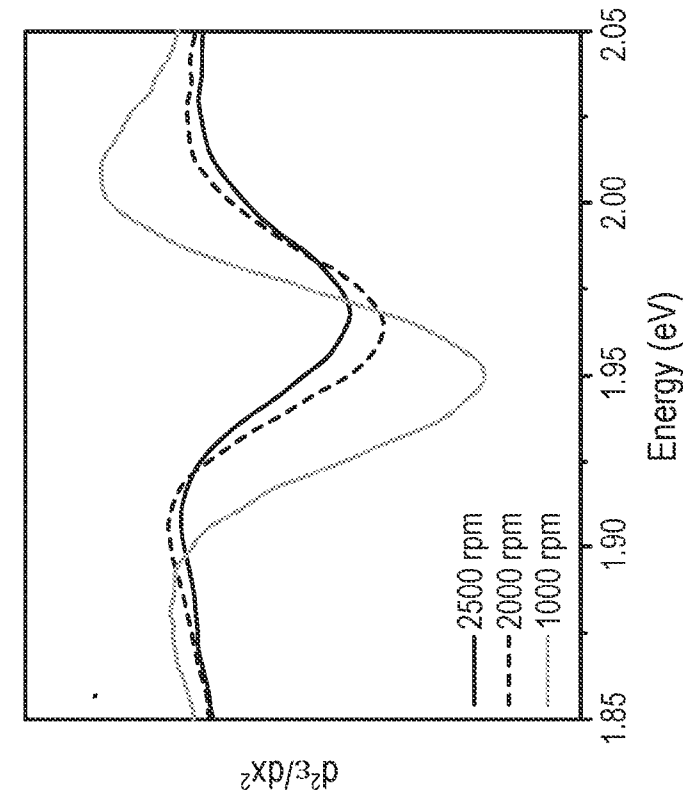


FIG. 31C

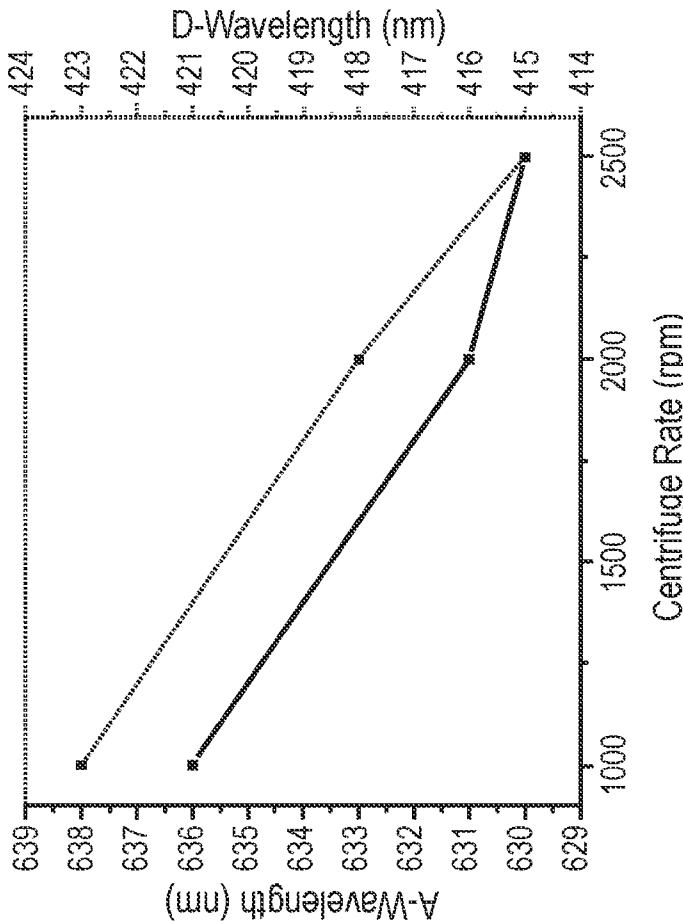


FIG. 32B

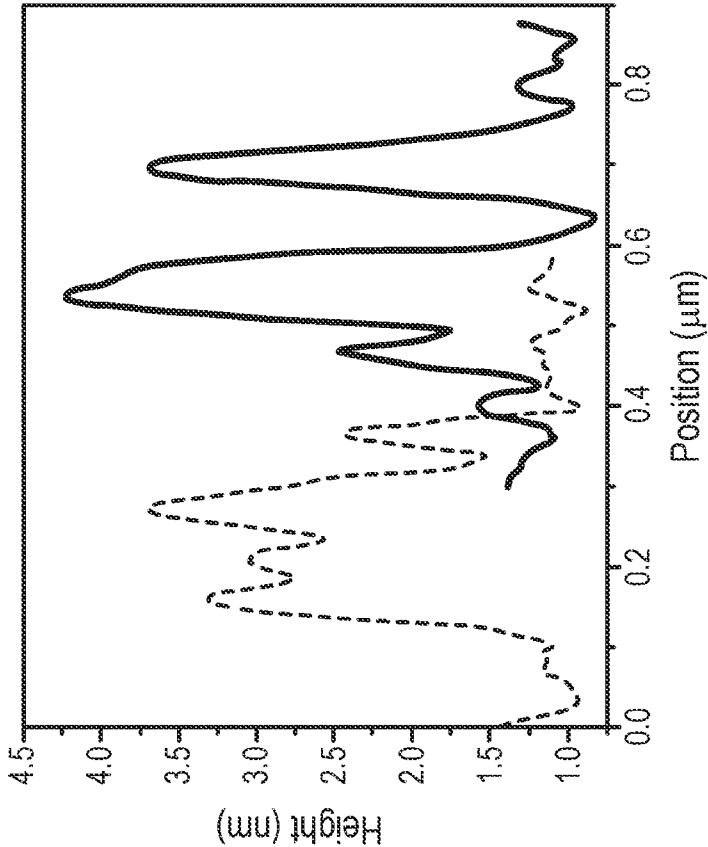


FIG. 32A

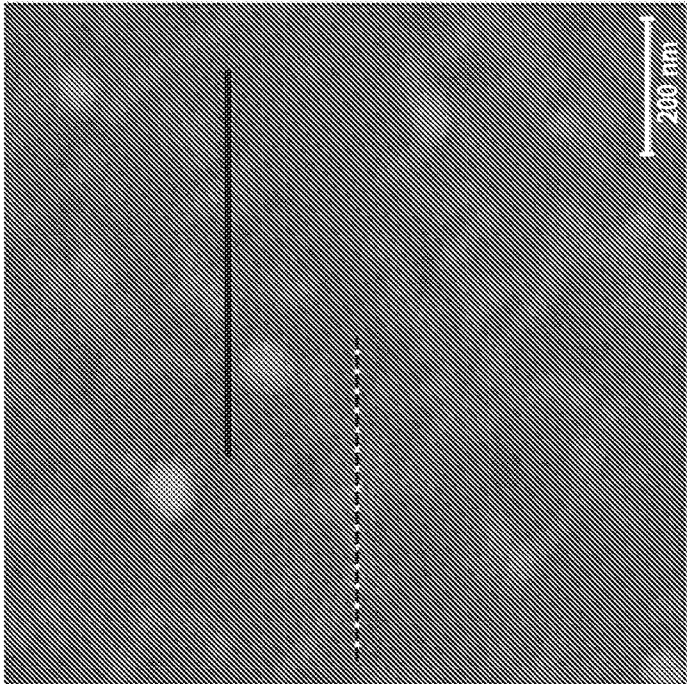


FIG. 32D

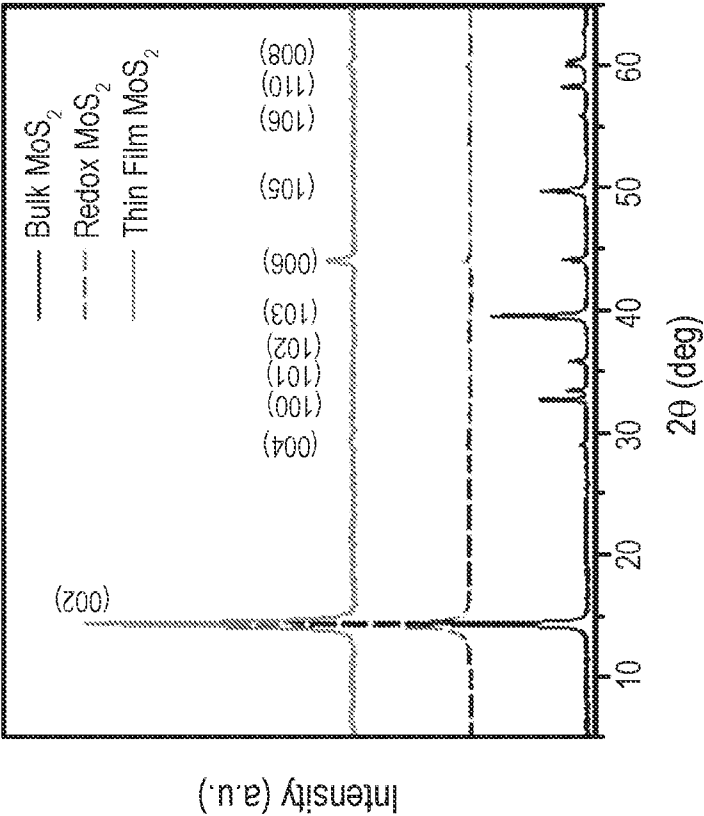


FIG. 32C

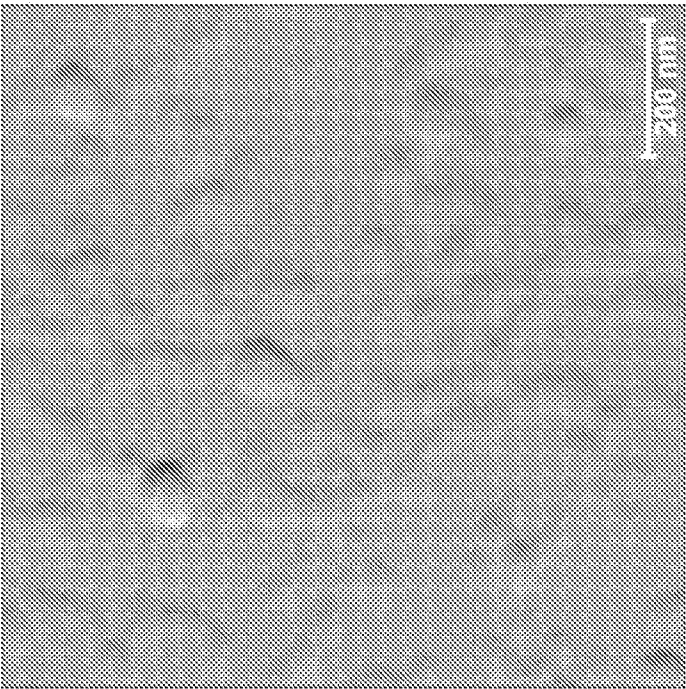


FIG. 33B

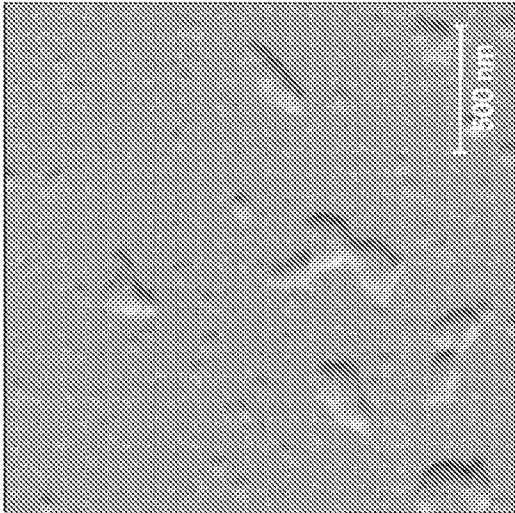


FIG. 33A

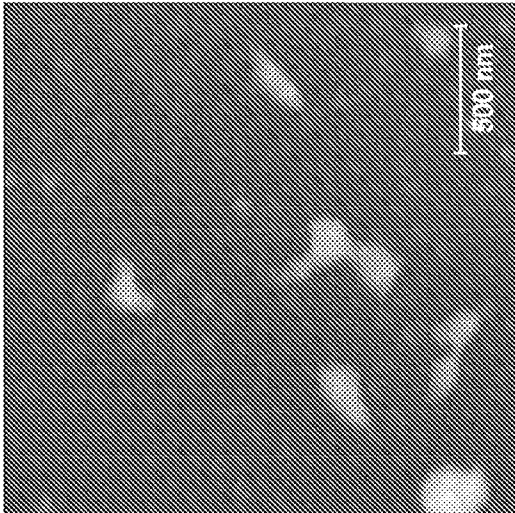


FIG. 32E

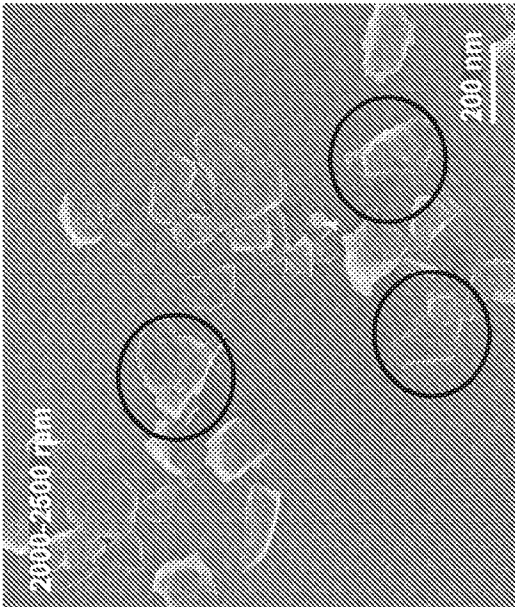


FIG. 34A

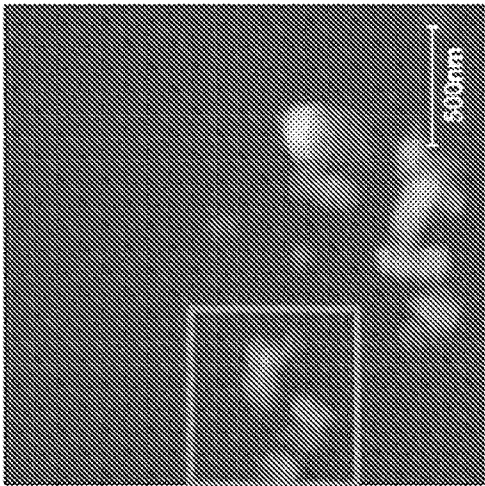


FIG. 34C

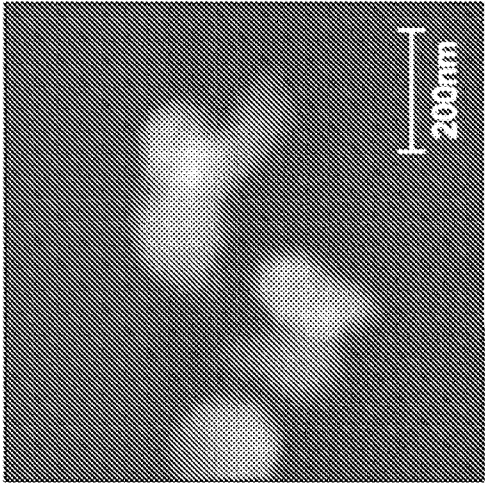


FIG. 34B

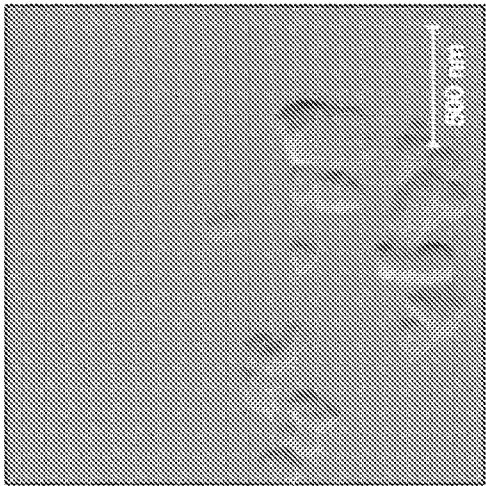


FIG. 34D

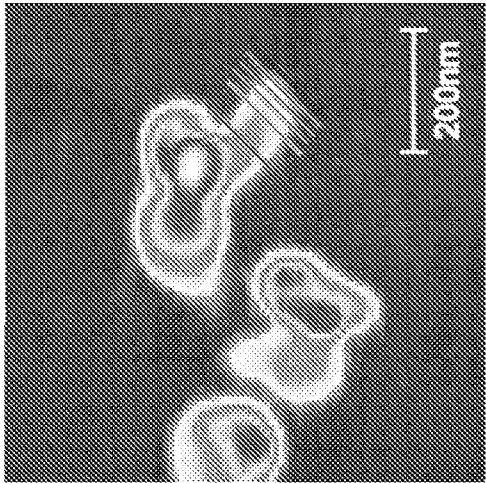


FIG. 34E

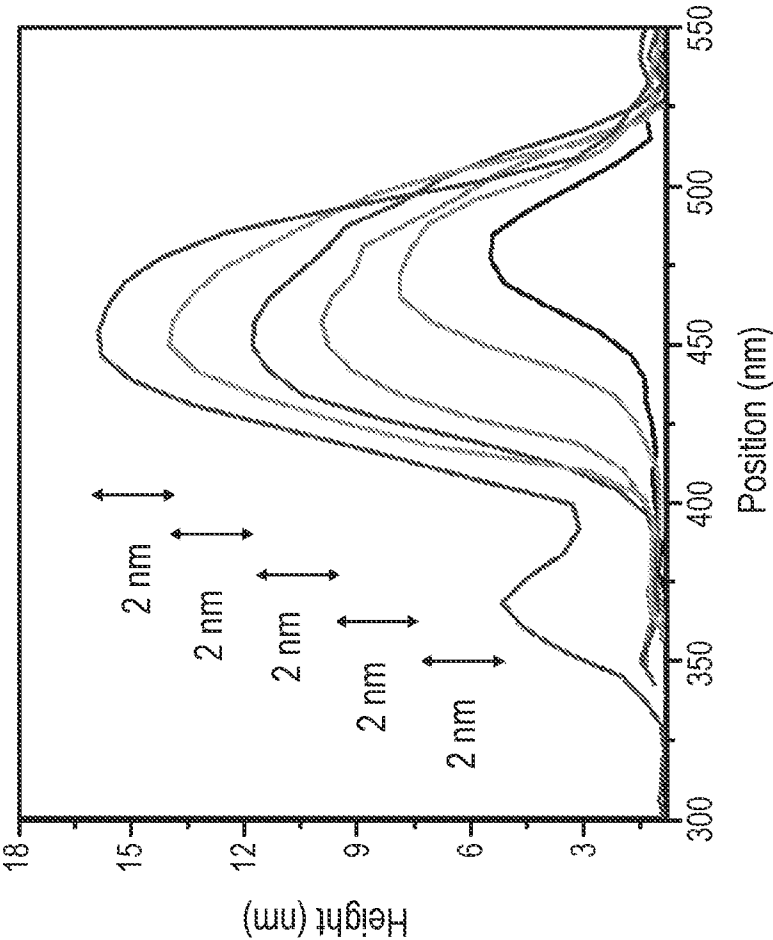


FIG. 35B

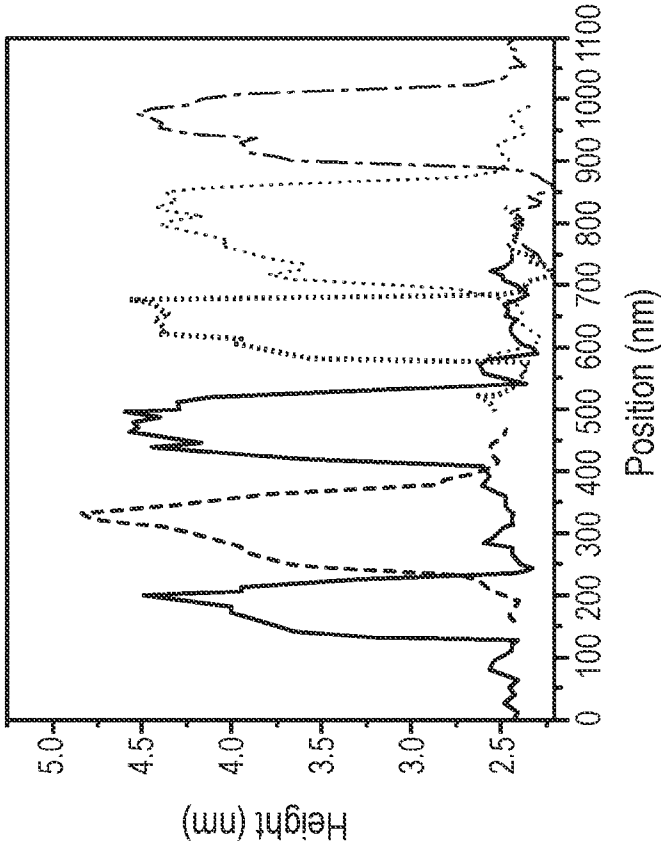


FIG. 35A

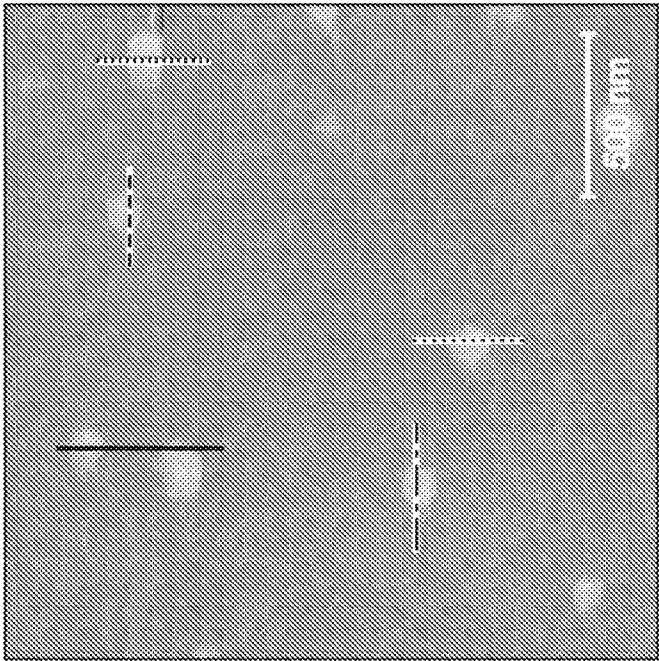


FIG. 35D

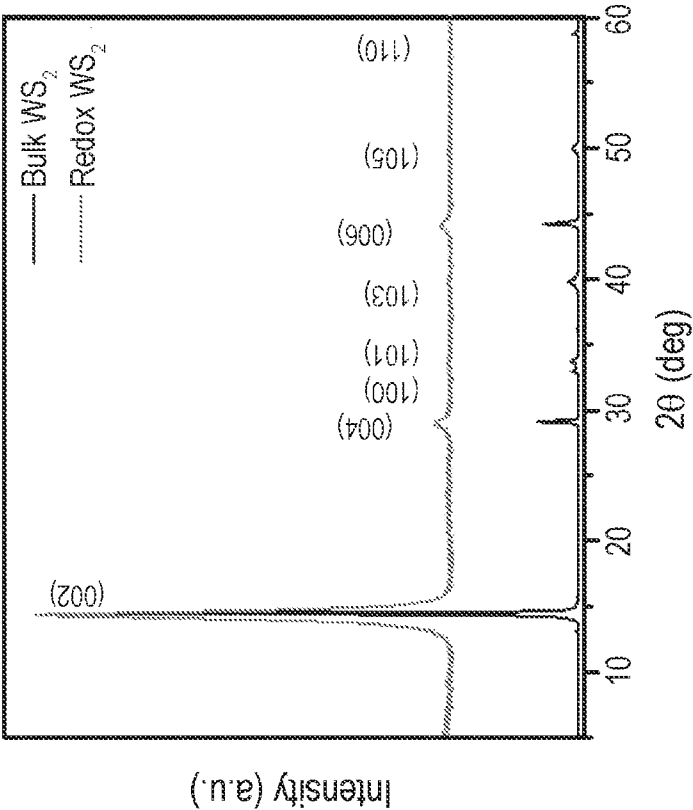


FIG. 35C

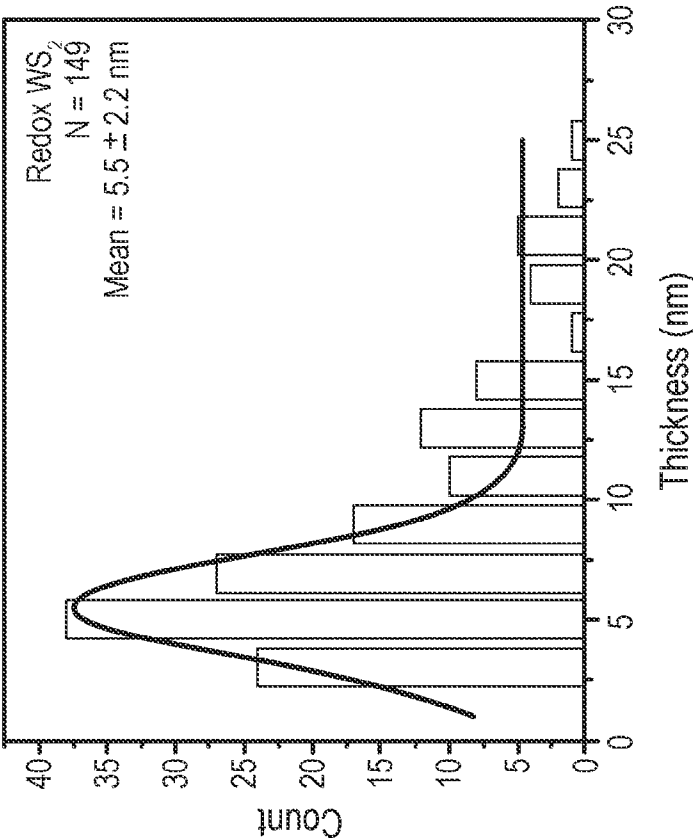
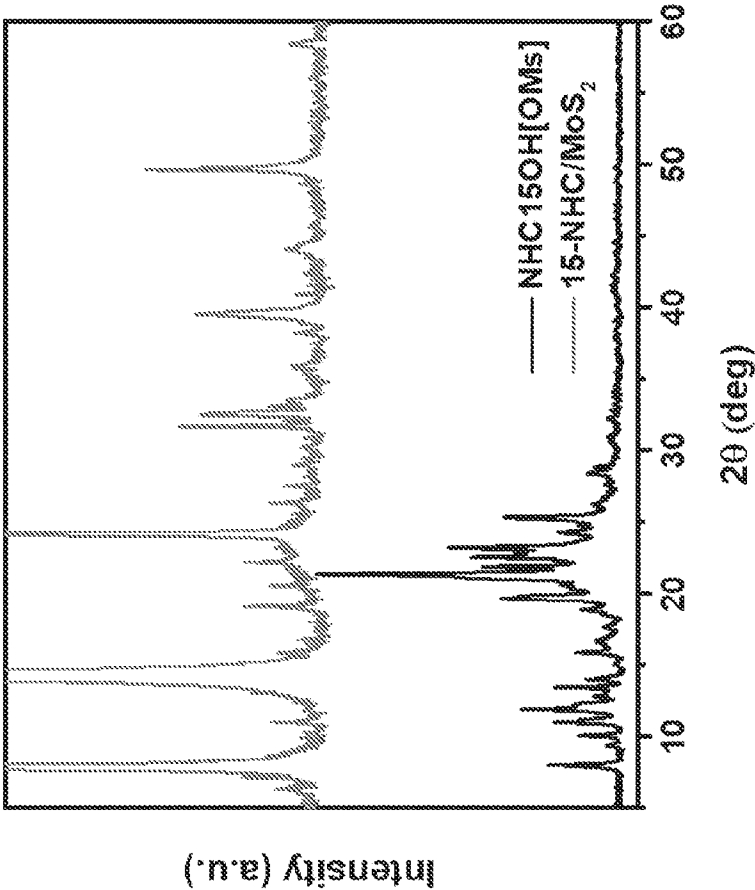


FIG. 36



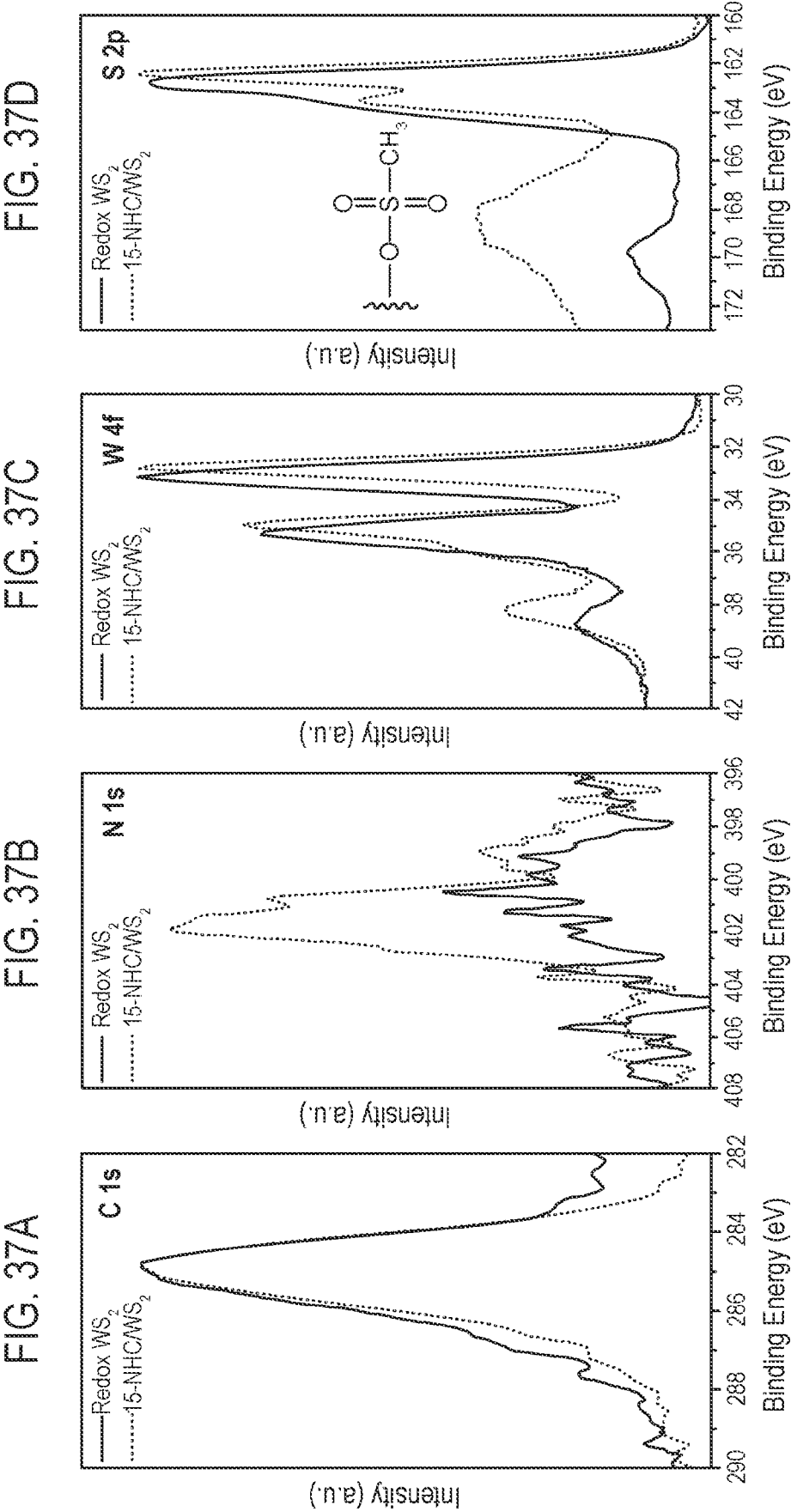


FIG. 38

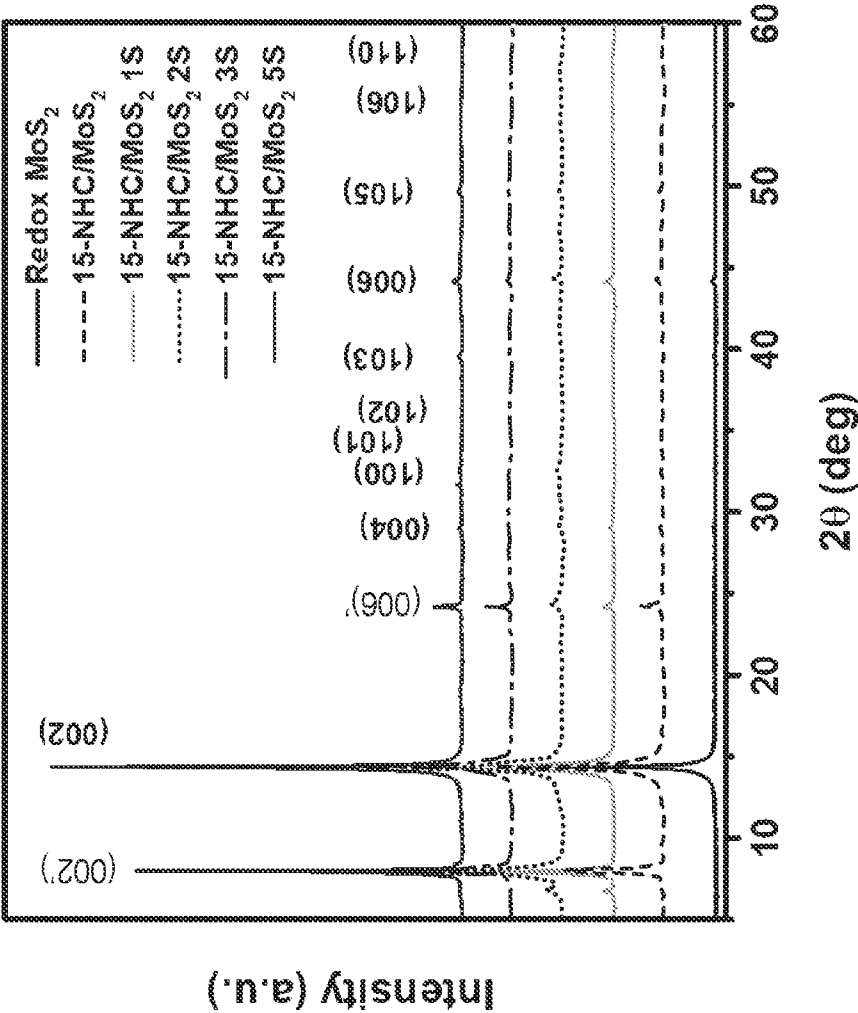


FIG. 39B

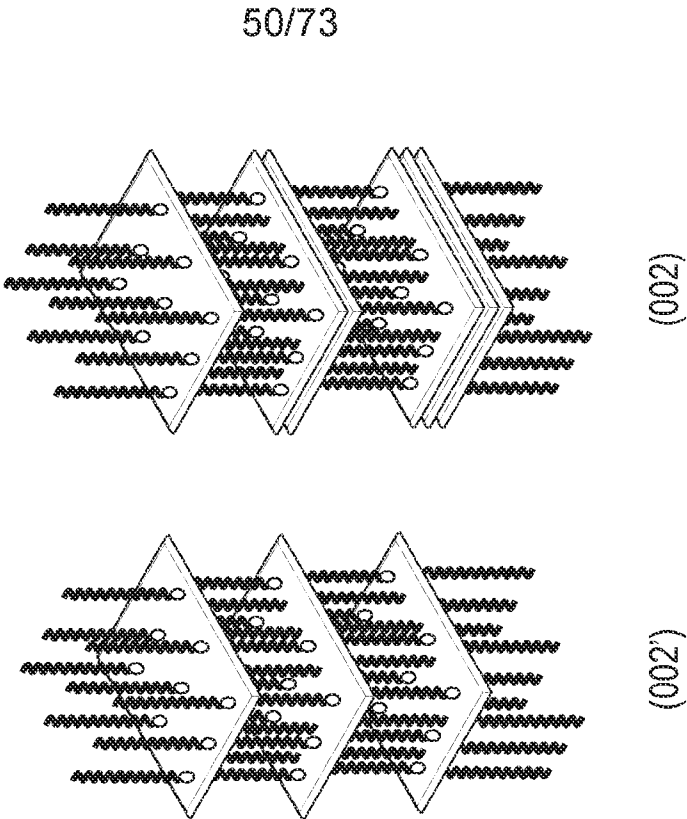


FIG. 39A

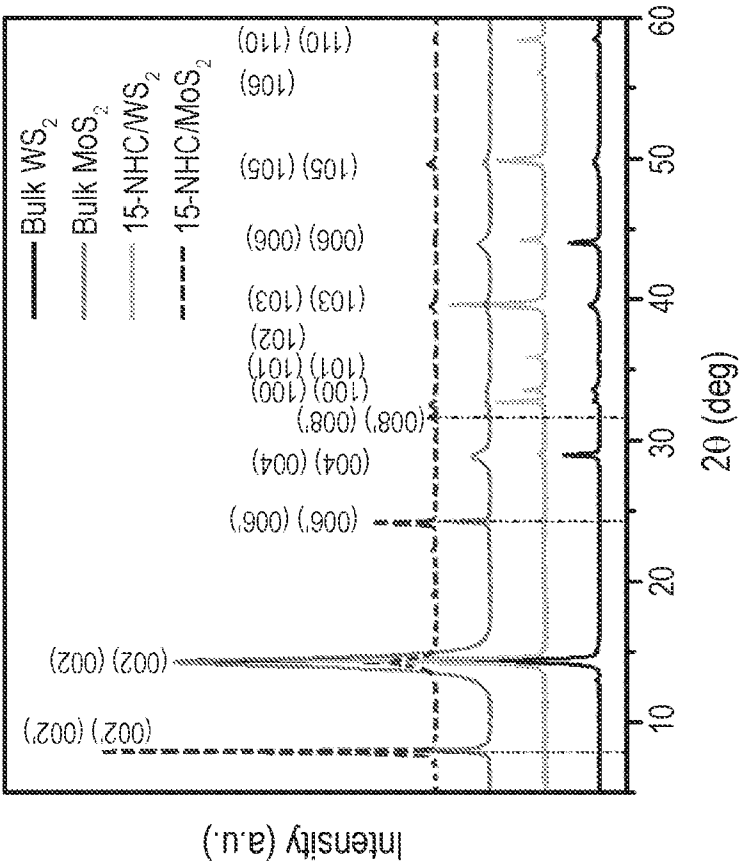


FIG. 40B

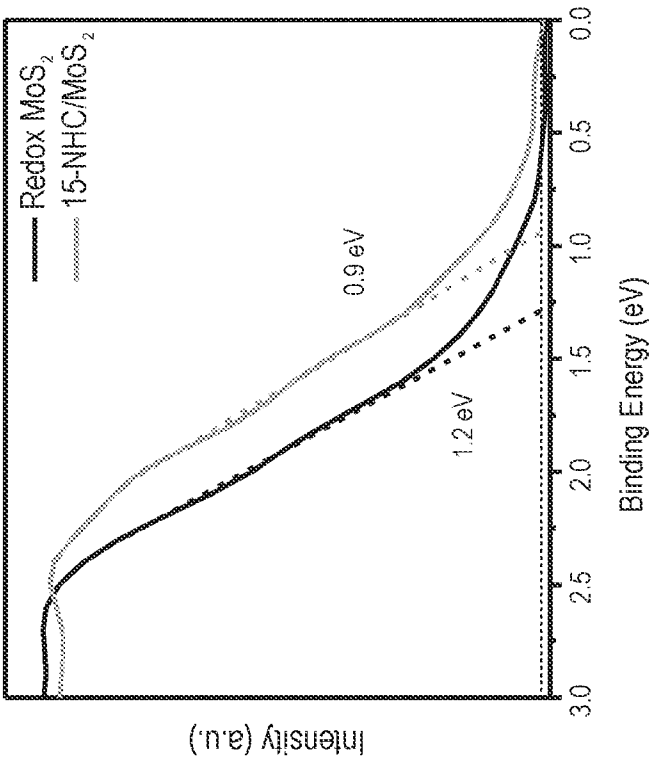


FIG. 40A

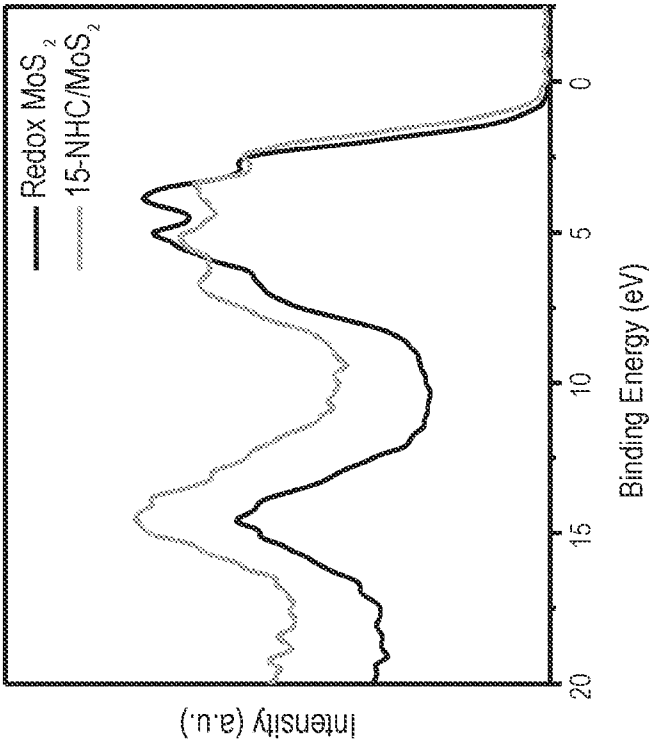


FIG. 40D

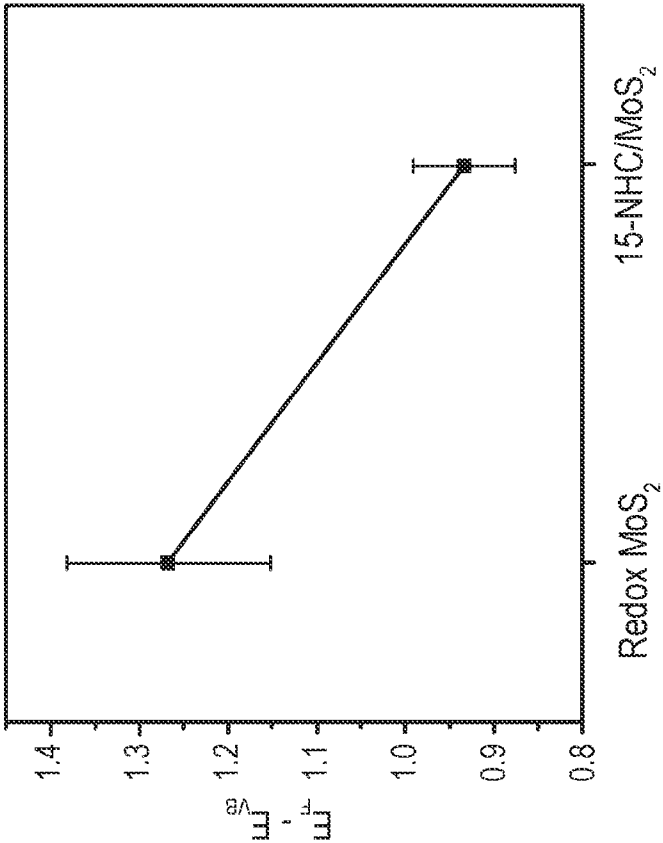


FIG. 40C

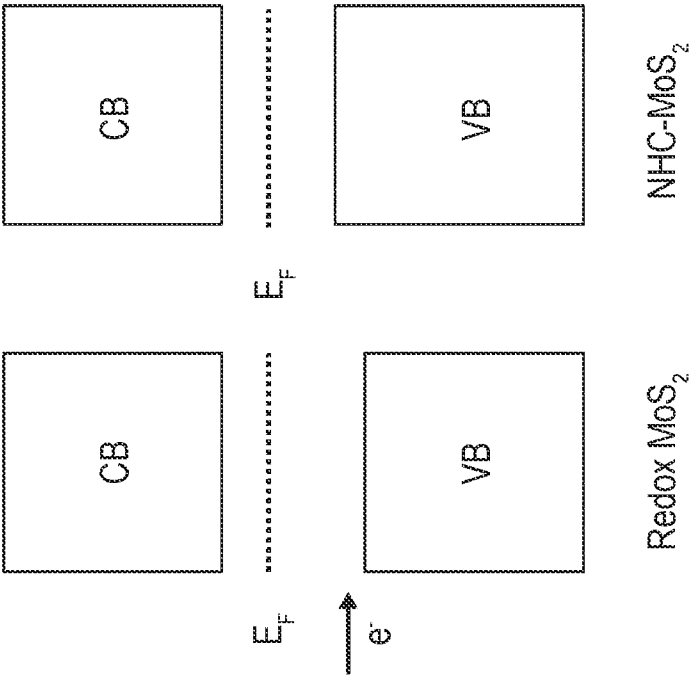


FIG. 41B

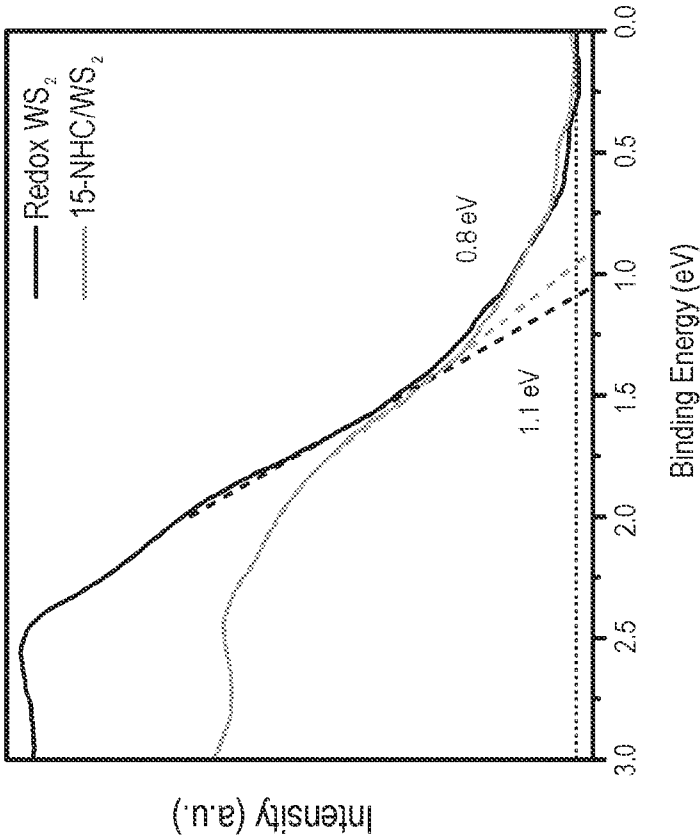
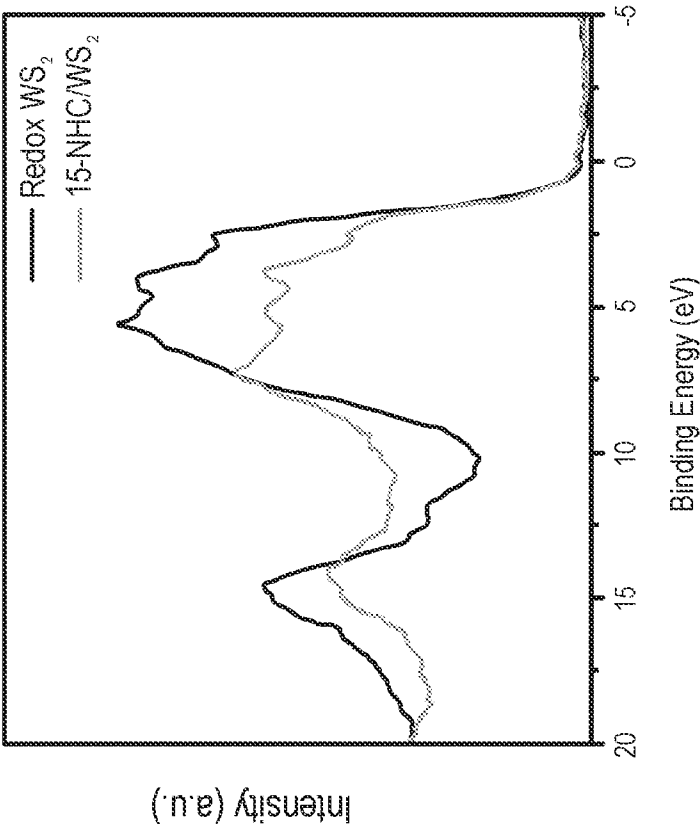


FIG. 41A



54/73

FIG. 42C

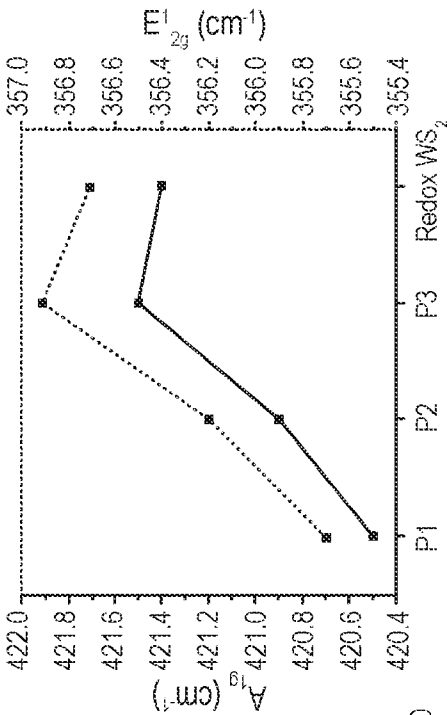


FIG. 42B

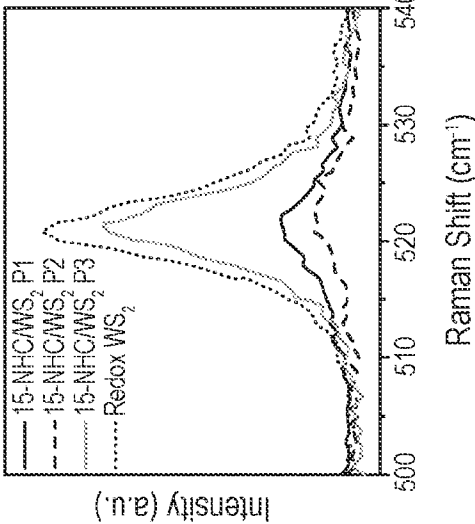


FIG. 42A

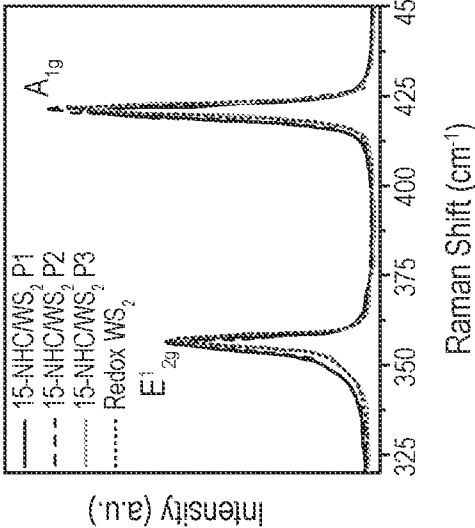


FIG. 42D

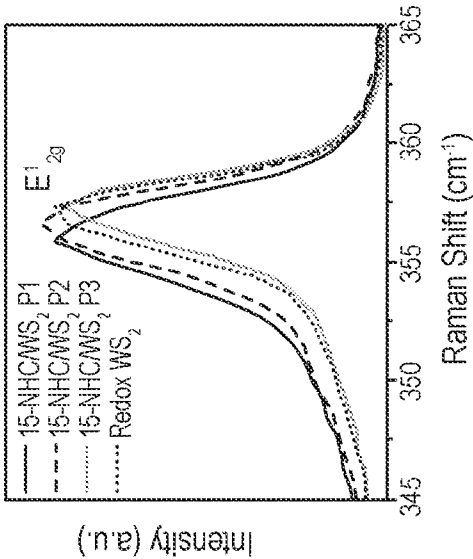


FIG. 42E

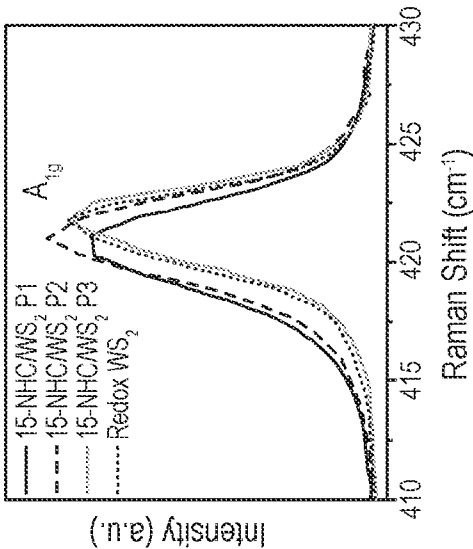


FIG. 42F

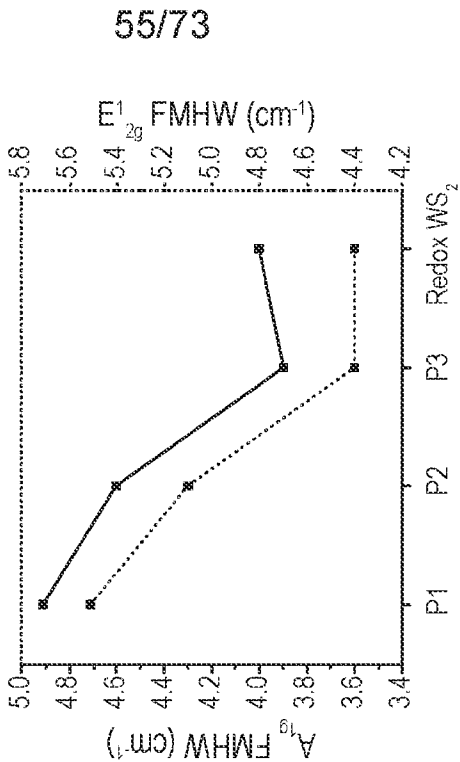


FIG. 43B

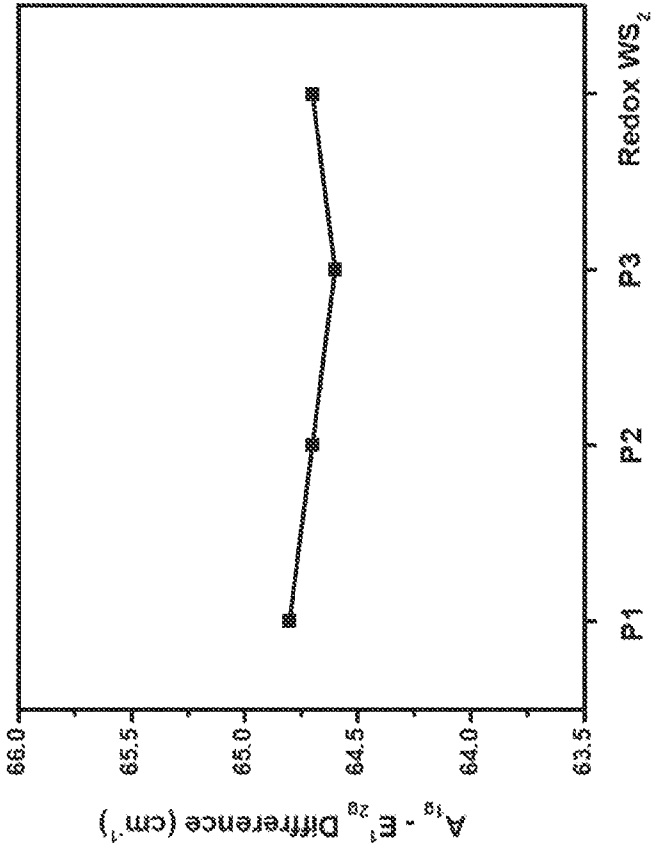


FIG. 43A

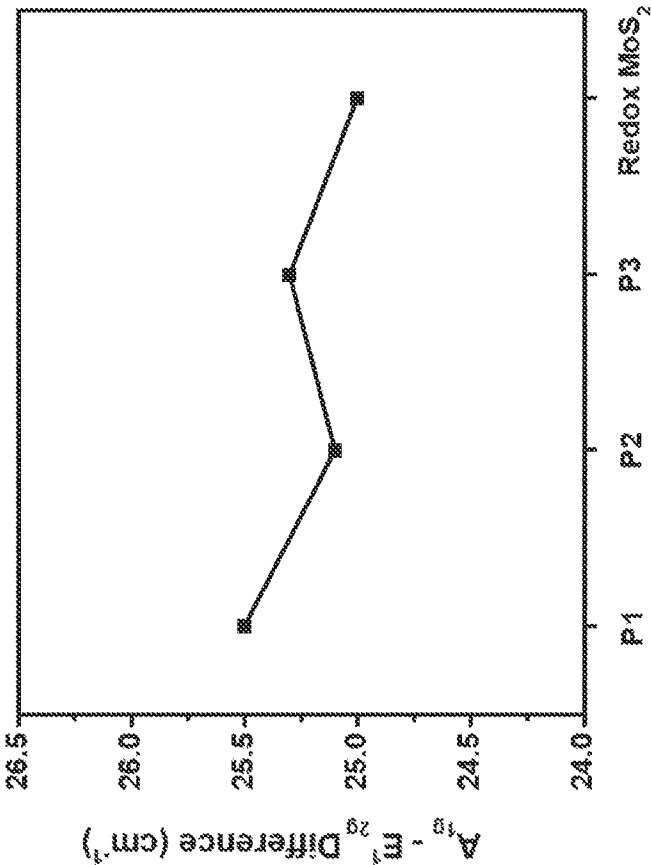


FIG. 44B

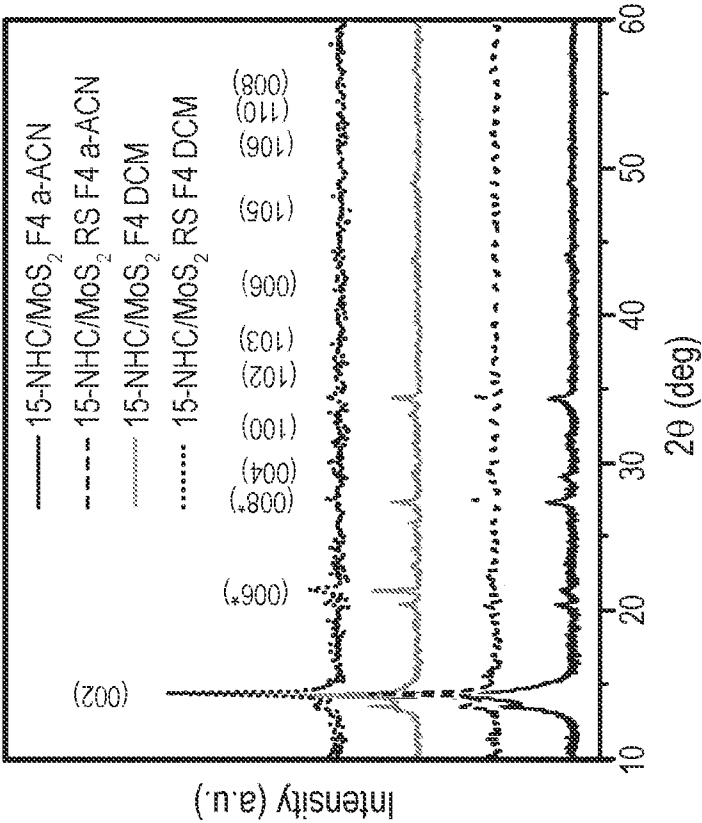


FIG. 44A

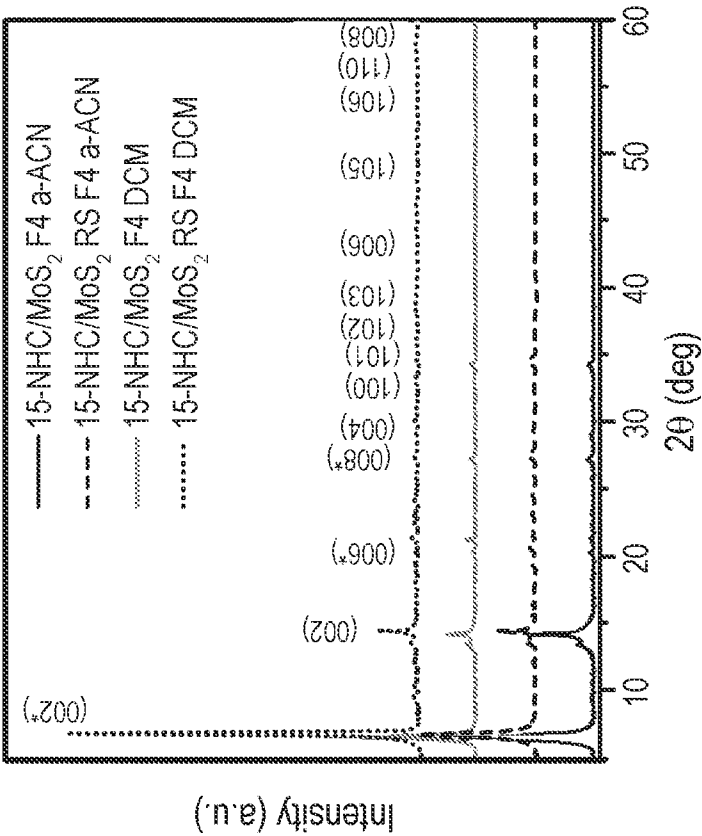


FIG. 45A

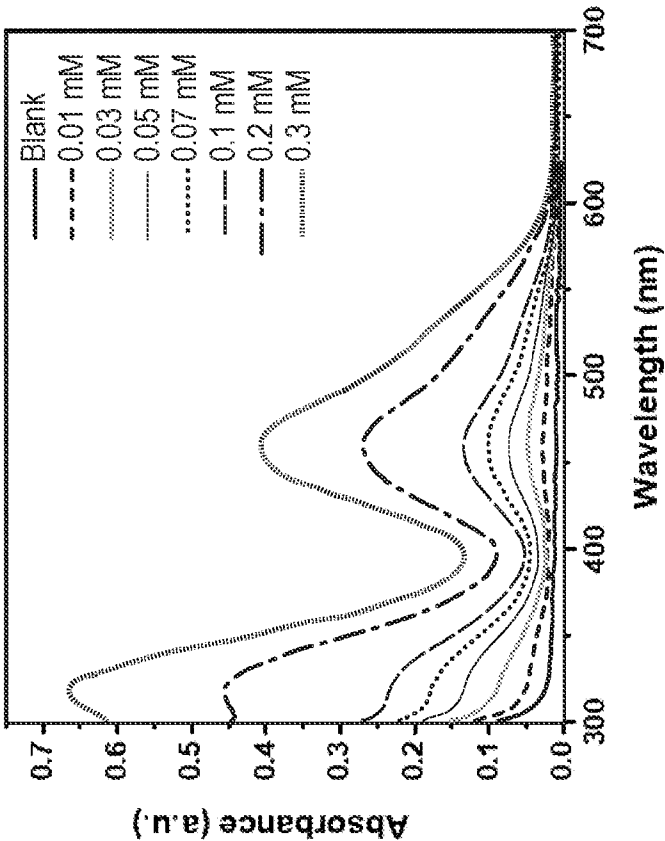


FIG. 45B

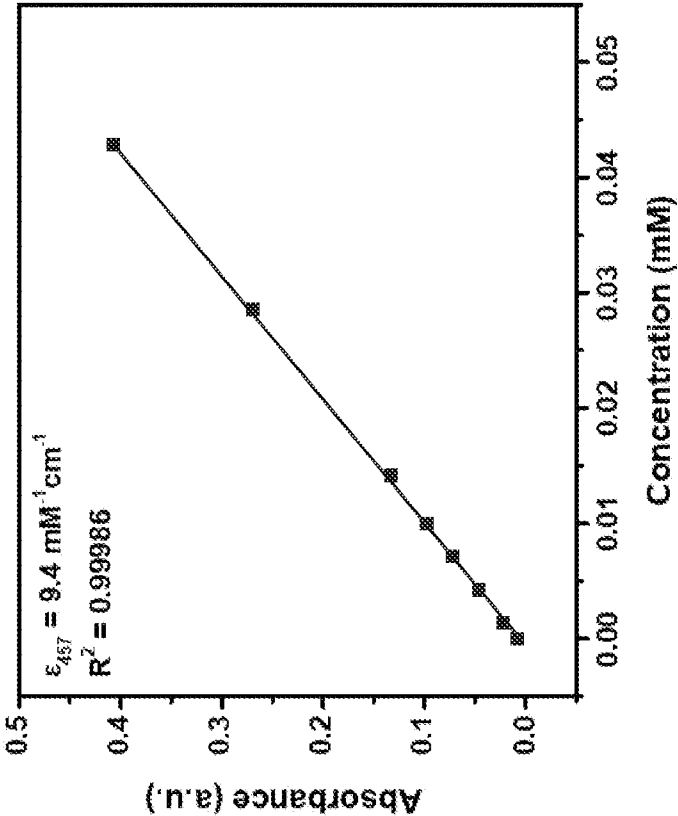


FIG. 45D

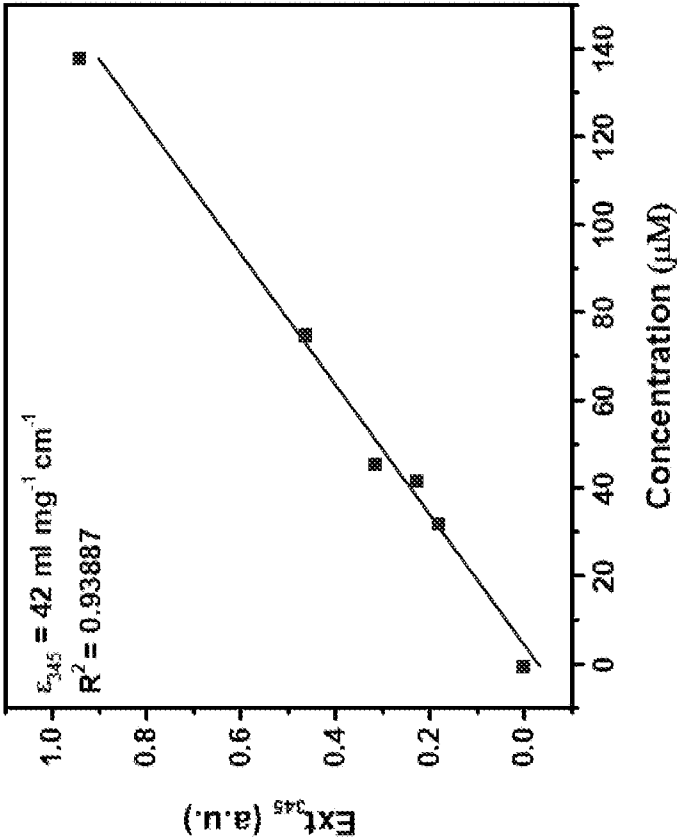


FIG. 45C

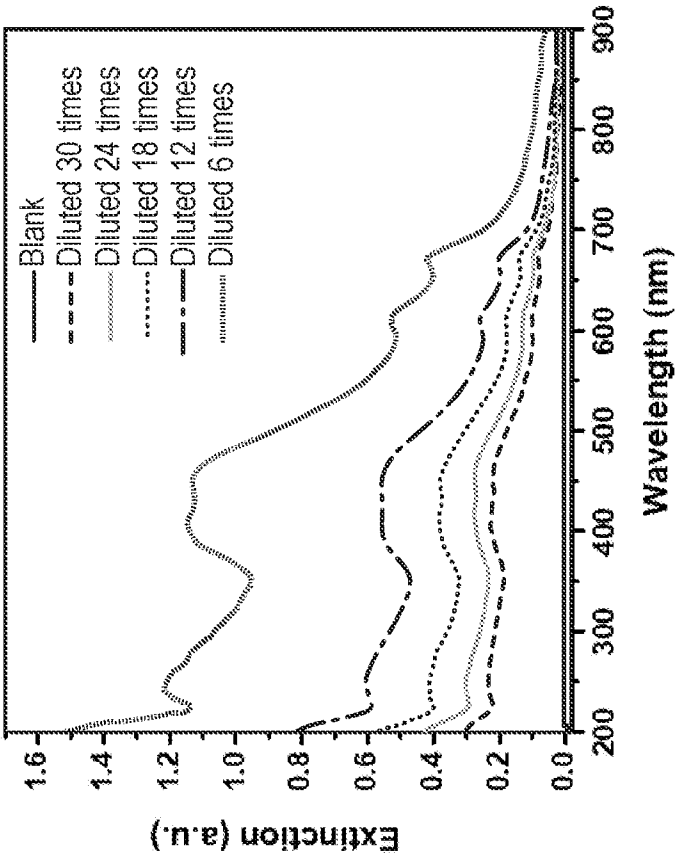


FIG. 46B

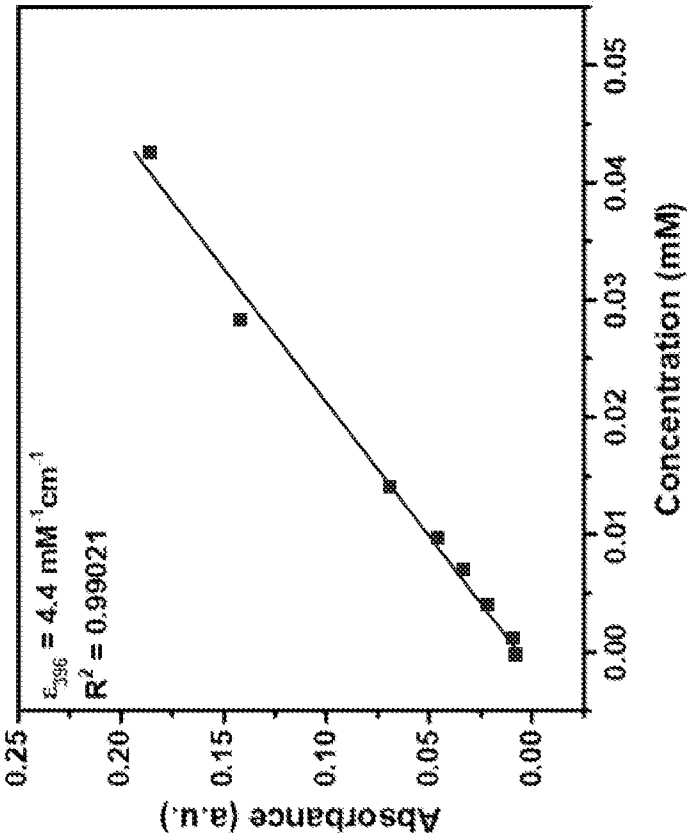


FIG. 46A

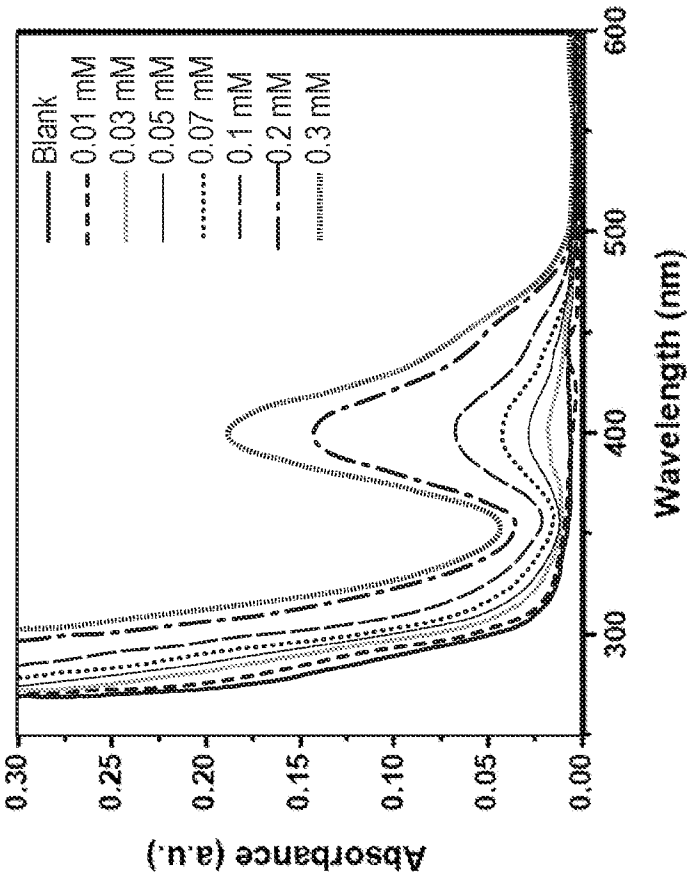


FIG. 46D

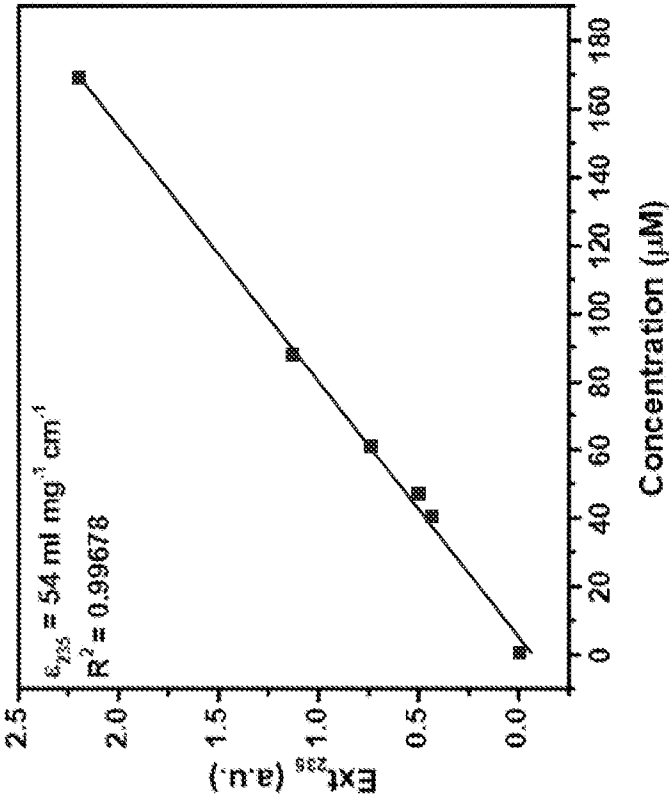
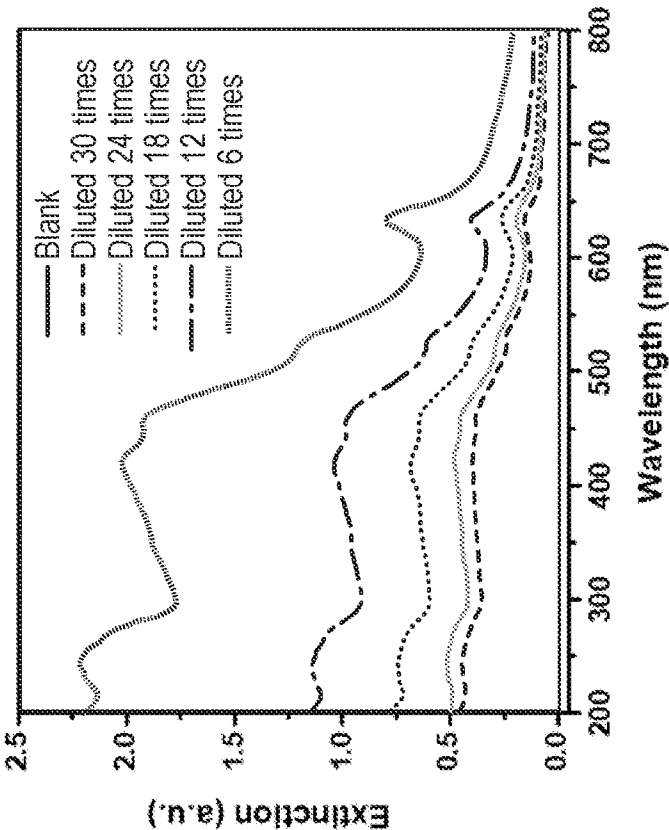


FIG. 46C



62/73

FIG. 47

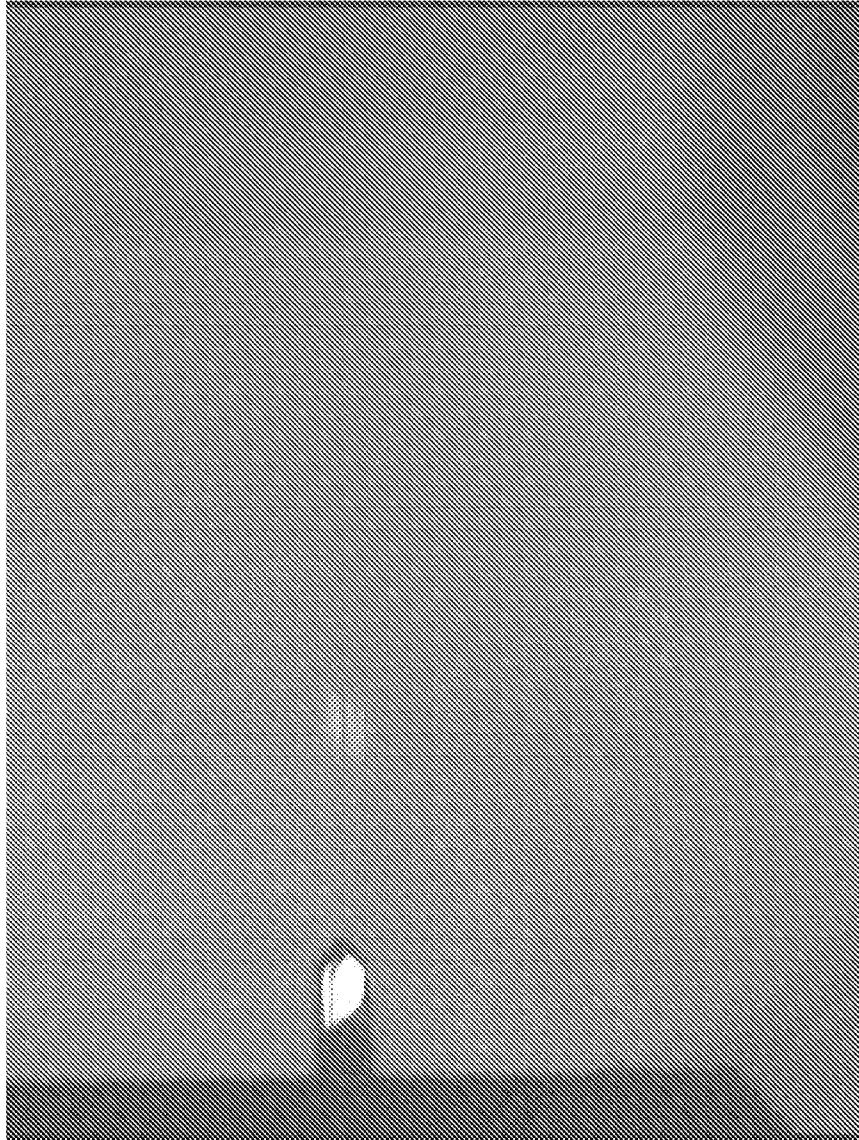


FIG. 48B

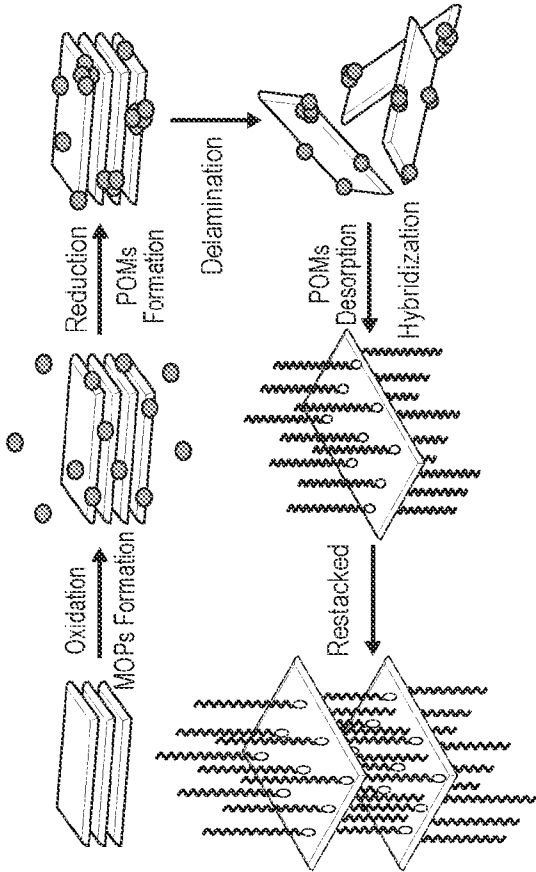


FIG. 48A

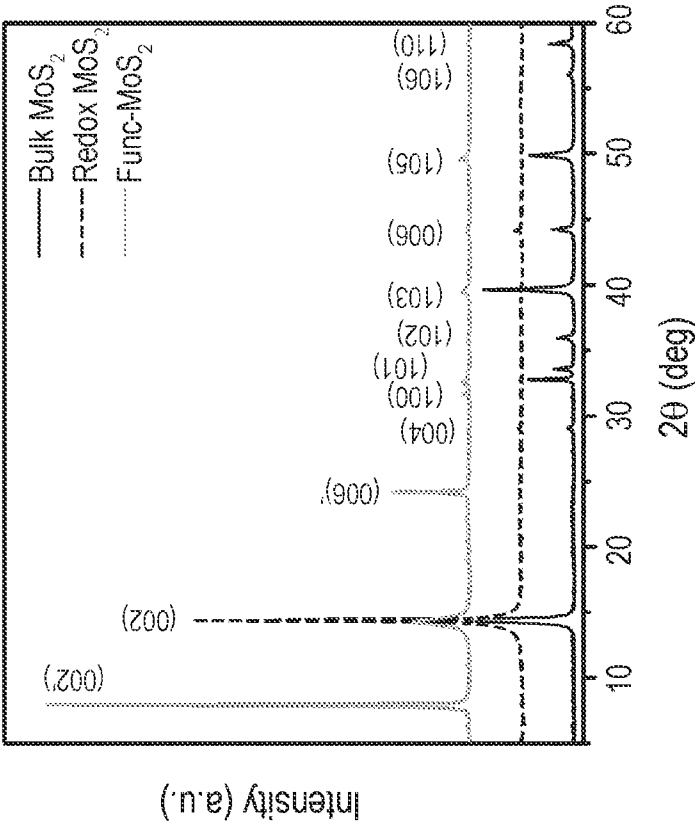


FIG. 49B

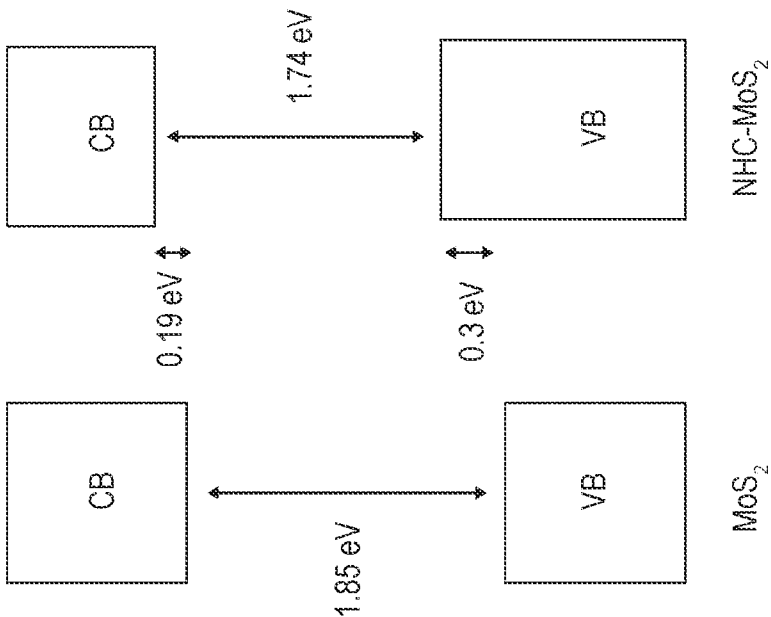


FIG. 49A

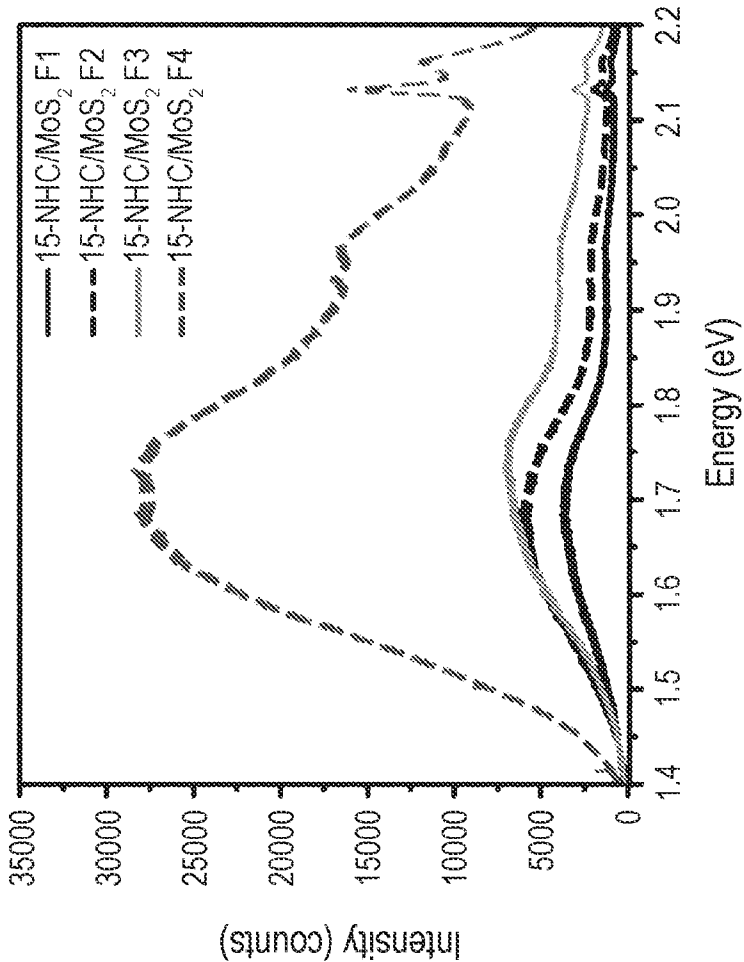


FIG. 50B

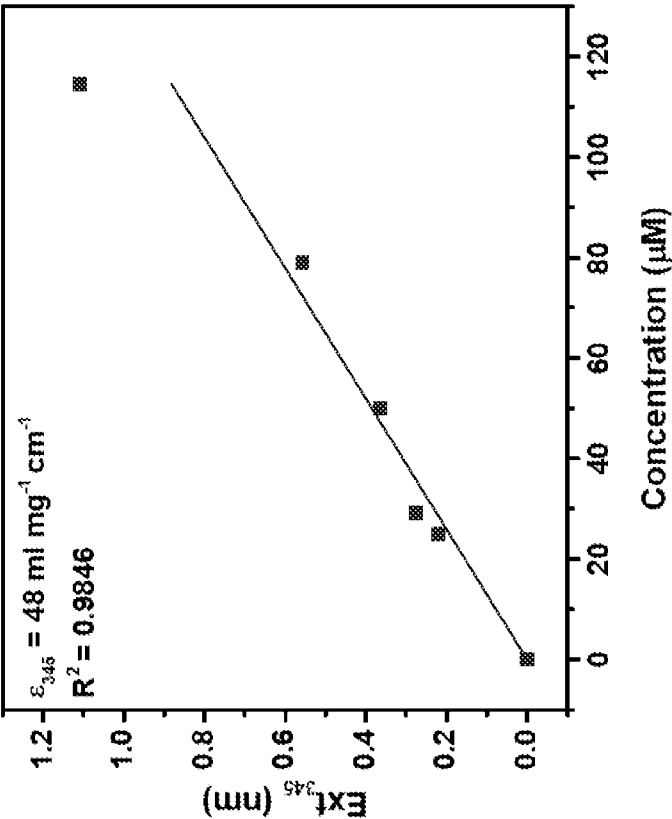


FIG. 50A

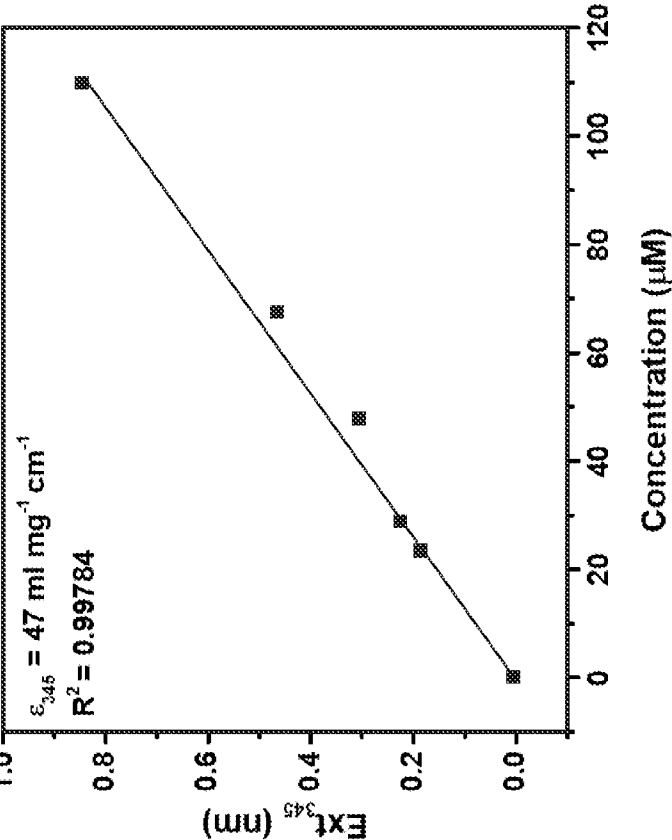


FIG. 51A

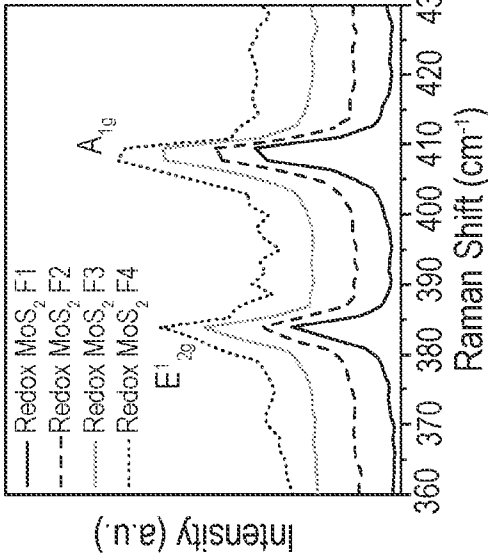


FIG. 51B

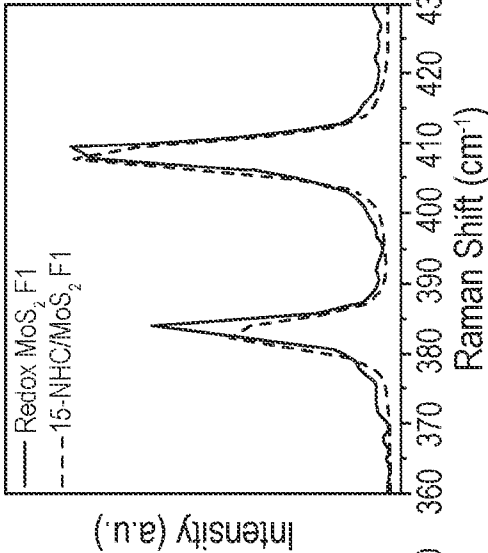
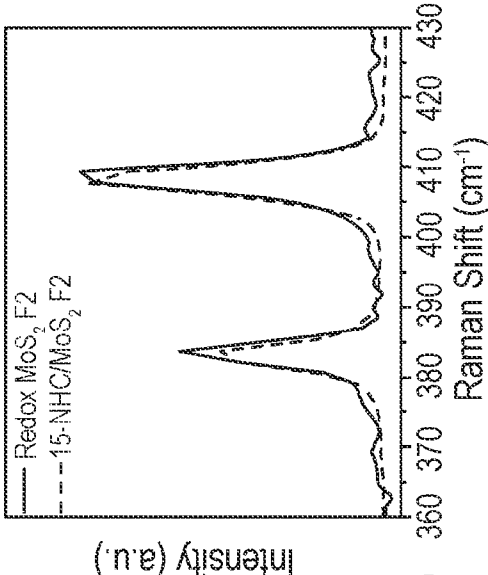


FIG. 51C



67/73

FIG. 51F

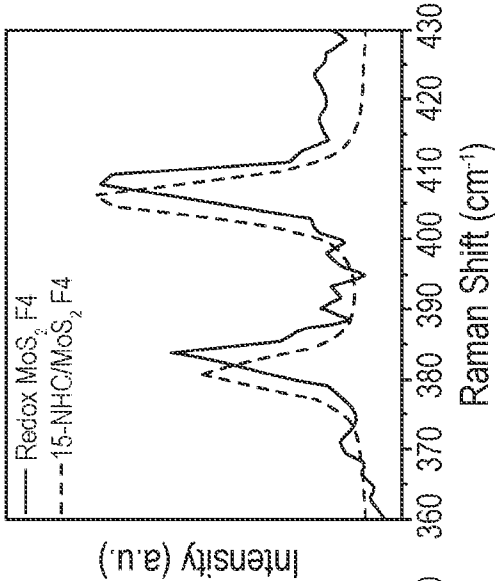


FIG. 51E

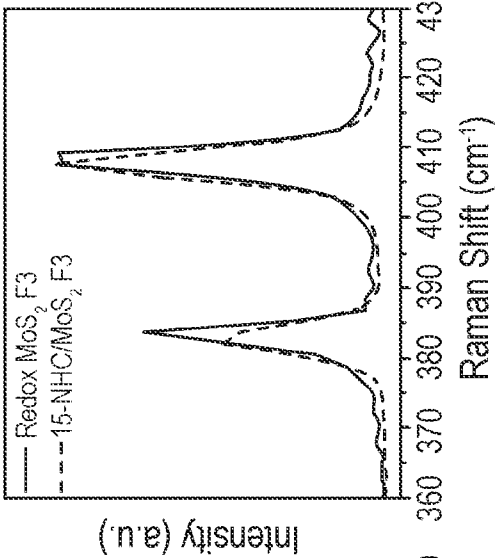


FIG. 51D

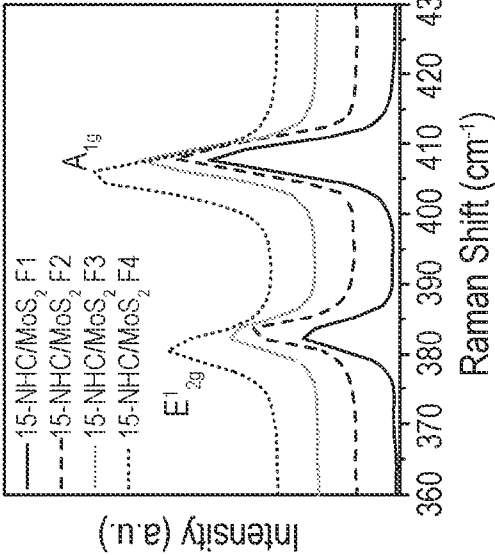


FIG. 51G

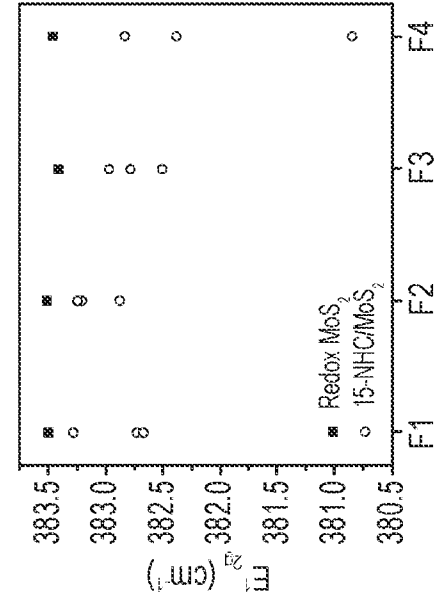


FIG. 51H

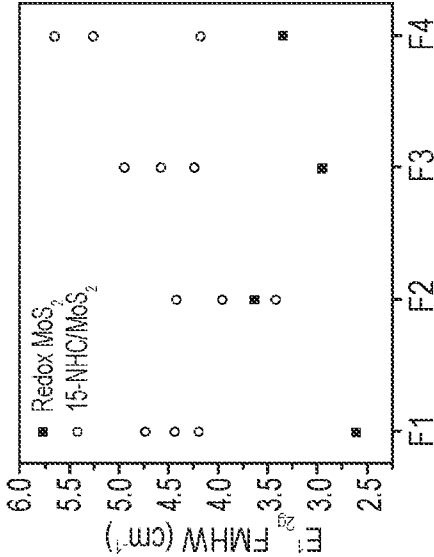


FIG. 51I

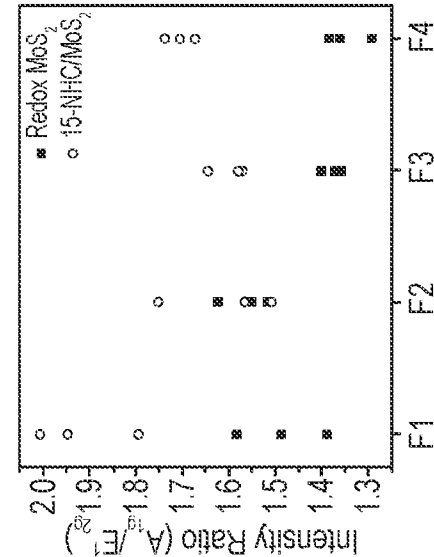


FIG. 51J

FIG. 51K

FIG. 51L

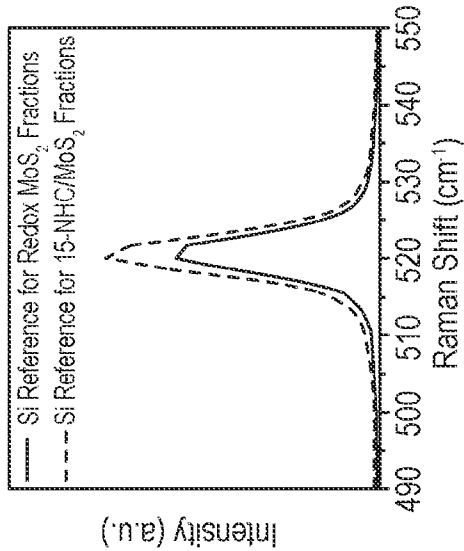
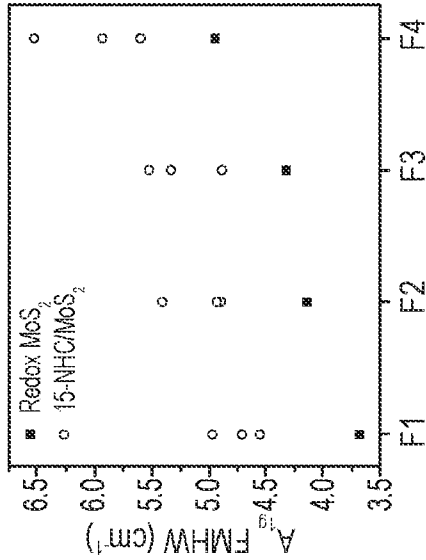
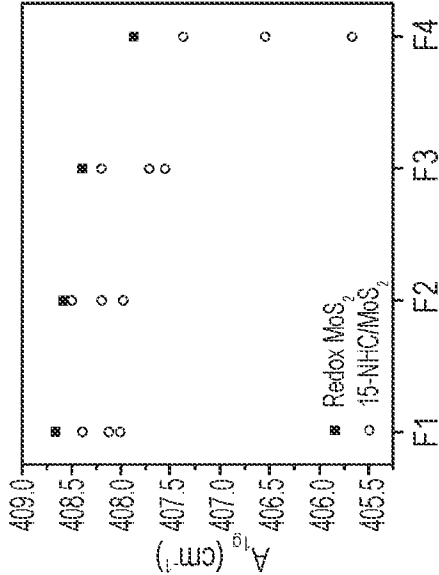


FIG. 52A

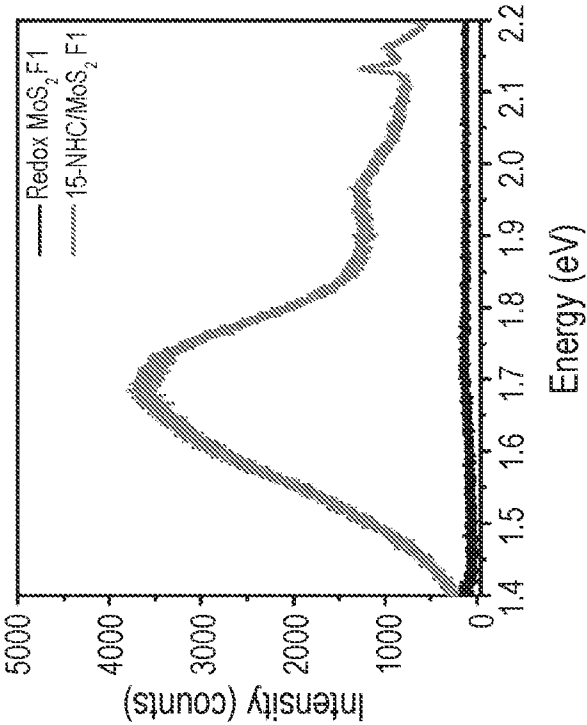


FIG. 52B

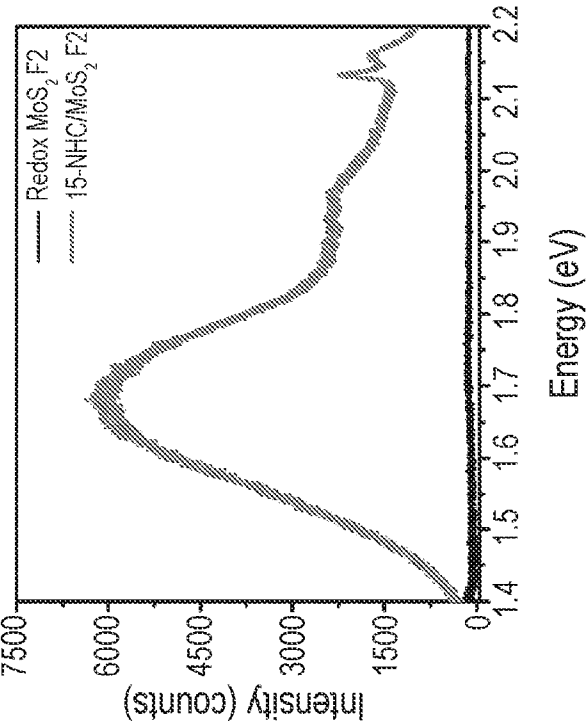


FIG. 52C

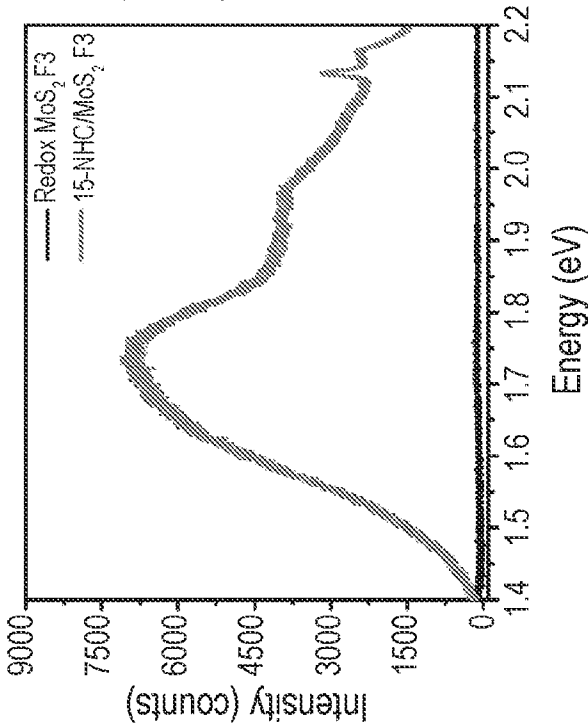


FIG. 52D

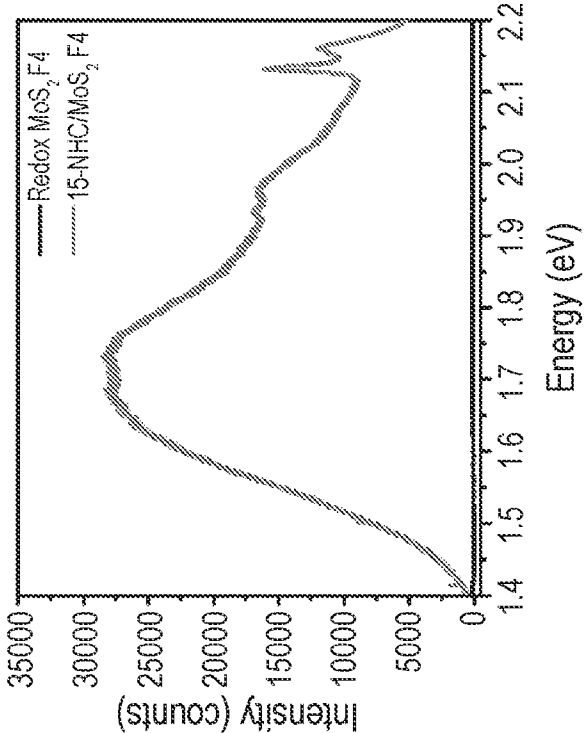
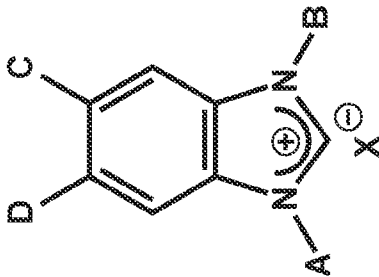


FIG. 53



N-Heterocyclic Carbene Precursors

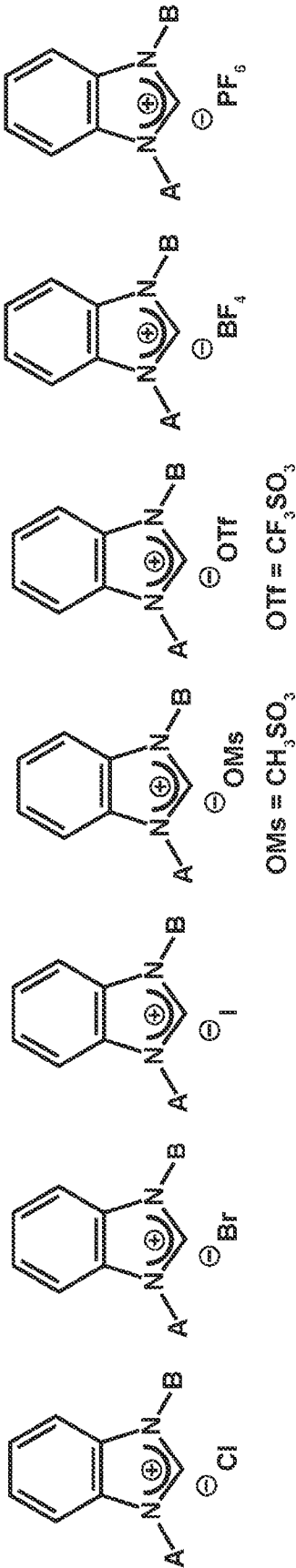


FIG. 54A

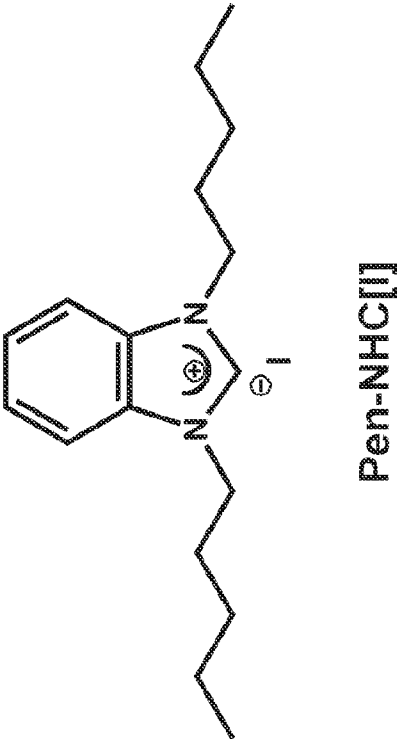
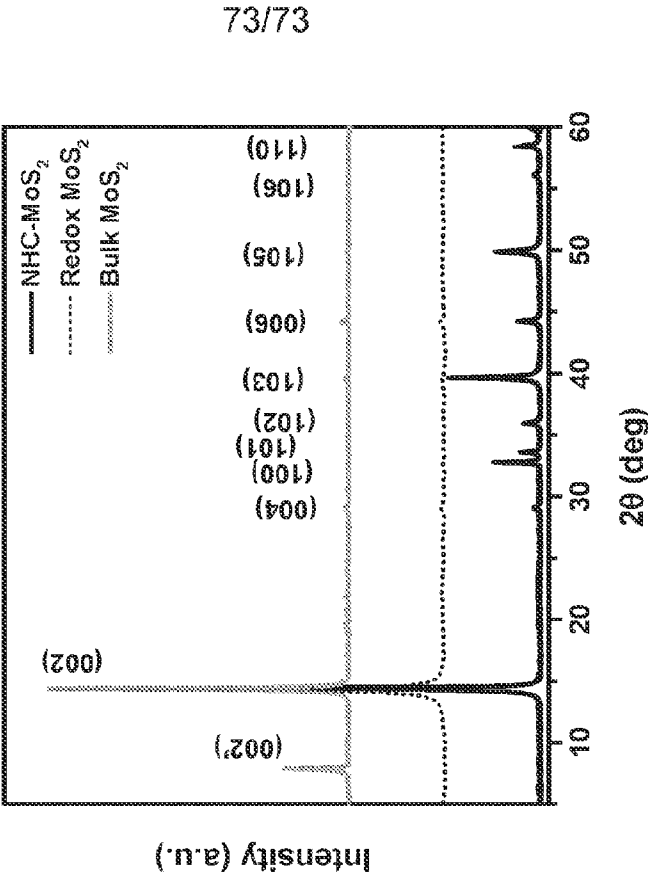


FIG. 54B



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2024/056611

A. CLASSIFICATION OF SUBJECT MATTERIPC: **B32B 15/04** (2025.01); **C23C 14/12** (2025.01); **C07D 235/04** (2025.01)CPC: **B32B 15/04**; **C23C 14/12**; **C07D 235/04**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

See Search History Document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

See Search History Document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

See Search History Document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2021/0181147 A1 (KOREA RESEARCH INSTITUTE OF BIOSCIENCE AND BIOTECHNOLOGY) 17 June 2021 (17.06.2021) abstract	1-3, 5, 7-15, (16-18)/(1-3, 5, 7-13)
A	US 2017/0044683 A1 (UCL BUSINESS PCL) 16 February 2017 (16.02.2017) entire document	1-3, 5, 7-15, (16-18)/(1-3, 5, 7-13)
A	Baek et al. "Highly Efficient, Surface Ligand Modified Quantum Dot Light-Emitting Diodes Driven by Type-Controllable MoTe2 Thin Film Transistors via Electron Charge Enhancer" Advanced Electronic Materials. 26 July 2021, vol 7, pg. 1-11 pg. 1, abstract, pg. 9, left col, para 1	1-3, 5, 7-15, (16-18)/(1-3, 5, 7-13)

☒ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"D" document cited by the applicant in the international application

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

31 March 2025 (31.03.2025)

Date of mailing of the international search report

07 April 2025 (07.04.2025)

Name and mailing address of the ISA/US

COMMISSIONER FOR PATENTS
MAIL STOP PCT, ATTN: ISA/US
P.O. Box 1450
Alexandria, VA 22313-1450
UNITED STATES OF AMERICA

Authorized officer

KARI RODRIQUEZ

Facsimile No. 571-273-8300

Telephone No. PCT Help Desk: 571-272-4300

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2024/056611

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Westmoreland et al. "Dynamic Tuning of the Bandgap of CdSe Quantum Dots through Redox-Active Exciton-Delocalizing N-Heterocyclic Carbene Ligands" Journal of the American Chemical Society. 07 March 2022, vol 144, pg. 4300-4304 pg. 4300, abstract, pg. 4300, Scheme 1	1-3, 5, 7-15, (16-18)/(1-3, 5, 7-13)
A	Garcia-Dali et al. "Molecular Functionalization of 2H-Phase MoS2 Nanosheets via an Electrolytic Route for Enhanced Catalytic Performance" ACS Applied Materials & Interfaces. 12 July 2021, vol 13, pg. 33157-33171 entire document	1-3, 5, 7-15, (16-18)/(1-3, 5, 7-13)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2024/056611

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1.

Group I+: Claims 1-18, directed to a N-heterocyclic carbene functionalized transition metal dichalcogenide. The compound of claim 1 will be searched to the extent that it encompasses the first species of claim 1, represented by N-heterocyclic carbene functionalized transition metal dichalcogenide comprising one transition metal dichalcogenide, which is the first transition metal dichalcogenide of claim 11, MoS₂; and one N-heterocyclic carbene, which is the first N-heterocyclic carbene of claim 3, formula II-A, wherein R_{1a} is H; R_{2a} is H; R_{3a} is H (in order to provide stable compound); R_{4a} is H; R_{5a} is H; R_{6a} is H (wherein optional groups are omitted). It is believed that claims 1-3, 5, 7-15 and (16-18)/(1-3, 5, 7-13) read on this first named invention, and thus these claims will be searched without fee. This first named invention has been selected based on the guidance set forth in section 10.54 of the PCT International Search and Preliminary Examination Guidelines. Applicant is invited to elect additional compounds of claim 1, wherein each additional compound elected will require one additional invention fee. Applicants must specify the claims that encompass any additionally elected compound. Applicants must further indicate, if applicable, the claims which encompass the first named invention, if different than what was indicated above for this group. Failure to clearly identify how any paid additional invention fees are to be applied to the '+' group(s) will result in only the first claimed invention to be searched. Additionally, an exemplary election wherein different actual variables are selected is suggested. An exemplary election would be a N-heterocyclic carbene functionalized transition metal dichalcogenide comprising one transition metal dichalcogenide, which is the first transition metal dichalcogenide of claim 11, MoS₂; and one N-heterocyclic carbene, which is the first N-heterocyclic carbene of claim 3, formula II-A, wherein R_{1a} is H; R_{2a} is H; R_{3a} is absent; R_{5a} is absent; R_{4a} and R_{6a} are taken together to form a ring which is a phenyl ring substituted with a C₄ alkoxy substituent (wherein optional groups are omitted) (i.e., claims 1-5, 7-15 and (16-18)/(1-5, 7-13)).

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.: **1-3, 5, 7-15 and (16-18)/(1-3, 5, 7-13)**

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.