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(54) **Title:** QUINOLINES, POLYQUINOLINES, MOLECULAR SEGMENTS OF FULLERENES AND GRAPHENE NANORIBBONS, AND GRAPHENE NANORIBBONS AND METHODS OF THEIR SYNTHESIS

(57) **Abstract:** Quinolines, polyquinolines, polybenzoquinolines, molecular segments of fullerenes and graphene nanoribbons, and processes for producing such materials are provided. The processes utilize a form of an aza-Diels-Alder (Povarov) reaction to first form quinolines and/or polyquinolines. In some such embodiments polyquinolines thus produced are used to form graphene nanoribbon precursors, and molecular segments and graphene nanoribbons. In many such embodiments the graphene nanoribbon precursors are formed from polybenzoquinolines.



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QUINOLINES, POLYQUINOLINES, MOLECULAR SEGMENTS OF FULLERENES
AND GRAPHENE NANORIBBONS, AND GRAPHENE NANORIBBONS AND
METHODS OF THEIR SYNTHESIS

FIELD OF THE INVENTION

[0001] The present disclosure is directed to quinolines, polyquinolines, benzoquinolines, polybenzoquinolines, molecular segments of fullerenes and graphene nanoribbons, and graphene nanoribbons as well as methods of synthesizing such compounds and materials.

STATEMENT OF FEDERAL FUNDING

[0002] This invention was made with Government support under Grant No. N00014-13-1-0650 awarded by the Office of Naval Research – N99914. The government has certain rights in the invention.

BACKGROUND OF THE INVENTION

[0003] Carbon-based materials, such as fullerenes, carbon nanotubes and graphene nanoribbons (GNRs)(FIG. 1A), have often been touted as the successors to inorganic semiconductors in solar cells and nanoscale transistors. (See, e.g., Pierre Delhaes, *Carbon-based Solids and Materials*, John Wiley & Sons, Inc., Hoboken, 2011; V. Georgakilas, et al., *Chem. Rev.* 2015, 115, 4744–4822; A. K. Geim, P. Kim, *Sci. Am.* 2008, April, 90–97; B.C.Thompson, J. M. J. Fréchet, *Angew. Chem. Int. Ed.* 2008, 47, 58–77; *Angew. Chem.* 2007, 120, 62–82; G. Dennler, et al., *Adv. Mater.* 2009, 21, 1323–1338; F. Schwierz, *Nat. Nanotechnol.* 2010, 5, 487–496; and A. C. Ferrari, et al., *Nanoscale* 2015, 7, 4598–4810, the disclosures of which are incorporated herein by reference.) Thus, much research effort has focused on either top-down lithographic approaches (see, e.g., L. Chen, et al. *Angew. Chem. Int.* 2012, 51 7640-7654; L. Ma, et al. *ChemPhysChem* 2013, 14, 47-54; Z. Chen, et al. *Physica E* 2007, 40, 223-232; M. Terronew, et al. *Nano Today* 2010, 5, 351-372; and K. Mullen, *ACS Nano* 2014, 8, 6531-6541, the disclosures of which are incorporated herein by reference), or the

bottom-up preparation of structurally and chemically well-defined variants of these carbon allotropes, as well as their molecular segments, via traditional organic chemistry techniques. (See, e.g., L.T. Scott, *Angew. Chem. Int. Ed.* 2004, 43, 4994–5007; L.T. Scott, *Angew. Chem.* 2004, 116, 5102–5116; A. Sygula, *Eur. J. Org. Chem.* 2011, 1611–1625; *Fragments of Fullerenes and Carbon Nanotubes: Designed Synthesis, Unusual Reactions, and Coordination Chemistry* (Eds.: M. A. Petrukhina, L. T. Scott), John Wiley & Sons, Inc., Hoboken, 2011; L. T. Scott, *Polycyclic Aromat. Compd.* 2010, 30, 247–259; M. Mojica, et al., *J. Phys. Org. Chem.* 2013, 26, 526–539; A. Narita, et al., *Chem. Soc. Rev.* 2015, 44, 6616–6643; L. Chen, et al., *Angew. Chem. Int. Ed.* 2012, 51, 7640–7654; J. Wu, et al., *Chem. Rev.* 2007, 107, 718–747; A. Narita, et al., *Chem. Rec.* 2015, 15, 295–309; and Z. Sun, et al., *Chem. Asian J.* 2013, 8, 2894–2904, the disclosure of which is incorporated herein by reference.) However, far fewer studies have demonstrated the solution-phase synthesis of analogous nitrogen-doped constructs. (See, e.g., T. H. Vo, et al., *Chem. Commun.* 2014, 50, 4172–4174; K. T. Kim, J. W. Lee, W. H. Jo, *Macromol. Chem. Phys.* 2013, 214, 2768–2773; D. J. Dibble, et al., *Angew. Chem. Int. Ed.* 2015, 54, 5883–5887; Q. Tan, et al., *Nat. Commun.* 2012, 3, 891; S. Ito, et al., *Angew. Chem. Int. Ed.* 2015, 54, 7256–7260; and R. Berger, et al., *Angew. Chem. Int. Ed.* 2014, 53, 10520–10524, the disclosures of which are incorporated herein by reference.) Given that substitutional doping is a classic strategy for tuning the properties of electronic materials, this gap in the literature is surprising and likely stems from the difficulties inherent to the synthetic incorporation of nitrogen heteroatoms at arbitrary locations in graphitic systems. (See, e.g., X. Wang, et al. *Chem. Soc. Rev.* 2014, 43, 7067–7098; O. Vostrowsky, A. Hirsch, *Chem. Rev.* 2006, 106, 5191–5207; J. C. Hummelen, C. Bellavia-Lund, F. Wudl, *Top. Curr. Chem.* 1999, 199, 93–134; P. T. Araujo, M. Terrones, M. S. Dresselhaus, *Mater. Today* 2012, 15, 98–109; R. Lv, M. Terrones, *Mater. Lett.* 2012, 78, 209–218, the disclosures of which are incorporated herein by reference.) Consequently, the development of new routes to nitrogen-containing segments of fullerenes and GNRs remains of paramount importance for the next generation of semiconductor devices and technologies.

[0004] Polyquinolines have been studied in both academia and industry since the early 1970s due to their impressive chemical stability as well as their excellent optical, electrical, and mechanical properties. Such favorable properties have enabled polyquinolines to demonstrate their promise for not only optoelectronic but also biomedical applications. (See, e.g., Stille, J.K. *Macromolecules* 1981, 14, 870–880; Kulkarni, A.P., et al. *Chem. Mater.* 2004, 16, 4556–4573; Rusanov, et al. *Russ. Chem. Rev.* 2005, 74, 671–683; Kimyonok, A., et al. *Macromol. Sci., Polym. Rev.* 2006, 46, 47–77; Zhao, X. and Zhan, X. *Chem. Soc. Rev.* 2011, 40, 3728–3743; Nalwa, H.S., et al. *Appl. Phys. Lett.* 1998, 72, 1311–1313; Parker, I.D. et al., *Appl. Phys. Lett.* 1994, 65, 1272–1274; Liu, M.S., et al. *Mater. Chem.* 1999, 9, 2201–2204; Tonzola, C.J. *Macromolecules* 2005, 38, 9539–9547; Tonzola, C.J., et al. *Adv. Funct. Mater.* 2007, 17, 863–874; Kim, J.L., et al. *Macromolecules* 2000, 33, 5880–5885; Zhang, X., et al. *Chem. Mater.* 1997, 9, 409–412; Kumar, S., et al. *Rev. Med. Chem.* 2009, 9, 1648–1654; Broch, S., et al. *Eur. J. Med. Chem.* 2010, 45, 1657–1662; Solomon, V.R. and Lee, H. *Curr. Med. Chem.* 2011, 18, 1488–1508.; Saugues, E., et al. *J. Med. Chem.* 2012, 57, 112–125; and Lu, J., et al., *Spectrochim. Acta, Part A* 2014, 130, 390–396, the disclosures of which are incorporated herein by reference.) To date, polyquinolines have been prepared via a limited number of synthetic strategies, including Suzuki couplings, the Sonogashira reaction, oxidative polymerizations, and the Friedländer synthesis, which are summarized in FIG. 1B. (See, e.g., Siemssen, B., et al. *Mol. Cryst. Liq. Cryst.* 2006, 462, 159–167; Tomar, M., et al. *J. Polym. Int.* 2012, 61, 1318–1325; Bangcuvo, C.G., et al. *Macromolecules* 2002, 35, 1563–1568; Bilici, A., et al. *React. Funct. Polym.* 2011, 71, 675–683; Beever, W.H. and Stille, J.K. *Macromolecules* 1979, 12, 1033–1038.; Marco-Contelles, J., et al. *Chem. Rev.* 2009, 109, 2652–2671; Sutherlin, D.M., et al. *Macromolecules* 1986, 19, 257–266; Jen, A.K.-Y., et al. *Chem. Mater.* 1998, 10, 471–473; Ma, H., et al. *Macromolecules* 1998, 31, 4049–4052; Ma, H., et al. *S. Chem. Mater.* 1999, 11, 2218–2225; and Agrawal, A.K. and Jenekhe, S.A. *Macromolecules* 1993, 26, 895–905, the disclosure of which are incorporated herein by reference.) The latter approach has proven particularly effective, as demonstrated in seminal studies by Jenekhe and co-workers. (See, e.g., Agrawal, A.K. and Jenekhe,

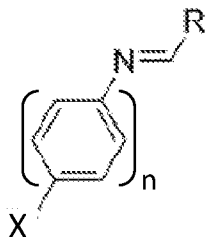
S.A. *Chem. Mater.* 1996, 8, 579–589; Zhang, X. and Jenekhe, S.A. *Macromolecules* 2000, 33, 2069–2082; Chen, X.L. and Jenekhe, S.A. *Macromolecules* 2000, 33, 4610–4612; and Jenekhe, S.A., et al. *Macromolecules* 2001, 34, 7315–7324, the disclosures of which are incorporated herein by reference.) However, the known routes to polyquinolines suffer from some disadvantages; they frequently necessitate difficult multi-step monomer syntheses, yield products with poor solubility, or provide access to only a limited number of structural motifs. For example, the Friedländer synthesis often requires the resulting polyquinolines to possess complex side chain substituents for enhanced solubility and cannot provide access to certain backbone architectures, such as those containing 4,6-linked quinoline subunits, as shown in FIG. 1C. (See, e.g., Tonzola, C.J., et al. *Adv. Mater.* 2002, 14, 1086–1090; Tonzola, C.J., et al. *Macromolecules* 2004, 37, 3554–3563; Krüger, H., et al. *Macromol. Chem. Phys.* 2003, 204, 1607–1615; Zhan, X., et al. *Macromolecules* 2002, 35, 2529–2537; Chen, C.-H. and Shu, C.-F. *J. Polym. Sci., Part A: Polym. Chem.* 2004, 42, 3314–3322; and Tonzola, C.J., et al. *Macromol. Chem. Phys.* 2005, 206, 1271–1279, the disclosure of which are incorporated herein by reference.) Thus, given the aforementioned limitations, there remains a need for the development of alternative routes to polyquinoline-type materials.

BRIEF SUMMARY OF THE INVENTION

[0005] The disclosure is generally directed generally to quinolines and polyquinolines, benzo- and polybenzoquinolines, molecular segments of fullerenes and graphene nanoribbons, and graphene nanoribbons and methods for the synthesis thereof.

[0006] Some embodiments of the disclosure are directed to methods of producing a quinoline including:

- providing a halogenated aromatic aldimine according to:



- wherein X is a halogen, n is an integer of at least 1, and R is an unsubstituted or substituted aromatic ring; and
- reacting the halogenated aromatic aldimine with an alkynyl in the presence of a Lewis acid mediator and an oxidant such that the imine group of the halogenated aromatic aldimine reacts with the alkyne group of the alkynyl yielding a quinoline wherein the nitrogen from the imine group is incorporated into the multicyclic quinoline ring.

[0007] In other embodiments n is at least 2 and the alkynyl comprises a multicyclic aromatic ring such that a benzoquinoline is formed.

[0008] In still other embodiments the alkynyl is a naphthyl alkyne such that a 2,4,6 substituted benzoquinoline is formed.

[0009] In yet other embodiments at least one of the substituents is selected from the group of electron withdrawing, electron donating, and aliphatic substituents.

[0010] In still yet other embodiments the halogenated aromatic comprises an ortho substituent on a pendant phenyl ring thereof.

[0011] In still yet other embodiments the method includes converting the halogen of the benzoquinoline to form an alkyne functionalized benzoquinoline and reacting such alkyne functionalized benzoquinolines with the halogenated aromatic aldimine in a Lewis acid mediator and an oxidant such that the imine group of the halogenated aromatic aldimine reacts with the alkyne group of the alkyne functionalized benzoquinoline yielding a dimeric oligobenzoquinoline.

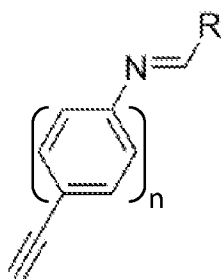
[0012] In still yet other embodiments the alkynyl further comprises an acetyl-protected amine; and the method further includes converting the acetyl-protected amine to an imine to form imine functionalized benzoquinoline and reacting such alkyne and

imine functionalized benzoquinolines in a Lewis acid mediator and an oxidant such that the imine group of the imine functionalized benzoquinoline reacts with the alkyne group of the alkyne functionalized benzoquinoline yielding a pentameric oligobenzoquinoline.

[0013] In still yet other embodiments the R group comprises a benzene having at least 5one further substitution selected from a heteroatom, a halogen, an alkyl chain, a methoxy (Me), an acetyl (Ac), an NHAc, an amines, an N(Me)₂, and a S(Me)₂.

[0014] Some other embodiments of the disclosure are directed to a method of producing polyquinoline including:

- providing a bifunctional monomer according to:



- wherein n is an integer of at least 1, and R is an unsubstituted or substituted aromatic ring; and
- polymerizing the bifunctional monomer in the presence of a Lewis acid mediator and a sacrificial oxidant such that the imine group of one bifunctional monomer reacts with the alkyne group of another bifunctional monomer, yielding a polyquinoline product wherein the nitrogen from the imine group is incorporated into each of the multicyclic quinoline rings of the polyquinoline.

[0015] In other embodiments the aromatic ring of R is further substituted with at least one of the following a heteroatom, a halogen, an alkyl chain, a methoxy (Me), an acetyl (Ac), an NHAc, an amine, an N(Me)₂, and a S(Me)₂.

[0016] In still other embodiments the aromatic ring of R has at least two substitutions.

[0017] In yet other embodiments the method further includes terminating the polymerization reaction to obtain a polyquinoline of specified length.

[0018] In still yet other embodiments n is at least 2 such that a polybenzoquinoline product is formed. In some such embodiments the second aromatic ring comprises a further substituent. In some other such embodiments the substituent is selected from the group of a heteroatom, a halogen, an alkyl chain, a methoxy (Me), an acetyl (Ac), an NHAc, an amine, an $N(Me)_2$, and a $S(Me)_2$. In still other such embodiments the bifunctional monomer further comprises an additional benzoquinoline subunit. In yet other such embodiments the additional benzoquinoline subunit further comprises an additional substituent group selected from the group of a heteroatom, a halogen, an alkyl chain, a methoxy (Me), an acetyl (Ac), an NHAc, an amines, an $N(Me)_2$, and a $S(Me)_2$.

[0019] In still yet other embodiments the individual quinolines of the polyquinoline are linked at the 4 and 6 positions.

[0020] Still some other embodiments of the disclosure are directed to a method of producing biquinoline including:

- providing an AA-type monomer comprising an aromatic bisaldimine and a BB-type monomer comprising an aromatic alkynyl; and
- reacting the AA-type monomer with the BB-type monomer in the presence of a Lewis acid mediator and an oxidant such that the imine group of AA-type monomer reacts with the alkyne group of the aromatic alkynyl yielding a biquinoline wherein the nitrogen from the imine group is incorporated into each of the multicyclic quinoline rings.

[0021] In other embodiments the aromatic rings of the AA-type monomer are further functionalized by a substituted or unsubstituted aromatic ring. In some such embodiments the aromatic ring is further substituted with at least one of the following a heteroatom, a halogen, an alkyl chain, a methoxy (Me), an acetyl (Ac), an NHAc, an amines an $N(Me)_2$, and a $S(Me)_2$.

[0022] In still other embodiments the bisaldimine comprises at least two aromatic rings.

[0023] Yet some other embodiments of the disclosure are directed to a method of producing polyquinoline including:

- providing an AA-type monomer comprising an aromatic bisaldimine and a BB-type monomer comprising an aromatic dialkynyl; and
- reacting the AA-type monomer with the BB-type monomer in the presence of a Lewis acid mediator and an oxidant such that the imine group of the AA-type monomer reacts with the alkyne group of the BB-type monomer yielding a polyquinoline wherein the nitrogen from the imine group is incorporated into each of the multicyclic quinoline rings of the polyquinoline.

[0024] In other embodiments the aromatic rings of the AA-type monomer are further functionalized by a substituted or unsubstituted aromatic ring. In some such embodiments the aromatic ring is further substituted with at least one of the following a heteroatom, a halogen, an alkyl chain, a methoxy (Me), an acetyl (Ac), an NHAc, an amine, an N(Me)₂, and a S(Me)₂.

[0025] In still other embodiments the bisaldimine comprises at least two aromatic rings.

[0026] Still yet some other embodiments of the disclosure are directed to a method of forming a molecular segment including:

- reacting a halogenated aromatic bisaldimine and an alkyne functionalized aromatic ring in the presence of a Lewis acid mediator and an oxidant such that the imine groups of the bisaldimine reacts with the alkyne group of the alkyne functionalized aromatic ring yielding a halogenated anthracene precursor having at least two pendant aromatic groups; and
- forming intramolecular C-C bonds between the acene cored and pendant aromatic groups to form a nitrogen-doped molecular segment.

[0027] In other embodiments the pendant aromatic groups are phenyls and the step of forming intramolecular C-C bonds utilizes a Heck reaction to yield a nitrogen-doped rubicene molecular segment product.

[0028] In still other embodiments the pendant aromatic groups are naphthyls and the step of forming intramolecular C-C bonds utilizes a base mediated

cyclodehydrogenation to yield a nitrogen-doped tetrabenzopentacene molecular segment product.

[0029] Still yet some other embodiments of the disclosure are directed to a method of forming a molecular segment including:

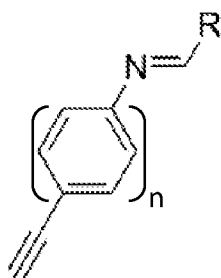
- reacting a halogenated anthracene bisalkyne and an aromatic adimine in the presence of a Lewis acid mediator and an oxidant such that the imine groups of the aldimine reacts with the alkyne group of the halogenated anthracene bisalkyne yielding a halogenated anthracene precursor having at least two pendant quinoline groups; and
- forming intramolecular C-C bonds between the acene cored and pendant quinoline groups to form a nitrogen-doped molecular segment.

[0030] In other embodiments the step of forming intramolecular C-C bonds utilizes a Heck reaction to yield a nitrogen-doped rubicene molecular segment product.

[0031] In still other embodiments the step of forming intramolecular C-C bonds utilizes a base mediated cyclodehydrogenation to yield a nitrogen-doped tetrabenzopentacene molecular segment product.

[0032] Still yet some other embodiments of the disclosure are directed to a method of forming graphene nanoribbon including:

- providing a bifunctional monomer according to:



- wherein n is an integer of at least 1, and R is an unsubstituted or substituted aromatic ring;
- polymerizing the bifunctional monomer in the presence of a Lewis acid mediator and a sacrificial oxidant such that the imine group of one bifunctional monomer reacts with the alkyne group of another bifunctional

monomer, yielding a polyquinoline product wherein the nitrogen from the imine group is incorporated into each of the multicyclic quinoline rings of the polyquinoline;

- continuing the polymerization of the polyquinoline to yield a polyquinoline precursor; and
- cyclodehydrogenating the polyquinoline precursor to yield a graphene nanoribbon.

[0033] In other embodiments n is at least 2 such that a polybenzoquinoline product is formed. In some such embodiments the benzoquinolines incorporate substituents at the 2 position, such that the substituents are disposed at edge locations along the graphene nanoribbon.

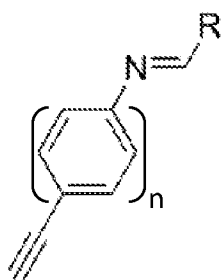
[0034] In still other embodiments the graphene nanoribbon is a nitrogen-doped $N=7$ armchair graphene nanoribbon. In some such embodiments the concentration of nitrogen doping can vary from 7 to 14%.

[0035] Still yet some other embodiments of the disclosure are directed to polyquinolines formed of a plurality of quinolines interlinked at the 4 and 6 positions.

[0036] Still yet some other embodiments of the disclosure are directed to polybenzoquinolines comprising two or more benzoquinolines interlinked at the 4 and 6 positions.

[0037] Still yet some other embodiments of the disclosure are directed to nitrogen-doped molecular segments selected from one of either rubicene or tetrapentacene.

[0038] Still yet some other embodiments of the disclosure are directed to quinoline monomers including:



wherein n is an integer of at least 1, and R is an unsubstituted or substituted aromatic ring.

[0039] In other embodiments the aromatic ring of R is further substituted with at least one of the following a heteroatom, a halogen, an alkyl chain, a methoxy (Me), an acetyl (Ac), an NHAc, an amine, an $N(Me)_2$, and a $S(Me)_2$. In some such embodiments the aromatic ring of R has at least two substitutions.

[0040] In still other embodiments n is at least 2. In some such embodiments the second aromatic ring comprises a further substituent. In other such embodiments the substituent is selected from the group of a heteroatom, a halogen, an alkyl chain, a methoxy (Me), an acetyl (Ac), an NHAc, an amine, an $N(Me)_2$, and a $S(Me)_2$.

[0041] In yet other embodiments the bifunctional monomer further comprises an additional benzoquinoline subunit. In some such embodiments the additional benzoquinoline subunit further comprises an additional substituent group selected from the group of a heteroatom, a halogen, an alkyl chain, a methoxy (Me), an acetyl (Ac), an NHAc, an amine, an $N(Me)_2$, and a $S(Me)_2$.

[0042] Additional embodiments and features are set forth in part in the description that follows, and in part will become apparent to those skilled in the art upon examination of the specification or may be learned by the practice of the invention. A further understanding of the nature and advantages of the present invention may be realized by reference to the remaining portions of the specification and the drawings, which forms a part of this disclosure.

BRIEF DESCRIPTION OF THE DRAWINGS

[0043] The description will be more fully understood with reference to the following figures and data graphs, which are presented as exemplary embodiments of the invention and should not be construed as a complete recitation of the scope of the invention, wherein:

[0044] FIG. 1A provides schematics of fullerenes, carbon nanotubes and graphene.

[0045] FIG. 1B provides synthesis schemes for conventional Sonogashira, Suzuki-Miyaura and Friedlander polyquinoline synthetic routes.

[0046] FIG. 1C provides synthesis schemes for molecular architectures available using a conventional Friedlander polyquinoline synthetic route.

[0047] FIG. 2A provides an overview of synthesis targets utilizing an aza-Diels-Alder (Povarov) reaction in accordance with embodiments of the invention.

[0048] FIG. 2B provides a synthesis scheme for an aza-Diels-Alder polyquinoline synthetic route in accordance with embodiments of the invention.

[0049] FIG. 3A provides a synthesis scheme for an aza-Diels-Alder quinoline synthetic route in accordance with embodiments of the invention.

[0050] FIG. 3B provides a flow-chart for a method for synthesizing quinolines in accordance with embodiments of the invention.

[0051] FIG. 4A provides a synthesis scheme for an aza-Diels-Alder polyquinoline synthetic route in accordance with embodiments of the invention.

[0052] FIG. 4B provides molecular diagrams for bifunctional monomers and polyquinolines in accordance with embodiments of the invention.

[0053] FIG. 5A provides an illustration of a retrosynthetic analysis of an AA/BB-type Friedländer polymerization.

[0054] FIG. 5B provides an illustration of a retrosynthetic analysis of an AA/BB-type aza-Diels-Alder polymerization in accordance with embodiments of the invention.

[0055] FIG. 6 provides a synthesis scheme for an AA/BB-type aza-Diels-Alder biquinoline synthetic route in accordance with embodiments of the invention.

[0056] FIG. 7 provides a synthesis scheme for an AA/BB-type aza-Diels-Alder polyquinoline synthetic route in accordance with embodiments of the invention.

[0057] FIGs. 8A and 8B provide synthesis schemes for model benzoquinoline compounds in accordance with embodiments of the invention.

[0058] FIGs. 9A and 9B provide synthesis schemes for polybenzoquinoline compounds in accordance with embodiments of the invention.

[0059] FIG. 10 provides a synthesis scheme for crowded benzoquinoline compounds in accordance with embodiments of the invention.

[0060] FIG. 11 provides a table of properties of various benzoquinoline compounds in accordance with embodiments of the invention.

[0061] FIG. 12 provides the chemical structure and HOMO and LUMO for various benzoquinoline compounds in accordance with embodiments of the invention.

[0062] FIGs. 13A and 13B provide illustrations of: A) tetrabenzopentacenes and graphene nanoribbons; and B) rubicenes and fullerenes of both a conventional design and designs in accordance with embodiments of the invention.

[0063] FIGs. 14A and 14B provide synthesis schemes for rubicenes and tetrabenzopentacenes in accordance with embodiments of the invention.

[0064] FIG. 15 provides a synthesis scheme for armchair graphene nanoribbons in accordance with embodiments of the invention.

[0065] FIGs. 16A and 16B provide synthesis schemes for nitrogen-doped graphene nanoribbons from bifunctional quinoline monomers in accordance with embodiments of the invention.

[0066] FIG. 17 provides a synthesis scheme for position 2 substituted benzoquinolines and methods of forming graphene nanoribbons therefrom in accordance with embodiments of the invention.

[0067] FIG. 18 provides bifunctional benzoquinoline monomers and graphene nanoribbon precursors formed therefrom in accordance with embodiments of the invention.

[0068] FIG. 19 provides illustrations of nitrogen-doped graphene nanoribbons in accordance with embodiments of the invention.

[0069] FIGs. 20A and 20B provide: A) the chemical structure and ^1H NMR spectrum; and B) the X-ray crystal structure of quinoline in accordance with embodiments of the invention.

[0070] FIG. 21 provides the results of an SEC-RI analysis of a polymerization reaction in accordance with embodiments of the invention.

[0071] FIG. 22 provides the results of an SEC-MALS analysis of polyquinoline in accordance with embodiments of the invention.

[0072] FIGs. 23A to 23C provide the structure and ^1H NMR of: A) a model quinoline; B) a quinoline monomer; and C) a polyquinoline in accordance with embodiments of the invention.

[0073] FIG. 24 provides FTIR spectra for a model quinoline, a quinoline monomer, and a polyquinoline in accordance with embodiments of the invention.

[0074] FIG. 25 provides normalized UV-vis absorbance spectra for a model quinoline, a quinoline monomer and a polyquinoline in accordance with embodiments of the invention.

[0075] FIGs. 26A and 26B provide: A) a chemical structure and ^1H NMR spectra; and B) a X-ray crystal structure for a biquinoline in accordance with embodiments of the invention.

[0076] FIGs. 27A and 27B provide an SEC-RI analysis: A) during a polymerization reaction; and B) after polymerization for a polyquinoline in accordance with embodiments of the invention.

[0077] FIGs. 28A and 28B provide the chemical structure and ^1H NMR spectra for: A) a model quinoline compound; and B) polyquinoline in accordance with embodiments of the invention.

[0078] FIG. 29 provides normalized UV-vis absorbance spectra for a model quinolines and polyquinolines in accordance with embodiments of the invention.

[0079] FIG. 30 provides cyclic voltammetry for thin films of a model quinoline and polyquinoline in accordance with embodiments of the invention.

[0080] FIGs. 31A and 31B provide: A) the energy minimized equilibrium for a model quinoline; and B) the HOMO and LUMO for the model quinoline in accordance with embodiments of the invention.

[0081] FIGs. 32A and 32B provide the X-ray crystal structures and chemical structures for two benzoquinolines in accordance with embodiments of the invention.

[0082] FIG. 33 provides SEC-RI chromatograms for polybenzoquinolines in accordance with embodiments of the invention.

[0083] FIG. 34 provides UV-vis absorbance spectra for benzoquinoline compounds in accordance with embodiments of the invention.

[0084] FIGs. 35A and 35B provide X-ray crystal structures for: A) an aldimine; and B) a benzoquinoline in accordance with embodiments of the invention.

[0085] FIG. 36 provides UV-vis absorbance spectra for benzoquinoline model compounds in accordance with embodiments of the invention.

[0086] FIG. 37 provides UV-vis absorption spectra for rubicene and tetrabenzopentacene compounds in accordance with embodiments of the invention.

[0087] FIG. 38 provides cyclic voltammograms for rubicene and tetrabenzopentacene compounds in accordance with embodiments of the invention.

[0088] FIGs. 39A to 39D provide the chemical structure, HOMO and LUMO for rubicenes and tetrabenzopentacene compounds in accordance with embodiments of the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0089] Turning now to the drawings, novel quinolines, polyquinolines, polybenzoquinolines, molecular segments of fullerenes (e.g., rubicenes) and graphene nanoribbons (e.g., and tetrobenzopentacenes), and graphene nanoribbons, and processes for producing such materials are provided. In many embodiments the processes utilize a form of an aza-Diels-Alder (Povarov) reaction to form quinolines, polyquinolines, benzoquinolines, polybenzoquinolines and oligobenzoquinolines. In some such embodiments polyquinolines thus produced are used to form molecular segments, graphene nanoribbon precursors and graphene nanoribbons. In many such embodiments the graphene nanoribbon precursors are formed from polybenzoquinolines and/or oligobenzoquinolines.

[0090] Many embodiments of the aza-Diels-Alder (Povarov) reaction utilize imine and alkynyl functionalized aromatic reagents in the presence of a Lewis acid mediator and a sacrificial oxidant to form the novel quinolines, polyquinolines, polybenzoquinolines, molecular segments, and graphene nanoribbons, as illustrated in FIG. 2A. In some such embodiments the imine and alkynyl functional groups may be collocated on a single bifunctional monomer. In other embodiments the imine and alkynyl functional groups may be located on separate compounds. These reagents may be further substituted as desired (e.g., alkyls, aromatic groups, heteroatoms, etc.) to

yield functionalized quinolines, biquinolines, benzoquinolines and polyquinolines that may then be used to form graphene ribbons.

[0091] An exemplary synthesis scheme in accordance with many embodiment is provided in FIG. 2B. In some such embodiments the reaction proceeds by either reacting a halogenated monomer with an R-group containing alkynyl or by polymerizing a bifunctional monomer (i.e., a monomer having both alkynyl and imine functional groups co-located on a single monomer molecule) in the presence of a Lewis acid mediator and a sacrificial oxidant such that the imine group of one bifunctional monomer reacts with the alkyne group of another bifunctional monomer, yielding a polyquinoline product wherein the nitrogen from the imine group is incorporated into each of the multicyclic quinoline rings of the polyquinoline. In some such embodiments:

- X may be a halogen or an alkynyl;
- n and m may be an integer of at least 1; and
- R is an unsubstituted or substituted aromatic ring.

[0092] In other embodiments the aromatic ring of R may be further substituted with at least one of the following a heteroatom, a halogen, an alkyl chain, a methoxy (Me), an acetyl (Ac), an NHAc, an amine, an N(Me)₂, and a S(Me)₂. In yet other embodiments the method further includes terminating the polymerization reaction to obtain a polyquinoline of specified length (designated by m in FIG. 2B). In still yet other embodiments n is at least 2 such that a polybenzoquinoline product may be formed. In some such embodiments the second aromatic ring may comprise a further substituent. In some other such embodiments the further substituent is selected from the group of a heteroatom, a halogen, an alkyl chain, a methoxy (Me), an acetyl (Ac), an NHAc, an amine, an N(Me)₂, and a S(Me)₂. In still other such embodiments the bifunctional monomer further may comprise an additional benzoquinoline subunit. In yet other such embodiments the additional benzoquinoline subunit may further comprise an additional substituent group selected from the group of a heteroatom, a halogen, an alkyl chain, a methoxy (Me), an acetyl (Ac), an NHAc, an amine, an N(Me)₂, and a S(Me)₂. In still yet other embodiments the individual quinolines of the polyquinoline are linked at the 4 and 6 positions.

[0093] In various other embodiments a cyclodehydrogenation reaction may be used to transform polyquinoline and/or polybenzoquinoline precursors into molecular segments and/or graphene nanoribbons.

[0094] The aza-Diels-Alder reactions described herein may be conducted under a variety of reaction conditions, including, temperatures (e.g., 30 to 130 °C), reaction times (e.g., 2 to 50 hours), etc. using a variety of Lewis acids (e.g., $\text{BF}_3 \cdot \text{OEt}_2$), non-polar solvents (e.g., toluene) and oxidants (e.g., chloranil). Likewise, the cyclodehydrogenation reactions described herein may be conducted under a variety of reaction conditions, including, various metallic catalysts (e.g., Pd and/or Fe). Further purification steps may also be incorporated in the methods to improve the reactant yield and purity (e.g., filtration, precipitation, chromatography, etc.).

[0095] These and other aspects of the embodiments will be described in greater detail in the following sections of the disclosure.

Synthesis of Quinolines and Polyquinolines

[0096] Quinoline is a heterocyclic aromatic organic compound with the chemical formula $\text{C}_9\text{H}_7\text{N}$. Quinoline itself has few applications, but many of its derivatives are useful in diverse applications. Polyquinolines are conjugated polymers of quinolines and are compounds with interesting electronic and optical products. However, until recently their synthesis has been constrained to cumbersome methods with limited flexibility for the synthesis of diverse compounds. Thus, there is a need in the art for facile methods of quinoline and polyquinoline synthesis that can be utilized to make a broad range of end products. Accordingly, many embodiments are provided which disclose novel quinoline and polyquinoline synthetic methods that enable the easy production of diverse quinoline and polyquinoline end products from inexpensive, commercially available starting materials.

[0097] Various embodiments of the synthetic methods for quinolines and polyquinolines incorporate an aza-Diels-Alder (Povarov) reaction. An exemplary synthesis scheme for such a reaction is provided in FIG. 2A. As shown, in many such embodiments the aza-Diels-Alder synthetic methods encompass a two-step process

whereby an aromatic compound having an aldimine functional group (e.g., a Schiff base) is reacted with a compound having an alkyne functional group in the presence of a Lewis acid mediator. In some embodiments the reaction further incorporates a sacrificial oxidant to prevent endogenous consumption of imine during the process. In embodiments where quinolines are to be produced the aromatic aldimine and alkyne functional groups are located on separate reagents. In other embodiments where polyquinolines are to be produced the aromatic aldimine and alkyne functional groups are co-located on a single bifunctional monomer. In many such embodiments the bifunctional monomer comprises a Schiff base having an alkyne substituent. Various embodiments methods implement an AB-type aza-Diels-Alder reaction to form quinolines and polyquinolines. In other embodiments methods implement an AA/BB-type aza-Diels Alder reaction to form biquinolines and polyquinolines. In still other embodiments modular benzo-, polybenzo- and oligobenzoquinolines are produced using an aza-Diels-Alder reaction. In some such embodiments, methods allow the incorporation of a variety of functional groups (R-groups) onto the aldimine/alkyne reagents or bifunctional monomer, and subsequently onto the polyquinoline ring produced therefrom.

Quinoline Synthesis

[0098] Turning now to methods for producing quinolines and quinolines produced therefrom, embodiments are provided that implement an aza-Diels-Alder (Povarov) reaction to yield a facile means of producing a wide-variety of quinoline compounds. An exemplary embodiment of such a process is shown schematically in FIG. 3A. As shown, in many embodiments a two-step process is utilized to produce quinolines from commercially available reactants. In many such embodiments the first-step comprises the production of one or more Schiff bases **1a** and **1b** from an amine substituted aromatic compound and an aldehyde containing a desired substituent group (hereinafter referred to as an “R-group”) utilizing standard protocols as will be known to those skilled in the art. (See, e.g., Taguchi, K. and Westheimer, F.H. *J. Org. Chem.* 1971, 36, 1570-1572, the disclosure of which is incorporated herein by reference.) In

many embodiments the R-group at least comprises an aromatic ring (e.g., a benzaldehyde) or an alkyl chain, and in many other embodiments the R-group is an aromatic ring having an alkyl substituent. The product of this initial reaction according to embodiments is a Schiff base having an aromatic substituent (e.g., an imine substitute aromatic structure) that is functionalized with the R-group.

[0099] In the second-step according to embodiments a compound comprising at least an alkyne functional group is reacted with the Schiff base **1a** and/or **1b** in the presence of a Lewis acid mediator. In accordance with embodiments of the process the resulting condensation results in the addition of the Schiff base with the alkyne substitute compound to form a quinoline heterocyclic ring **2a** and/or **2b** wherein the R-group is substituted on the heterocyclic ring ortho to the nitrogen, as shown in FIG. 3A.

[00100] It should be understood that although specific compounds are shown in the reaction diagram provided in FIG. 3A, these species are merely exemplary. It will be understood that the synthesis scheme may be generalized by altering the nature of the aromatic aldimine, the aldehyde and the alkyne containing reagents. For example, although an amine substitute benzene ring is shown as one of the initial reagents in FIG. 3A, it should be understood that any suitable amine substitute aromatic may be used. Likewise, although the R-groups attached to the aldehyde reagent are shown to be functionalized benzene, it should be understood that any suitable substituent may be used in accordance with embodiments, including, for example, alternative substituted aromatic groups. In addition, although the R-group in the exemplary embodiment provided in FIG. 3A comprises a further 8-carbon alkyl substituent attached to the aromatic group, it should be understood that the R-group in accordance with embodiments may further comprise one or more para- or meta- substituted substituents, such as, for example alkyl chains of a suitable length, heteroatoms or other functional groups. In some embodiments, for example, an alkyl chain of 2 to 50 carbons is used, while in other embodiments an alkyl chain of 5 to 10 carbons is used. In many embodiments the R-group may be chosen to selectively engineer one or more properties of the quinoline. For example, although not to be bound by theory, generally the longer the alkyl chain(s), the more soluble the end products will be, as may be

understood by one of ordinary skill in the art. Finally, although phenylacetylene is used as an example of a suitable alkyne containing molecule, it should be understood that any suitable alkyne containing molecule may be thus provided. Thus, by altering the functional groups of the R-group or alkyne any number of quinolines may be produced, such as, for example, bicyclic, tricyclic, and other multicyclic aromatic structures, for example with any number of additional substituent functional groups. Including, for example, heteroatoms (e.g., N, S, etc.) halogens (e.g., F, Cl, etc.), alkyl chains, methoxys (Me), acetyls, NHAc, amines, N(Me)₂, and S(Me)₂, among others may be inserted into the aromatic aldimine and/or alkyl reagents.

[00101] A flow-chart is provided in FIG. 3B that provides a flow-chart for forming quinolines in accordance with embodiments. As shown, in many embodiments as an initial step a Schiff base having an aromatic functional group is formed from commercially available reagents (e.g., an amine functionalized aromatic and a substituted aldehyde). The Schiff base is then reacted with an alkyne substituted compound in the presence of a Lewis acid mediator to form quinoline via a Povarov reaction. Finally, purification of one or both of the Schiff base or the final quinoline product may optionally be performed. Such purification may be performed by any suitable method, such as, for example, filtering, chromatography, and precipitation, as will be described in greater detail in the Exemplary Embodiments, below. Some exemplary embodiments of purification procedures include, for example, filtering the reaction mixture through celite and solvent removal, for example by vacuum, or flash chromatography using deactivated silica gel with pure hexanes as the mobile phase.

[00102] Although specific embodiments of reaction conditions, reagents and solvents will be described in detail in the Exemplary Embodiments, it will be understood that there is a great deal of flexibility in such parameters. For example, the first reaction may comprise the use of any suitable non-polar solvent such as, for example, toluene. The reaction may be carried out at any suitable temperature, such as, for example, from 90-150°C. In some specific embodiments the reaction may be carried out at a temperature of around 130°C. In some embodiments the reaction may be facilitated utilizing a molecular sieve to remove side products and water, when forming the Schiff

base. Any suitable mesh size for the molecular sieve may be used, such as, for example such as, for example a 3 Angstrom molecular sieve. Any reaction time may be used, for example reaction times of 4 to 50 hours are used in some exemplary embodiments, while in others the exemplary reaction time is 16 hours. Likewise, although a $\text{BF}_3\text{-OEt}_2$ Lewis acid is provided in the exemplary embodiments, it should be understood that any number of Lewis acids known to mediate the Povarov reaction may be used. (See, e.g., Kouznetsov, V.V. *Tetrahedron* 2009, 65, 2721-2750, the disclosure of which is incorporated herein by reference.) Finally, the exemplary embodiments show the condensation reaction being performed in the presence of a sacrificial oxidant, such as, for example, chloranil. It should be understood that any suitable sacrificial oxidant may be used. (See, e.g., *Chloranil Encyclopedia of Reagents for Organic Synthesis*, John Wiley & Sons; Braude, E.A., et al. *J. Chem. Soc.* 1960, 32, 49-3257; Huisgen, R., et al. *Tetrahedron* 1962, 17, 3-29; Fryer, R.I., et al. *J. Org. Chem.* 1970, 35, 2455-2459; and Landberg, B.E. and Lown, J.W. *J. Chem. Soc., Perkin Trans.* 11975, 1326-1333, the disclosure of which is incorporated herein by reference.)

[00103] As will be understood, regardless of the specific reagents and techniques used it will be understood that the methods for forming quinolines in accordance with embodiments provides a simple two-step aza-Diels-Alder synthetic route that requires only commercially available starting materials. In addition, the procedures allow for the use of a large number of commercially available benzaldehyde derivatives (e.g., having various R-groups), which can provide facile access to a diverse library of new quinoline materials.

Polyquinoline Synthesis (AB-Type Polymerization)

[00104] Turning now to methods for producing polyquinolines and polyquinolines produced therefrom, embodiments are provided that implement an aza-Diels-Alder (Povarov) reaction to yield a wide-variety of polyquinoline-type compounds. An exemplary embodiment of such a process is shown schematically in FIG. 4A. It will be understood that the synthesis scheme may be generalized by altering the nature of the aromatic aldimine, the aldehyde and the alkyne containing reagents. As shown, in many

embodiments a two-step process is utilized to produce polyquinolines from commercially available reactants. In many such embodiments the first-step comprises the production of a Schiff base **3** having both alkyne and aldimine functional groups, which will be referred to herein as a “bifunctional monomer.” Although the embodiment provided in FIG. 4A shows a specific bifunctional AB-type monomer, as will be described in greater detail, these bifunctional monomers may take many forms and types, including, for example, aza-Diels-Alder AA/BB-type monomers.

[00105] In this first reaction, an aldehyde functionalized R-group is combined with a bifunctional aromatic compound having at least amine and alkyne functional groups (e.g., alkyne functionalize aniline). In this reaction, the aldehyde on the R-group facilitates bonding of the R-group to the nitrogen on the bifunctional aromatic compound. As illustrated in FIG. 4A, the resulting product of the first reaction comprises the bifunctional monomer with its nitrogen substituent double bonded to the aromatic constituent of the R-group, such that the bifunctional monomer **3** comprises at least one aromatic ring (e.g. a benzene ring or the like), with an imine substituent and a substituted alkyne. Although the exemplary embodiment shows the alkyne being para-substituted, it will be understood that in other embodiments meta-substituted alkyne groups may also be used.

[00106] Although in the exemplary embodiment of the process shown in FIG. 4A the bifunctional monomer comprises at least one benzene ring with an imine substituent and a para-substituted alkyne, it should be understood that alternative arrangements might be used with the reaction described in accordance with embodiments. For example, the monomer may comprise any suitable aromatic group. Moreover, the bifunctional monomer may comprise bicyclic, tricyclic, and other multicyclic aromatic structures, such as are depicted, for example, in monomers E1 to E4 provided in FIG. 4B. In addition, although the R-group in the exemplary embodiment provided in FIG. 4A comprises a further 8-carbon alkyl substituent, it should be understood that the R-group in accordance with embodiments may further comprise one or more para- or meta-substituted substituents, such as, for example alkyl chains of a suitable length. In some embodiments, for example, an alkyl chain of 2 to 50 carbons is used, while in other

embodiments an alkyl chain of 5 to 10 carbons is used. In many embodiments the R-group may be chosen to selectively engineer one or more properties of the end product. For example, although not to be bound by theory, generally the longer the alkyl chain(s), the more soluble the end products will be, as may be understood by one of ordinary skill in the art. Finally, as shown in FIG. 4B, many other substitutions and substituents may be made to the bifunctional monomers in accordance with embodiments, including the introduction of halogens (e.g., F, Cl, etc.), alkyl chains, OMe, NHAc, amines, N(Me)₂, and S(Me)₂, among others.

[00107] As will be understood, regardless of the specific reagents and techniques used methods for forming bifunctional monomers in accordance with embodiments provide a simple synthetic route that requires only commercially available starting materials. In addition, the procedures allow for the use of a large number of commercially available benzaldehyde derivatives (e.g., for use as R-groups), which provides facile access to a diverse library of alternative bifunctional monomer compounds.

[00108] As shown in the flow-chart in FIG. 4C, the first-step of the reaction in accordance with embodiments may be completed by combining the reactants (e.g., R-group and bifunctional aromatic) into solution with a suitable polar solvent (e.g., toluene) to form the bifunctional monomer. The reactants are allowed to react under suitable conditions (e.g., reaction temperature such as 90-150 °C for 16 hours) followed by cooling the reaction vessel to room temperature. Purification of the bifunctional monomer may then be performed prior to performance of the second reaction.

[00109] Although specific embodiments of reaction conditions, reagents and solvents of this first-step of the reaction will be described in detail below, it will be understood that there is a great deal of flexibility in such parameters. For example, the first reaction may comprise the use of any suitable non-polar solvent such as, for example, toluene. The reaction may be carried out at any suitable temperature, such as, for example, from 90-150°C. In some specific embodiments the reaction may be carried out at a temperature of around 130°C. In some embodiments the reaction may be facilitated utilizing a molecular sieve to remove side products and water, when forming the

bifunctional monomer. Any suitable mesh size for the molecular sieve may be used, such as, for example a 3 Angstrom molecular sieve. Any reaction time may be used, for example reaction times of 4 to 50 hours are used in some exemplary embodiments, while in others the exemplary reaction time is 16 hours.

[00110] Turning to the second-step of the method, as shown in FIG. 4A, in many embodiments a polyquinoline is produced from the bifunctional monomer via a Diels-Alder AB-type polymerization reaction wherein the imine group of one bifunctional monomer combines with the alkyne group of a second bifunctional monomer. As shown in the reaction diagram, the second-step of the reaction according to embodiments results in the incorporation of the nitrogen from the imine group into a multicyclic quinoline group, with the R-group as a substituent, adjacent (i.e., ortho) to the nitrogen. In many embodiments this allows for polyquinolines that are linked at the 4,6 positions of the quinoline ring, as shown for example in FIG. 4A.

[00111] As shown in the diagram provided in FIG. 4A, the bifunctional Schiff base monomer **3** is reacted in the presence of a Lewis acid mediator to form the polyquinoline **4** via an AB-type Diels-Alder polymerization (Povarov) reaction. In embodiments of the process this second polymerization step may be halted and the reaction products isolated or purified using any means known in the art. For example, the reaction may be halted by cooling the reaction mixture to room temperature and dilution with a suitable solvent, such as, for example, CH₂Cl₂. Reagents may be quenched with saturated NaHCO₃ and the organics may then be washed with saturated NaHCO₃. Finally, purification of the polyquinolines may then optionally be performed. Purification may be performed by any suitable method, such as, for example, filtering, chromatography, and precipitation, as will be described in greater detail in the Exemplary Embodiments, below. Some exemplary embodiments of purification procedures include, for example, filtering the reaction mixture through cotton and solvent removal, for example by vacuum, or size-exclusion chromatography where the mixture is dissolved in CHCl₃ and, after being purified, is precipitated from ethanol to yield the product. Using purification techniques in accordance with such embodiments it is possible to obtain nearly monodisperse polyquinoline products.

[00112] Although specific embodiments of reaction conditions, reagents and solvents of this second-step of the reaction will be described in detail in the Exemplary Embodiments, it will be understood that there is a great deal of flexibility in such parameters. For example, the first reaction may comprise the use of any suitable non-polar solvent such as, for example, toluene. The reaction may be carried out at any suitable temperature, such as, for example, from 70-130 °C. In some specific embodiments the reaction may be carried out at a temperature of around 110 °C. Any reaction time may be used, for example reaction times of 2 to 50 hours are used in some exemplary embodiments, while in others the exemplary reaction time is 24 hours. Likewise, although a BF₃-OEt₂ Lewis acid is provided in the exemplary embodiments, it should be understood that any number of Lewis acids known to mediate the Povarov reaction may be used. (See, e.g., Kouznetsov, V.V. *Tetrahedron* 2009, 65, 2721-2750, the disclosure of which is incorporated herein by reference.) Finally, the exemplary embodiments show the condensation reaction being performed in the presence of a sacrificial oxidant, such as, for example, chloranil. It should be understood that any suitable sacrificial oxidant may be used. (See, e.g., *Chloranil Encyclopedia of Reagents for Organic Synthesis*, John Wiley & Sons; Braude, E.A., et al. *J. Chem. Soc.* 1960, 32, 49-3257; Huisgen, R., et al. *Tetrahedron* 1962, 17, 3-29; Fryer, R.I., et al. *J. Org. Chem.* 1970, 35, 2455-2459; and Landberg, B.E. and Lown, J.W. *J. Chem. Soc., Perkin Trans.* 11975, 1326-1333, the disclosure of which is incorporated herein by reference.)

[00113] Regardless of the specific reaction conditions used, it should be understood that utilizing the bifunctional monomers and AB-type Diels-Alder polymerization methods described herein in accordance with embodiments allows for the facile production of a wide-variety of polyquinolines. In particular, as the structure of the polyquinolines in accordance with embodiments is determined by the structure of the bifunctional monomer including the substituent R-group, a number of diverse starting materials may be used in order to synthesize a large number of different polyquinoline materials as illustrated by exemplary monomers E1 to E4 and associated polyquinolines in FIG. 4B.

Biquinoline and Polyquinoline Synthesis (AA/BB-Type Polymerization)

[00114] Although the above discussion focused on the use of an AB-type bifunctional monomer to form polyquinolines via an AB-type Diels-Alder polymerization reaction (i.e. having single imine and alkyne functionalities), other embodiments are directed to methods of forming polyquinolines that implement an AA/BB-type Diels-Alder polymerization (i.e., using reagents having multiple imine and alkyne functionalities).

[00115] A conventional AA/BB-type polymerization is used in the Friedländer approach, which to date has served as the workhorse of polyquinoline synthesis. (See, e.g., J. K. Stille, *Macromolecules*, 1981, 14, 870; and L. S. Povarov, *Russ. Chem. Rev.*, 1967, 36, 656, the disclosures of which are incorporated herein by reference.) FIG. 5A provides an illustration of a retrosynthetic analysis of a typical AA/BB-type Friedländer polymerization, entailing the reaction of an AA-type bis(amino ketone) monomer with a BB-type bis(keto methylene) monomer. However, as previously discussed, the Friedländer synthesis often requires the resulting polyquinolines to possess complex side chain substituents and cannot provide access to certain backbone architectures (as previously described with respect to FIG. 1C).

[00116] Methods according to embodiments implement an AA/BB-type aza-Diels-Alder polymerization as illustrated in FIG. 5B that provide a simple method of obtaining a wide-variety of polyquinolines, including polyquinolines containing 4,6-linked quinoline subunits. As shown, such embodiments comprise the reaction of an AA-type aromatic diimine monomer with a BB-type dialkynyl monomer to furnish a polyquinoline. It will be understood that the synthesis scheme shown in FIG. 5B is merely exemplary and may be generalized by altering the nature of the AA-type aromatic diimine monomer and the BB-type dialkynyl monomer reagents.

[00117] Some embodiments of an AA/BB-type aza-Diels-Alder reaction are utilized to form biquinolines. An exemplary embodiment of such a biquinoline synthetic route is provided in FIG. 6. Again it will be understood that the synthesis scheme shown in FIG. 6 is merely exemplary and may be generalized by altering the nature of the aromatic diimine monomer and the alkynyl monomer reagents. As shown, the process according to embodiments utilizes the aza-Diels-Alder reaction previously described above but

wherein bis(aldimines) **1a-c** are reacted with an alkyne functionalized compound (e.g. phenylacetylene) in the presence of a Lewis acid mediator (e.g., $\text{BF}_3 \cdot \text{OEt}_2$) and a sacrificial oxidant (e.g., chloranil) to yield biquinolines **2a-c**. It should be understood that although certain bis(aldimines) **1a-c** are used to form the biquinolines in these exemplary embodiments, any suitable aromatic bisaldimine may be formed in accordance with established methods known to those skilled in the art. (See, e.g., D. J. Dibble, et al., *Macromolecules*, 2015, 48, 557 and D. J. Dibble, et al., *Angew. Chem. Int. Ed.*, 2015, 54, 5883, the disclosures of which are incorporated herein by reference.) In particular, it will be understood that the R-groups used in the bis(aldimines) allow for the installation of nearly arbitrary substituents on the peripheral aromatic (e.g., phenyl) groups, including electron donating, electron withdrawing, sterically hindered and saturated alkyl moieties as will be discussed in greater detail below. As will be discussed in greater detail in the Exemplary Embodiments the AA/BB-type aza-Diels-Alder biquinoline synthesis in accordance with embodiments utilized mild conditions and commercial starting materials to produce regioisomerically pure products in excellent yield.

[00118] Other embodiments implement this AA/BB-type aza-Diels-Alder reaction to prepare polyquinolines, as illustrated in FIG. 7. In these embodiments a diimine **1c** is reacted with a dialkynyl (e.g. diethynyl benzene) in an AA/BB-type polymerization under the conditions discussed above for the synthesis of biquinolines to yield the polyquinoline **3c**. It will be understood that the synthesis scheme shown in FIG. 7 is merely exemplary and may be generalized by altering the nature of the aromatic diimine monomer and the BB-type dialkynyl monomer reagents, as previously discussed.

[00119] In both embodiments of the biquinoline synthesis and the polyquinoline synthesis, it should be understood that alternative reagents might be used with the reaction described in accordance with embodiments. For example, the imine and alkynyl containing reagents may comprise any suitable aromatic group. Moreover, the reagents may comprise bicyclic, tricyclic, and other multicyclic aromatic structures. In addition, although certain R-groups are provided in the exemplary embodiment provided in FIGs. 6 and 7, it should be understood that the R-group in accordance with embodiments may

further comprise one or more para- or meta- substituted substituents, such as, for example alkyl chains of a suitable length. In some embodiments, for example, an alkyl chain of 2 to 50 carbons is used, while in other embodiments an alkyl chain of 5 to 10 carbons is used. In many embodiments the R-group may be chosen to selectively engineer one or more properties of the end product. For example, although not to be bound by theory, generally the longer the alkyl chain(s), the more soluble the end products will be, as may be understood by one of ordinary skill in the art. Finally, as will be discussed in greater detail below, many other substitutions and substituents may be made to the bifunctional monomers in accordance with embodiments, including the introduction of heteroatoms, halogens (e.g., F, Cl, etc.), alkyl chains, OMe, NHAc, amines, N(Me)₂, and S(Me)₂, among others.

[00120] Finally, as in the other embodiments thus far discussed, although specific embodiments of reaction conditions, reagents and solvents will be described in detail in the Exemplary Embodiments, it will be understood that there is a great deal of flexibility in such parameters including, for example: the nature of the non-polar solvent (e.g., toluene), the reaction temperature (which may range for example from 70-130 °C), the reaction times (e.g., 2 to 50 hours), the Lewis acid used (e.g., BF₃-OEt₂), the presence of a sacrificial oxidant (e.g., chloranil), etc.

Benzoquinoline Synthesis

[00121] Many embodiments are directed to novel benzoquinolines and polybenzoquinolines and methods of their manufacture. More particularly, embodiments provide methods for the modular synthesis of polybenzoquinolines, which, as will be discussed in greater detail later, constitute a generic class of GNR precursor polymers. In various embodiments a general aza-Diels–Alder reaction for the synthesis of a series of benzoquinoline compounds is provided. In other embodiments an AB-type bifunctional monomer and methods for synthesizing congested polybenzoquinoline via a Diels–Alder-type polymerization reaction from such monomers are also provided. Methods are also provided for the modular preparation of polybenzoquinolines of varying size and

having variable peripheral substituents. Finally, molecules and methods are provided in various embodiments capable of serving as precursors to a nitrogen-doped GNR.

[00122] Some embodiments directed to benzoquinoline compounds and their method of manufacture are shown in the diagram provided in FIG. 8A. As described in previous embodiments benzoquinoline compounds (such as those shown by example at FIG. 8A, **3a** and **3b**) are formed by the reaction of an aldimine having at least two aromatic groups (e.g. naphthalene) (FIG. 8A, **1a** and **1b**) with an alkyne having one or more aromatic groups (e.g., naphthylalkyne)(FIG. 8A, **2**) in the presence of a suitable Lewis acid mediator ($\text{BF}_3 \cdot \text{OEt}_2$) and a sacrificial oxidant (e.g., chloranil). It will be understood that the synthesis scheme shown in FIG. 8A is merely exemplary and may be generalized by altering the nature of the reagents and their substituents

[00123] Although the production of single benzoquinolines have been described, as shown in FIGs. 8A (compounds **5a** and **5b**) and FIG. 8B (compound **8**), in other embodiments oligobenzoquinolines and methods of their manufacture are also provided. In such embodiments the pendant bromides of the benzoquinolines (e.g., compounds **3a** and **3b** in FIG. 8A) are converted to alkynes, forming an alkyne functionalize benzoquinoline (e.g., compounds **4a** and **4b** of FIG. 8A). The alkyne functionalized benzoquinoline is then reacted with the aldimine (e.g., compound **1a** or **1b** in FIG. 8A) again using a Lewis acid mediator and sacrificial oxidant to produce oligobenzoquinolines (compounds **5a** and **5b**.)

[00124] This linear synthetic strategy in accordance with embodiments is capable of producing regioisomerically pure products, and may be utilized to produce compounds having an arbitrary number of benzoquinolines interconnected. For example, FIG. 8B provides a diagram of a process for producing pentameric benzoquinolines (FIG. 8B, compound **8a**) in accordance with embodiments of the method. It will be understood that the synthesis scheme shown in FIG. 8B is merely exemplary and may be generalized by altering the nature of the reagents and their substituents. As shown, in this embodiment the dimeric benzoquinoline (FIG. 8B, compound **5b**) is used as the starting material to generate complementary benzoquinoline reagents having alkyne (FIG. 8B, compound **6**) and imine (FIG. 8B, compound **7**) functionalities. Thus in

embodiments an alkyne functionalized benzoquinoline reagent is formed by converting the pendant bromide of the benzoquinoline (FIG. 8b, compound **5b**) to an alkyne, and an imine functionalized benzoquinoline reagent is formed by converting the acetyl-protected amine of the benzoquinoline (FIG. 8B, compound **5b**) to an aldimine using reactions and reagents that will be known to those skilled in the art. These imine and alkyne functionalize benzoquinoline reagents are then combined under the Povarov reaction conditions (e.g., in the presence of a Lewis acid and a sacrificial oxidant) to furnish a pentameric benzoquinoline (FIG. 8B, compound **8**). Accordingly, using embodiments, it is not only possible to prepare benzoquinoline macromolecules using a linear synthetic strategy, but also to more facilely create larger benzoquinoline macromolecules by independently modifying the bromide and amine termini of such benzoquinoline precursors.

[00125] In addition to such benzoquinoline macromolecules, in other embodiments elongated benzoquinoline macromolecules and methods of producing the same are also provided. In many such embodiments, as shown in the schematic provided in FIGs. 9A and 9B, an AB-type aza-Diels-Alder (Povarov) polymerization reaction is implemented using an aromatic bifunctional monomer. It will be understood that the synthesis schemes shown in FIGs. 9A and 9B are merely exemplary and may be generalized by altering the nature of the reagents and their substituents.

[00126] In such embodiments, the aromatic bifunctional monomer having both alkyne and aldimine functionalities (e.g., compound **10a** in FIG. 9A) is produced in a first-step from a suitable amine functionalized aromatic reagent (e.g., an 4-iodonaphthylamine: compound **9** in FIG. 9A) and a suitable aldehyde reagent. In many preferred embodiments the bifunctional monomer has both the requisite alkyne and aldimine functional groups within a single substrate, as well as an alkyl chain for enhanced solubility. Using the bifunctional monomer thus provided an AB-type aza-Diels-Alder (Povarov) polymerization reaction (as described above) is implemented to polymerize the bifunctional monomer and yield a polybenzoquinoline (FIG. 9A, compound **11a**).

[00127] Many embodiments of the methods of polymerization allow for a modularity that provides for the accommodation of different peripheral substituents within the

benzoquinolines and polybenzoquinolines. In many such embodiments bifunctional monomers are provided that incorporate desired substituent groups, such as, for example, branched alkyl chains (FIG. 9A, compound **11b**) and/or fluorine substituents (FIG. 9A, compound **11c**). In such embodiments the methods described above in relation to embodiments for producing benzoquinolines and polybenzoquinolines (e.g., FIGs. 8A, 8B and 9A, compounds **3b**, **5b**, **8** and **11a**) may be adapted to furnish substituted polybenzoquinolines (e.g., FIG. 9A, compounds **11b** from **10b** and polybenzoquinoline **11c** from **10c**) by simply altering the functional R-groups attached to the bifunctional monomer. For example, many other substitutions and substituents may be made to the bifunctional monomers in accordance with embodiments by simply altering the R-group of the aldehyde reagent utilized to produce the bifunctional monomer. Some examples of such substitutions may include the introduction of heteroatoms, halogens (e.g., F, CL, etc.), alkyl chains, OMe, NHAc, amines, N(Me)₂, and S(Me)₂, among others. Accordingly, embodiments of such methods allow for the preparation of distinct polybenzoquinolines under similar conditions underscoring the potential general scope of embodiments of the approach.

[00128] In other embodiments the polymerization strategy for producing polybenzoquinolines outlined above may also be used in the preparation of longer, sequence-variable polybenzoquinoline macromolecules. In such embodiments (an example of which is provided in FIG. 9B) the procedure for the preparation of the bifunctional monomer (e.g., compounds **10a–10c** in FIG. 9A) is slightly modified. In such embodiments the bifunctional monomer comprising the requisite alkyne and aldimine functional groups incorporates an expanded aromatic core containing an additional benzoquinoline subunit. In some such embodiments this additional benzoquinoline subunit also comprises an alternating substituent group of interest (R²-group), such as linear and/or branched alkyl sidechains (e.g., FIG. 9B, compound **12**), or other desired R-groups as previously discussed (e.g., heteroatoms, halogens (e.g., F, CL, etc.), alkyl chains, OMe, NHAc, amines, N(Me)₂, and S(Me)₂, etc.). Once the expanded bifunctional monomer is prepared, polymerization may be undertaken via the aza-Diels-Alder (Povarov) reaction described earlier to yield a polybenzoquinoline

having incorporated therein the desired additional functionality (e.g., R²-group in compound **13** of FIG. 9B).

[00129] Other embodiments are directed to 2,4,6 substituted benzoquinolines and methods of their production. In such embodiments, a methodology is provided for the installation of varying chemical substituents at the 2 position of 4,6-linked benzoquinolines (corresponding to edge locations in GNRs formed therefrom, as will be discussed in greater detail below). Given the well-known sensitivity of the electronic structure of GNRs to edge modification, embodiments that allow for such edge modification provide the further ability to control the electrical functionality of the envisioned GNR materials.

[00130] As shown in FIG. 10, in many embodiments an aza-Diels–Alder reaction is provided that allows for the synthesis of 2,4,6-substituted benzoquinoline compounds via a Lewis acid-promoted Povarov reaction as described elsewhere herein. It will be understood that the synthesis schemes shown in FIG. 10 is merely exemplary and may be generalized by altering the nature of the reagents and their substituents. Thus, in accordance with embodiments an aromatic aldimine precursor (compound **1a** in FIG. 10) is produced from commercially available starting materials (e.g., 4-bromonaphthylamine and octyl benzaldehyde) through known literature protocols. (See, e.g., See, e.g., D. J. Dibble, et al., *Macromolecules*, 2015, 48, 557 and D. J. Dibble, et al., *Angew. Chem. Int. Ed.*, 2015, 54, 5883, cited above.) The aromatic aldimine is then reacted with an aromatic alkyne having a further aldehyde functionality attached thereto (e.g., naphthyl alkyne, compound **2** in FIG. 10) in the presence of a Lewis acid to furnish the crowded benzoquinoline (e.g., compound **3a** in FIG. 10). As previously described, a sacrificial oxidant (e.g., chloranil) may also be provided to ensure the benzoquinoline is fully aromatized. As described previously, a number of suitable Lewis acids may be used to promote the cycloaddition of the alkyne to the aldimine. The table provided in FIG. 11 provides the results from several Lewis acids (entries 1 to 4 in Table 1). As shown a number of the Lewis acids resulted in measurable yields. In particular, good yields and regioselectivity were obtained for the following Lewis acids: AgOTf (67%),

ZnCl₂ (75%), and BF₃•OEt₂ (83%) (entries 6-8 in Table 1) showing that a range of possible Lewis acids are usable with embodiments of the methods.

[00131] As discussed previously, many different commercially available benzaldehyde derivatives may be utilized to prepare distinct aromatic aldimines (e.g., compounds **1b** to **1i** in FIG. 11). Embodiments allow for these structurally variant aromatic aldimines to be combined with the aromatic alkyne to furnish a vast array of regioisomerically pure 2,4,6-substituted benzoquinolines (e.g., compounds **3b** - **3i** in FIG. 11). Notably methods according to embodiments allow for the preparation of benzoquinolines featuring both electron withdrawing (e.g., entries 8, 9, 10, and 12 in Table 1 of FIG. 11) and electron donating (e.g., entry 15 in Table 1 of FIG. 11) substituents in good yields of > 65 %. Moreover, embodiments of the protocol are also capable of accommodating sterically hindered aldimines featuring ortho substituents on their pendant phenyl rings (e.g., entries 8 and 13 in Table 1), with little deleterious effect on the yields. Embodiments of methods also accommodate aliphatic substituents (e.g., entry 14 in Table 1 of FIG. 11). Accordingly, embodiments readily accommodate varying chemical functionalities, including electron donating, electron withdrawing, sterically hindered, and saturated alkyl moieties.

[00132] Studies on the electronic properties of these exemplary compounds with ultra-violet-visible (UV-vis) spectroscopy, as described in greater detail in the Exemplary Embodiments, establish that steric effects can be utilized in accordance with embodiments to alter the electronic properties of the benzoquinoline compounds. For example, FIG. 12 provides the chemical structures and corresponding HOMO and LUMO isosurface plots for compounds a number of exemplary compounds made in accordance with embodiments (e.g., compounds **3b**, **3e**, **3g**, **3h**, and **3i**, from FIG. 11). As shown, the orientation of the naphthyl substituent relative to the benzoquinoline core was similar for these molecules, with a typical dihedral angle of ~74°, however, the dihedral angle between the pendant phenyl ring and benzoquinoline core could be roughly correlated with the localization of the HOMO and LUMO (FIG. 12). Overall, this analysis indicates that steric effects play an important role in dictating the electronic properties of the exemplary compounds. Accordingly, although not to be bound by

theory, in some embodiments steric interactions between the crowded benzoquinoline core and the 2,6 substituents of the pendant phenyl rings can increase the dihedral angle between the two systems, twisting them out of co-planarity thereby decoupling the phenyl and benzoquinoline aromatic systems and reducing the overall size of the pi-conjugated framework and altering the electronic properties of the compounds. As such, some embodiments are directed to methods of utilizing steric effects to alter the electronic properties of crowded benzoquinolines, and for the use of such engineered compounds as precursors to provide for the rational design and bottom-up preparation of nitrogen-doped GNRs and their electronic properties.

[00133] In summary, embodiments have been developed for the preparation of polybenzoquinolines implementing an aza-Diels–Alder (Povarov) reaction capable of synthesizing modular polybenzoquinolines in relatively few steps using inexpensive precursor materials, and straightforward reaction conditions. Utilizing such embodiments it is possible to prepare a variety of benzoquinoline compounds, including crowded yet soluble polymers with variable peripheral substituents and sizes. Indeed, given the large number of commercially available benzaldehyde derivatives, embodiments of methods allow access to a diverse family of novel benzoquinoline-based materials. Moreover, as will be discussed in greater detail below, the polybenzoquinolines constitute a novel class of precursor polymers for N=7 armchair GNRs, which conventionally have been prepared exclusively from polyanthracenes, some of which have a known propensity to oxidation and undesirable photochemistry. (See, e.g., J.C.C. Atherton and S. Jones, *Tetrahedron* 2003, 59, 9039-9057; and A.R. Reddy and M. Bendikov, *Chem. Commun.* 2006, 1179-1181, the disclosures of which are incorporated herein by reference.) Finally, embodiments provide methods of altering the electronic structures of substituted benzoquinolines by controlling steric factors, which embodiments allow for the control of and ability to rationally design the electronic properties of materials such as GNRs from such building blocks. Finally, given the known general utility of the quinoline motif in medicinal, inorganic, and materials chemistry, embodiments provide broad relevance not only for carbon-based electronics but also for a wide range of other chemical disciplines.

Syntheses of Molecular Segments of Fullerenes and Graphene Nanoribbons

[00134] Carbon-based materials, such as fullerenes and graphene nanoribbons (GNRs), have often been touted as the successors to inorganic semiconductors in solar cells and nanoscale transistors. Thus, much research effort has focused on the bottom-up preparation of structurally and chemically well-defined variants of these carbon allotropes, as well as their molecular segments, via traditional organic chemistry techniques. In particular, graphene nanoribbons (GNRs), which are narrow strips of graphene that feature a quantum confinement-induced band gap, constitute a promising class of materials for the next generation of semiconductor devices. The electronic properties of GNRs are exquisitely sensitive to their width, heteroatom content, and edge character. Thus, much research effort has been devoted to the preparation of GNRs that are structurally and chemically defined at the atomic level. Although traditional top-down lithographic approaches have exhibited only limited success in this regard, more recent studies have demonstrated the bottom-up preparation of pristine GNRs via the surface-assisted or solution-phase synthesis of nanoribbon precursor polymers, followed by their cyclodehydrogenation. To date, these bottom-up strategies have primarily focused on all-carbon systems, with only a limited number of studies describing the preparation of nitrogen-containing GNR frameworks. Given the immense potential of substitutional nitrogen doping for tailoring the properties of GNRs, this sparse literature precedent is surprising and likely arises from the substantial challenges associated with the incorporation of heteroatoms at arbitrary locations in graphitic materials.

[00135] Accordingly, embodiments are directed to molecular segments of fullerenes and graphene nanoribbons, and methods for the rational design and preparation of such materials and their precursors. In many such embodiments, the molecular segments (e.g., rubicene and tetrabenzopentacenederivatives), which constitute molecular segments of C₇₀ fullerenes and the graphene nanoribbons (e.g., N=7 armchair graphene nanoribbons) are nitrogen-doped as illustrated in FIG. 13. Some such embodiments implement the formation of molecular segments and graphene

nanoribbons using a combination of an aza-Diels-Alder reaction to form quinoline precursors followed by the cyclodehydrogenation of the quinoline precursor to the molecular segments and/or graphene nanoribbons, as will be described in greater detail below.

[00136] Various embodiments of methods of forming such molecular segments and graphene nanoribbons encompass bifunctional quinoline and/or monomers, wherein the monomers comprise at least one aromatic ring incorporating at least an imine and an alkyne substituent. In many such embodiments the aromatic ring is a fused aromatic ring and the imine and aldehyde substituents are collocated on a first of said aromatic rings at the 1 and 4 positions. In other embodiments the second aromatic ring may comprise all carbons or may comprise one or more heteroatoms, including, for example, nitrogen. The monomers may also comprise more than two aromatic rings. The monomers may be polymerized using an aza-Diels-Alder reaction, as described herein, to create a variety of graphene nanoribbon precursors and molecular segments of fullerenes. Many embodiments are thus directed to such quinoline monomers as well as precursors based on such structures and molecular segments and graphene nanoribbons formed therefrom.

Synthesis of Molecular Segments

[00137] In some aspects, embodiments provide doped molecular segments and methods of the rational design and preparation of such molecular segments. Some embodiments of such molecular segments include, for example, nitrogen-doped molecular segments, including, rubicene and tetrabenzopentacene derivatives, which constitute molecular segments of C70 fullerenes and N=7 armchair graphene nanoribbons, respectively. Embodiments of these molecular segments are illustrated in FIGs. 13A and 13B. Embodiments of methods for forming molecular segments provide facile access to previously unknown polycyclic aromatic hydrocarbons (PAHs), which hold promise both as organic electronic functional materials and as model compounds for the ultimate construction of larger carbonaceous systems, such as, for example, graphene nanoribbons. It will be understood that embodiments of such molecular

segments and graphene nanoribbons are formed as alternatives to classic all-carbon rubicene (FIG. 13A, left) and tetrabenzopentacene (FIG. 13B, left) motifs. In such embodiments, these molecules incorporate nitrogen heteroatoms within their aromatic systems (FIG. 13A, right and FIG. 13B, right). Such PAHs constitute molecular segments of nitrogen-doped C70 fullerenes (FIG. 13A, bottom) and N=7 armchair graphene nanoribbons (FIG. 13B, bottom), which have been difficult historically to access synthetically.

[00138] In many such embodiments the methods involve a two-step process wherein a first step comprises the synthesis of bifunctional halogenated building blocks followed by the conversion of these building block to form highly derivatized anthracene precursors via the aza-Diels-Alder (Povarov) reaction previously described. (See, e.g., D. J. Dibble, et al., *Macromolecules* 2015, 48, 557–561, the disclosure of which is incorporated herein by reference.) Embodiments of such two-step processes further incorporate a second step wherein the precursors formed in the first Povarov conversion step are used to form two 5-membered fused rings via a Heck reaction (see, e.g., X. Chen, et al., *Angew. Chem. Int. Ed.* **2009**, 48, 5094–5115; *Angew. Chem.* **2009**, 121, 5196–5217; D. McCartney, P. J. Guiry, *Chem. Soc. Rev.* 2011, 40, 5122–5150; and R. F. Heck, *Org. React.* 1982, 27, 345–390, the disclosures of which are incorporated herein by reference), or to form two 6-membered fused rings via a base-mediated cyclodehydrogenation reaction (see, e.g., A. Studer, D. P. Curran, *Nat. Chem.* 2014, 6, 765–773; O. R. Luca, et al., *Org. Chem. Front* 2015, 2, 823–848; and M. Kivala, et al., *Cyclodehydrogenation in the Synthesis of Graphene-Type Molecules In Materials Science and Technology*, 2013, pp. 373–420, the disclosures of which are incorporated herein by reference) within the obtained anthracene skeletal frameworks, furnishing nitrogen-containing molecular segments, such as, for example, rubicene or tetrabenzopentacene derivatives, respectively.

[00139] Exemplary embodiments of such synthetic schemes are provided in FIGs. 14A and 14B. It will be understood that the synthesis schemes shown in FIGs. 14A and 14B are merely exemplary and may be generalized by altering the nature of the reagents and their substituents. As shown in FIG. 14A, molecular segments (e.g.,

rubicene **3** and tetrabenzopentacene **5** in FIG. 14A) are formed via a Povarov reaction as previously described. More specifically, in embodiments the molecular segments (FIG. 14A) are formed by first preparing a bis(aldimine) **1** through known literature procedures as previously described. Subsequently, anthracene precursor compound **2** is obtained by reacting the aldimine with an alkyne functionalize single ring aromatic compound (e.g., phenylacetylene) in the presence of a Lewis acid mediator (e.g., $\text{BF}_3 \cdot \text{OEt}_2$) and an oxidant (e.g., chloranil) under suitable reaction times and temperatures (as previously described), while anthracene precursor compound **4** is obtained by reacting bis(aldimine) **1** with an alkyne functionalized double ring aromatic compound (e.g., 1-ethynylnaphthalene) in the presence of a Lewis acid (e.g., FeCl_3) and an oxidant (e.g., a TEMPO oxonium salt), again under suitable reaction conditions.

[00140] Once the highly derivatized anthracene precursors, having at least halogen, aromatic groups and desired R-group substituents functionalized along the central anthracene ring are formed, the precursors are then transformed into the desired molecular segment. For example, in some such embodiments the anthracene precursor may be transformed via a palladium-catalyzed Heck reaction to form intramolecular C-C bonds between the acene core and pendant phenyls of the anthracene precursor to form a rubicene material **3**. In analogous embodiments, tetrabenzopentacene (e.g., compound **5** in FIG. 14A) may be obtained using base-mediated cyclodehydrogenation to form intramolecular C-C bonds between the acene core and pendant naphthyls of precursor compound **4**.

[00141] Although the above embodiments describe methods of forming different molecular segments via separate anthracene precursors, in other embodiments a single multifunctional anthracene precursor may be utilized capable of producing different molecular segments. One exemplary embodiment of such a method is provided in FIG. 14B. As shown, in this embodiment rubicene (compound **9** in FIG. 14B) and tetrabenzopentacene (compound **10** in FIG. 14B) are produced via a common anthracene precursor having at least halogen and quinoline substituents having desired R-groups attached thereto along the central anthracene ring. In such embodiments a Povarov reaction, is utilized to form the anthracene precursor as illustrated in FIG. 14B.

As shown, to obtain the molecular segments, a halogenated bis(alkyne) anthracene **6** is first prepared according to known techniques. Then an aldimine **7** is formed and reacted with the bis(alkyne), again in the presence of a Lewis acid mediator and an oxidant, producing the anthracene precursor **8**. A rubicene (compound **9** in FIG. 14B) is then prepared in accordance with embodiment using a palladium-catalyzed Heck reaction to form intramolecular C-C bonds between the acene core and pendant quinolines of the anthracene precursor. In alternative embodiments a tetrabenzopentacene (compound **10** in FIG. 14B) is produced using base-mediated cyclodehydrogenation to form intramolecular C-C bonds between the acene core and pendant quinolines of the anthracene precursor.

[00142] In summary, embodiments of methods provide a novel Povarov reaction-based methodology for the preparation of nitrogen-doped rubicenes and tetrabenzopentacenes, which are molecular segments of C70 fullerenes and N=7 armchair graphene nanoribbons, respectively. These embodiments represent the first examples of nitrogen-doped rubicenes and tetrabenzopentacenes. In addition, the method according to embodiments utilizes the formation of intramolecular carbon-carbon bonds between arene moieties, facilitating the selective installation of 5- and 6-membered rings in nitrogen-containing PAHs. In contrast, the alternative oxidative cyclodehydrogenation strategies for bond formation in arenes are well-known to be extremely difficult (or impossible) to control for electron-deficient nitrogen-containing heterocycles. (See, e.g., M. Grzybowski, K. Skonieczny, H. Butenschön, D. T. Gryko, *Angew. Chem. Int. Ed.* **2013**, 52, 9900–9930; *Angew. Chem.* **2013**, 125, 10084–10115, the disclosure of which is incorporated herein by reference.) Embodiments also provide two distinct yet complementary synthetic pathways, which allow for synthetic flexibility and access to molecules that feature nitrogen heteroatoms at different locations and/or possess modular peripheral alkyl substituents, further allowing for the rational, multifaceted tuning of the materials' self-assembly and electronic properties.

[00143] Embodiments are also directed to the novel nitrogen-doped molecular segments. It is known that organic electronic materials that exhibit n-type and ambipolar behavior remain quite rare, and the incorporation of nitrogen heteroatoms

has been extensively validated as a design strategy for coaxing such behavior from acenes. (See, e.g., J. E. Anthony, *Chem. Rev.* 2006, 106, 5028–5048; J.E. Anthony, *Angew. Chem. Int. Ed.* 2008, 47, 452–483; *Angew. Chem.* 2008, 120, 460–492; U. H. F. Bunz, *Acc. Chem. Res.* 2015, 48, 1676–1686; *Polycyclic Arenes and Heteroarenes: Synthesis, Properties, and Applications* (Ed.: Q. Miao), Wiley-VCH, Weinheim, 2015. J. E. Anthony, A. Facchetti, M. Heeney, S. R. Marder, X. Zhan, *Adv. Mater.* 2010, 22, 3876–3892; Y. Zhao, Y. Guo, Y. Liu, *Adv. Mater.* 2013, 25, 5372–5391; and X. Gao, Y. Hu, *J. Mater. Chem. C* 2014, 2, 3099–3117, the disclosures of which are incorporated herein by reference.) Consequently, embodiments of such nitrogen-doped analogues are promising for use in bulk organic semiconductors. Finally, embodiments of the modular constructs allow for the construction of a variety of atomically-defined nitrogen-doped molecular segments of fullerenes and graphene nanoribbons. Accordingly, many embodiments are directed to extended carbonaceous frameworks formed using such molecular segment.

Synthesis of Graphene Nanoribbon Precursors and Graphene Nanoribbons

[00144] As previously discussed, many embodiments describe the modular synthesis of polyquinolines and polybenzoquinolines, in other embodiments such compounds are utilized as a generic class of GNR precursor polymers. As discussed in the sections above, embodiments according to the disclosure provide methods of forming such polyquinoline and polybenzoquinoline precursors via a general aza-Diels-Alder reaction. In addition, embodiments of methods also provide AB-type bifunctional monomers and AA/BB-type reagents to synthesize congested but soluble polybenzoquinoline also via a Diels-Alder-type polymerization reaction. Finally, embodiments are also provided that demonstrate the scope and modularity of such methods by preparing polybenzoquinolines and oligobenzoquinolines of various sizes and that feature different peripheral substituents. Overall, these embodiments enable facile and rapid access to a large family of quinoline- and benzoquinoline-based materials, which can then be used as precursors for polymerization reactions to produce graphene nanoribbons, as will be described herein.

[00145] Accordingly, in some embodiments various graphene nanoribbons may be produced by polymerizing a quinoline or benzoquinoline-based compound. In some such embodiments quinoline-based compounds may be used as precursors to form polyquinolines and polybenzoquinolines via a Diels-Alder polymerization reaction and then these precursors may in turn be used to form graphene nanoribbons, such as through surface-assisted or solution-based cyclodehydrogenation of the polymeric quinoline-based precursor. (See, e.g., J. Cai, P. et al., *Nature* **2010**, 466, 470–473; and X. Yang, et al., *J. Am. Chem. Soc.* **2008**, 130, 4216–4217, the disclosures of which are incorporated herein by reference.)

[00146] As shown in FIG. 15 by varying the nature of the quinoline-based compounds used in forming the precursors various types of graphene nanoribbons may be formed. For example, in some embodiments a polybenzoquinoline precursor is utilized to form a nitrogen-doped N=7 armchair GNR via cyclodehydrogenation, as shown in FIG. 15. As shown, in such embodiments the formation of a well-defined nitrogen-doped GNR is implemented via a precursor consisting of benzoquinoline subunits linked at their 4 and 6 positions (FIG. 15).

[00147] Regardless of the specific GNR to be formed, in embodiments the quinoline-based precursors are produced via a aza-Diels-Alder (Povarov) reaction that constructs the quinoline and benzoquinoline precursor subunits from alkyne- and aldimine-modified monomers (FIG. 16A). Consequently, polymerization of the bifunctional monomers according to embodiments furnishes the desired quinoline or polybenzoquinoline precursor (FIG. 16A, middle), which can then be cyclodehydrogenated into a GNR (e.g., nitrogen-doped N=7 armchair GNR) (FIG. 16A, left). An exemplary synthesis scheme for producing polybenzoquinoline precursors from bifunctional monomers and then cyclization of such polybenzoquinoline precursors into GNRs via the Scholl reaction is provided in FIG. 16B. It should be understood that although specific reagents, R-groups, solvents (e.g., toluene) catalysts (Fe(III)), oxidants (chloranil), Lewis acids (BF₃·OEt₂) and reaction conditions are listed in the synthesis scheme of FIG. 16B, suitable alternatives may be utilized as is described within this disclosure.

[00148] In embodiments previously described the aza-Diels-Alder (Povarov) reaction is utilized to synthesize the envisioned polybenzoquinoline precursor polymers. In alternative embodiments the methodology is used to modularly install varying chemical substituents at the 2 positions of the 4,6-linked benzoquinolines (as shown schematically in FIG. 17). As shown in the illustration the insertion of a substituent at the 2 position corresponds to edge locations in the proposed final GNRs (FIG. 17, left). Given the well-known sensitivity of the electronic structure of GNRs to edge modification, (see, e.g., Castro Neto, et al. *Rev. Mod. Phys.* 2009, 81, 109–162; Chen, L., et al. *Angew. Chem. Int. Ed.* 2012, 51, 7640–7654; Narita, A. et al. *Chem. Rec.* 2015, 15, 295–309; and Narita, A. et al. *Chem. Soc. Rev.* 2015, 44, 6616–6643, the disclosures of which are incorporated herein by reference) embodiments according to such a methodology allows for the potential control of the electrical functionality of such GNR materials.

[00149] As previously described, many different functionalities can be substituted into the monomers in accordance with embodiments. In turn, these functionalities can thereby be inserted into the graphene nanoribbon precursors and ultimately the GNRs formed therefrom. Some exemplary variant monomer functionalities and how they are modularly incorporated into GNR precursors formed therefrom are shown schematically in FIG. 18. As demonstrated, the modular nature of such functionalities allows for a wide-variety of substitution, including, for example, various alkyl chains, heteroatoms such as halogens, and various other substituents including: OMe, NHAc, NH₂, N(Me)₂ and S(Me)₂, etc.

[00150] Utilizing the modular nature of the monomers produced in accordance with embodiment it is then possible in accordance with other embodiments to engineer specific substituents within the GNRs produced therefrom. For example, some embodiments are directed to methods of controlling the amount of nitrogen doping in the GNR. Some exemplary nitrogen-doped GNRs are shown schematically in FIG. 19. In many embodiments variable nitrogen doping of from ~7% to 14% may be provided for N=7 armchair GNRs by altering the nitrogen content of the quinoline-based monomers described herein and from which the GNRs are formed.

[00151] The above embodiments therefore provide a framework for the rational, design and modular construction of GNRs from quinoline-based precursor building blocks having exquisite variability and variety.

EXEMPLARY EMBODIMENTS

[00152] The following provides information about the methods and materials used to conduct the exemplary studies that produced the data discussed. It will be understood that this data and the accompanying examples are only provided as illustration and are not meant to limit the scope of the systems, methods and apparatus described throughout the disclosure.

Materials and General Experimental Procedures.

Materials

[00153] All chemicals were purchased from Acros Organics or Sigma–Aldrich, and all solvents were obtained from Fisher Scientific and used as received unless otherwise noted. The toluene used to prepare the model systems and polymer was dried with 3 Å molecular sieves and stored under argon. All glassware was oven dried at 150 °C overnight. The reactions were performed under dry argon unless otherwise noted.

Compound Purification Procedures

[00154] Flash chromatography was performed using a CombiFlash Rf 200 purification system manufactured by Teledyne Isco. Deactivated silica gel was prepared by flushing the silica gel cartridge with 1/9 triethylamine/hexanes, followed by hexanes to remove excess triethylamine. Preparatory size exclusion chromatography for polyquinolines was performed with chloroform as the mobile phase using a gravity fed column (70 mm x 254 mm) containing BioBeads SX-1 resin (200–400 mesh, Bio-Rad Laboratories, Hercules, CA). Additional purification-relevant information and protocols are noted below as required.

Reaction Product Characterization Procedures

[00155] All intermediates and products were characterized with a combination of nuclear magnetic resonance (NMR) spectroscopy, mass spectrometry, Fourier transform infrared (FTIR) spectroscopy, and/or ultraviolet-visible (UV-Vis) spectroscopy. The ¹H NMR spectra were obtained on a Bruker AVANCE400, a Bruker DRX500, or an AVANCE600 instrument. The ¹³C NMR spectra were obtained on a Bruker DRX500 outfitted with a CryoProbe (Bruker TCI 500 MHz, 5 mm diameter tubes). Chemical shifts were reported in ppm for ¹H and ¹³C NMR. The chemical shifts for the NMR data were referenced as follows: for samples in CDCl₃, the ¹H NMR were referenced to tetramethylsilane (TMS) at 0.00, and the ¹³C NMR were referenced to CDCl₃ at 77.16; for samples in CD₂Cl₂, the ¹H NMR were referenced to the solvent peak at 5.32, and the ¹³C NMR were referenced to the solvent peak at 54.00. The data are labeled as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, br s = broad singlet), the coupling constants (in Hertz), and the integration value. The high resolution electrospray mass spectrometry (HRMS ESI) data was obtained at the University of California, Irvine Mass Spectrometry Facility on a Waters LCT Premier electrospray time-of-flight instrument. FTIR spectra were obtained on a Nicolet Nexus 670 FTIR spectrophotometer. The UV-Vis spectra were collected on an Agilent Cary 100 Series spectrophotometer in tetrahydrofuran (THF) at room temperature.

Polymer Characterization and Analysis Procedures

[00156] The polyquinolines were analyzed with size exclusion chromatography (SEC). For the crude polymer, the SEC analysis was performed in THF using an Agilent Technologies 1260 Infinity Series separations module equipped with two ResiPore GPC columns connected in series (7.5 mm x 300 mm, multiple pore size, 3 μm) from Agilent Technologies (Santa Clara, CA). The separations module was connected to an Agilent 1260 infinity dual angle light scattering, refractive index, and viscometer detectors in series. The flow rate was 1.0 mL/min with an injection volume of 50–100 μL and sample concentration of 1.0 mg/mL.

[00157] The purified polymer was characterized by size exclusion chromatography via multi-angle light scattering (SEC-MALS). The SEC analysis was performed using an Agilent Technologies 1260 Infinity Series separations module equipped with two GPC columns (7.8 mm x 300 mm, 104 Å pore size, 5 µm & 7.8 mm x 300 mm, 100 Å pore size, 5 µm) from MZ Analysentechnik (Mainz, Germany). The separations module was connected to a DAWN HELEOS II MALS detector equipped with a 785 nm laser and 20 nm bandpass interference filters to minimize fluorescence effects (Wyatt Technology Corp., Santa Barbara, CA). The concentration was measured by the Optilab TrEX differential refractive index detector at 785 nm (Wyatt Technology Corp., Santa Barbara, CA). The flow rate was 0.7 mL/min with an injection volume of 100 µL and sample concentration of 3.0 mg/mL. The above system was used to determine the molecular weight (M_w and M_n) and PDI values reported for the purified polymer. The molecular weight data was analyzed with the Astra 6.1.2 software suite by using a dn/dc of 0.27 mL/g. For purified polyquinoline 4, corresponding to Figure 3, the analysis yielded values of $M_n = 10.1 \text{ kg mol}^{-1}$, $M_w = 10.4 \text{ kg mol}^{-1}$, and $M_w/M_n = 1.04$.

Example 1: Quinoline/Polyquinioline Studies

[00158] Model quinoline compounds were synthesized via the aza-Diels–Alder (Povarov) reaction, as illustrated in FIG. 3A. Schiff bases **1a** and **1b** (FIG. 3A) were formed in a single step from commercially available reagents by using known literature protocols. The Schiff bases were reacted with phenylacetylene in the presence of a Lewis acid mediator and the sacrificial oxidant chloranil, which helped avoid endogenous consumption of the imine. A number of Lewis acids known to mediate the Povarov reaction, were screened. Overall, the reaction exclusively produced **2a** and **2b** (FIG. 3A) as the products in good yields.

[00159] Model compound **2a** (FIG. 3A) was characterized with ^1H NMR spectroscopy (FIG. 20). The ^1H NMR spectrum featured three apparent doublets at 8.19 ppm, 8.11 ppm, and 7.80 ppm; a broad apparent singlet at 8.04 ppm; and a singlet at 7.84 ppm. The doublet at 8.19 ppm was assigned to the ortho position of one of the quinoline's pendant phenyl groups (Ha), and the narrow singlet at 8.04 ppm to position 3 on the

quinoline ring (Hb). The remaining doublets at 8.11 ppm and 7.80 ppm were assigned to positions 7 and 8 of the quinoline ring, respectively (Hd and He), and the broad apparent singlet at 8.04 ppm to position 5 of the quinoline ring (Hc). These assignments were validated for all of the proton resonance peaks were further validated via 2D Correlation Spectroscopy (COSY) experiments.

[00160] It is important to note that the NMR spectra obtained for the reaction mixtures indicated the presence of a single regioisomer. To confirm this observation, the regioisomers' identities were evaluated via 1D-Nuclear Overhauser Effect (NOE) experiments. For compound **2a** (FIG. 3A), a 2% enhancement in the NOE signal was observed between protons Ha and Hb on the quinoline ring, indicating their proximity. However, an enhancement in the NOE signal was not observed between Hb and Hc. These findings confirmed that only a single regioisomer was produced during the course of the reaction.

[00161] The absolute configuration of the product was further confirmed by growing crystals of compound **2a** (FIG. 3A) and determining its structure with standard X-ray crystallography techniques (FIG. 20B). An analysis of the structure indicated that the pendant phenyl substituents were twisted out of planarity relative to the quinoline ring system, with the phenyl ring at position 2 of the quinoline possessing a smaller dihedral angle (24°) than the phenyl ring at position 4 (45°). This difference was likely due to the absence of a hydrogen on the pyridinic nitrogen and the consequent reduced allylic strain at position 2. Thus, the X-ray crystallographic analysis unequivocally confirmed the identity of compound **2a** (FIG. 3A).

[00162] Having validated the regioselectivity of the reaction conditions, the bifunctional AB-type monomer necessary for the polymerization reaction illustrated in FIG. 4A was prepared. The design of this monomer incorporated the requisite alkyne and aldimine functional groups within a single substrate, as well as an alkyl chain for enhanced solubility. By adapting the reaction conditions used to synthesize compound **1** (FIG. 3A), a Schiff base (compound **3** in FIG. 4A) was prepared in 43% isolated yield. Notably, the preparation of the monomer required inexpensive, commercially available reagents and only a single synthetic step.

[00163] Then the reaction conditions optimized for the synthesis of compound **2** (FIG. 3A) were used to polymerize AB-type monomer **3** (FIG. 4A). The reaction progress was monitored by size exclusion chromatography with a refractive index detector (SEC-RI), as illustrated in FIG. 21. Initially, a chromatogram of a sample of the pure monomer showed a single sharp peak, as expected. Subsequently, 2 hours after the start of the reaction, monomer consumption was accompanied by the appearance of small oligomers. After 4 hours, the chromatogram indicated the presence of higher molecular weight species, and after 6 hours, the monomer was completely consumed, leading to the appearance of additional higher molecular weight species. Furthermore, after 10 hours, the chromatogram showed only a slight enhancement in the size of the polymeric product, with essentially no further increase observed after 24 hours. The gradual molecular weight build-up during the polymerization, as well as the high apparent polydispersity of the crude product, were consistent with a step-growth mechanism and closely resembled literature reports for Diels–Alder AB-type polymerizations. (See, e.g., Bailey, W. J. *Step Growth Polymerization*; Marcel Dekker: New York, 1972; Vol. 3; Schlüter, A. D. *In Synthesis of Polymers*; Wiley-VCH Verlag GmbH: 2008, p 459-483; and Tasdelen, M. A. *Polym. Chem.* 2011, 2, 2133–2145, the disclosures of which are incorporated herein by reference.)

[00164] Polymer **4** (FIG. 4A) was purified for further analysis. The reaction mixture was first quenched after a period of 24 hours by addition of aqueous sodium bicarbonate. Per literature precedent, the crude mixture was then treated with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), definitively ensuring the rearomatization of the reaction products and the elimination of any potential remaining defects. (See, e.g., Meyers, A. I.; Wettlaufer, D. G. *J. Am. Chem. Soc.* 1984, 106, 1135–1136, the disclosure of which is incorporated herein by reference.) In turn a two-step chromatography/ethanol precipitation procedure was used to remove low molecular weight contaminants and isolate purified polymer **4** (FIG. 4A) in moderate yield. After purification, the polyquinoline was analyzed with size exclusion chromatography via a multi-angle light scattering detector (SEC-MALS) to obtain its unambiguous molecular weight; a representative light scattering chromatogram is shown in FIG. 22. The purified

material possessed a number average molecular weight (M_n) of 10.1 kg mol⁻¹ with a polydispersity index (PDI) of 1.04, corresponding to a degree of polymerization of 32. This material was used for all subsequent characterization steps.

[00165] Purified polymer **4** (FIG. 4A) was then analyzed with ¹H NMR spectroscopy by comparing its spectrum to the spectra of model quinoline **2b** (FIG. 3A) and monomer **3** (FIG. 4A) as summarized in FIG. 23. First, it is noted that the NMR spectrum of compound **4** featured signal broadening, as expected for a polymeric material (FIG. 23C). The resonances of the aromatic peaks between 7.0 and 8.5 ppm (FIG. 23C) were also shifted downfield relative to the aromatic region of the monomer (FIG. 23B) but were in a similar location to those found for the aromatic region of the model quinoline (FIG. 23A). In addition, the NMR spectra of model compound **2b** (FIG. 23A) and **4** (FIG. 23C) lacked the characteristic peaks at 3.15 ppm and 8.41 ppm associated with the alkyne and aldimine proton resonances, respectively. These peaks were prominent in the spectrum of monomer **3** (Hf and Hg in FIG. 23B). Finally, the integration ratio between the aromatic and aliphatic regions of compound **4** (FIG. 23C) was ~1:2, as would be expected based on the postulated structure and repeat unit of the polymer. In their totality, these observations indicate the formation of an extended aromatic system consisting of 4,6-linked quinoline subunits.

[00166] Polyquinoline (compound **4**, FIG. 4A) was analyzed with FTIR spectroscopy, comparing its spectrum (FIG. 24) to those obtained for quinoline model compound **2b** (FIG. 3A) and monomer **3** (FIG. 4A). The spectrum of compound **4** (FIG. 4A) revealed a cluster of peaks at 1500 cm⁻¹ – 1600 cm⁻¹, which could be attributed in part to its aromatic quinoline core. This spectrum also featured broad peaks at 1616 cm⁻¹, 2216 cm⁻¹, and 3298 cm⁻¹ that can be assigned based on literature precedent to the polymer's imine, alkyne CC, and alkyne CH terminal functionalities, respectively (FIG. 24, polymer trace). These proposed assignments were corroborated by the spectrum of monomer **3** (FIG. 4A), which featured peaks at 1626 cm⁻¹, 2146 cm⁻¹, and 3319 cm⁻¹, presumably corresponding to its imine, alkyne CC, and alkyne CH functionalities, respectively (FIG. 24, monomer trace). The assignments were further supported by the spectrum of model compound **2b** (FIG. 3A), which lacked the imine and alkyne peaks but did feature a

cluster of peaks at 1500 cm^{-1} – 1600 cm^{-1} , likely in part due to its quinoline core (FIG. 24, model quinoline trace). Together, the observations provided additional confirmation of the identity of compound **4** (FIG. 4A) and indicated that some of the polymer's imine and alkyne terminal groups (which were not readily detected with ^1H NMR) probably remained intact after the reaction and workup.

[00167] Finally, the optical properties of polymer **4** (FIG. 4A) were investigated with UV-Vis spectroscopy (FIG. 25). The spectrum obtained for compound **4** (FIG. 4A) featured broad peaks at 275 nm and 338 nm, with an absorption onset at 460 nm (FIG. 25, polymer trace). In comparison, the spectrum of model quinoline **2b** (FIG. 3A) featured sharper peaks at 275 nm, 335 nm, and 348 nm, with an absorption onset at 365 nm (FIG. 25, model quinoline); and the spectrum of monomer **3** (FIG. 4A) featured peaks at 277 nm and 327 nm, with an absorption onset at 386 nm (FIG. 25, monomer trace). The red shift in the absorption onset and the broadening observed for the polyquinoline's spectrum, relative to the spectra of both the monomer and the model quinoline, were indicative of the formation of a macromolecule with an extended π -conjugated system.

Example 2: AA/BB-Type aza-Diels-Alder Reaction

[00168] Model crowded biquinoline (FIG. 6 compounds **2a-c**) were synthesized via the Povarov reaction, as illustrated in FIG. 6. Established literature protocols were used to form bis(aldimines) **1a-c** (FIG. 6). Next, compounds **1a-c** (FIG. 6) were reacted with phenylacetylene in the presence of $\text{BF}_3 \cdot \text{OEt}_2$ as a Lewis acid mediator and chloranil as an oxidant, furnishing biquinolines **2a-c** (FIG. 6). Overall, the synthesis utilized mild conditions and commercial starting materials to produce regioisomerically pure products in excellent yield.

[00169] Model compounds **2a-c** (FIG. 6) were characterized with nuclear magnetic resonance (NMR) spectroscopy and mass spectrometry. As an example, the aromatic region of the ^1H NMR spectrum for compound **2b** (FIG. 6) is illustrated in FIG. 26A. This spectrum featured two apparent doublets at 8.15 and 7.99 ppm; a broad singlet at 7.94 ppm; a sharp singlet at 7.88 ppm; and a singlet, which presumably overlapped with a

multiplet, at 7.60 ppm. The doublet at 8.15 ppm was tentatively to the protons at the ortho positions of the quinolines' tert-butyl-substituted phenyl groups (Ha) and the doublet at 7.99 ppm to the proton at position 7 of the quinoline cores (Hb). In turn the broad singlet at 7.94 ppm was assigned to the proton at position 5 of the quinoline cores (Hc) and the sharp singlet at 7.88 ppm to position 2 of the quinoline cores (Hd). Finally, the complex signal at 7.60 ppm was attributed to the proton at the para positions of the quinolines' tert-butyl-substituted phenyls (He), as well as to an overlapping multiplet from the quinolines' unsubstituted pendant phenyls. The assignments for all of the proton resonances were further validated by 2D correlation spectroscopy (COSY) experiments.

[00170] To gain insight into the regioisomeric identity of the products, w the Nuclear Overhauser Effect (NOE) was observed (Figure 26A). For these experiments, compound **2b** (FIG. 6) was analyzed because its spectrum was more straightforward to interpret. A clear enhancement in the NOE signal between proton Ha of the quinoline systems and proton Hd of the pendant tert-butyl-substituted phenyl groups can be observed, confirming their proximity (FIG 26A). This observation suggested that the reaction conditions likely produced only a single regioisomer, in agreement with previous findings for analogous quinoline and benzoquinoline systems.

[00171] The connectivity and absolute configurations of the compounds was further confirmed with X-ray crystallography (FIG. 26B). For these experiments, compound **2a** (FIG. 6) was analyzed because it readily produced crystals of sufficient quality for X-ray diffraction analysis. The crystal structure revealed that the quinolines featured pendant methyl-substituted phenyl rings at the 2 position and pendant unsubstituted phenyl rings at the 4 position, validating the NOE analysis (FIG. 26B). Moreover, it was found that the connected aromatic systems (quinolines and phenyls) were all twisted out of planarity relative to one another, presumably due to steric interactions (FIG. 26B). Together with the COSY experiments, the crystal structure definitively confirmed the identity of compound **2a** (FIG. 6), and thus, the regioselectivity of the reaction conditions.

[00172] Having evaluated the regiospecificity of the strategy, polyquinolines were prepared, as illustrated in FIG. 7. Here, diimine **1c** (FIG. 7) was reacted with diethynyl benzene in an AA/BB-type polymerization under the conditions developed for the synthesis of compounds **2a-c** (FIG. 6). The progress of this polymerization was monitored by size exclusion chromatography with a refractive index detector (SEC-RI), as illustrated by the representative chromatograms in FIG. 27A. Initially, a chromatogram of the starting materials showed a single sharp peak, corresponding to monomer **1c** (FIG. 27A, 0h trace). Subsequently, after 2 h, monomer consumption was accompanied by the appearance of low molecular weight oligomers (FIG. 27A). In turn, after 4 h, the monomer was nearly completely consumed, leading to the appearance of additional higher molecular weight species (FIG. 27A). Furthermore, after 8 h, the chromatogram showed only a slight enhancement in the size of the polymeric product (FIG. 27A), with an additional modest increase found after 24 h (FIG. 27A). The buildup in molecular weight observed during the reaction was consistent with a step-growth mechanism and resembled literature precedent for Diels–Alder AA/BB-type polymerizations.

[00173] Polymer **3c** (FIG. 7) was processed and analyzed with SEC-RI. To this end, the reaction was first quenched through the addition of aqueous sodium bicarbonate after a period of 72 h. Subsequently, compound **3c** (FIG. 7) was treated with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), ensuring rearomatization of the quinoline core, and then precipitation this polymer from ethanol, ensuring removal of any residual low molecular weight contaminants. FIG. 27B shows a representative chromatogram obtained for compound **3c** (FIG. 7) after precipitation; the polyquinoline possessed a weight average molecular weight (M_w) of 33.2 kg mol^{-1} , a number average molecular weight (M_n) of 14.8 kg mol^{-1} , and a polydispersity index (PDI) of 2.24. The polydispersity of the polymer further supported the notion of a step-growth mechanism and again matched literature precedent for Diels–Alder AA/BB-type polymerizations.

[00174] Polyquinoline **3c** was further analyzed (FIG. 7) via ^1H NMR spectroscopy, with model biquinoline **2c** (FIG. 6) serving as a useful reference. It is first noted that the ^1H NMR spectra of both compound **3c** (FIG. 28B) and compound **2c** (FIG. 28A)

featured resonances between 7.0 and 8.5 ppm in the aromatic region, which could be associated with the quinoline and phenyl moieties, as well as resonances between 0.0 and 3.0 ppm in the alkyl region, which could be associated with the methyl and dodecyl functionalities. Although the observed signals were in similar positions for both the polymer and the model compound, the spectrum of compound **3c** (FIG. 28B) featured significant broadening relative to the spectrum of compound **2c** (FIG. 28A), as expected for a polymeric material. Moreover, the integration ratio between the aromatic and alkyl regions of compound **3c** was ~1:6, matching predictions based on the structure of the model biquinoline and the repeat unit of the polyquinoline. Overall, the analysis confirmed the formation of an extended macromolecule comprised of linked biquinoline and phenyl subunits.

[00175] The electronic properties of polyquinoline **3c** (FIG. 7) and model biquinoline **2c** (FIG. 6) were investigated with UV-vis spectroscopy (FIG. 29). The spectrum obtained for compound **3c** featured peaks at 291 nm and 363 nm, as well as an absorption onset at 435 nm (FIG. 29, solid **3c**). In comparison, the spectrum obtained for compound **2c** featured peaks at 288 nm and 363 nm, as well as an absorption onset of 425 nm (FIG. 29, solid **2c**). Moreover, the spectrum of the polyquinoline was broadened and tailed into the red, relative to the one of the model biquinoline. Overall, the observations were consistent with the formation of a π -conjugated macromolecule.

[00176] Next the photophysical properties of polyquinoline **3c** and model biquinoline **2c** (FIGs. 6 & 7) were observed with fluorescence spectroscopy. The emission spectrum obtained for compound **3c** featured a peak at 419 nm (FIG. 29, dashed **3c**), while the emission spectrum obtained for compound **2c** featured a peak at 446 nm (FIG. 29, dashed **2c**). Thus, the polyquinolines possessed a more substantial Stokes shift, compared to the biquinoline. These findings were again consistent with the formation of a π -conjugated macromolecule.

[00177] In addition, the electrochemical properties of thin films from both polyquinoline **3c** (FIG. 7) and model biquinoline **2c** (FIG. 6) were studied with cyclic voltammetry (FIG. 30). At reductive potentials, the voltammogram obtained for compound **3c** featured a quasi-reversible redox couple with a midpoint potential of -1.83 V vs. Ag/AgCl and an

irreversible cathodic wave with a peak potential of -2.13 V vs. Ag/AgCl (FIG. 30, **3c** trace). The voltammogram obtained for compound **2c** was similar and featured two quasi-reversible redox couples with midpoint potentials of -1.81 V vs. Ag/AgCl and -2.04 V vs. Ag/AgCl (FIG. 30, **2c** trace). Moreover, within the accessible potential window, the voltammograms obtained for both the polyquinoline and the biquinoline did not exhibit any redox activity at oxidative potentials. Overall, the electrochemical measurements demonstrated that the redox properties of the polymers and model compounds were similar.

[00178] Finally, to gain additional insight into the electronic properties of the materials and interpret the electrochemical findings, density functional theory (DFT) calculations were performed for model biquinoline **2c** (FIG. 6). From these calculations, the equilibrium molecular geometry were obtained, as well as the shapes and energies of this molecule's highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) (FIG. 31). It was thus possible to assign the first redox couple observed at -1.81 V vs. Ag/AgCl for the biquinoline to its LUMO. It was found that the electrochemically-determined LUMO energy of -2.6 eV was similar to the theoretically-calculated LUMO energy of -2.0 eV, indicating that compound **2c** possessed a large electron affinity (FIG. 31B). Moreover, a HOMO energy of -5.7 eV was extracted from the DFT calculations (FIG. 31B), indicating that compound **2c** (FIG. 6) possessed a large ionization potential. This analysis suggested that materials based on the crowded biquinoline motif hold promise as n-type organic semiconductors.

Example 3: Polybenzoquinolines

[00179] benzoquinoline model compounds **3a,b** and **5a,b** were synthesized via the Povarov reaction, as illustrated in FIG. 8A. To prepare model compounds **3a** and **3b** (FIG. 8), first aldimines **1a** and **1b** were formed via a known literature protocol. Then naphthyl alkyne **2** was reacted with **1a** or **1b** in the presence of $\text{BF}_3 \cdot \text{OEt}_2$ as the Lewis acid mediator and chloranil as the sacrificial oxidant, producing monomeric benzoquinolines **3a** or **3b** (FIG. 8), respectively. Next, to prepare dimeric model compounds **5a** and **5b** (FIG. 8), the pendant bromides of compounds **3a** and **3b** are

converted to alkynes, forming compounds **4a** and **4b** (FIG. 8), respectively. Alkyne **4a** was then reacted with aldimine **1a** and alkyne **4b** with aldimine **1b**, producing benzoquinolines **5a** and **5b** (FIG. 8). This linear synthetic strategy furnished the desired regioisomerically pure products in moderate yields.

[00180] Pentameric compound **8** was then prepared as a longer model benzoquinoline (FIG. 8B). To construct compound **8**, compound **5b** was used as the sole starting material and generated complementary building blocks **6** and **7**. Thus, to synthesize compound **6**, the pendant bromide of **5b** was converted to an alkyne, and to synthesize compound **7**, the acetyl-protected amine of **5b** was converted to an aldimine. Subsequently alkyne **6** and aldimine **7** were combined under Povarov conditions, furnishing compound **8**. Here, by independently modifying the bromide and amine termini of the precursors, an arduous linear synthesis was avoided to produce a benzoquinoline macromolecule.

[00181] Benzoquinoline model compounds (**3a**, **3b**, **5a**, **5b**, and **8** from FIG. 8) were characterized with ¹H and ¹³C nuclear magnetic resonance (NMR) spectroscopy, mass spectrometry (MS), and/or X-ray crystallography. In particular, crystals of **3a** and **5a** were grown and their solid-state structures determined through standard X-ray crystallography techniques (FIG. 32). Although the resolution for compound **5a** was quite poor, both crystal structures confirmed that the reaction conditions produced only the desired regioisomers and connectivity, as further supported by a detailed NMR analysis for compound **3b**. The crystal structures also revealed that the naphthyl moieties of both compounds **3a** and **5a** were almost completely orthogonal with respect to their neighboring benzoquinoline subunits (FIG. 32A & 32B) and that the two constituent benzoquinoline subunits of compound **5a** were twisted out of planarity with respect to one another in the solid state (FIG. 32B). Altogether, these experiments definitively confirmed the identity of the model compounds.

[00182] With the model compounds in hand, elongated benzoquinoline macromolecules were synthesized. Thus, polybenzoquinoline **11a** was prepared through polymerization of AB-type bifunctional monomers via the Povarov reaction. Therefore it was possible to produce monomer **10a** from 4-iodonaphthylamine **9** in only

three steps (FIG. 8B). The design of this monomer incorporated the requisite alkyne and aldimine functional groups within a single substrate, as well as an alkyl chain for enhanced solubility. The reaction conditions optimized for the synthesis of compounds **3b**, **5b**, and **8** (FIG. 8A) were then used to polymerize 10a (FIG. 8B). The resulting reaction mixture was analyzed via size exclusion chromatography with a refractive index detector (SEC-RI), and through calibration with standards, an M_n of 2730 g mol⁻¹, an M_w of 5420 g mol⁻¹, and a PDI of 1.98 were obtained for compound **11a**. This product's polydispersity was consistent with a step-growth polymerization mechanism, as expected for a Diels-Alder-type reaction.

[00183] Polybenzoquinoline **11a** was subsequently processed and again characterized. The reaction was terminated by addition of phenylacetylene and purified the resulting material through sequential precipitation/chromatography. Then compound **11a** was analyzed via SEC-RI with respect to calibration standards. The measurement yielded an M_n of 7840 g mol⁻¹, an M_w of 10500 g mol⁻¹, and a PDI of 1.34, corresponding to ~ 21 benzoquinoline subunits for purified compound **11a** (Figure 3 and Table 1). For comparison, the same measurement for monodisperse benzoquinoline model compound **8** yielded an M_n of 2110 g mol⁻¹, an M_w of 2120 g mol⁻¹, and a PDI of 1.01, reinforcing the accuracy of the analysis (FIG. 33 and Table 2, below). Notably, despite its aromatic character and crowded architecture, compound **11a** was readily soluble in most common organic solvents, presumably due to a partially contorted geometry, as observed for the model compounds. The observations were consistent with the preparation of an extended polybenzoquinoline.

TABLE 2: Compound Properties				
Compound	M_n [g mol ⁻¹]	M_w [g mol ⁻¹]	PDI	$N^{[b]}$
8	2110	2120	1.01	5
11a	7840	10500	1.34	21
11b	15500	22300	1.44	25
11c	8960	10900	1.22	22
13	29600	36200	1.22	60

[00184] Compounds **3b**, **5b**, **8**, and **11a** were further characterized with ultraviolet-visible (UV-vis) spectroscopy (FIG. 34). The spectra obtained for compounds **3b**, **5b**, and **8** showed characteristic absorbance peaks with maxima at nearly identical positions of 297 nm, 314 nm, 352 nm, and 370 nm. By comparison, the spectrum obtained for **11a** featured broadened absorption maxima at similar positions and an onset of absorption that was red-shifted from ~380 nm to ~450 nm. Together, these measurements corroborated the formation of an extended polybenzoquinoline system for compound **11a**.

[00185] To demonstrate that the polymerization strategy was modular and capable of accommodating different peripheral substituents the reaction conditions already validated for the synthesis of compound **10a** was utilized to prepare monomers **10b** and **10c**, which incorporated branched alkyl chain and fluorine substituents, respectively (FIG. 9A). These conditions were then used similar to those developed for the synthesis of compounds **3b**, **5b**, **8**, and **11a** to furnish polybenzoquinolines **11b** and **11c** from monomers **10b** and **10c**, respectively (FIG. 9A). Standard purification and analysis procedures yielded the data shown in FIG. 33 and Table 2 for compounds **11b** and **11c**, confirming the success of the polymerization reactions. The preparation of distinct polybenzoquinolines under similar reaction conditions underscored the potential general scope of the approach.

[00186] Finally, the polymerization strategy was applied to the preparation of an even longer, sequence-variable polybenzoquinoline macromolecule. The procedure was slightly modified to convert **3b** into bifunctional monomer **12** in four steps (FIG. 9B). The design of **12** incorporated the requisite alkyne and aldimine functional groups, an expanded aromatic core containing an additional benzoquinoline subunit, and alternating linear and branched alkyl side chains. Polymerization of **12** under standard reaction conditions furnished polybenzoquinoline **13**. Per the SEC-RI measurement, this polymer featured an M_n of 29600 g mol⁻¹, an M_w of 36200 g mol⁻¹, and a PDI of 1.22, corresponding to ~ 60 repeating main chain benzoquinoline subunits (FIG. 33 and Table 2). Moreover, despite its increased size relative to compounds **11a-11c**, and **13**

exhibited good solubility in common organic solvents. Overall, these findings demonstrated the potential modularity of the approach, portending favorably for the synthesis of polybenzoquinoline-based graphene nanoribbon precursors with tunable sequence contexts.

Example 4: Crowded Benzoquinolines

[00187] A model 2,4,6-substituted benzoquinoline **3a** is first synthesized via the Lewis acid-promoted Povarov reaction, as illustrated in FIG. 10. Thus, an aldimine precursor **1a** was first prepared from commercially available starting materials (4-bromonaphthylamine and octyl benzaldehyde) through a known literature protocol. To furnish **3a**. A variety of Lewis acid promoters were screened for the cycloaddition of naphthyl alkyne **2** to aldimine **1a** (FIG. 11); here, the sacrificial oxidant chloranil was included to ensure that compound **3a** was fully aromatized. Although several Lewis acids (entries 1 to 4 in FIG. 11) resulted in modest yields for compound **3a**, good yields and regioselectivity were obtained for AgOTf (67%), ZnCl₂ (75%), and BF₃•OEt₂ (83%) (entries 6-8 in FIG. 11). Based on these observations, BF₃•OEt₂ was selected as the most promising Lewis acid for the subsequent experiments.

[00188] Having determined the optimal reaction conditions for the regioselective production of benzoquinoline **3a**, the scope of the reaction was determined. Therefore different commercially available aldehyde derivatives were used to prepare distinct aldimines **1b-1i**. Each of these aldimines was coupled with alkyne **2** to furnish regioisomerically pure 4,6-substituted benzoquinolines **3b-3i**, as confirmed by ¹H and ¹³C nuclear magnetic resonance (NMR) spectroscopy. Notably, the reaction conditions readily enabled the preparation of benzoquinolines featuring both electron withdrawing (entries 8, 9, 10, and 12 in FIG. 11) and electron donating (entry 15 in FIG. 11) substituents in good yields of > 65 %. Moreover, the protocol was capable of accommodating sterically hindered aldimines featuring ortho substituents on their pendant phenyl rings (entries 8 and 13 in FIG. 11), with little deleterious effect on the yields. Finally, it was discovered that the conditions could even accommodate aliphatic substituents (entry 14 in FIG. 11). Together, the above observations underscored the

general applicability of the overall procedure for the production of varied crowded benzoquinolines.

[00189] With the compounds in hand, insight into their absolute configurations was determined. Thus, the solid-state structures obtained were analyzed and compared for aldimine **1a** and benzoquinoline **3e** with standard X-ray crystallography techniques (FIG. 35). For aldimine **1a**, it was found that the pendant phenyl ring was only slightly out of plane with the naphthyl system (FIG. 35A). Thus, pi-conjugation along the imine backbone appeared to be maintained. For benzoquinoline **3e**, it was found that there was a small dihedral angle of $\sim 15^\circ$ between the pendant phenyl ring and the newly formed benzoquinoline system (FIG. 35B). Moreover, the crystal structure further confirmed the regioselectivity of the general reaction conditions (FIG. 35B). These crystallographic studies provided additional confirmation for the identity of the molecules.

[00190] Next the electronic properties of benzoquinolines **3a–3i** were investigated with UV-vis spectroscopy. As a specific example, the spectrum measured for compound **3e** featured absorption peaks with maxima at 224 nm, 240 nm, 295 nm, 313 nm, 351 nm, and 370 nm (FIG. 36). This spectrum also differed somewhat from the spectrum of the benzo[h]quinoline core due to the presence of additional and/or redshifted peaks; the difference could be readily rationalized by considering the aromatic substituents and expanded pi-conjugated system of **3e** (relative to the benzo[h]quinoline). In general, the spectra of the benzoquinoline compounds all featured clusters of peaks at 220 – 300 nm and 300 – 375 nm but were blue- or red-shifted with respect to one another, as illustrated for compounds **3b**, **3e**, **3g**, **3h**, and **3i** (FIG. 36). Overall, the spectra of the compounds were qualitatively quite similar.

[00191] When analyzing the molecules' spectroscopic properties, the spectra of compounds **3b** and **3g** were both substantially blue shifted with respect to that of compound **3e**, and even generally resembled the spectrum of compound **3h** (FIG. 36). Indeed, based only on a straightforward analysis of electron withdrawing and electron donating groups, one might expect a change in the positions of the HOMO and LUMO levels for halogen-substituted compound **3b** and methyl-substituted compound **3g**, but

not necessarily a dramatic change in their spectra and HOMO-LUMO gap (all with respect to the spectrum of unsubstituted **3e**). Here, based on the solid state structure of compound **3e** in FIG. 35B, it is hypothesized that steric interactions between the crowded benzoquinoline core and the 2,6 substituents of the pendant phenyl rings of compounds **3b** and **3g** increased the dihedral angle between the two systems, twisting them out of co-planarity. This effect would decouple the phenyl and benzoquinoline aromatic systems and reduce the overall size of the pi-conjugated framework for compounds **3b** and **3g**, inducing the observed blue shifts in the spectra.

[00192] To provide theoretical validation for the hypothesis, DFT calculations were performed for all of the crowded 2,4,6-substituted benzoquinolines. As illustrative examples, FIG. 12 shows the chemical structures and corresponding HOMO and LUMO isosurface plots for compounds **3b**, **3e**, **3g**, **3h**, and **3i**. First, it is found that the orientation of the naphthyl substituent relative to the benzoquinoline core was similar for these molecules, with a typical dihedral angle of $\sim 74^\circ$. This observation indicated that the naphthyl moiety likely played a minor role in the unexpected blue shift observed for compounds **3b** and **3g**. Second, it is found that the dihedral angle between the pendant phenyl ring and benzoquinoline core for compounds **3b**, **3e**, **3g**, and **3i** could be roughly correlated with the localization of the HOMO and LUMO (FIG. 12). Indeed, these molecular orbitals were more likely to encompass the pendant phenyl ring for compounds **3b** and **3e**, than for compounds **3g** and **3i**. Moreover, the HOMO and LUMO orbitals of compound **3g** resembled those of compound **3h**, indicating that the pendant phenyl of compound **3g** was electronically decoupled from its benzoquinoline core (FIG. 12). Overall, this analysis indicated that steric effects play an important role in dictating the electronic properties of the compounds.

Example 5: Molecular Segments and Graphene Nanoribbons

[00193] Rubicene and tetrabenzopentacene were synthesized via the Povarov reaction, as illustrated in FIG. 14A. To prepare compounds **3** and **5** in FIG. 14A, bis(aldimine) **1** was first formed through a known literature procedure. Subsequently, compound **2** was obtained by reacting the bis(aldimine) **1** with phenylacetylene in the

presence of $\text{BF}_3 \cdot \text{OEt}_2$ as a Lewis acid mediator and chloranil as an oxidant, and compound **4** was obtained by reacting bis(aldimine) **1** with 1-ethynylnaphthalene in the presence of FeCl_3 as Lewis acid and a TEMPO oxonium salt as an oxidant. Next, compound **3** was synthesized by using the palladium-catalyzed Heck reaction to form intramolecular C-C bonds between the acene core and pendant phenyls of compound **2**. In an analogous approach, compound **5** was synthesized by using base-mediated cyclodehydrogenation to form intramolecular C-C bonds between the acene core and pendant naphthyls of compound **4**. This pathway furnished desired products **3** and **5** in moderate yields.

[00194] Rubicene **9** and tetrabenzopentacene **10** were also synthesized via the Povarov reaction, as illustrated in FIG. 14B. To obtain compounds **9** and **10** (FIG. 14B), a bis(alkyne) **6** is first prepared. Then aldimine **7** is formed and reacted with bis(alkyne) **6**, again in the presence of a Lewis acid mediator and an oxidant, producing anthracene intermediate **8**. Rubicene (compound **9** in FIG. 14B) was prepared using the palladium-catalyzed Heck reaction to form intramolecular C-C bonds between the acene core and pendant quinolines of anthracene precursor **8**. In an analogous approach tetrabenzopentacene compound **10** was synthesized using base-mediated cyclodehydrogenation to form intramolecular C-C bonds between the acene core and pendant quinolines of anthracene precursor **8**.

[00195] The electronic properties of compounds **3**, **5**, **9**, and **10** were investigated with ultraviolet-visible (UV/Vis) spectroscopy. For compounds **3** and **9**, it was found that the spectra generally resembled those reported for rubicene and its derivatives. For example, the spectrum obtained for compound **3** featured characteristic clusters of absorption peaks at 341 nm, 399 nm, and 483 nm (FIG. 37). By comparison, the spectrum obtained for compound **9** was broadened and red-shifted (presumably due to the molecule's expanded aromatic system), with prominent absorption peaks at 400 nm and 524 nm (FIG. 37). Likewise, it is found that the spectra for compounds **5** and **10** were similar to the classic ones reported for tetrabenzopentacene and other pentacene derivatives. The spectrum obtained for compound **5** featured a cluster of three characteristic absorption peaks at 555 nm, 600 nm, and 650 nm (FIG. 37). The

spectrum obtained for compound **10** was slightly blue-shifted but comparable to compound **5**, with absorption peaks at 543 nm, 588 nm, and 638 nm (FIG. 37). Overall, these findings indicated that the electronic properties of the nitrogen-doped rubicene and tetrabenzopentacene variants generally resembled those of their all-carbon parent molecules.

[00196] The electrochemical behavior of compounds **3**, **5**, **9**, and **10** were next investigated with cyclic voltammetry (CV) (FIG. 38). Interestingly, it was found that compounds **3** and **9** were easier to reduce but more difficult to oxidize compared to previously reported all-carbon rubicene derivatives (Table 3, below). For compound **3**, the voltammogram featured two quasi-reversible redox couples at reductive potentials of -0.83 V vs. Ag/AgCl and -1.24 V vs. Ag/AgCl, but no obvious reversible redox couples at oxidative potentials. For compound **9**, the voltammogram was similar, with two quasi-reversible redox couples at reductive potentials of -0.73 V vs. Ag/AgCl and -1.04 V vs. Ag/AgCl, and, again, no obvious reversible redox couples at oxidative potentials. Likewise, it was found that compounds **5** and **10** were easier to reduce but more difficult to oxidize than previously reported all-carbon pentacene derivatives. For compound **5**, the voltammogram featured two quasi-reversible redox couples at reductive potentials of -0.99 V vs. Ag/AgCl and -1.41 V vs. Ag/AgCl, as well as one quasi-reversible redox couple at oxidative potentials of 0.70 V vs. Ag/AgCl. For compound **10**, the voltammogram was similar, with two quasi-reversible redox couples at reductive potentials of -0.91 V vs. Ag/AgCl and -1.16 V vs. Ag/AgCl, as well as one quasi-reversible redox couple at oxidative potentials of 0.91 V vs. Ag/AgCl. Overall, these findings indicated that the incorporation of nitrogen heteroatoms enhanced the molecules' electron accepting properties, in agreement with literature precedent for various heteroacenes.

TABLE 3: Molecular Orbital Energy Summary				
Compound	HOMO [eV]	LUMO [eV]	HOMO ^(DFT) [eV]	LUMO ^(DFT) [eV]
Rubcene	-5.51	-3.40	-5.54	-2.80
3	-5.71	-3.68	-5.60	-3.01
9	-5.74	-3.77	-5.80	-3.25
Tetrabenzopentacene	-	-	-4.71	-2.71
5	-4.94	-3.50	-4.89	-2.87
10	-5.23	-3.58	-5.13	-3.11

[00197] To gain further insight into the electronic structure of the molecules, density functional theory (DFT) calculations were performed for compounds **3**, **5**, **9**, and **10** (FIG. 39), as well as for their all-carbon analogues. From these calculations, the shapes and energies of the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) were obtained for all six molecules (FIG. 39 and Table 3, below). It was thus possible to assign the redox couples observed with cyclic voltammetry for compounds **3**, **5**, **9**, and **10** to the HOMO and LUMO, as appropriate (Table 1). The DFT calculations indicated that, regardless of the presence of heteroatoms, the HOMO and LUMO were similar in shape and localized on the aromatic core for both the three rubicenes and the three terabenzopentacenes. However, it was found that the energies of the theoretically-predicted HOMO and LUMO for all of the nitrogen-doped compounds were lowered with respect to their all-carbon parent molecules, as also suggested by the electrochemical measurements (FIG. 38 and Table 1). Notably, the electronic properties of the molecules appeared to be influenced by the precise location of the nitrogen dopants, with compound **9** featuring a lower lying LUMO and HOMO than compound **3**, and compound **10** featuring a lower lying LUMO and HOMO than compound **5**, again in agreement with the electrochemical measurements (FIG. 28 and Table 1). Overall, the theoretical calculations supported the experimental findings and implied that the molecules constitute exciting candidate n-type organic semiconductor materials.

INCORPORATION BY REFERENCE

[00198] All patents, patent applications, and publications cited in this specification are herein incorporated by reference in their entirety to the same extent as if each independent patent, patent application, or publication was specifically and individually indicated to be incorporated by reference.

DOCTRINE OF EQUIVALENTS

[00199] Having described several embodiments, it will be recognized by those skilled in the art that various modifications, alternative constructions, and equivalents may be used without departing from the spirit of the invention. Additionally, a number of well-known processes and elements have not been described in order to avoid unnecessarily obscuring the present invention. Accordingly, the above description should not be taken as limiting the scope of the invention.

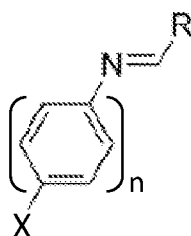
[00200] Those skilled in the art will appreciate that the presently disclosed embodiments teach by way of example and not by limitation. Therefore, the matter contained in the above description or shown in the accompanying drawings should be interpreted as illustrative and not in a limiting sense. The following claims are intended to cover all generic and specific features described herein, as well as all statements of the scope of the present method and system, which, as a matter of language, might be said to fall there between.

WHAT IS CLAIMED IS:

1. A method of producing a quinoline comprising:

providing a halogenated aromatic aldimine according to:

wherein X is a halogen, n is an integer of at least 1, and R is an unsubstituted or



substituted aromatic ring; and

reacting the halogenated aromatic aldimine with an alkynyl in the presence of a Lewis acid mediator and an oxidant such that the imine group of the halogenated aromatic aldimine reacts with the alkyne group of the alkynyl yielding a quinoline wherein the nitrogen from the imine group is incorporated into the multicyclic quinoline ring.

2. The method of claim 1, wherein n is at least 2 and the alkynyl comprises a multicyclic aromatic ring such that a benzoquinoline is formed.

3. The method of claim 2, wherein the alkynyl is a naphthyl alkyne such that a 2,4,6 substituted benzoquinoline is formed.

4. The method of claim 3, wherein at least one of the substituents is selected from the group of electron withdrawing, electron donating, and aliphatic substituents.

5. The method of claim 3, wherein the halogenated aromatic comprises an ortho substituent on a pendant phenyl ring thereof.

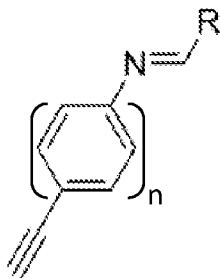
6. The method of claim 2, further comprising converting the halogen of the benzoquinoline to form an alkyne functionalized benzoquinoline and reacting such alkyne functionalized benzoquinolines with the halogenated aromatic aldimine in a Lewis acid mediator and an oxidant such that the imine group of the halogenated aromatic aldimine reacts with the alkyne group of the alkyne functionalized benzoquinoline yielding a dimeric oligobenzoquinoline.

7. The method of claim 6, wherein the alkynyl further comprises an acetyl-protected amine; and

further comprising converting the acetyl-protected amine to an imine to form imine functionalized benzoquinoline and reacting such alkyne and imine functionalized benzoquinolines in a Lewis acid mediator and an oxidant such that the imine group of the imine functionalized benzoquinoline reacts with the alkyne group of the alkyne functionalized benzoquinoline yielding a pentameric oligobenzoquinoline.

8. The method of claim 1, wherein the R group comprises a benzene having at least one further substitution selected from a heteroatom, a halogen, an alkyl chain, a methoxy (Me), an acetyl (Ac), an NHAc, an amine, an N(Me)₂, and a S(Me)₂.

9. A method of producing polyquinoline comprising:
providing a bifunctional monomer according to:



wherein n is an integer of at least 1, and R is an unsubstituted or substituted aromatic ring; and

polymerizing the bifunctional monomer in the presence of a Lewis acid mediator and a sacrificial oxidant such that the imine group of one bifunctional monomer reacts with the alkyne group of another bifunctional monomer, yielding a polyquinoline product wherein the nitrogen from the imine group is incorporated into each of the multicyclic quinoline rings of the polyquinoline.

10. The method of claim 9 wherein the aromatic ring of R is further substituted with at least one of the following a heteroatom, a halogen, an alkyl chain, a methoxy (Me), an acetyl (Ac), an NHAc, an amine, an N(Me)₂, and a S(Me)₂.

11. The method of claim 10, wherein the aromatic ring of R has at least two substitutions.

12. The method of claim 9, further comprising terminating the polymerization reaction to obtain a polyquinoline of specified length.

13. The method of claim 9, wherein n is at least 2 such that a polybenzoquinoline product is formed.

14. The method of claim 13, wherein the second aromatic ring comprises a further substituent.

15. The method of claim 14, wherein the substituent is selected from the group of a heteroatom, a halogen, an alkyl chain, a methoxy (Me), an acetyl (Ac), an NHAc, an amine, an N(Me)₂, and a S(Me)₂.

16. The method of claim 13, wherein the bifunctional monomer further comprises an additional benzoquinoline subunit.

17. The method of claim 16, wherein the additional benzoquinoline subunit further comprises an additional substituent group selected from the group of a heteroatom, a halogen, an alkyl chain, a methoxy (Me), an acetyl (Ac), an NHAc, an amine, an N(Me)₂, and a S(Me)₂.
18. The method of claim 9, wherein the individual quinolines of the polyquinoline are linked at the 4 and 6 positions.
19. A method of producing biquinoline comprising:
providing an AA-type monomer comprising an aromatic bisaldimine and a BB-type monomer comprising an aromatic alkynyl; and
reacting the AA-type monomer with the BB-type monomer in the presence of a Lewis acid mediator and an oxidant such that the imine group of AA-type monomer reacts with the alkyne group of the aromatic alkynyl yielding a biquinoline wherein the nitrogen from the imine group is incorporated into each of the multicyclic quinoline rings.
20. The method of claim 19, wherein the aromatic rings of the AA-type monomer are further functionalized by a substituted or unsubstituted aromatic ring.
21. The method of claim 20, wherein the aromatic ring is further substituted with at least one of the following a heteroatom, a halogen, an alkyl chain, a methoxy (Me), an acetyl (Ac), an NHAc, an amine, an N(Me)₂, and a S(Me)₂.
22. The method of claim 19, wherein the bisaldimine comprises at least two aromatic rings.
23. A method of producing polyquinoline comprising:
providing an AA-type monomer comprising an aromatic bisaldimine and a BB-type monomer comprising an aromatic dialkynyl;

reacting the AA-type monomer with the BB-type monomer in the presence of a Lewis acid mediator and an oxidant such that the imine group of the AA-type monomer reacts with the alkyne group of the BB-type monomer yielding a polyquinoline wherein the nitrogen from the imine group is incorporated into each of the multicyclic quinoline rings of the polyquinoline.

24. The method of claim 23, wherein the aromatic rings of the AA-type monomer are further functionalized by a substituted or unsubstituted aromatic ring.

25. The method of claim 24, wherein the aromatic ring is further substituted with at least one of the following a heteroatom, a halogen, an alkyl chain, a methoxy (Me), an acetyl (Ac), an NHAc, an amine, an N(Me)₂, and a S(Me)₂.

26. The method of claim 23, wherein the bisaldimine comprises at least two aromatic rings.

27. A method of forming a molecular segment comprising:

reacting a halogenated aromatic bisaldimine and an alkyne functionalized aromatic ring in the presence of a Lewis acid mediator and an oxidant such that the imine groups of the bisaldimine reacts with the alkyne group of the alkyne functionalized aromatic ring yielding a halogenated anthracene precursor having at least two pendant aromatic groups; and

forming intramolecular C-C bonds between the acene cored and pendant aromatic groups to form a nitrogen-doped molecular segment.

28. The method of claim 27, wherein the pendant aromatic groups are phenyls and the step of forming intramolecular C-C bonds utilizes a Heck reaction to yield a nitrogen-doped rubicene molecular segment product.

29. The method of claim 27, wherein the pendant aromatic groups are naphthyls and the step of forming intramolecular C-C bonds utilizes a base mediated cyclodehydrogenation to yield a nitrogen-doped tetrabenzopentacene molecular segment product.

30. A method of forming a molecular segment comprising:

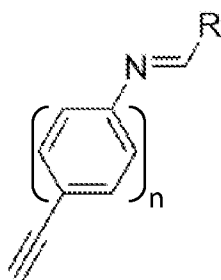
reacting a halogenated anthracene bisalkyne and an aromatic adimine in the presence of a Lewis acid mediator and an oxidant such that the imine groups of the aldimine reacts with the alkyne group of the halogenated anthracene bisalkyne yielding a halogenated anthracene precursor having at least two pendant quinoline groups; and

forming intramolecular C-C bonds between the acene cored and pendant quinoline groups to form a nitrogen-doped molecular segment.

31. The method of claim 30, wherein the step of forming intramolecular C-C bonds utilizes a Heck reaction to yield a nitrogen-doped rubicene molecular segment product.

32. The method of claim 30, wherein the step of forming intramolecular C-C bonds utilizes a base mediated cyclodehydrogenation to yield a nitrogen-doped tetrabenzopentacene molecular segment product.

33. A method of forming graphene nanoribbon comprising:
providing a bifunctional monomer according to:



wherein n is an integer of at least 1, and R is an unsubstituted or substituted aromatic ring;

polymerizing the bifunctional monomer in the presence of a Lewis acid mediator and a sacrificial oxidant such that the imine group of one bifunctional monomer reacts with the alkyne group of another bifunctional monomer, yielding a polyquinoline product wherein the nitrogen from the imine group is incorporated into each of the multicyclic quinoline rings of the polyquinoline;

continuing the polymerization of the polyquinoline to yield a polyquinoline precursor; and

cyclodehydrogenating the polyquinoline precursor to yield a graphene nanoribbon.

34. The method of claim 33, wherein n is at least 2 such that a polybenzoquinoline product is formed.

35. The method of claim 34, wherein the benzoquinolines incorporate substituents at the 2 position, such that the substituents are disposed at edge locations along the graphene nanoribbon.

36. The method of claim 33, wherein the graphene nanoribbon is a nitrogen-doped N=7 armchair graphene nanoribbon.

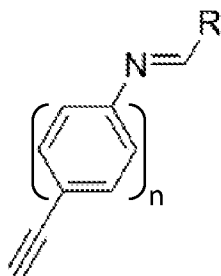
37. The method of claim 36, wherein the concentration of nitrogen doping can vary from 7 to 14%.

38. A polyquinoline formed of a plurality of quinolines interlinked at the 4 and 6 positions.

39. A polybenzoquinoline comprising two or more benzoquinolines interlinked at the 4 and 6 positions.

40. A nitrogen-doped molecular segment selected from one of either rubicene or tetrapentacene.

41. A quinoline monomer comprising:



wherein n is an integer of at least 1, and R is an unsubstituted or substituted aromatic ring.

42. The monomer of claim 41, wherein the aromatic ring of R is further substituted with at least one of the following a heteroatom, a halogen, an alkyl chain, a methoxy (Me), an acetyl (Ac), an NHAc, an amines, an $N(Me)_2$, and a $S(Me)_2$.

43. The monomer of claim 42, wherein the aromatic ring of R has at least two substitutions.

44. The monomer of claim 41, wherein n is at least 2.

45. The monomer of claim 44, wherein the second aromatic ring comprises a further substituent.

46. The monomer of claim 45, wherein the substituent is selected from the group of a heteroatom, a halogen, an alkyl chain, a methoxy (Me), an acetyl (Ac), an NHAc, an amine, an $N(Me)_2$, and a $S(Me)_2$.

47. The monomer of claim 44, wherein the bifunctional monomer further comprises an additional benzoquinoline subunit.

48. The monomer of claim 47, wherein the additional benzoquinoline subunit further comprises an additional substituent group selected from the group of a heteroatom, a halogen, an alkyl chain, a methoxy (Me), an acetyl (Ac), an NHAc, an amine, an N(Me)₂, and a S(Me)₂.

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FIG. 1A

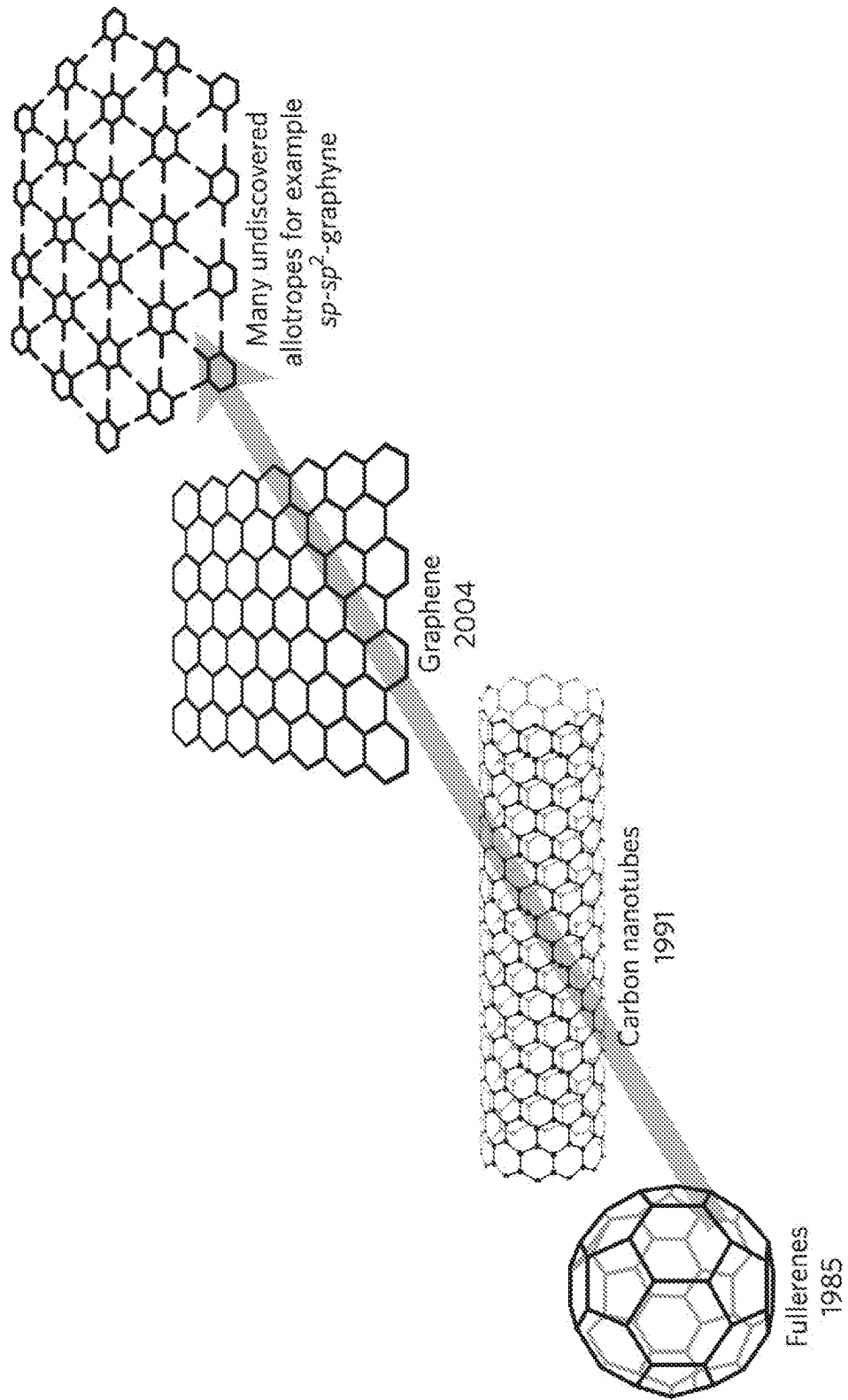
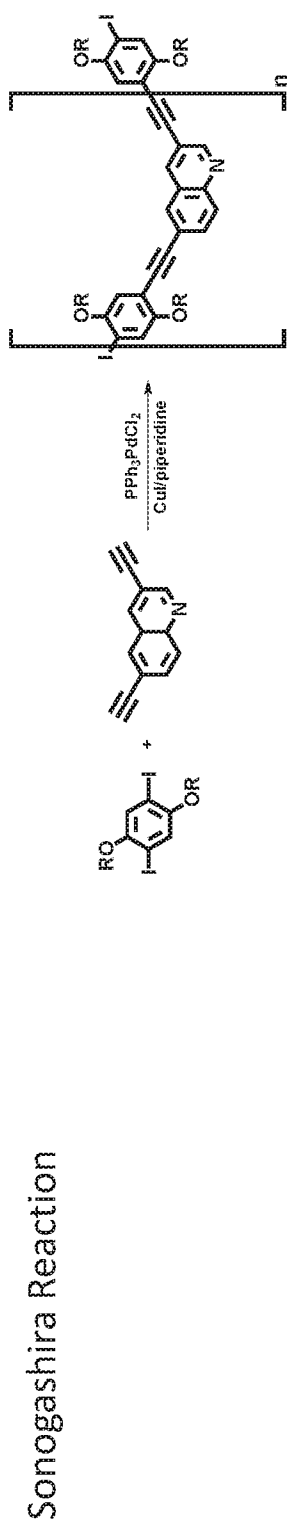
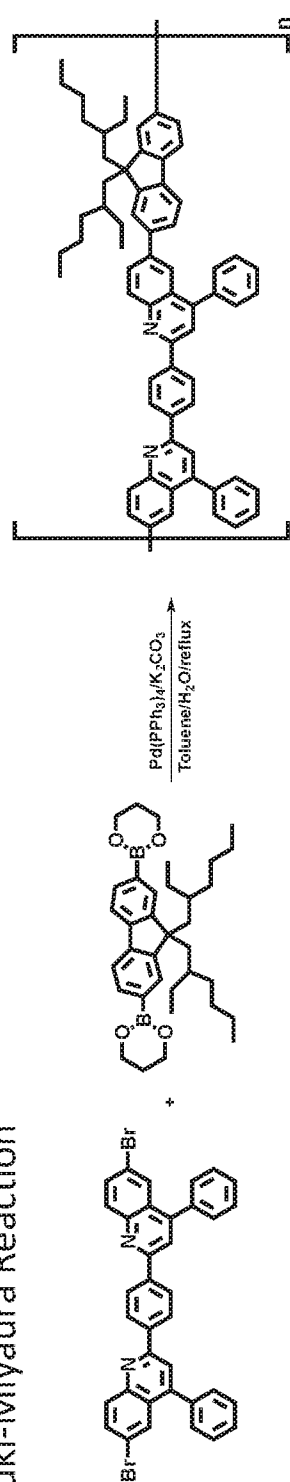
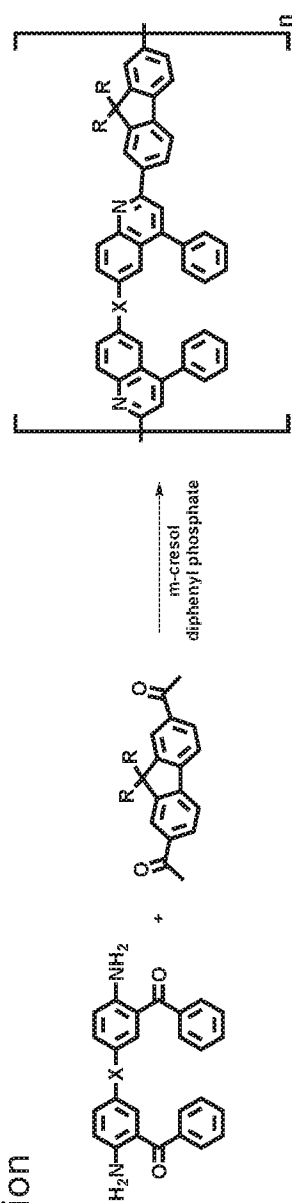


FIG. 1B
PRIOR ART

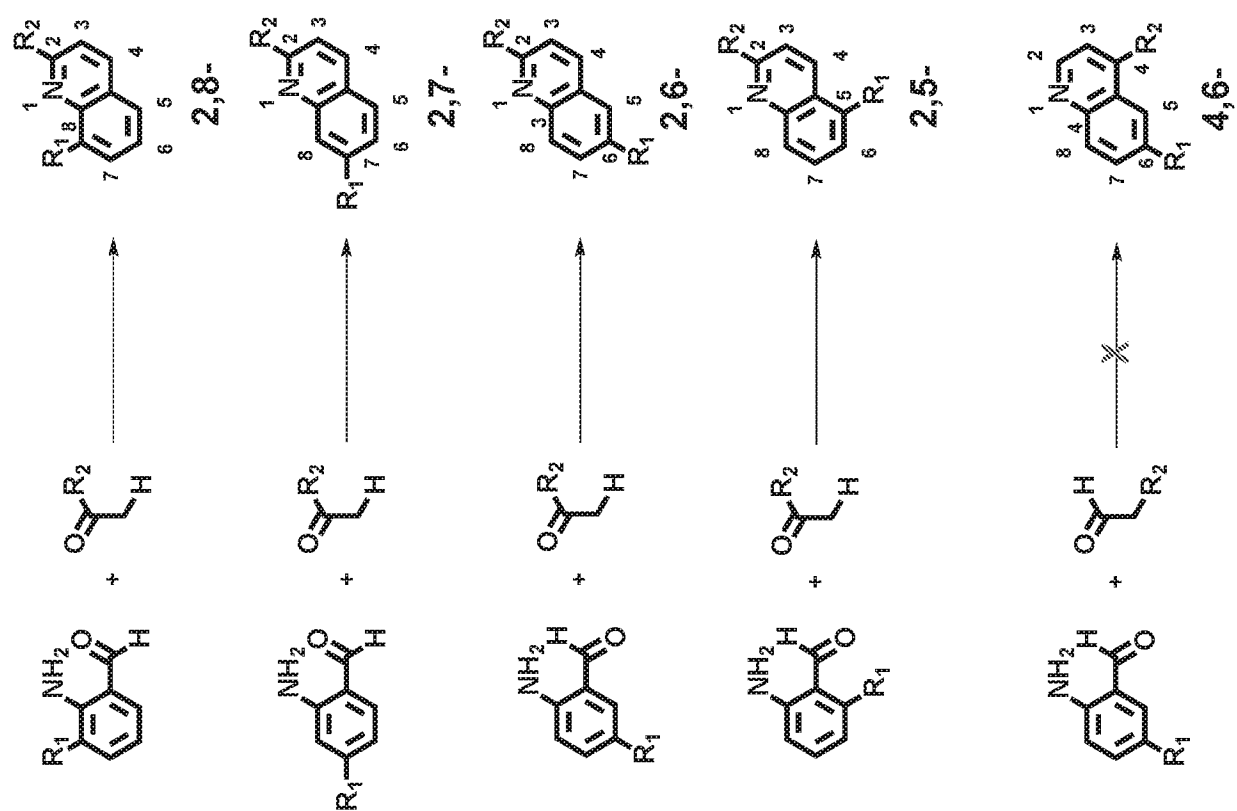
Suzuki-Miyaura Reaction



Friedlander Reaction



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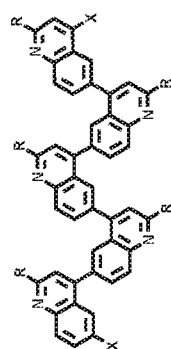
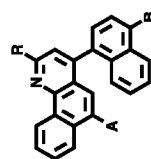
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FIG. 2A

Polyquinolines

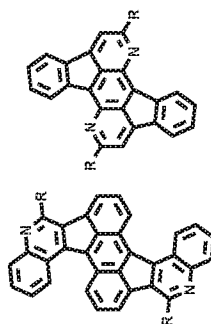
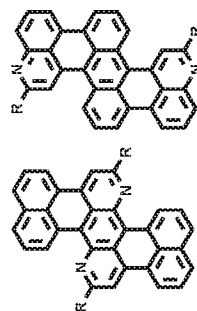
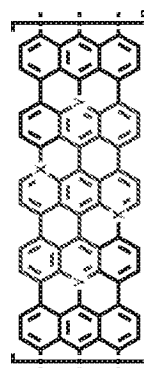
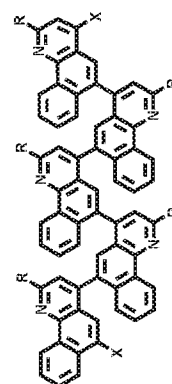
Synthesis of

4,6-linked polyquinolines

BenzoquinolinesSynthesis of benzoquinolines
via the Povarov reactionRubicones

Synthesis of

nitrogen doped rubicones

TetrobenzopentacenesSynthesis of
tetrobenzopentacenesGraphene NanoribbonsSynthesis of
nitrogen doped GNRsPolybenzoquinolinesSynthesis of
oligobenzoquinolines and
polybenzoquinolines

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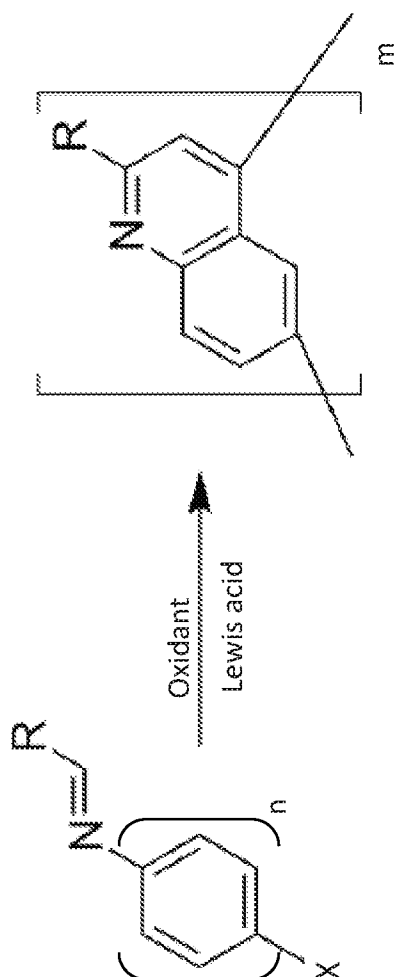


FIG. 2B

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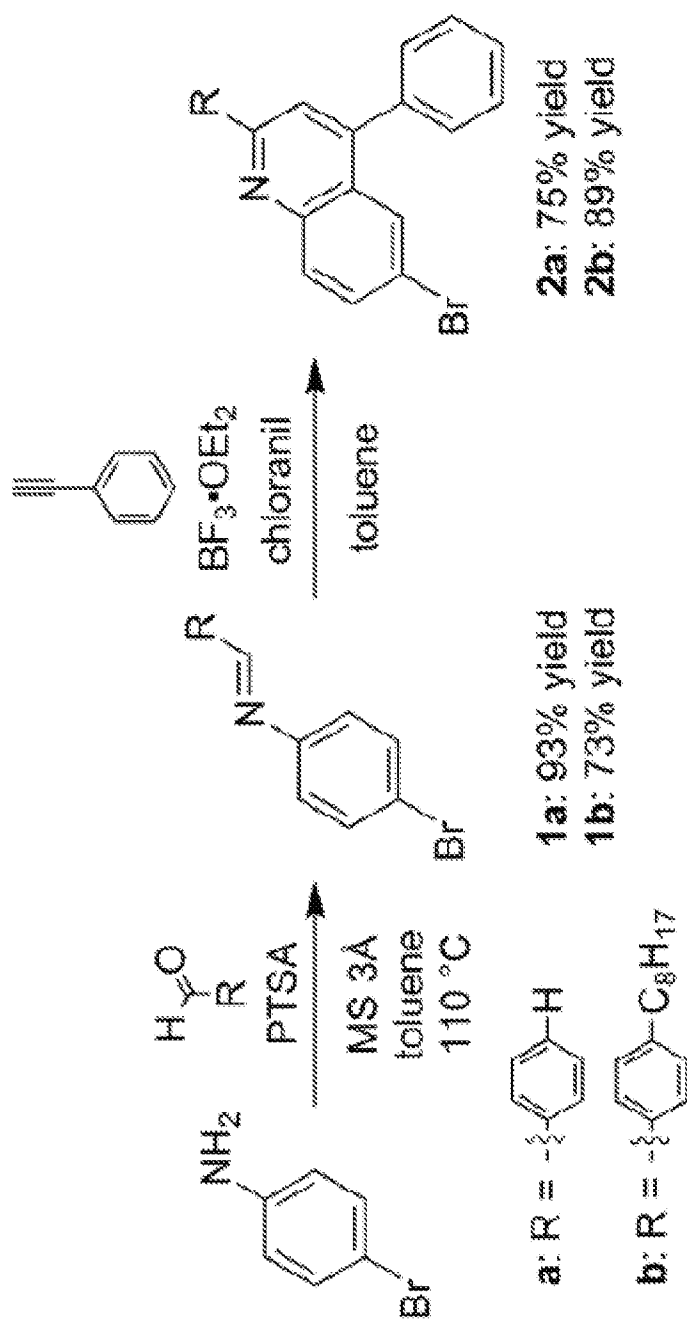


FIG. 3A

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FIG. 3B

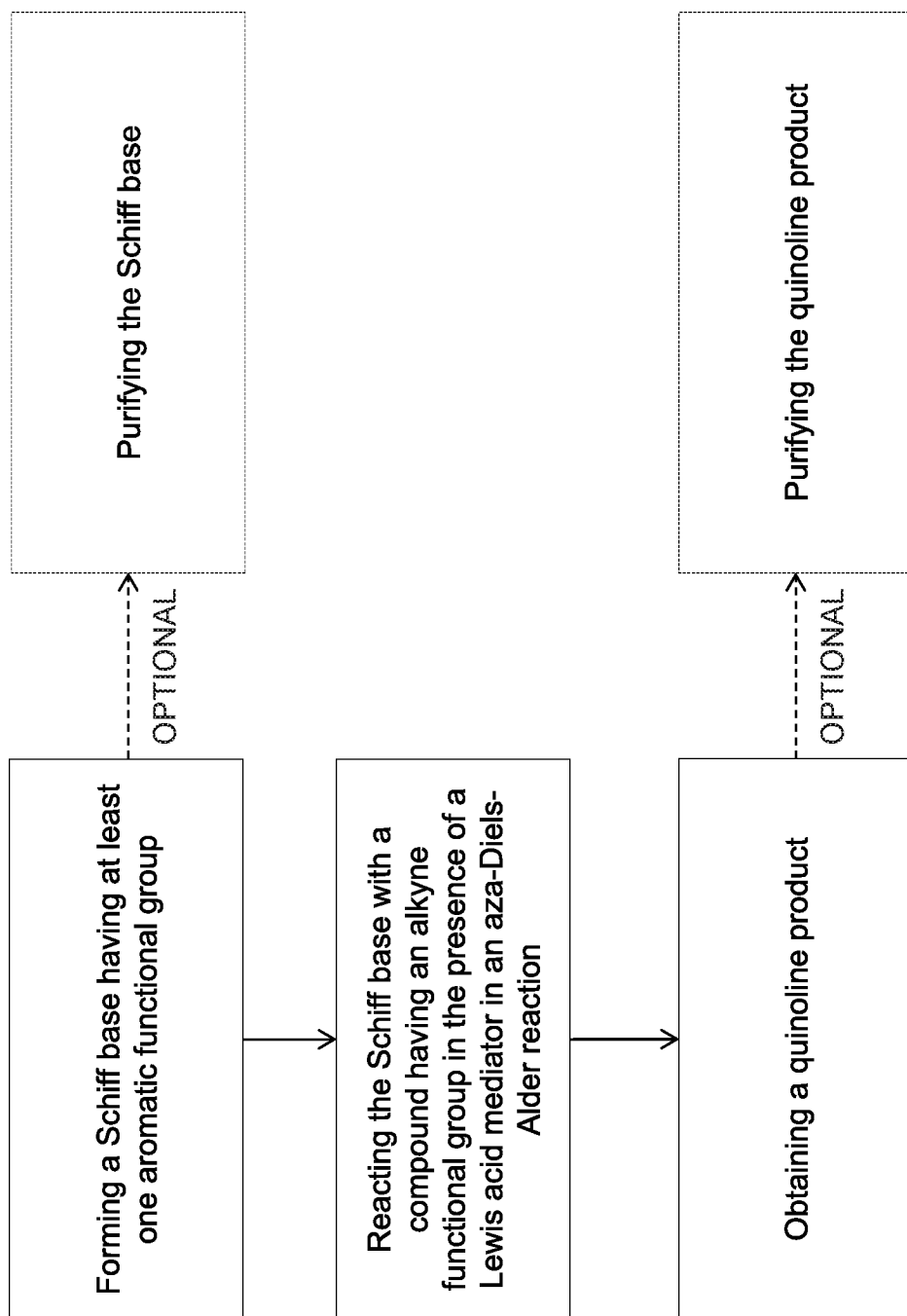
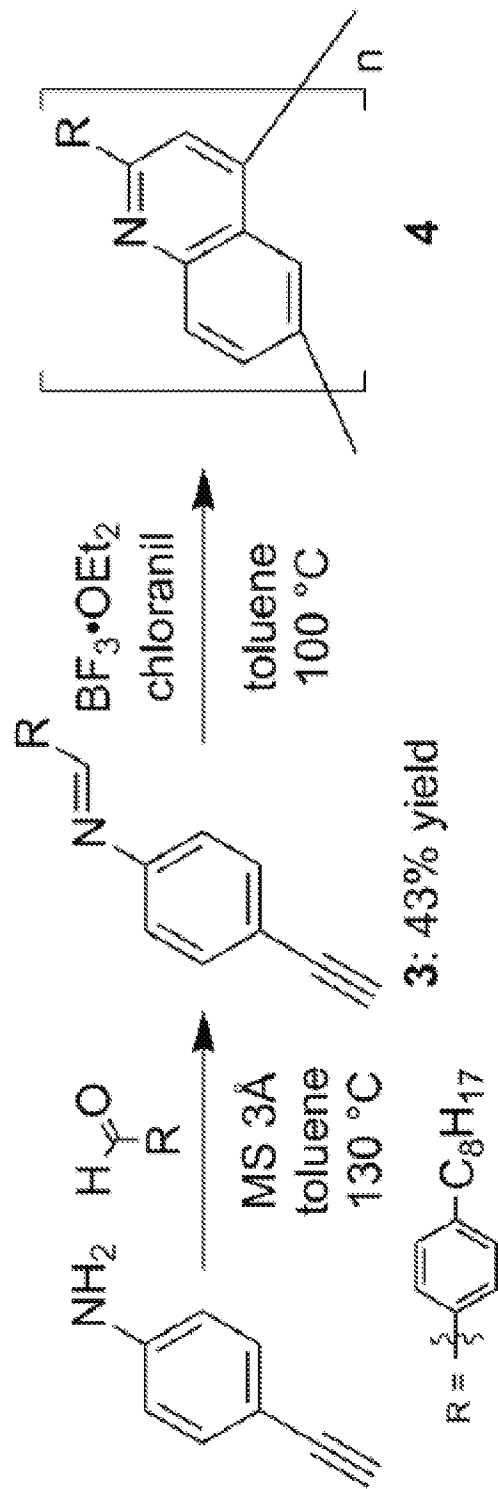
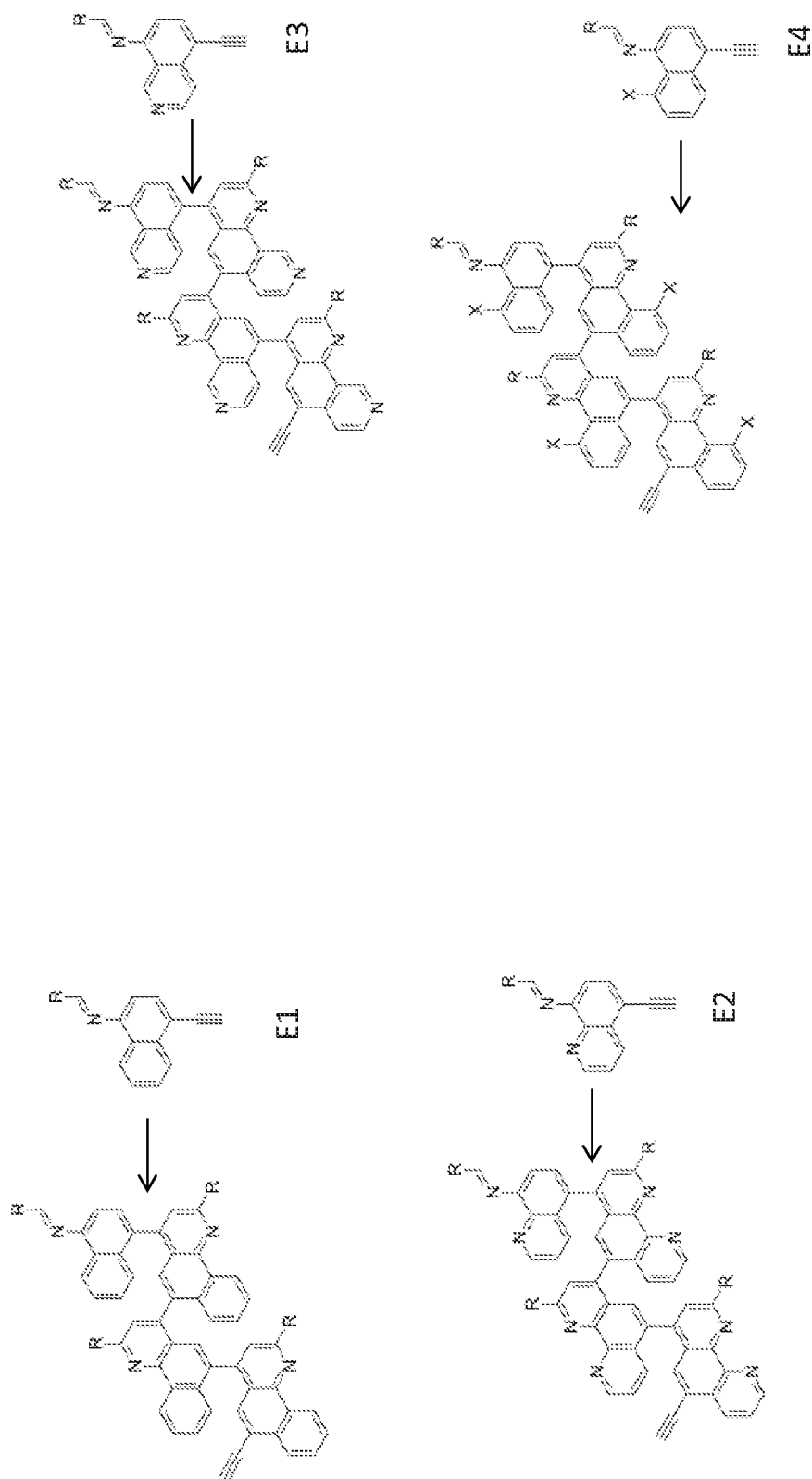


FIG. 4A



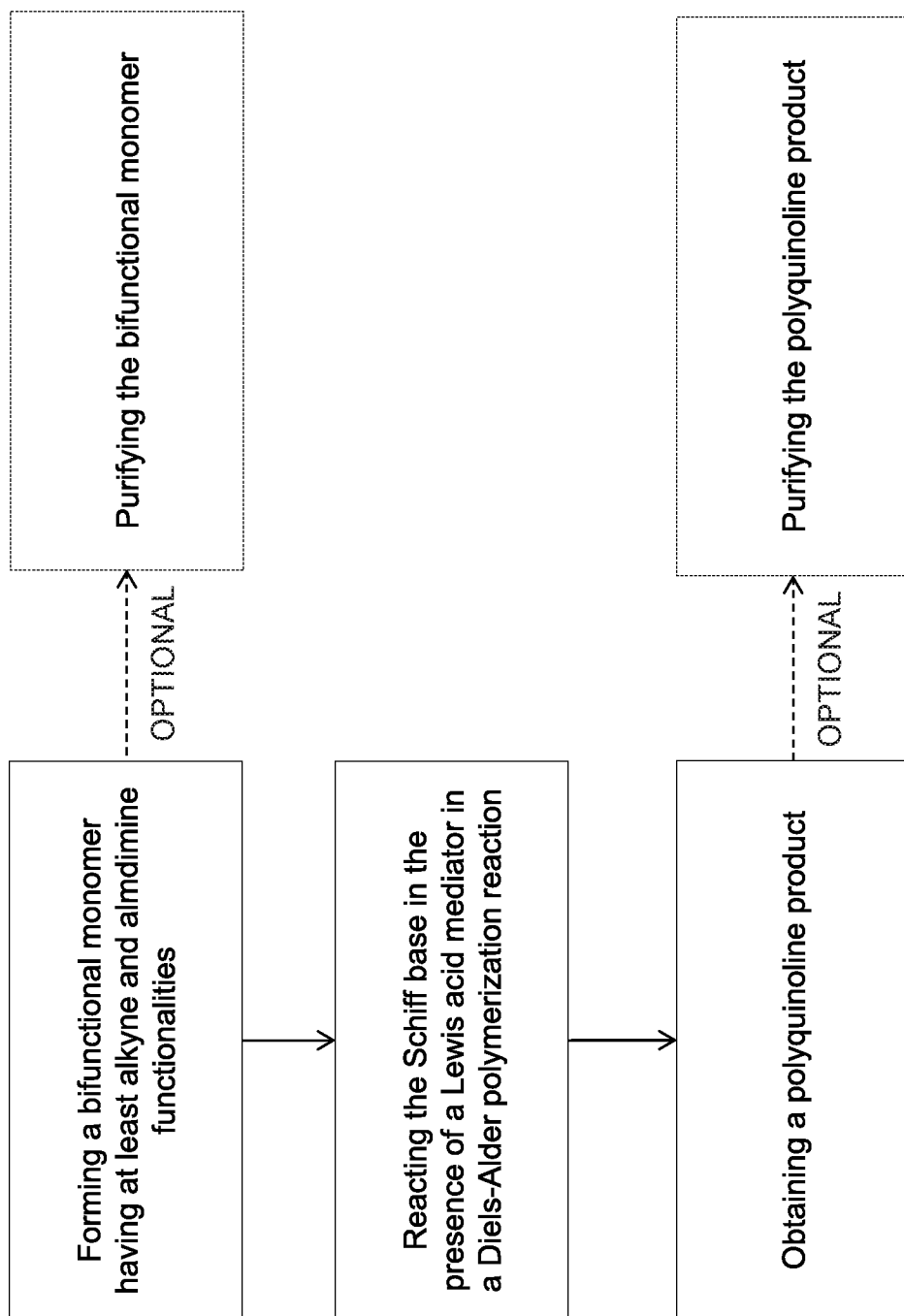
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FIG. 4B



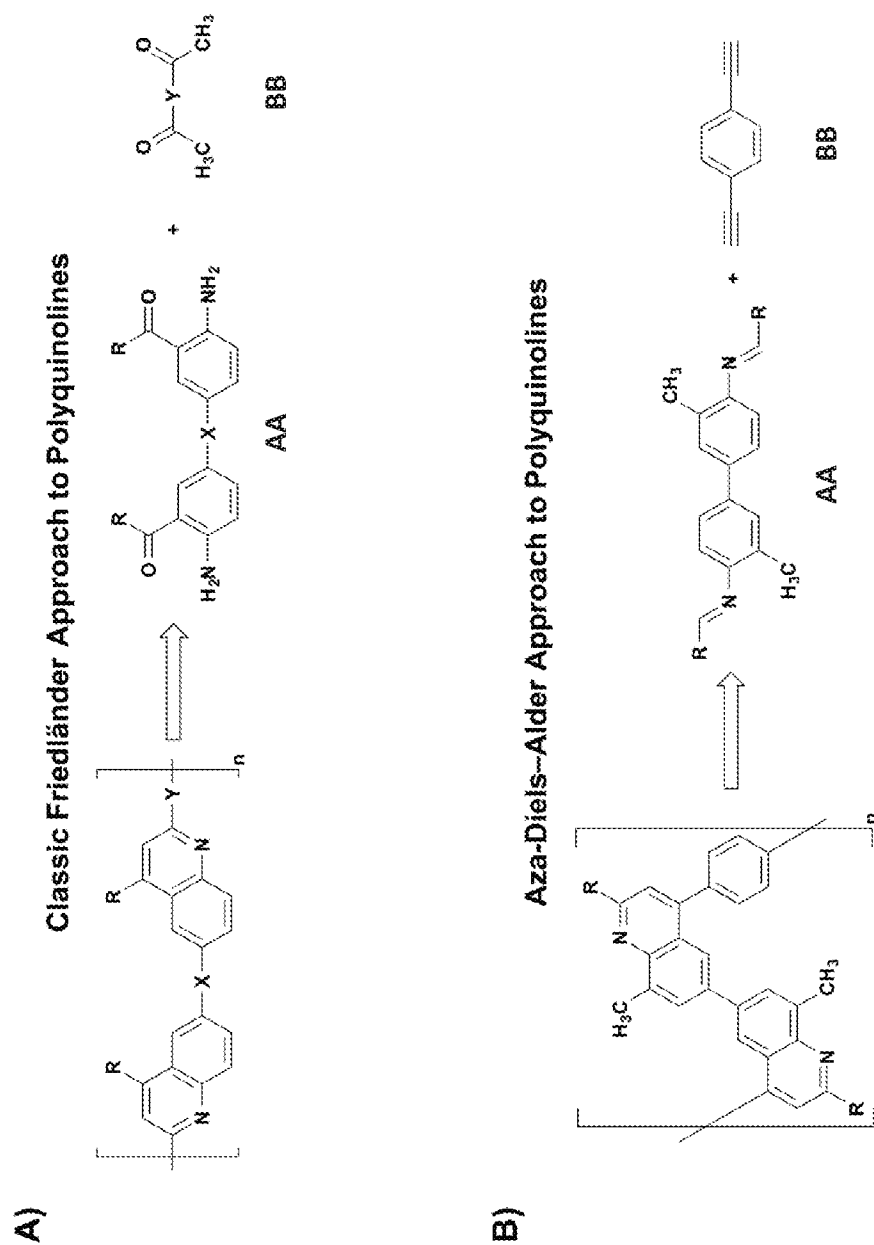
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FIG. 4C



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FIG. 5



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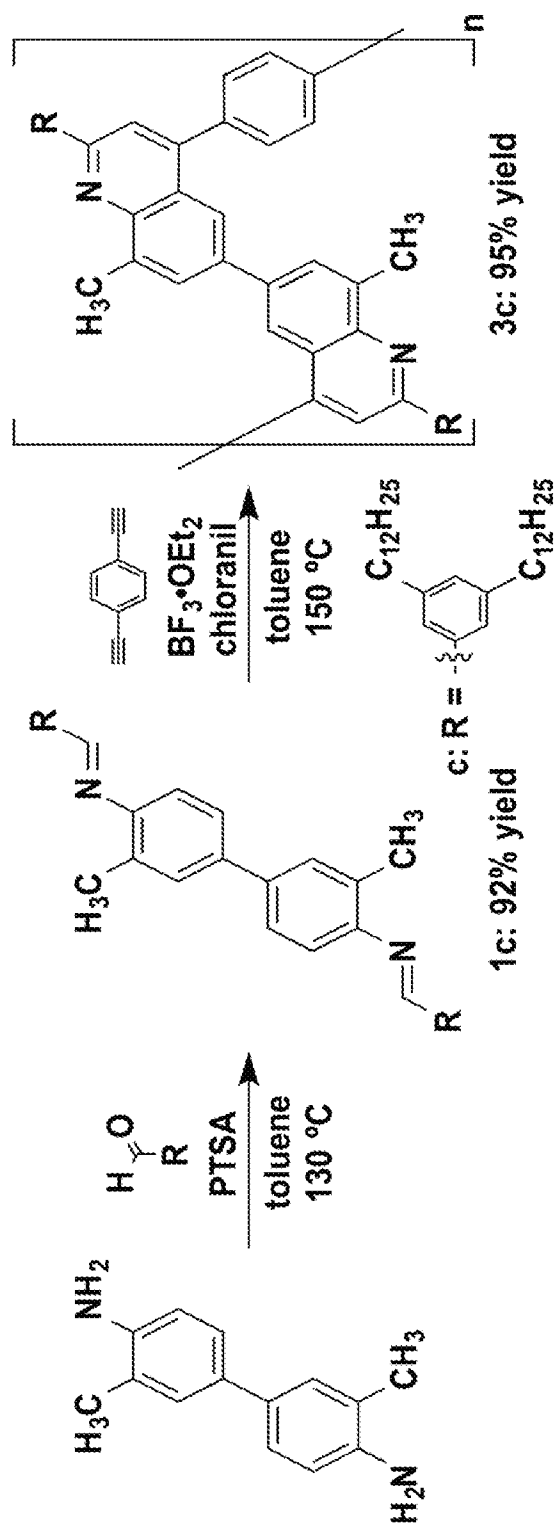
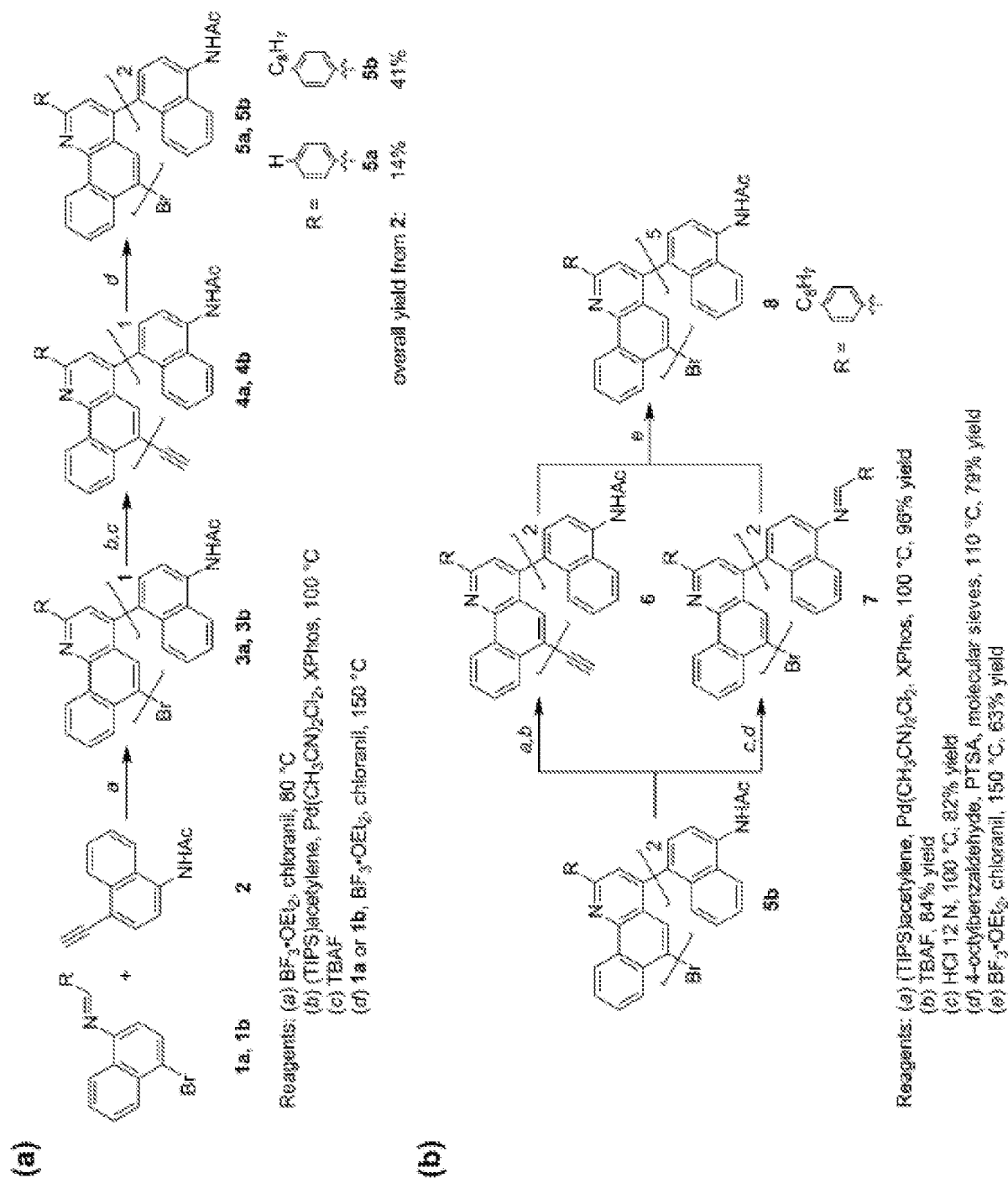
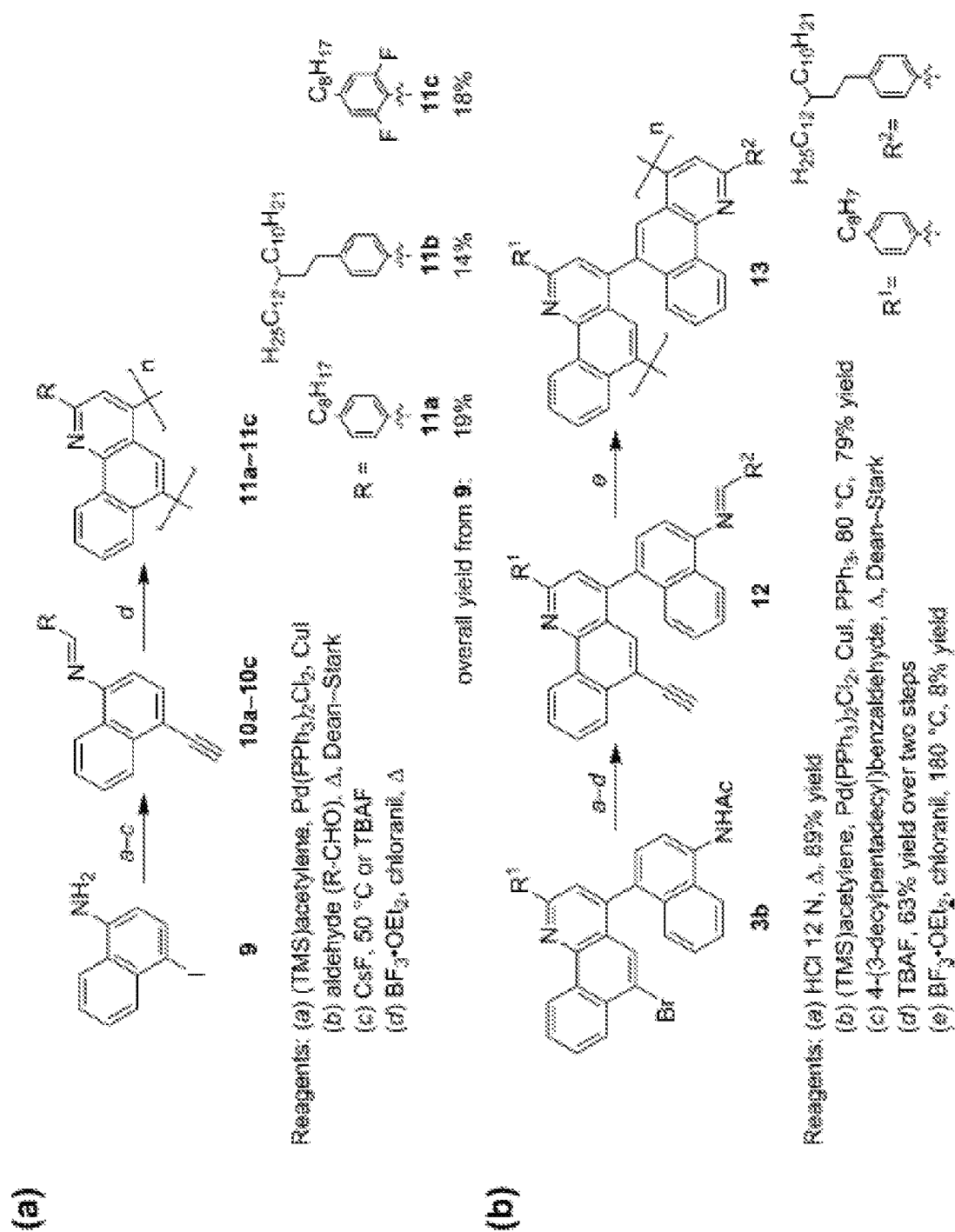


FIG. 7

FIG. 8



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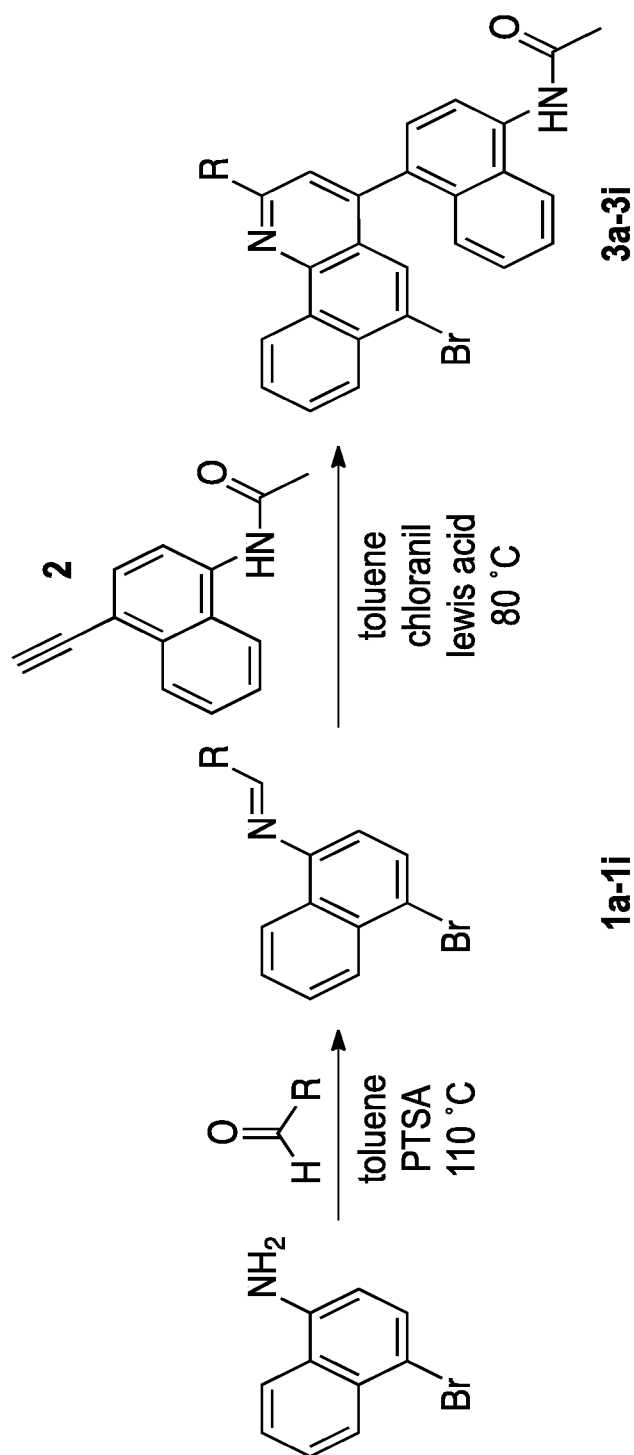


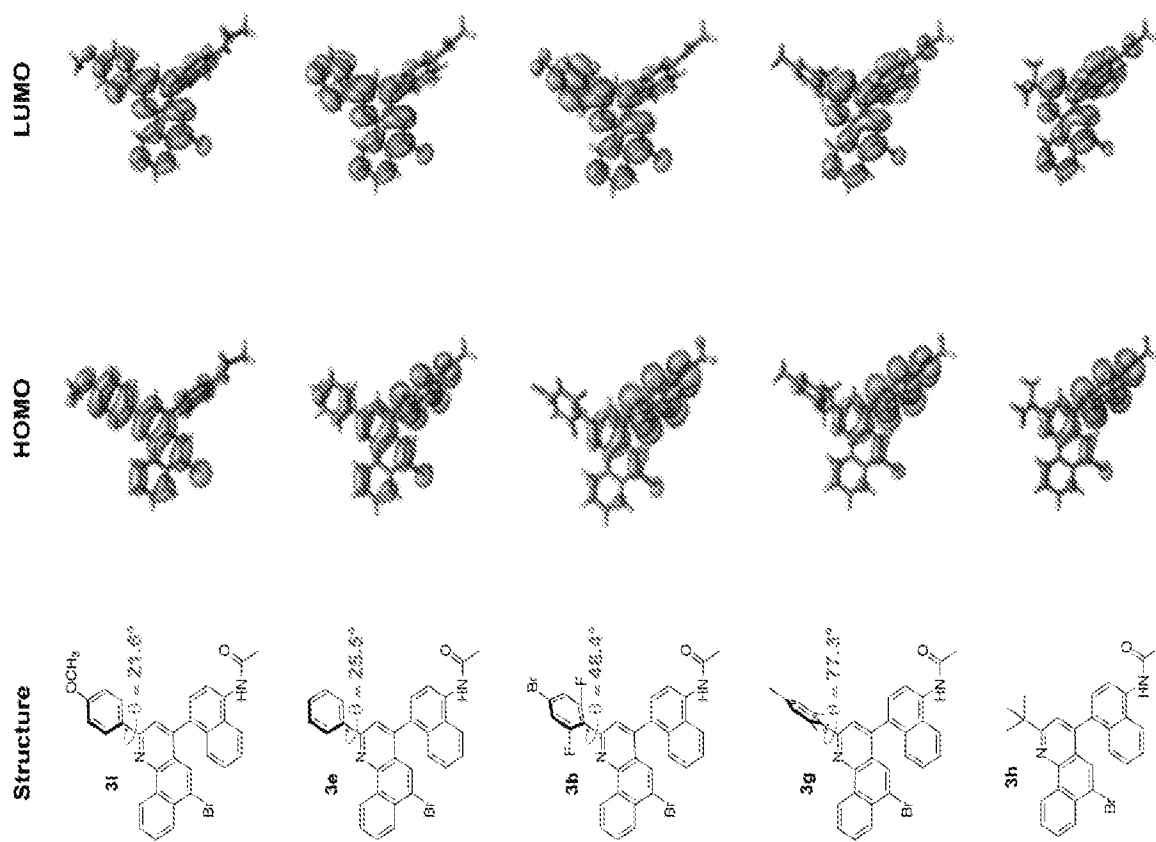
FIG. 10

FIG. 11

Entry	Compound ^a	L.A.	R	Yield ^b (%)
1	3a	AlCl ₃		0
2	3a	Y(OTf)		38
3	3a	FeCl ₃		53
4	3a	SnCl ₂		33
5	3a	Ag(OTf)		67
6	3a	ZnCl ₂		75
7	3a	BF ₃ •OEt ₂		83
8	3b	BF ₃ •OEt ₂		82
9	3c	BF ₃ •OEt ₂		82
10	3d	BF ₃ •OEt ₂		76
11	3e	BF ₃ •OEt ₂		76
12	3f	BF ₃ •OEt ₂		75
13	3g	BF ₃ •OEt ₂		70
14	3h	BF ₃ •OEt ₂		68
15	3i	BF ₃ •OEt ₂		68

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FIG. 12



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FIG. 13

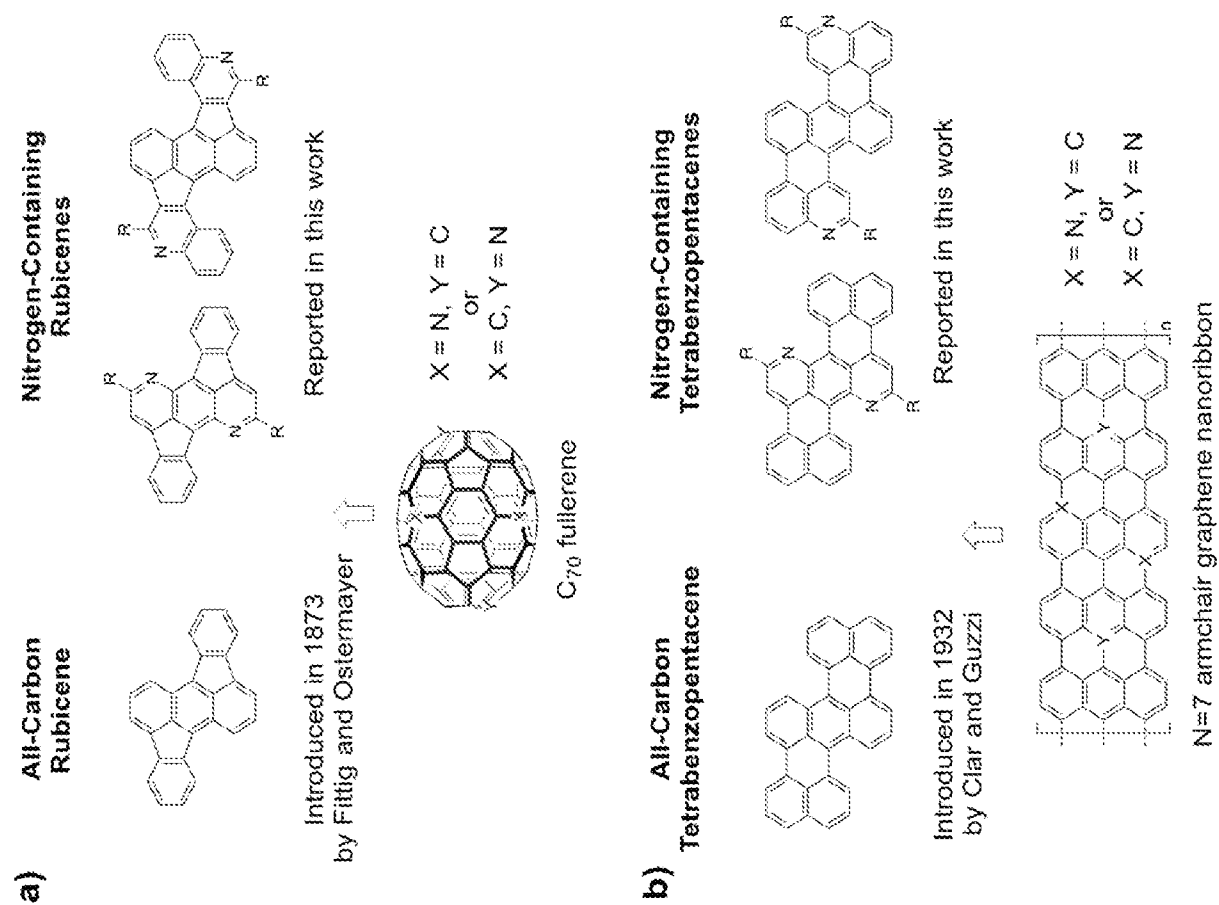


FIG. 14

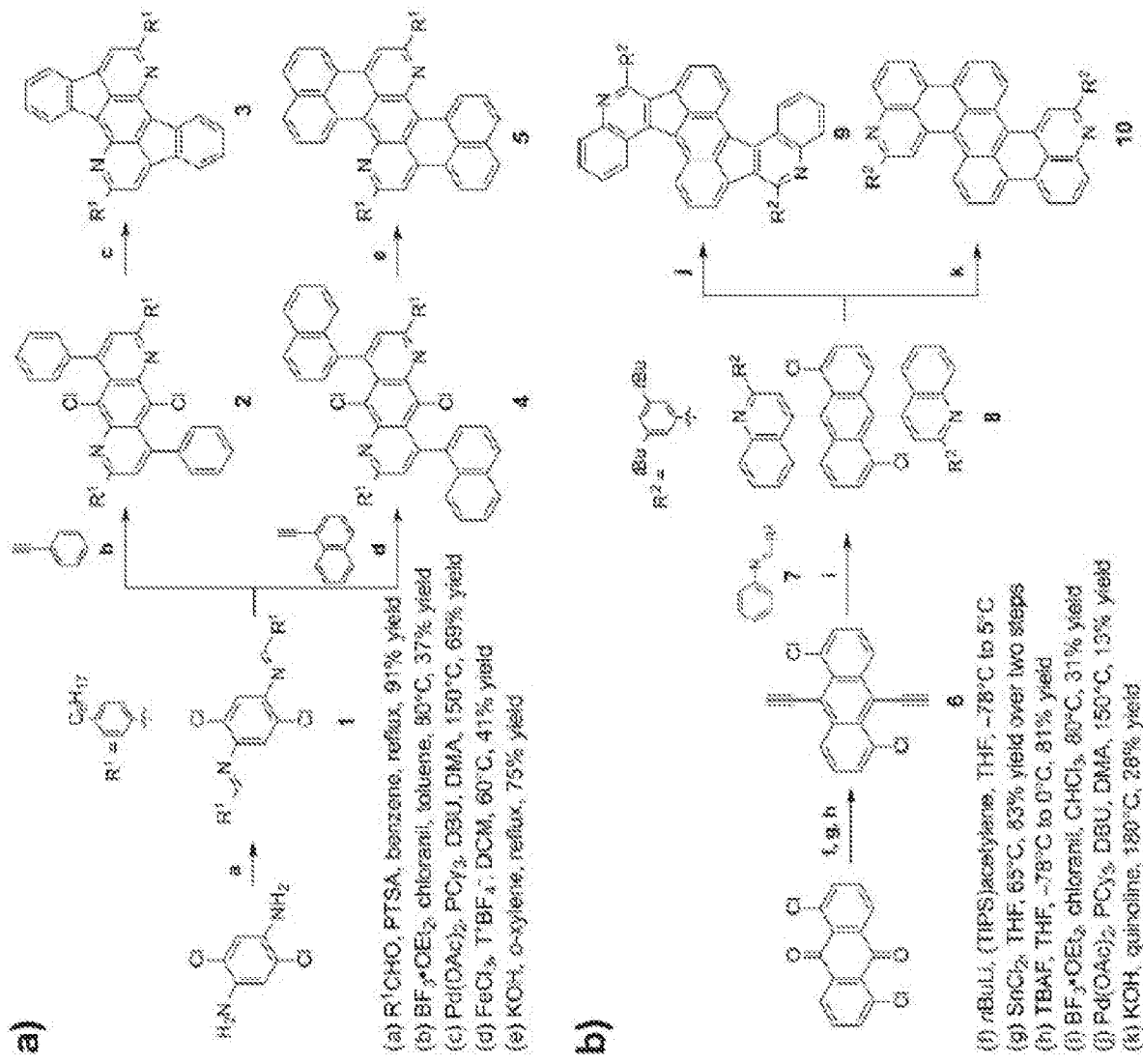
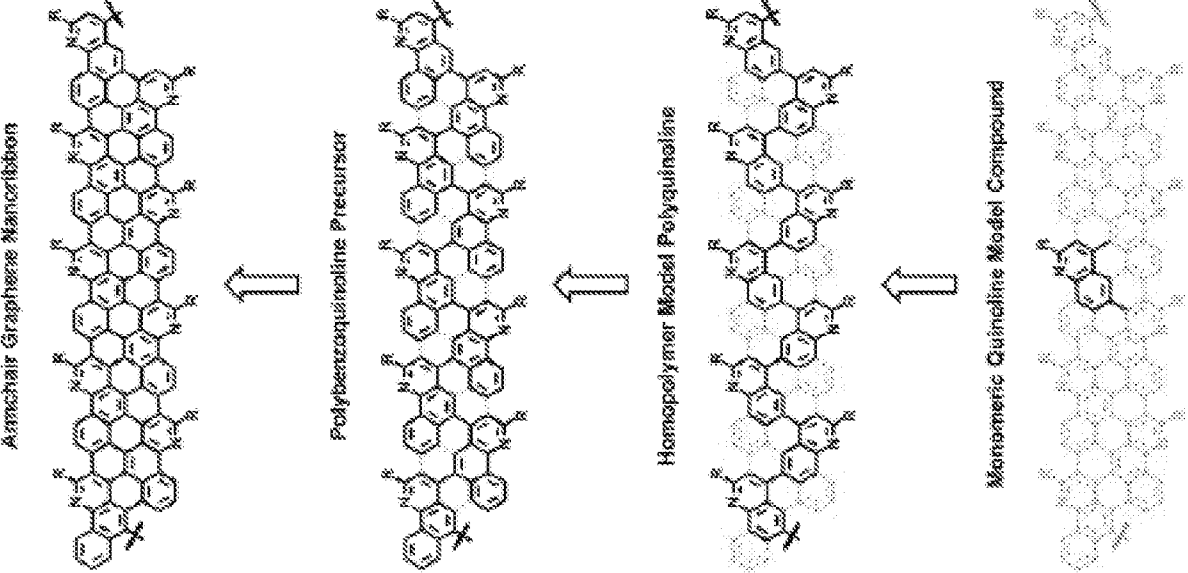


FIG. 15



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FIG. 16A

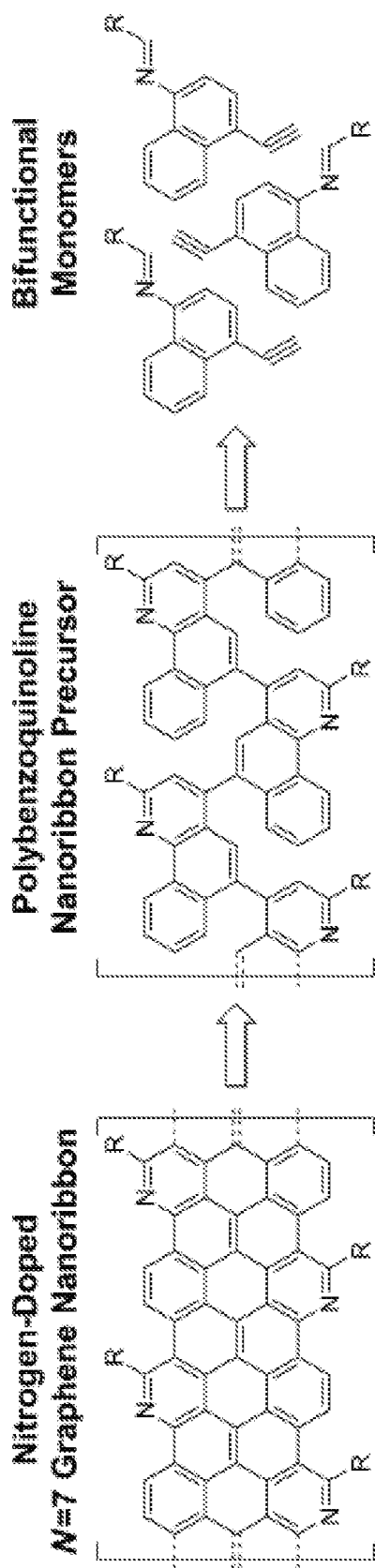


FIG. 16B

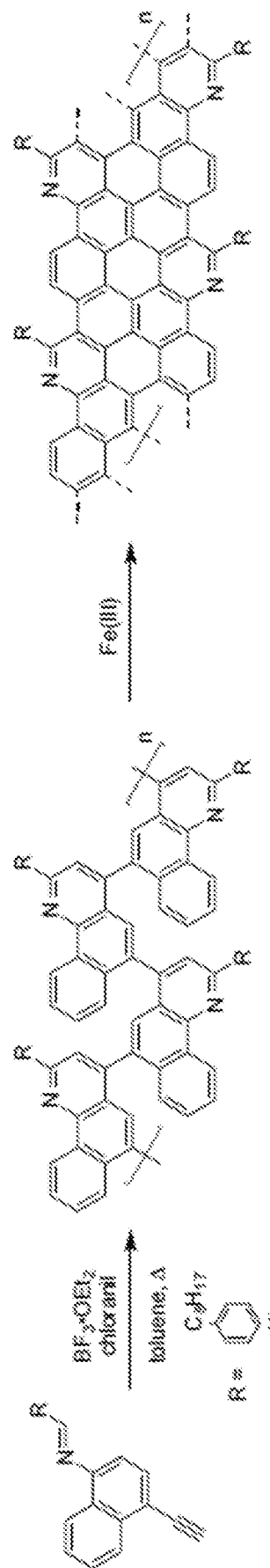
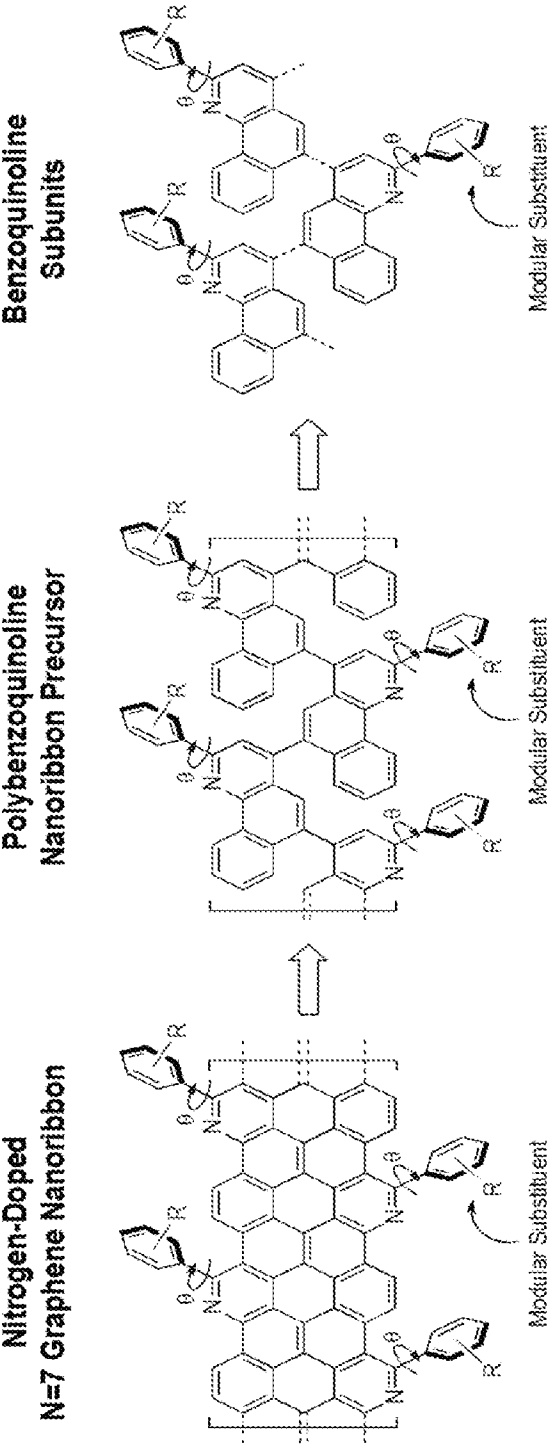
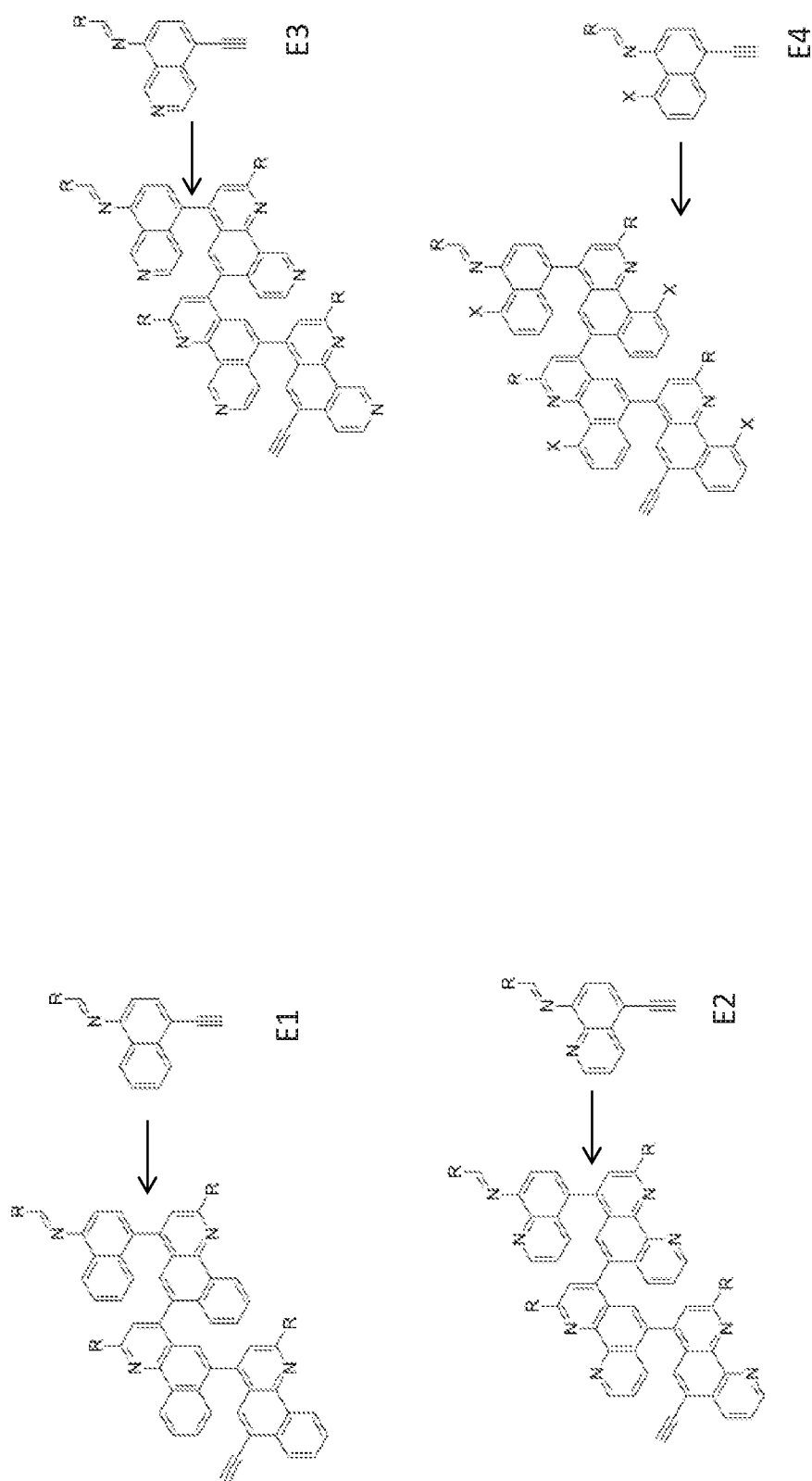


FIG. 17



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FIG. 18



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FIG. 19

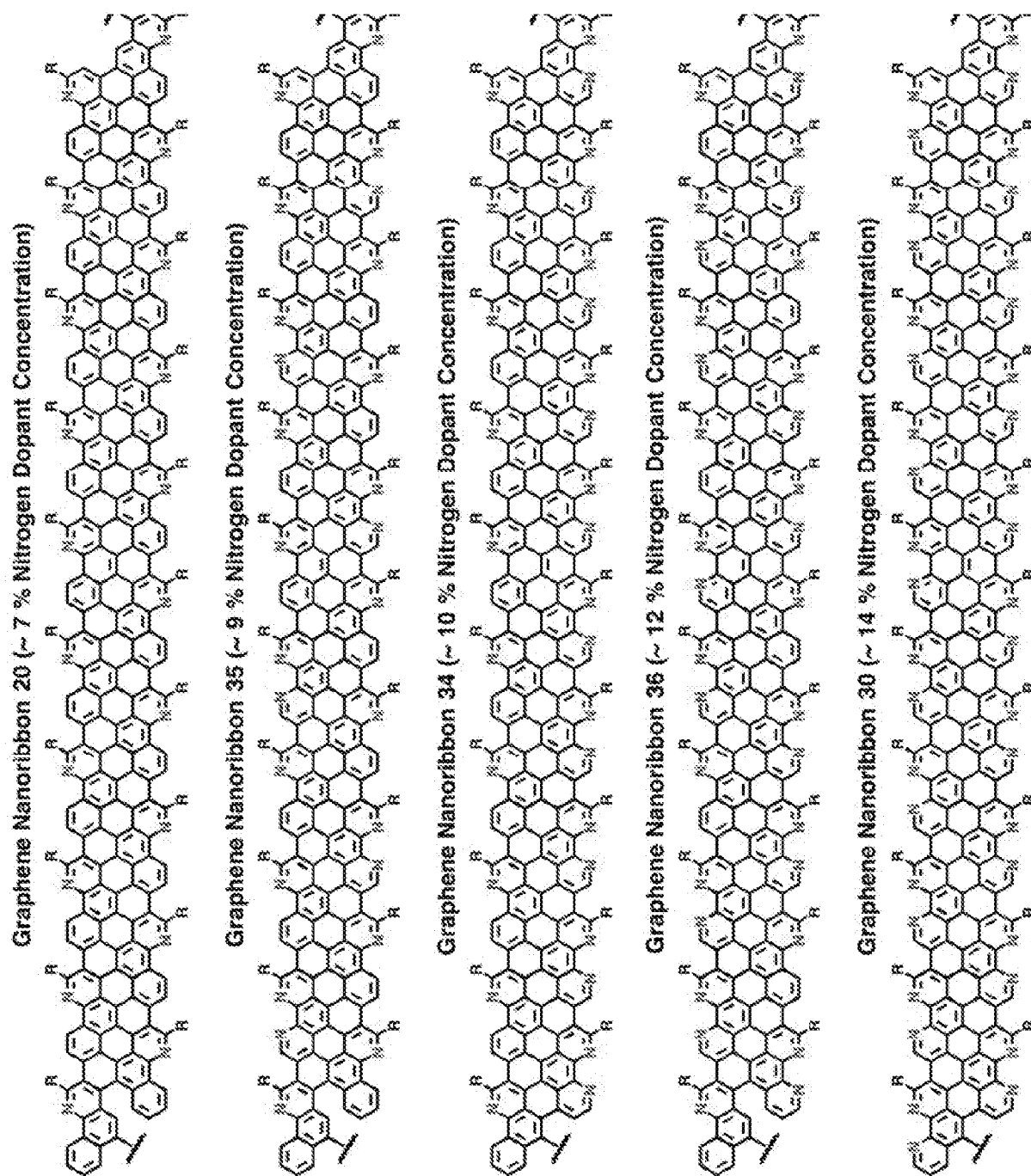
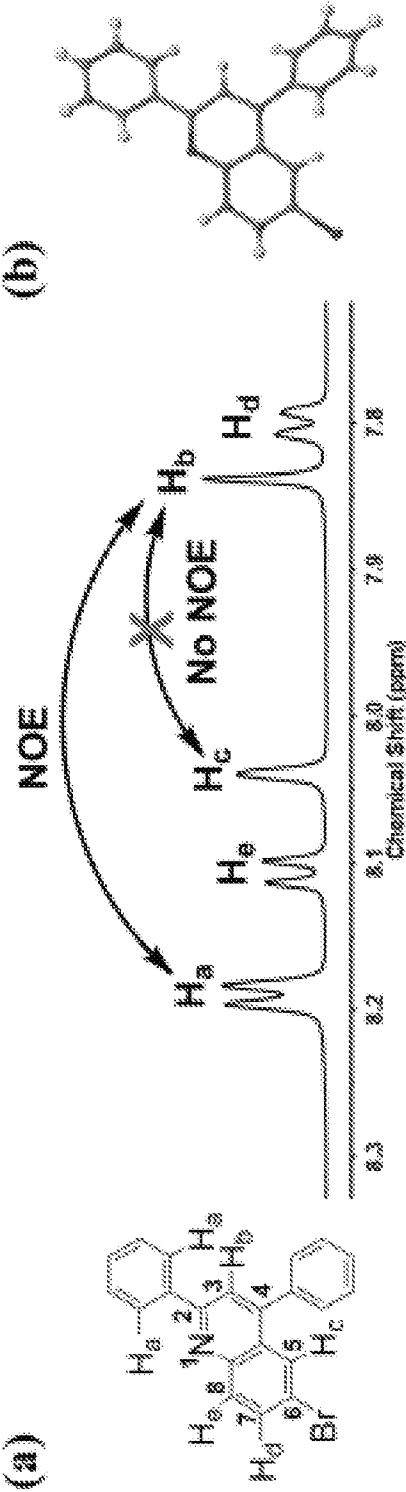


FIG. 20



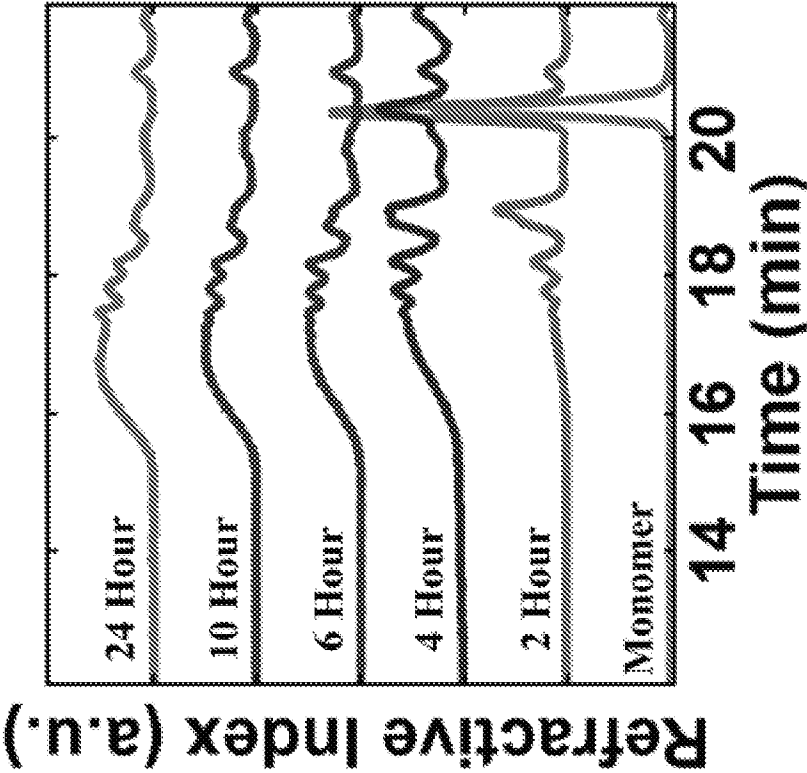


FIG. 21

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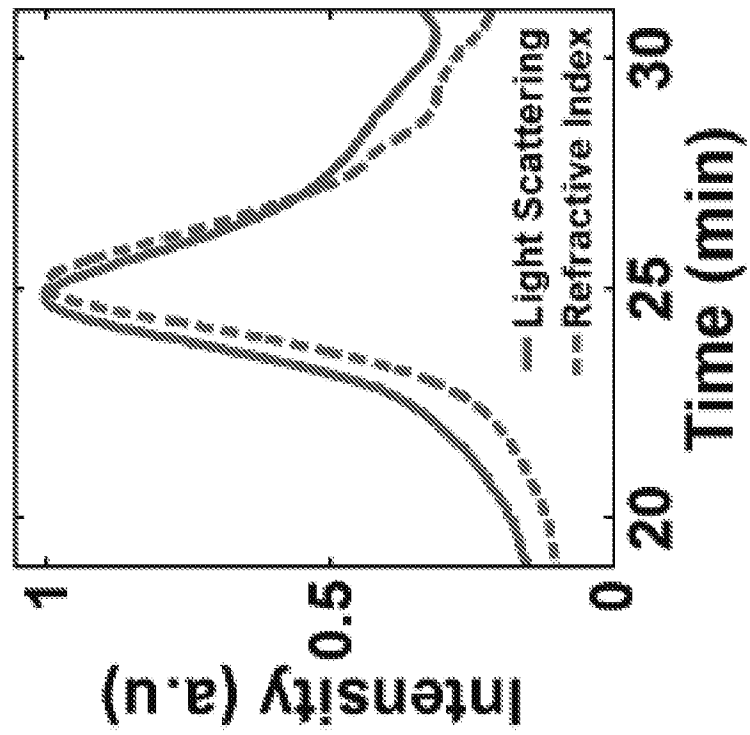
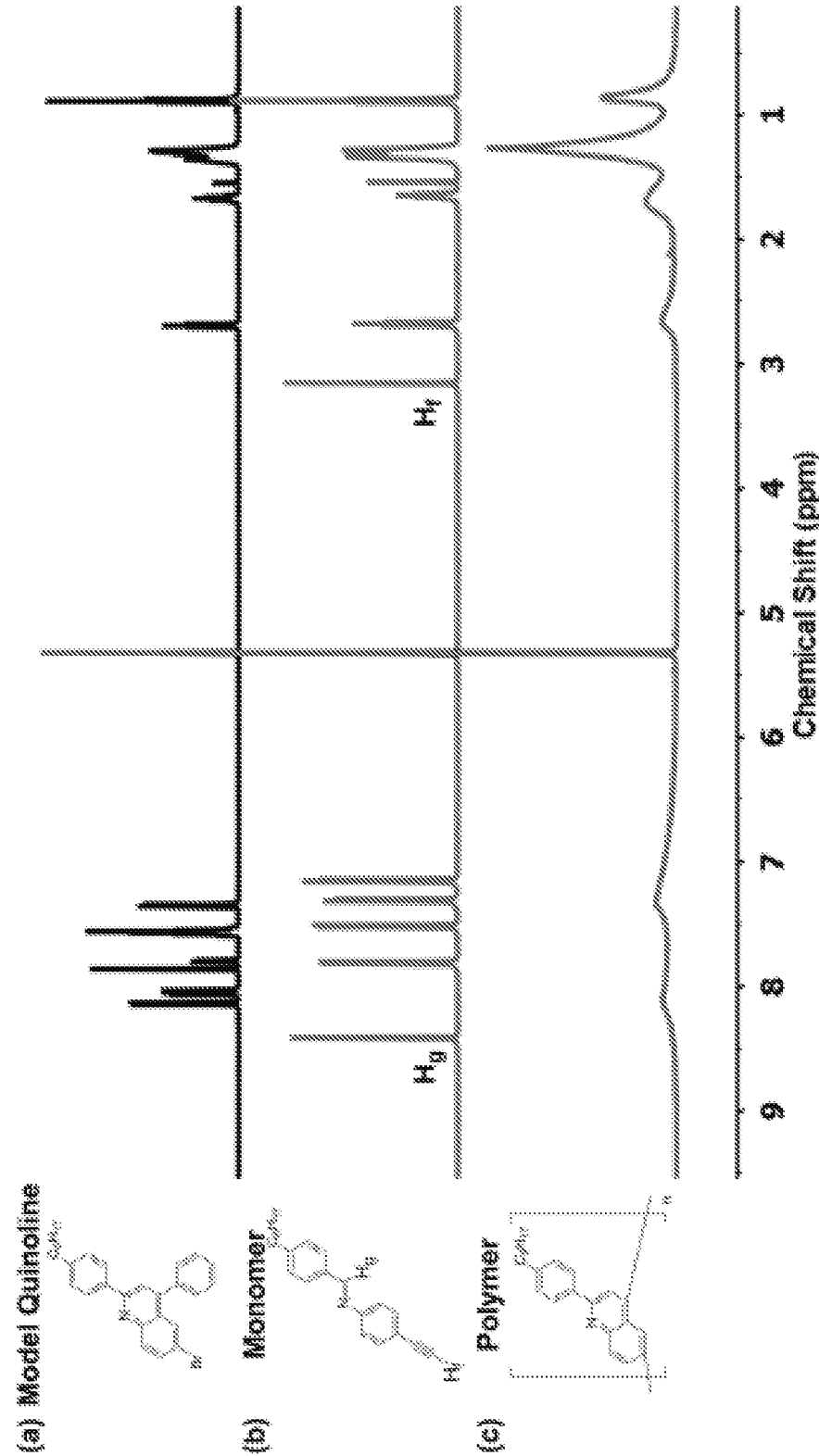


FIG. 22

FIG. 23



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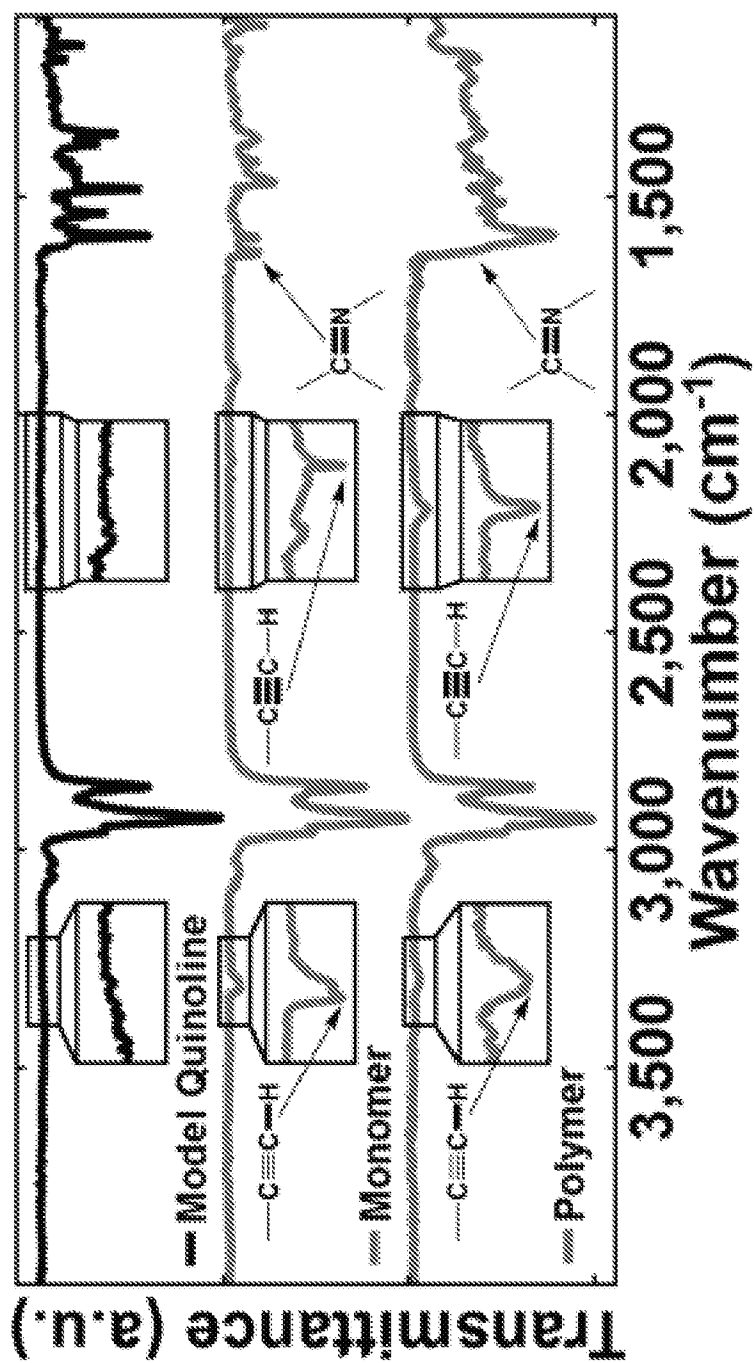


FIG. 24

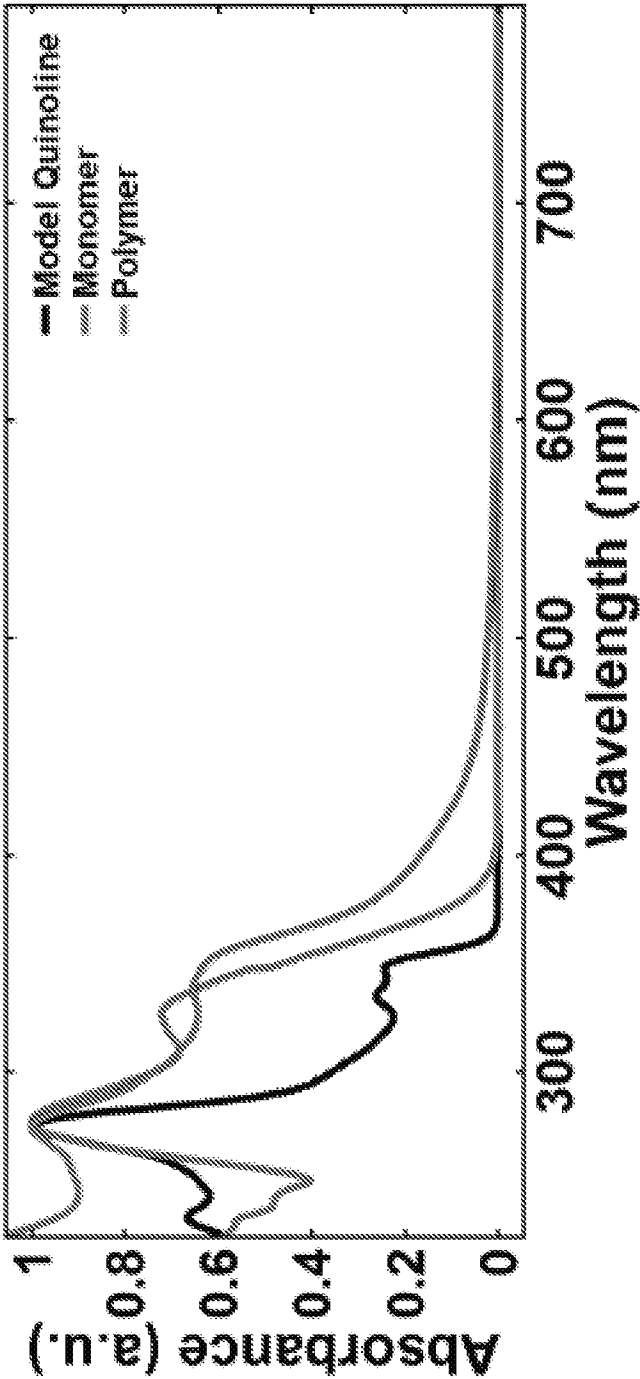
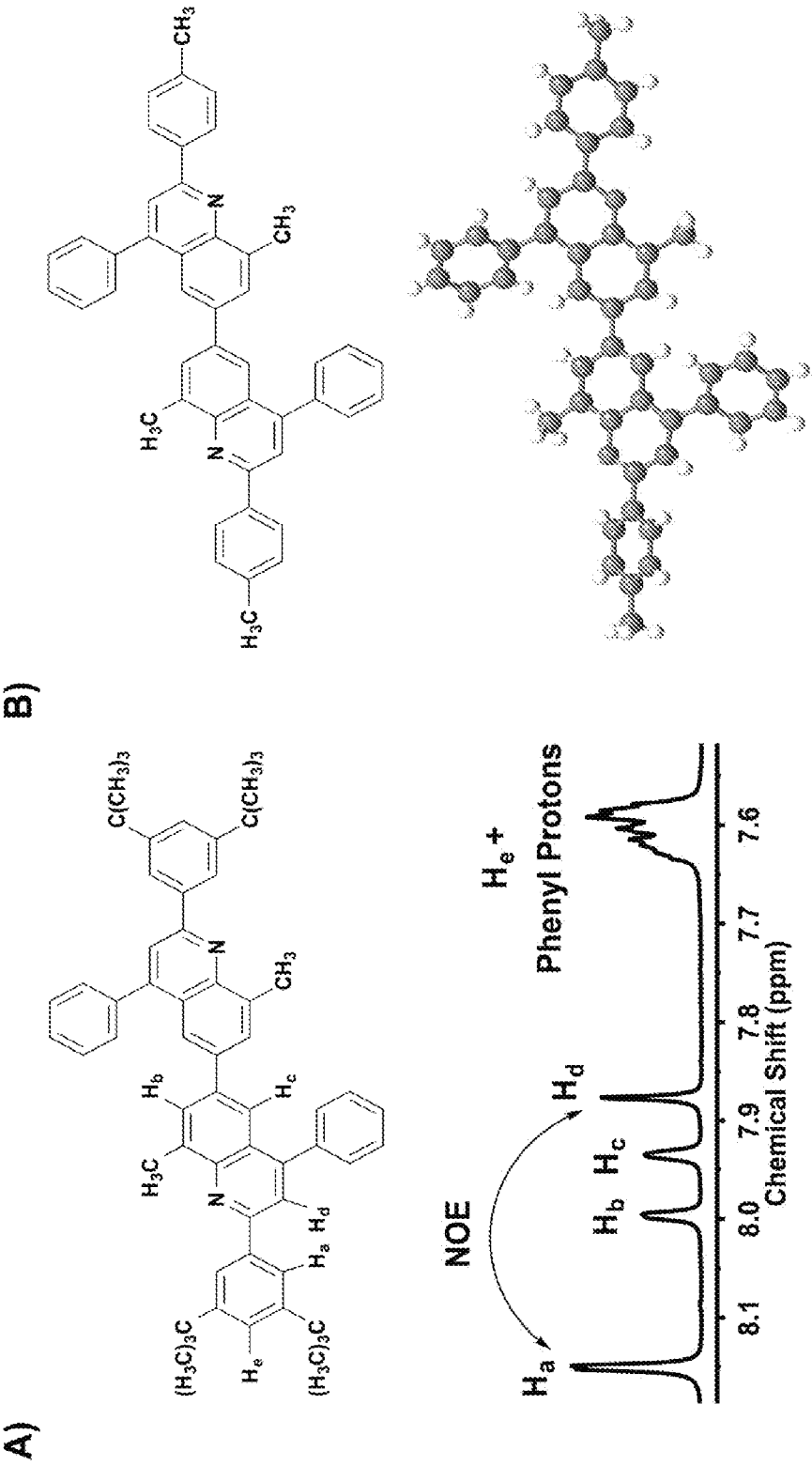


FIG. 25

FIG. 26



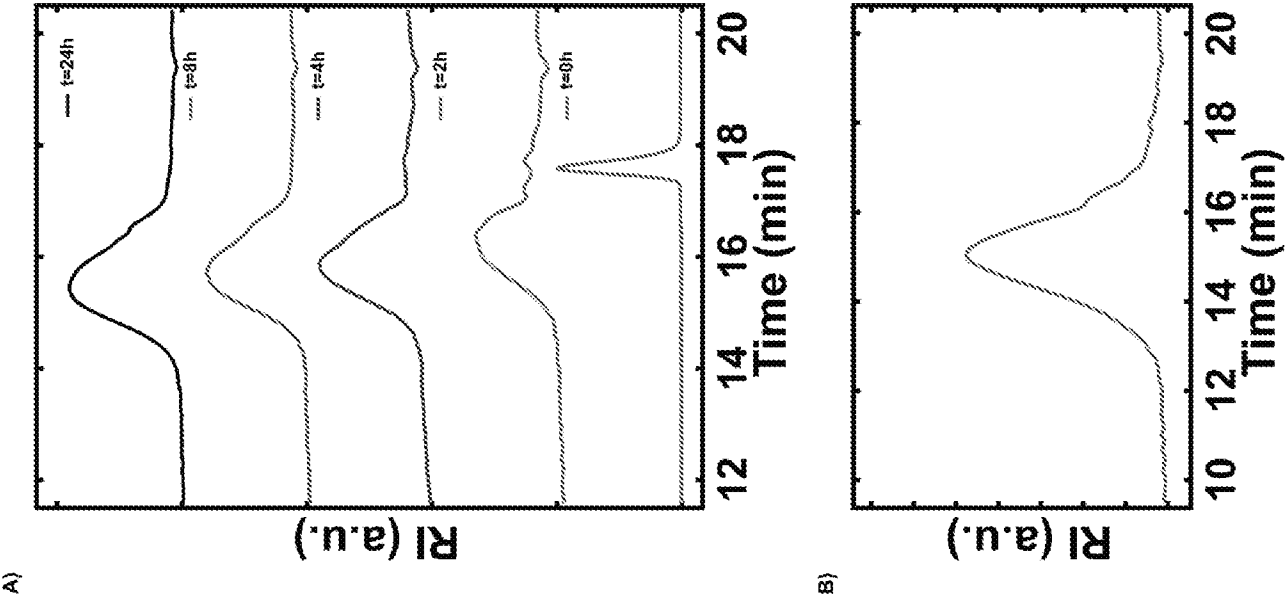
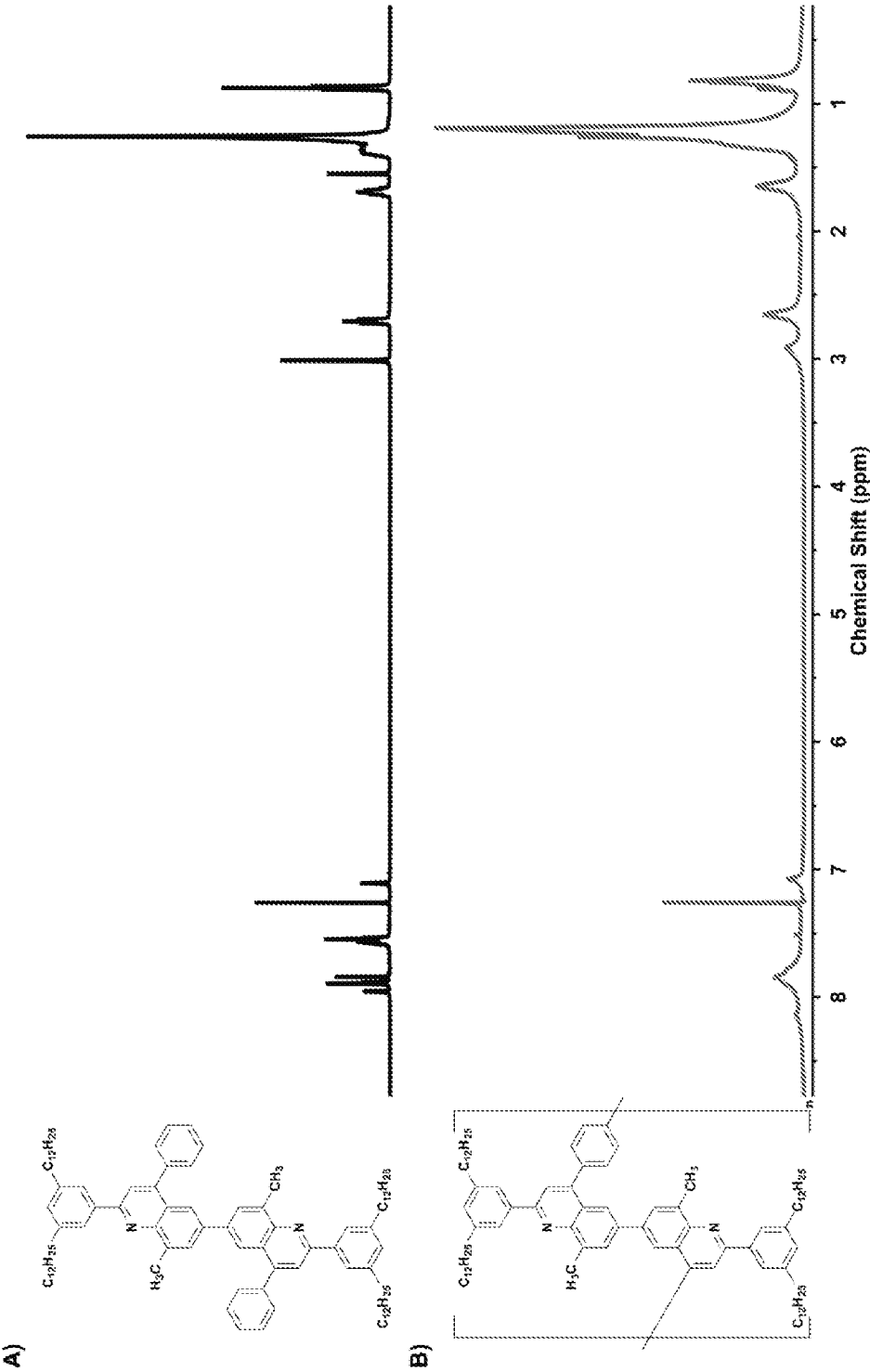


FIG. 27

FIG. 28



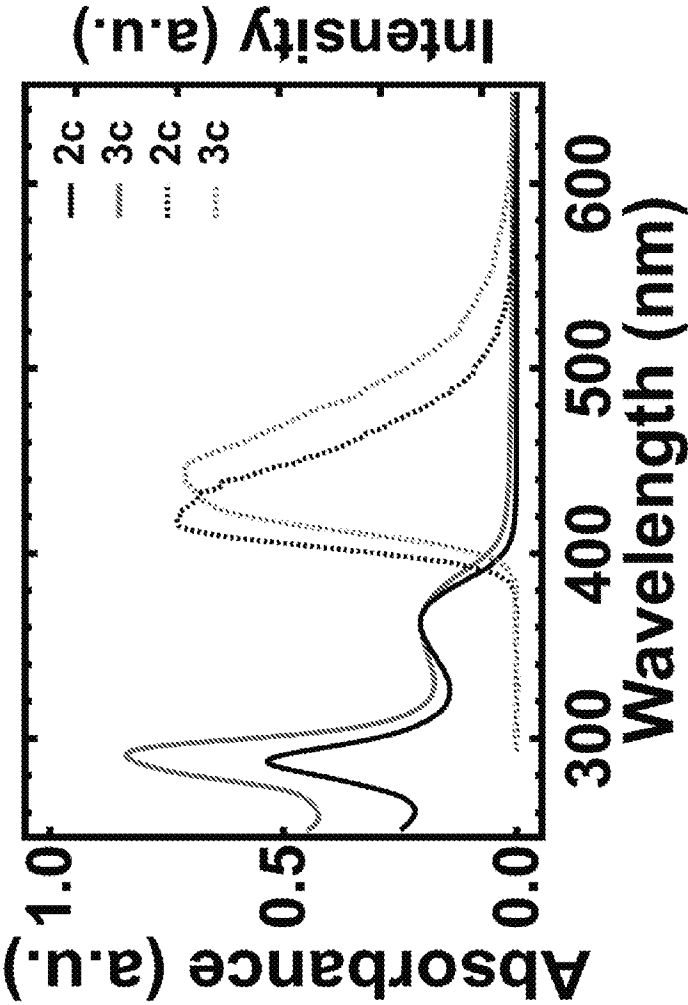
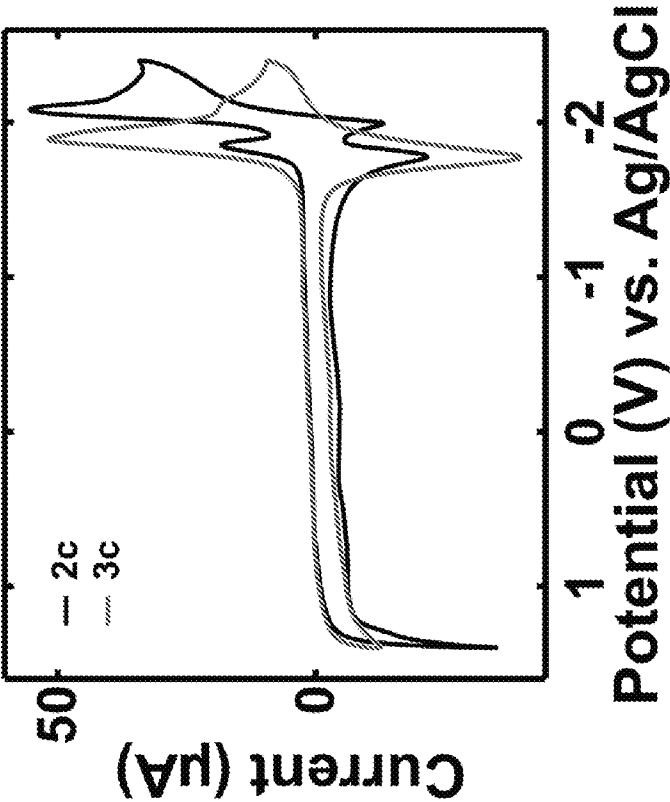


FIG. 29

FIG. 30



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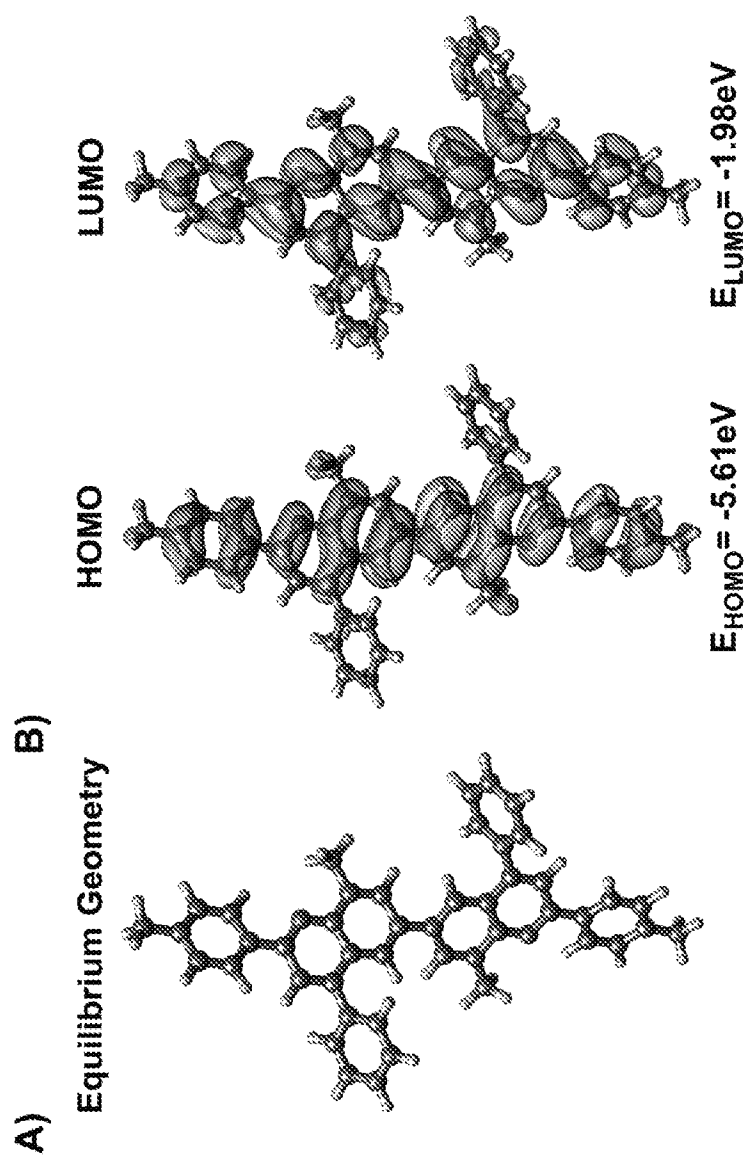
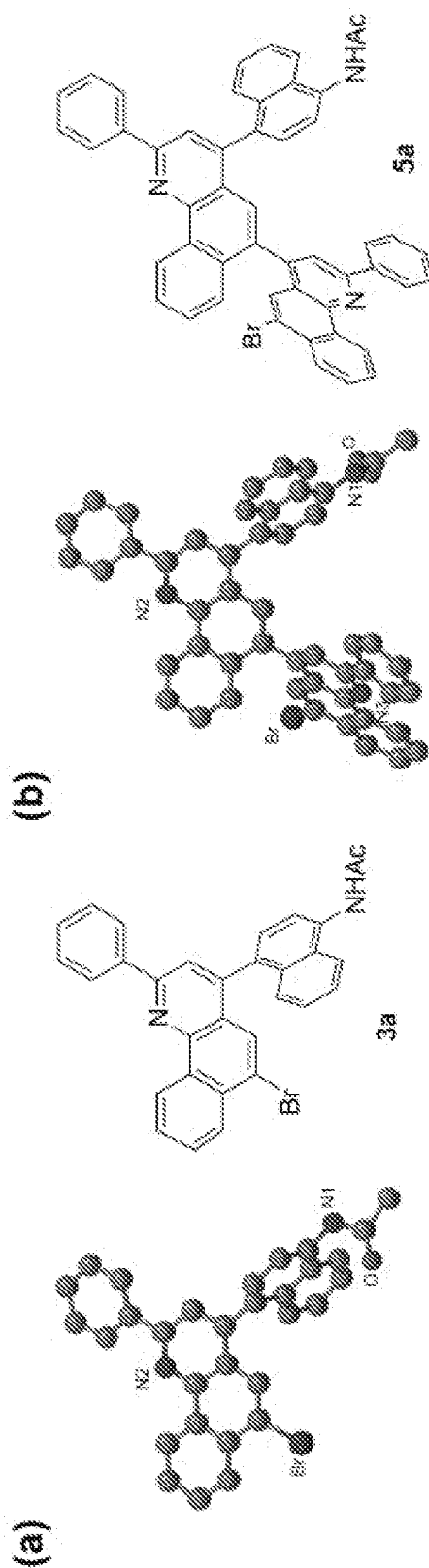


FIG. 31

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FIG. 32



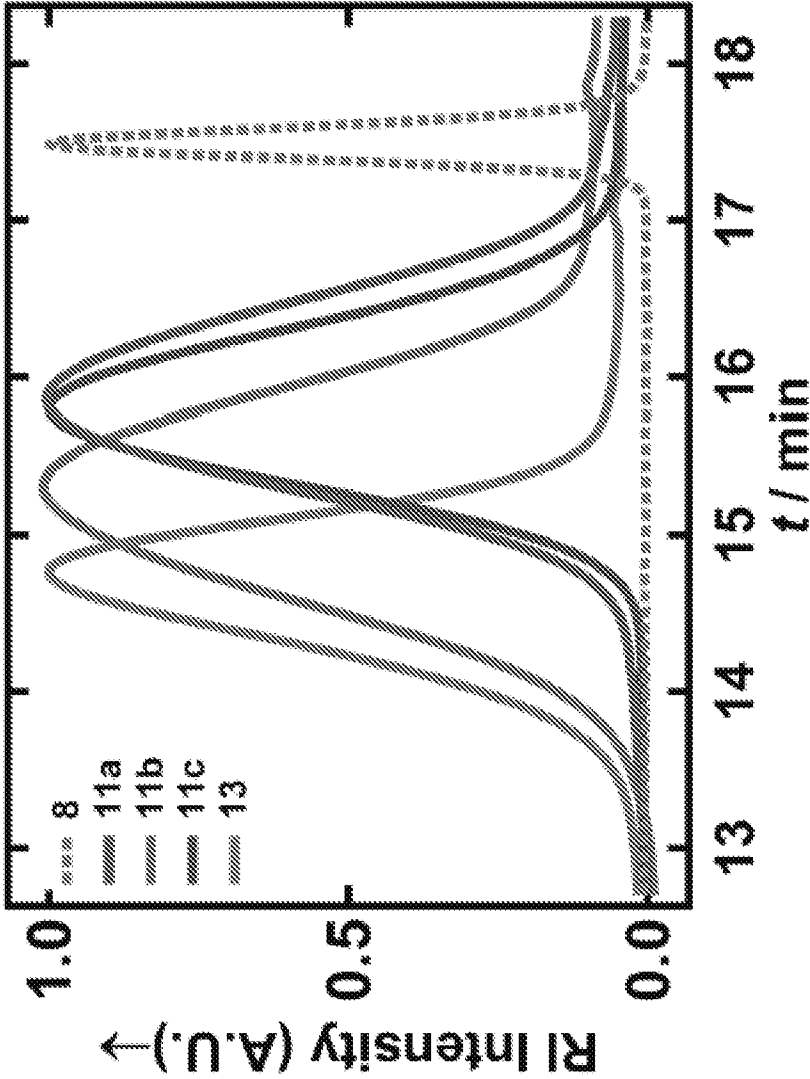


FIG. 33

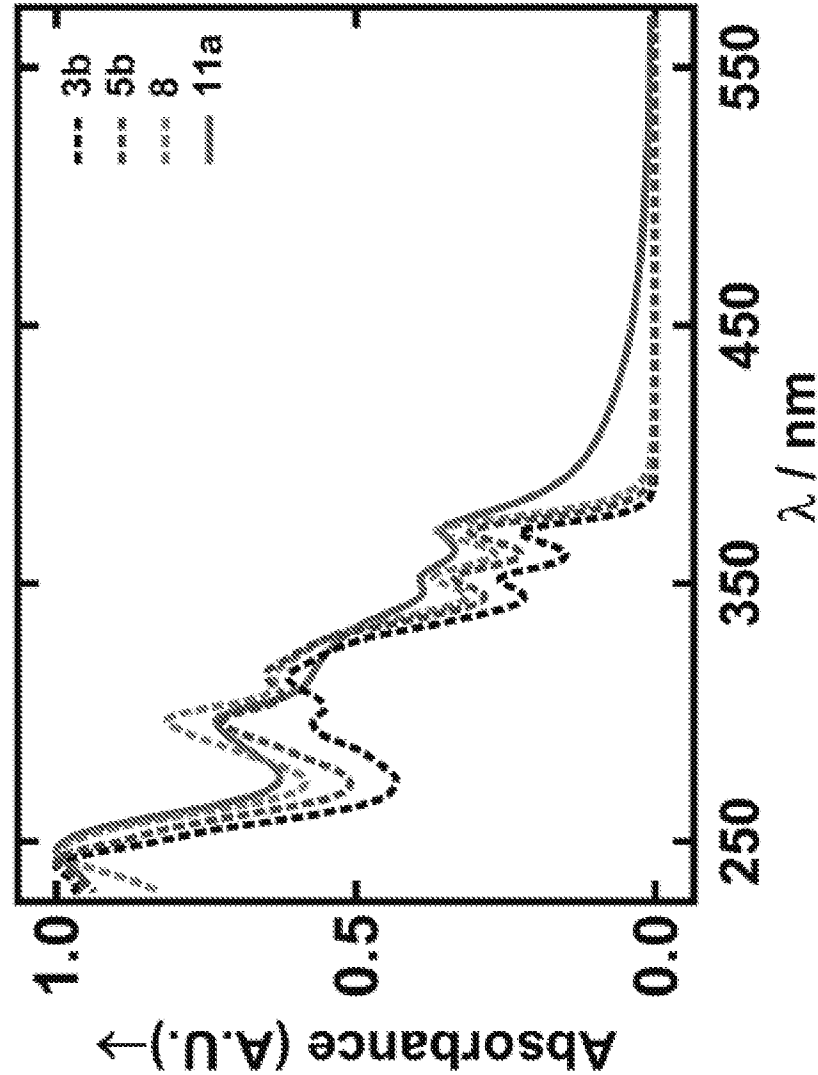


FIG. 34

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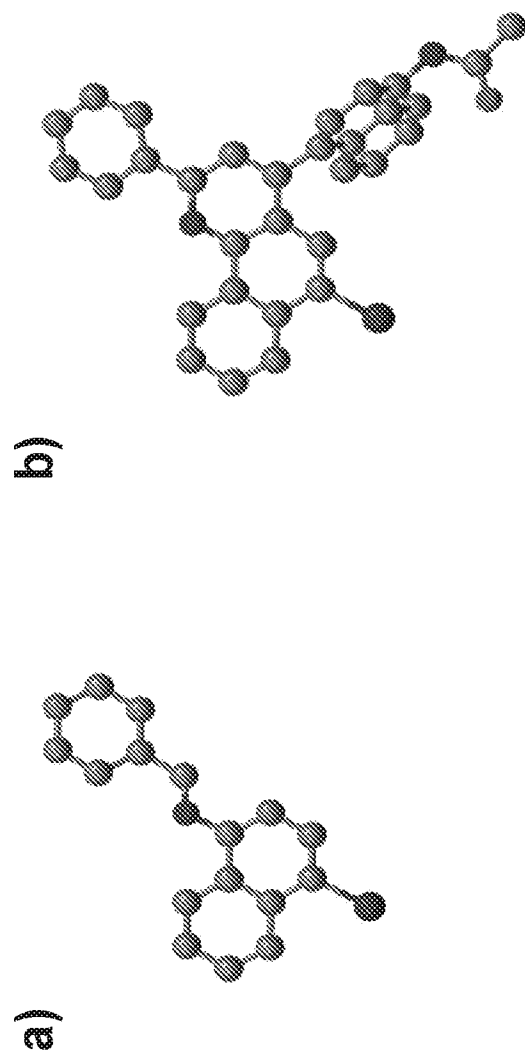


FIG. 35

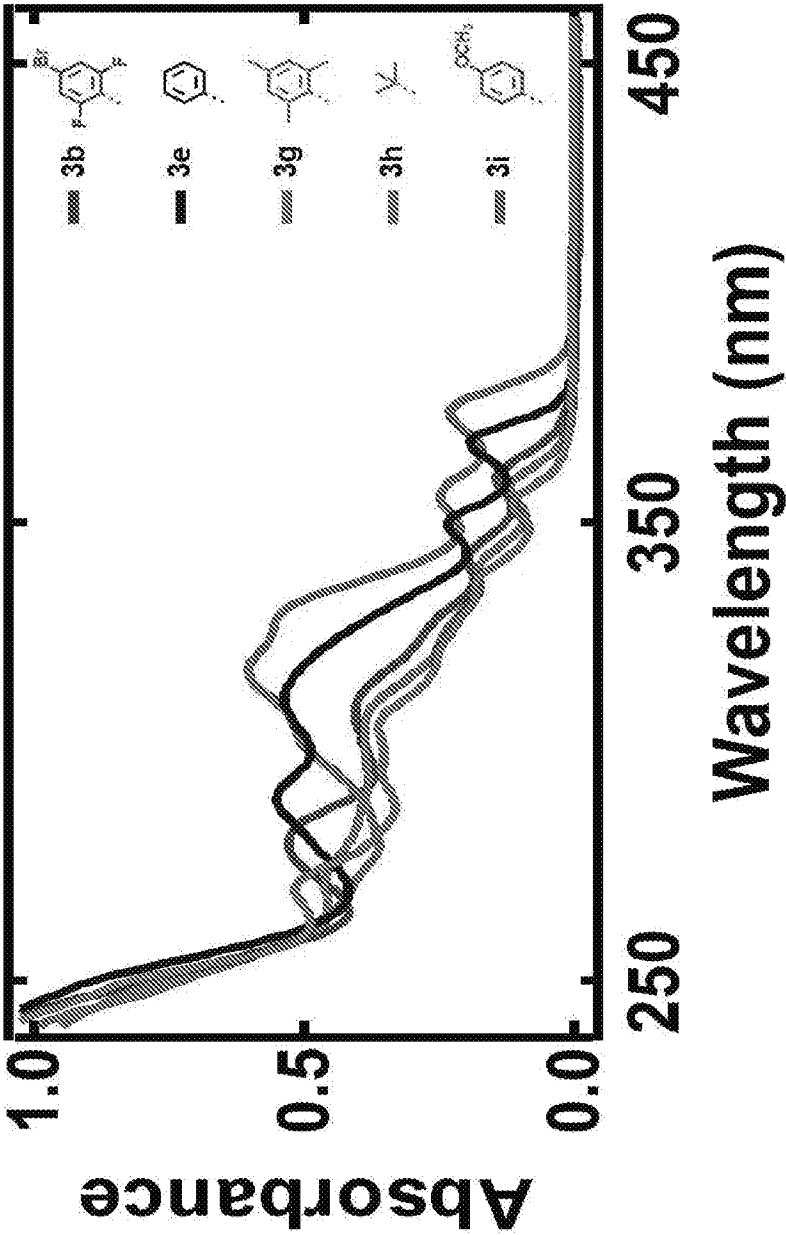
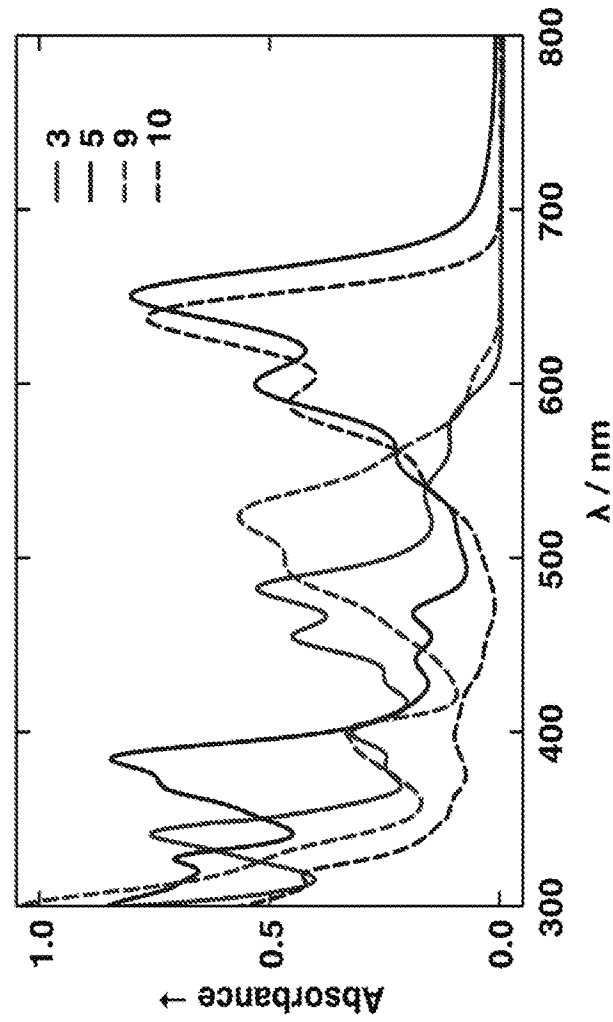


FIG. 36

FIG. 37



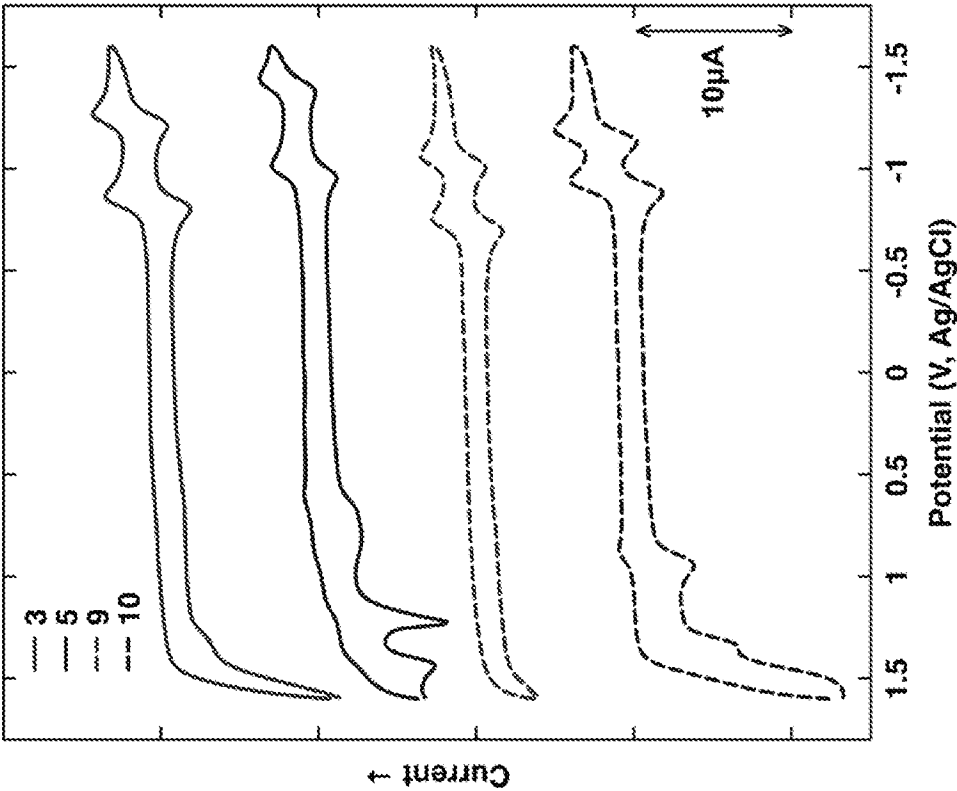


FIG. 38

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FIG. 39

