



(51) International Patent Classification:

G01J 1/42 (2006.01)

B05D 3/06 (2006.01)

F21L 4/02 (2006.01)

(21) International Application Number:

PCT/US2023/067306

(22) International Filing Date:

22 May 2023 (22.05.2023)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

63/365,112

20 May 2022 (20.05.2022)

US

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(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ,
CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM,
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG,
KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY,
MA, MD, MG, MK, MN, MU, MW, MX, MY, MZ, NA,
NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO,
RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH,
TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS,
ZA, ZM, ZW.

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

(54) Title: SYSTEMS AND METHODS FOR ULTRAVIOLET LIGHT EMISSION

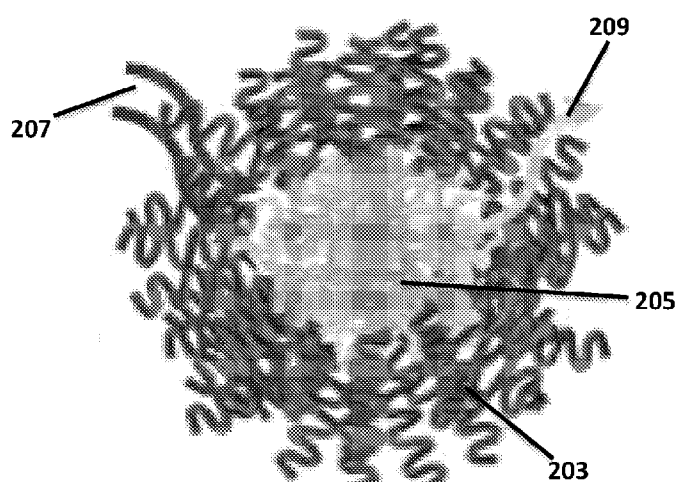


Fig. 2 201

(57) Abstract: Systems and methods for ultraviolet light emission are provided. Generally, amphiphilic vesicles contain an organic core. The organic core can incorporate organic compounds for performing triplet-triplet annihilation upconversion for emitting ultraviolet light. Accordingly, input light is impinged upon the amphiphilic vesicle, resulting in upconversion of the input light photons into UV light photons.



Published:

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

SYSTEMS AND METHODS FOR ULTRAVIOLET LIGHT EMISSION

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Application Ser. No. 63/365,112, entitled Systems and Methods for Ultraviolet Light Emission, filed May 20, 2022, which is incorporated herein by reference in its entirety.

TECHNICAL FIELD

[0002] The disclosure is generally directed to systems and methods for localized ultraviolet light emission and more specifically to systems of UV-emitting vesicles and methods of synthesis and use.

BACKGROUND

[0003] Ultraviolet (UV) light is high-energy electromagnetic radiation having a wavelength between approximately 10 nm and 400 nm. Short-wave UV light can provide ionizing radiation capable of providing sufficient energy to ionize atoms or molecules by detaching electrons. Long-wave UV light is not considered ionizing radiation but does provide sufficient energy to catalyze a number of chemical and biological reactions. Accordingly, UV radiation is utilized in to provide energy for numerous biological, chemical, and industrial applications.

[0004] Photon upconversion is a process in which the sequential absorption of two or more photons leads to the emission of light at a shorter wavelength. Various organic and inorganic materials can perform upconversion through various mechanisms. Organic molecules can achieve photon upconversion through triplet-triplet annihilation, which is an energy transfer mechanism between two molecules in their triplet state (Fig. 1). To achieve photon upconversion through triplet-triplet annihilation, two types of molecules are often combined: a sensitizer and an emitter (annihilator). The sensitizer absorbs the low energy photon and populates its first excited triplet state (T₁) through intersystem crossing. The sensitizer then transfers the excitation energy to the emitter, resulting in a triplet excited emitter and a ground state sensitizer. Two triplet excited emitters then can

undergo triplet-triplet annihilation, and if a singlet excited state (S1) of the emitter is populated fluorescence results in an upconverted photon.

SUMMARY

[0005] Several embodiments are directed to a system for providing localized UV emission. The system can include an amphiphilic vesicle having an organic core encapsulated by an outer hydrophilic region. The organic core can include a sensitizer and an annihilator for performing triplet-triplet annihilation upconversion to emit UV light. The system can be solubilized in an aqueous solution, an aqueous gel, an aqueous sol, or an aqueous emulsion.

[0006] Many embodiments are directed to methods of localized light emission. A system for localized UV emission can be provided. The system includes a sensitizer and an annihilator for performing triplet-triplet annihilation upconversion to emit UV light. Input light can be impinged on the system, photons of the input light are upconverted, resulting in UV emission. The input light can traverse through a medium or a material that is incapable of being traversed by light having the same wavelength of the emitted UV light.

[0007] In some implementations, a system is for localized UV emission. The system comprises an amphiphilic vesicle having an inner organic core encapsulated by an outer hydrophilic region. The system comprises a sensitizer. The system comprises an annihilator.

[0008] In some implementations, the sensitizer and annihilator are within the inner organic core of the amphiphilic vesicle.

[0009] In some implementations, annihilator is capable of releasing photons of UV light when the sensitizer is stimulated with input light

[0010] In some implementations, the system further comprises : an aqueous solution, an aqueous gel, an aqueous sol, or an aqueous emulsion. The amphiphilic vesicle is solubilized within the solution, the aqueous gel, the aqueous sol, or the aqueous emulsion.

[0011] In some implementations, the sensitizer is stimulated by light having a wavelength between 400 nm and 1000 nm.

[0012] In some implementations, the sensitizer is stimulated by infrared light.

[0013] In some implementations, a method provides localized UV light. The method comprises providing a UV emitting system comprising. The UV emitting system comprises an amphiphilic vesicle having an inner organic core encapsulated by an outer hydrophilic region, a sensitizer, and an annihilator. The sensitizer and annihilator are within the inner organic core of the amphiphilic vesicle. The amphiphilic vesicle is solubilized within an aqueous solution, an aqueous gel, an aqueous sol, or an aqueous emulsion. The method comprises impinging an input light on the UV emitting system such that photons of the input light come into contact with the inner organic core resulting in emission of UV light.

[0014] In some implementations, the method further comprises, prior to impinging the input light on the UV emitting system, traversing the input light through a medium that cannot be traversed by UV light having a wavelength equivalent the wavelength emitted by the annihilator.

[0015] In some implementations, the method further comprises,

[0016] In some implementations, prior to impinging the input light on the UV emitting system, penetrating the input light to a depth within a medium or material that cannot be reached by UV light having a wavelength equivalent to the wavelength emitted by the annihilator.

[0017] In some implementations, the input light has a wavelength of between 400 nm and 1000 nm.

[0018] In some implementations, the input light is infrared light.

[0019] In some implementations, the amphiphilic vesicle is a micelle that comprises an amphiphilic polymer.

[0020] In some implementations, the amphiphilic polymer comprises one of: polyethylene glycol (PEG), polyvinyl pyrrolidone (PVP), poly *N*-isopropyl acrylamide (pNIPAM), polylactic acid (PLA), or a polyamide.

[0021] In some implementations, the amphiphilic polymer comprises *block*-poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol).

[0022] In some implementations, the amphiphilic polymer comprises F127 polymer.

[0023] In some implementations, the sensitizer is one of: bis(2-phenylpyridine)(acetylacetonate)iridium(III), Ir(ppy)₂(acac) (ppy₂); bis(2-(3,5-dimethylphenyl)-4-propylpyridine)(2,2,6,6-tetramethylheptane-3,5-diketone)iridium(III),

Ir(dmppy-pro)₂tmd (tmd); tris(2-phenylpyridine)iridium(III), Ir(ppy)₃ (ppy₃); 1,2,3,5-Tetrakis(carbazol-9-yl)-4,6-dicyanobenzene, 2,4,5,6-tetra(carbazol-9-yl)benzene-1,3-dicarbonitrile (4CzIPN); or 3,3'-carbonylbis(7-diethylaminocoumarin) (CBDAC).

[0024] In some implementations, the sensitizer is one of: bis(2-phenylpyridine)(acetylacetonate)iridium(III), Ir(ppy)₂(acac) (ppy₂) or bis(2-(3,5-dimethylphenyl)-4-propylpyridine)(2,2,6,6-tetramethylheptane-3,5-diketonate)iridium(III), Ir(dmppy-pro)₂tmd (tmd).

[0025] In some implementations, the annihilator is one of: pyrene; 2,7-di-tert-butylpyrene (DBP); 2,5-Diphenyloxazole (PPO); 1,4-bis((triisopropylsilyl)ethynyl)naphthalene (TIPS-Nph); or ([1,1'-Biphenyl]-4-ylethynyl)triisopropylsilane (p-TIPS-BP).

[0026] In some implementations, the sensitizer is tris(2-phenylpyridine)iridium(III), Ir(ppy)₃ (ppy₃) and the annihilator is one of: pyrene; 2,7-di-tert-butylpyrene (DBP); 2,5-Diphenyloxazole (PPO); or 1,4-bis((triisopropylsilyl)ethynyl)naphthalene (TIPS-Nph).

[0027] In some implementations, the sensitizer is bis(2-phenylpyridine)(acetylacetonate)iridium(III), Ir(ppy)₂(acac) (ppy₂) and the annihilator is one of: pyrene; 2,7-di-tert-butylpyrene (DBP); 2,5-Diphenyloxazole (PPO); 1,4- or bis((triisopropylsilyl)ethynyl)naphthalene (TIPS-Nph).

[0028] In some implementations, the sensitizer is bis(2-(3,5-dimethylphenyl)-4-propylpyridine)(2,2,6,6-tetramethylheptane-3,5-diketonate)iridium(III), Ir(dmppy-pro)₂tmd (tmd) and the annihilator is one of: pyrene; 2,7-di-tert-butylpyrene (DBP); 2,5-Diphenyloxazole (PPO); or 1,4-bis((triisopropylsilyl)ethynyl)naphthalene (TIPS-Nph).

[0029] In some implementations, the sensitizer is 1,2,3,5-Tetrakis(carbazol-9-yl)-4,6-dicyanobenzene, 2,4,5,6-tetra(carbazol-9-yl)benzene-1,3-dicarbonitrile (4CzIPN) and the annihilator is one of: pyrene; 2,7-di-tert-butylpyrene (DBP); 2,5-Diphenyloxazole (PPO); 1,4-bis((triisopropylsilyl)ethynyl)naphthalene (TIPS-Nph); or ([1,1'-Biphenyl]-4-ylethynyl)triisopropylsilane (p-TIPS-BP).

[0030] In some implementations, the sensitizer is 3,3'-carbonylbis(7-diethylaminocoumarin) (CBDAC) and the annihilator is one of: pyrene, 2,7-di-tert-butylpyrene (DBP); or 1,4-bis((triisopropylsilyl)ethynyl)naphthalene (TIPS-Nph).

BRIEF DESCRIPTION OF THE DRAWINGS

[0031] The description and claims 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.

[0032] Figure 1 provides a schematic of triplet-triplet annihilation photon upconversion.

[0033] Figure 2 provides a schematic of a system for localized UV emission.

[0034] Figure 3 provides molecular structures of sensitizers and annihilators and various combinations of use. Fig. 3 further provides data on mix-and-match sensitizer/annihilator pairings for blue-to-UV upconversion micelles. UCPL of various annihilator (each column) and sensitizer (each row) pairings under 447 nm laser excitation. The UCPL was collected through a 425 nm short pass filter. UC intensities were normalized to each spectrum emission counts at 425 nm (set to be 0.5). The concentrations used for data presented in this figure are summarized in Fig. 17.

[0035] Figure 4 provides a schematic depicting the ability to provide localized UV emission in a location that cannot be reached by traditional UV emission sources.

[0036] Figure 5 provides a schematic for generating systems for localized UV emission.

[0037] Figures 6A and 6B provide a mechanism of triplet-triplet annihilation upconversion (TTA-UC) and newly identified iridium-based sensitizers for blue-to-UV upconversion. 6A: The process of triplet-triplet annihilation upconversion (TTA-UC): Sensitizers (Sen) absorb lower energy photons and generate triplets *via* intersystem crossing (ISC). Annihilators (Ann) are promoted to their triplet states through triplet energy transfer (TET) from Sen. Two Ann triplets can annihilate to an excited singlet. The Ann singlet emits a higher energy photon, returning to the ground state. 6B: Normalized absorption (Abs) and photoluminescence (PL) spectra of three iridium complexes (ppy3, ppy2, and tmd) and 2,7-di-tert-butylpyrene (DBP). The iridium complexes were excited at 365 nm, and DBP was excited at 335 nm.

[0038] Figure 7 provides a data table of solubility of three iridium complexes in organic solvents at room temperature determined by UV-vis absorption spectroscopy.

[0039] Figure 8 provides a theoretical prediction of the number of molecules per micelle based on concentrations in solutions added for micelle fabrication using a Poisson distribution. In this model, the total number of available molecules are distributed among nanodroplets of TCB according to a Poisson probability distribution. An upper boundary of the number of nanodroplets available is determined by the TCB solution volume (20 μ L) used to make micelles (for simplicity, we assume all the chloroform initially added evaporates). In this simulation, we estimate a nanodroplet diameter of 25 nm based on DLS. This is an upper boundary condition, as it is difficult to estimate the true volume of the nanodroplet in the F-127 micelle core.

[0040] Figures 9A to 9C provide data of screening iridium-based sensitizers reveals versatile TTA-UC pairings with the annihilator DBP in toluene. 9A: Normalized upconversion photoluminescence (UCPL) of sensitizer/annihilator pairs ppy3/DBP, ppy2/DBP, and tmd/DBP in toluene under 447 nm laser excitation with different power densities. UCPL was collected through a 425 nm short pass filter. 9B: UC quantum yields (Φ_{UC}) of ppy3/DBP, ppy2/DBP, and tmd/DBP UC systems in toluene. 9C: UC intensity dependence on incident power for ppy3/DBP, ppy2/DBP, and tmd/DBP UC systems in toluene. We performed measurements in A, B, and C with optimized sensitizer and annihilator concentrations based on upconverted light output, which are summarized in Fig. 10.

[0041] Figure 10 provides a data table of optimized concentrations of [Sensitizer]/[Annihilator] in bulk solution (toluene) and for TCB/chloroform solutions used to prepare micelles.

[0042] Figure 11 provides data results of Stern-Volmer quenching tests on the sensitizers. All three sensitizers were kept at the same concentration (100 μ M). DBP was used as the annihilator at varying concentration.

[0043] Figures 12A and 12B provide data of nanoencapsulation of iridium complexes with DBP to form UV-emitting UC micelles. 12A: Upconversion (UC) and phosphorescence (Ph) of sensitizers in both micelles and solutions (1,2,4-trichlorobenzene (TCB)) under 447 nm excitation. Constant concentrations of UC materials were used to compare TTA-UC in TCB solutions as compared to micelles (i.e., the same total quantity of UC materials was used and diluted to a constant volume). A

425 nm short pass filter was used when collecting UC emission, and a 475 nm long pass filter was used when collecting sensitizer phosphorescence. The gray dashed line separates UC and phosphorescence. The counts of UC and phosphorescence were scaled to the highest count of ppy3/DBP micelle UC (set to 1.0). 12B: A comparison of UC and phosphorescence intensities of the three UV-emitting micelles. The concentrations used for data presented in 12A and 12B are summarized in Fig. 10.

[0044] Figure 13 provides a data table of representative dynamic light scattering (DLS) data for micelles with different encapsulated species.

[0045] Figure 14 provides a data table of upconversion-to-phosphorescence ratios of [Sensitizer]/[Annihilator] in TCB and micelles.

[0046] Figure 15 provides data of UV-emitting upconversion micelles exhibit energetic losses to phosphorescence. UC and phosphorescence intensities of three UV-emitting micelles plotted on the same y-axis scale. UC and Ph are separated by the gray dashed line. The counts of UC and Ph are scaled to the highest count of ppy3/DBP micelle UC.

[0047] Figure 16 provides data of upconversion intensity dependence on incident power for ppy3/DBP, ppy2/DBP, and tmd/DBP upconversion micelles. The optimized sensitizer and annihilator concentrations are summarized in Fig. 10.

[0048] Figure 17 provides a data table of concentrations of [Sensitizer]/[Annihilator] in TCB/chloroform solutions used to fabricate UV-emitting UC micelles in Fig. 3.

[0049] Figures 18A to 18F provide data showing blue incident light performs UV photochemistry with ppy2/PPO micelles as demonstrated by photolysis of caged fluorescein. 18A: Ortho-nitrobenzyl caged fluorescein is non-fluorescent until UV-triggered photolysis, which produces the uncaged product fluorescein. 18B: Schematic demonstrating that caged fluorescein undergoes photolysis upon exposure to a 365 nm LED and displays visible color changes (top), whereas caged fluorescein does not photolyze upon exposure to 470 nm LED (middle). Incorporating ppy2/PPO upconversion micelles into a caged fluorescein solution causes fluorescein photolysis upon exposure to a 470 nm LED and subsequent blue-to-UV upconversion (bottom). 18C: 365 nm UV light (19.7 mW) photolyzed caged fluorescein in solution (top). 470 nm blue light (50.4 mW) did not photolyze caged fluorescence over a 30-minute interval (middle), but 470 nm blue light successfully photolyzed caged fluorescein when ppy2/PPO upconversion

micelles were incorporated in solution (bottom). All cuvettes contained 2.5 mL of 0.2 mM caged fluorescein in 1× phosphate-buffered saline (PBS). 18D, 18E, and 18F: UV-vis absorption spectra corresponding to the top, middle, and bottom rows of cuvettes shown in 4C, respectively. The black lines in 18E and 18F are micelle-only controls that do not contain fluorescein. A characteristic fluorescein absorbance peak near 490 nm is evident after photolysis of caged fluorescein with UV light (18D) or blue-to-UV upconversion (18F).

[0050] Figure 19 provides data of optimizing upconverted PPO emission in micelles. Upconversion photoluminescence (UCPL) measurements with 447 nm laser incident light demonstrate that the maximum upconversion intensity (<425 nm) is achieved with micelles made with 200 mM PPO in chloroform. No distinguishable improvement was observed upon increasing the concentration to 250 mM, so ppy2/PPO upconversion micelles were fabricated with saturated ppy2 in TCB and 200 mM PPO in chloroform. A 425 nm short pass filter was placed in front of an Ocean Optics QE Pro detector, resulting in low intensities between 425 nm and 650 nm and influencing the spectral shape of the sensitizer luminescence above 650 nm. Each micelle UCPL spectrum was scaled by the maximum of the 50 mM spectrum to preserve relative intensity.

[0051] Figure 20 provides a data table of estimation of Φ_{UC} of the optimized micelles using a relative method.

[0052] Figure 21 provides data of fluorescence changes of caged fluorescein solutions indicate successful photolysis with incident UV light or blue light with ppy2/PPO micelles. Fluorescence data of samples presented in Fig. 18C. Top: 365 nm UV light (19.7 mW) photolyzed caged fluorescein in solution, as demonstrated by a drastic increase in fluorescence. Middle: 470 nm blue light (50.4 mW) did not photolyze caged fluorescence over a 30-minute interval. Bottom: 470 nm blue light (50.4 mW) photolyzed caged fluorescein when ppy2/PPO upconversion micelles were incorporated in solution. All curves on each graph are scaled by the maximum fluorescence intensity for the 0-minute cuvette to preserve relative fluorescence intensity. Emission spectra for the top panel were taken with 470 nm excitation to prevent detector saturation, whereas the middle panel and the bottom panel used 494 nm excitation.

[0053] Figures 22A to 22E provide data of upconversion micelles enhance the penetration depth and spatial confinement of UV radiation to perform localized UV photochemistry. 22A: Schematic of the experimental setup for B: light beam penetration through cuvettes. 22B: UV light (365 nm) attenuates more substantially across a 1 cm cuvette than blue light (470 nm). Both samples contain 0.2 mM caged fluorescein in 1× PBS, and the sample irradiated by blue light also contained ppy2/PPO upconversion micelles. The UV beam is visualized by fluorescence, whereas the blue beam is visualized by fluorescence, sensitizer luminescence, and annihilator upconversion emissions. Both LED sources were operated at 32 mW. 22C: Schematic of the experimental setup for C: light focused with a 50× 0.55 numerical aperture (NA) objective. 22D: Photographic images of focused UV light photolysis of caged fluorescein throughout the light path, whereas blue-to-UV upconversion confines photolysis to a voxel deep within the solution. The UV beam is visualized by fluorescence, and the blue beam is visualized by fluorescence and sensitizer luminescence. To demonstrate photolysis, a fluorescein solution (top) and fluorescein and ppy2/PPO micelles solution (bottom) were irradiated with the same power (2.2 mW) of 365 nm UV LED and 470 nm blue LED, respectively. All cuvettes contained 1.5 mL of 0.67 mM caged fluorescein. The light was focused by a 50× 0.55 NA objective. The scientific camera was equipped with a 500 nm long pass filter. 22E: False-colored maps of fluorescein luminescence intensities after background subtraction (the intensity at $t = 0$ s was treated as background) illustrate that photolysis deep within a solution is enabled by an encapsulated blue-to-UV UC system.

[0054] Figure 23 provides data showing UV and blue light excite uncaged fluorescein. Excitation spectrum of the sample irradiated by 365 nm light for 30 s (Fig. 18C, top row) shows that blue and UV light excite uncaged fluorescein. Emission intensity at 512 nm was monitored, and the displayed spectrum was scaled by the maximum measured emission intensity.

[0055] Figure 24 provides data of normalized intensity of the incident beams across the quartz cuvettes in Fig. 22B. ImageJ was used to split images into blue, green, and red color channels. Then, gray values of the green channel were extracted to quantify the attenuation of incident beams across the quartz cuvettes.

[0056] Figure 25 provides a schematic of four measurements taken for each sample to calculate the UC quantum yield.

DETAILED DESCRIPTION

[0057] Turning now to the drawings and data, systems of localized UV emission in accordance with various embodiments are described. In several embodiments, localized UV emission is achieved via triplet-triplet annihilation photon upconversion (TTA-UC). In many embodiments, to emit localized light, vesicles comprising TTA-UC sensitizers and annihilators are utilized. In several embodiments, a sensitizer-annihilator combination is capable of converting longer wavelength light (e.g., visible light) into UV light. Several embodiments are also directed to methods of using and/or synthesizing systems of localized UV emission.

[0058] Many of the various embodiments of the disclosure are capable of providing UV light emission in locations in which UV light is normally incapable of reaching. UV light is incapable of penetrating through most materials and thus the utility of UV light energy has historically been limited to superficial applications. One mechanism to obtain deeper UV emission is to utilize photon upconversion, especially TTA-UC. To emit UV energy beyond the surface, TTA-UC sensitizers and annihilators can be strategically positioned in a location in which longer wavelength light (e.g., visible light), but not UV light, is capable of reaching. The longer wavelength light can be upconverted to higher energy UV light via TTA-UC, providing UV light emission.

[0059] While TTA-UC provides a means for UV light emission in locations that UV light cannot normally reach, most TTA-UC sensitizers and annihilators are organic molecules with low solubility in water. For chemical, biochemical and industrial applications that occur in aqueous environments, organic sensitizers and annihilators are unusable due to their lack of solubility and an inability to achieve high concentrations therein. Accordingly, there is a need for a non-superficial UV-emitting system that is water soluble.

[0060] Several embodiments of the disclosure are directed to a UV light emitting vesicle that comprises organic sensitizers and annihilators encapsulated within the interior portion of the vesicle. By formulating soluble vesicles with sensitizers and annihilators, the vesicles can be utilized in non-superficial aqueous environments and

require less input light, allowing for robust UV emission in locations that are difficult to provide UV energy but are reachable via longer wavelength light. Furthermore, and in accordance with many embodiments, the vesicles unexpectedly allow for mixing and matching of combinations of sensitizers and annihilators for emitting UV light due to their good solubility in the vesicle's organic solvent-filled core.

Systems of localized UV emission

[0061] Many embodiments are directed to systems of localized UV light emission. In several embodiments, a system of localized UV light emission comprises an amphiphilic vesicle having an outer hydrophilic region and inner organic core, the outer hydrophilic portion encapsulating the inner organic core. In many embodiments, a system of localized UV light emission comprises organic compounds of photon upconversion. In many of these embodiments, the organic compounds of photon upconversion comprise a sensitizer and an annihilator for providing TTA-UC.

[0062] An example of a schematic of a system of localized UV emission is provided in Fig. 2. The exemplary system 201 includes an outer hydrophilic region 203 and an inner hydrophobic organic region 205. Inner organic region 205 includes organic compounds for photon upconversion, such as sensitizers and annihilators for providing TTA-UC. To emit UV light, two longer wavelength photons 207 contact organic region 205 resulting in upconversion longer wavelength photons 207 into a UV photon 209 that is emitted. Upconversion can be performed by utilizing the TTA-UC mechanism, as shown in Fig. 1.

[0063] Several embodiments of systems of localized UV light emission comprise an amphiphilic vesicle, such as (for example) micelles and liposomes. Any molecules capable of forming amphiphilic vesicles can be utilized. Examples of molecules used to form amphiphilic vesicles include (but are not limited to) detergents, phospholipids, and polymers. Examples of polymers used for forming micelles include (but are not limited to) polyethylene glycol (PEG), polyvinyl pyrrolidone (PVP), poly *N*-isopropyl acrylamide (pNIPAM), polylactic acid (PLA), and polyamides (e.g., poly L-lysine). In some embodiments, an amphiphilic block copolymer is utilized. An example of an amphiphilic block copolymer is *block*-poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol). Any appropriate block lengths can be utilized such that a micelle

having an inner organic core and a hydrophilic outer region is formed. In some embodiments, the F127 polymer is utilized, comprising the formula *block*-poly(ethylene glycol)₁₀₁-*block*-poly(propylene glycol)₅₆-*block*-poly(ethylene glycol)₁₀₁. Further, the overall size of a system of localized UV light emission can be any size, but generally in the nanometer to micrometer range. In various embodiments, the diameter of a system of localized UV light emission is less than 1000 nm, is less than 500 nm, is less than 200 nm, is less than 100 nm, or is less than 50 nm.

[0064] Many embodiments of systems of localized UV light emission comprise organic compounds within the organic core. In several embodiments, the organic core provides a means to perform photon upconversion. In many embodiments, the organic core comprises one or more sensitizers and one or more annihilators; the sensitizer and annihilator are paired to perform photon upconversion via TTA-UC. Accordingly, the sensitizer is capable of receiving longer wave light photons then transferring the energy of the photons to the annihilator such that it emits UV light photons (see Fig. 1).

[0065] Several sensitizers and annihilators have been found to provide capability of receiving longer wave light photons and upconverting into UV light photons.

[0066] In many embodiments, sensitizers that can be utilized within the organic core include (but are not limited to) bis(2-phenylpyridine)(acetylacetonate)iridium(III), Ir(ppy)₂(acac) (ppy₂); bis(2-(3,5-dimethylphenyl)-4-propylpyridine)(2,2,6,6-tetramethylheptane-3,5-diketonate)iridium(III), Ir(dmppy-pro)₂tmd (tmd); tris(2-phenylpyridine)iridium(III), Ir(ppy)₃ (ppy₃); 1,2,3,5-Tetrakis(carbazol-9-yl)-4,6-dicyanobenzene, 2,4,5,6-tetra(carbazol-9-yl)benzene-1,3-dicarbonitrile (4CzIPN); and 3,3'-carbonylbis(7-diethylaminocoumarin) (CBDAC).

[0067] In many embodiments, annihilators that can be utilized within the organic core include (but are not limited to) pyrene, 2,7-di-tert-butylpyrene (DBP); 2,5-Diphenyloxazole (PPO); 1,4-bis((triisopropylsilyl)ethynyl)naphthalene (TIPS-Nph), and ([1,1'-Biphenyl]-4-ylethynyl)triisopropylsilane (p-TIPS-BP).

[0068] Any combination of sensitizer and annihilator capable of receiving longer wave light photons and upconverting into UV light photons can be utilized (see Figs. 3). In

certain embodiments, the following combinations of sensitizer and annihilator, which provide good upconversion results, are utilized within the organic core:

- ppy3 + pyrene
- ppy3 + DBP
- ppy3 + TIPS-Nph
- ppy3 + PPO
- ppy2 + pyrene
- ppy2 + DBP
- ppy2 + TIPS-Nph
- ppy2 + PPO
- tmd + pyrene
- tmd + DBP
- tmd + TIPS-Nph
- tmd + PPO
- CBDAC + pyrene
- CBDAC + DBP
- CBDAC + TIPS-Nph
- 4CzIPN + pyrene
- 4CzIPN + DBP
- 4CzIPN + TIPS-Nph
- 4CzIPN + PPO
- 4CzIPN + p-TIPS-BP

[0069] Many embodiments are directed to an aqueous solution, an aqueous gel, an aqueous sol, or an aqueous emulsion having one or more systems of localized UV light emission solubilized therein. Each system of localized UV light emission can comprise an amphiphilic vesicle having an outer hydrophilic region and inner organic core, the outer hydrophilic portion encapsulating the inner organic core and providing the solubility within the aqueous solution. An aqueous solution, gel, sol, or emulsion can comprise a collection of systems of localized UV light emission in which the collection of systems is dispersed

throughout. In some embodiments, each system of the collection contains the same sensitizer and annihilator combination such that the solution is capable of producing a particular wavelength of UV light. In some embodiments, at least two systems of the collection each contain a unique sensitizer and annihilator combination such that the solution is capable of producing at least two wavelengths of light, or alternatively the solution is capable of producing a particular wavelength of UV light from at least two wavelengths of input light.

Methods of producing localized UV emission

[0070] Several embodiments are directed to producing localized UV emission via a system comprising an amphiphilic vesicle, a sensitizer, and an annihilator. In many of these embodiments, a collection of systems is utilized to produce localized UV emission, in which the collection is provided in an aqueous solution, gel, sol, or emulsion.

[0071] To produce localized UV emission, input light is transmitted to and impinged upon a system where at least two photons of the input light are received by a sensitizer. The sensitizer can transmit the energy of the two photon of the input light to an annihilator, resulting in upconversion and emission of a photon of UV light. In various embodiments, the input light has a wavelength longer than emitted UV light wavelength.

[0072] In some embodiments, the input light is visible light. In some embodiments, the input light is infrared light. In some embodiments, the input light has a wavelength of between 400 nm and 1000 nm. In some embodiments, the input light is laser light having a particular wavelength (or short range of wavelengths). In some embodiments, the input light is narrowband, or is broadband, or is multiband. In several embodiments, the selection of input light is determined by the compatibility of the sensitizer and/or the desired UV light emission.

[0073] A number of embodiments are directed to localized UV emission in locations that are generally unreachable by nonlocalized UV light source. Accordingly, in several embodiments, the input light traverses through a medium or material that cannot be traversed by UV light having a wavelength equivalent the wavelength emitted by the annihilator. In several embodiments, the input light penetrates to a depth within a medium or material that cannot be reached by UV light having a wavelength equivalent to the

wavelength emitted by the annihilator. In some these embodiments, UV emitting systems can be provided at a location that is reachable by the input light but not by UV light having a wavelength equivalent the wavelength produced by the emitter, and thus producing the UV light at the unreachable location via the input light and UV emitting systems.

[0074] An exemplary schematic showing UV emission at an unreachable location is provided in Fig. 4. In this example, UV emission is desired at a particular location 401 that is unreachable by UV light 403 due to the inability of UV light 403 to penetrate and/or traverse medium 405. To achieve UV emission in location 401, micelles 407 comprising an organic core with a sensitizer and annihilator are dispersed within location 401. Visible light 409 is provided to traverse through medium 405 to impinge upon and stimulate the organic core of micelles 407, resulting in UV emission 411 in location 401.

Methods of generating systems of localized UV emission

[0075] Several embodiments are directed to methods of generating systems of localized UV emission. As described in the preceding section, a system of localized UV emission can comprise an amphiphilic vesicle having an organic core and hydrophilic outer region. The organic core can comprise organic molecules for performing photon up conversion.

[0076] Any method to generate an amphiphilic vesicle having an organic core and hydrophilic outer region can be utilized, many of which are known and described in the art. Generally, amphiphilic molecules are utilized to form the amphiphilic vesicles and organic compounds are localized to the organic core using an organic solvent. The organic solvent can be removed yielding an amphiphilic vesicle with organic core.

[0077] Provided in Fig. 5 is a schematic of an example of a method to generate micelles for localized UV emission. In this example, the amphiphilic block copolymer F127 is utilized for formulate micelles by stirring the polymer in water. The generated micelles have an organic core formed of the poly(propylene glycol) block encapsulated by a hydrophilic region formed of the poly(ethylene glycol) blocks. A upconversion mixture comprising the sensitizer and annihilator are provided in the organic solvent mixture of chloroform and trichlorobenzene. The upconversion mixture is mixed with the micelles in their solution, resulting in the upconversion mixture centralizing in the organic core of the

micelles. Chloroform is evaporated to yield micelles for localized UV emission. Although a specific method is described, any method for generating micelles with an organic core can be utilized and the various reagents can be exchanged for similar reagents. For example, the trichlorobenzene can be substituted with toluene and the water can be substituted with a buffered solution (e.g., phosphate buffered solution). Likewise, any amphiphilic polymer or polymer combinations capable of forming micelles with an organic core can be utilized.

EXAMPLES

[0078] The embodiments of the disclosure will be better understood with the several examples provided within. Many exemplary results of systems and methods to provide localized UV are described. As can be readily discerned from various particular implementations of micelles comprising various sensitizer-annihilator combinations, the systems and methods as described herein are capable of outperforming traditional complexes for performing upconversion.

Spatially Controlled UV Light Generation at Depth Using Upconversion Micelles

[0079] The triplet-triplet annihilation upconversion (TTA-UC) process is illustrated in Fig. 6A. Sensitizers absorb low energy photons, generate triplets *via* spin-orbit coupling, and transfer the triplet states to annihilators through triplet energy transfer. Two annihilator triplet states can then undergo triplet-triplet annihilation to generate one high energy singlet excited state, which can radiatively decay and emit light at a higher energy than the incident photon energy. This process must obey energy conservation laws, where the upconverted emission energy is lower than twice the sensitizer triplet energy. Annihilators for TTA-UC are usually small organic molecules like acenes, whereas sensitizers span a range of materials such as metallic complexes, thermally activated delayed fluorescence (TADF) molecules, and inorganic nanoparticles.

[0080] The TTA-UC process is extremely sensitive to the local chemical environment, which has posed major challenges to deploy TTA-UC into aqueous solutions. First, highly polar solvents tend to facilitate electron transfer reactions, which compete with the desired triplet energy transfers between sensitizers and annihilators for TTA-UC. Additionally,

high local concentrations of materials are required for efficient TTA-UC, but organic TTA-UC molecules have low solubility in polar solvents. Instead, TTA-UC molecules are most soluble in nonpolar organic solvents. While sensitizer and annihilator solubility can be tuned by appending different functional groups (e.g., sulfate, carboxylate for water solubility), this approach requires substantial synthetic efforts for each sensitizer and annihilator pair that could result in undesirable changes to their energetic properties and ultimate UC performance.

[0081] Nanoencapsulation can overcome these challenges to expand the scope of chemical environments for TTA-UC. After encapsulation, the chemical compatibility of the resultant nanomaterials with a system dictate the ability to deliver upconverted light, thereby overcoming the limitations of individual molecules. For instance, micelles comprised of poly(propylene oxide) cores surrounded by poly(ethylene oxide) coronas can be utilized.

[0082] For UC emission in the UV, a range of sensitizer and annihilator pairs for both blue-to-UV UC and green-to-UV UC demonstrate the flexibility of materials options, excitation wavelengths, and emission ranges available to accommodate distinct requirements for different light-driven applications. Despite this apparent versatility, there are few reports for deploying UV-emitting UC systems to accomplish challenging photochemistry.

[0083] As described herein, the encapsulation of UV-emitting UC materials enhance the spatial control of UV light generation in aqueous solutions. Using the block copolymer Pluronic F-127 to form self-assembled micelles in water, it was found that the solubility of UC materials in the hydrophobic solvent used during micelle fabrication dictates the accessible upconverted light output. Enhanced UC performance is observed from materials with high solubility in a high-boiling point organic solvent (1, 2, 4-trichlorobenzene; TCB) due to partitioning into the hydrophobic core environment of F-127 micelles. Two new iridium-based sensitizers are described for blue-to-UV UC with outstanding solubilities in organic solvents, including toluene and TCB. These iridium-based sensitizers enable the fabrication of bright, UV-emitting micelles. For UC materials with sufficient solubility in the micelle core solvent, this encapsulation method allows facile customization of the excitation wavelengths and UV emission ranges required for different

contexts. Specifically, the two newly identified sensitizers are paired with four unique annihilators to generate UV light with wavelengths as low as 350 nm. This greatly expands the accessible UC emission ranges, while the smallest UC emission wavelength in prior reports of TTA-UC nanoparticles is 430 nm (violet). Finally, the benefits of the technology are shown by the photolysis of caged fluorescein with upconverted UV light at a focal point deep within an aqueous solution containing UV-emitting micelles. This demonstration validates the opportunity to use TTA-UC for the in-depth and spatially confined manipulation of UV-responsive materials in aqueous environments. With a growing suite of available UV emitters, these nanomaterials have potential to enable a wide range of emerging UV-light-triggered photochemical and biological applications.

[0084] Two promising sensitizers for blue-to-UV UC were identified: bis(2-phenylpyridine)(acetylacetonate)iridium(III), Ir(ppy)₂(acac) (ppy₂) and bis(2-(3,5-dimethylphenyl)-4-propylpyridine)(2,2,6,6-tetramethylheptane-3,5-diketonate)iridium(III), Ir(dmppy-pro)₂tmd (tmd), which were assessed along with tris(2-phenylpyridine)iridium(III), Ir(ppy)₃ (ppy₃), (Fig. 6B). These two iridium complexes are structurally similar to ppy₃, but with drastically improved solubilities in the TCB solvent used for micelle fabrication (Fig. 7). During the micelle fabrication process, upconversion molecules are not dispersed evenly across all micelles; rather, upconversion molecules are dispersed following a Poisson distribution. If solubility in TCB is limited, it is difficult to encapsulate enough sensitizers and annihilators within each micelle to enable TTA-UC. For instance, the solubility of ppy₃ in both toluene and TCB is less than 1 mM (Fig. 7). Although this solubility is sufficient for UC in bulk solutions (UC materials dissolved in solvents without nanoencapsulation), much higher solubilities are necessary for encapsulation. Modeling the Poisson distribution of ppy₃, ppy₂, and tmd based on their solubilities in TCB (Fig. 7), average number of molecules per micelle were predicted to be 3, 28, and 74, respectively (Fig. 8). This drastic increase in encapsulation efficiency of ppy₂ and tmd suggests their potential to improve UC emission in micelles.

[0085] Initially, the UC properties of the iridium complexes ppy₂ and tmd were characterized with a single annihilator, 2,7-di-tert-butylpyrene (DBP) in toluene, which is a favorable nonpolar solvent for screening TTA-UC. The UC properties of the ppy₃/DBP system were also measured to serve as a reference. All three iridium complexes

displayed similar absorption ranges and emission profiles with slightly red-shifted emission peaks from ppy3 to ppy2 to tmd, suggesting that ppy2 and tmd should also possess energetically favorable properties for blue-to-UV UC (Fig. 6B). Fig. 9A presents the normalized UC photoluminescence (UCPL) of the three sensitizers. Each sensitizer is paired with DBP in toluene under 447 nm excitation with varying power densities. The sensitizer concentrations in this experiment were optimized to maximize UCPL (Fig. 10), and the DBP concentration was held constant between the three systems to maintain consistency and to minimize self-absorption effects from DBP. All UCPL spectra had identical shapes when compared to photoluminescence of DBP (335 nm excitation, Fig. 6B). The spectral shape of the UC emission remained consistent across excitation power densities. The UC quantum yield (Φ_{UC}) of these systems was quantified as:

$$\Phi_{UC} (\%) = \frac{\text{Number of upconverted photons}}{\text{Number of absorbed photons}} \times 100$$

[0086] Since TTA-UC efficiency is inherently limited by the requirement to absorb two photons to emit one photon, the maximum achievable Φ_{UC} is 50%. Φ_{UC} of ppy3, ppy2, and tmd are 1.4%, 2.0%, and 3.2%, respectively (Fig. 9B), indicating the ppy2/DBP and tmd/DBP systems had higher UC efficiencies than the ppy3/DBP system. Another important TTA-UC metric is the threshold (I_{th}), or the power density of incident light at which UC intensity transitions from a quadratic regime (inefficient TTA) to a linear regime (efficient TTA). I_{th} for the ppy3/DBP, ppy2/DBP, and tmd/DBP systems were 156, 51.5, and 115 mW/cm², respectively (Fig. 9C), which means the ppy2/DBP and tmd/DBP systems exhibited lower thresholds to achieve efficient UC than the ppy3/DBP system. It is emphasized that these I_{th} were measured at concentrations that maximize upconverted light output. I_{th} is dependent on sensitizer concentration, and ppy2 and tmd concentrations are adjustable by virtue of their enhanced solubilities compared to ppy3; therefore, I_{th} in bulk solutions can be further reduced if dictated by an application. In summary, using either ppy2 or tmd as a sensitizer with DBP reduced the threshold values and increased UC quantum yields compared to using ppy3 as a sensitizer.

[0087] To better understand the sensitizers' relative TET transfer efficacy, Stern-Volmer quenching tests were conducted while keeping three sensitizers at the same concentration (100 μ M). Phosphorescence intensities were measured as a function of

annihilator concentration and compared to the phosphorescence intensity without the quencher, i.e., annihilator in this context. A greater slope indicates an enhanced quenching effect by the annihilator, suggesting more efficient triplet energy transfer. The results (Fig. 11) indicated similar energy transfer efficiency between ppy2 and ppy3, whereas tmd exhibited less efficient triplet energy transfer. This difference might be due to lower triplet energy of tmd, which has red-shifted photoluminescence compared to ppy2 and ppy3 (Fig. 6B).

[0088] Moving beyond bulk solutions, it was found that encapsulation significantly increased upconverted light output when using either ppy2 or tmd as sensitizers. ppy3, ppy2, and tmd were encapsulated with DBP into micelles to compare UC performance of micelles to TCB solutions. Although toluene is generally a better solvent for solution upconversion due to its low polarity (Figs. 9A to 9C), the core solvent was switched for micelle integration to TCB because it provides better solubility for sensitizers (Fig. 7) and facilitates the formation of more consistent and stable micelles. The encapsulation process is shown schematically in Fig. 5. Freshly fabricated micelles were approximately 25 nm in diameter (Fig. 13) allowing for facile dispersion in water to produce suspensions with excellent optical clarity. The spectroscopic characterization of these micelles is shown in Fig. 12A, with the counts of UC and phosphorescence scaled to the highest counts of ppy3/DBP micelle UC.

[0089] The concentrations of materials used for micelle integration were re-optimized for each system to maximize emitted light: the TTA-UC material concentrations required for efficient micelle fabrication were consistently higher than the optimal concentrations in toluene (Fig. 11), indicating the importance of high solubility of the UC materials. More efficient upconverting micelles were produced by ppy2/DBP and tmd/DBP systems instead of ppy3/DBP because ppy2/DBP and tmd/DBP have higher intrinsic UC efficiencies (Fig. 9B) and higher solubilities in the TCB solvent used for micelle integration (Fig. 8). Additionally, when adding the same total quantity of UC materials, the magnitude of UCPL was lower from TCB solution than from micelles (Fig. 12A).

[0090] Encapsulation also reduced sensitizer phosphorescence (Fig. 12A) and increased the UC-to-phosphorescence ratio by an order of magnitude (Fig. 14). This enhanced performance implies fewer losses from the encapsulated UC system compared

to UC in TCB solution. Dramatically reduced phosphorescence has been observed in other nanoencapsulated UC systems, suggesting the generalizability of these findings. This effect is attributed to higher local concentrations of the TTA-UC materials after nanoencapsulation, which reduces the average intermolecular distances between sensitizers and annihilators. The high local concentrations facilitate triplet energy transfer and enhance UC efficiency. However, for blue-to-UV upconversion, phosphorescence is still a significant energetic loss pathway as shown in Fig. 15.

[0091] The performance of the three UV-emitting UC micelles is summarized in Fig. 12B, where ppy2/DBP micelles produced the highest UC emissions and tmd/DBP micelles generated the highest UC-to-phosphorescence ratio. Furthermore, I_{th} of the optimized ppy3/DBP, ppy2/DBP, and tmd/DBP micelles were 664, 787, and 622 mW/cm², respectively, as shown in Fig. 16. Considering TCB is a relatively unfavorable solvent for UC due to its polarity, it is unsurprising that the threshold values are slightly higher in micelles than in toluene bulk solutions. Significant scattering effects and low absorption coefficients hindered the measurement of micelle Φ_{UC} using the absolute measurement method. However, the relative UC efficiencies of the optimized micelles were estimated by comparing UC intensities and absorption of micelles to those of toluene bulk solutions. These estimations neglect scattering by micelles during UC intensity and absorption measurements. Using this approximation, the relative Φ_{UC} were found to be lower for micelles than toluene solutions (Table 16). This result is consistent with the known tradeoff between maximum overall light output and quantum yield upon increasing sensitizer loading. Still, it is emphasized that Φ_{UC} of micelles containing ppy2 and tmd were much higher than Φ_{UC} of micelles containing ppy3 (Table 16).

[0092] Deployment into diverse applications involves different requirements such as specific UV emission ranges, elimination of metal sensitizer complexes to promote biocompatibility, or reduced costs for scalable production. Towards this end, the results show an enormous flexibility to “mix and match” sensitizers and annihilators that generate UV UC emission. To assess the generalizability of the encapsulation method, five sensitizers and four annihilators—twenty distinct UC pairs—were integrated into micelles (Figs. 3 and 17). In addition to the aforementioned iridium complexes, two pure organic

were selected sensitizers, 3,3'-carbonylbis(7-diethylaminocoumarin) (CBDAC) and 2,4,5,6-tetra(carbazol-9-yl)benzene-1,3-dicarbonitrile (4CzIPN), to investigate the scope of materials compatible with this encapsulation method. Annihilators were encapsulated with different UV emission ranges: pyrene, 1,4-bis((triisopropylsilyl)ethynyl)naphthalene (TIPS-Nph), and 2,5-Diphenyloxazole (PPO). PPO emits photons at wavelengths shorter than 350 nm, which is a particularly attractive range for photochemical reactions. UC emissions from all 20 encapsulated UC systems are shown in Fig. 3, with each spectrum normalized to its emission at 425 nm. All but one of the systems formed successful UV-emitting UC micelles. The only unsuccessful combination of CBDAC and PPO did not show UCPL in the micelle precursor TCB solution nor in toluene. Slightly red-shifted UC emissions were observed from pyrene and TIPS-Nph and are attributed to molecular aggregation. Towards biological applications, more biocompatible organic solvents, such as hexane, octane, or dodecane, can be further investigated for micelle core solvents, as well as integrating heavy metal-free sensitizers. Overall, this incredible flexibility to mix-and-match sensitizers and annihilators in micelles presents opportunities to meet the diverse requirements of a wide range of applications.

[0093] Next, the utility of an encapsulated blue-to-UV system to trigger a UV-sensitive photochemical reaction in aqueous solution was demonstrated. Specifically, a caged fluorophore with a photocleavable protecting group was selected as a UV upconversion reporter, such that removal of the protecting group using UV photolysis results in visible color changes and measurable absorbance and fluorescence changes. The UV upconversion reporter was fluorescein bis-(5-carboxymethoxy-2-nitrobenzyl) ether, hereafter referred to as caged fluorescein (Fig. 18A). It was hypothesized that blue incident light would photolyze caged fluorescein only when UV upconversion micelles were integrated into the solution (Fig. 18B). For this demonstration, the ppy2/PPO sensitizer/annihilator pair was selected due to its upconversion emission profile extending deepest into the UV spectrum (Fig. 3), where caged fluorescein has high absorptivity. The fabrication of ppy2/PPO micelles was optimized to maximize upconversion counts (Fig. 19).

[0094] In a control experiment, solutions of caged fluorescein were irradiated with a 365 nm LED, which led to photolysis of caged fluorescein and visible changes from

transparent to yellow (Fig. 18C, top row). An absorbance peak near 490 nm emerged and grew with increased UV irradiation, indicating increased concentrations of uncaged fluorescein (Fig. 18D). The absorbance spectrum was consistent with the spectrum of fluorescein, the uncaged product. Samples containing caged fluorescein and ppy2-only micelles (non-upconverting) did not change color (Fig. 18C, middle row) or absorbance (Fig. 18E) when irradiated with a 470 nm LED, suggesting that blue light was insufficient to photolyze caged fluorescein in the absence of a complete upconversion system. In contrast, samples containing caged fluorescein and ppy2/PPO upconversion micelles progressively changed to yellow (Fig. 18C, bottom row) and developed an absorbance peak near 490 nm (Fig. 18F) with continued exposure to a 470 nm LED. Fluorescence emission spectra showed that both UV light and blue light with ppy2/PPO upconversion micelles photolyzed caged fluorescein, with longer light exposure times corresponding to greater fluorescence intensity (Fig. 21). Direct irradiation with UV light photolyzed caged fluorescein more quickly than irradiation with blue light with ppy2/PPO upconversion micelles, even when the photon flux of blue incident light exceeded that of UV incident light (Fig. 18C, top and bottom rows, respectively). This difference in photolyzing kinetics between direct UV irradiation and upconversion micelles is attributed to relatively low UC quantum yields (Fig. 20). Yet, this attribute can still be potentially advantageous in some contexts. Low UC quantum yields provide larger dynamic ranges available to control photolysis kinetics by adjusting micelle concentration and input power. The potentially large dynamic range of UC photon flux is favorable for applications such as spatiotemporal control over drug delivery, in which a high flux of UV light can be damaging to surrounding cells.

[0095] Finally, the command of in-depth and spatially confined UV light generation using blue-to-UV UC micelles was demonstrated. Blue-to-UV upconversion is a powerful method for triggering UV photochemistry in scenarios that require greater incident light penetration depths than direct irradiation with UV light can achieve (Fig. 22A). A 365 nm LED beam was visualized with fluorescence triggered by the beam (Fig. 23) and noticeably attenuated across a 1 cm cuvette containing a solution of caged fluorescein (Fig. 22B, top). In contrast, a 470 nm LED beam did not attenuate as severely through a 1 cm cuvette containing a solution of caged fluorescein and ppy2/PPO upconversion

micelles (Fig. 22B, bottom). The visualized 470 nm LED beam was a combination of the beam itself, sensitizer fluorescence, and upconverted UV emission. While the UV light intensity reduced by 50% after penetrating 3 mm deep into the solution, the blue light intensity decreased by less than 5% (Fig. 24). Surprisingly, the presence of absorptive sensitizer molecules did not significantly impact the transmission of a 470 nm beam through the cuvette containing ppy2/PPO upconversion micelles. An apparent benefit of encapsulating upconversion materials is that the overall concentration of absorptive compounds in the path of incident light is minimized, while sufficient concentrations are maintained locally in the micelle core to facilitate upconversion. These images demonstrate the potential for blue-to-UV upconversion to trigger UV photochemistry deeper within media than direct UV excitation.

[0096] UV photochemistry was further demonstrated in localized volume elements by leveraging the quadratic nature of blue-to-UV TTA-UC. Since upconversion only proceeds efficiently at regions of high intensity, the photolysis of caged fluorescein was localized to the focal point of blue input light in a system with blue-to-UV upconversion micelles (Fig. 22C). Focused UV light photolyzed the caged fluorescein primarily where the beam entered the solution (Fig. 22D, top row), and background-subtracted images revealed minimal photolysis at the focal point (Fig. 22E, top row). In contrast, focused blue light enabled photolysis primarily at the focal point in a solution containing ppy2/PPO micelles (Fig. 22D, bottom row), which became more apparent after background subtraction (Fig. 22E, bottom row). In summary, encapsulated blue-to-UV upconversion systems offer exquisite control over the volume and location of UV-triggered photochemical reactions. This technology enables opportunities for the precise photochemical manipulation of light-responsive materials that are currently inaccessible with direct excitation.

[0097] In conclusion, a generalized approach was developed to encapsulate blue-to-UV upconversion systems, which were deployed to conduct spatially controlled photochemical reactions in aqueous environments at depth. Specifically, two iridium complexes with excellent solubilities in organic solvents (e.g., toluene and TCB) were identified as sensitizers for blue-to-UV UC. The TTA-UC efficiencies of sensitizers ppy2 and tmd paired with the annihilator DBP in toluene led to both higher UC quantum yields and lower thresholds than a previously reported system, ppy3/DBP. The increased

solubility of ppy2 and tmd in TCB enabled encapsulation of more molecules into Pluronic F-127 micelles, resulting in micelles with improved UC light output and reduced phosphorescence compared to unencapsulated UC pairs in organic solvents. To demonstrate the generalizability of the encapsulation method for UV-emitting TTA-UC systems, nineteen different UV UC pairs were successfully integrated into Pluronic F-127 micelles, allowing customizability in excitation wavelengths and UV emission ranges to satisfy the requirements of versatile applications. As a proof of concept, ppy2/PPO micelles were used to trigger photolysis of caged fluorescein with upconverted UV light at a focal point deep within an aqueous solution. UV-emitting micelles provide the unique advantage of enhanced penetration depth and spatially confined light generation with low incident powers, which are inaccessible with direct excitation due to absorption and scattering effects. Although blue light is not the most ideal wavelength for biological applications, a recent report demonstrates the use of blue light (405 nm) to penetrate through biological tissues to photolytically degrade a hydrogel up to 0.5 cm in animal skin. These upconversion micelles still greatly improve the penetration depth of UV light in biological systems. While currently rare, as more sensitizers for UV-emitting UC are discovered (such as green-to-UV sensitizers), integrating these systems into micelles is worth further investigation to further increase the input light depth penetration for biological applications. Precise, localized UV light generation at depth with TTA-UC has the potential to revolutionize a myriad of burgeoning fields, such as volumetric 3D printing, spatially controlled drug delivery, and precise optogenetic activation.

Methods supporting the Data Examples

Chemicals

[0098] All chemicals were used as received.

[0099] Bis(2-phenylpyridine)(acetylacetonate)iridium(III), Ir(ppy)₂(acac) (ppy₂) and bis(2-(3,5-dimethylphenyl)-4-propylpyridine)(2,2,6,6-tetramethylheptane-3,5-diketonate)iridium(III), Ir(dmppy-pro)₂tmd (tmd) were purchased from Luminescence Technology Corp.

[0100] Tris(2-phenylpyridine)iridium(III), Ir(ppy)₃ (ppy₃) and 2,4,5,6-tetra(carbazol-9-yl)benzene-1,3-dicarbonitrile (4CzIPN) were purchased from Ossila.

[0101] 2,7-di-tert-butylpyrene (DBP) and 3,3'-carbonylbis(7-diethylaminocoumarin) (CBDAC) were purchased from Tokyo Chemical Industry (TCI).

[0102] Pyrene, 2,5-Diphenyloxazole (PPO), Pluronic® F-127, toluene (anhydrous, 99.8%), 1,2,4-trichlorobenzene (TCB) (anhydrous, >99%), and chloroform (anhydrous, >99%, stabilized) were purchased from Sigma-Aldrich.

[0103] 1,4-bis((triisopropylsilyl)ethynyl)naphthalene (TIPS-Nph) was purchased from HAARES ChemTech Inc. following a standard synthetic protocol.

[0104] Fluorescein bis-(5-carboxymethoxy-2-nitrobenzyl) ether, dipotassium salt (CMNB-caged fluorescein) was purchased from ThermoFisher Scientific.

Micelle fabrication

[0105] Given the sensitivity of upconversion to oxygen, all solvents used for micelle fabrication were either sparged with nitrogen on a Schlenk line (>99% N₂ purity, sparge 20 mL at a time for approximately 15 minutes) or purchased anhydrous to maintain low oxygen content. Furthermore, micelle fabrication was performed in a glovebox with <0.5 ppm O₂. First, 60 mg/mL Pluronic F-127 was dissolved in MilliQ ultrapure water (18.2 MΩ·cm) with vigorous stirring. Next, a sensitizer solution with desired concentration was prepared in 1,2,4-trichlorobenzene (TCB), while an annihilator solution was prepared in chloroform. If a saturated solution was used for micelle fabrication, excess materials were added to the solvent, and the solution was rigorously stirred and subsequently filtered with 0.22 μm PTFE filters to produce a homogenous and saturated solution. Sensitizer solutions were used within one week of preparation, whereas annihilator solutions were immediately discarded after use due to chloroform volatility. The sensitizer and annihilator solutions were mixed with a 2:3 volume ratio, respectively, to yield an upconversion solution. For a typical small-scale fabrication, 50 μL of upconversion solution was added to 2 mL F-127 in water (60 mg/mL). Then, the solution was stirred overnight at 800 rpm without the lid to allow the chloroform to evaporate. Finally, the UC micelle solution was filtered by 0.45 μm PVDF filters, yielding a transparent solution.

[0106] This fabrication method can be adapted to different scales. However, stirring speed and stirring time should be adjusted accordingly for different scales to ensure adequate mixing and micelle formation. For example, a 20-mL solution was stirred at

1600 rpm for more than 24 h before filtering. Solutions containing micelles were characterized in quartz cuvettes with lids secured by PTFE sealant tape before removal from the glovebox, unless otherwise specified.

Photoluminescence measurements

[0107] Photoluminescence (PL) measurements were collected on a custom setup. A 447 nm laser (MDL-F-447-2W, Dragon Lasers) excited the sample, PL was collected at 90 degrees using a collection lens, and the appropriate filter was used to avoid saturating the spectrometer (425 nm short pass filter for upconversion PL; 475 nm long pass filter for phosphorescence), QE Pro (QEPRO-XR, Ocean Insight).

Threshold measurements

[0108] Threshold measurements were collected on a custom setup, where a 447 nm laser was focused on the sample, and UCPL was collected at 90 degrees by the spectrometer with a 425 nm short pass filter. The power of the laser at the focal point was measured using an optical power detector (818-SL, Newport Corporation) threaded with an OD3 attenuator if necessary, and the photocurrent was reported by a Keithley 2400 sourcemeter. The image of the laser spot was captured by a CMOS scientific camera (CS165MU, ThorLabs, Inc.) and analyzed in ImageJ to determine the spot size. Different beam intensities were achieved by attenuating the laser with neutral density filters (NEK01, ThorLabs, Inc.).

[0109] The upconversion peak was integrated and plotted against excitation intensity in a log-log plot. The resulting plot was analyzed to find the linear and quadratic regimes, and the intersection between these regimes was used to interpolate the threshold intensity.

UC quantum yield measurements

[0110] UC quantum yield measurements were collected on a custom setup where a 447 nm laser excited the sample in an integrating sphere, and the resulting emission spectrum was collected by a spectrometer. Upconversion solutions were loaded into quartz cuvettes with 2 mm path lengths. The integrating sphere was calibrated using a

radiometric source (HL-3P-CAL, Ocean Insight), which emits a known power at specific wavelengths. This calibration was used to convert arbitrary counts into absolute irradiance ($\mu\text{W}/\text{nm}$). Four measurements shown below were taken for each sample to calculate the UC quantum yield (Fig. 25, which are modified from PLQY measurements developed by de Mello).

- Exp A: There was no sample in the integrating sphere, and the emission collected from the sphere was cut off by a 425 nm short pass filter to prevent saturation of the detector.
- Exp B: There was a sample in the integrating sphere but not in the light path, and the emission collected from the sphere was cut off by a 425 nm short pass filter to prevent saturation of the detector.
- Exp C: There was a sample in the integrating sphere and in the light path, and the emission collected from the sphere was cut off by a 425 nm short pass filter.
- Exp C': There was a sample in the integrating sphere and in the light path, and the emission collected from the sphere was not cut off by any filters (the detector would not saturate due to high absorption of the upconversion solution).

[0111] For each type of measurement, both UC and laser luminescence are captured by the spectrometer. The UC quantum yield was calculated as follows (L refers to the integrated area under the UC emission or laser profile):

$$R = \text{filter cutoff ratio on laser light} = \frac{L_{C' \text{ laser}}}{L_{C \text{ laser}}}$$

$$A = \text{absorption coefficient} = 1 - \frac{L_{C \text{ laser}}}{L_{B \text{ laser}}}$$

$$\Phi_{\text{UC}} (\%) = \frac{\text{Number of upconverted photons}}{\text{Number of absorbed photons}} \times 100 = \frac{L_{C \text{ UC}} - (1 - A) \times L_{B \text{ UC}}}{L_{A \text{ laser}} \times A \times R} \times 100$$

[0112] The UC quantum yield measurement was performed once at a relatively high-power density, denoted as Φ_{UC} . The power density was measured in the same way as described in the threshold measurement section. UC quantum yields (Φ'_{UC}) of other data points were calculated using the following equation by comparing their UCPL intensities and power densities with the known one:

$$\Phi'_{UC} = \Phi_{UC} \times \frac{UCPL'}{UCPL} \times \frac{\text{power density}}{\text{power density'}}$$

Dynamic light scattering

[0113] As-fabricated micelles were diluted 5 times with DI water and filtered with 0.22- μm PVDF filters prior to taking measurements. Samples were loaded in polystyrene cuvettes sealed with PTFE tape. A NanoBrook Omni particle size and zeta potential analyzer was used to measure micelle size distributions. Each sample was measured using three separate runs of 60 seconds each.

Other spectroscopic measurements

[0114] UV-vis absorption spectra were collected with an Agilent Cary 6000i UV/Vis/NIR. Photoluminescence data presented in Fig. 6B were collected with a Horiba FluoroLog Fluorimeter.

Ortho-nitrobenzyl caged fluorescein as a UV upconversion reporter

[0115] Caged fluorescein samples were prepared in a glovebox under red light conditions to prevent premature uncaging and degradation. To aid the preparation of upconversion reporter solutions, 2 mM caged fluorescein was prepared by suspending caged fluorescein powder in 1 $\times$ phosphate-buffered saline (PBS) and stirring for several hours to aid dissolution. Caged fluorescein powder was stored at $-20\text{ }^{\circ}\text{C}$ between uses. Pluronic F-127 micelles were suspended in 1 $\times$ PBS by adding 1 volume of 10 $\times$ PBS to 9 volumes of freshly fabricated micelles in DI water.

[0116] Three distinct caged fluorescein solutions were prepared for the experiment in Fig. 18C:

- Positive control (Fig. 18C, top row): 0.2 mM caged fluorescein was produced by tenfold dilution of 2 mM caged fluorescein with nitrogen-sparged 1 $\times$ PBS.
- Negative control (Fig. 18C, middle row): 0.2 mM caged fluorescein with sensitizer-only micelles were prepared by tenfold dilution of 2 mM caged fluorescein with nitrogen-sparged sensitizer-only micelles in 1 $\times$ PBS. Sensitizer-only micelles were fabricated with saturated ppy2 in TCB and neat chloroform, in lieu of an annihilator

solution.

- UC reporter (Fig. 18C, bottom row): 0.2 mM caged fluorescein with UC micelles were prepared by tenfold dilution of 2 mM caged fluorescein with nitrogen-sparged UC micelles in 1× PBS. UC micelles were fabricated with saturated ppy2 in TCB and 200 mM PPO in chloroform (see Fig. 19 for concentration optimization).

[0117] From each solution, 2500 µL was distributed into four quartz cuvettes. Each cuvette was irradiated by an LED for a different amount of time. The positive control was irradiated by a 365 nm LED (ThorLabs, Inc.) at 19.7 mW. The negative control and experiment were irradiated by a 470 nm LED (ThorLabs, Inc.) at 50.4 mW. Power measurements were taken with a standard photodiode power sensor and compact power and energy meter console (S120VC and PM100D, ThorLabs, Inc.). All images were taken using a Canon EOS Rebel T6i. The reported images are unedited.

DOCTRINE OF EQUIVALENTS

[0118] While the above description contains many specific embodiments of the invention, these should not be construed as limitations on the scope of the invention, but rather as an example of one embodiment thereof. Accordingly, the scope of the invention should be determined not by the embodiments illustrated, but by the appended claims and their equivalents.

WHAT IS CLAIMED IS:

1. A system for localized UV emission, comprising:
an amphiphilic vesicle having an inner organic core encapsulated by an outer hydrophilic region;
a sensitizer; and
an annihilator;
wherein the sensitizer and annihilator are within the inner organic core of the amphiphilic vesicle;
wherein the annihilator is capable of emitting photons of UV light when the sensitizer is stimulated with input light.
2. The system of claim 1, wherein the amphiphilic vesicle is a micelle that comprises an amphiphilic polymer.
3. The system of claim 2, wherein the amphiphilic polymer comprises one of: polyethylene glycol (PEG), polyvinyl pyrrolidone (PVP), poly *N*-isopropyl acrylamide (pNIPAM), polylactic acid (PLA), or a polyamide.
4. The system of claim 3, wherein the amphiphilic polymer comprises *block*-poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol).
5. The system of claim 4, wherein the amphiphilic polymer comprises F127 polymer.
6. The system of any one of claims 1 to 5, wherein the sensitizer is one of: bis(2-phenylpyridine)(acetylacetonate)iridium(III), Ir(ppy)₂(acac) (ppy₂); bis(2-(3,5-dimethylphenyl)-4-propylpyridine)(2,2,6,6-tetramethylheptane-3,5-diketonate)iridium(III), Ir(dmppy-pro)₂tmd (tmd); tris(2-phenylpyridine)iridium(III), Ir(ppy)₃ (ppy₃); 1,2,3,5-Tetrakis(carbazol-9-yl)-4,6-dicyanobenzene, 2,4,5,6-tetra(carbazol-9-yl)benzene-1,3-dicarbonitrile (4CzIPN); or 3,3'-carbonylbis(7-diethylaminocoumarin) (CBDAC).

7. The system of claim 6, wherein the sensitizer is one of: bis(2-phenylpyridine)(acetylacetonate)iridium(III), Ir(ppy)₂(acac) (ppy₂) or bis(2-(3,5-dimethylphenyl)-4-propylpyridine)(2,2,6,6-tetramethylheptane-3,5-diketonate)iridium(III), Ir(dmppy-pro)₂tmd (tmd).

8. The system of any one of claims 1 to 5, wherein the annihilator is one of: pyrene; 2,7-di-tert-butylpyrene (DBP); 2,5-Diphenyloxazole (PPO); 1,4-bis((triisopropylsilyl)ethynyl)naphthalene (TIPS-Nph); or ([1,1'-Biphenyl]-4-ylethynyl)triisopropylsilane (p-TIPS-BP).

9. The system of any one of claims 1 to 5, wherein the sensitizer is tris(2-phenylpyridine)iridium(III), Ir(ppy)₃ (ppy₃) and the annihilator is one of: pyrene; 2,7-di-tert-butylpyrene (DBP); 2,5-Diphenyloxazole (PPO); or 1,4-bis((triisopropylsilyl)ethynyl)naphthalene (TIPS-Nph),.

10. The system of any one of claims 1 to 5, wherein the sensitizer is bis(2-phenylpyridine)(acetylacetonate)iridium(III), Ir(ppy)₂(acac) (ppy₂) and the annihilator is one of: pyrene; 2,7-di-tert-butylpyrene (DBP); 2,5-Diphenyloxazole (PPO); 1,4- or bis((triisopropylsilyl)ethynyl)naphthalene (TIPS-Nph).

11. The system of any one of claims 1 to 5, wherein the sensitizer is bis(2-(3,5-dimethylphenyl)-4-propylpyridine)(2,2,6,6-tetramethylheptane-3,5-diketonate)iridium(III), Ir(dmppy-pro)₂tmd (tmd) and the annihilator is one of: pyrene; 2,7-di-tert-butylpyrene (DBP); 2,5-Diphenyloxazole (PPO); or 1,4-bis((triisopropylsilyl)ethynyl)naphthalene (TIPS-Nph).

12. The system of any one of claims 1 to 5, wherein the sensitizer is 1,2,3,5-Tetrakis(carbazol-9-yl)-4,6-dicyanobenzene, 2,4,5,6-tetra(carbazol-9-yl)benzene-1,3-dicarbonitrile (4CzIPN) and the annihilator is one of: pyrene; 2,7-di-tert-butylpyrene (DBP); 2,5-Diphenyloxazole (PPO); 1,4-bis((triisopropylsilyl)ethynyl)naphthalene (TIPS-Nph); or ([1,1'-Biphenyl]-4-ylethynyl)triisopropylsilane (p-TIPS-BP).

13. The system of any one of claims 1 to 5, wherein the sensitizer is 3,3'-carbonylbis(7-diethylaminocoumarin) (CBDAC) and the annihilator is one of: pyrene, 2,7-di-tert-butylpyrene (DBP); or 1,4-bis((triisopropylsilyl)ethynyl)naphthalene (TIPS-Nph).
14. The system of any one of claims 1 to 13 further comprising: an aqueous solution, an aqueous gel, an aqueous sol, or an aqueous emulsion, wherein the amphiphilic vesicle is solubilized within the aqueous solution, the aqueous gel, the aqueous sol, or the aqueous emulsion.
15. The system of any one of claims 1 to 14, wherein the sensitizer is stimulated by light having a wavelength between 400 nm and 1000 nm.
16. The system of claim 15, wherein the sensitizer is stimulated by infrared light.
17. A method for providing localized UV light, comprising:
providing a UV emitting system comprising:
an amphiphilic vesicle having an inner organic core encapsulated by an outer hydrophilic region;
a sensitizer; and
an annihilator;
wherein the sensitizer and annihilator are within the inner organic core of the amphiphilic vesicle, wherein the amphiphilic vesicle is solubilized within an aqueous solution, an aqueous gel, an aqueous sol, or an aqueous emulsion; and
impinging an input light on the UV emitting system such that photons of the input light contact the inner organic core resulting in emission of UV light.
18. The method of claim 17 further comprising:
prior to impinging the input light on the UV emitting system, traversing the input light through a medium that cannot be traversed by UV light having a wavelength equivalent the wavelength emitted by the annihilator.

19. The method of claim 17 further comprising:
prior to impinging the input light on the UV emitting system, penetrating the input light to a depth within a medium or material that cannot be reached by UV light having a wavelength equivalent to the wavelength emitted by the annihilator.
20. The method of claim 17, 18 or 19, wherein the input light has a wavelength of between 400 nm and 1000 nm.
21. The method of claim 20, wherein the input light is infrared light.
22. The method of any one of claims 17 to 21, wherein the amphiphilic vesicle is a micelle that comprises an amphiphilic polymer.
23. The method of claim 22, wherein the amphiphilic polymer comprises one of: polyethylene glycol (PEG), polyvinyl pyrrolidone (PVP), poly *N*-isopropyl acrylamide (pNIPAM), polylactic acid (PLA), or a polyamide.
24. The method of claim 23, wherein the amphiphilic polymer comprises *block*-poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol).
25. The method of claim 24, wherein the amphiphilic polymer comprises F127 polymer.
26. The method of any one of claims 17 to 25, wherein the sensitizer is one of: bis(2-phenylpyridine)(acetylacetonate)iridium(III), Ir(ppy)₂(acac) (ppy₂); bis(2-(3,5-dimethylphenyl)-4-propylpyridine)(2,2,6,6-tetramethylheptane-3,5-diketonate)iridium(III), Ir(dmppy-pro)₂tmd (tmd); tris(2-phenylpyridine)iridium(III), Ir(ppy)₃ (ppy₃); 1,2,3,5-Tetrakis(carbazol-9-yl)-4,6-dicyanobenzene, 2,4,5,6-tetra(carbazol-9-yl)benzene-1,3-dicarbonitrile (4CzIPN); or 3,3'-carbonylbis(7-diethylaminocoumarin) (CBDAC).

27. The method of claim 26, wherein the sensitizer is one of: bis(2-phenylpyridine)(acetylacetonate)iridium(III), Ir(ppy)₂(acac) (ppy₂) or bis(2-(3,5-dimethylphenyl)-4-propylpyridine)(2,2,6,6-tetramethylheptane-3,5-diketonate)iridium(III), Ir(dmppy-pro)₂tmd (tmd).

28. The method of any one of claims 17 to 25, wherein the annihilator is one of: pyrene; 2,7-di-tert-butylpyrene (DBP); 2,5-Diphenyloxazole (PPO); 1,4-bis((triisopropylsilyl)ethynyl)naphthalene (TIPS-Nph); or ([1,1'-Biphenyl]-4-ylethynyl)triisopropylsilane (p-TIPS-BP).

29. The method of any one of claims 17 to 25, wherein the sensitizer is tris(2-phenylpyridine)iridium(III), Ir(ppy)₃ (ppy₃) and the annihilator is one of: pyrene; 2,7-di-tert-butylpyrene (DBP); 2,5-Diphenyloxazole (PPO); or 1,4-bis((triisopropylsilyl)ethynyl)naphthalene (TIPS-Nph).

30. The method of any one of claims 17 to 25, wherein the sensitizer is bis(2-phenylpyridine)(acetylacetonate)iridium(III), Ir(ppy)₂(acac) (ppy₂) and the annihilator is one of: pyrene; 2,7-di-tert-butylpyrene (DBP); 2,5-Diphenyloxazole (PPO); 1,4- or bis((triisopropylsilyl)ethynyl)naphthalene (TIPS-Nph).

31. The method of any one of claims 17 to 25, wherein the sensitizer is bis(2-(3,5-dimethylphenyl)-4-propylpyridine)(2,2,6,6-tetramethylheptane-3,5-diketonate)iridium(III), Ir(dmppy-pro)₂tmd (tmd) and the annihilator is one of: pyrene; 2,7-di-tert-butylpyrene (DBP); 2,5-Diphenyloxazole (PPO); or 1,4-bis((triisopropylsilyl)ethynyl)naphthalene (TIPS-Nph).

32. The method of any one of claims 17 to 25, wherein the sensitizer is 1,2,3,5-Tetrakis(carbazol-9-yl)-4,6-dicyanobenzene, 2,4,5,6-tetra(carbazol-9-yl)benzene-1,3-dicarbonitrile (4CzIPN) and the annihilator is one of: pyrene; 2,7-di-tert-butylpyrene (DBP); 2,5-Diphenyloxazole (PPO); 1,4-bis((triisopropylsilyl)ethynyl)naphthalene (TIPS-Nph); or ([1,1'-Biphenyl]-4-ylethynyl)triisopropylsilane (p-TIPS-BP).

33. The method of any one of claims 17 to 25, wherein the sensitizer is 3,3'-carbonylbis(7-diethylaminocoumarin) (CBDAC) and the annihilator is one of: pyrene, 2,7-di-tert-butylpyrene (DBP); or 1,4-bis((triisopropylsilyl)ethynyl)naphthalene (TIPS-Nph).

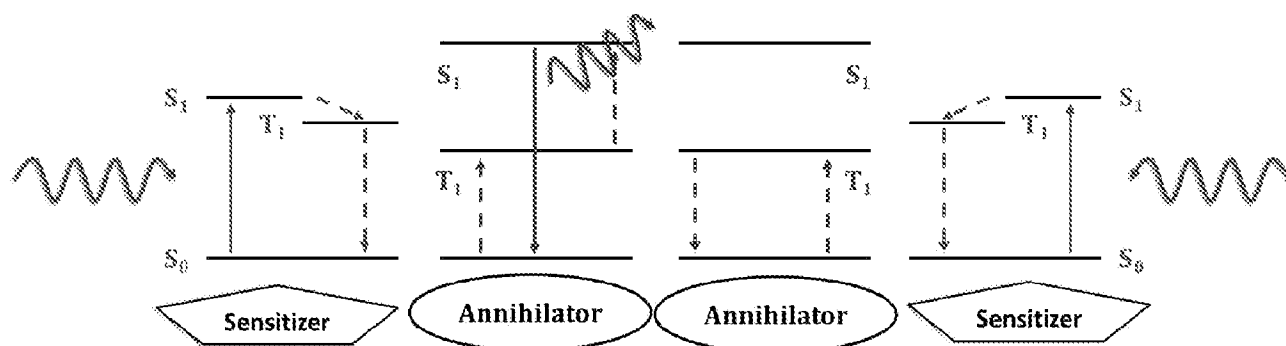
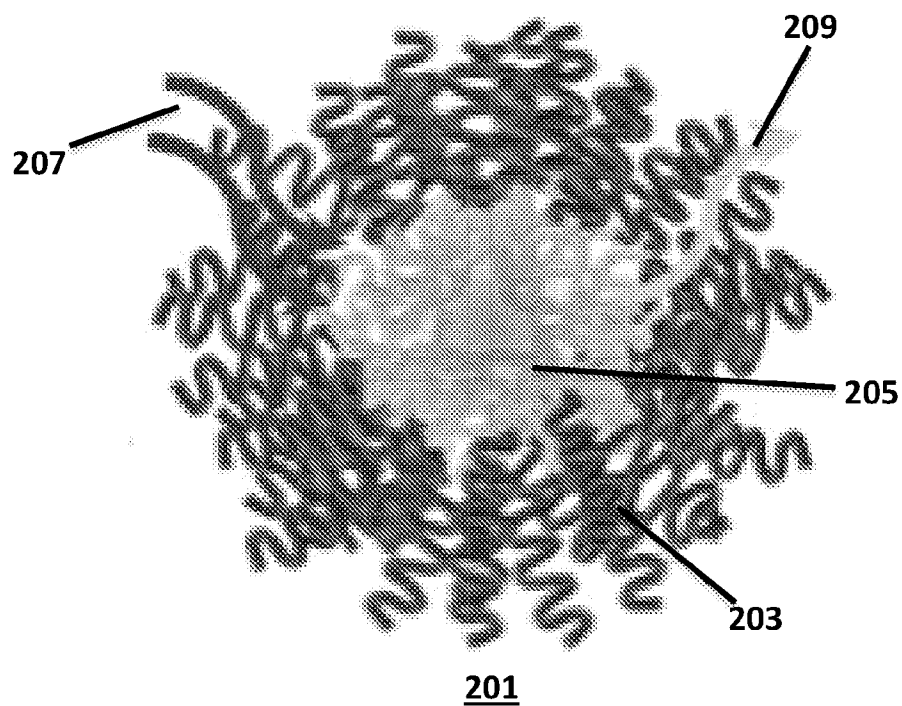
Fig. 1**Fig. 2**

Fig. 3

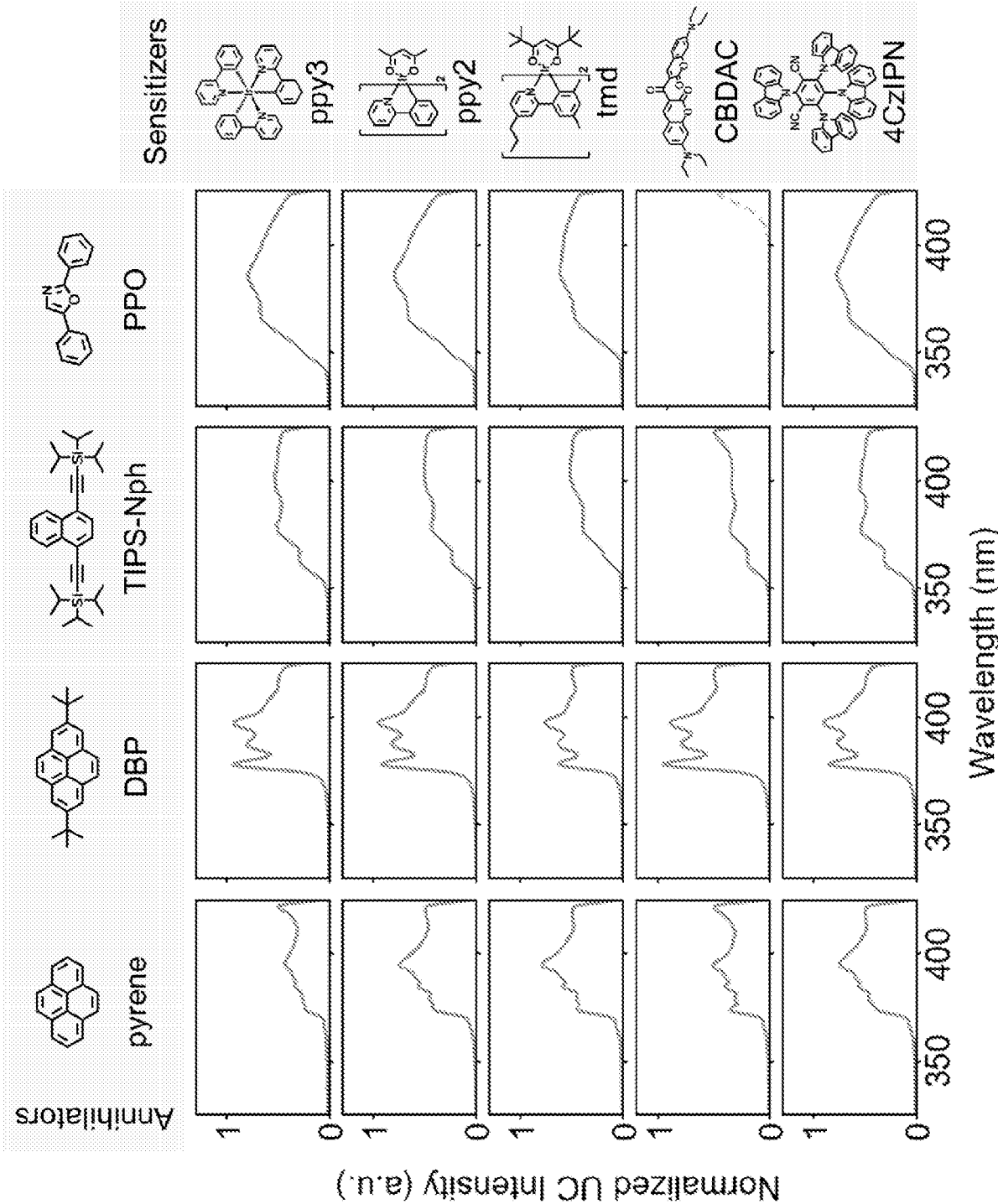


Fig. 4

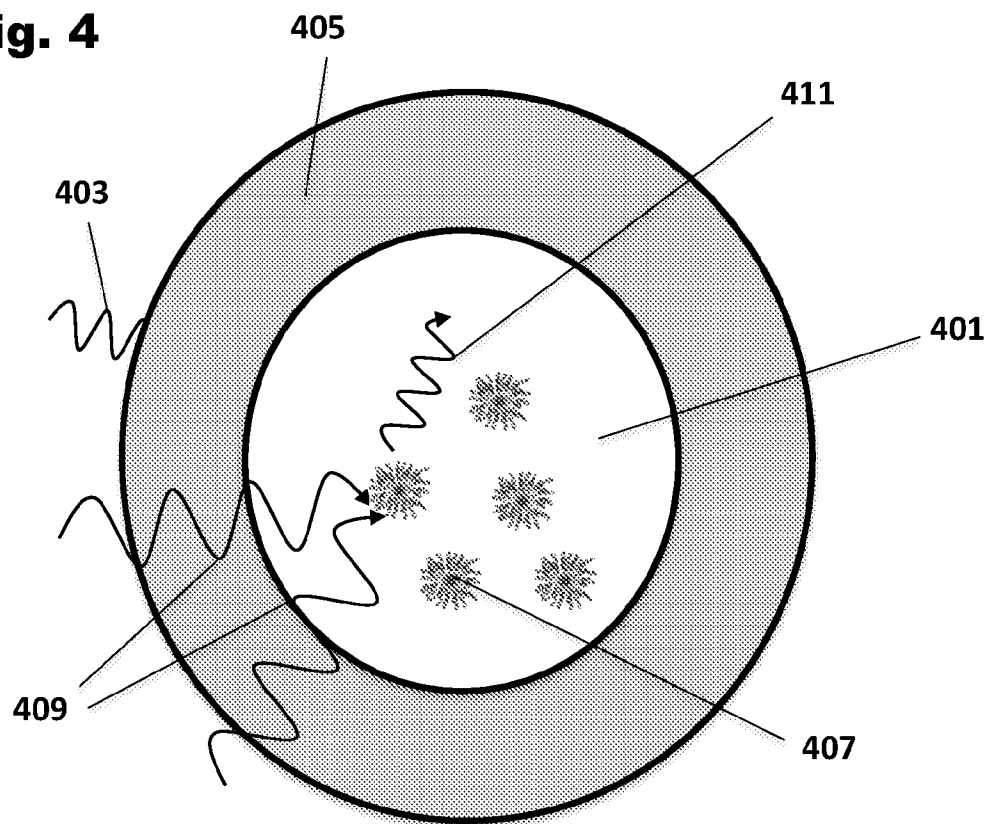


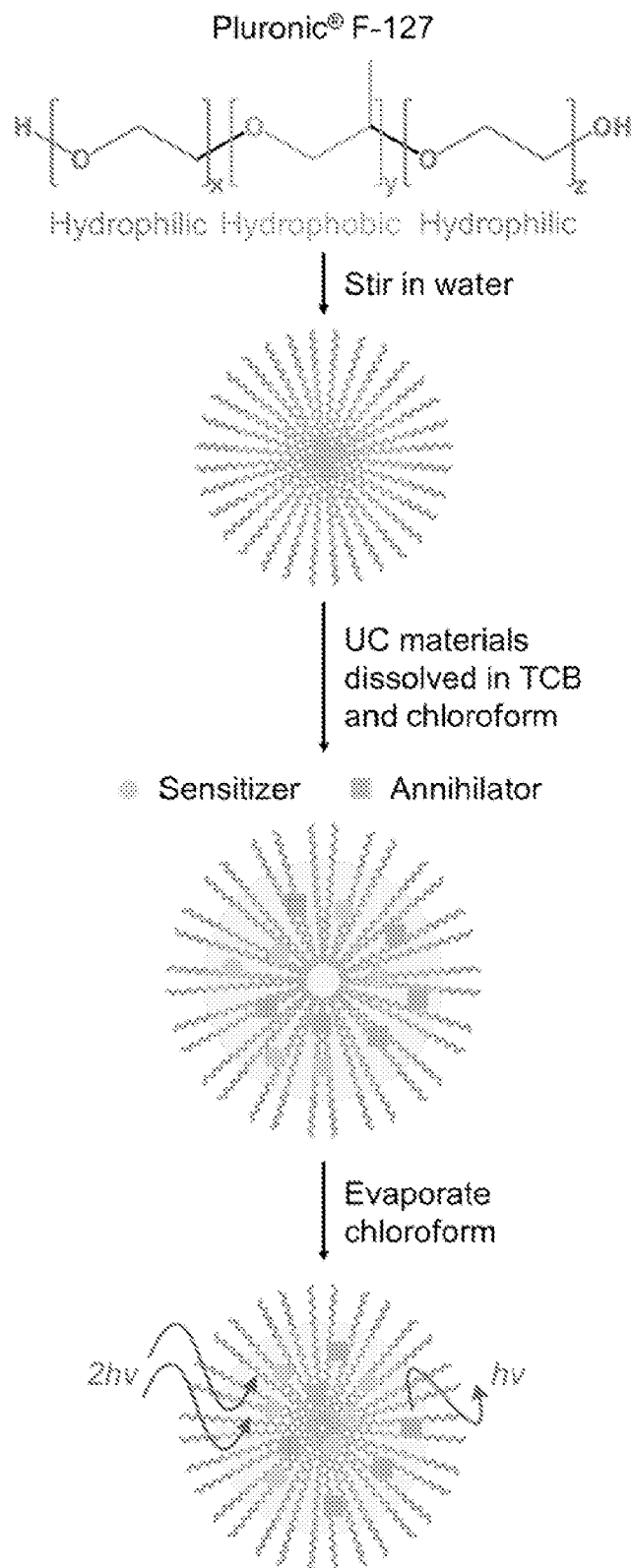
Fig. 5

Fig. 6A

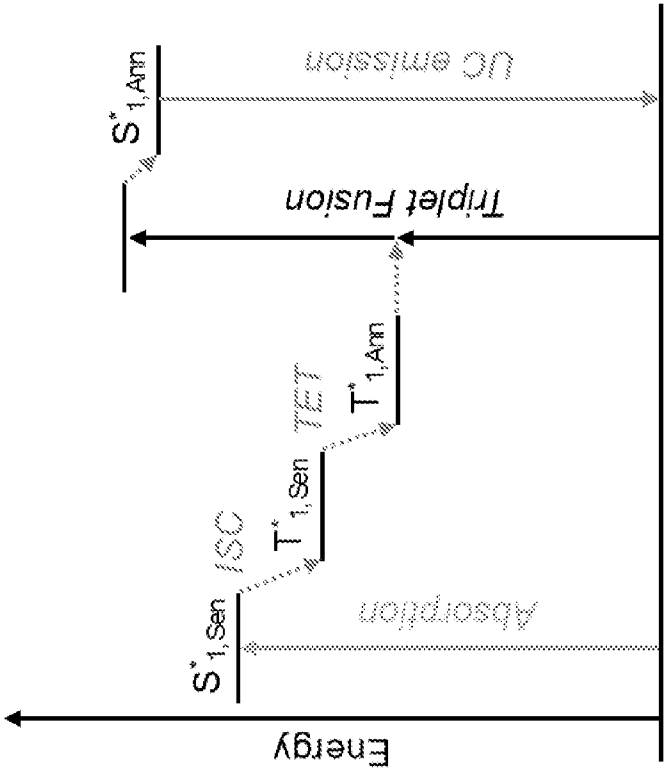


Fig. 6B

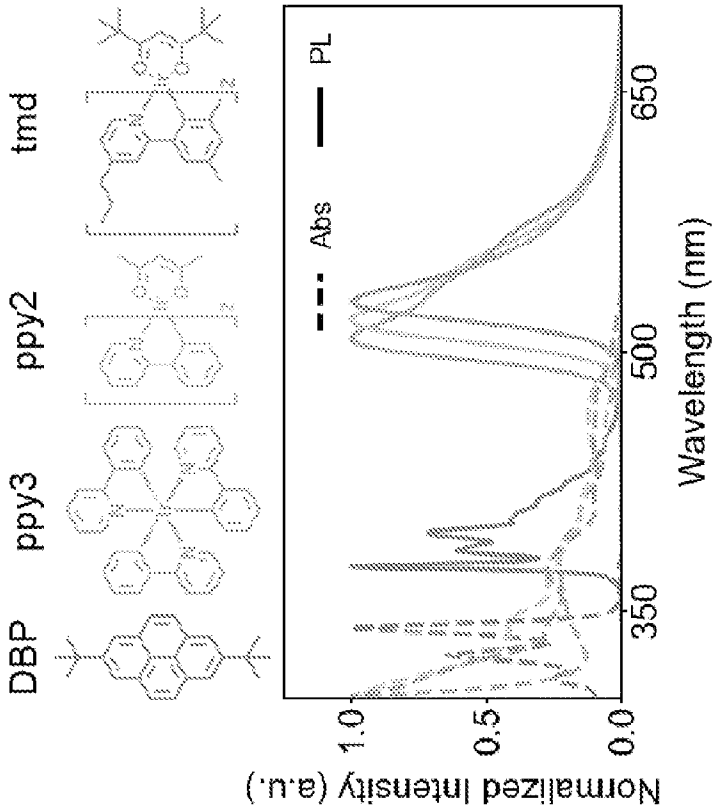


Fig. 7

Table. Solubility of three iridium complexes in organic solvents at room temperature determined by UV-vis absorption spectroscopy.

Complex	Toluene (mM)	1,2,4-trichlorobenzene (TCB) (mM)
ppy3	< 0.3	< 0.7
ppy2	< 2.0	< 5.6
tmd	> 15	> 15

Fig. 8

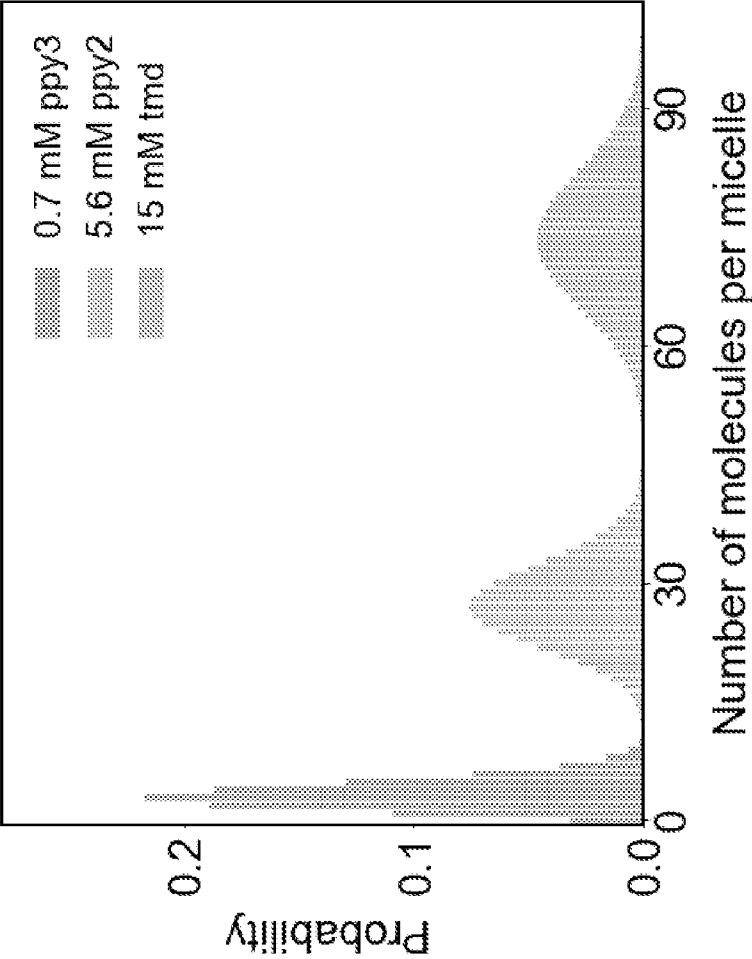


Fig. 9A

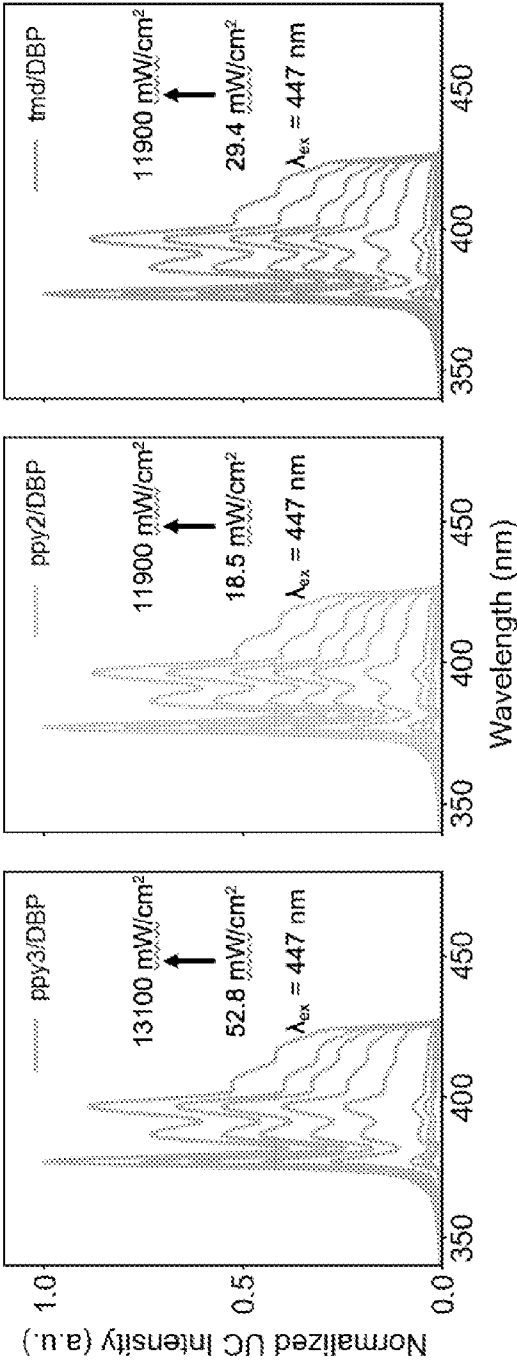


Fig. 9B

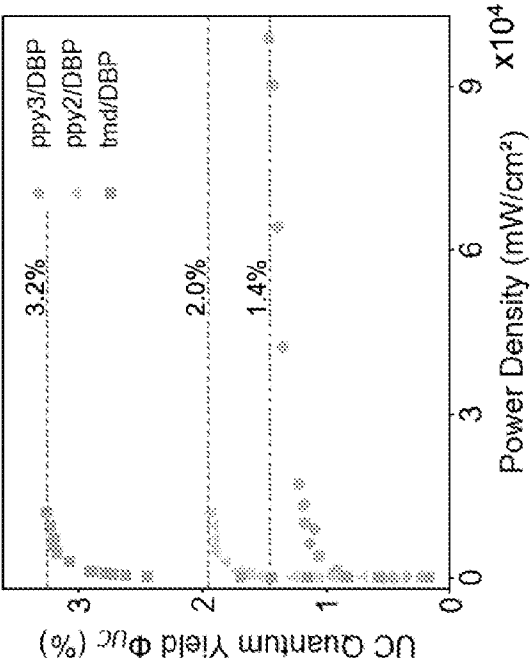


Fig. 9C

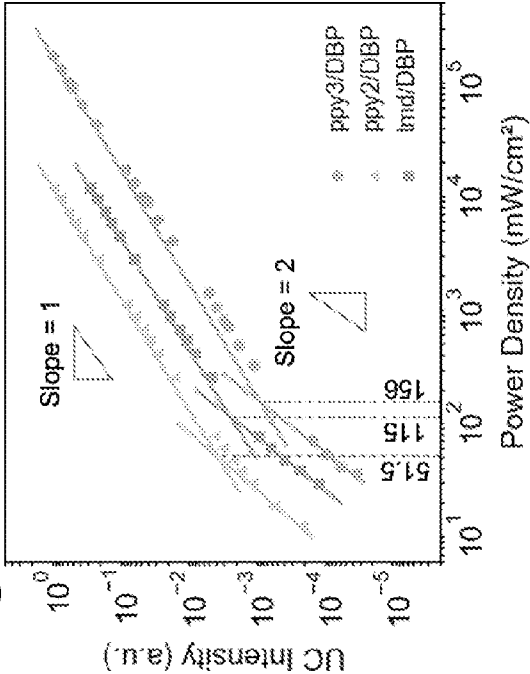


Fig. 10

Table. Optimized concentrations of [Sensitizer]/[Annihilator] in bulk solution (toluene) and for TCB/chloroform solutions used to prepare micelles.

Sensitizer/Annihilator pair	Solution (toluene)	Micelles (TCB/chloroform)
ppy3/DBP	[100 μ M]/[1 mM]	[0.7 mM]/[50 mM]
ppy2/DBP	[200 μ M]/[1 mM]	[5.6 mM]/[60 mM]
tmd/DBP	[80 μ M]/[1 mM]	[15 mM]/[300 mM]

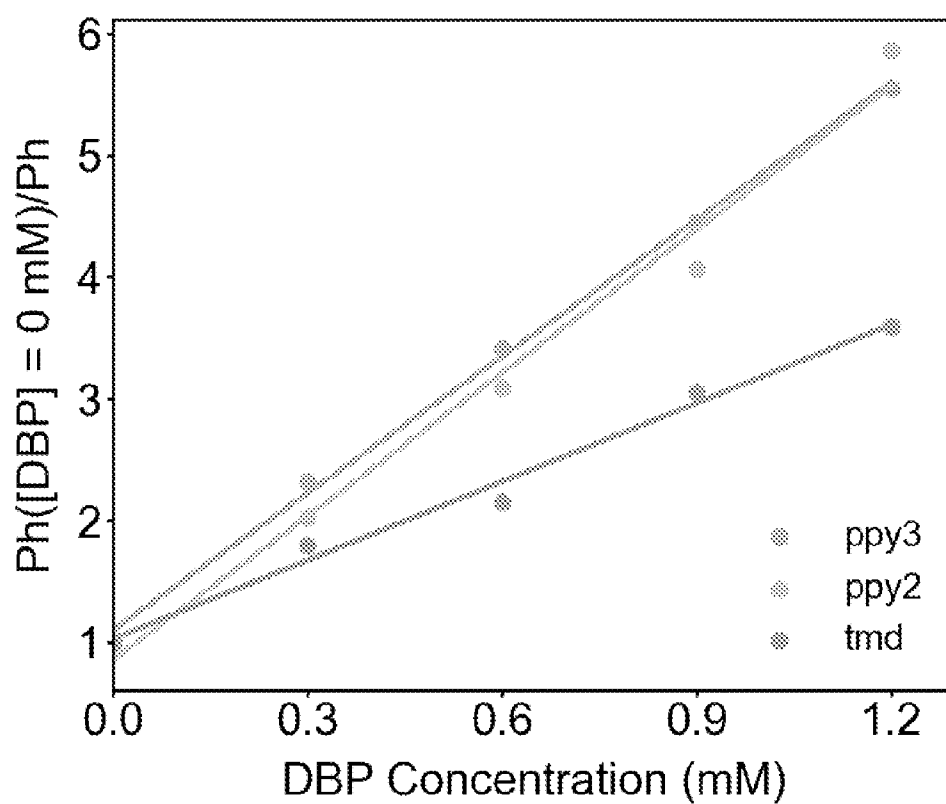
Fig. 11

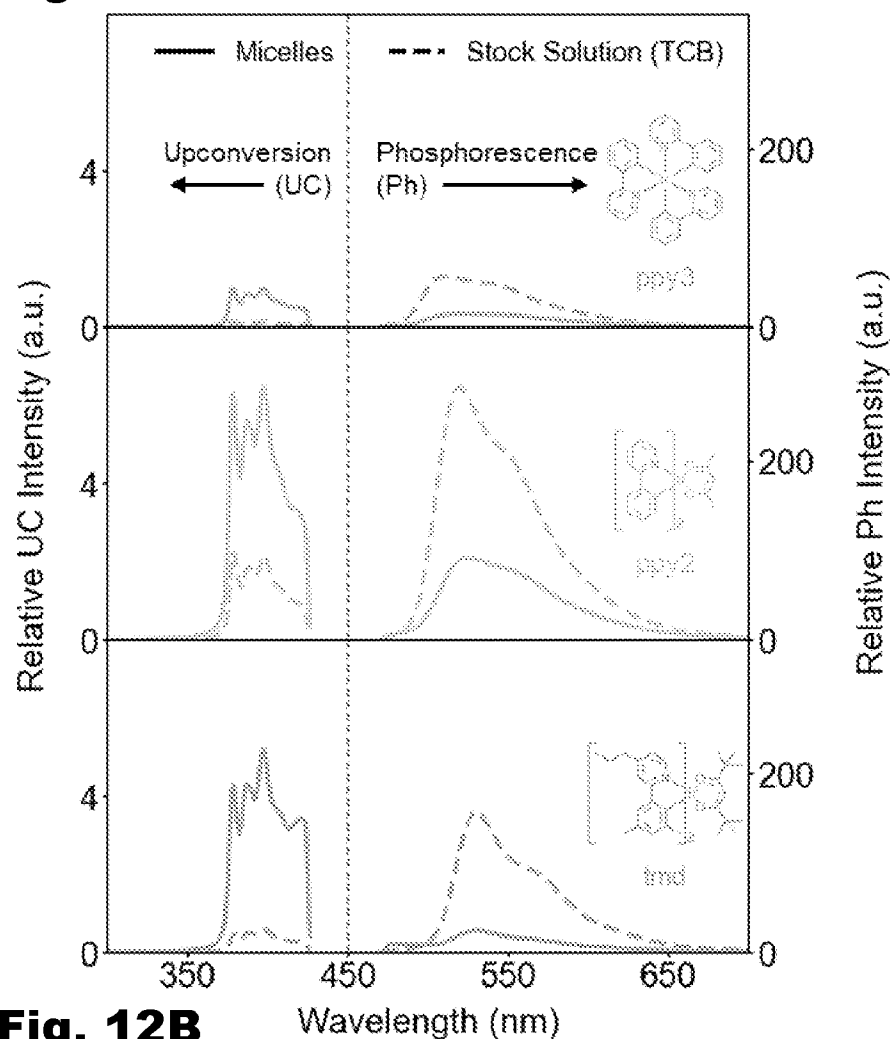
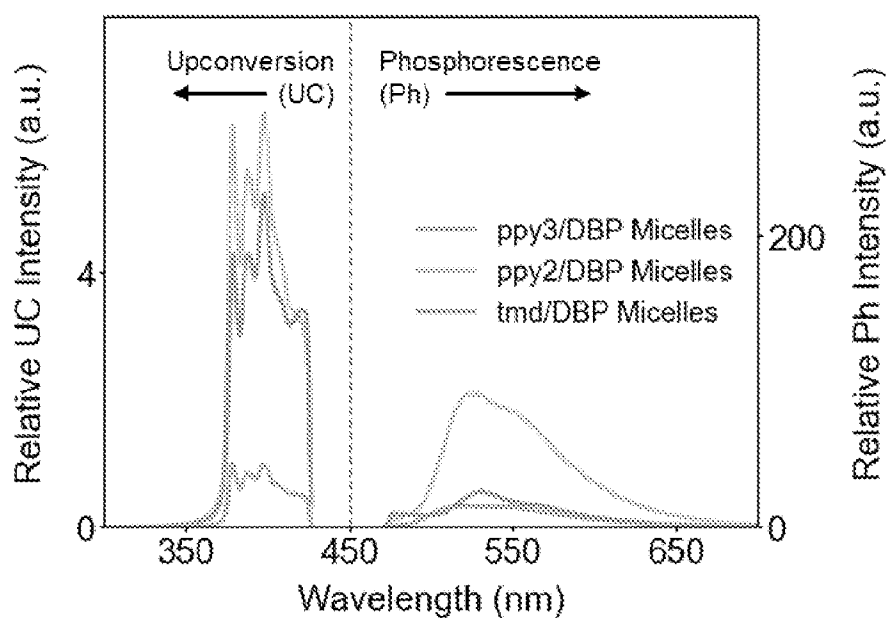
Fig. 12A**Fig. 12B**

Fig. 13**Table. Representative dynamic light scattering (DLS) data for micelles with different encapsulated species.**

Micelle Contents	TCB/CHCl₃ only	ppy2/PPO in TCB/CHCl₃	ppy2 in TCB/CHCl₃	PPO in TCB/CHCl₃
Effective diameter (nm)	23.8 ± 0.2	25.6 ± 0.2	25.0 ± 0.2	24.6 ± 0.3
Polydispersity	0.12 ± 0.02	0.105 ± 0.004	0.09 ± 0.01	0.09 ± 0.02
Data retained (%)	95.2	91.8	94.8	93.3

Fig. 14**Table. UC-to-phosphorescence ratios of [Sensitizer]/[Annihilator] in TCB and micelles**

Sensitizer/Annihilator pair	Solution (x10⁻⁵) (TCB)	Micelles (x10⁻⁵)
ppy3/DBP	1.3	25
ppy2/DBP	3.8	31
tmd/DBP	2.1	98

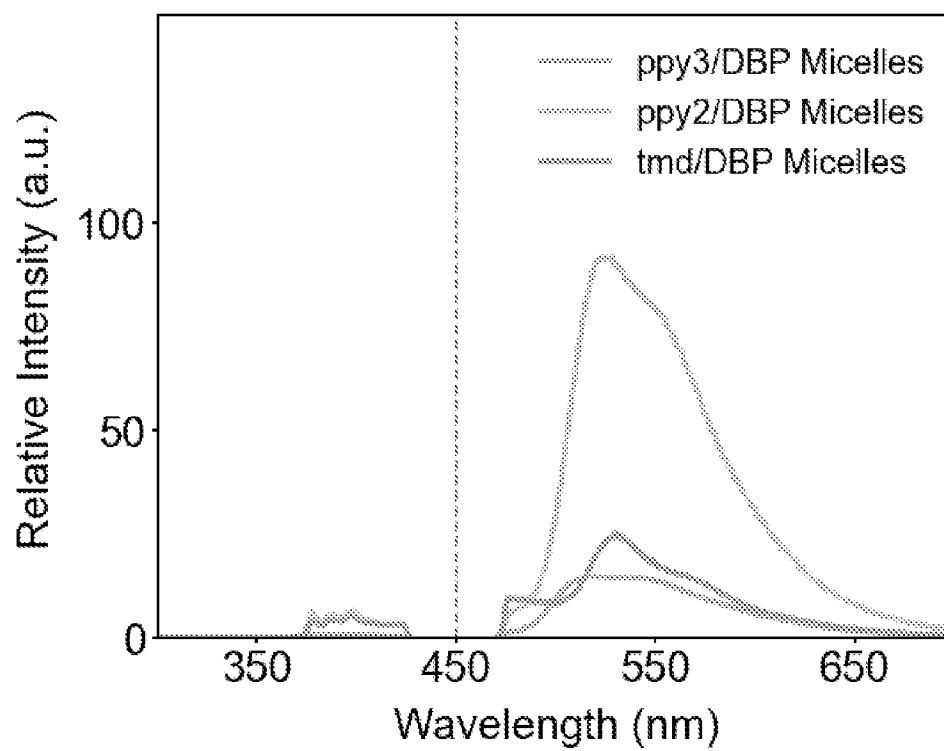
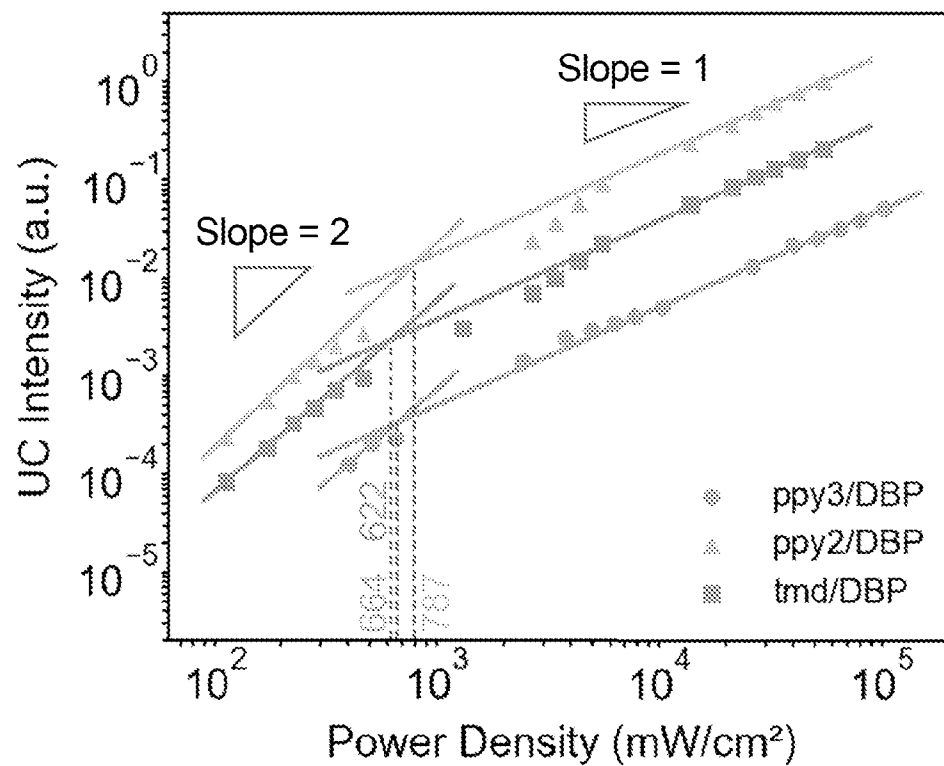
Fig. 15**Fig. 16**

Fig. 17

Table. Concentrations of [Sensitizer]/[Annihilator] in TCB/chloroform solutions used to fabricate UV-emitting UC micelles in Fig. 17B.

Sensitizer/ Annihilator	Pyrene	DBP	TIPS-Nph	PPO
ppy3	[0.7 mM]/[25 mM]	[0.7 mM]/[50 mM]	[0.7 mM]/[25 mM]	[0.7 mM]/[100 mM]
ppy2	[5.6 mM]/[25 mM]	[5.6 mM]/[60 mM]	[5.6 mM]/[25 mM]	[5.6 mM]/[100 mM]
tmd	[15 mM]/[25 mM]	[15 mM]/[300 mM]	[15 mM]/[125 mM]	[15 mM]/[600 mM]
CBDAC	[2 mM]/[25 mM]	[2 mM]/[50 mM]	[2 mM]/[25 mM]	[2 mM]/[100 mM]
4CzIPN	[4.3 mM]/[25 mM]	[4.3 mM]/[50 mM]	[4.3 mM]/[25 mM]	[4.3 mM]/[100 mM]

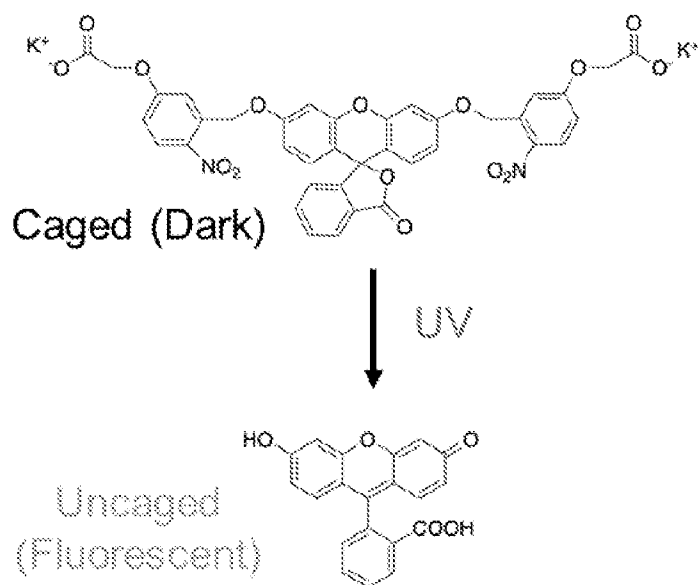
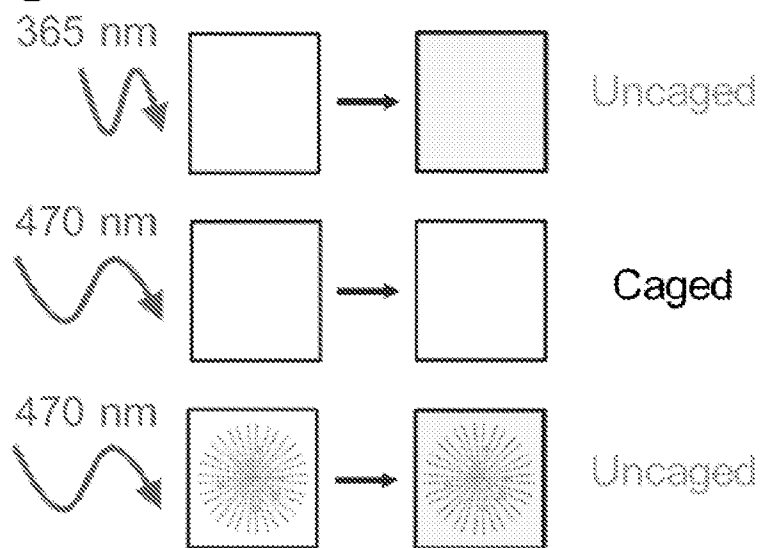
Fig. 18A**Fig. 18B**

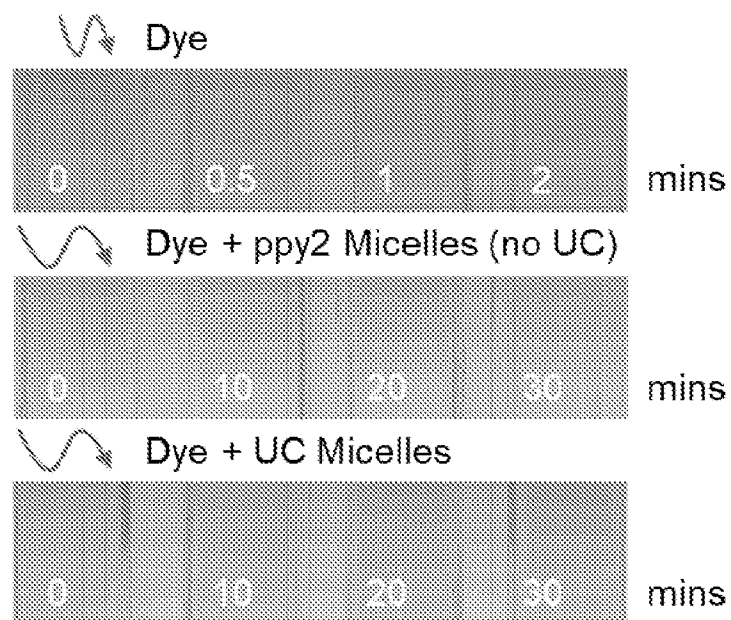
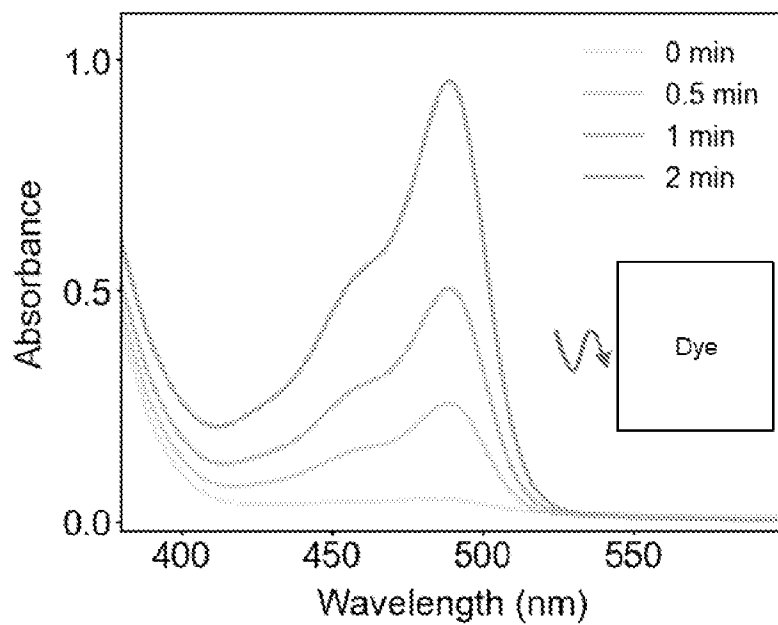
Fig. 18C**Fig. 18D**

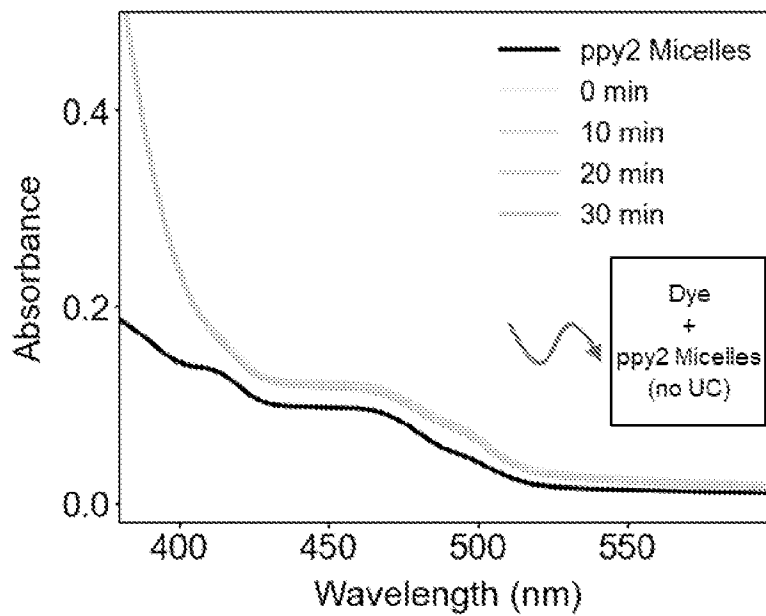
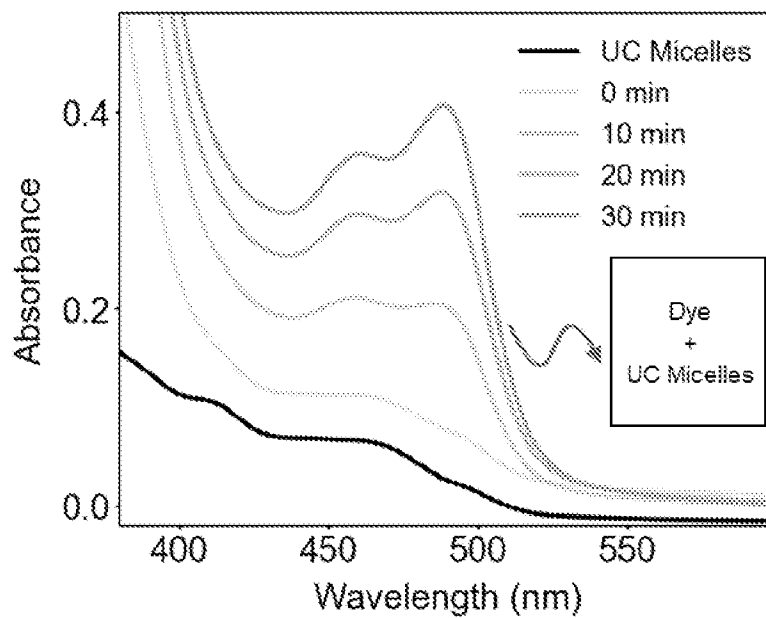
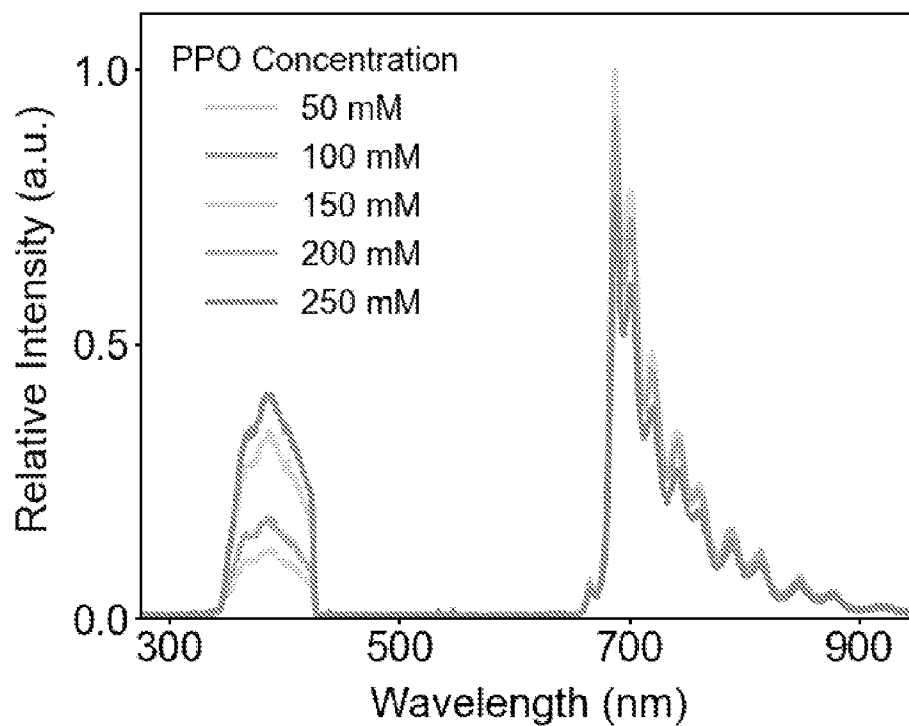
Fig. 18E**Fig. 18F**

Fig. 19**Fig. 20****Table. Estimation of Φ_{UC} of the optimized micelles using a relative method.**

	Bulk solution (toluene)			Micelles		
	UC intensity (a.u.)	Abs _{447 nm}	Measured Φ_{UC}	Relative UC intensity	Abs _{447 nm}	Calculated Φ_{UC}
ppy3	1	0.0789	1.4%	0.00061	0.0074	0.0091%
ppy2	1	0.188	2.0%	0.0085	0.0252	0.13%
tmd	1	0.0625	3.2%	0.012	0.0382	0.064%

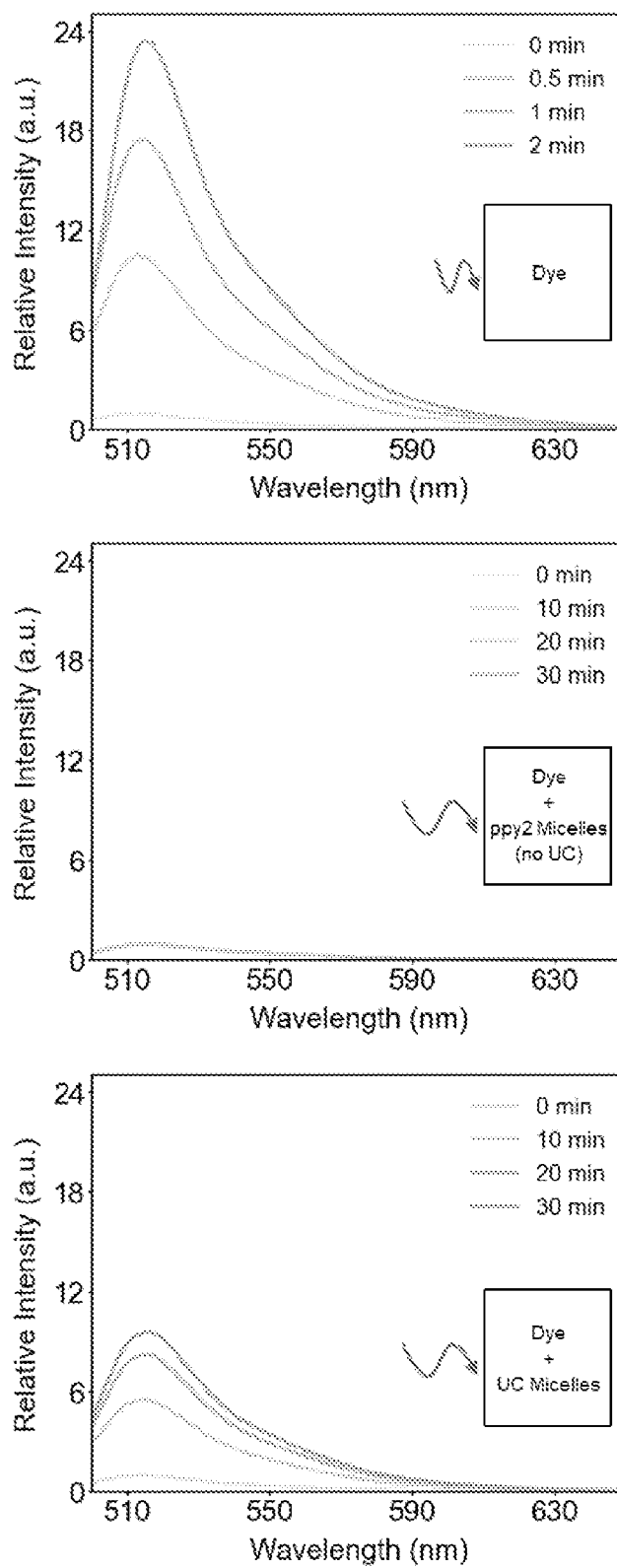
Fig. 21

Fig. 22C

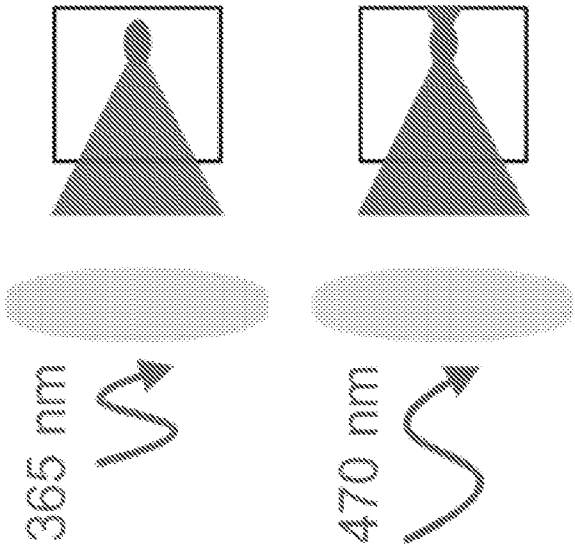


Fig. 22B

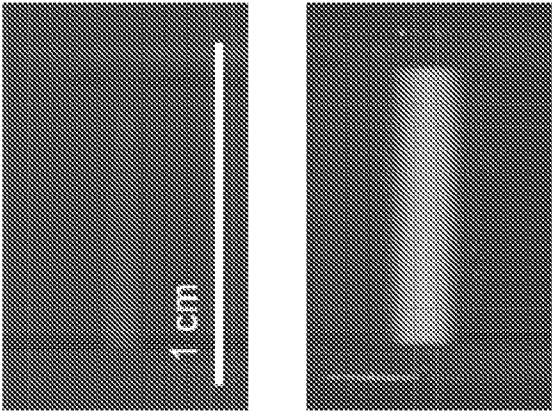


Fig. 22A

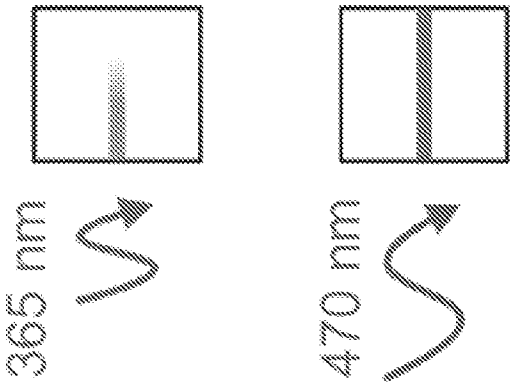


Fig. 22D

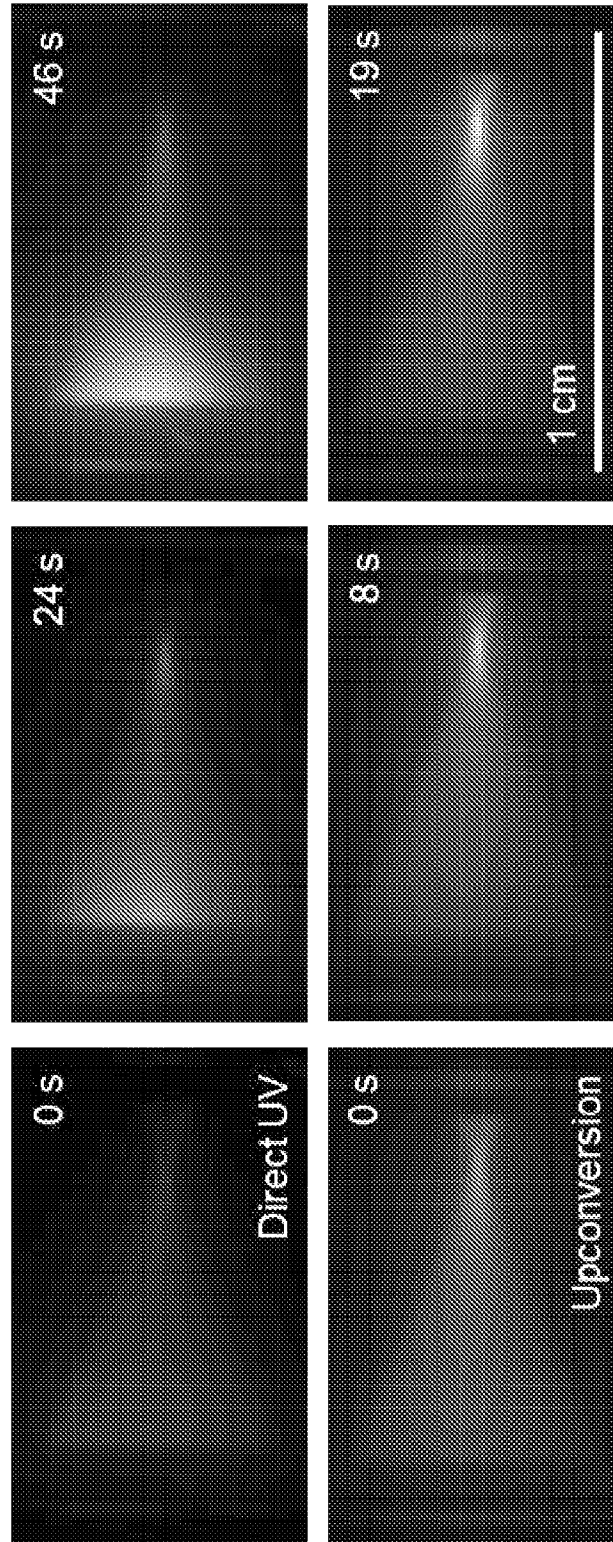


Fig. 22E

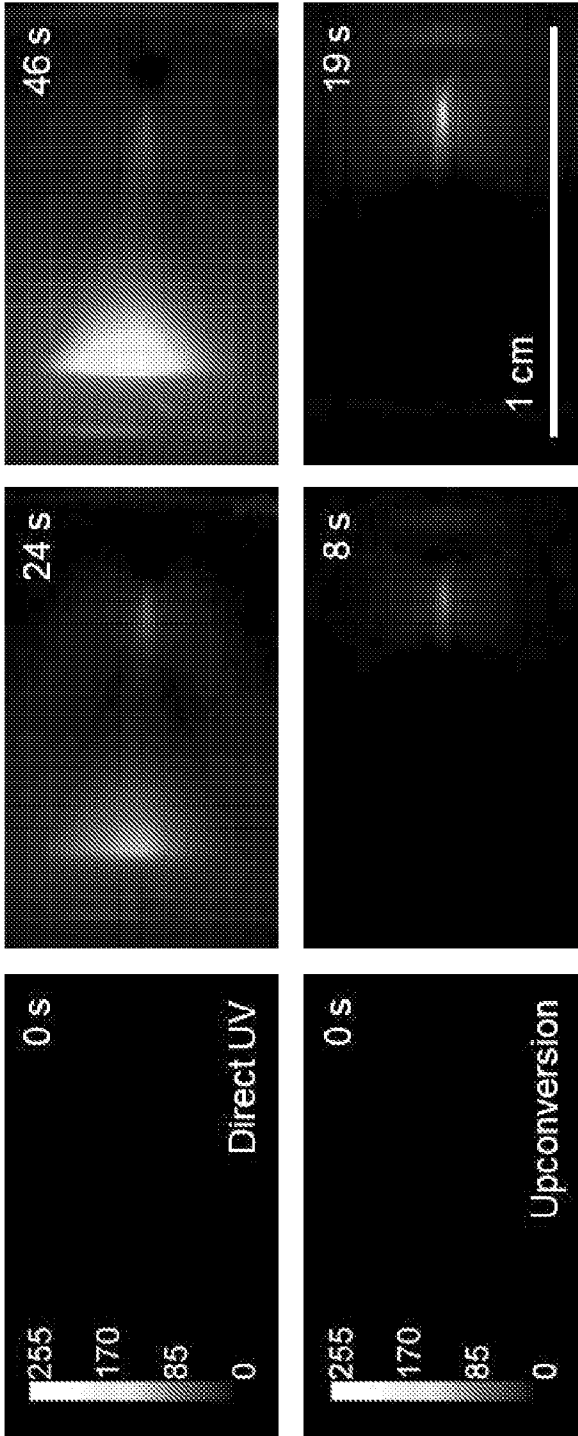


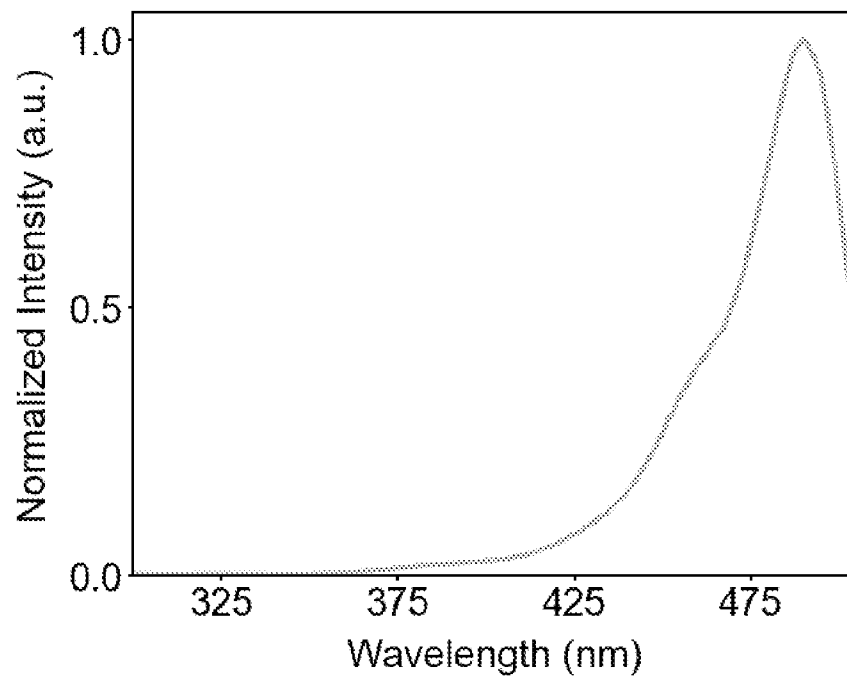
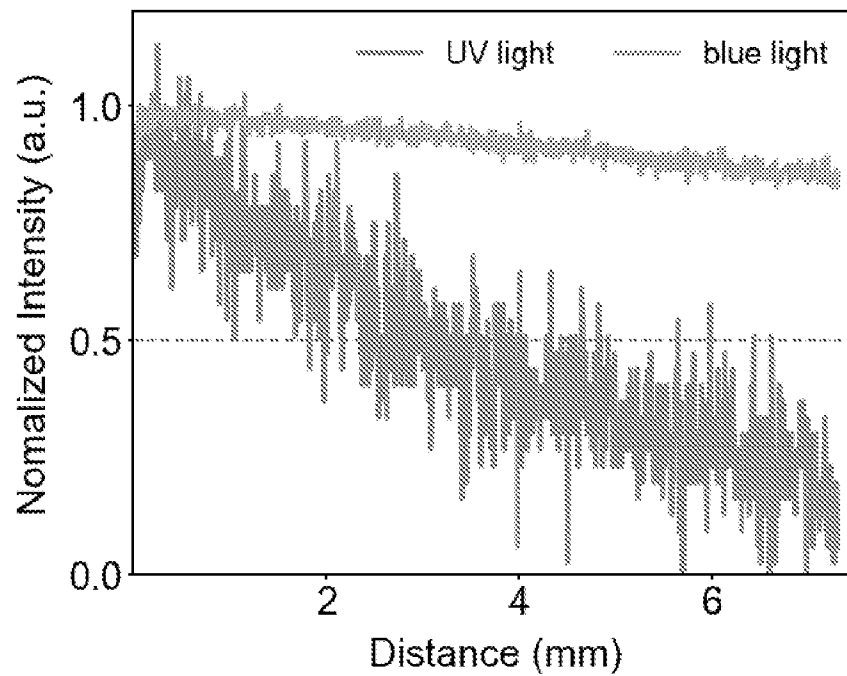
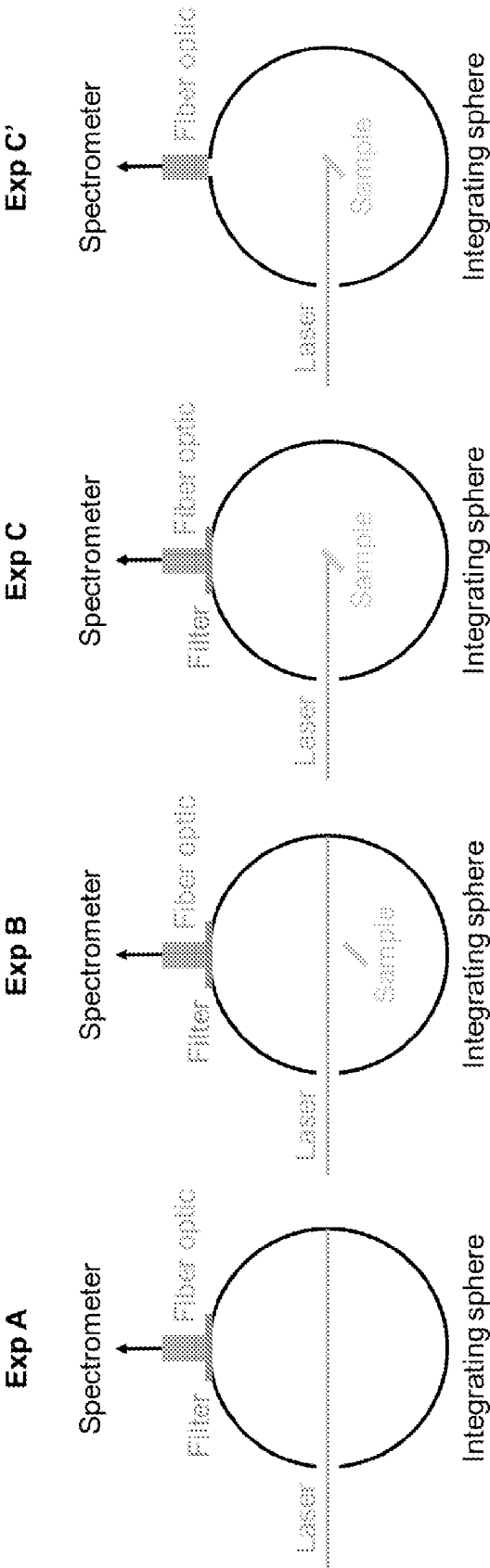
Fig. 23**Fig. 24**

Fig. 25



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 23/67306

A. CLASSIFICATION OF SUBJECT MATTER

IPC - INV. G01J 1/42, F21L 4/02 (2023.01)

ADD. B05D 3/06 (2023.01)

CPC - INV. G01J 1/429, G01J 1/42, F21L 4/02

ADD. B05D 3/061

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

See Search History document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

See Search History document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2022/0025255 A1 (PRESIDENT AND FELLOWS OF HARVARD COLLEGE) 27 January 2022 (27.01.2022); para [0005]-[0006], [0023]-[0025], [0028], [0032]-[0033], [0035], [0038]-[0039], [0045]-[0047], [0058]-[0059], [0067], [0071]-[0072], [0092]; Figs. 1 and 2B	1-6, 8-9, 17-21
Y		7, 10-13
Y	US 2021/0159438 A1 (NANOCO TECHNOLOGIES LTD.) 27 May 2021 (27 May 2021); para [0039], [0042], [0080], [0082]	7, 10-11
Y	US 2019/0169495 A1 (ADOLPHE MERKLE INSTITUTE, UNIVERSITY OF FRIBOURG) 06 June 2019 (06.06.2019); para [0050]	12
Y	WO 2021/154897 A1 (QUADRATIC 3D, INC.) 05 August 2021 (05.08.2021); pg 11 para 6; pg 15 para 1	13
A	US 2021/0228719 A1 (THE UNIVERSITY OF HONG KONG) 29 July 2021 (29.07.2021); see entire document	1-13, 17-21
A	US 2019/0275151 A1 (CAMPOS et al.) 12 September 2019 (12.09.2019); see entire document	1-13, 17-21
A	US 2018/0311353 A1 (CHILDRENS MEDICAL CENTER CORPORATION) 01 November 2018 (01.11.2018); see entire document	1-13, 17-21
A	US 2017/0236653 A1 (THE FLORIDA STATE UNIVERSITY RESEARCH FOUNDATION INC.) 17 August 2017 (17.08.2017); see entire document	1-13, 17-21
A	US 2016/0222286 A1 (MAX-PLANCK-GESELLSCHAFT ZUR FORDERUNG DER WISSENSCHAFTEN) 14 August 2016 (04.08.2016); see entire document	1-13, 17-21

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"D" document cited by the applicant in the international application

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

28 August 2023

Date of mailing of the international search report

SEP 27 2023

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents

P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-8300

Authorized officer

Karl Rodriguez

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 23/67306

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 14-16, 22-33
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.