Electronic Supplementary Material (ESI) for Nanoscale.

Supplemental Information

Controlling the Durability and Optical Properties of Triplet-Triplet Annihilation Upconversion Nanocapsules

Authors: Tracy H. Schloemer[a], Samuel N. Sanders[b], Pournima Narayanan[a,c], Qi Zhou[a], Manchen Hu[a], and Daniel N. Congreve[a,b*]

Affiliations:
[a]Department of Electrical Engineering, Stanford University, Stanford, CA 94305

[b]Rowland Institute at Harvard University, Cambridge, MA 02142

[c]Department of Chemistry, Stanford University, Stanford, CA 94305

*congreve@stanford.edu

Materials and Methods

Materials: All chemicals were used as received. 9,10-bis((triisopropylsilyl)ethynyl)anthracene) (TIPS-an), Coumarin 30, and anhydrous (3-aminopropyl)triethyoxysilane (APTES) were purchased from Sigma Aldrich. PdTPTBP and PtOEP were purchased from Frontier Scientific. 99% oleic acid (OA) was purchased from Beantown Chemical. Anhydrous tetraethyl orthosilicate (TEOS), anhydrous acetone, and tetra-*tert*-butylperylene (TTBP) were purchased from Acros Organics. Bis(9,10-phenylethynyl)anthracene (BPEA), tetrahydrofuran (THF), and anhydrous ethanol were purchased from Thermo Fisher Scientific. 2-bromo-9,10-diphenylanthracene (Br-DPA) and Coumarin 153 were purchased from TCI Chemicals. 10K MPEG-Silane was purchased from Nanosoft Polymers. BODIPY 505/515 (BODIPY) was purchased from Cayman Chemicals. 2,5-Bis(2-ethylhexyl)-3,6-di(furan-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (DPP) was purchased from Ambeed Chemical. Water was purified using a Millipore Milli-Q lab water system.

Measurements:

Photographs were taken with a with a Canon EOS Rebel T6i. All images presented are unedited.

Upconversion Photoluminescence spectra were recorded with an Ocean Optics QE Pro. No variation in emission shape or time was observed throughout the measurement. A Thorlabs Power meter PM100D with a S120VC photodiode was used to measure the laser power as a function of the laser dial setting. To determine the spot size, a knife-edge measurement was performed by measuring the total power seen as a blade edge was moved along the diameter of the spot. The resulting power vs. distance plot was used to calculate the beam width.

Samples for the upconversion emission spectra and corresponding photographs in **Figs. 2-3** were prepared in the glovebox as follows. The vials containing the capsule reaction mixture were sealed and brought into the glovebox (<0.5 ppm O_2). After vigorously shaking the vial containing the capsule reaction mixture, 20 µL of the solution was added to 1980 µL of anhydrous acetone in a 10 mm pathlength quartz cuvette unless noted otherwise. The cuvette was sealed before removing from the glovebox. The samples were irradiated at 635 nm at a power density of 66 W cm^{-2}.

Samples for the upconversion emission spectra in **Fig. S4** was prepared by diluting capsule paste in degassed MilliQ ultrapure water (100 mg mL^{-1}) and diluting it 3:1 (v/v) in anhydrous acetone in a 10 mm pathlength quartz cuvette unless noted otherwise. The cuvette was sealed before removing from the glovebox. The samples were irradiated at 635 nm at a power density of 66 W cm^{-2}.

Samples for the upconversion emission spectra in **Fig. 5** was prepared by diluting 500 µL of the nanocapsule reaction supernatant in 1 mL MilliQ water and 1.5 mL acetone.

The geometry of the setup was fixed to compare relative emission intensities of reaction aliquots and capsule paste solutions respectively. We note that we could not use an integrating sphere/external calibration light source to make quantitative comparisons, as we could not generate a detectible upconversion emission signal due to the low absolute concentration of UC materials

in the nanocapsule dispersion. Due to this experimental setup, we emphasize relative trends within a particular experiment and make no quantitative claims regarding absolute light output.

Emission spectra in **Fig. S7** were collected using a Horiba FluoroLog Fluorimeter. Capsules previously dispersed in ethanol/water (1 mL) were further diluted in ethanol (2 mL) and transferred to a 10 mm pathlength quartz cuvette.

UV-Vis Absorption spectra in **Fig. S9** were collected using an Agilent Cary 6000i UV/Vis/NIR Spectrophotometer using either a 2 mm or 10 mm pathlength quartz cuvette.

Atomic Force Microscopy After vigorous agitation, a sample of the reaction mixture was diluted by a factor of $1x10^4$ (Fig. 4C-F) or $5x10^5$ (Fig. 4A-B) in MilliQ water by means of serial dilutions. 10 µL of each unfiltered mixture was drop-cast on a clean glass microscope cover slip. The samples were dried under light vacuum for 20 min at room temperature, and then for >48 hours in an ambient atmosphere at room temperature. AFM images were collected in ambient air using a Park Systems Park NX10 in tapping mode. Particle diameters were extracted using ImageJ software with data from at least 50 particles used to prepare **Fig. 5**.

Dynamic Light Scattering Directly from the capsule reaction mixture after vigorous agitation, 300 µL of the solution was removed from the glovebox. In an ambient atmosphere, 2700 µL of fresh, ultrapure (MilliQ) water was added. The mixture was filtered with a 220 nm PVDF syringe filter into 10 mm polystyrene cuvette. The data was collected on a Brookhaven Instruments 90Plus Nanoparticle Size Analyzer. The temperature was held at 25 °C with a 1 s equilibration time and 3 total measurements per sample. Apparent nanoparticle aggregation was not observed when analyzing samples fabricated with 3.0 mL TEOS/0.4 g PEG-silane with an order of magnitude difference in concentration. After the initial DLS characterization, some samples were diluted 2x by volume in acetone and re-characterized by DLS (**Table S4**, **Fig. S2**).

Upconversion Nanocapsule Fabrication:

Stock Solution Preparation:

1. *TIPS-An/PdTPTBP Nanocapsules:* Fresh upconversion stock solutions were prepared for each batch of capsules. Under red lighting in the glovebox (<0.5 ppm O_2), saturated solutions of the sensitizer (PdTPTBP, ~2 mg mL^{-1}) and annihilator (TIPS-anthracene, ~5 mg mL^{-1}) were prepared in 99% oleic acid at room temperature and the mixtures were allowed to stir for at least 4 hours before filtering with a 0.45 μm PTFE filter. Red lighting was used to prevent demetallation of PdTPTBP.[1] Stock solutions for the capsule fabrication were prepared with 0.4 mL TIPS-an, 0.5 mL PdTPTBP, and 1.6 mL OA for fabrication Method 1. After the stock solutions were prepared, rigorous red lighting was no longer required and ambient lighting was used. These volume ratios can be scaled down for use in fabrication Method 2.
2. *TTBP/PdTPTBP Nanocapsules:* Fresh upconversion stock solutions were prepared for each batch of capsules. The saturated PdTPTBP solution was prepared as described for TIPS-an/PdTPTBP nanocapsules. An 11.5 mg mL^{-1} solution of TTBP was prepared in 99% oleic acid at room temperature and the mixture was allowed to stir for at least 4 hours before filtering with a 0.45 μm PTFE filter. Stock solutions for the capsule fabrication were prepared with 150 μL TTBP, 75 μL PdTPTBP, and 25 μL OA for fabrication Method 2.
3. *BPEA/PdTPTBP Nanocapsules*: Fresh upconversion stock solutions were prepared for each batch of capsules. The saturated PdTPTBP solution was prepared as described for TIPS-an/PdTPTBP nanocapsules. A saturated solution of BPEA (0.45 mg mL^{-1}) was prepared in 99% oleic acid at room temperature and the mixture was allowed to stir for at least 4 hours before filtering with a 0.45 μm PTFE filter. Stock solutions for the capsule fabrication were prepared with 300 μL BPEA and 150 μL PdTPTBP for fabrication Method 2.
4. *BrDPA/PtOEP Nanocapsules*: Fresh upconversion stock solutions were prepared for each batch of capsules. Under red lighting in the glovebox (<0.5 ppm O_2), solutions of the sensitizer (saturated PtOEP, ~5 mg mL^{-1}) and annihilator (BrDPA, 18.4 mg mL^{-1}) were prepared in 99% oleic acid at 90 ºC. The mixtures were allowed to stir for 2 hours before cooling and filtering with a 0.45 μm PTFE filter. Stock solutions for the capsule fabrication were prepared with 75 μL BrDPA, 150 μL PtOEP, and 25 μL OA for fabrication Method 2.
5. *Coumarin 153 Nanocapsules*: A 10 mg mL^{-1} solution of Coumarin 153 was prepared in 99% oleic acid at room temperature and the mixture was allowed to stir for at least 4 hours before filtering with a 0.45 μm PTFE filter. This stock solution was used without further dilution for fabrication Method 2.
6. *Coumarin 30 Nanocapsules*: A saturated solution of Coumarin 30 (~5 mg mL^{-1}) was prepared in 99% oleic acid at room temperature and the mixture was allowed to stir for at least 4 hours before filtering with a 0.45 μm PTFE filter. This stock solution was used without further dilution for fabrication Method 2.
7. *BODIPY Nanocapsules*: A saturated solution of BODIPY (~2 mg mL^{-1}) was prepared in 99% oleic acid at room temperature and the mixture was allowed to stir for at least 4 hours before filtering with a 0.45 μm PTFE filter. This stock solution was used without further dilution for fabrication Method 2.

8. *DPP Nanocapsules*: A saturated solution of DPP (~5 mg mL^{-1}) was prepared in 99% oleic acid at room temperature and the mixture was allowed to stir for at least 4 hours before filtering with a 0.45 μm PTFE filter. This stock solution was used without further dilution for capsule fabrication Method 2.

Capsule Fabrication General Comments:

- Samples were prepared in one of two methods based upon the required synthetic scale, adapted from Ref.[2,3]. By DLS and UC photoluminescence over multiple batches, the methods are comparable. The pH of the water after nanocapsule fabrication is typically between 5 and 6.
- We choose to discuss the feed quantities of APTES, TEOS, and MPEG-silane in terms of masses and volumes, and not concentrations, because the concentrations change as each material is added to the oleic acid/water emulsion.
- Nanoparticles synthesized *via* oil/water emulsification do not contain the same number of solutes (i.e., each nanocapsule does not all contain the same number of sensitizer molecules). Instead, during the emulsification process, the solutes are expected to distribute among nanodroplets according to a Poisson distribution.[4] Because of this phenomenon, the concentrations of sensitizers and annihilators required to observe upconversion in nanocapsules is different than in previous reports[5] where studies were performed in a bulk solution (i.e., no nanoparticles).

Capsule Fabrication Method 1- Large Scale (TIPS-an capsules): Milli-Q water (200 mL) was chilled over an ice bath for at least one hour (temperature ~5 °C) and then poured into to a Vitamix Blender (Amazon.com) in a nitrogen filled glovebox (<0.5 ppm O_2). The upconversion stock solution containing sensitizer and annihilator (1.45 mL) was carefully dispensed into the water in one portion. The solution was blended for 60 s at the maximum speed. The emulsion was split into 20 mL portions and added to 40 mL clear scintillation vials and immediately stirred at 1100 rpm. To each reaction, (3-aminopropyl)triethoxysilane (APTES) (75 μL) was added until the mixture became transparent. Then, 10K MPEG-silane was immediately added and stirred vigorously/shaken to disperse evenly (see **Table S1**). Within 5 minutes of the MPEG-silane addition, anhydrous tetraethyl orthosilicate (TEOS) was added in one portion (see **Table S1**). The flask was sealed and the solution stirred vigorously at room temperature. After approximately 10 mins, the flask was sealed with parafilm before removing from the glovebox and was stirred vigorously at 1100 rpm at a temperature of 65 °C for 42 hours.

Sample	Mass PEG-Silane (g)	Volume TEOS (mL)
1	0.4	0.0
2	0.4	0.4
3	0.4	0.8
4	0.4	1.6
5	0.4	3.0
6	0.4	4.0
7	0.1	3.0
8	0.2	3.0
9	0.8	3.0
10	1.2	3.0

Table S1: A summary of the PdTPTBP/TIPS-anthracene capsules presented in this work using Method 1 (20 mL reaction volumes). All other quantities were held constant (i.e., volume oleic acid stock solutions, volume APTES).

To isolate the upconversion nanocapsule paste characterized in **Fig. S4**, the reaction was allowed to cool to room temperature and was centrifuged for one hour at 8670 × *g*. After discarding the pellet, the supernatant was centrifuged for 14 hours at 8670 × *g* to isolate a paste containing upconversion nanocapsules and water (summarized **Table S2**).

Mass PEG-Silane (g)	Volume TEOS (mL)	Mass Recovered Capsule Paste After Purification (g)
0.4	0.4	0.4214
0.4	0.8	0.8820
0.4	1.6	0.7367
0.4	3.0	0.5807
0.4	4.0	0.3504
1.2	3.0	0.4669

Table S2: A summary of the capsule paste mass recovered after the second centrifugation for nanocapsules using Method 1 (20 mL reaction volumes).

Then, the paste was diluted to a 100 mg mL^{-1} solution in MilliQ water. The solutions were immediately brought into a glovebox (<0.5 ppm O_2) and sparged with nitrogen using a fishtank bubbler for 60s.

Capsule Fabrication Method 2- Small Scale: Fresh upconversion stock solutions were prepared for each batch of capsules. Milli-Q water (20 mL) was sparged under nitrogen for 30 minutes in a 40 mL clear vial before sealing and bringing into a nitrogen filled glovebox (<0.5 ppm O_2). The upconversion stock solution containing sensitizer and annihilator (145 μL) was carefully dispensed into the water in one portion. An emulsion was generated by vortexing the solution at the maximum speed for 7 minutes (VWR Analog Vortex Mixer, VWR). Then, the emulsion was immediately stirred at 1100 rpm. To each reaction, (3-aminopropyl)triethoxysilane (APTES) (75 μL) was added until the mixture became transparent. Then, 0.4 g 10K MPEG-silane was immediately added and stirred vigorously/shaken to disperse evenly. Within 5 minutes of the MPEG-silane addition, 3.0 mL of anhydrous tetraethyl orthosilicate (TEOS) was added in one portion. The flask was sealed and the solution stirred vigorously at room temperature. After approximately 10 mins, the flask was sealed with parafilm before removing from the glovebox and was stirred vigorously at 1100 rpm at a temperature of 65 °C for 42 hours.

For the Coumarin 30, Coumarin 153, BODIPY, and DPP capsules, the capsules were washed to remove residual unencapsulated dye. The reactions were allowed to cool to room temperature and was centrifuged for one hour at 8670 × *g*. After discarding the pellet, the supernatant was centrifuged for 14 hours at 8670 × *g* to isolate a paste containing upconversion nanocapsules and water. After discarding the supernatant, this pellet was dispersed in EtOH/water (17.5 mL, 1:1 v/v) and was centrifuged for 14 hours at 8670 × *g*. The supernatant was discarded, and the pellet was again dispersed in EtOH/water (7.5 mL, 1:1 v/v).

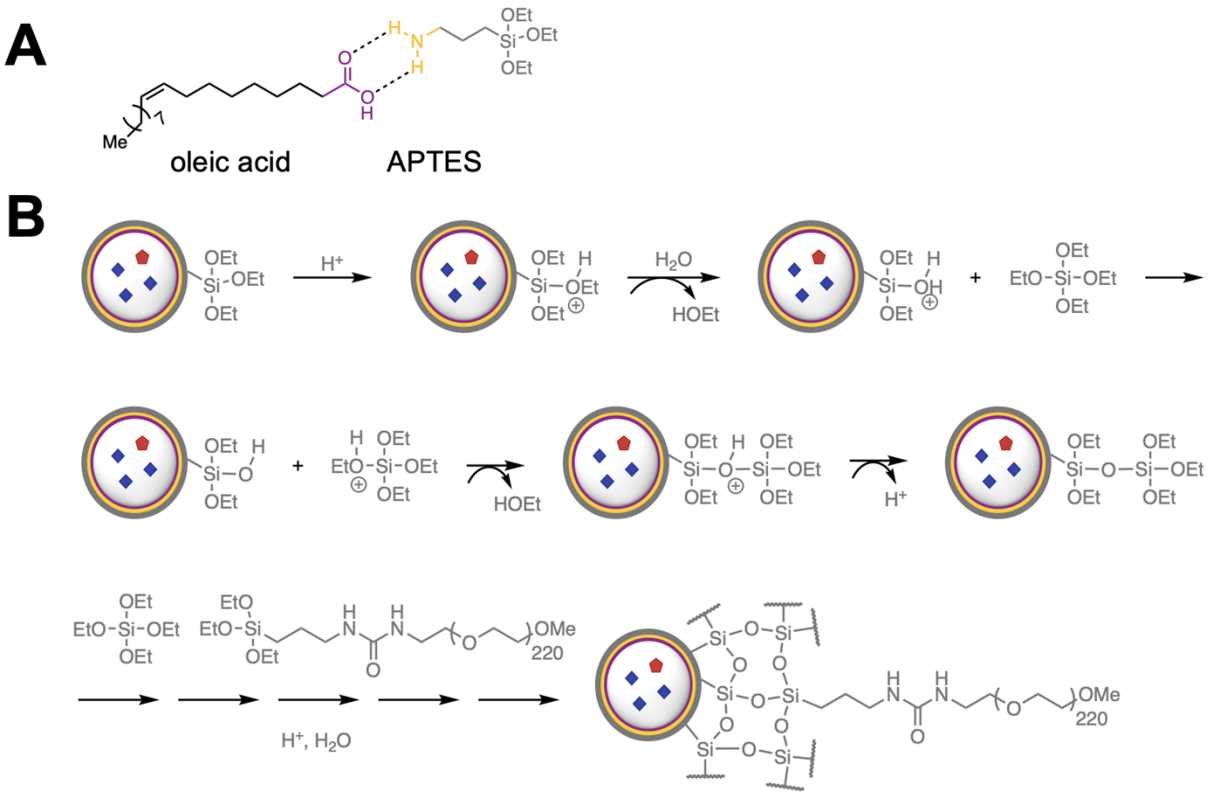


Figure S1: A) Hydrogen bonding between oleic acid and (3-aminopropyl)triethoxysilane (APTES) stabilizes oleic acid nanodroplets and provides triethoxysilane sites upon which silica can grow. B) A simplified reaction scheme depicting the formation of the silica shell around a nanocapsule which ignores the contributions of oligomeric and cyclic species.[6–8] The degree of substitution of silica is shown to be 4 for illustrative purposes and not meant to represent the actual structure where the degree of substitution is likely lower.[6–8] PEG-silane incorporates into the shell to provide steric hindrance, preventing significant nanocapsule aggregation. These condensation reactions also lead to the formation of amorphous, high molecular weight silica that is not incorporated into the nanocapsule shell, depicted in **Figure 1D**.

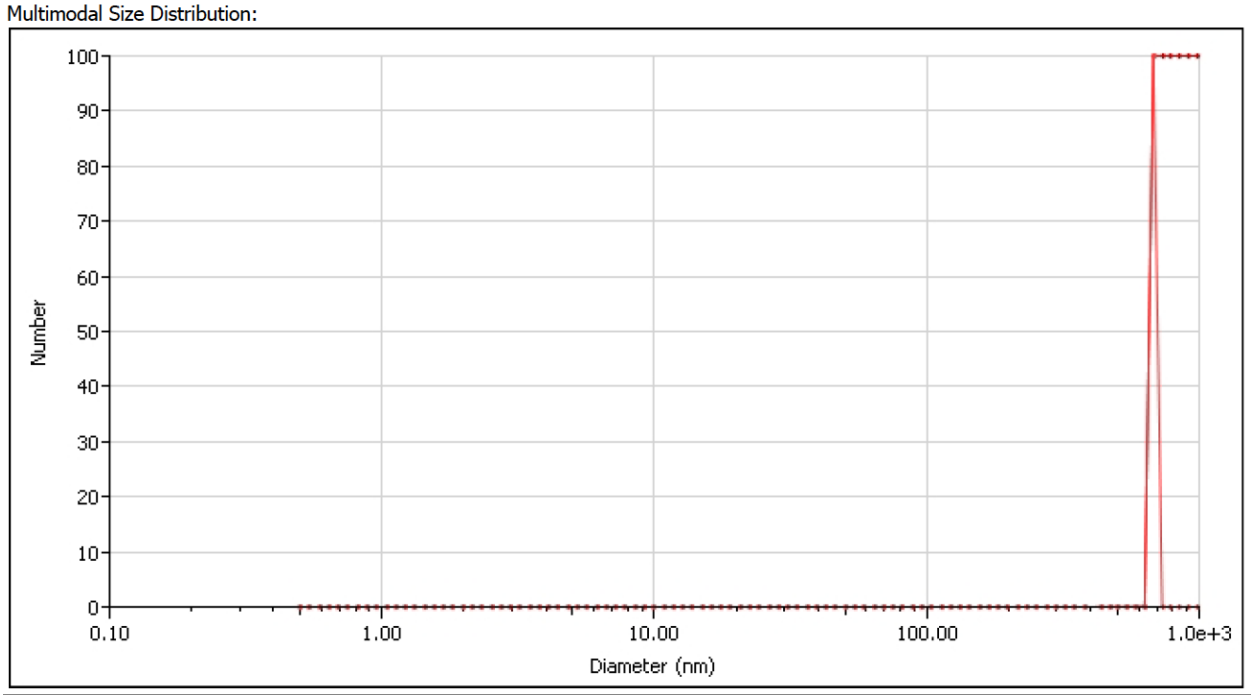
Fig. 2 Sample	Feed Volume TEOS (mL)	Feed Mass MPEG-silane (g)	UC Emission (a.u) at 474 nm	PdTPTBP Phosphorescence (a.u) at 800 nm	Ratio of UCPL (474 nm) to Phosphorescence (800 nm)	Laser Scatter ($x10^2$ a.u.) at 635 nm
UC Emission:Phosphorescence < 0.5						
n/a	0.0	0.4	5.95	62.15	0.10	4.97
A	0.4	0.4	5.02	33.42	0.15	4.23
B	0.8	0.4	4.62	242.42	0.02	6.62
E	4.0	0.4	12.58	47.78	0.26	4.25
0.5 < UC Emission:Phosphorescence < 3						
C	1.6	0.4	287.50	176.70	1.63	10.42
G	3.0	0.2	267.90	130.50	2.05	20.20
I	3.0	0.8	1306.25	850.45	1.54	150.15
J	3.0	1.2	102.77	132.57	0.78	31.27
UC Emission:Phosphorescence > 3						
F	3.0	0.1	753.80	173.40	4.35	217.98
D/H	3.0	0.4	650.60	161.80	4.02	64.51

Table S3: A quantitative comparison of the upconverted emission as compared to sensitizer phosphorescence for the samples presented in **Fig. 2-3**.

Entry	Mass PEG-Silane (g)	Volume TEOS (mL)	Effective Diameter (nm)	PDI
1	0.4	0	566.1 ± 25.8	0.24 ± 0.01
2	0.4	0.4	168.1 ± 3.0	0.22 ± 0.02
3	0.4	3.0	137.1 ± 1.8	0.17 ± 0.01

Table S4: The average effective diameters based upon dynamic light scattering characterization of TIPS-anthracene/PdTPTBP upconversion nanocapsules sampled from the reaction crude diluted in *water and acetone*. Acetone was added immediately before the measurement, which emphasizes the coalescing of oleic acid which is miscible in acetone (Entry 1). Entry 3 represents a control batch which contains a large population of durable nanocapsules. Each entry represents an average of three measurements and the standard deviation. Because we diluted the samples in acetone, larger effective diameters are obtained compared to DLS performed with samples diluted in only water presented elsewhere in this manuscript. This technique is highly dependent upon the solution viscosity per the Stokes-Einstein equation.[9] In this experiment, the viscosity of water was used as a proxy for the true viscosity of the mixed acetone/solvent system when extracting the diffusion coefficient.

A.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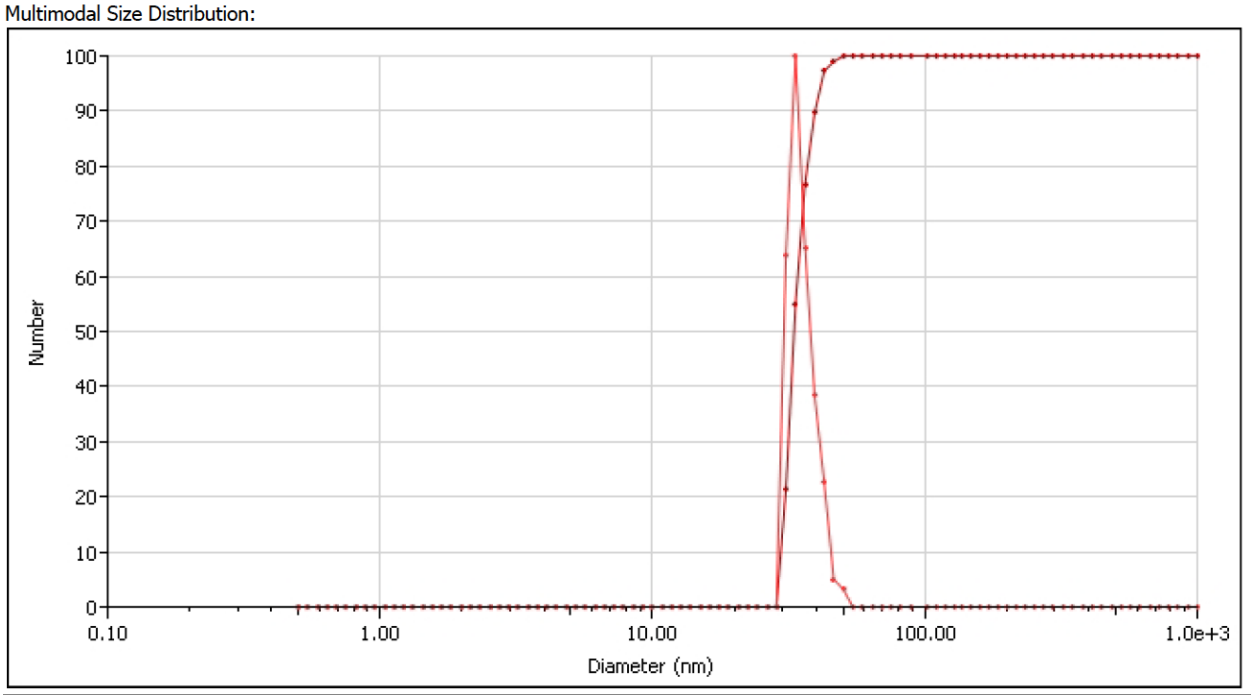
B.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C.

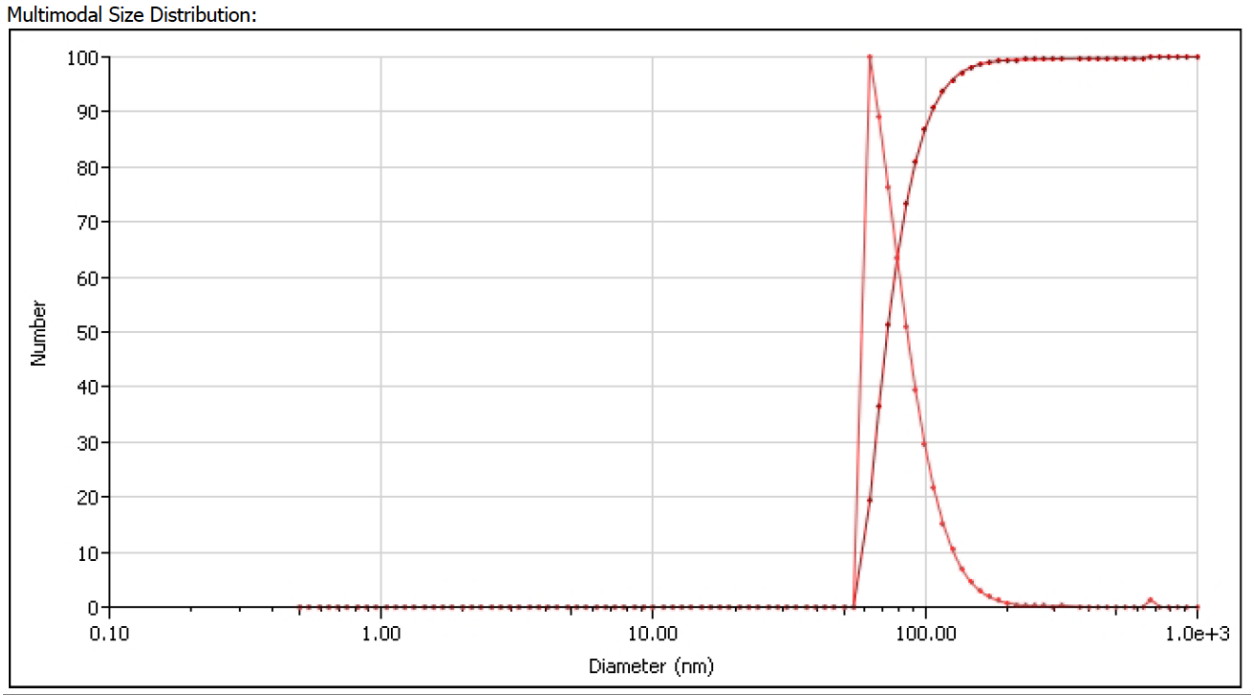


Figure S2: Representative dynamic light scattering traces of TIPS-anthracene/PdTPTBP upconversion nanocapsules sampled from the reaction crude diluted in *water and acetone* presented in **Table S4**.

Mass SiO_2 in purified capsule paste (g)	Molar Mass SiO_2 (g/mol)	Moles SiO_2 (x 10^{-3} mol)	Moles TEOS (x 10^{-3} mol)	Molar Mass TEOS (g/mol)	Mass TEOS (g)	Density TEOS (g/mL)[10]	Volume TEOS (mL)
0.2	60.08	3.33	3.33	208.33	0.7	0.933	0.7
0.3		4.99	4.99		1.0		1.1
0.4		6.66	6.66		1.4		1.5

Table S5: A rough estimate of the TEOS volume required to make nanocapsules. The mass of silica recovered is based upon the mass solids that have been recovered from the purified paste (c.a. 50% of the capsule paste by mass is comprised of solid species[2]). Of course, the mass of the recovered solid is comprised of silica, PEG, oleic acid, PdTPTBP, and TIPS-an, but for simplicity, it is assumed 100% of the mass is silica (SiO_2). While imperfect, it provides a decent approximation of the TEOS volume required to fabricate nanocapsule shells on the scale presented in the **Materials and Methods**.

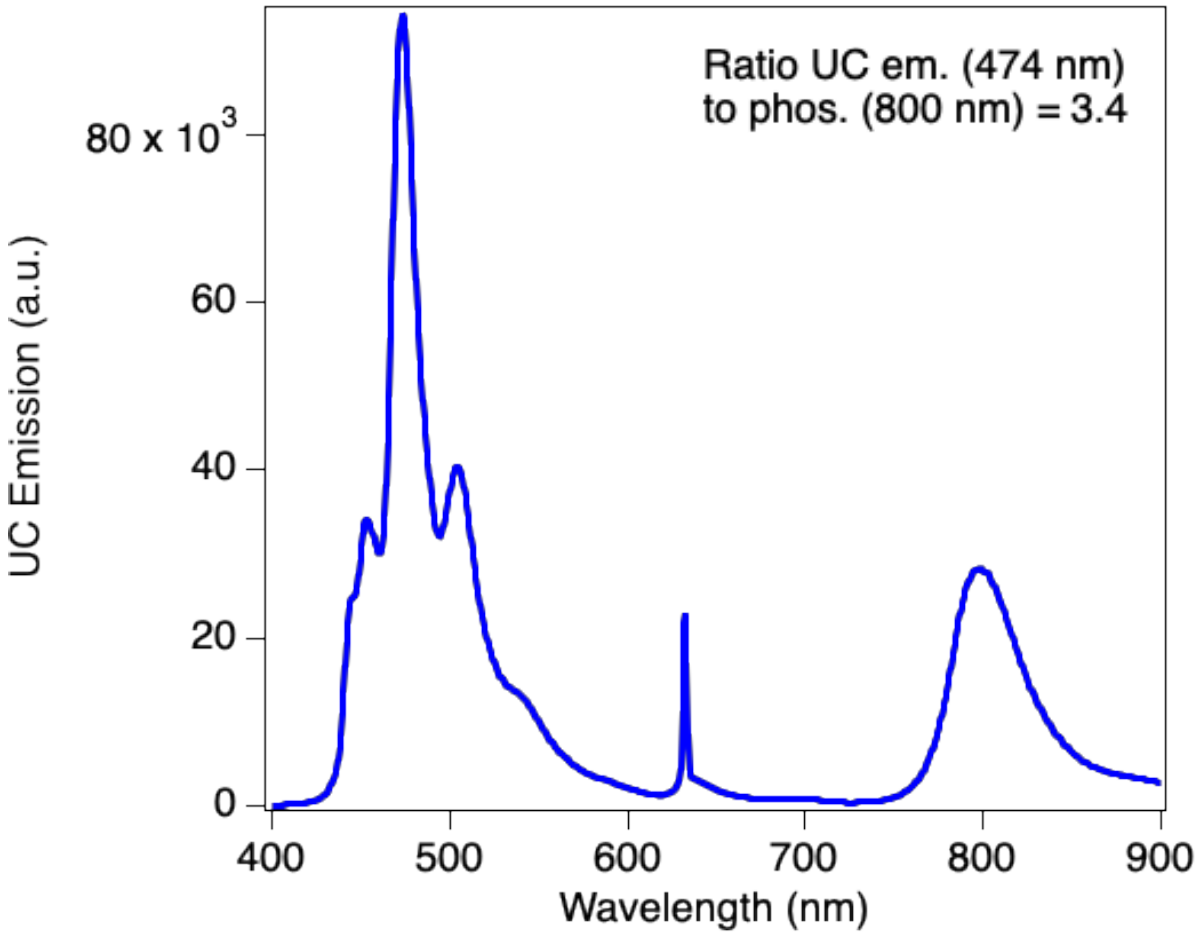


Figure S3: Upconversion emission of the oleic acid solution containing PdTPTBP and TIPS-an used to prepare nanocapsules. TIPS-an upconversion emission is observed from 450-550 nm. The emission peak at 450 nm is significantly reduced in magnitude and distorted due to overlapping sensitizer absorption as well as self-absorption at high concentrations. A 2 mm pathlength quartz cuvette was used to minimize these impacts. PdTPTBP phosphorescence is observed from 750-850 nm. The peak centered at 635 nm originates from laser scatter.

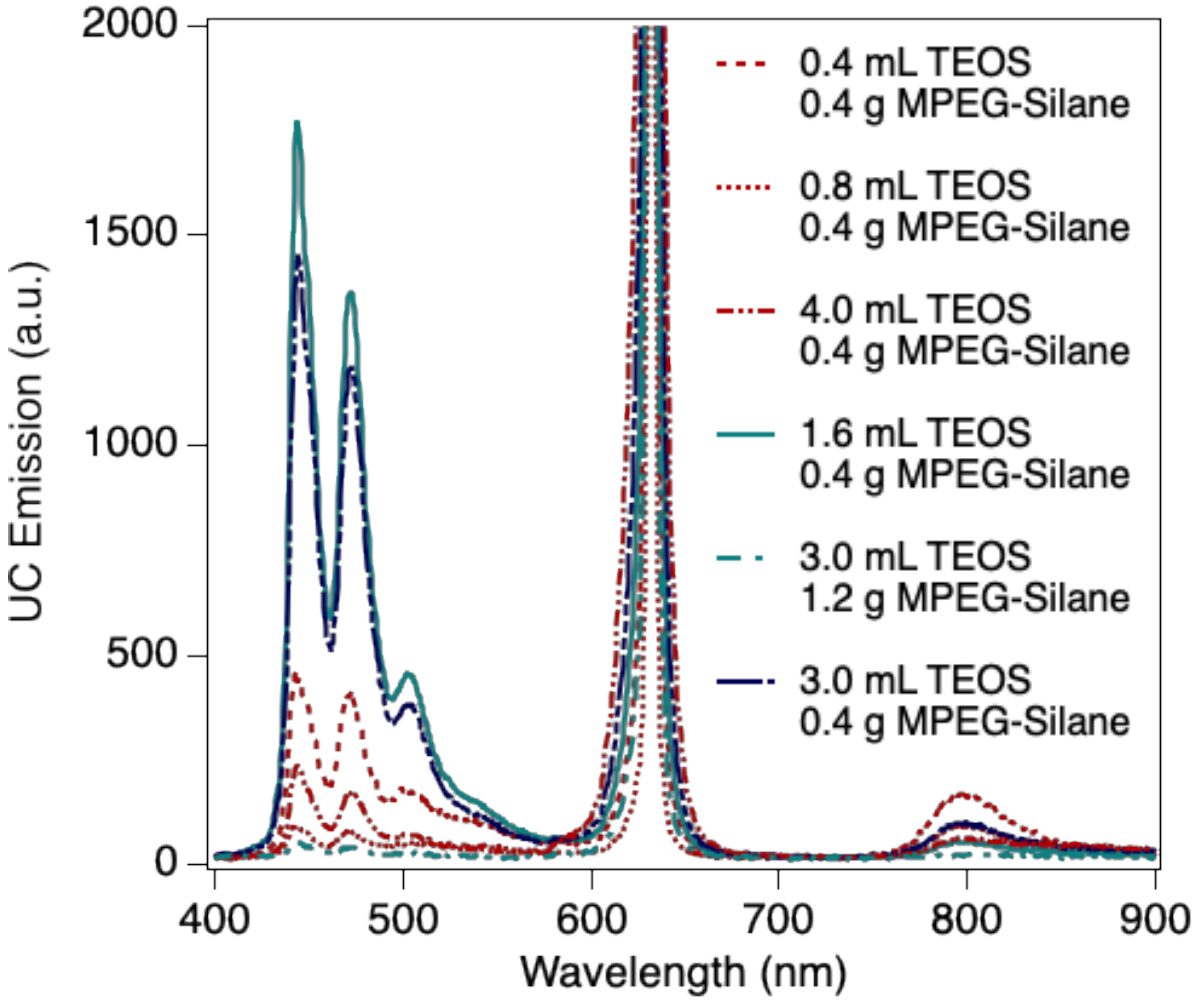
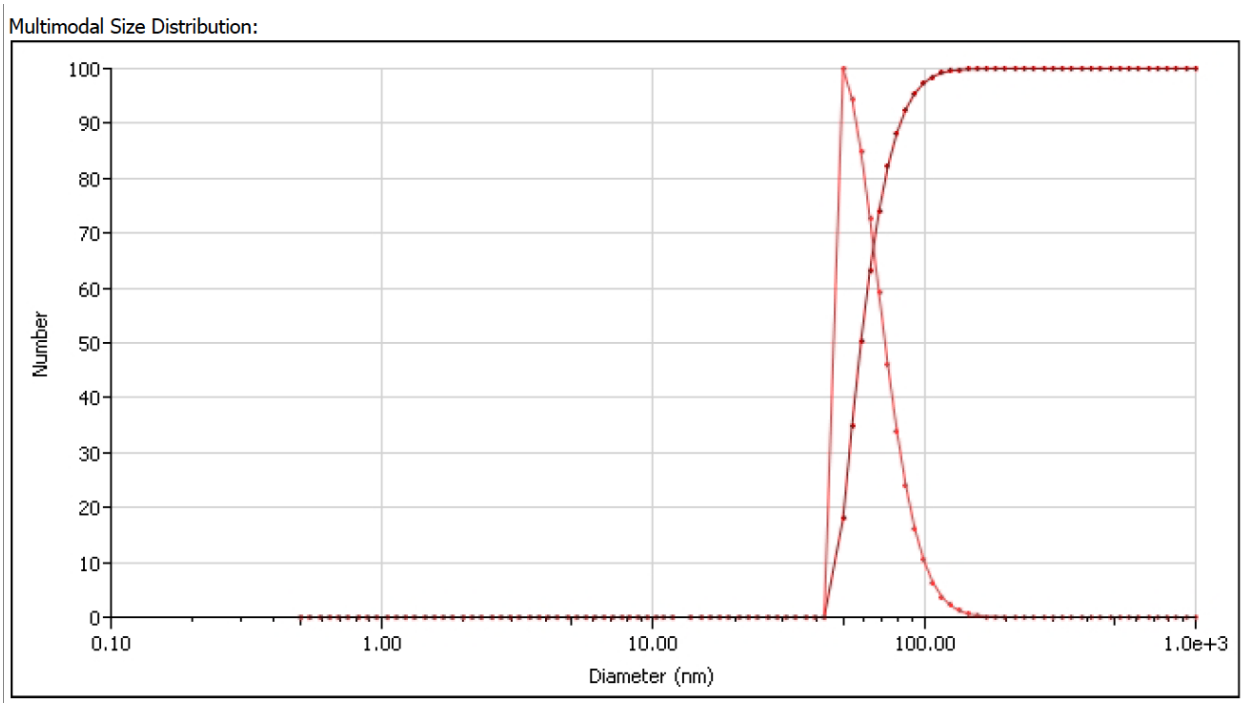


Figure S4: The upconversion photoluminescence spectra for purified upconversion nanocapsules synthesized with varying quantities of tetraethyl orthosilicate and PEG-silane. The capsule paste solution (25 mg mL^{-1}, 3:1 acetone:water) was irradiated with a 635 nm laser over a pathlength of 10 mm at 66 W cm^{-2}. TIPS-an upconversion emission is observed from 450-550 nm and PdTPTBP phosphorescence is observed from 750-850 nm. The peak centered at 635 nm originates from laser scatter.

Fig. 2 Sample	Feed Volume TEOS (mL)	Feed Mass PEG-Silane (g)	Effective Diameter (nm)	PDI
UC Emission:Phosphorescence < 0.5				
n/a	0.0	0.4	77.44 ± 1.0	0.27 ± 0.02
A	0.4	0.4	96.7 ± 2.0	0.18 ± 0.01
B	0.8	0.4	80.7 ± 1.7	0.13 ± 0.04
E	4.0	0.4	93.2 ± 1.1	0.12 ± 0.02
0.5 < UC Emission:Phosphorescence < 3				
C	1.6	0.4	79.6 ± 0.4	0.05 ± 0.03
G	3.0	0.2	111.9 ± 0.9	0.13 ± 0.01
I	3.0	0.8	87.40 ± 0.3	0.19 ± 0.02
J	3.0	1.2	87.4 ± 1.5	0.17 ± 0.01
UC Emission:Phosphorescence > 3				
F	3.0	0.1	151.7 ± 7.0	0.19 ± 0.05
D/H	3.0	0.4	88.8 ± 0.3	0.12 ± 0.02

Table S6: The average effective diameters based upon dynamic light scattering characterization of TIPS-anthracene/PdTPTBP upconversion nanocapsules sampled from the reaction crude diluted in *water* for the samples presented in **Fig. 2-3**. Each entry represents an average of three measurements and the standard deviation.

A.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Diameter (nm)

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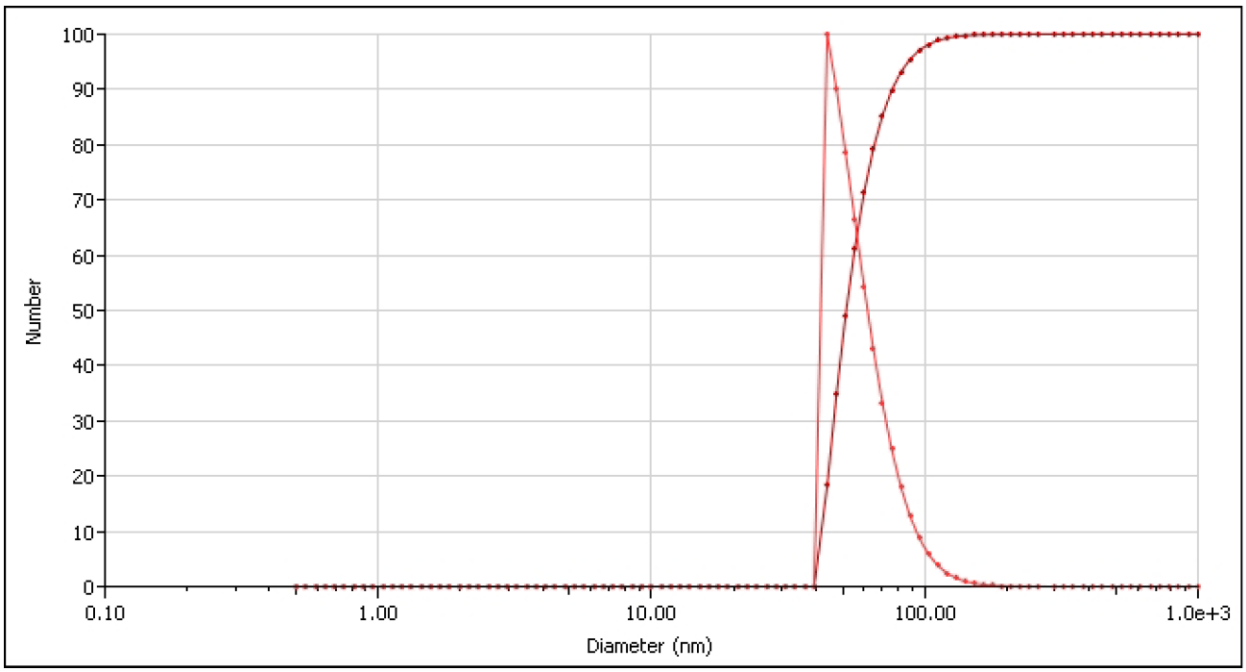
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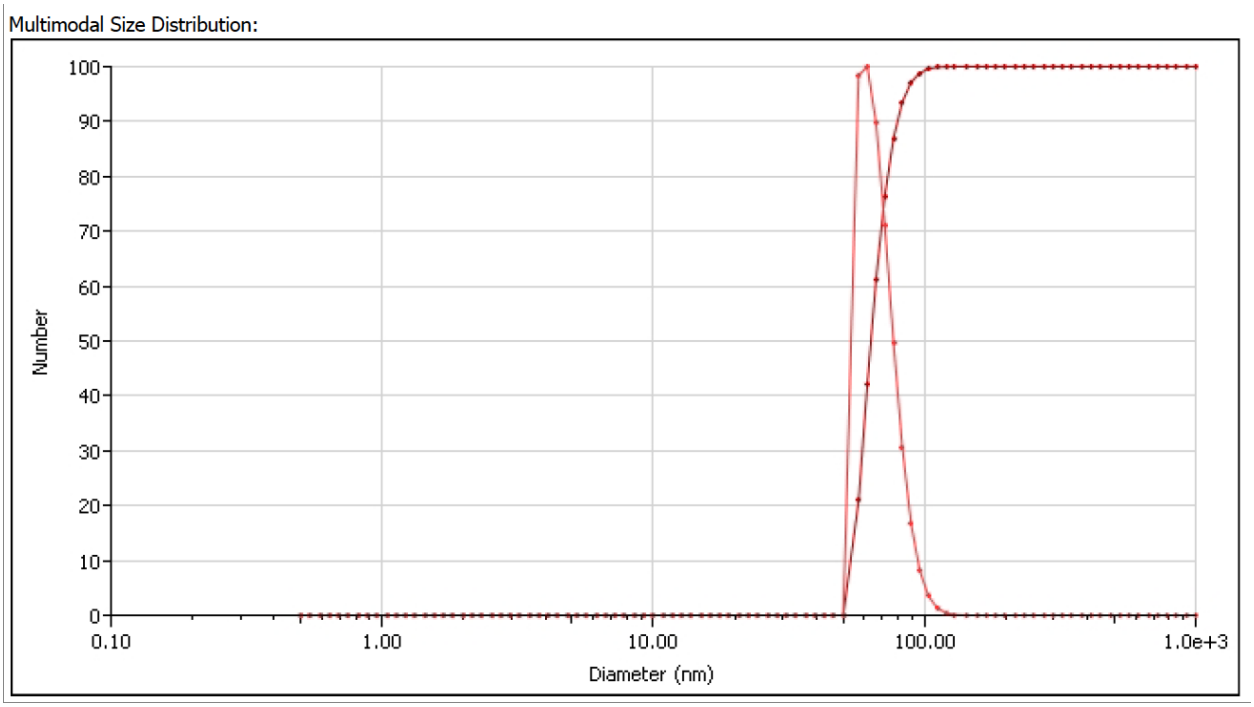
Diameter (nm)

C.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Diameter (nm)

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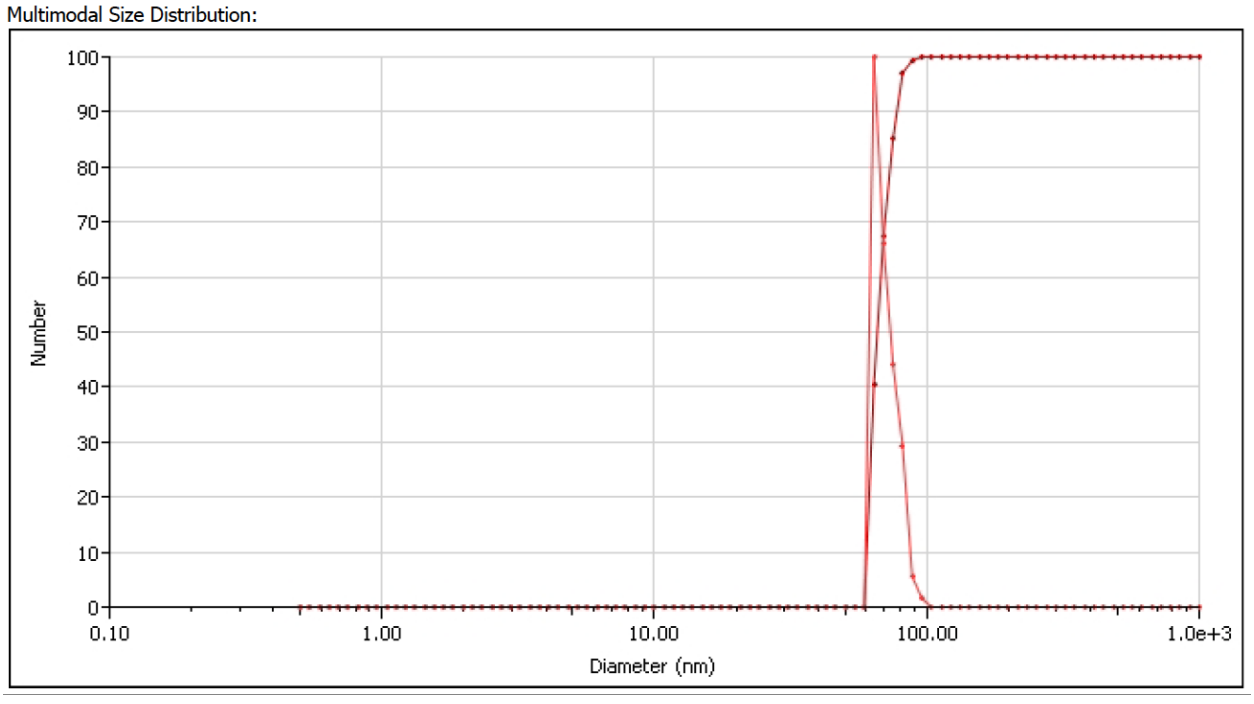
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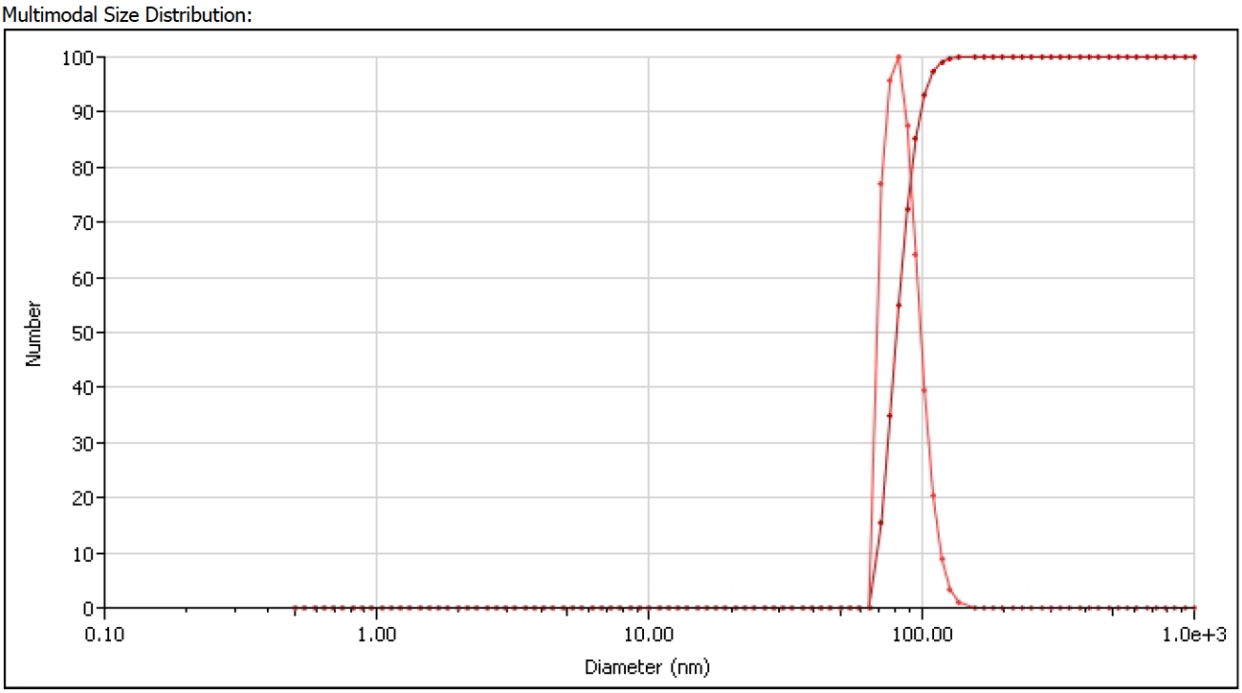
E.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Diameter (nm)

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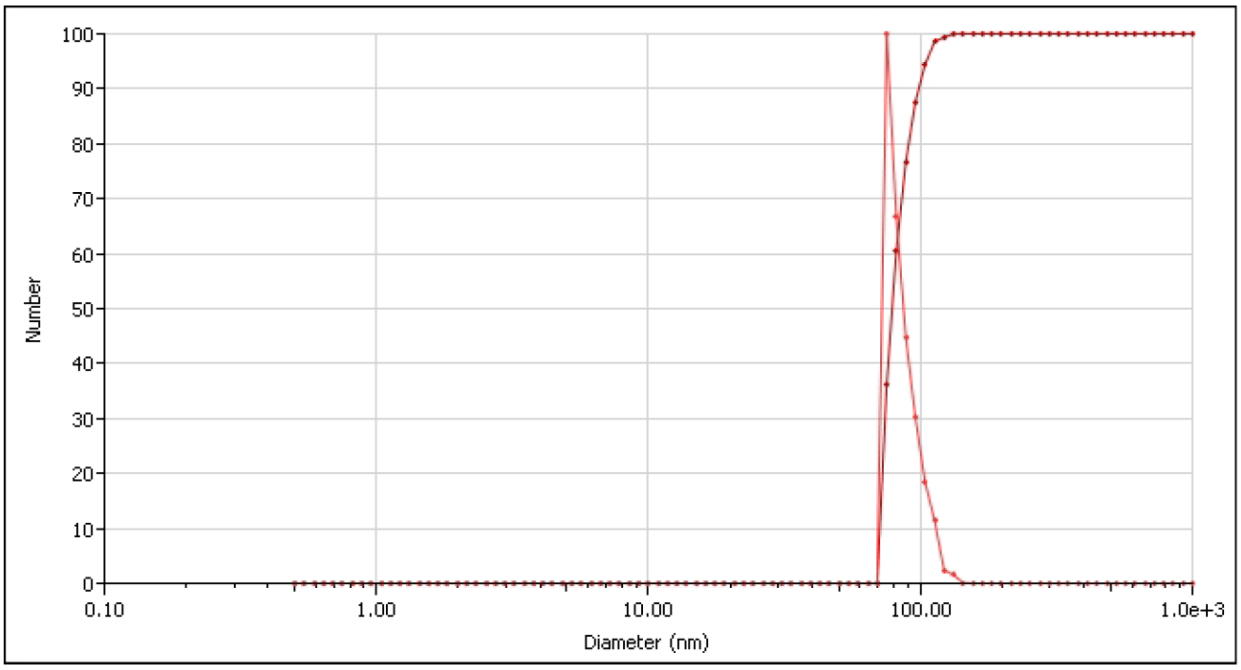
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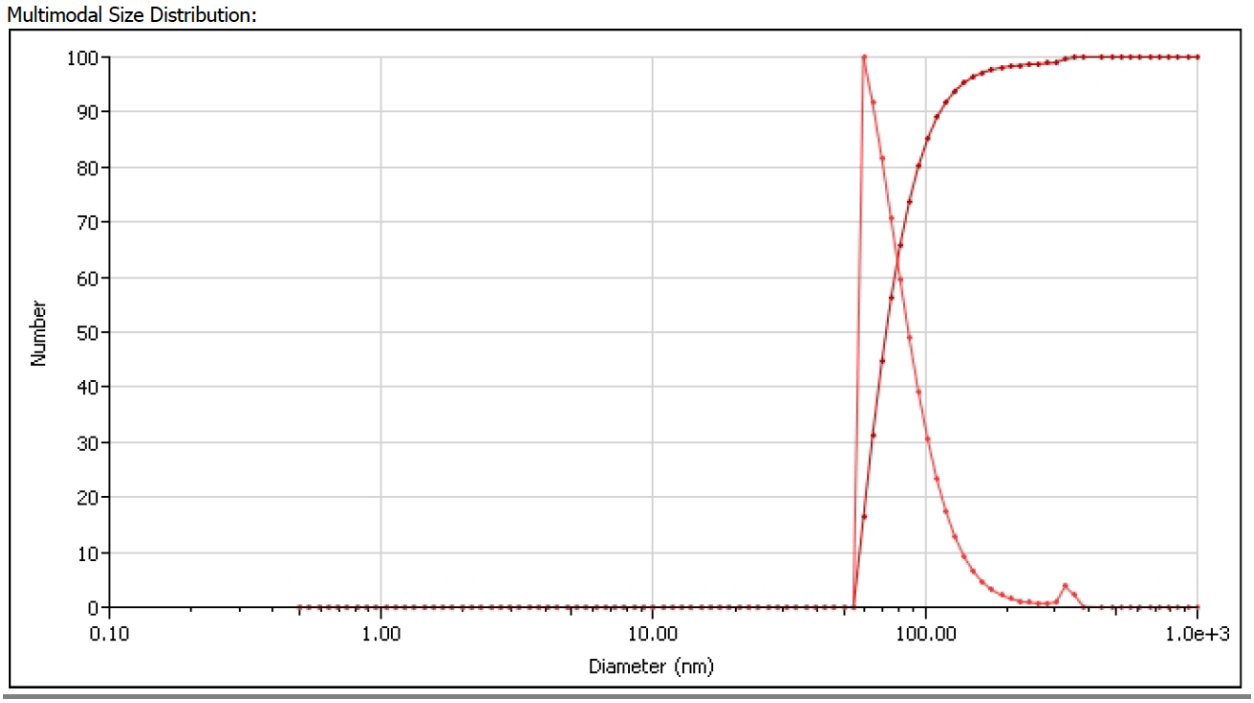
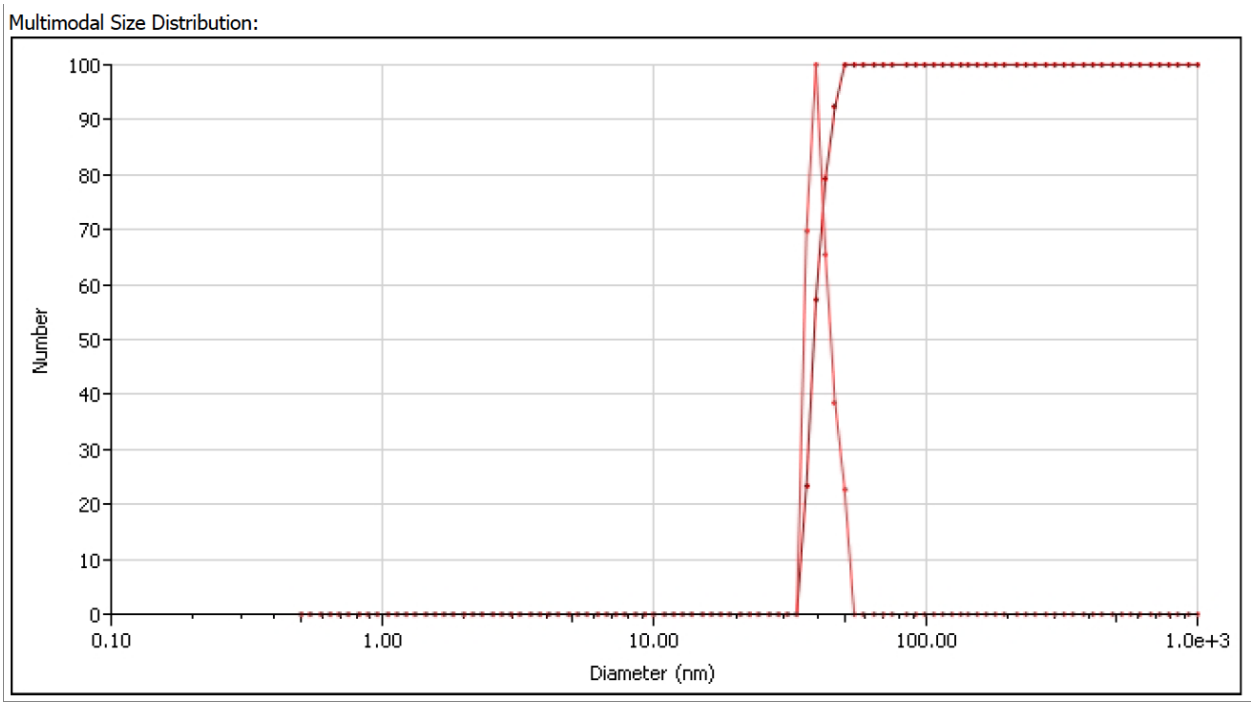
Diameter (nm)

G.


Multimodal Size Distribution:
Number
100
90
80
70
60
50
40
30
20
10
0
0.10
1.00
10.00
100.00
1.0e+3
Diameter (nm)

H.


Multimodal Size Distribution:
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90
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60
50
40
30
20
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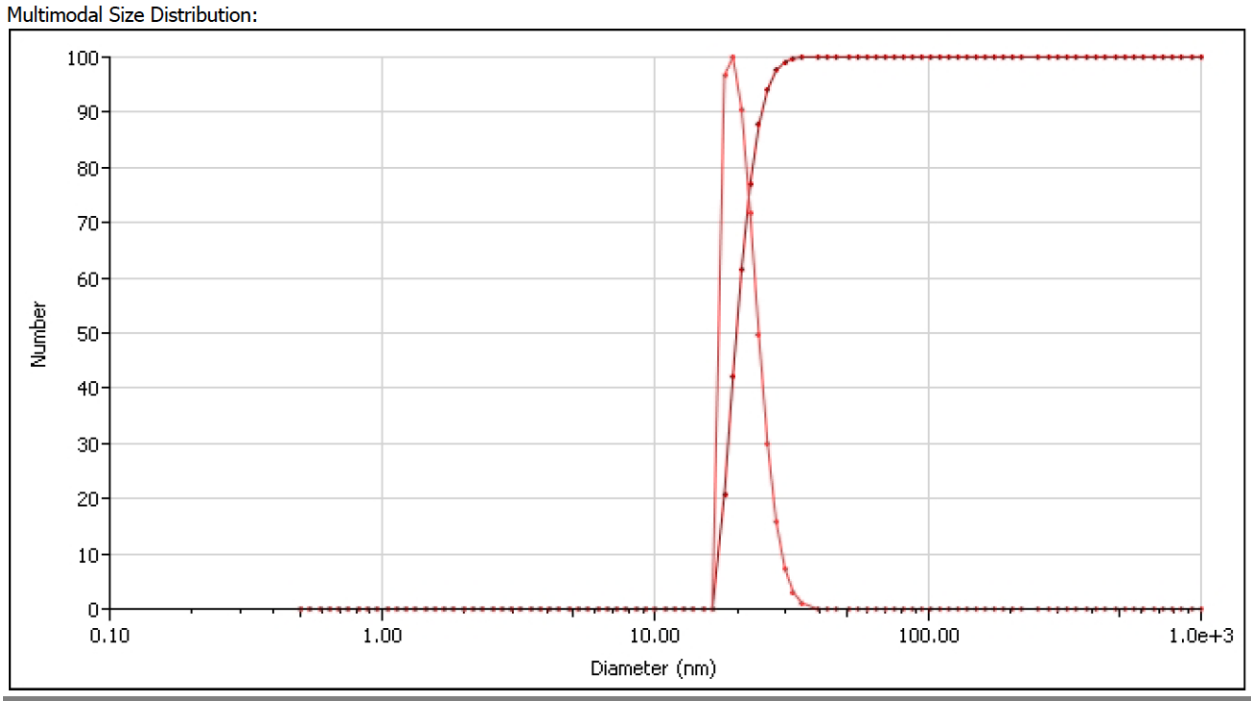
0
0.10
1.00
10.00
100.00
1.0e+3
Diameter (nm)

I.



J.

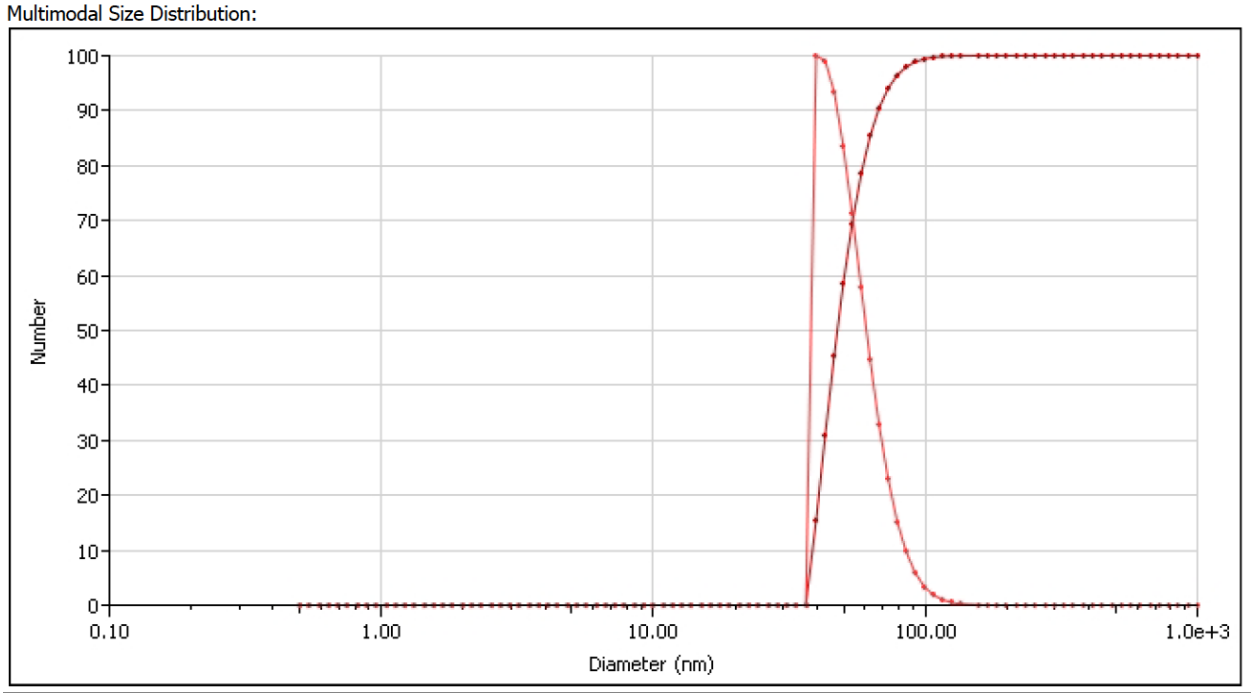


Figure S5: Representative dynamic light scattering traces of TIPS-anthracene/PdTPTBP upconversion nanocapsules sampled from the reaction crude diluted in *water* for samples 1-10 (A-J respectively). The sample entry number corresponds to the numbering in **Table S1**.

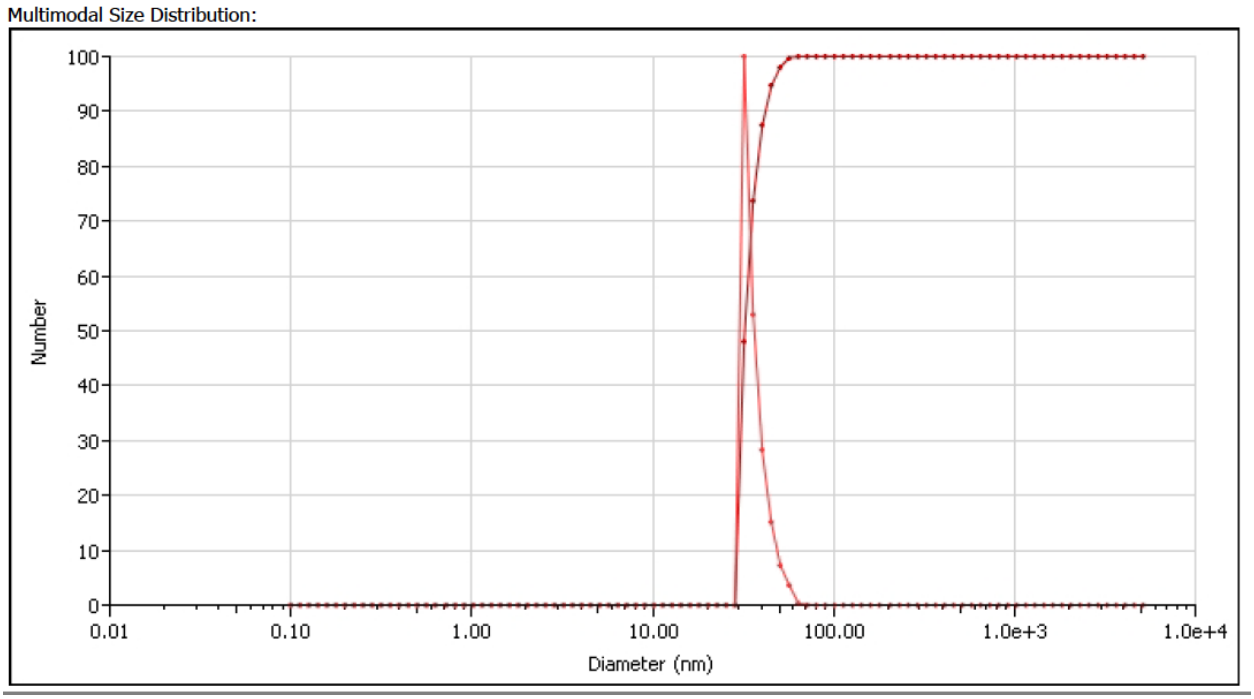
Effective Diameter (nm)	PDI
4.68 ± 2.0	0.89 ± 0.26

Table S7: The average effective diameter based upon dynamic light scattering characterization of the polymer PEG-silane diluted in *water*. This entry represents an average of three measurements and the standard deviation. To mimic nanocapsule fabrication conditions, 400 mg of PEG-silane was added to 20 mL of fresh MilliQ water and stirred at 65 ºC for 48 hours before the size characterization.

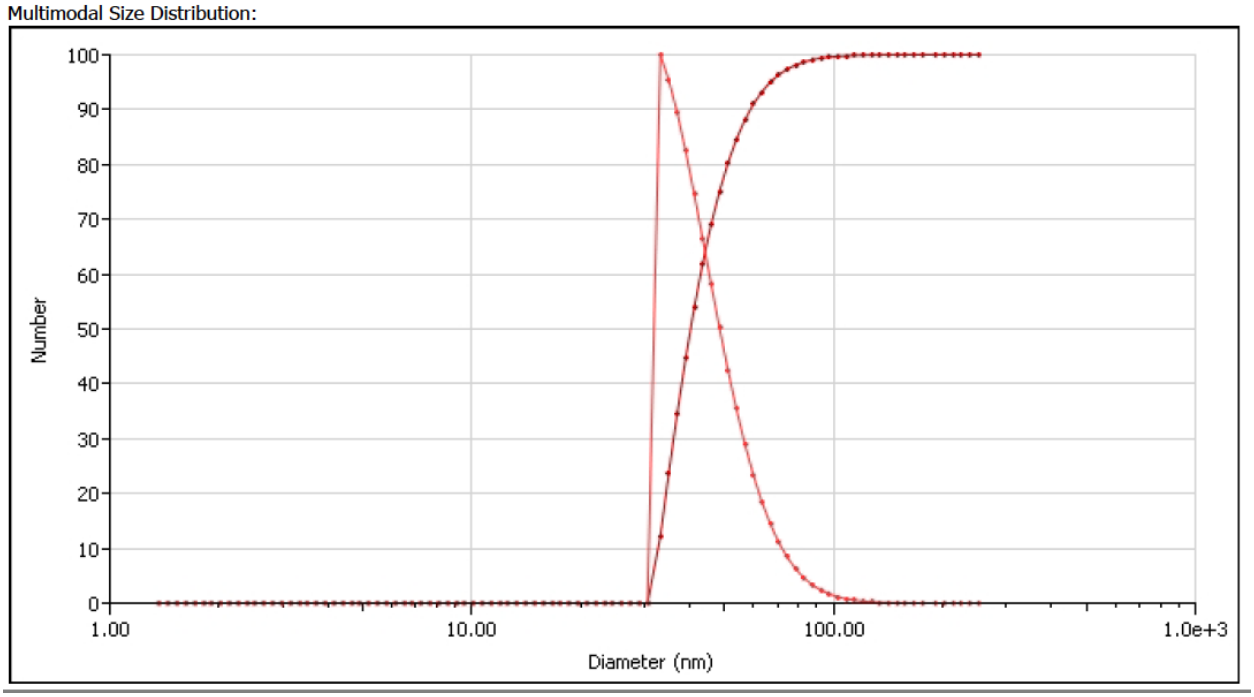
	Effective Diameter (nm)	PDI
PtOEP/BrDPA	125.2 ± 1.7	0.26 ± 0.01
PdTPTBP/TTBP	75.2 ± 1.1	0.16 ± 0.01
PdTPTBP/BPEA	151.1 ± 2.8	0.17 ± 0.01

Table S8: The average effective diameters based upon dynamic light scattering characterization of upconversion nanocapsules sampled from the reaction crude diluted in *water* for the samples presented in **Fig. 5**. Each entry represents an average of three measurements and the standard deviation.

A.


Multimodal Size Distribution:
Number
100
90
80
70
60
50
40
30
20
10
0
0.01
0.10
1.00
10.00
100.00
1.0e+3
1.0e+4
Diameter (nm)

B.


Multimodal Size Distribution:
Number
100
90
80
70
60
50
40
30
20
10
0
1.00
10.00
100.00
1.0e+3
Diameter (nm)

C.

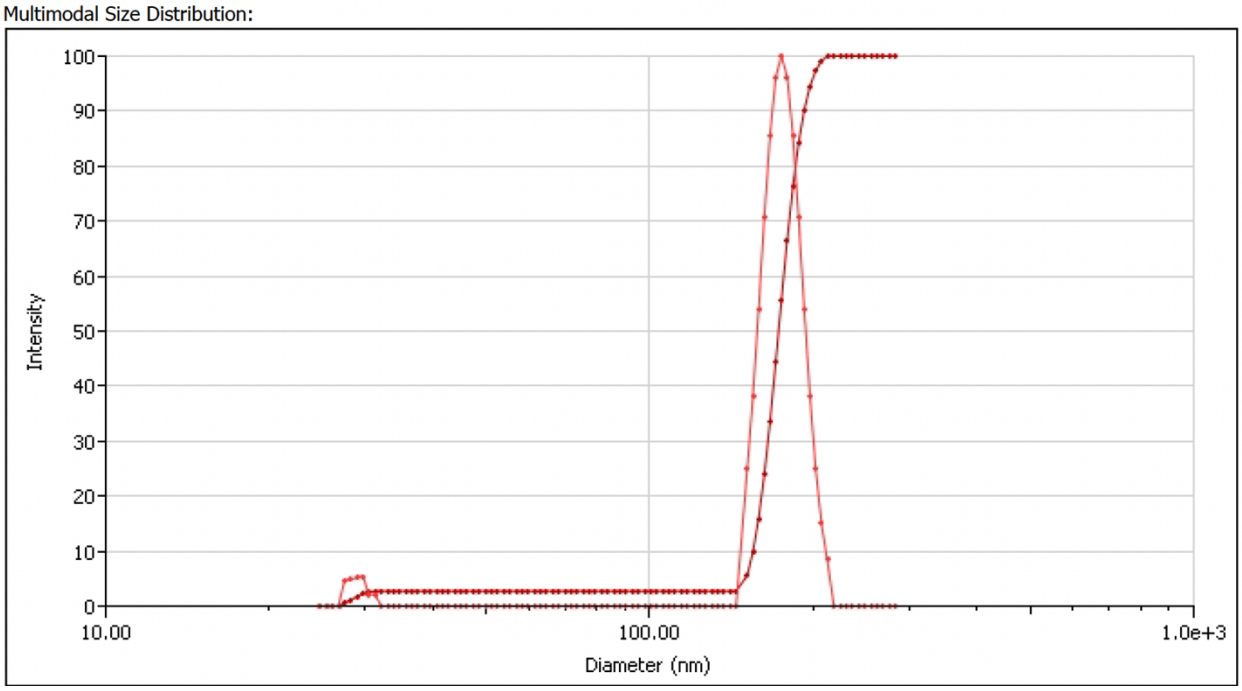


Figure S6: Representative dynamic light scattering traces of PtOEP/BrDPA (A), PdTPTBP/TTBP (B), and PdTPTBP/BPEA (C) upconversion nanocapsules sampled from the reaction crude diluted in *water*.

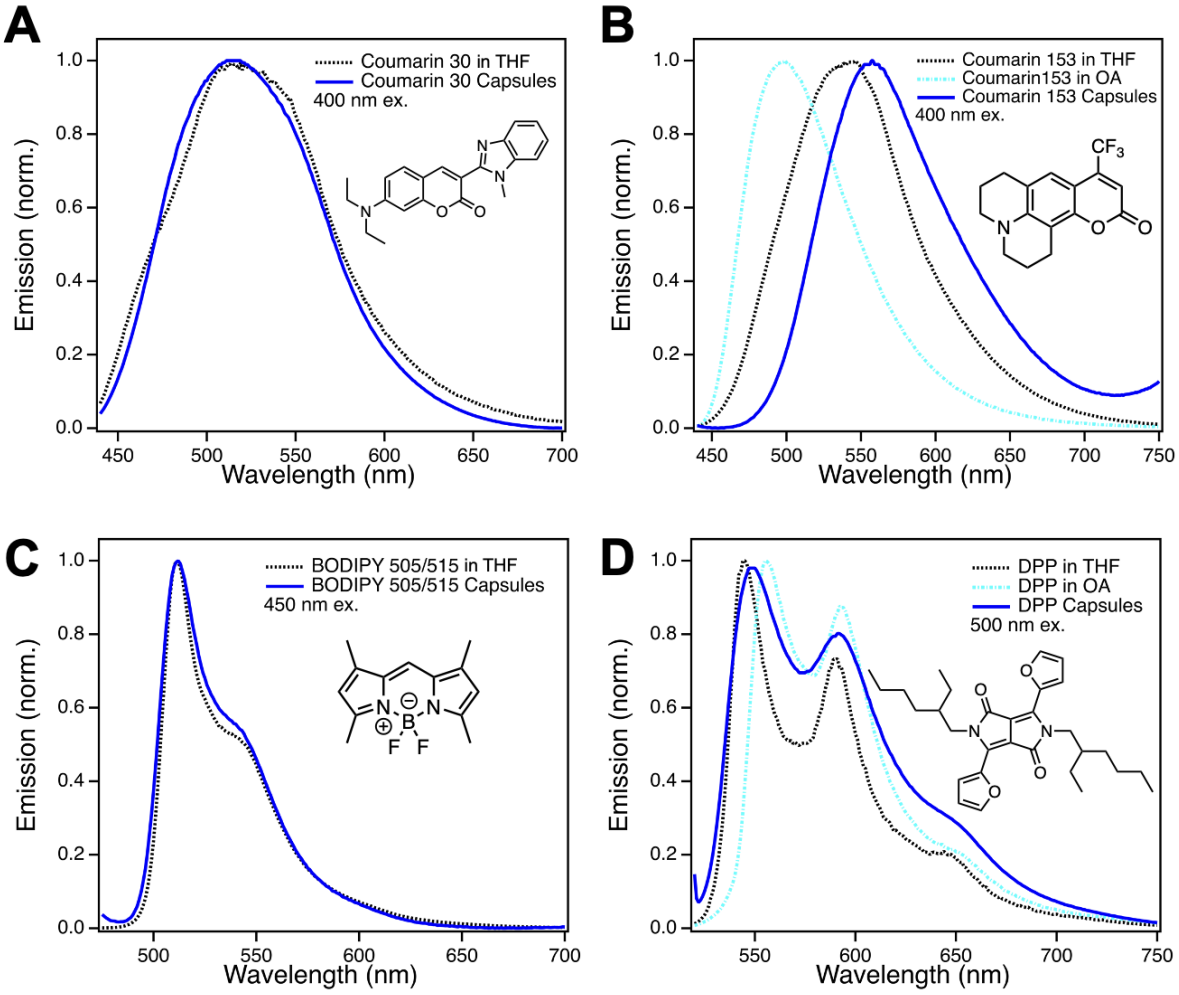
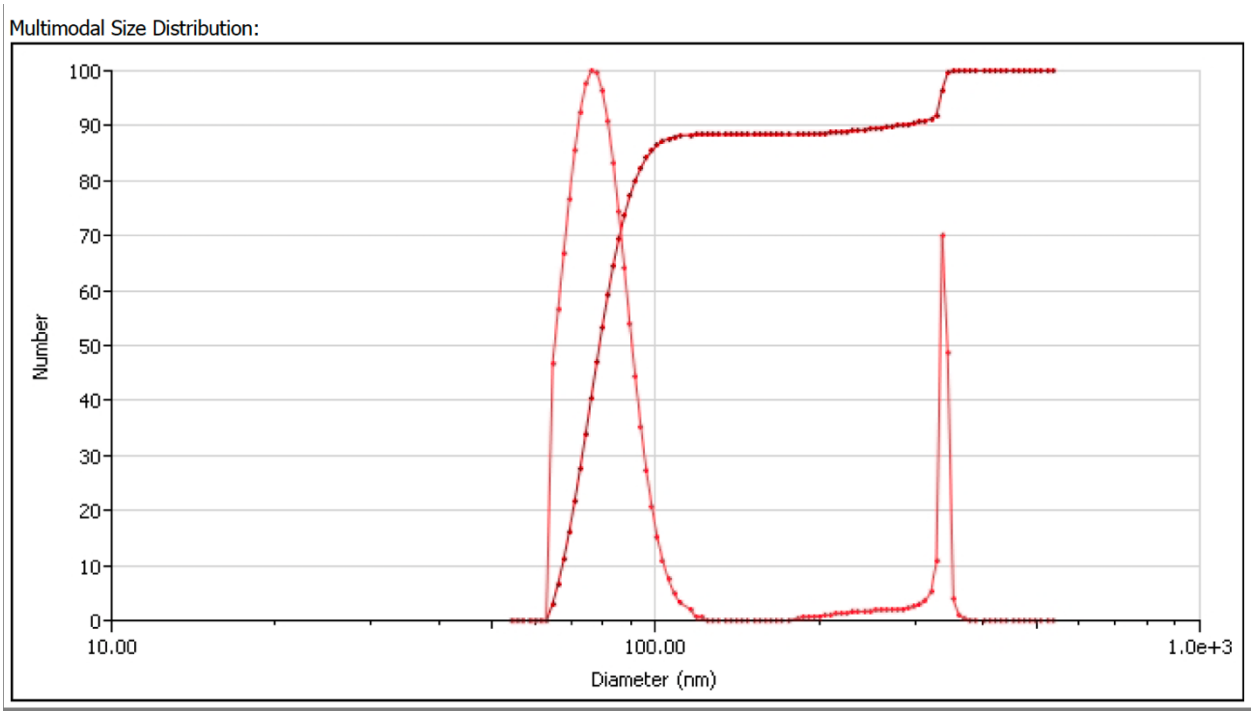


Figure S7: Emission spectra of nanocapsules dispersed in EtOH/water containing Coumarin 30 (A), Coumarin 153 (B), BODIPY (C), or DPP (D) overlaid with the emission spectra of the unencapsulated material (dissolved in THF and/or oleic acid, OA). The excitation wavelength is denoted in the panel.

	Effective Diameter (nm)	PDI
Coumarin 30	166.7 ± 0.4	0.20 ± 0.02
Coumarin 153	115.1 ± 2.0	0.23 ± 0.01
BODIPY	206.0 ± 1.1	0.27 ± 0.02
DPP	111.4 ± 1.2	0.25 ± 0.02

Table S9: The average effective diameters based upon dynamic light scattering characterization of upconversion nanocapsules sampled from the reaction crude diluted in *water* for the samples presented in **Fig. S7**. Each entry represents an average of three measurements and the standard deviation.

A.


Multimodal Size Distribution:
Number
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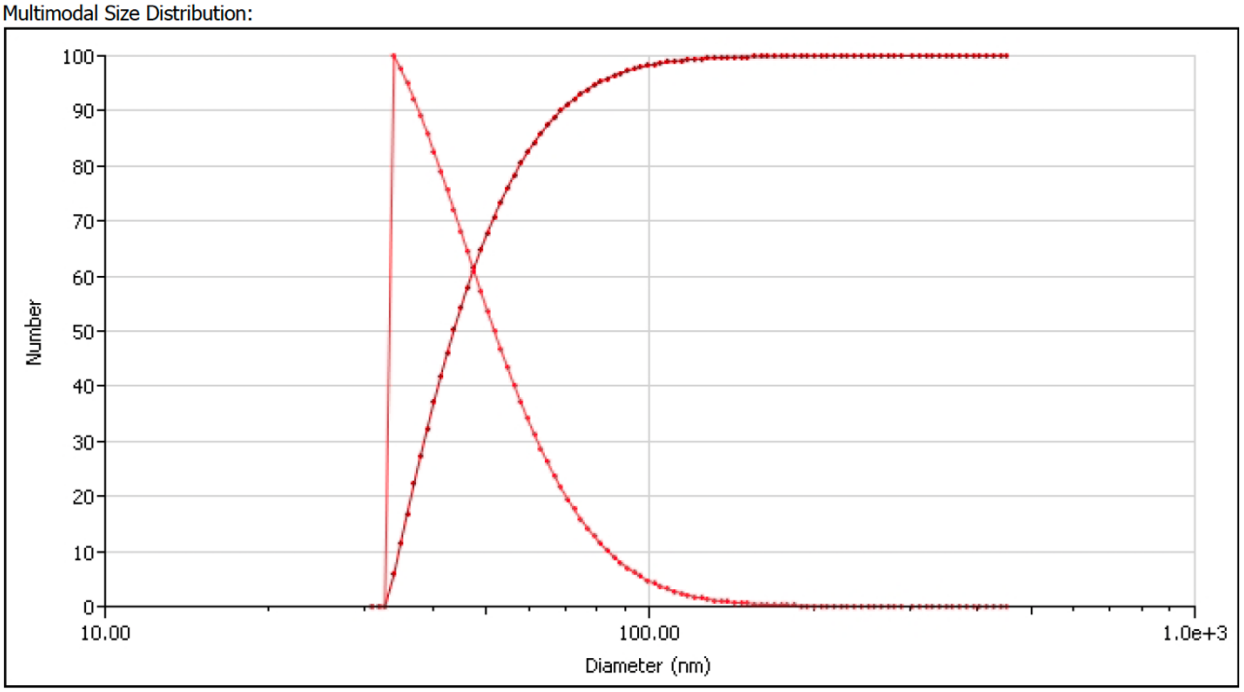
60
50
40
30
20
10
0
10.00
100.00
1.0e+3
Diameter (nm)

B.


Multimodal Size Distribution:
Number
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80
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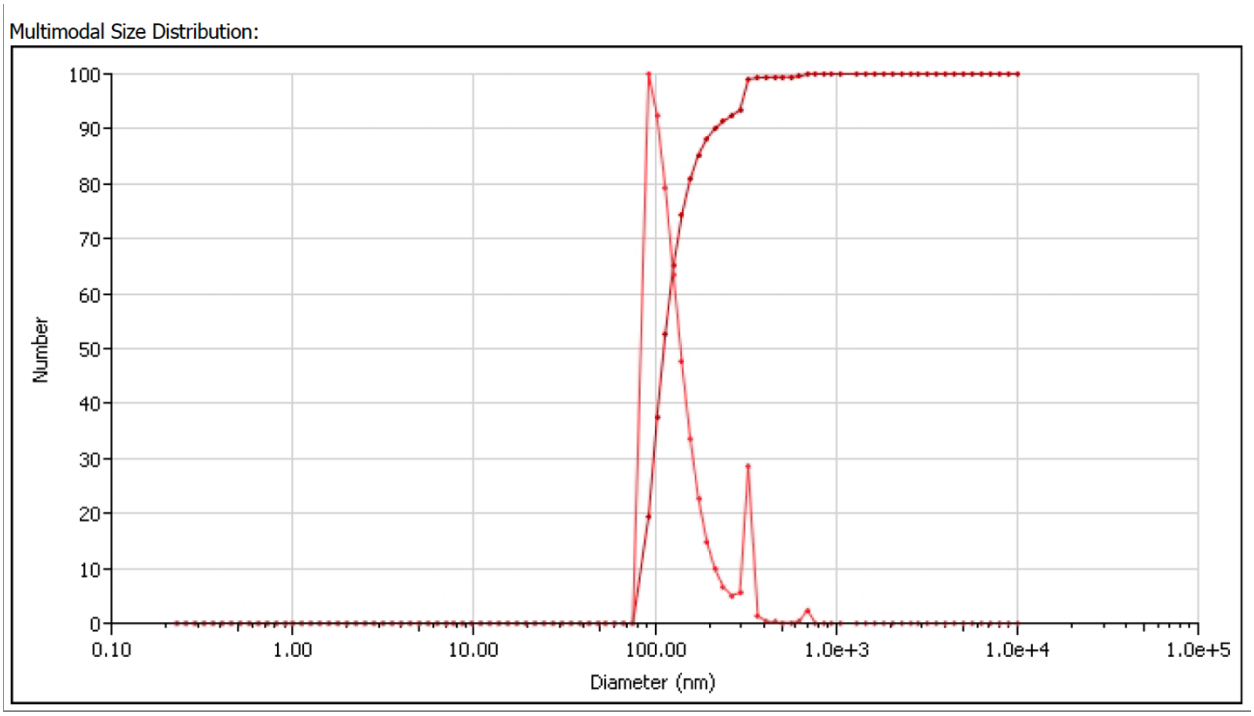
60
50
40
30
20
10
0
10.00
100.00
1.0e+3
Diameter (nm)

C.



D.

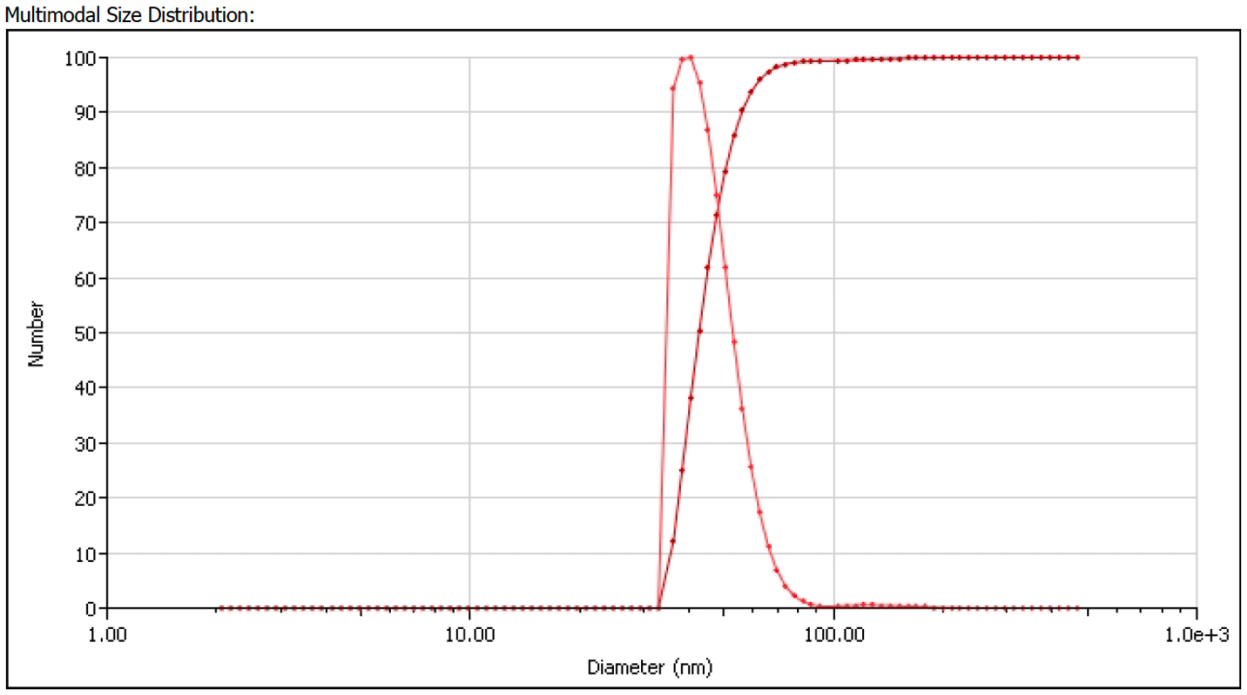
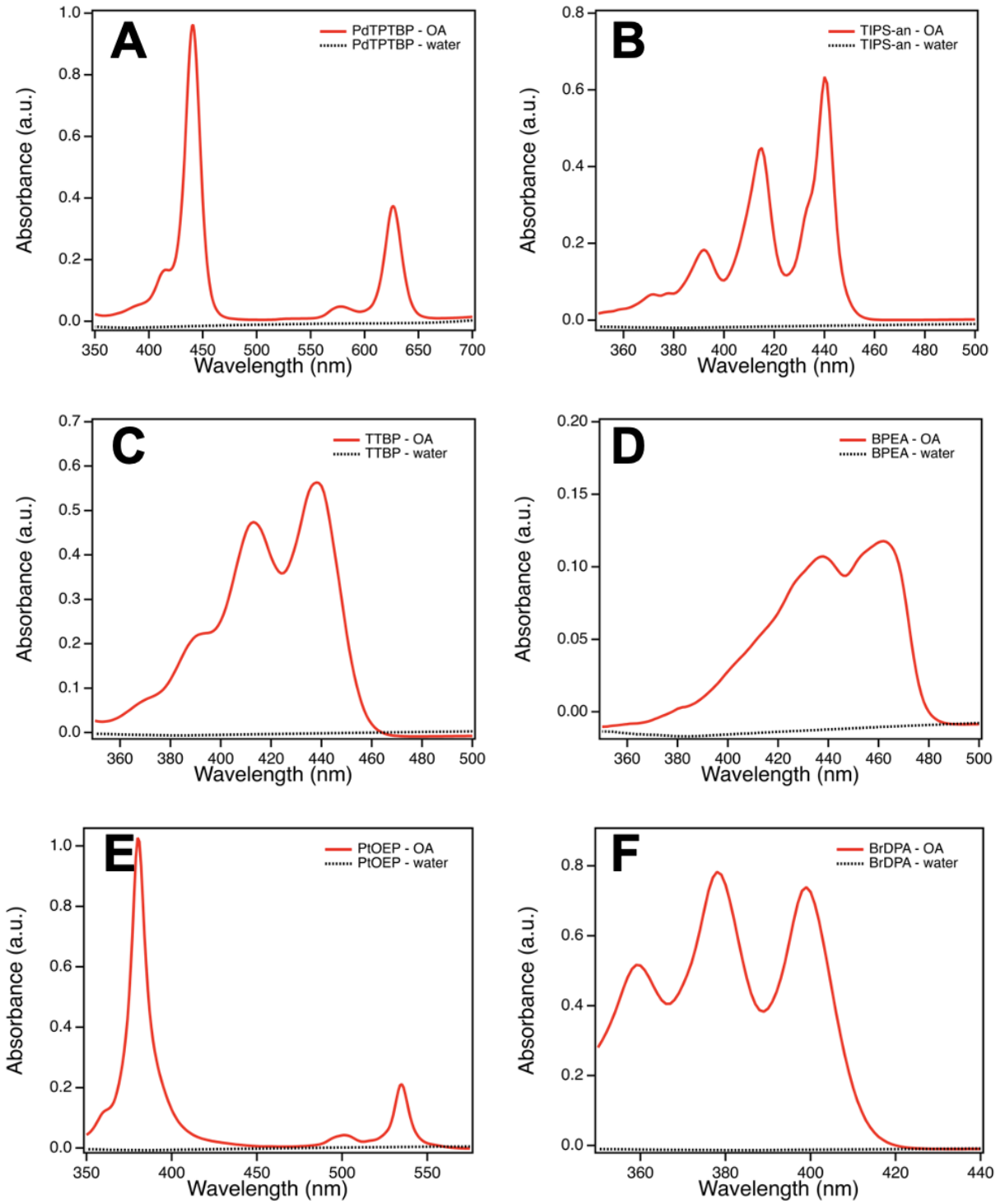


Figure S8: Representative dynamic light scattering traces of Coumarin 30 (A), Coumarin 153 (B), BODIPY (C), and DPP (D) nanocapsules sampled from the reaction crude diluted in *water*.


A
PdTPTBP - OA
PdTPTBP - water
Absorbance (a.u.)
Wavelength (nm)
B
TIPS-an - OA
TIPS-an - water
Absorbance (a.u.)
Wavelength (nm)
C
TTBP - OA
TTBP - water
Absorbance (a.u.)
Wavelength (nm)
D
BPEA - OA
BPEA - water
Absorbance (a.u.)
Wavelength (nm)
E
PtOEP - OA
PtOEP - water
Absorbance (a.u.)
Wavelength (nm)
F
BrDPA - OA
BrDPA - water
Absorbance (a.u.)
Wavelength (nm)

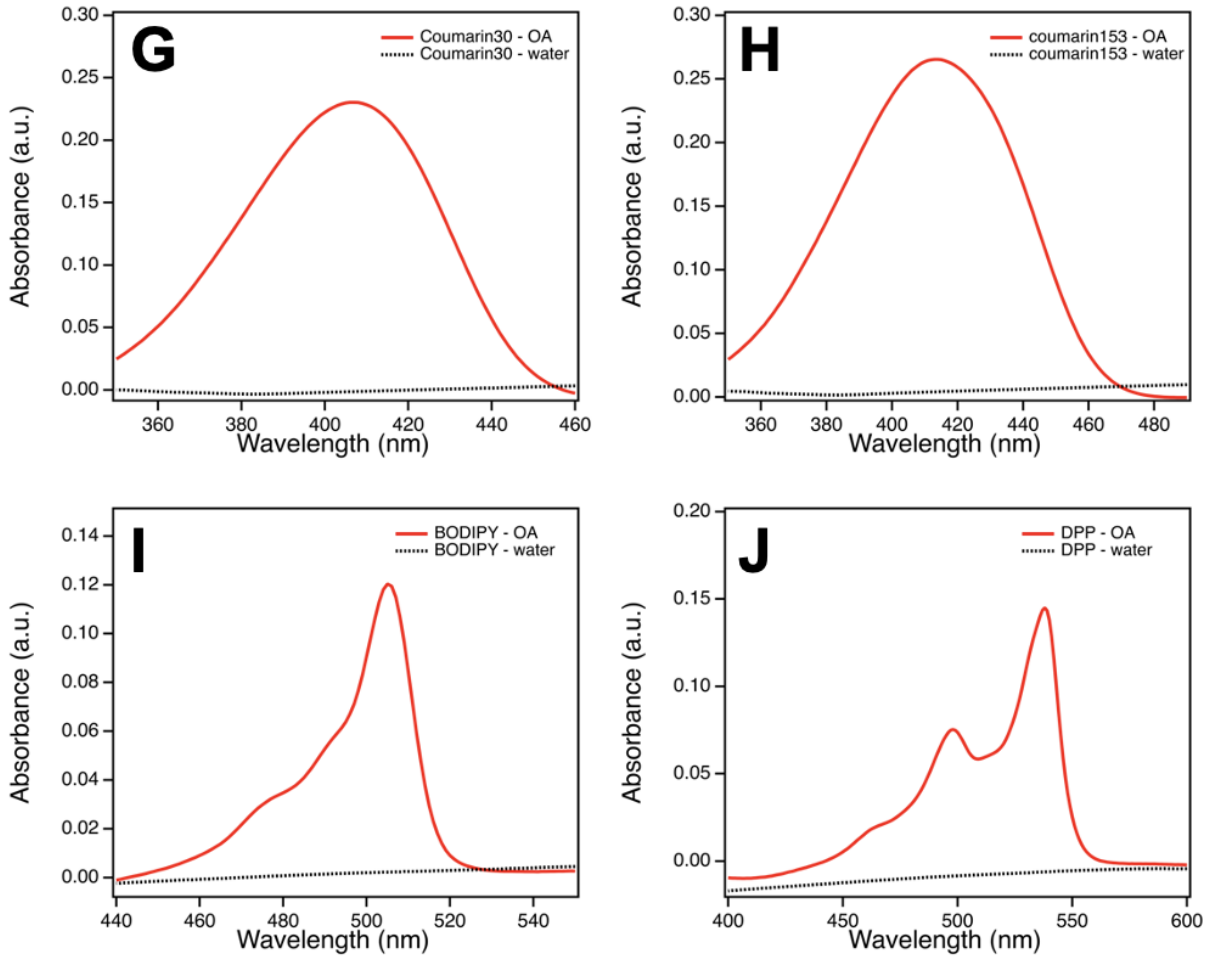


Figure S9: UV-Vis absorption spectra used to extract partition coefficients of each compound in equilibrium among oleic acid and water phases (A-J). Each compound was dissolved in oleic acid (OA), filtered with a 0.45 µm PTFE syringe filter, and stirred with an equal volume of water before diluting samples of equal volume in THF for characterization. For every sample shown, no detectible quantity partitions from the oleic acid layer into the water layer.

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