Unimolecular Submersible Nanomachines. Synthesis, Actuation and Monitoring

Supporting Information

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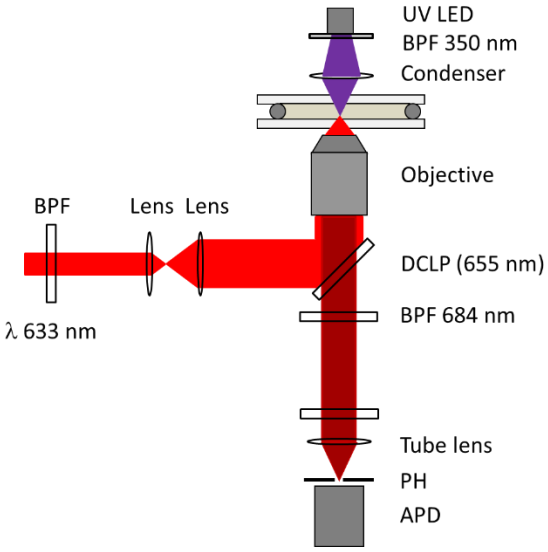


Figure S1. Schematic of the confocal single molecule fluorescence microscope with UV illumination. The excitation can be provided by a HeNe laser (633 nm) or an Ar^+ laser (514 nm) focused to the diffraction limited spot. BPF: bandpass filter; DCLP: dichroic mirror (long pass); PH: pinhole; APD: avalanche photodiode detector.

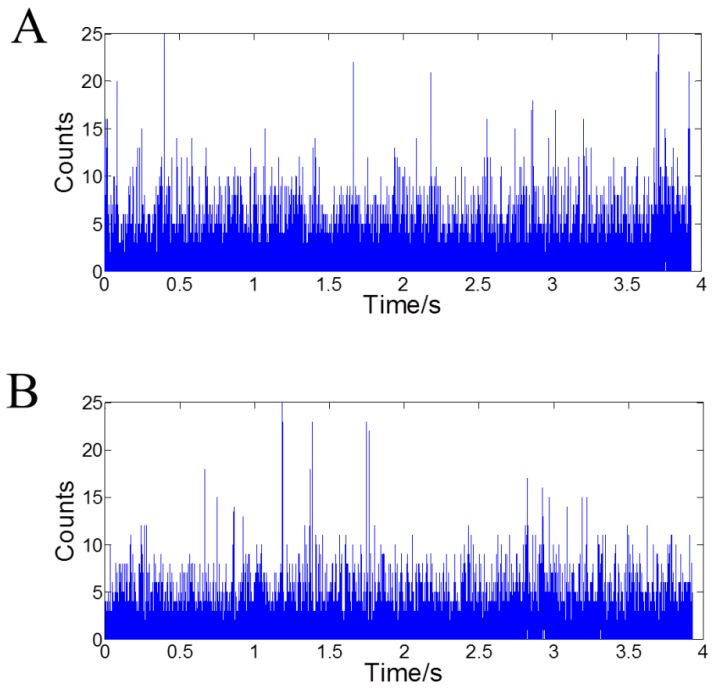


Figure S2. Selected fluorescence intensity trace of USN-**1** molecules diffusing in bulk solution. (A) Without UV activation, (B) with UV activation. Integration time: 60 μs.

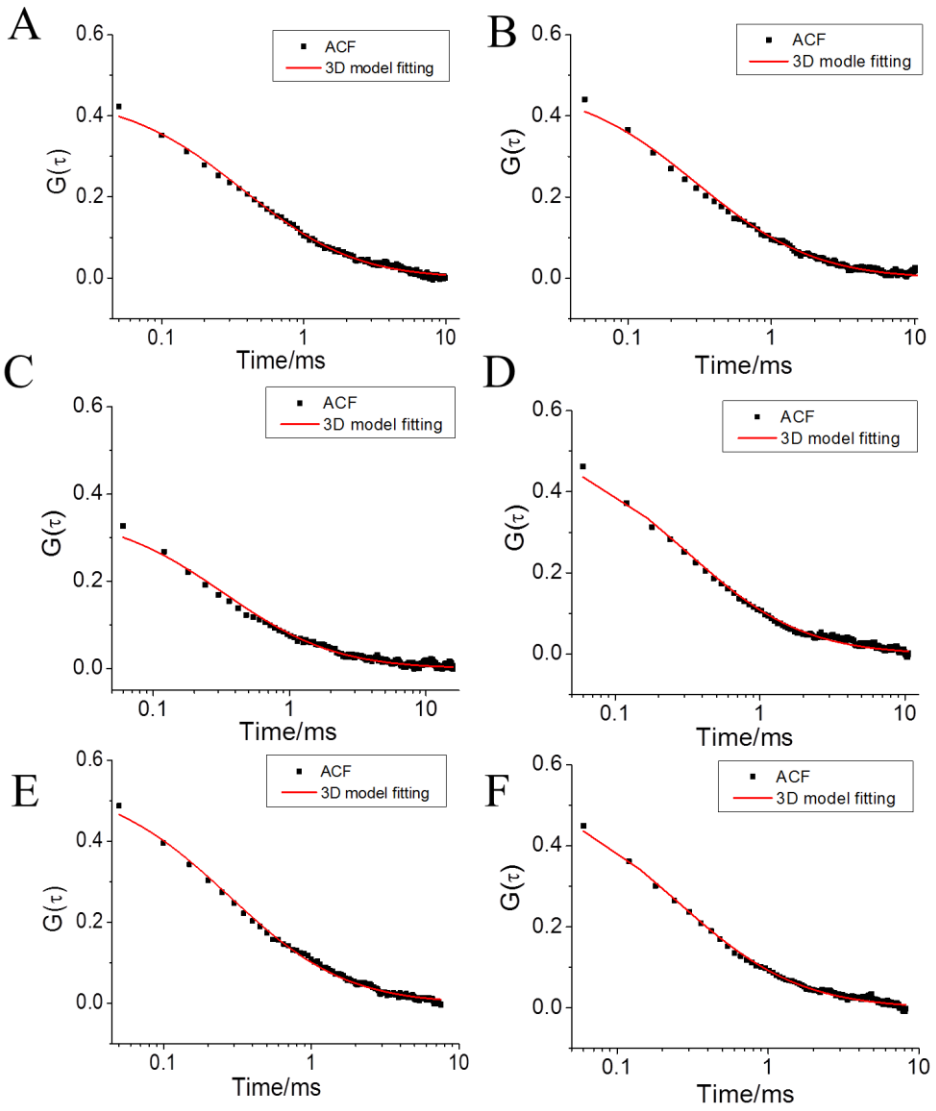


Figure S3. Selected NLLS fitting of the ACFs of the USN molecules using the 3D diffusion model. (A) USN-**1** without UV. (B) CM-**2** without UV. (C) USN-**3** without UV. (D) USN-**4** without UV. (E) USN-**1** with UV. (F) USN-**4** with UV.

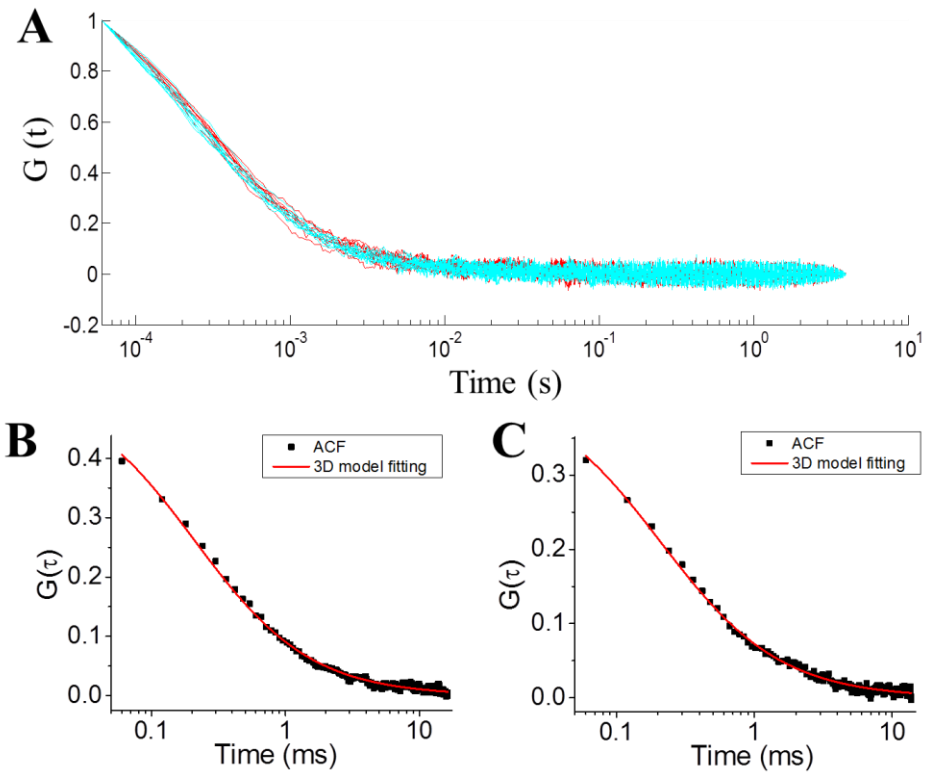


Figure S4. Heating effect of the excitation laser beam at 633 nm. A) Typical ACF curves of USN-**1** molecule diffusion collected at 3.0 mW (red lines) and 1.2 mW (cyan lines) laser powers, respectively. B) A selected ACF curve and corresponding NLLS fitting with 3D diffusion model in the presence of 3.0 mW laser power; and C) in the presence of 1.2 mW laser power. The statistical diffusion coefficient is 0.91 ± 0.11 × 10^{-10} $m^2 \cdot s^{-1}$ and 0.93 ± 0.10 × 10^{-10} $m^2 \cdot s^{-1}$, respectively, from the fitting of 10 measurements each. There is no significant difference with respect to the excitation laser power, indicating the heating effect of the excitation laser power is negligible.

Molar absorptivity estimation

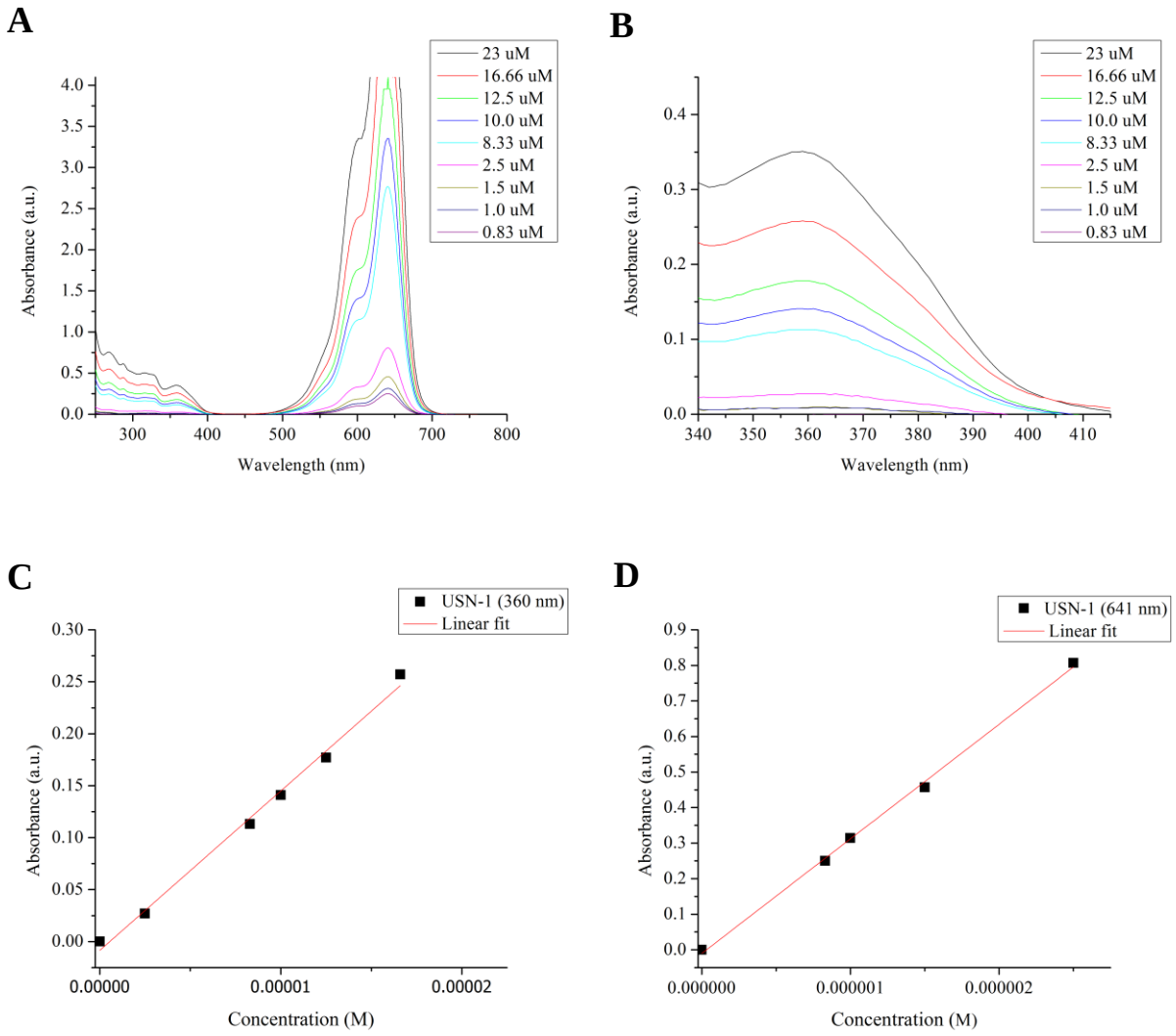


Figure S5. A) UV-vis spectra of USN-**1**. B) UV-vis spectra of USN-**1** in the motor region. C) Calibration curve at 360 nm. D) Calibration curve at 641 nm.

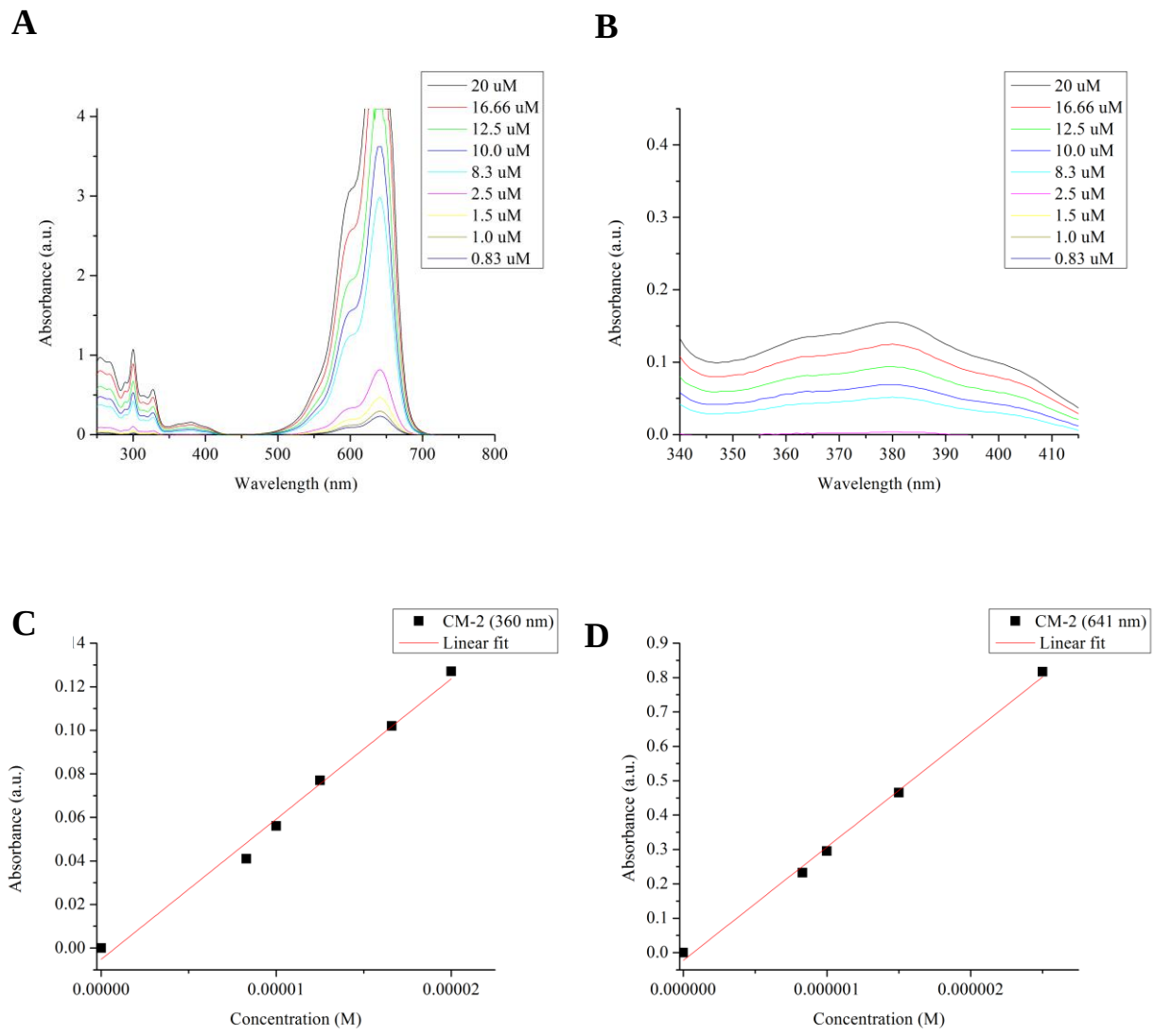


Figure S6. A) UV-vis spectra of CM-**2**. B) UV-vis spectra of CM-**2** in the motor region. C) Calibration curve at 360 nm. D) Calibration curve at 641 nm.

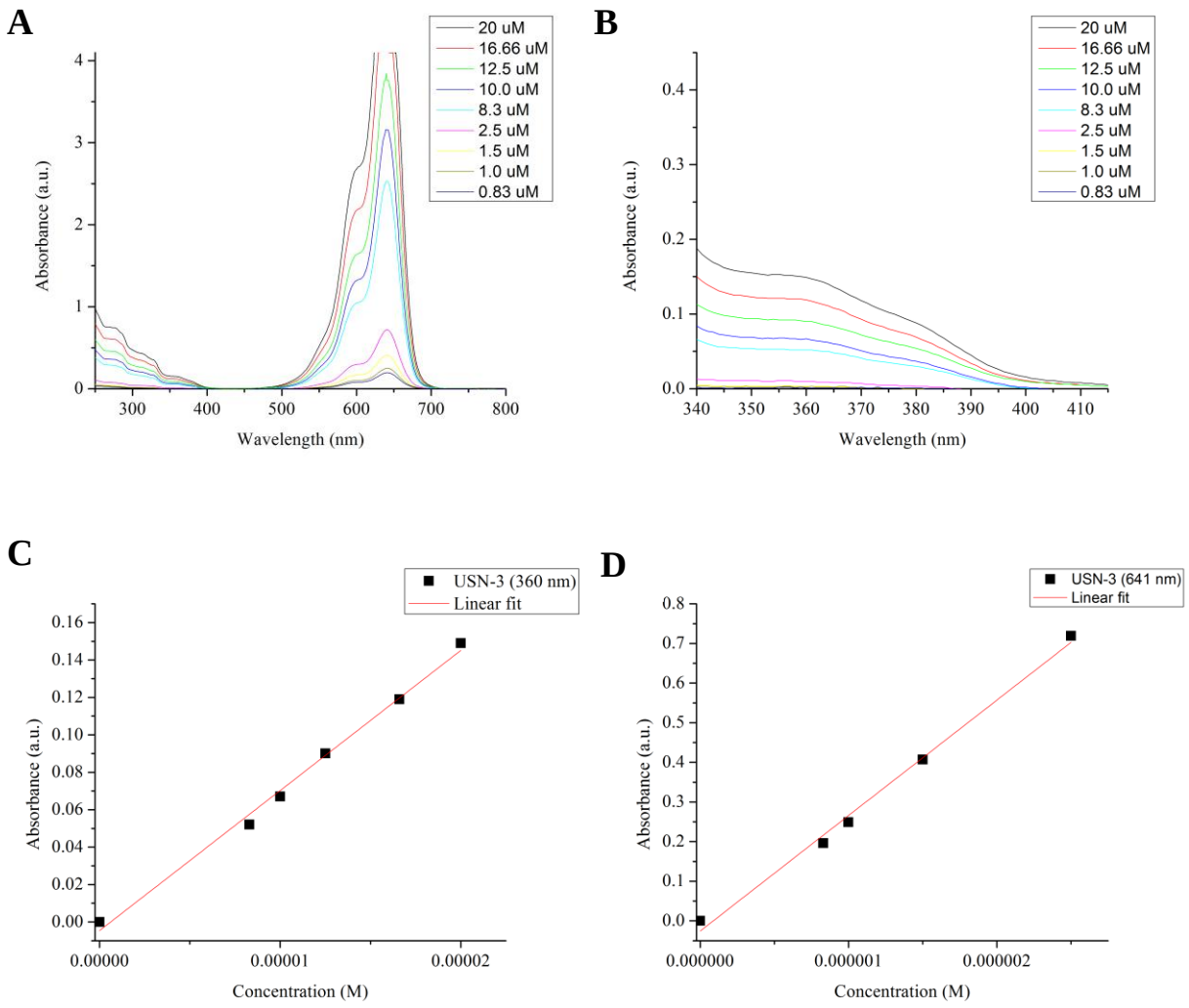


Figure S7. A) UV-vis spectra of USN-**3**. B) UV-vis spectra of USN-**3** in the motor region. C) Calibration curve at 360 nm. D) Calibration curve at 641 nm.

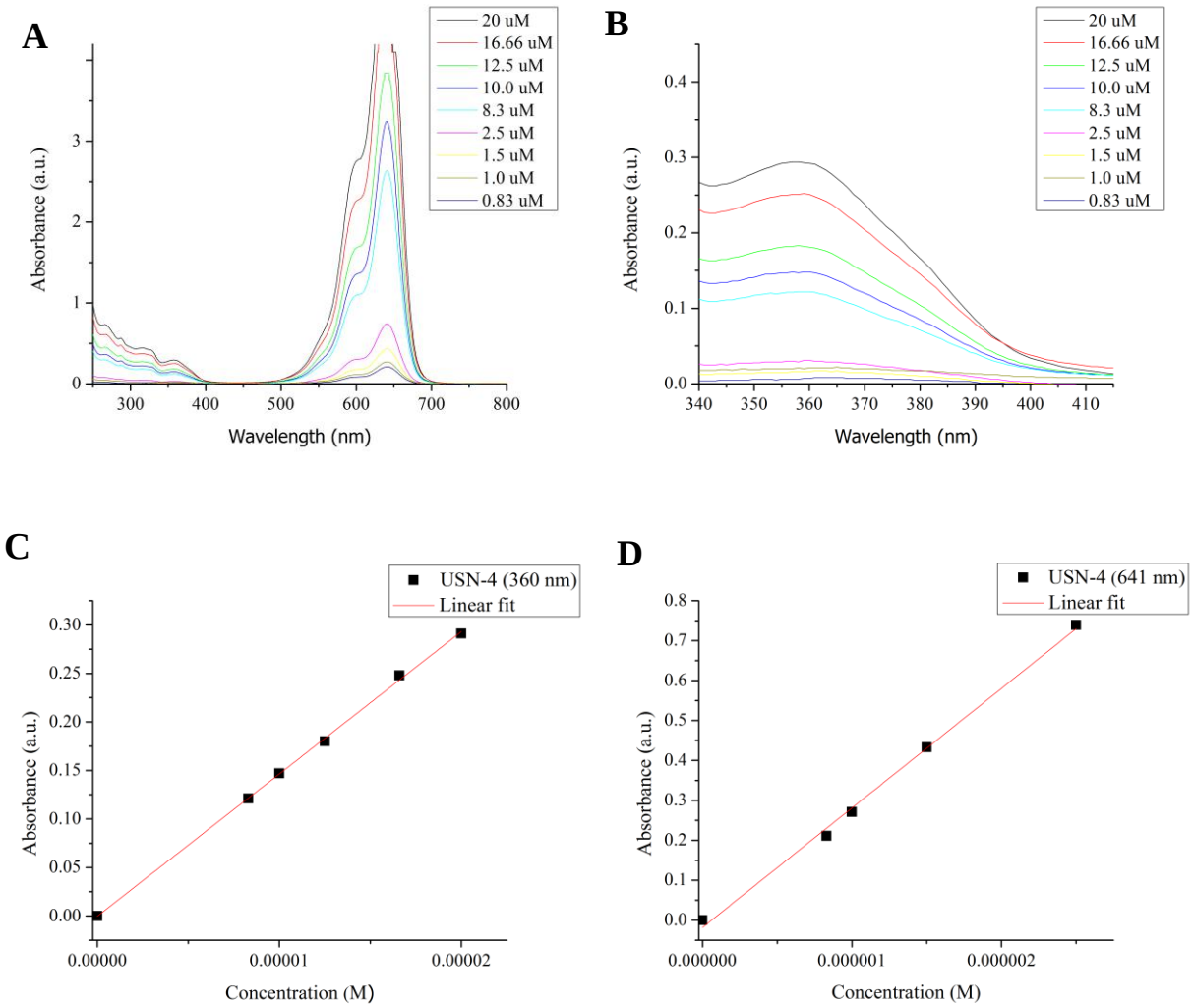


Figure S8. A) UV-vis spectra of USN-**4**. B) UV-vis spectra of USN-**4** in the motor region. C) Calibration curve at 360 nm. D) Calibration curve at 641 nm.

Table S1. Molar absorptivity of USNs at 360 nm and 641 nm

	USN-1	**CM-2**	**USN-3**	**USN-4**
$\varepsilon_{360\ nm}$ **($M^{-1}cm^{-1}$)**	15,400	6,400	7,500	14,700
$\varepsilon_{641\ nm}$**($M^{-1}cm^{-1}$)**	322,000	330,000	291,000	299,000

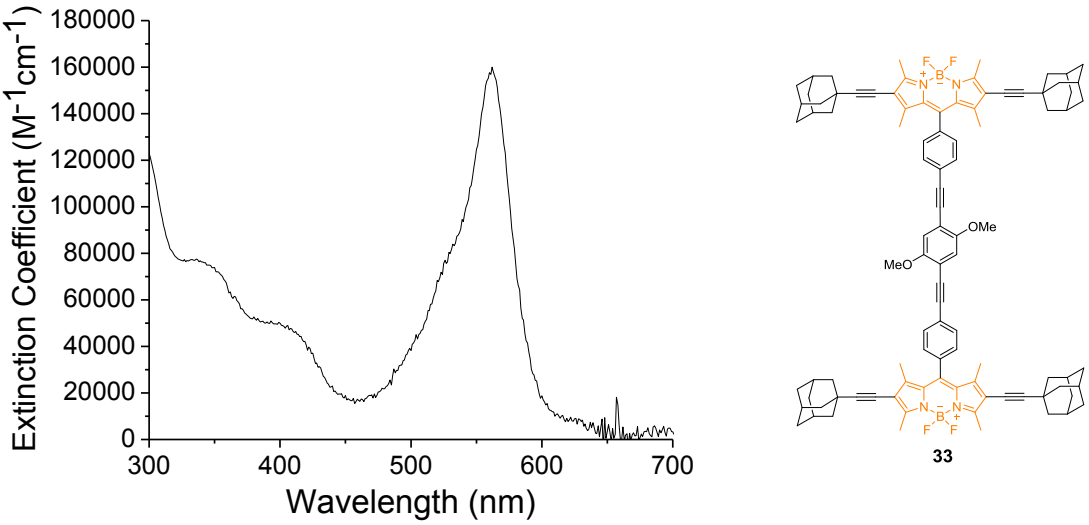


Figure S9. UV-Vis spectrum of 2.0 µM of nanocar **33** in ACN. Nanocar **33** has 4 admantane wheels and two BODIPY dyes.

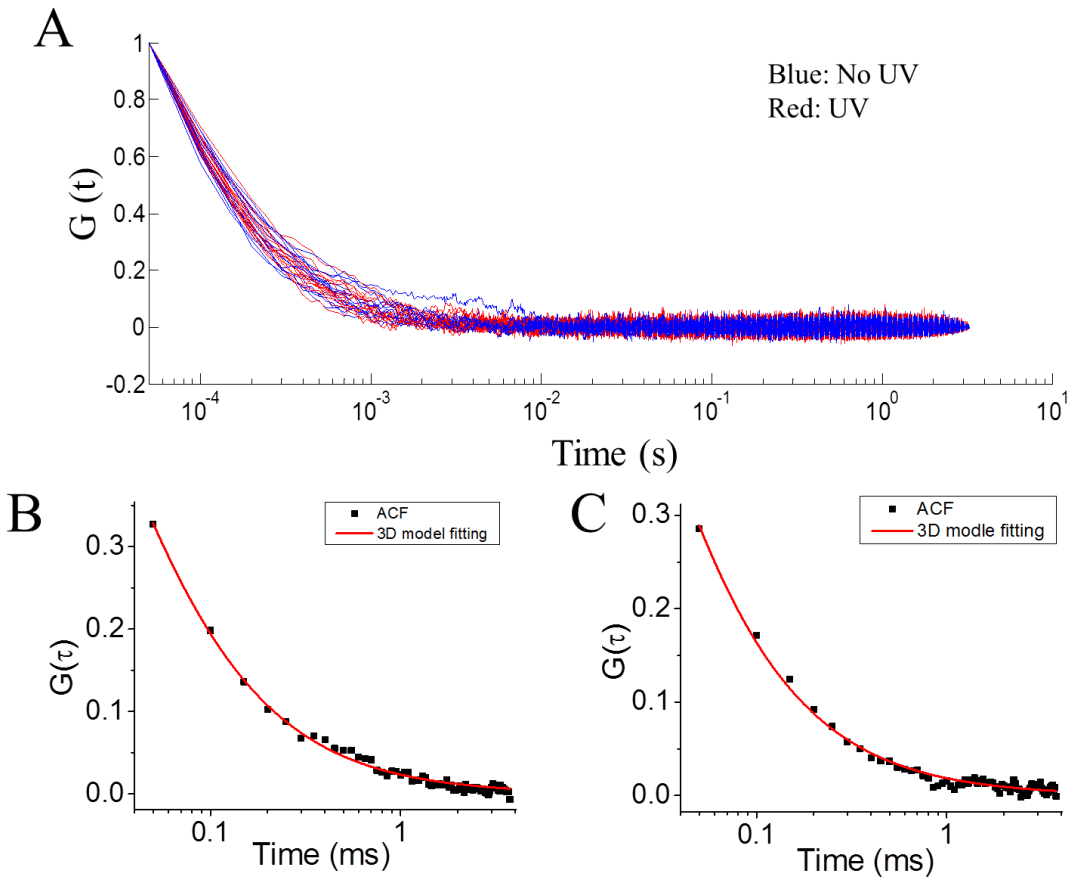
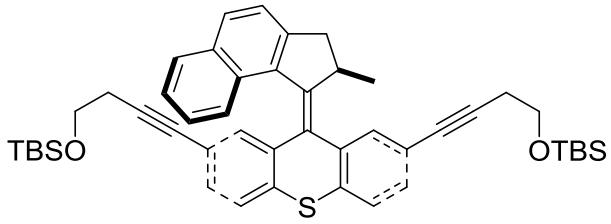


Figure S10. Heating effect of the UV excitation light at 365 nm. The selected molecule is nanocar **33** in ACN with an extinction coefficient of 64,900 $M^{-1}cm^{-1}$ at 360 nm, more than 4× larger than that of the USN-**1**. A) Typical ACF curves of **33** diffusion in the presence (red) and absence (blue) of UV light excitation, respectively. B) A selected ACF curve and corresponding NLLS fitting with a 3D diffusion model without UV light excitation; and (C) with UV light excitation. The statistical diffusion coefficient is 1.11± 0.04 $\times 10^{-10}$ $m^2 \cdot s^{-1}$ and 1.10 ± 0.05 $\times 10^{-10}$ $m^2 \cdot s^{-1}$, respectively, from the fitting of 10 measurements each. There is no significant difference between with and without UV light excitation, indicating the heating effect of the UV excitation is negligible.

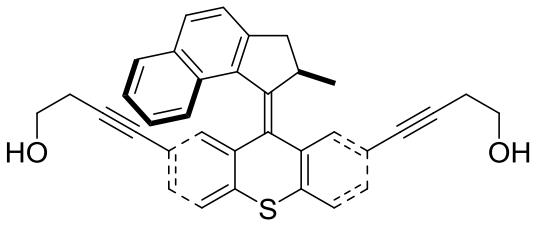
Experimental Data for Compound Synthesis

1. Synthesis of USN-1



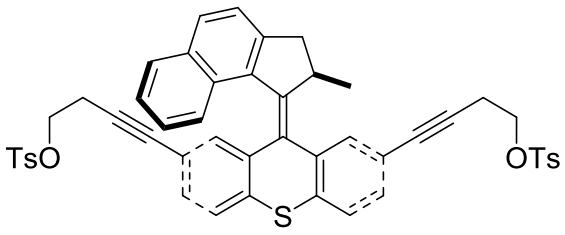
(4,4'-(9-(2-Methyl-2,3-dihydro-1*H*-cyclopenta[a]naphthalen-1-ylidene)-9*H*-thioxanthene-2,7-diyl)bis(but-3-yne-4,1-diyl))bis(oxy)bis(*tert*-butyldimethylsilane) (6). An oven dried Schlenk tube equipped with a stir bar was charged with motor **5**[7] (750 mg, 1.4 mmol), tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct (25.6 mg, 0.028 mmol), CuI (5.4 mg, 0.028 mmol), triphenylphosphine (26.3 mg, 0.14 mmol) and 4-(*tert*-butyldimethylsilyloxy)-but-1-yne (1.44 ml, 7.0 mmol). NEt_3 (7 mL) was added and the mixture was stirred at 70 °C overnight. The resulting mixture was partitioned between CH_2Cl_2 (40 mL) and saturated NH_4Cl (aq) (40 mL). The organic layer was dried over anhydrous $MgSO_4$, concentrated, and purified by column chromatography (silica gel; 30% CH_2Cl_2 in hexanes) to afford **6** as a pale-yellow solid (915 mg, 90%): m.p. 207–209 °C; FTIR (neat) 3052, 2954, 2930, 2856, 1588, 1472, 1454, 1388, 1362, 1252, 1218, 1100, 1058, 1006 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, J = 1.7 Hz, 1H), 7.75 (d, J = 8.2 Hz, 1H), 7.70 (d, J = 8.2 Hz, 1H), 7.50 (dd, J_1 = 8.0, J_2 = 0.4 Hz, 1H), 7.47 (dt, J_1 = 8.0, J_2 = 0.4 Hz, 1H), 7.44 (d, J = 8.2 Hz, 1H), 7.26 (dd, J_1 = 8.1, J_2 = 1.8, 1H), 7.19 (ddd, J_1 = 8.1, J_2 = 5.7, J_3 = 2.2 Hz, 1H), 7.03 (dd, J_1 = 8.1, J_2 = 1.8 Hz, 1H), 6.87 – 6.78 (m, 2H), 6.73 (dd, J_1 = 1.8, J_2 = 0.5 Hz, 1H), 4.24 (p, J = 6.7 Hz, 1H), 3.86 (t, J = 6.9 Hz, 2H), 3.64 (dd, J_1 = 15.4, J_2 = 6.2 Hz, 1H), 3.56 (td, J = 7.2, 1.1 Hz, 2H), 2.67 (t, J = 6.9 Hz, 2H), 2.63 (d, J = 15.4 Hz, 1H), 2.34 (t, J = 7.1 Hz, 2H), 0.94 (d, J = 0.4 Hz, 9H), 0.84 (d, J = 0.4 Hz, 9H), 0.78 (d, J = 6.8 Hz, 3H), 0.13 (s, 6H), -0.02 (s, 3H), -0.03 (s, 3H). ^{13}C NMR

(125 MHz, $CDCl_3$) δ 147.00, 146.11, 139.96, 137.72, 135.37, 134.85, 134.70, 133.11, 131.55, 130.77, 130.43, 129.38, 129.19, 128.78, 127.91, 127.62, 127.30, 127.16, 125.94, 124.90, 124.41, 123.69, 122.09, 122.04, 88.02, 87.07, 81.35, 80.68, 61.92, 61.76, 39.77, 37.94, 25.96, 25.89, 23.99, 23.68, 19.53, 18.44, 18.32, -5.15, -5.16, -5.27, -5.28. HRMS (APCI) *m*/*z* calculated for $[M+H]^+$ $C_{47}H_{57}O_2SSi_2$ 741.3612, found 741.3584.



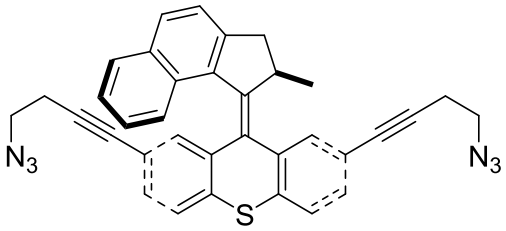
4,4'-(9-(2-Methyl-2,3-dihydro-1*H*-cyclopenta[a]naphthalen-1-ylidene)-9*H*-thioxanthene-2,7-diyl)dibut-3-yn-1-ol (7). A 100 mL round-bottomed flask equipped with a stir bar was charged with **6** (544 mg, 0.73 mmol). THF (10 mL) and a solution of TBAF (1.83 mL, 1.83 mmol, 1.0 M in THF) were added, and the mixture was stirred at rt for 1.5 h. The mixture was poured into water (50 mL) and filtered. The solid was collected, washed with water (20 mL ×2) and dried under vacuum to afford desired product **7** as a pale-yellow solid (358 mg, 95%): m.p. 240 °C (decomposition.); FTIR (neat) 3302, 3050, 2954, 2922, 2894, 2838, 1702, 1586, 1516, 1454, 1386, 1338, 1256, 1170, 1042, 1020 cm^{-1}; ^1H NMR (600 MHz, THF-d_8) δ 7.87 (d, *J* = 1.6 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.26 (dd, J_1 = 8.0, J_2 = 1.7 Hz, 1H), 7.15 (ddd, J_1 = 8.0, J_2 = 6.5, J_3 = 1.2 Hz, 1H), 7.03 (dd, J_1 = 8.1, J_2 = 1.8 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.80 – 6.75 (m, 1H), 6.68 (d, *J* = 1.7 Hz, 1H), 4.28 (p, *J* = 6.8 Hz, 1H), 4.02 (s, 1H), 3.75 – 3.65 (m, 4H), 3.39 (t, *J* = 7.3 Hz, 2H), 2.64 (d, *J* = 15.4 Hz, 1H), 2.60 (t, *J* = 7.0 Hz, 2H), 2.26 (t, *J* = 7.2 Hz, 2H), 0.76 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (150 MHz, THF-d_8) δ 148.04, 147.38, 141.26, 138.93, 136.38, 136.04, 135.53, 134.45, 132.35, 131.65, 131.55, 130.52, 130.28, 129.96,

128.91, 128.54, 128.50, 128.26, 126.82, 125.81, 125.21, 124.62, 123.68, 123.62, 89.25, 88.25, 81.81, 81.21, 61.79, 61.63, 40.53, 39.11, 24.89, 24.54, 19.79. HRMS (APCI) *m*/*z* calculated for $[M+H]^+$ $C_{35}H_{29}O_2S$ 513.1883, found 513.1879.



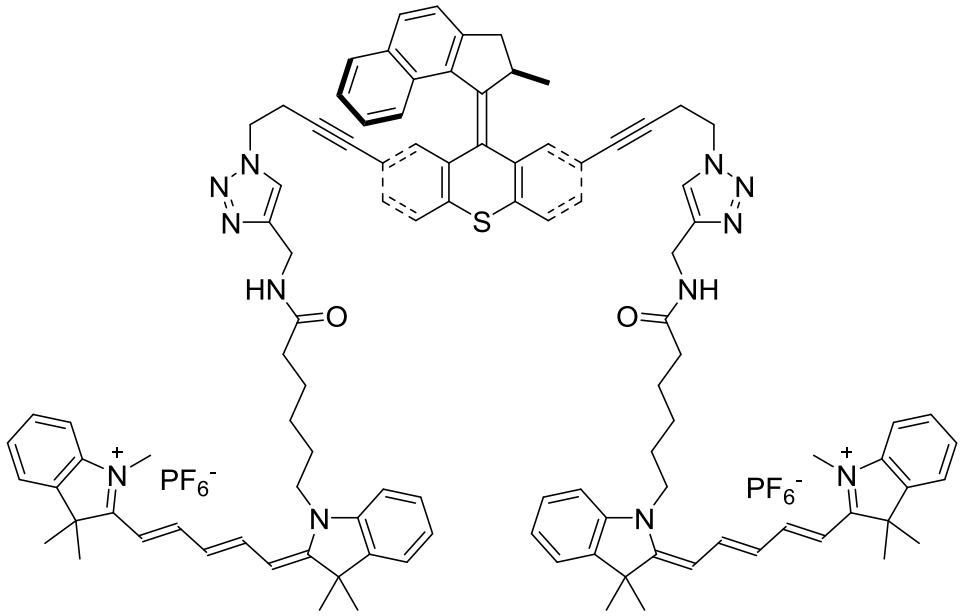
4,4'-(9-(2-Methyl-2,3-dihydro-1*H*-cyclopenta[a]naphthalen-1-ylidene)-9*H*-thioxanthene 2,7-diyl)bis(but-3-yne-4,1-diyl) bis(4-toluenesulfonate) (8). An oven dried 100 mL round-bottom flask equipped with a stir bar was charged with **7** (357 mg, 0.7 mmol), 4-toluenesulfonyl chloride (663 mg, 3.5 mmol), DMAP (4.28 mg, 0.0335 mmol) and CH_2Cl_2 (20 mL). After cooling to 0 °C, NEt_3 (0.97 mL, 6.97 mmol) was added. The suspension was stirred vigorously for 18 h in the absence of light. The resulting yellow solution was partitioned between CH_2Cl_2 (50 mL) and water (40 mL). The organic phase was dried over anhydrous $MgSO_4$, concentrated and purified by column chromatography (SiO_2; 20% hexanes in CH_2Cl_2) to afford **8** as a pale yellow solid (475 mg, 85%): m.p. 181–183 °C; FTIR (neat) 3050, 2956, 2922, 1598, 1454, 1356, 1188, 1174, 1098, 1070, 1038 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.78 – 7.74 (m, 2H), 7.72-7.67 (m, 3H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.27-7.25 (m, 2H), 7.20-7.18 (td, *J* = 8.3, 1.6 Hz, 2H), 6.97 (dd, *J* = 8.1, 1.8 Hz, 1H), 6.81 (td, *J* = 7.5, 6.6, 1.3 Hz, 1H), 6.77 (d, *J* = 8.2 Hz, 1H), 6.66 (d, *J* = 1.7 Hz, 1H), 4.27 – 4.17 (m, 3H), 3.92 (td, *J* = 7.3, 1.6 Hz, 2H), 3.66 (dd, *J* = 15.4, 6.1 Hz, 1H), 2.83 (t, *J* = 7.0 Hz, 2H), 2.65 (d, *J* = 15.4 Hz, 1H), 2.48 (t, *J* = 7.3 Hz, 2H), 2.391 (s, 3H), 2.388 (s, 3H), 0.79 (d, *J* = 6.8 Hz, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ 147.38, 146.18, 144.98, 144.83, 139.87, 137.67, 135.93, 135.43, 134.50,

133.10, 132.95, 132.89, 131.63, 130.85, 130.58, 129.91, 129.84, 129.40, 129.24, 128.69, 127.97, 127.90, 127.66, 127.32, 126.72, 125.83, 124.89, 124.41, 123.72, 121.27, 121.24, 84.59, 83.58, 82.47, 81.78, 67.69, 67.49, 39.75, 37.87, 21.63, 20.55, 20.16, 19.55. HRMS (APCI) *m*/*z* calculated for $[M+H]^+$ $C_{49}H_{41}O_6S_3$ 821.2060, found 821.2066.



2,7-Bis(4-azidobut-1-ynyl)-9-(2-methyl-2,3-dihydro-1*H*-cyclopenta[a]naphthalen-1-ylidene)-9*H*-thioxanthene (9). An oven-dried round-bottom flask equipped with a stir bar was charged with ditosylate **8** (180 mg, 0.22 mmol) and NaN_3 (57 mg, 0.88 mmol). DMF (5 mL) was added, and the mixture was stirred at 80 °C overnight. After cooling to rt, the mixture was partitioned between Et_2O (20 mL) and then washed with water (30 mL × 3). The organic phase was dried over anhydrous $MgSO_4$, and concentrated under vacuum to afford **9** as a pale yellow solid (118 mg, 95%): m.p. 199–200 °C; FTIR (neat) 3048, 2922, 2190, 1738, 1586, 1452, 1336, 1270, 1066 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 1.6 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.1 Hz, 1H), 7.27 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.20 (ddd, *J* = 8.0, 6.4, 1.4 Hz, 1H), 7.05 (dd, *J* = 8.1, 1.8 Hz, 1H), 6.83 (ddd, *J* = 7.9, 6.5, 1.3 Hz, 1H), 6.81 – 6.77 (m, 1H), 6.73 (d, *J* = 1.7 Hz, 1H), 4.23 (p, *J* = 6.8 Hz, 1H), 3.64 (dd, *J* = 15.3, 6.2 Hz, 1H), 3.51 (t, *J* = 6.8 Hz, 2H), 3.21 (t, *J* = 6.9 Hz, 2H), 2.76 (t, *J* = 6.7 Hz, 2H), 2.63 (d, *J* = 15.4 Hz, 1H), 2.41 (t, *J* = 6.9 Hz, 2H), 0.79 (d, *J* = 6.8 Hz, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) 147.28, 146.14, 139.87, 137.70, 135.84, 135.29, 134.61, 133.12, 131.64, 130.84, 130.44, 129.35, 129.16, 128.73, 127.87, 127.67, 127.33, 126.85,

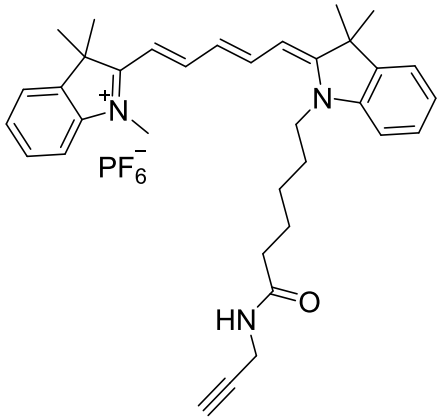
125.91, 124.90, 124.38, 123.69, 121.45, 121.43, 86.51, 85.58, 82.35, 81.62, 49.92, 49.69, 39.72, 37.87, 20.84, 20.39, 19.55.; HRMS, (APCI) *m*/*z* calcd for $[M+Na]^+$ $C_{35}H_{26}N_6SNa$ 585.1832, found 585.1839.



USN-1. A 2 mL vial charged with diazide **9** (18 mg, 0.032 mmol), cy5 dye **10** (47 mg, 0.071 mmol), $CuSO_4$(s) (0.8 mg, 0.0032 mmol) and sodium ascorbate (1.9 mg, 0.0096 mmol) was sealed with a rubber septum cap. A well degassed mixture of CH_2Cl_2 (0.08 mL) and water (0.08 mL) was added to the vial, and the vial was shaken by a wrist-action shaking machine for 48 h. The mixture was partitioned between CH_2Cl_2 (5 mL) and water (5 mL). The organic phase was dried over anhydrous $MgSO_4$, filtered, and the filtrate was concentrated under vacuum. The crude product was purified by column chromatography (silica gel, 2% to 3% MeOH in CH_2Cl_2). The blue solid was dissolved in a 1:1 mixture of CH_3CN:H_2O (4 mL) and NH_4PF_6 (104 mg, 0.64 mmol) was added for the ion exchange step. The organic phase was removed by vacuum and the solid was filtered, collected and washed with water (5 mL × 5) and CH_2Cl_2 (5 mL × 3). The solid was collected and dried to afford the desired USN-**1** as a blue

solid (54 mg, 89%): m.p. 165 °C (decomp.); FTIR (neat): 3426, 2954, 2922, 2852, 1480, 1446, 1368, 1332, 1216, 1144, 1084, 1038, 1014 cm^{-1}; ^{1}H NMR (500 MHz, CD_3CN) δ 8.08–8.00 (m, 4H), 7.84 (d, *J* = 1.5 Hz, 1H), 7.82 (br s, 1H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.76–7.72 (m, 1H), 7.50 (s, 1H), 7.48 (s, 1H), 7.49–7.32 (m, 10H), 7.26–7.10 (m, 10H), 6.98 (dd, J_1 = 8.1 Hz, J_2 = 1.8 Hz, 1H), 6.95 (br t, *J* = 5.5 Hz, 1H), 6.84 (br t, *J* = 5.6 Hz, 1H), 6.80 (ddd, J_1 = 8.5 Hz, J_2 = 6.7 Hz, J_3 = 1.3 Hz, 1H), 6.75–6.71 (m, 1H), 6.61 (d, *J* = 1.6 Hz, 1H), 6.52–6.43 (m, 2H), 6.17–6.09 (m, 4H), 4.56 (t, *J* = 6.4 Hz, 2H), 4.46–4.20 (m, 6H), 4.19 (qd, J_1 = 6.9 Hz, J_2 = 6.2 Hz, 1H), 3.92–3.80 (m, 4H), 3.71 (dd, J_1 = 15.6 Hz, J_2 = 6.2 Hz, 1H), 3.51 (s, 3H), 3.49 (s, 3H), 2.99 (t, *J* = 6.4 Hz, 2H), 2.65 (t, *J* = 6.5 Hz, 2H), 2.61 (d, *J* = 15.6 Hz, 1H), 2.07–2.03 (m, 4H), 1.68–1.59 (m, 28H), 1.56–1.46 (m, 4H), 1.36–1.24 (m, 4H), 0.65 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, CD_3CN) δ 174.98, 174.96, 174.14, 174.10, 173.4, 173.4, 154.8, 148.5, 148.2, 146.3, 146.0, 144.07, 144.06, 143.28, 143.26, 142.40, 142.39, 142.300, 142.296, 141.2, 138.6, 136.443, 136.436, 135.2, 134.1, 132.1, 131.59, 131.57, 130.6, 130.3, 129.57, 129.56, 129.2, 128.8, 128.7, 127.7, 126.3, 126.0, 125.972, 125.966, 125.59, 125.55, 125.4, 125.2, 123.9, 123.7, 123.3, 123.2, 122.6, 122.2, 112.0, 111.9, 111.850, 111.846, 104.15, 104.14, 103.93, 103.9, 87.9, 87.2, 83.2, 82.8, 50.19, 50.184, 50.177, 49.6, 49.4, 44.83, 44.82, 40.4, 39.0, 36.4, 36.3, 35.6, 35.5, 32.03, 32.01, 27.81, 27.80, 27.7, 27.64, 27.61, 27.0, 25.94, 25.92, 22.1, 21.8, 19.6; HRMS (ESI) *m*/*z* calculated for $[M-2PF_6]^{+2}$ $C_{105}H_{110}N_{12}S$ 801.4292, found 801.4268. Note: 1. Two pairs of considerably broader and consequently shorter signals at δ 146.4 (quaternary carbon) and 146.0 (quaternary carbon), and δ 123.9 (CH) and 123.7 (CH) were observed. These signals to the carbons in the 1,2,3-triazole rings, with the breadth resulting from rapid relaxation caused by the directly attached ^{14}N (a quadrupolar nucleus)[1]. These assignments were consistent with the observation in the ^{13}C NMR spectrum

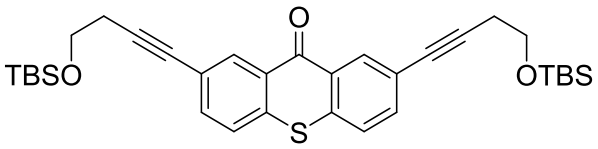
of USN-**3**. 2. The assignments were tentatively determined by comparing ^{13}C NMR spectrum and DEPT-135 spectra of **USN-1, USN-3, 10** and **9**.



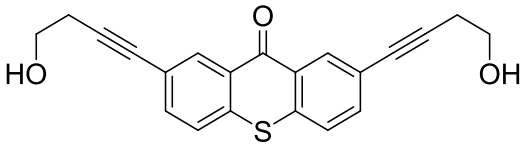
2-((1*E*,3*E*,5*Z*)-5-(3,3-Dimethyl-1-(6-oxo-6-(prop-2-ynylamino)hexyl)indolin-2-ylidene)penta-1,3-dienyl)-1,3,3-trimethyl-3*H*-indolium hexafluorophosphate (10). An oven-dried round-bottom flask charged with Cy5 **11**[2] (340 mg, 0.54 mmol), *N*,*N*′-dicyclohexylcarbodiimide (116 mg, 0.55 mmol) and 4-dimethylaminopyridine (7 mg, 0.057 mmol) was added CH_2Cl_2 (10 mL) and propargylamine (58 μL, 0.92 mmol) in sequence. The solution was stirred at rt for 12 h. The solvent was removed by vacuum and the crude material was purified by column chromatography (silica gel, 3% MeOH in CH_2Cl_2). The blue solid was dissolved in a 1:1 mixture of CH_3CN:H_2O (5 mL) and NH_4PF_6 (880 mg, 5.4 mmol) was added. The organic phase was removed by vacuum and the solid was filtered, collected and washed with water (5 mL × 5) and Et_2O (5 mL × 3). The solid was collected and dried to afford **10** as a blue solid (288 mg, 80%): m.p. 98 °C (decomposition); FTIR (neat) 3426, 3320, 3286, 2928, 2850, 1480, 1446, 1367, 1332, 1213, 1142, 1086, 1036, 1014 cm^{-1}; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.15–8.08 (m, 2H), 7.51–7.47 (m, 2H), 7.43–7.37 (m, 2H), 7.28–7.23 (m, 4H), 6.90 (br t, *J* = 5.7Hz, 1H), 6.59 (t, *J* = 12.5 Hz, 1H), 6.25 (d, *J* = 13.8 Hz, 1H), 6.21 (d, *J* = 13.9 Hz, 1H), 4.02 (t, *J* = 7.6Hz, 2H), 3.89 (dd, J_1 = 5.7 Hz, J_2 = 2.5 Hz, 2H), 3.55 (s, 3H), 2.41 (t, *J* = 2.5 Hz, 1H), 2.16 (t, *J* = 7.4 Hz, 2H), 1.81–1.74 (m, 2H), 1.687 (s, 6H), 1.686 (s, 6H), 1.66–

1.60 (m, 2H), 1.47–1.40 (m, 2H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 174.9, 174.3, 173.3, 154.9, 154.8, 144.1, 143.4, 142.5, 142.3, 129.6, 129.5, 125.960, 125.957, 125.7, 123.3, 123.2, 112.1, 111.8, 103.2, 104.1, 81.8, 71.6, 50.24, 50.19, 44.9, 36.3, 32.2, 29.0, 27.83, 27.77, 27.7, 27.0, 25.9; HRMS (APCI) *m*/*z* calculated for $[M-PF_6]^+$ $C_{35}H_{42}N_3O$ 520.3322, found 520.332.

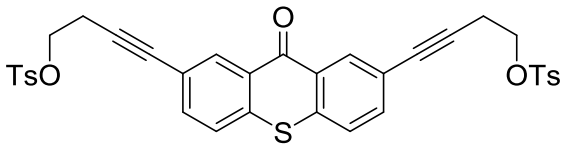
2. Synthesis of CM-2



2,7-Bis(4-((tert-butyldimethylsilyl)oxy)but-1-yn-1-yl)-9*H*-thioxanthen-9-one (13). Following the procedure described in the synthesis of **6**, **12** (500 mg, 1.34 mmol), tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct (24.7 mg, 0.027 mmol), CuI (5.22 mg, 0.027 mmol), triphenylphosphine (35.4 mg, 0.135 mmol), 4-(*tert*-butyldimethylsilyloxy)-but-1-yne (1.39 mL, 6.72 mmol) and NEt_3 (6 mL) were used in the reaction to afford **13** as a yellow solid (719 mg, 93%): m.p. 102-105 °C; FTIR (neat) 2930, 2860, 1630, 1590, 1470, 1410, 1330, 1250, 1220, 1100, 1090, 1000 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (dd, *J* = 1.9, 0.5 Hz, 2H), 7.59 (dd, *J* = 8.3, 1.9 Hz, 2H), 7.48 (dd, *J* = 8.3, 0.5 Hz, 2H), 3.84 (t, *J* = 7.1 Hz, 4H), 2.66 (t, *J* = 7.1 Hz, 4H), 0.92 (s, 18H), 0.11 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.70, 136.06, 134.92, 132.98, 128.93, 126.04, 122.35, 89.08, 80.46, 61.84, 25.93, 23.90, 18.41, -5.19. HRMS (ESI) *m*/*z* calculated for $[M+H]^+$ $C_{33}H_{45}O_3SSi_2$ 577.2622 found 577.2599.

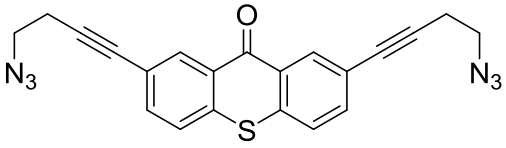


2,7-Bis(4-hydroxybut-1-yn-1-yl)-9*H*-thioxanthen-9-one (14). Following the procedure described in the synthesis of **7**, **13** (600 mg, 1.04 mmol), THF (15 mL), and TBAF (2.6 mL, 1.0 M in THF) were used in the reaction to yield **14** as a yellow solid (351 mg, 97%): m.p. 185 °C (decomposition); FTIR (neat) 3410, 2960, 2930, 2900, 2860, 1620, 1580, 1470, 1420, 1390, 1330, 1220, 1160, 1120, 1090,1050 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.35 – 8.30 (d, J = 1.9 Hz, 2H), 7.79 (dd, J_1 = 8.3, J_2 = 0.6 Hz, 2H), 7.70 (dd, J_1 = 8.4, J_2 = 1.9 Hz, 2H), 4.97 (t, J = 5.6 Hz, 2H), 3.61 (td, J_1 = 6.7, J_2 = 5.4 Hz, 4H), 2.59 (t, J_1 = 6.7 Hz, 4H). δ ^{13}C NMR (125 MHz, DMSO-d_6) δ 177.97, 136.27, 135.51, 132.00, 128.56, 127.62, 122.23, 91.05, 80.34, 60.09, 23.84. HRMS (ESI) *m*/*z* calculated for $[M+H]^+$ $C_{21}H_{17}O_3S$ 349.0893, found 349.0882.

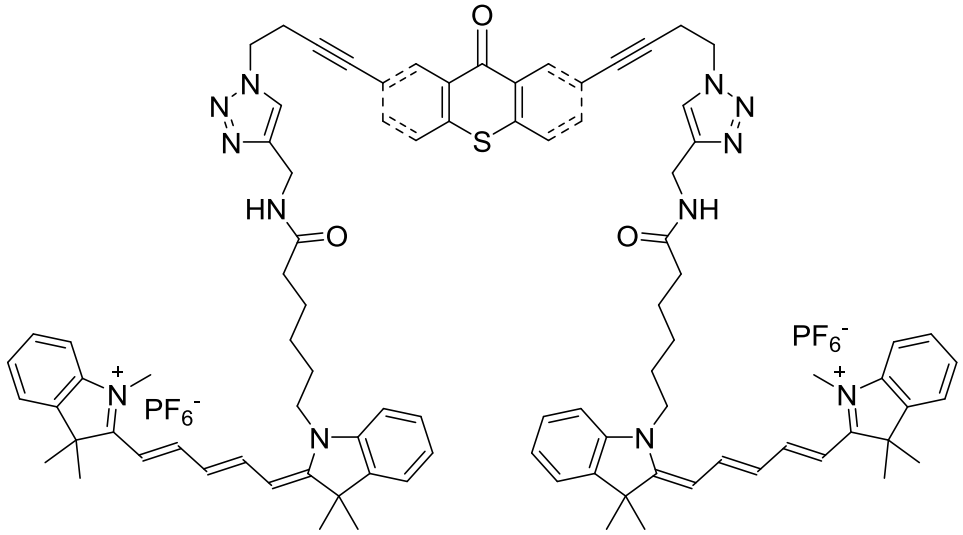


9-(Oxo-9*H*-thioxanthene-2,7-diyl)bis(but-3-yne-4,1-diyl)bis(4-methylbenzenesulfonate) (15). Following the procedure described in the synthesis of **8**, **14** (350 mg, 1.0 mmol), 4-toluenesulfonyl chloride (762 mg, 4.0 mmol), DMAP (6.10 mg, 0.05 mmol), NEt_3 (1.39 mL, 10.0 mmol), and CH_2Cl_2 (20 mL) were used in the reaction to yield **15** as a yellow solid (574 mg, 87%): m.p. 98-100 °C; FTIR (neat) 2970, 2930, 2850, 1640, 1590, 1470, 1410, 1350, 1120, 1100, 1090 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (dd, J_1 = 1.9, J_2 = 0.5 Hz, 2H), 7.87 – 7.81 (m, 4H), 7.56 (dd, J_1 = 8.3, J_2 = 1.9 Hz, 2H), 7.49 (dd, J_1 = 8.3, J_2 = 0.6 Hz, 2H), 7.39 – 7.32 (m, 4H), 4.20 (t, J = 7.0 Hz, 4H), 2.82 (t, J = 6.9 Hz, 4H), 2.43 (s, 6H).^{13}C NMR (125 MHz, $CDCl_3$) δ 178.47, 145.09, 136.51, 134.94, 133.02, 132.74, 129.98, 128.83, 128.00, 126.13,

121.55, 85.71, 81.43, 67.56, 21.68, 20.43. HRMS (ESI) *m/z* calculated for $[M+Na]^+$ $C_{35}H_{28}O_7S_3Na$ 679.0889, found 679.0868.

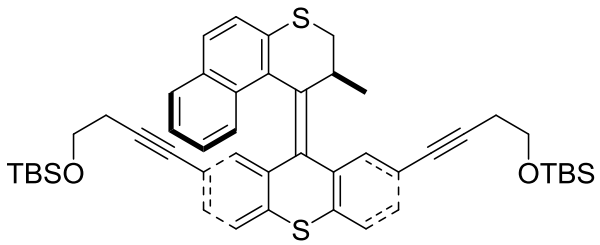


2,7-Bis(4-azidobut-1-yn-1-yl)-9H-thioxanthen-9-one (16). Following the procedure described in the synthesis of **9**, **15** (100 mg, 0.15 mmol), NaN_3 (39 mg, 0.6 mmol), and DMF (7 mL) were used in the reaction to yield **16** as a pale yellow solid (56 mg, 94%): m.p. 105-108 °C; FTIR (neat) 3040, 2980, 2940, 2888, 2090, 1630, 1590, 1470, 1410, 1330, 1280, 1220, 1120, 1080, 1030 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.63 (d, *J* = 1.9 Hz, 2H), 7.62 (dd, J_1 = 8.3, J_2 = 1.9 Hz, 2H), 7.50 (dd, J_1 = 8.3, J_2 = 0.6 Hz, 2H), 3.52 (t, *J* = 6.8 Hz, 4H), 2.76 (t, *J* = 6.8 Hz, 4H).^{13}C NMR (125 MHz, $CDCl_3$) δ 178.56, 136.44, 134.89, 133.06, 128.89, 126.12, 121.73, 87.59, 81.35, 49.79, 20.66. HRMS (ESI) *m/z* calculated for $[M+Na]^+$ $C_{21}H_{14}N_6OSNa$ 421.0842, found 421.0842.

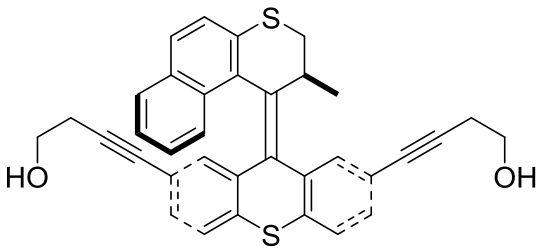


CM-2. Following the procedure described in the synthesis of USN-**1**, **16** (20 mg, 0.050 mmol), **10** (73 mg, 0.11 mmol), $CuSO_4 \cdot 5H_2O$ (1.26 mg, 0.005 mmol), sodium ascorbate (2.1 mg, 0.01 mmol), CH_2Cl_2 (0.15 mL), and water (0.15 mL) were used in the reaction to yield CM-**2** as a blue solid. A 1:1 mixture of CH_3CN:H_2O (4 mL) and NH_4PF_6 (163 mg, 1 mmol) was used for the ion exchange step to afford the desired CM-**2** (67 mg, 77%): m.p. 160 °C (decomposition); FTIR (neat) 2970, 2940, 2870, 1680, 1600, 1480, 1450, 1370, 1330, 1210, 1150, 1090, 1040, 1020 cm^{-1}; ^1H NMR (600 MHz, CD_3CN) δ 8.32 – 8.26 (m, 2H), 7.98 (q, *J* = 12.5, Hz, 4H), 7.79 (s, 2H), 7.57 – 7.51 (m, 4H), 7.44 (dd, J_1 = 16.9, J_2 = 7.4 Hz, 4H), 7.39 (tt, J_1 = 7.8, J_2 = 1.2 Hz, 2H), 7.33 (td, J_1 = 7.7, J_2 = 1.4 Hz, 2H), 7.27 – 7.18 (m, 6H), 7.14 (d, *J* = 7.9 Hz, 2H), 6.96 (dd, J_1 = 11.1, J_2 = 5.1 Hz, 2H), 6.39 (td, J_1 = 12.4, J_2 = 2.4 Hz, 2H), 6.07 (ddd, J_1 = 13.8, J_2 = 6.7, J_3 = 2.4 Hz, 4H), 4.54 (td, J_1 = 6.4, J_2 = 1.8 Hz, 4H), 4.42 (d, *J* = 5.9 Hz, 4H), 3.86 (t, *J* = 7.7 Hz, 4H), 3.51 (s, 6H), 2.96 (td, J_1 = 6.4, J_2 = 3.2 Hz, 4H), 2.11-2.14 (m, 4H), 1.71 – 1.53 (m, 32H), 1.40 – 1.32 (m, 4H). ; ^{13}C NMR (150 MHz, $CDCN_3$) δ 178.69, 174.52, 173.64, 173.10, 154.29, 154.26, 146.02, 143.62, 142.78, 141.93, 141.85, 137.26, 135.54, 132.69, 129.21, 129.10, 129.08, 127.39, 126.43, 125.59, 125.51, 125.07, 123.41, 122.78, 122.71, 122.09, 111.46, 111.40, 103.65, 103.39, 88.34, 81.97, 49.72, 48.98, 44.38, 35.91, 35.14, 31.58, 29.77, 27.32, 27.17, 27.09, 26.54, 25.40, 21.57. HRMS (ESI) *m*/*z* calculated for $[M-2PF_6]^{+2}$ $C_{91}H_{98}N_{12}O_3S$ 719.3797, found 719.3806.

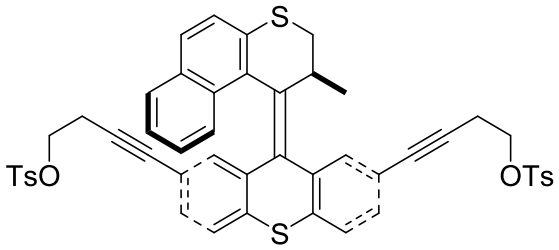
3. Synthesis of USN-3



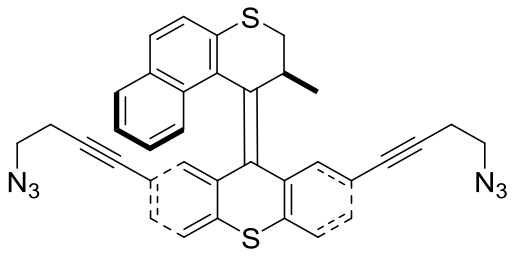
(4,4'-(9-(2-Methyl-2,3-dihydro-1*H*-benzo[f]thiochromen-1-ylidene)-9*H*-thioxanthene-2,7-diyl)bis(but-3-yne-4,1-diyl))bis(oxy)bis(tert-butyldimethylsilane) (18). Following the procedure described in the synthesis of **6**, motor **17** (*30*) (700 mg, 1.24 mmol), bis(triphenylphosphine)palladium(II) dichlodride (88 mg, 0.13 mmol), copper(I) iodide (48 mg, 0.26mmol), 4-(*tert*-butyldimethylsilyloxy)-1-butyne (1.02 mL, 4.96 mmol), and triethyl amine (6.5 mL) were used in the reaction to yield **18** as a white solid (782 mg, 82%) m.p. 72–74 °C; FTIR (neat) 3052, 2952, 2928, 2856, 1588, 1504, 1456, 1388, 1360, 1332, 1250, 1102, 1058, 1006 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62-7.56 (m, 3H), 7.51 (dd, J_1 = 8.0 Hz, J_2 = 0.3 Hz, 1H), 7.50–7.47 (m, 1H), 7.38 (d, J = 8.5 Hz, 1H), 7.31 (dd, J_1 = 8.0 Hz, J_2 = 1.7 Hz, 1H), 7.15 (dd, J_1 = 8.1 Hz J_2 = 0.5 Hz, 1H), 7.12 (ddd, J_1 = 8.1 Hz, J_2 = 6.8 Hz, J_3 = 1.2 Hz, 1H), 6.99 (ddd, J_1 = 8.5 Hz, J_2 = 6.8 Hz, J_3 = 1.3 Hz, 1H), 6.73 (dd, J_1 = 8.1 Hz, J_2 = 1.8 Hz, 1H), 6.35 (dd, J_1 = 1.8 Hz, J_2 = 0.3 Hz, 1H), 4.10 (dqd, J_1 = 7.4 Hz, J_2 = 6.8 Hz, J_3 = 3.5 Hz, 1H), 3.85 (t, J = 6.9 Hz, 2H), 3.70 (dd, J_1 = 11.4 Hz, J_2 = 7.4 Hz, 1H), 3.62 (t, J = 7.1 Hz, 2H), 3.06 (dd, J_1 = 11.4 Hz, J_2 = 3.5 Hz, 1H), 2.67 (t, J = 6.9 Hz, 2H), 2.39 (t, J = 7.1 Hz, 2H), 0.94 (s, 9H), 0.88 (s, 9H), 0.79 (d, J = 6.8 Hz, 3H), 0.12 (s, 6H), 0.04 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.9, 137.6, 135.8, 135.6, 135.2, 133.6, 132.0, 131.6, 131.2, 130.9, 130.6, 130.5, 130.0, 129.2, 127.71, 127.69, 127.5, 126.1, 125.8, 125.5, 124.4, 124.0, 121.9, 121.1, 88.4, 86.8, 81.1, 80.5, 61.84, 61.82, 37.2, 32.6, 25.93, 25.90, 24.0, 23.7, 19.2, 18.4, 18.3, −5.17, −5.18, −5.22, −5.23; HRMS (APCI) *m/z* calculated for $[M+H]^+$ $C_{47}H_{57}O_2S_2Si_2$ 773.3333, found 773.3331.



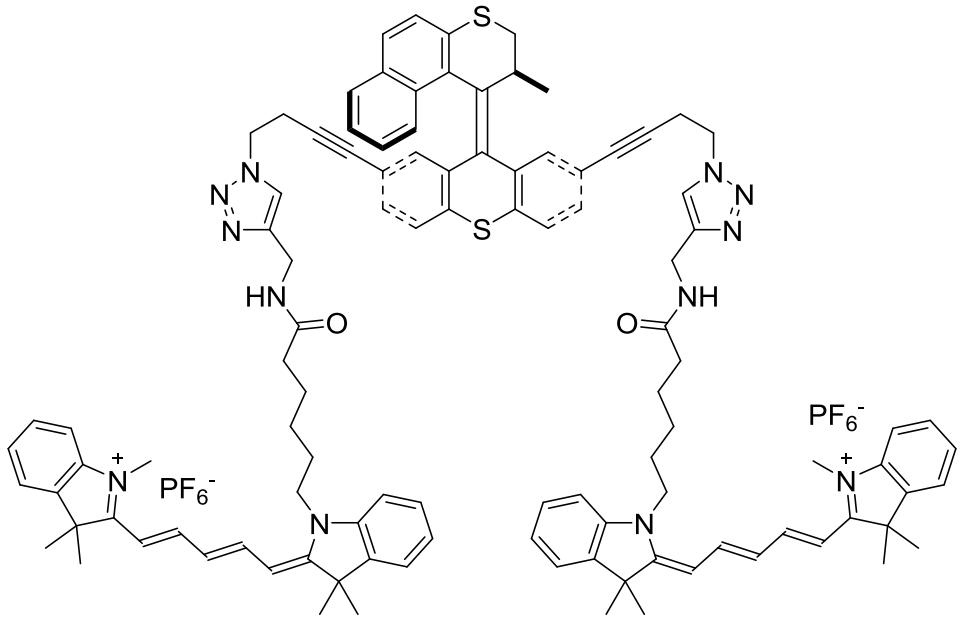
4,4'-(9-(2-Methyl-2,3-dihydro-1*H*-benzo[f]thiochromen-1-ylidene)-9*H*-thioxanthene-2,7-diyl)dibut-3-yn-1-ol (19). Following the procedure described in the synthesis of **7**, **18** (386 mg, 0.5 mmol), THF (2 mL), and TBAF (1.5 mL, 1.0 M in THF) were used in the reaction to yield **19** as a white solid (220 mg, 97%): m.p. 190 °C (decomposition); FTIR (neat) 3286, 3046, 2918, 2878, 2228, 1616, 1588, 1550, 1504, 1454, 1388, 1328, 1242, 1166, 1136, 1076, 1044, 1022 cm^{-1}; ^{1}H NMR (500 MHz, d4-THF) δ 7.66 (d, J = 1.6 Hz,1H), 7.64 (br d, J = 8.4 Hz, 1H), 7.59–7.56 (m, 1H), 7.54 (dd, J_1 = 8.0 Hz, J_2 = 0.3 Hz,1H), 7.53–7.49 (m, 1H), 7.37 (d, J = 8.6 Hz, 1H), 7.32 (dd, J_1 = 8.0 Hz, J_2 = 1.7 Hz, 1H), 7.16 (dd, J_1 = 8.1 Hz J_2 = 0.5 Hz, 1H), 7.06 (ddd, J_1 = 8.1 Hz, J_2 = 6.8 Hz, J_3 = 1.1 Hz,1H), 6.94 (ddd, J_1 = 8.5 Hz, J_2 = 6.8 Hz, J_3 = 1.3 Hz, 1H), 6.72 (dd, J_1 = 8.1 Hz, J_1 = 1.8 Hz, 1H), 6.33 (d, J = 1.7 Hz, 1H), 4.09 (dqd, J_1 = 7.2 Hz, J_2 = 6.7 Hz, J_3 = 3.4 Hz, 1H), 4.00 (t, J = 5.7 Hz, 1H), 3.77 (dd, J_1 = 11.5 Hz, J_2 = 7.3 Hz, 1H), 3.73 (t, J = 5.9 Hz, 1H), 3.68 (dt, J_1 = 7.0 Hz, J_2 = 5.7 Hz, 2H), 3.45 (dd, J_1 = 7.2 Hz, J_2 = 5.9 Hz, 2H), 3.05 (dd, J_1 = 11.5 Hz, J_2 = 3.4 Hz, 1H), 2.59 (t, J = 7.0 Hz, 2H), 2.30 (t, J = 7.2 Hz, 2H), 0.75 (d, J= 6.7 Hz, 3H); ^{13}C NMR (125 MHz, dϐ-THF) δ 139.0, 138.8, 136.8, 136.7, 136.4, 134.6,132.7, 132.6, 132.1, 131.7, 131.6, 131.3, 130.8, 130.1, 128.6, 128.5, 128.4, 127.0, 126.6, 126.1, 125.1, 124.7, 123.3, 122.4, 89.5, 87.9, 81.4, 80.9, 61.6, 61.5, 37.5, 33.6, 24.7, 24.4, 19.2; HRMS (APCI) *m*/*z* calculated for $[M+H]^+$ $C_{35}H_{29}O_2S_2$ 545.1603, found 545.1591.



4,4'-(9-(2-Methyl-2,3-dihydro-1*H*-benzo[f]thiochromen-1-ylidene)-9*H*-thioxanthene-2,7-diyl)bis(but-3-yne-4,1-diyl)bis(4-toluenesulfonate) (20). Following the procedure described in the synthesis of **8**, **19** (164 mg, 0.3 mmol), 4-toluenesulfonyl chloride (172 mg, 0.9 mmol), NEt_3 (0.17 mL, 1.2 mmol), and CH_2Cl_2 (6 mL) were used in the reaction to yield **20** as a pale-yellow solid (230 mg, 90%): m.p. 84–86 °C; FTIR (neat) 3052, 2960, 2924,1598, 1454, 1188, 1174, 1098, 1066 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.86–7.81 (m, 2H), 7.76–7.72 (m, 2H), 7.61 (d, J = 8.4 Hz, 1H), 7.59–7.55 (m, 2H), 7.51 (d, J = 8.1 Hz, 1H), 7.48–7.44 (m, 1H), 7.39 (d, J = 8.6 Hz, 1H), 7.35–7.31 (m, 2H), 7.28–7.24 (m, 3H), 7.15 (dd, J_1 = 8.1 Hz, J_2 = 0.4 Hz, 1H), 7.11 (ddd, J_1 = 8.0 Hz, J_2 = 6.8 Hz, J_3 = 1.2 Hz, 1H), 6.99 (ddd, J_1 = 8.5 Hz, J_2 = 6.8 Hz, J_3 = 1.3 Hz, 1H), 6.65 (dd, J_1 = 8.1 Hz, J_1 = 1.8 Hz, 1H), 6.29 (d, J = 1.5 Hz, 1H), 4.27–4.18 (m, 2H), 4.07 (dqd, J_1 = 7.5 Hz, J_2 = 6.8 Hz, J_3 = 3.5 Hz, 1H), 4.03–3.98 (m, 2H), 3.69 (dd, J_1 = 11.5 Hz, J_2 = 7.5 Hz, 1H), 3.05 (dd, J_1 = 11.5 Hz, J_2 = 3.5 Hz, 1H), 2.84 (t, J = 7.0 Hz, 2H), 2.59–2.49 (m, 2H), 2.41 (s, 3H), 2.40 (s, 3H), 0.80 (d, J = 6.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.0,144.8, 138.1, 137.8, 136.1, 135.7, 134.1, 132.9, 132.8, 132.2, 131.6, 130.4, 130.9, 130.8, 130.7, 130.5, 130.0, 129.93, 129.87, 129.2, 128.0, 127.9, 127.83, 127.82, 127.6, 126.1, 125.9, 125.6, 124.4, 123.9, 121.1, 120.2, 85.0, 83.5, 82.2, 81.6, 67.61, 67.56, 37.1, 32.8, 21.7, 21.6, 20.6, 20.2, 19.3; HRMS (APCI) *m*/*z* calculated for $[M+H]^+$ $C_{49}H_{41}O_6S_4$ 853.1780, found 853.1773.



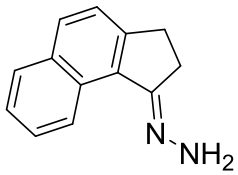
(2,7-Bis(4-azidobut-1-ynyl)-9*H*-thioxanthen-9-ylidene)-2-methyl-2,3-dihydro-1*H*-benzo[f]thiochromene (21). Following the procedure described in the synthesis of **9**, **20** (85.3 mg, 0.100 mmol), NaN_3 (20 mg, 0.31 mmol), and DMF (3 mL) were used in the reaction to yield **21** as a pale yellow solid (57 mg, 96%): m.p. 96–98 °C; FTIR (neat) 3052, 2870, 2926, 2088, 1738, 1586, 1444, 1426, 1414, 1366, 1218, 1064 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.64–7.56 (m, 3H), 7.51 (dd, J_1 = 8.0 Hz, J_2 = 0.3 Hz, 1H), 7.49–7.46 (m,1H), 7.39 (d, J = 8.5 Hz, 1H), 7.32 (dd, J_1 = 8.0 Hz, J_2 = 1.7 Hz, 1H), 7.15 (dd, J_1 = 8.1 Hz, J_2 = 0.5 Hz, 1H), 7.11 (ddd, J_1 = 8.1 Hz, J_2 = 6.8 Hz, J_3 = 1.2 Hz, 1H), 6.99 (ddd, J_1 = 8.5 Hz, J_2 = 6.8 Hz, J_3 = 1.2 Hz, 1H), 6.75 (dd, J_1 = 8.1 Hz, J_2 = 1.8 Hz, 1H), 6.37 (d, J = 1.6 Hz, 1H), 4.09 (dqd, J_1 = 7.4 Hz, J_2 = 6.8 Hz, J_3 = 3.4 Hz, 1H), 3.70 (dd, J_1 = 11.5 Hz, J_2 = 7.4 Hz, 1H), 3.50 (t, J = 6.6 Hz, 2H), 3.27 (t, J = 6.9 Hz, 2H), 3.05 (dd, J_1 = 11.5 Hz, J_2 = 3.4 Hz, 1H), 2.76 (t, J = 6.6 Hz, 2H), 2.47 (t, J = 6.9 Hz, 2H), 0.79 (d, J = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.92, 137.85, 136.00, 135.72, 135.37, 133.99, 132.12, 131.56, 130.92, 130.81, 130.58, 130.55, 129.92, 129.12, 127.72, 127.70, 127.61, 126.18, 125.87, 125.52, 124.41, 123.92, 121.30, 120.46, 86.94, 85.45, 82.13, 81.43, 49.79, 49.73, 37.09, 32.56, 20.88, 20.40, 19.22; HRMS (APCI) *m*/*z* calculated for $[M+Na]^+$ $C_{35}H_{26}N_6S_2Na$ 617.1553, found 617.1570.



6.4. USN-3. Following the procedure described in the synthesis of USN-**1**, **21** (11.9 mg, 0.02 mmol), **10** (29.3 mg, 0.044 mmol), $CuSO_4 \cdot 5H_2O$ (0.5 mg, 0.002 mmol), sodium ascorbate (1.5 mg, 0.06 mmol), CH_2Cl_2 (0.05 mL), and water (0.05 mL) were used in the first step. A 1:1 mixture of CH_3CN:H_2O (4 mL) and NH_4PF_6 (65.2 mg, 0.4 mmol) was used for the ion exchange step to afford USN-**3** as a blue solid (29 mg, 76%): m.p. 155 °C (decomposition); FTIR (neat) 3426, 2926, 2854, 1480, 1446, 1368, 1332, 1216, 1144, 1088, 1038, 1014 cm^{-1}; ^1H NMR (500 MHz, CD_3CN) δ 8.10–8.00 (m, 4H), 7.81 (br s, 1H), 7.68-7.65 (m,1H), 7.63–7.60 (m, 1H), 7.56 (d, J = 1.5 Hz, 1H), 7.55 (s, 1H), 7.51 (d, J = 8.0 Hz, 1H), 7.48–7.43 (m, 5H), 7.42–7.34 (m, 5H), 7.27–7.20 (m, 7H), 7.19-7.15 (m, 3H), 7.11 (ddd, J_1 = 8.1 Hz, J_2 = 6.8 Hz, J_3 = 1.1 Hz, 1H), 6.97 (ddd, J_1 = 8.6 Hz, J_2 = 6.8 Hz, J_3 = 1.3 Hz, 1H), 6.87 (br t, J = 5.7 Hz, 1H), 6.83 (br t, J = 5.7 Hz, 1H), 6.68 (dd, $J1$ = 8.1 Hz, J_2 = 1.8 Hz, 1H), 6.53–6.44 (m, 2H), 6.28 (d, J = 1.7 Hz, 1H), 6.18–6.10 (m, 4H), 4.57 (t, J = 6.4 Hz, 2H), 4.43–4.29 (m, 6H), 3.99 (dqd, J_1 = 7.2 Hz, J_2 = 6.7 Hz, J_3 = 3.0 Hz, 1H), 3.91–3.85 (m, 4H), 3.82 (dd, J_1 = 11.5 Hz, J_2 = 7.2 Hz, 1H), 3.50 (br s, 6H), 3.10 (dd, J_1 = 11.5 Hz, J_2 = 3.0 Hz, 1H), 3.00 (t, J = 6.3 Hz, 2H), 2.72 (t, J = 6.5 Hz, 2H), 2.07–2.03 (m, 4H), 1.71–1.60 (m, 28H), 1.56–1.47 (m, 4H),

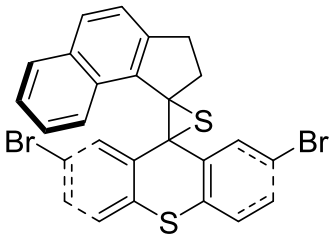
1.36–1.28 (m, 4H), 0.67 (d, J = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.01, 175.00, 174.18, 174.15, 173.44, 173.40, 154.8, 144.4, 143.30, 143.29, 142.43, 142.41, 142.314, 142.310, 139.22, 139.20, 136.7, 136.6, 136.5, 135.4, 132.7, 132.5, 131.7, 131.6, 131.5, 131.4, 131.1, 130.2, 129.6, 129.0, 128.9, 128.7, 127.7, 127.0, 126.4, 126.1, 125.994, 125.985, 125.6, 124.7, 123.9, 123.7, 123.282, 123.280, 123.2, 122.5, 121.3, 111.98, 111.96, 111.86, 104.16, 104.15, 103.94, 103.93, 88.2, 87.1, 83.1, 82.5, 55.4, 50.21, 50.20, 49.6, 49.5, 44.9, 37.7, 36.37, 36.34, 35.6, 35.5, 33.1, 32.0, 27.8, 27.7, 27.6, 27.02, 27.00, 25.9, 22.2, 21.8, 19.1; HRMS (APCI) m/z calculated for $[M-2PF_6]^{+2}$ $C_{105}H_{110}N_{12}S_2$ 817.4153, found 817.4147. Note: 1. Two considerably broader and consequently shorter signals at δ 123.9 (CH) and 123.6 (CH) were observed. These signals are the carbons in the 1,2,3-triazole rings, with the breadth resulting from rapid relaxation caused by the directly attached ^{14}N (a quadrupolar nucleus). Compared to the signals at δ 123.9 and δ 123.7 in the ^{13}C NMR of USN-**1**, the signals at δ 123.9 (CH) and 123.6 (CH) were even more severely broadened. In the ^{13}C spectrum of USN-**3**, we did not observe any carbon signals at the δ ~146.5 region corresponding to the quaternary carbon in the 1,2,3-triazole rings, which were found in the case of USN-**1**. 2. The assignments were determined by comparing ^{13}C and DEPT-135 spectra of USN-**1**, USN-**3**, and **21**.

4. Synthesis of USN-4



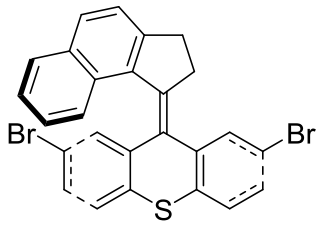
Hydrazone 24. A 50 mL round-bottomed flask equipped with a stir bar was charged with ketone **23**[3] (2.0 g, 10.97 mmol), hydrazine monohydrate (54.8 mL, 1130 mmol) and ethanol

(21.9 mL). The mixture was stirred under reflux for 2 d and permitted to cool to rt. The ethanol was removed under reduced pressure. The mixture was partitioned between CH_2Cl_2 (50 mL) and water (30 mL × 3). The organic phase was dried over anhydrous $MgSO_4$, and concentrated under vacuum to afford **24** as a yellow solid (1.95 g, 91%): m.p. 94-95 °C; FTIR (neat) 3360, 3310, 3190, 3050, 2920, 1630, 1590, 1510, 1440, 1420, 1380, 1330, 1250, 1180, 1120, 1090, 1030, 1000 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 9.24 (d, J = 8.33, 1H), 7.89 – 7.81 (m, 1H), 7.75 (d, J = 8.3 Hz, 1H), 7.57 (ddd, J_1 = 8.4, J_2 = 6.8, J_3 = 1.4 Hz, 1H), 7.48 (ddd, J_1 = 8.2, J_2 = 6.8, J_3 =1.3 Hz, 1H), 7.42 – 7.36 (m, 1H), 5.25 (brs, 2H), 3.23 – 3.12 (m, 2H), 2.84 – 2.78 (m, 2H).^{13}C NMR (125 MHz, $CDCl_3$) δ 159.73, 147.05, 133.07, 132.44, 129.99, 129.03, 128.20, 127.31, 125.65, 125.52, 123.45, 28.89, 25.45. HRMS (ESI) *m*/*z* calculated for $[M+H]^+$ $C_{13}H_{13}N_2$ 197.1073, found 197.1070.



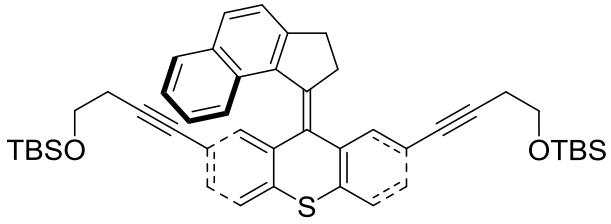
Episulfide 26. To an oven dried round-bottom flask charged with hydrazone **24** (300 mg, 1.5 mmol) and $MgSO_4$ (157 mg, 1.3 mmol) was added CH_2Cl_2 (15 mL). To this suspension was added quickly MnO_2 (522 mg, 6 mmol) at *ca*. 5 °C. The flask was immersed and stirred in a cold bath ranging from –12 °C to –10 °C for 2 h. After that, the mixture was cooled to – 50 °C and then transferred to a Schlenk filtration tube connected to an oven dried three-neck round bottom flask. The filtrate was collected and the Schlenk tube was rinsed with pre-cooled CH_2Cl_2 (20 mL, -50 °C). To the flask containing the filtrate, thione **25** (290 mg, 0.75 mmol) was added until no more N_2 evolved. The mixture was stirred for an additional 2 h at rt. The mixture was poured

into methanol (70 mL) and stirred vigorously until formation of a precipitant. The solid was filtered, washed with methanol (25 mL) and dried under vaccum. The crude product was purified by column chromatography (SiO_2; 10% EtOAc in hexanes) to afford **26** (228 mg, 55 %): m.p. 176-177 °C; FTIR (neat) 3060, 2990, 2860, 1630, 1520, 1440, 1380, 1250, 1160, 1080 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 8.90 (d, *J* = 8.6 Hz, 1H), 8.02 (d, *J* = 2.2 Hz, 1H), 7.86 (d, *J* = 2.2 Hz, 1H), 7.57 – 7.51 (m, 2H), 7.40 – 7.33 (m, 2H), 7.29 (d, *J* = 8.2 Hz, 1H), 7.22 (ddd, J_1 = 8.0, 6.7, J_2 = 1.2 Hz, 1H), 7.18 (d, *J* = 8.2 Hz, 1H), 6.86 (dd, J_1 = 8.1, J_2 = 2.1 Hz, 1H), 6.78 (d, *J* = 8.1 Hz, 1H), 3.18 (ddd, J_1 = 14.1, J_2= 9.9, J_3 = 6.8 Hz, 1H), 2.76 – 2.63 (m, 2H), 1.55 – 1.47 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.14, 140.69, 136.20, 135.59, 134.63, 134.08, 132.53, 132.37, 131.69, 130.19, 129.99, 129.72, 129.47, 128.19, 127.78, 127.75, 124.63, 124.48, 124.04, 122.89, 120.91, 120.06, 65.13, 60.53, 37.48, 30.69. HRMS (ACPI) *m*/*z* calculated for $[M+H]^+$ $C_{26}H_{17}Br_2S_2$ 550.9133, found 550.9131.



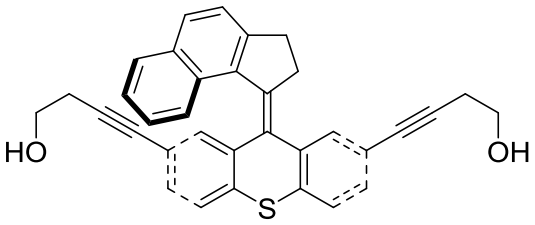
2,7-Dibromo-9-(2,3-dihydro-1H-cyclopenta[a]naphthalen-1-ylidene)-9H-thioxanthene (27). To a 200 mL screw-capped tube charged with **26** (200 mg, 0.36 mmol) was added trimethyl phosphite (5 mL, 42.4 mmol) and the mixture was stirred at 130 °C for 12 h. After the reaction mixture was cooled to room temperature, it was poured into methanol (50 mL). The precipitate was filtered and washed with methanol (15 mL). The solid was purified by column chromatography (silica gel, 10% CH_2Cl_2 in hexanes) to afford motor **27** as a yellow solid (131 mg, 70%): m.p. 190 °C (decomposition); FTIR (neat) 3060, 3020, 2960, 2840,1610, 1580, 1510, 1440, 1380,1280, 1260, 1210, 1160, 1130, 1080, 1030 cm^{-1}; ^1H NMR

(500 MHz, $CDCl_3$) δ 7.86 (d, J = 2.1 Hz, 1H), 7.78 (d, J = 8.2, 1H), 7.75 (m, 1H), 7.48 (d, J = 8.0, 1H), 7.46 (d, J = 8.0, 1H), 7.43 – 7.39 (m, 1H), 7.36 (dd, J_1 = 8.3, J_2 = 2.1, 1H), 7.25 – 7.21 (m, 1H), 7.13 (dd, J_1 = 8.3, J_2 = 2.1 Hz, 1H), 6.88 (ddd, J_1 = 8.2, J_2 = 6.7, J_3 = 1.3 Hz, 1H), 6.82 (dd, J_1 = 8.6, J_2 = 1.1 Hz, 1H), 6.79-6.75 (m, 1H), 3.25 (br m, 4H).^{13}C NMR (125 MHz, $CDCl_3$) δ 147.93, 143.45, 141.34, 139.82, 135.90, 134.71, 134.16, 132.99, 131.64, 131.02, 130.74, 129.21, 129.15, 129.14, 128.68, 128.11, 127.73, 126.07, 125.77, 125.16, 124.61, 123.14, 120.55, 120.35, 33.68, 32.09. HRMS (ACPI) *m*/*z* calculated for $[M+H]^+$ $C_{26}H_{17}Br_2S$ 518.9412, found 518.9391.



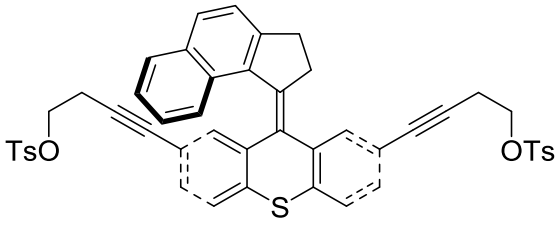
(((9-(2,3-Dihydro-1H-cyclopenta[a]naphthalen-1-ylidene)-9H-thioxanthene-2,7-diyl)bis(but-3-yne-4,1-diyl))bis(oxy))bis(tert-butyldimethylsilane) (28). Following the procedure described in the synthesis of **6**, **27** (185 mg, 0.35 mmol), tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct (16.3 mg, 0.017 mmol), triphenylphosphine (23.31 mg, 0.087 mmol), CuI (6.87 mg, 0.035 mmol), 4-(*tert*-butyldimethylsilyloxy)-but-1-yne (0.37 mL,1.75 mmol) and NEt_3 (5 mL) were used in the reaction to afford **28** as a yellow solid (235 mg, 88%): m.p. 56-58 °C; FTIR (neat) 3070, 2960, 2930, 2860, 1590, 1520, 1460, 1390, 1360, 1250, 1220, 1100, 1070, 1010 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 – 7.72 (m, 2H), 7.69 (d, J = 8.1 Hz, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.46 (d, J = 8.1 Hz, 2H), 7.25 – 7.22 (m, 1H), 7.19 (ddd, J_1 = 8.0, J_2 = 5.6, J_3 = 2.3 Hz, 1H), 7.02 (dd, J_1 = 8.0, J_2 = 1.7 Hz, 1H), 6.84 (dd, J_1 = 5.7, J_2 = 1.4 Hz, 2H), 6.69 (d, J = 1.6 Hz, 1H), 3.85 (t, J = 6.9 Hz, 2H), 3.55 (t, J = 7.1 Hz, 2H), 3.22 (br m, 4H), 2.66 (t, J = 6.9

Hz, 2H), 2.33 (t, *J* = 7.1 Hz, 2H), 0.94 (s, 9H), 0.84 (s, 9H), 0.13 (s, 6H), -0.02 (s, 6H).^{13}C NMR (150 MHz, $CDCl_3$) 147.67, 142.22, 139.71, 138.12, 136.52, 135.27, 134.68, 132.96, 131.64, 131.11, 130.22, 129.36, 129.20, 127.92, 127.89, 127.59, 127.37, 127.25, 125.96, 125.01, 124.45, 122.99, 122.07, 122.04, 88.04, 87.02, 81.29, 80.64, 61.90, 61.74, 33.94, 32.19, 25.94, 25.87, 23.97, 23.66, 18.40, 18.29, -5.17, -5.30. HRMS (ESI) *m*/*z* calculated for $[M+Na]^+$ $C_{46}H_{54}O_2SSi_2Na$ 749.3275, found 749.3286.

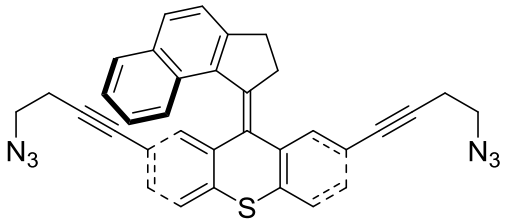


4,4'-(9-(2,3-Dihydro-1H-cyclopenta[a]naphthalen-1-ylidene)-9H-thioxanthene-2,7-diyl)bis(but-3-yn-1-ol) (29). Following the procedure described in the synthesis of **7**, **28** (200 mg, 0.275 mmol), THF (10 mL), and TBAF (0.69 mL, 1.0 M in THF) were used in the reaction to yield **29** as a yellow solid (116 mg, 84%): m.p. 200 °C (decomposition); FTIR (neat) 3320, 3060, 2930, 2910, 2850, 1740, 1590, 1510, 1460, 1390, 1340, 1250, 1140, 1070, 1040,1020 cm^{-1}; ^{1}H NMR (600 MHz, THF-d_8) δ 7.82 (d, *J* = 1.6 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.1 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.25 (dd, J_1 = 8.1, J_2 = 1.7 Hz, 1H), 7.15 (ddd, J_1 = 8.0, J_2 = 6.6, J_3 = 1.2 Hz, 1H), 7.01 (dd, J_1 = 8.1, J_2 = 1.8 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.79 (ddd, J_1 = 8.2, J_2 = 6.6, J_3 = 1.3 Hz, 1H), 6.65 (d, *J* = 1.7 Hz, 1H), 3.99 (s, 1H), 3.68 (t, *J* = 7.0 Hz, 3H), 3.39 (t, *J* = 7.2 Hz, 2H), 3.24 (br m, 4H), 2.60 (t, *J* = 7.1 Hz, 2H), 2.25 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (150 MHz, THF-d_8) δ 148.91, 143.13, 140.85, 139.12, 137.18, 136.13, 135.72, 134.11, 132.29, 131.84, 131.13, 130.32, 130.07, 128.91, 128.74, 128.42, 128.33, 128.04, 126.68, 125.69, 125.07, 123.80, 123.46, 123.36, 89.09, 88.02, 81.62, 81.02, 61.62, 61.46, 34.67, 32.76,

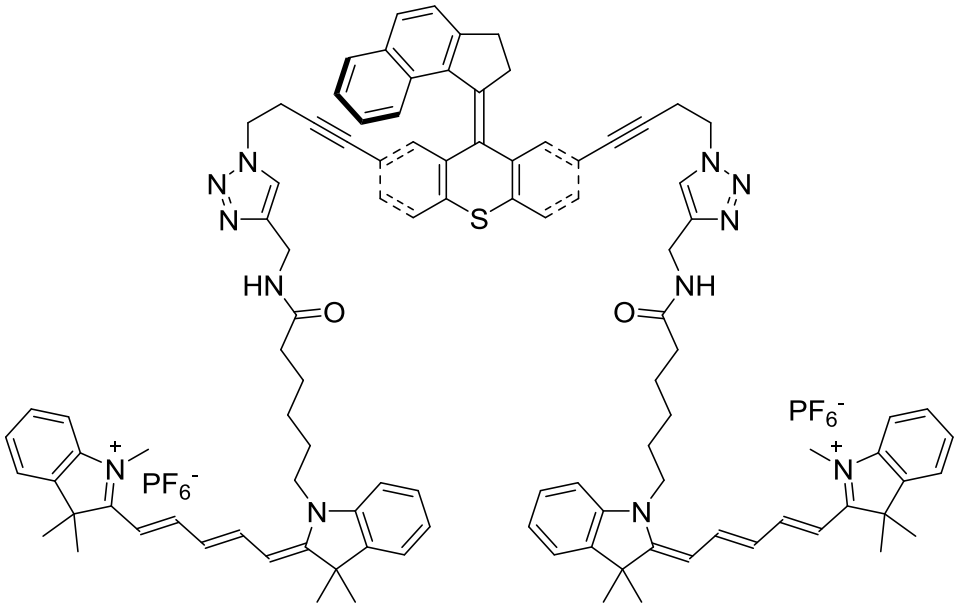
24.71, 24.36. HRMS (ESI) *m*/*z* calculated for $[M+Na]^+$ $C_{34}H_{26}O_2SNa$ 521.1546, found 521.1527.



(9-(2,3-Dihydro-1H-cyclopenta[a]naphthalen-1-ylidene)-9H-thioxanthene-2,7-diyl)bis(but-3-yne-4,1-diyl) bis(4-methylbenzenesulfonate) (30). Following the procedure described in the synthesis of **8**, **29** (100 mg, 0.2 mmol), 4-toluenesulfonyl chloride (153 mg, 0.8 mmol), DMAP (1.22 mg, 0.01 mmol) NEt_3 (0.28 mL, 2 mmol), and CH_2Cl_2 (20 mL) were used in the reaction to yield **30** as a yellow solid (137 mg, 85%): m.p. 160-162 °C; FTIR (neat) 3060, 2930, 2850, 1600, 1460, 1360, 1190, 1170, 1100, 1070, 1020 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.86 – 7.80 (m, 2H), 7.75 (d, J = 8.2 Hz, 1H), 7.73 – 7.70 (m, 3H), 7.70 – 7.67 (m, 1H), 7.50 (dd, J_1 = 8.0, 0.4 Hz, 1H), 7.48 – 7.45 (m, 2H), 7.34 – 7.29 (m, 2H), 7.28 – 7.24 (m, 2H), 7.18 (ddd, J_1 = 8.1, J_2 = 6.2, J_3 = 1.8 Hz, 2H), 6.96 (dd, J_1 = 8.1, J_2 = 1.8 Hz, 1H), 6.85 – 6.77 (m, 2H), 6.63 (dd, J_1 = 1.8, J_2 = 0.5 Hz, 1H), 4.22 (t, J = 7.0 Hz, 2H), 3.92 (t, J = 7.3 Hz, 2H), 3.24 (br m, 4H), 2.83 (t, J = 7.0 Hz, 2H), 2.48 (t, J = 7.3 Hz, 2H), 2.40 (s, 3H), 2.39 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) 147.80, 145.02, 144.88, 142.64, 139.63, 138.06, 136.31, 135.83, 135.25, 132.96, 132.89, 132.83, 131.74, 131.23, 130.42, 129.94, 129.87, 129.41, 129.27, 128.01, 128.00, 127.92, 127.80, 127.68, 127.33, 126.93, 125.87, 125.04, 124.49, 123.10, 121.28, 121.17, 84.64, 83.56, 82.43, 81.74, 67.72, 67.50, 33.86, 32.19, 21.67, 20.55, 20.16. HRMS (ESI) *m*/*z* calculated for $[M+Na]^+$ $C_{48}H_{38}O_6S_3Na$ 829.1723, found 829.1724.



2,7-Bis(4-azidobut-1-yn-1-yl)-9-(2,3-dihydro-1H-cyclopenta[a]naphthalen-1-ylidene)-9H-thioxanthene (31). Following the procedure described in the synthesis of **9**, **30** (200 mg, 0.25 mmol), NaN_3 (65 mg, 1.0 mmol), and DMF (7 mL) were used in the reaction to yield **31** as a yellow solid (123 mg, 90%): m.p. 137-138 °C; FTIR (neat) 3050, 2930, 2860, 2090, 1620, 1590, 1460, 1390, 1260, 1140, 1070 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, J = 1.7 Hz, 1H), 7.76 (d, J = 8.2 Hz, 1H), 7.73 – 7.69 (m, 1H), 7.51 (dd, J_1 = 8.0, J_2 = 0.4 Hz, 1H), 7.49 – 7.47 (m, 1H), 7.47 – 7.45 (m, 1H), 7.29 – 7.25 (m, 1H), 7.21 (ddd, J_1 = 8.1, J_2 = 5.9, J_3 = 2.1 Hz, 1H), 7.04 (dd, J_1 = 8.0, J_2 = 1.8 Hz, 1H), 6.89 – 6.79 (m, 2H), 6.70 (dd, J_1 = 1.8, J_2 = 0.5 Hz, 1H), 3.51 (t, J = 6.7 Hz, 2H), 3.37 – 3.07 (m, 6H), 2.76 (t, J = 6.7 Hz, 2H), 2.41 (t, J = 6.9 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.78, 142.54, 139.63, 138.10, 136.43, 135.74, 135.12, 132.98, 131.74, 131.21, 130.28, 129.36, 129.19, 127.91, 127.84, 127.70, 127.35, 127.06, 125.96, 125.05, 124.47, 123.07, 121.45, 121.39, 86.57, 85.58, 82.32, 81.58, 49.92, 49.69, 33.90, 32.16, 20.88, 20.41. HRMS (ESI) *m*/*z* calculated for $[M+H]^+$ $C_{34}H_{25}N_6S$ 549.1856, found 549.1876.



USN-4. Following the procedure described in the synthesis of USN-**1**, **31** (13.77 mg, 0.025 mmol), **10** (36 mg, 0.55 mmol), $CuSO_4 \cdot 5H_2O$ (0.63 mg, 0.0025 mmol), sodium ascorbate (1.0 mg, 0.0075 mmol), CH_2Cl_2 (0.1 mL), and water (0.1 mL) were used in the reaction to yield USN-**4** as a blue solid. A 1:1 mixture of CH_3CN:H_2O (4 mL) and NH_4PF_6 (82 mg, 0.5 mmol) was used for the ion exchange step to afford the desired USN-**4** (38 mg, 80%): m.p. 158 °C (decomposition); FTIR (neat) 3430, 2980, 2930, 2870, 1480, 1450, 1370, 1330, 1220, 1150, 1080, 1040, 1010 cm^{-1}; ^1H NMR (600 MHz, CD_3CN) δ 8.03 (tt, J_1 = 13.1, J_2 = 3.9 Hz, 4H), 7.82 – 7.72 (m, 4H), 7.51 – 7.33 (m, 12H), 7.26 – 7.11 (m, 10H), 6.96 (dd, J_1 = 8.1, J_2 = 1.8 Hz, 1H), 6.85 – 6.72 (m, 4H), 6.58 (d, J = 1.8 Hz, 1H), 6.46 (td, J_1 = 12.4, J_2 = 2.0 Hz, 2H), 6.18 – 6.05 (m, 4H), 4.56 (t, J = 6.4 Hz, 2H), 4.38 (d, J = 5.8 Hz, 2H), 4.31 – 4.24 (m, 4H), 3.86 (dt, J_1 = 22.9, J_2 = 7.7 Hz, 4H), 3.50 (d, J = 13.4 Hz, 6H), 3.25 (br s, 4H), 2.99 (t, J = 6.3 Hz, 2H), 2.65 (t, J = 6.4 Hz, 2H), 2.05 (q, J = 7.5 Hz, 4H), 1.68 – 1.60 (m, 28H), 1.57-1.47 (m, 6H), 1.33-1.27 (m, 2H).; ^{13}C NMR (150 MHz, $CDCN_3$) δ 174.56, 174.53, 173.74, 173.68, 173.06, 172.99, 154.34, 149.39, 145.98, 145.54, 143.63, 143.42, 142.85, 141.97, 141.86, 140.52, 138.57, 136.60, 135.92, 135.88, 133.48, 131.80, 131.54, 130.92, 130.48, 130.16, 129.89, 129.12, 128.74, 128.33,

128.28, 127.34, 126.44, 126.00, 125.65, 125.61, 125.53, 125.14, 125.00, 124.09, 123.41, 123.22, 122.82, 122.72, 122.15, 121.71, 111.52, 111.50, 111.40, 103.70, 103.49, 103.46, 87.47, 86.65, 82.79, 82.31, 49.73, 49.14, 48.94, 44.37, 35.91, 35.87, 35.15, 35.02, 34.85, 34.24, 34.18, 32.38, 31.55, 29.78, 27.35, 27.17, 27.14, 26.53, 25.44,25.42, 21.69, 21.38.; HRMS (ESI) *m*/*z* calculated for $[M\text{-}2PF_6]^{+2}$ $C_{104}H_{108}N_{12}O_2S$ 794.4214, found 794.4243.

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