

**Materials and methods:** All the reagents were from commercial source and used as received.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker DPX-400 MHz NMR spectrometer using the residual proton resonance of the solvent as the internal standard. All molecules without characterization data mentioned below were synthesized through well-established synthesis procedures previously reported by our group.<sup>S1, S2, S3</sup> UV-vis absorption spectra were obtained by a Carry 100 Scan spectrometer. Fluorescence spectra were recorded on a PerkinElmer LS 55 spectrofluorimeter. Mass spectrometric data were collected by Capillary LC (Thermo Dionex Ultimate 3000)-ESI-MS (Bruker AmaZon quadrupole ion trap).

**Dynamic Light Scattering (DLS) Study:** For the DLS measurements, 2  $\mu\text{mol}$  of **3**, **4** or **5** was dissolved in 10 mL PBS buffer (pH 7.4, 10 mM) and stirred at 4 °C for overnight and then stored in room temperature as 200  $\mu\text{M}$  stock solution. Then these oligomeric amphiphile solutions were diluted to 50  $\mu\text{M}$  with PBS buffer and filtered using hydrophilic membrane (pore size 0.450  $\mu\text{m}$ ) before experiment was performed. The diluted samples were treated with UV irradiation (Black Ray UV lamp, 365 nm, 115 V ~ 60 Hz); bCA; UV irradiation followed the addition of bCA or UV irradiation followed the addition of BSA. The sizes of each solution were recorded overtime by a Malvern Nanozetasizer ZS90 with a 637-nm laser source with non-invasive backscattering technology detected at 173° using disposable sizing cuvette. Standard operating procedures (SOP) are set up including following parameters: the sample was equilibrated for 120 s at 25 °C before each measurement; the sizes were reported as the hydrodynamic diameter ( $D_H$ ) and each measurement average 16 runs were repeated three times; the data was automatically analyzed by the zetasizer software through Mie model which then give the view of count rate, correlation function, intensity particle size distribution (PSD), volume PSD and Number PSD after each measurement.

**Transmission Electron Microscope (TEM) Study:** The same sample for DLS measurement was dropped onto carbon-coated copper grid. The grid was dried by slow evaporation in air, and then dry separately in a vacuum overnight. Images were recorded on a JEOL-2000FX electron microscopy operated at 200 kV and at a nominal magnification of 5000X. At least 10 locations on the TEM grid were examined. The assembly diameter was calculated using ImageJ software.

**Atomic force microscopy (AFM):** AFM images were taken using a Bruker Dimensions 3000 Scanning Probe Microscope under tapping mode. Silicon wafers [Cemat Silicon S.A., (111)-oriented] were pre-cleaned by sonication in ethanol and acetone for 20 min, respectively. Then the wafers were dried with Ar flow and treated with UV-O3 for 15 min. For AFM measurement, the oligomers at a concentration of 50  $\mu\text{M}$  was drop-cast onto the corresponding substrate.

**Dil encapsulation:** 50  $\mu\text{M}$  oligomeric amphiphile solutions in PBS buffer were stirred at room temperature and Dil stock solution (1 mg/mL in acetone, 5 wt% to **3**, **4** or **5**) was added in each solution. The solutions were stirred for 8 h in room temperature, open to the atmosphere allowing the organic solvent to evaporate, and then filtered

through hydrophilic membranes with pore size of 0.45  $\mu\text{m}$  to remove unencapsulated Dil.

**Guest release study:** Dil-encapsulated oligomeric amphiphile solutions (50  $\mu\text{M}$ ) were treated with 15 min UV irradiation; 60  $\mu\text{M}$  bCA; 15 min UV irradiation followed the addition of 60  $\mu\text{M}$  bCA or 15 min UV irradiation followed the addition of 60  $\mu\text{M}$  BSA. The absorption spectra of Dil were recorded overtime.

The % release of Dil was calculated by using the following equations:

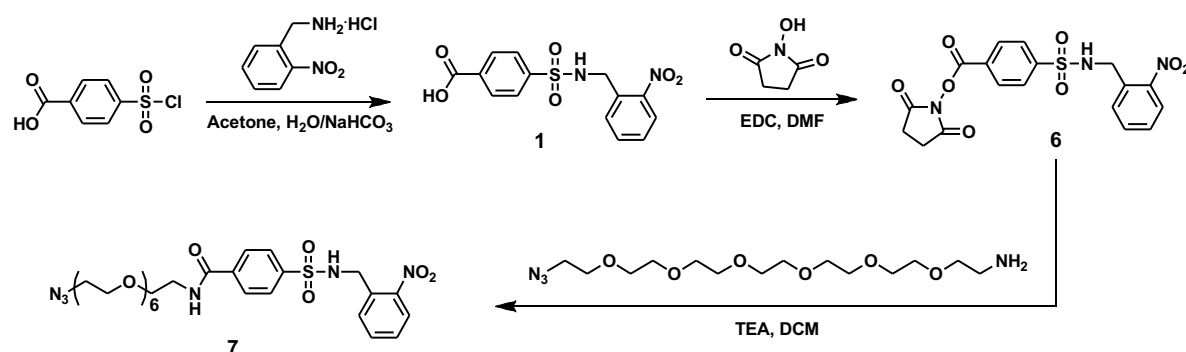
$$\% \text{ Release of Dil} = (I_t - I_0) / I_t * 100$$

Where  $I_0$  = the highest absorbance of Dil

$I_t$  = the highest absorbance of Dil at each time point

**Calculation of critical aggregation concentration (CAC):** A stock solution (1 mM) of **3/4/5** micelle was prepared was diluted into various solutions of different concentrations. The concentration range of polymer was maintained from 0.1 mM to 0.001 mM. Nile Red was encapsulated to the micelle by adding 10  $\mu\text{L}$  of Nile Red stock solution (20  $\mu\text{M}$  in acetone). All the micelle solutions were kept uncapped overnight to evaporate the acetone. Then emission spectrum was recorded for each solution and emission maxima of each spectrum were plotted as a function of the concentration of **3/4/5**. The inflection point of the plot was taken as CAC of polymer **3/4/5**.

**Synthesis of masked ligand:** Synthetic protocol of masked ligand is outlined in scheme 1:



**Scheme 1:** Synthetic protocol of masked ligand

**Synthesis of compound 1:** 4-(Chlorosulfonyl) benzoic acid (2.2 g, 10 mmol) was taken into a round bottomed flask along with 2-Nitrobenzylamine hydrochloride (1.89 g, 10 mmol) and dissolved in the co-solvent of acetone (100 mL) and  $\text{H}_2\text{O}$  (25 mL).  $\text{NaHCO}_3$  (1.68 g, 20 mmol) in  $\text{H}_2\text{O}$  was then added to the reaction mixture. The solution was stirred for overnight, concentrated, followed with the addition of 100 mL  $\text{H}_2\text{O}$ . The residue was extracted with 3 $\times$ 200 mL ethyl acetate, the organic phase was combined, concentrated and purified by combiflash using DCM/methanol as eluant. The product was eluted at a polarity of 11% methanol in DCM and obtained as a

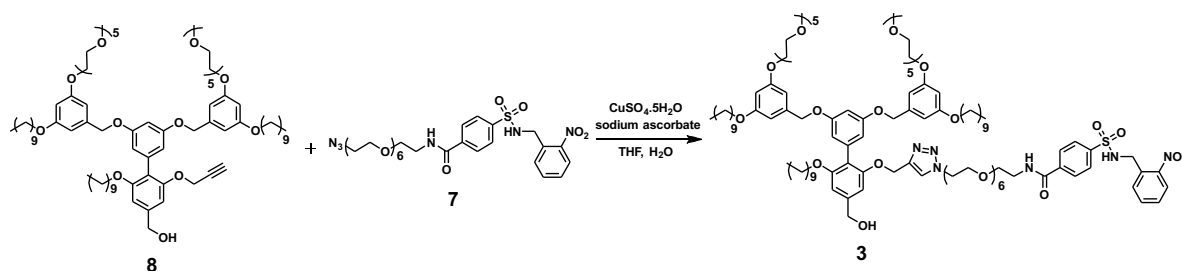
light yellow solid. Yield: 27%.  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-}d_6$ , TMS):  $\delta$  (ppm) = 8.49 (t, 1H), 8.08 (d, 2H), 7.97 (d, 1H), 7.69 (t, 1H), 7.63 (d, 1H), 7.52 (t, 1H), 4.36 (d, 2H).

**Synthesis of compound 6:** Compound 1 (268 mg, 0.8 mmol) and N-Hydroxysuccinimide (138 mg, 0.96 mmol) were dissolved in DMF (15 mL), followed with the addition of EDC·HCl (184 mg, 1.2 mmol). The solution was allowed to stir in room temperature for overnight. The reaction mixture was mixed with 50 mL DCM and washed with 3×30 mL  $\text{H}_2\text{O}$ , 3×30 mL saturated  $\text{NaHCO}_3$  solution and 3×30 mL brine. The organic layer was collected and dried over anhydrous  $\text{Na}_2\text{SO}_4$ , concentrated and purified by combiflash using hexanes/ethyl acetate as eluant. The product was eluted at polarity of 50% ethyl acetate in hexanes and obtained as a light yellow solid. Yield: 88%.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  (ppm) = 8.19 (d, 2H), 8.00 (d, 1H), 7.91 (d, 2H), 7.56 (m, 2H), 7.44 (t, 1H), 4.48 (d, 2H), 2.93 (s, 4H).

**Synthesis of compound 7:** Compound 2 (260 mg, 0.6 mmol) and triethylamine (112  $\mu\text{L}$ , 0.8 mmol) were dissolved in 10 mL DCM and stirred. O-(2-Aminoethyl)-O'-(2-azidoethyl) pentaethylene glycol (175 mg, 0.5 mmol) was dissolved in 5 mL DCM and added to the reaction mixture dropwise with the help of an addition funnel. The reaction was allowed to go on for overnight at room temperature, after which it was washed with 2×10 mL  $\text{H}_2\text{O}$  and 2×10 mL brine. The DCM layer was then dried over  $\text{Na}_2\text{SO}_4$ , concentrated and purified by combiflash using hexanes/ethyl acetate as eluant. The product was eluted at a polarity of 100% ethyl acetate and obtained as amber liquid. Yield: 78%.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  (ppm) = 7.98 (d, 1H), 7.92 (d, 2H), 7.87 (d, 2H), 7.60 (d, 2H), 7.47 (m, 1H), 7.15 (s, 1H), 5.66 (t, 1H), 4.44 (d, 2H), 3.70-3.59 (m, 26H), 3.36 (m, 2H).

**General procedure for click reaction:** The mixture of dendritic acetylene compound (1.0 eq), azide (2 eq for 1 acetylene group),  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (0.5 equiv.) and sodium ascorbate (0.5 eq.) in THF/ $\text{H}_2\text{O}$  (1:1) solvent mixture was heated at 50  $^\circ\text{C}$  for 24 h. The reaction progress was monitored by TLC. After completion of the reaction, the reaction mixture was partitioned between ethyl acetate and saturated aqueous  $\text{NH}_4\text{Cl}$  solution. The aqueous layer was extracted twice with ethyl acetate and the combined organic layer was dried over  $\text{Na}_2\text{SO}_4$  and evaporated to dryness. The crude product was purified by silica gel column chromatography.

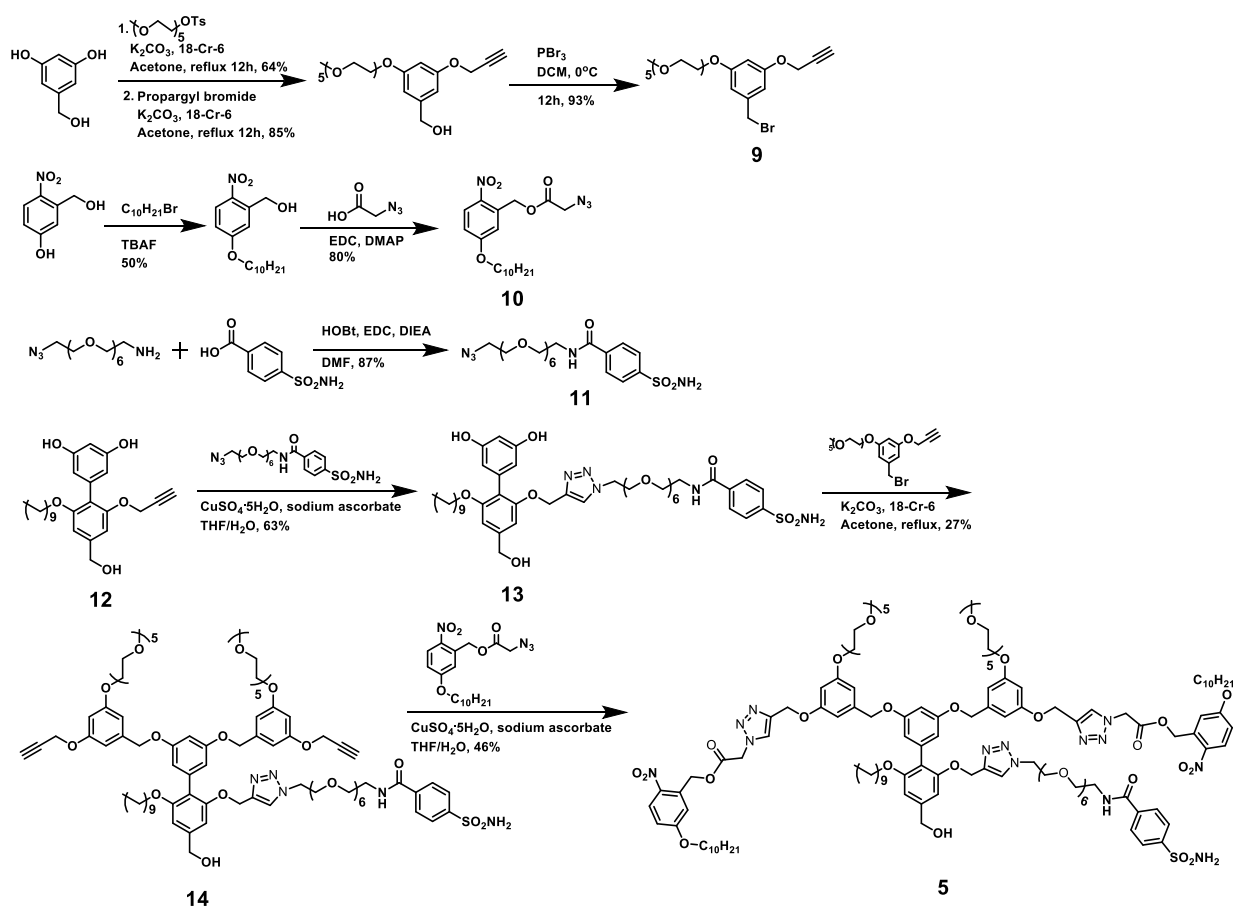
**Synthesis of 3:** Synthetic protocol of 3 is outlined in scheme 2:



**Scheme 2:** Synthetic protocol of targeted oligomer 3

**Synthesis of D1 (compound 5):** Compound **8** was synthesized according to our previous report<sup>1</sup>. According to general procedure for click reaction, compound **8** (50 mg, 35  $\mu$ mol) was treated with azide **7** (47 mg, 70  $\mu$ mol) to give 52 mg of **3**. Yield: 72%. NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.96 (t, 3H), 7.82 (d, 2H), 7.71 (br, 1H), 7.59 (d, 2H), 7.54 (m, 1H), 7.40 (t, 1H), 6.32 (s, 1H), 6.61 (m, 8H), 6.39 (t, 1H), 6.17 (t, 1H), 5.15 (s, 2H), 4.89 (s, 4H), 4.66 (s, 2H), 4.41 (m, 4H), 4.09 (t, 4H), 3.90-3.36 (m, 68H), 3.36 (s, 6H), 1.76-1.18 (m, 48H), 0.95-0.80 (m, 9H); <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  166.0, 160.4, 160.0, 159.0, 157.2, 156.3, 147.9, 142.6, 142.4, 139.4, 138.4, 135.8, 134.0, 132.5, 131.6, 128.9, 128.2, 126.9, 125.0, 119.3, 110.3, 106.2, 105.8, 104.8, 104.7, 100.9, 100.7, 71.9, 70.7, 70.6, 70.5, 70.5, 70.4, 70.4, 70.3, 69.7, 67.9, 67.4, 65.0, 59.0, 53.4, 50.3, 44.8, 40.1, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 29.3, 29.3, 26.1, 26.0, 25.6, 22.7, 22.4, 14.1; ESI-TOF m/z 1067.4 [M+2Na]<sup>2+</sup>: Calculated: 1067.32, found: 1067.4 [M]<sup>+</sup>+Na: Calculated: 2111.64, found: 2112.0.

**Synthesis of D2:** Synthetic protocol of **5** is outlined in scheme 3:



**Scheme 3:** Synthetic protocol of targeted dendrimer D2

**Synthesis of compound 11:** EDC·HCl (328 mg, 1.68 mmol) and N, N-diisopropylethylamine (0.60 ml, 3.36 mmol) were added to a solution O-(2-Aminoethyl)-O'-(2-azidoethyl) pentaethylene glycol (500 mg, 1.4 mmol) and 4-carboxybenzenesulfonamide (287 mg, 1.4 mmol) and HOBt (262 mg, 1.68 mmol) in dimethylformamide (5 ml) and stirred for 24 hours at room temperature under

nitrogen. The solvent was removed in vacuo and the residue purified by column chromatography on silica gel eluting with dichloromethane:methanol (95:5) (by volume) to give compound **11** as a colorless oil. Yield 87%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.77-7.84 (m, 4H), 7.56 (s, 1H), 6.24 (s, 1H), 3.36-3.73 (m, 24H). ESI-MS  $m/z$  calcd for  $\text{C}_{47}\text{H}_{69}\text{N}_5\text{O}_{14}\text{SNa}$   $[\text{M}+\text{Na}]^+$ : 556.21; found: 556.3718.

**Synthesis of compound 13:** Compound **12** was prepared following our previously reported procedure<sup>1</sup>. According to general procedure for click reaction, compound **12** (400 mg, 0.94 mmol) was treated with azide **11** (600 mg, 1.18 mmol) to give 560 mg of **13**. Yield: 63%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.91 (br s, 1H), 7.77 (m, 4H), 7.56 (s, 1H), 6.7 (s, 1H), 6.58 (s, 1H), 6.30 (m, 3H), 6.10 (br s, 1H), 4.64 (s, 2H), 4.53 (s, 2H), 4.46 (t, 2H), 4.21 (s, 4H), 3.93 (m, 4H), 3.78-3.83 (m, 6H), 3.52-3.73 (m, 50H), 3.35 (s, 6H), 1.55 (m, 2H), 1.2-1.4 (m, 14H), 0.88(m, 3H). ESI-MS  $m/z$  calcd for  $\text{C}_{47}\text{H}_{69}\text{N}_5\text{O}_{14}\text{SNa}$   $[\text{M}+\text{Na}]^+$ : 959.45; found: 982.4715.

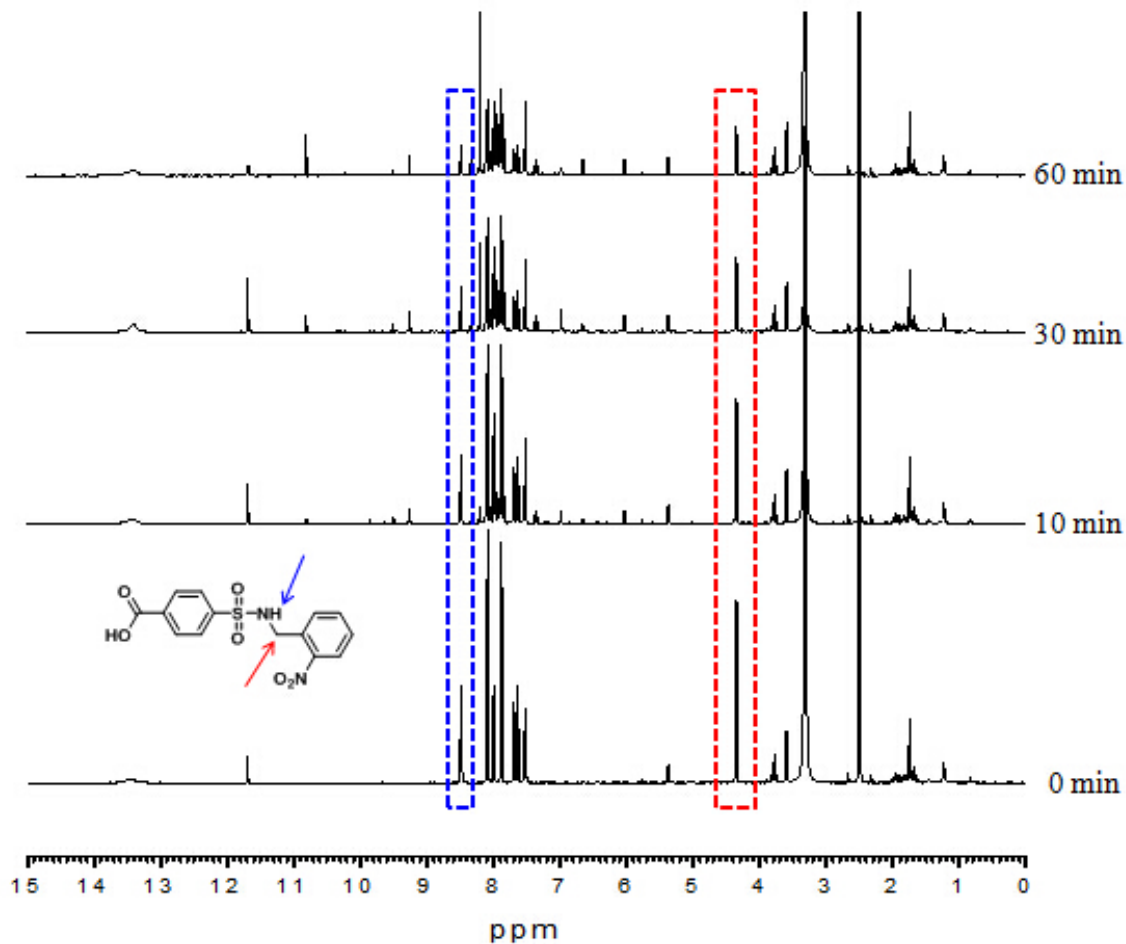
**Synthesis of compound 14:** Compound **10** (280 mg, 0.29 mmol),  $\text{K}_2\text{CO}_3$  (121 mg, 0.87 mmol), 18-crown-6 (38 mg, 0.145 mmol) and compound **9** (305 mg, 0.638 mmol) were mixed together in anhydrous acetone (50 mL) and refluxed for 12 h under argon. After slowly cooling the reaction to room temperature and evaporating the solvent, the resultant mixture was dissolved in ethyl acetate and washed with water. The combined organic layers were dried over  $\text{Na}_2\text{SO}_4$ , concentrated under reduced pressure and the crude mixture was purified by silica gel chromatography with MeOH/ethyl acetate (6:94 v/v) to give compound **14** (135 mg, 27%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.94 (d, 2H), 7.79 (d, 2H), 7.56 (br s, 1H), 7.53 (s, 1H), 6.72 (s, 1H), 6.63 (s, 1H), 6.17~6.39 (m, 9H), 5.08 (s, 2H), 4.64 (s, 2H), 4.53 (s, 2H), 4.46 (t, 2H), 4.21 (s, 4H), 3.93 (m, 4H), 3.78-3.83 (m, 6H), 3.52-3.73 (m, 50H), 3.35 (s, 6H), 1.55 (m, 2H), 1.2-1.4 (m, 14H), 0.88(m, 3H). ESI-MS  $m/z$  calcd for  $\text{C}_{89}\text{H}_{129}\text{N}_5\text{O}_{28}\text{SNa}$   $[\text{M}+\text{Na}]^+$ : 1770.85; found: 1771.5027,  $[\text{M}+2\text{Na}]^{2+}$  896.7148.

**Synthesis of 5:** According to general procedure for click reaction, compound **14** (100 mg, 56  $\mu\text{mol}$ ) was treated with azide **10** (66 mg, 168  $\mu\text{mol}$ ) to give 66 mg of **5**. Yield: 46%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  8.15 (d, 2H), 7.94 (d, 2H), 7.89 (s, 2H), 7.79 (d, 2H), 7.53 (s, 1H), 7.48 (br s, 1H), 6.94 (m, 4H), 6.72 (s, 1H), 6.62 (s, 1H), 6.17~6.37 (m, 9H), 5.60 (s, 4H), 5.48 (s, 4H), 5.02 (d, 6H), 4.63 (s, 2H), 4.4 (t, 2H), 4.15 (s, 4H), 4.02 (t, 6H), 3.91 (m, 4H), 3.81 (m, 8H), 3.51-3.7 (m, 50H), 3.35 (s, 6H), 1.8 (m, 4H), 1.55 (m, 2H), 1.46 (m, 4H), 1.2-1.5 (m, 38H), 0.88 (m, 9H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  166.2, 165.95, 163.70, 159.97, 159.15, 157.16, 156.75, 156.35, 144.49, 144.10, 142.8, 139.82, 138.27, 137.91, 136.06, 133.82, 128.37, 128.18, 127.08, 125.00, 124.05, 119.64, 114.67, 113.76, 110.49, 107.54, 107.37, 104.95, 104.86, 101.77, 101.31, 71.89, 70.68, 70.54, 70.45, 70.38, 70.30, 70.04, 69.79, 69.56, 69.30, 69.15, 68.79, 67.42, 65.06, 64.92, 63.57, 61.64, 58.99, 55.99, 53.44, 51.25, 50.77, 50.18, 40.09, 31.89, 29.70, 29.59, 29.35, 29.31, 29.09, 28.98, 25.93, 22.68, 14.13. ESI-MS  $m/z$  calcd for  $\text{C}_{127}\text{H}_{185}\text{N}_{13}\text{O}_{38}\text{SNa}$   $[\text{M}+\text{Na}]^+$ : 2555.26; found: 2555.9831.

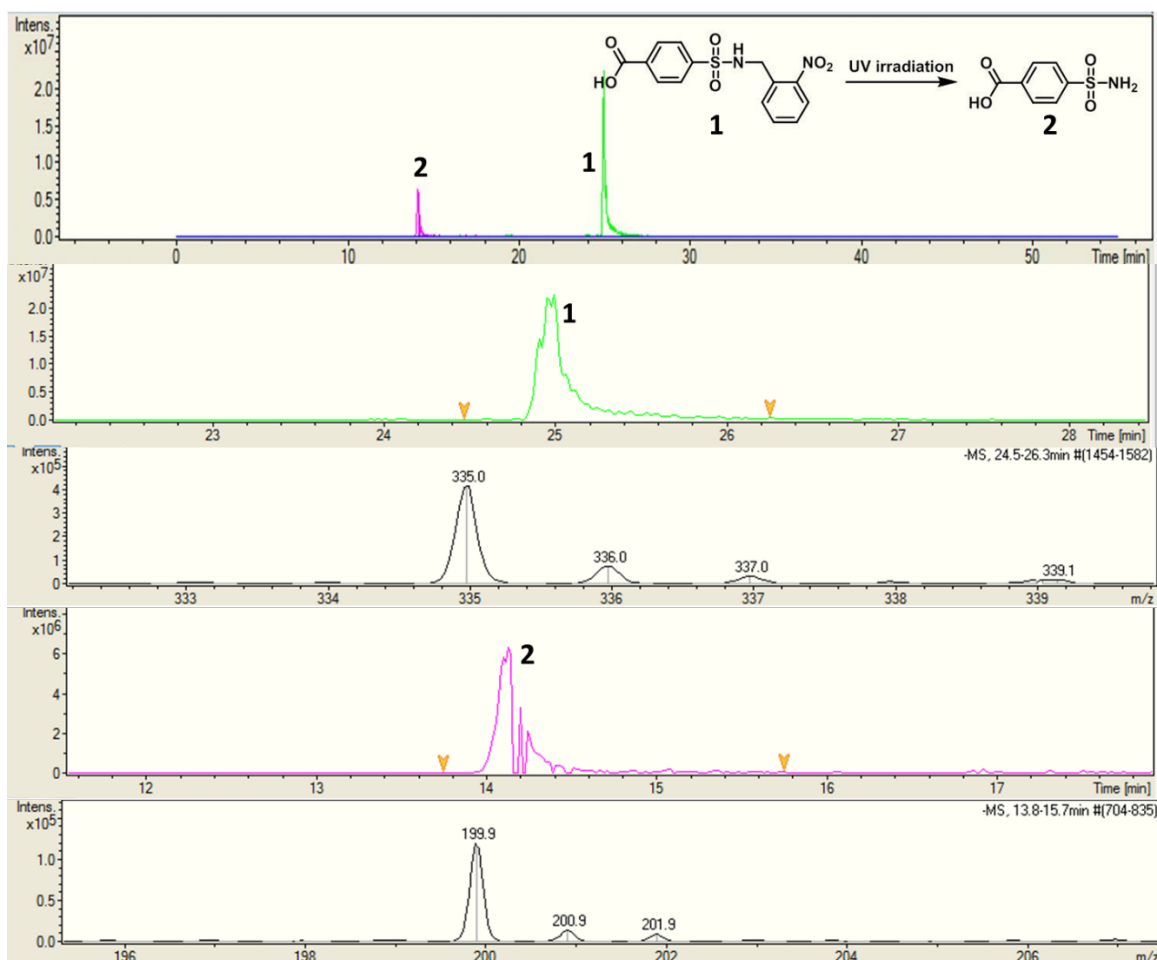
**Synthesis of control 4:** **4** was prepared following our previously reported procedure<sup>3</sup>.

### Photo-cleavage ligand unmasking studies:

10 mg of compound **1** was dissolved in 5 mL D-DMSO and sealed in a NMR tube. The compound was irradiated with UV light and  $^1\text{H}$ NMR spectra were recorded overtime. After irradiation, the residue was analyzed by LC-ESI-MS.

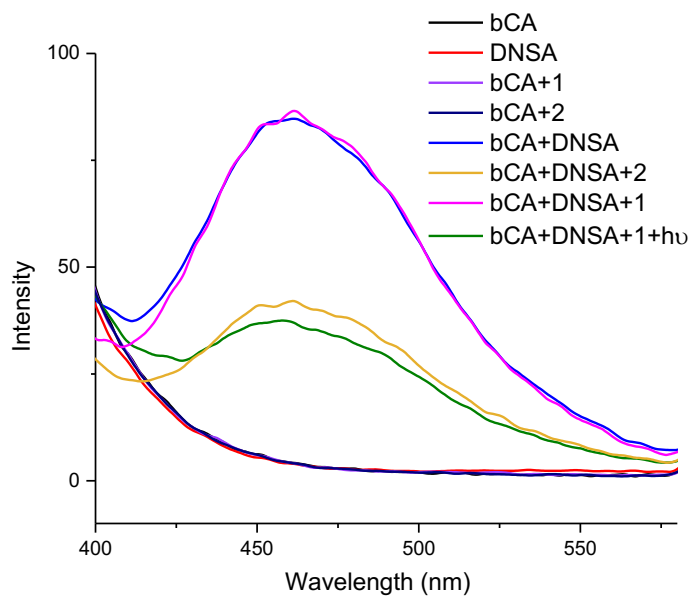


**Figure S1:**  $^1\text{H}$  NMR spectra of compound **1** in D-DMSO at various UV irradiation periods. The gradual decrease of peaks at 8.49 and 4.36 ppm, which is corresponding to imino and methylene group, indicated the photo-cleavage of o-nitrobenzyl group.

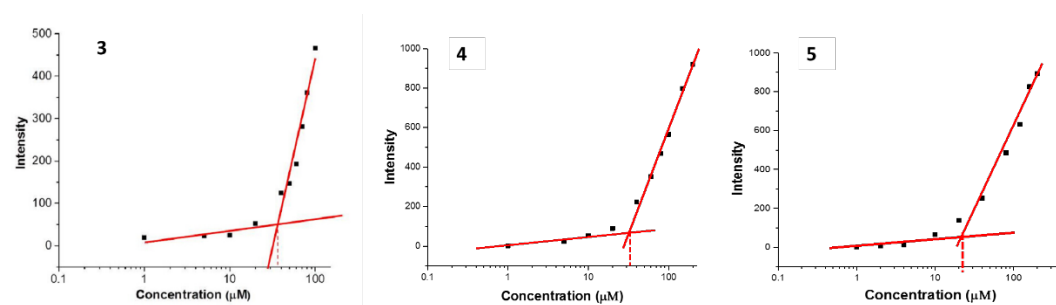


**Figure S2:** LC-ESI-MS results of compound **1** upon UV irradiation. Green peak ( $m/z = 335.0$ ) is corresponding to compound **1**. Pink peak ( $m/z = 200.0$ ) is corresponding to compound **2**: 4-carboxylbenzene-sulfonamide. This result indicated that sulfonamide is generated after UV irradiation.

**Ligand-bCA competitive binding assay:** A 1 mM stock solution of bCA was prepared in 0.1 M phosphate buffer (pH 7.4), stock solution of 10 mM 5-dimethylaminonaphthalene-1-sulfonamide (DNSA), 10 mM compound **1** and 10 mM **2** were prepared in DMSO. The fluorescence intensities and spectra were measured in fluorimeter. DNSA was first added to the 10  $\mu$ M bCA solution at a molar ratio 1:1, the fluorescence intensities of the CA-DNSA complex were measured at 460 nm with excitation at 280 nm. Then compound **1** was added to the mixture and treated with UV light (365 nm) for 15 minutes, the emission spectra of this solution was recorded both before and after shining UV light. Control experiments such as the mixture of bCA-compound **1**, bCA-compound **2** were done following the same method.

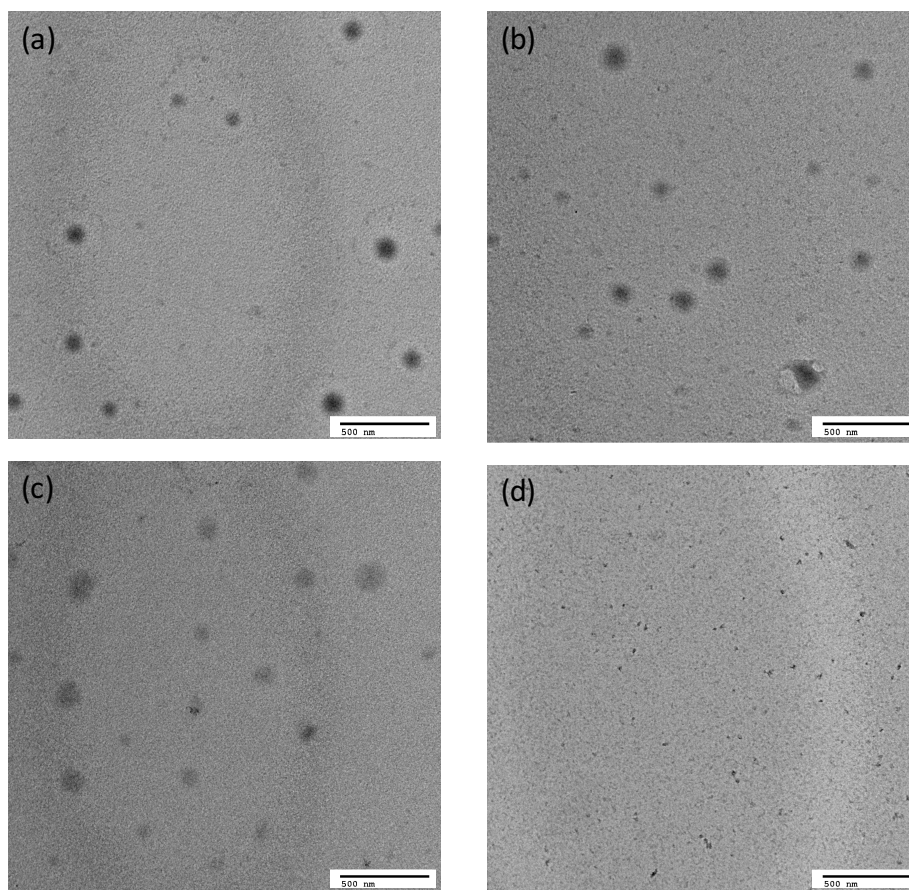


**Figure S3:** Emission spectra of bCA, DNSA, bCA-DNSA complex, bCA-2 complex, competitive binding between **2** and DNSA.

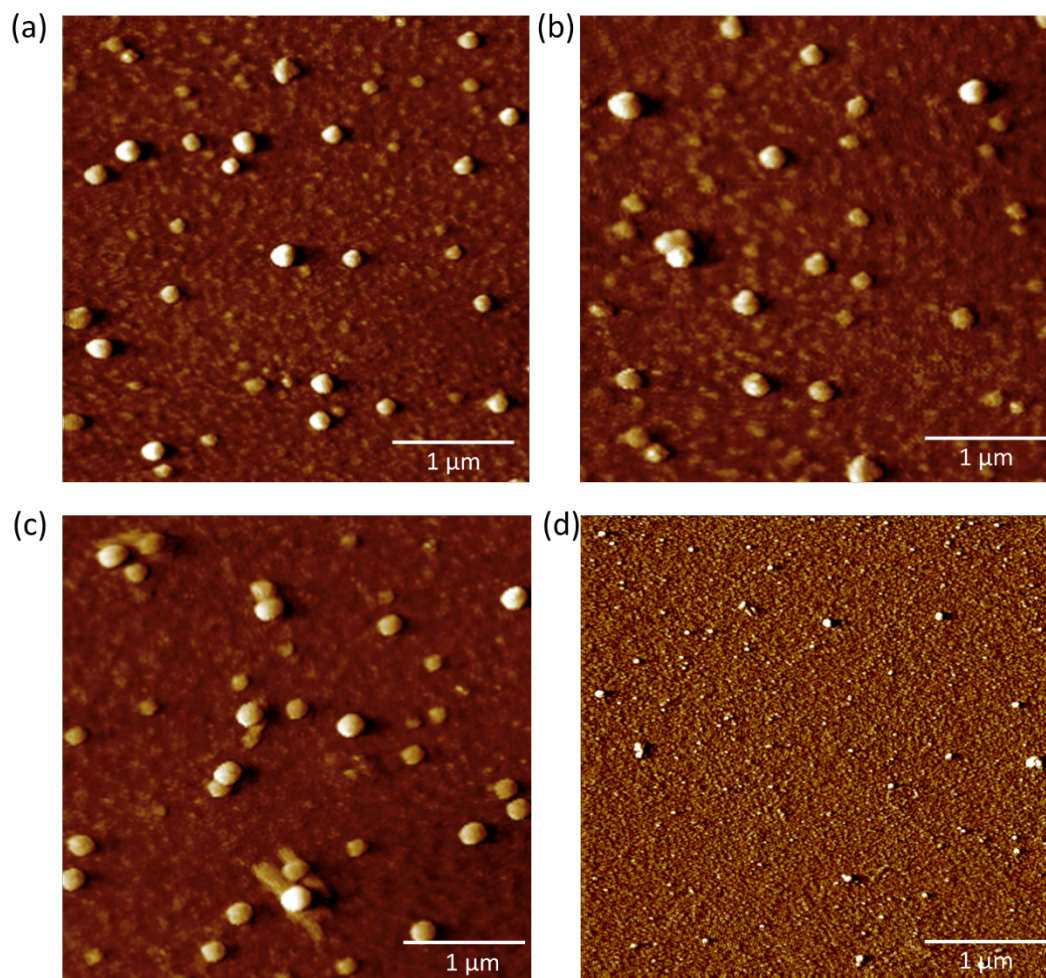


**Figure S4:** Plots of fluorescence intensity of Nile Red vs concentrations of oligomers. CAC of 3 was calculated to be 36 μM, CAC of 4 was calculated to be 32 μM, CAC of 5 was calculated to be 23 μM.

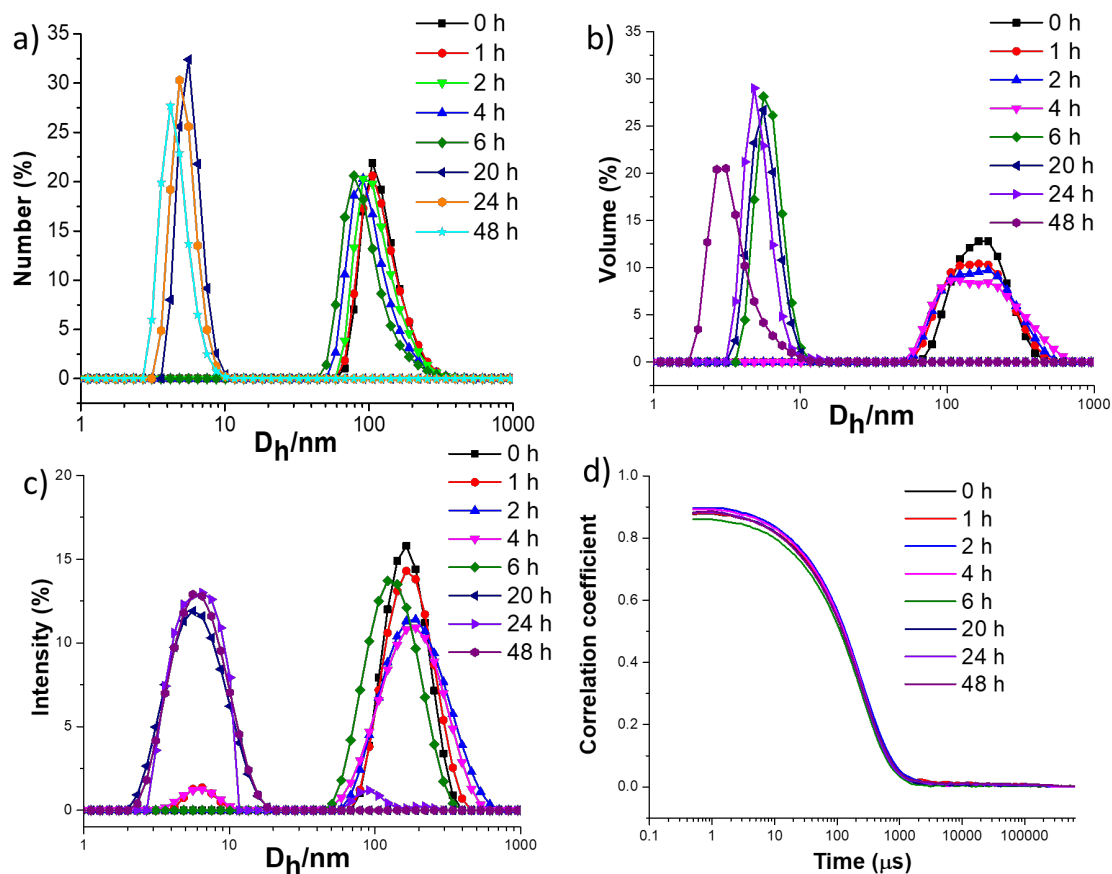




**Figure S5:** TEM images (scale bar: 500 nm) of **3** (50  $\mu$ M) supramolecular micellar structures in aqueous solution in presence of (a) no inputs, (b) bCA, (c) UV light, (d) bCA and UV light.



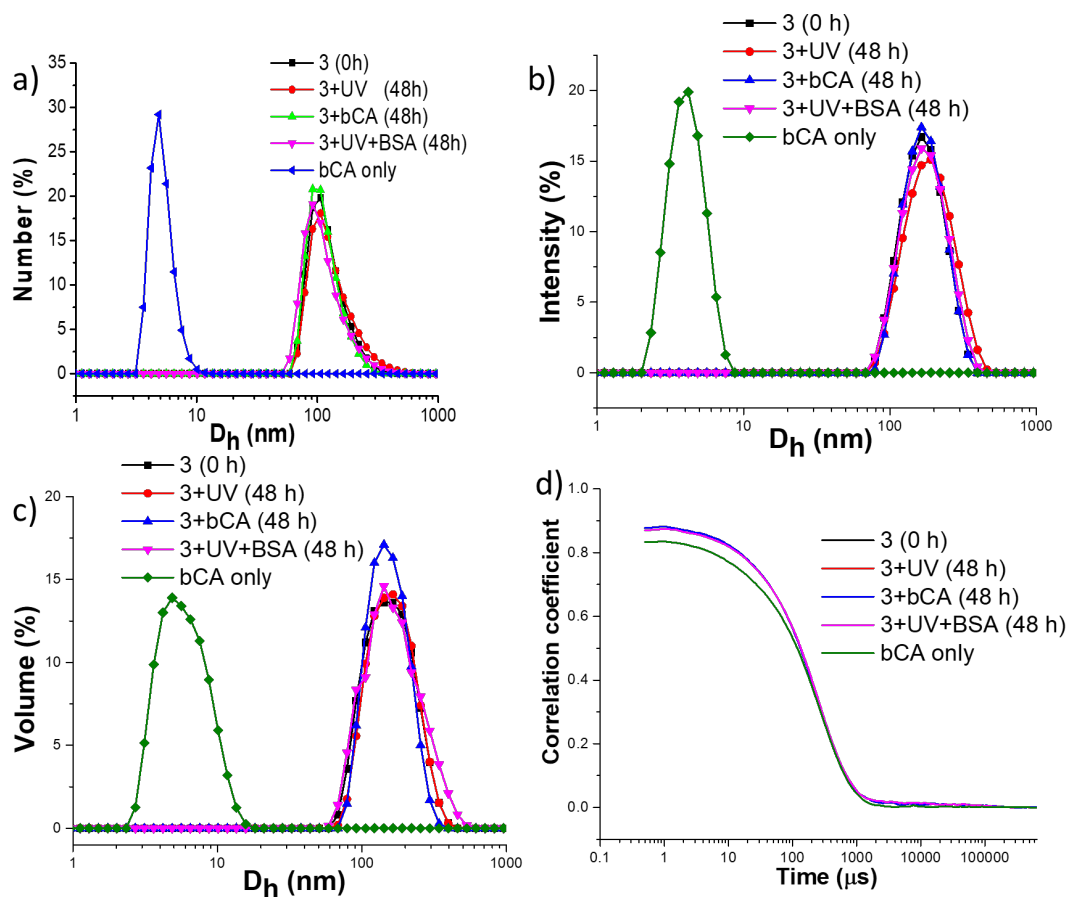
**Figure S6:** AFM images of **3** (50  $\mu\text{M}$ ) supramolecular micellar structures in aqueous solution in presence of (a) no inputs, (b) bCA, (c) UV light, (d) bCA and UV light.



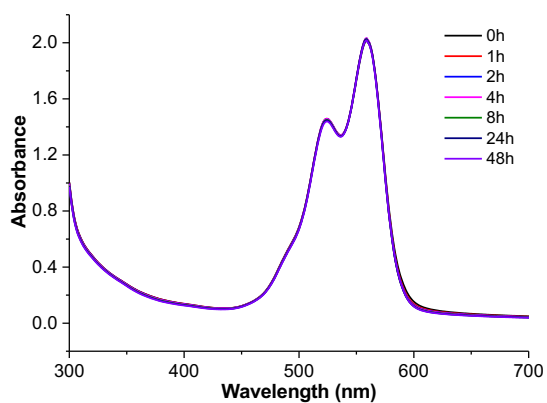
**Figure S7:** DLS profile of **3** in presence of UV and bCA in aqueous solution in (a) number distribution, (b) volume distribution, (c) intensity distribution, (d) auto-correlation curve.

**Table S1:** PDI of each measurement in DLS.

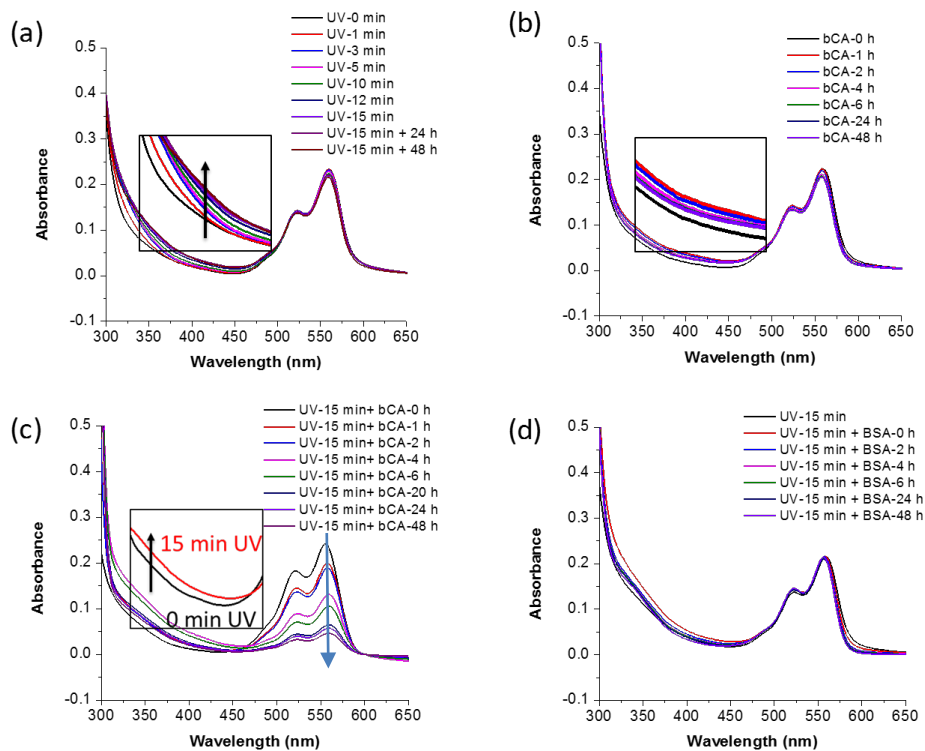
	3	4	5	bCA
No inputs	0.162	0.203	0.124	0.106
bCA	0.264	0.243	0.360	N/A
UV	0.36	0.175	0.516	N/A
UV+bCA	0.410	0.232	0.495	N/A



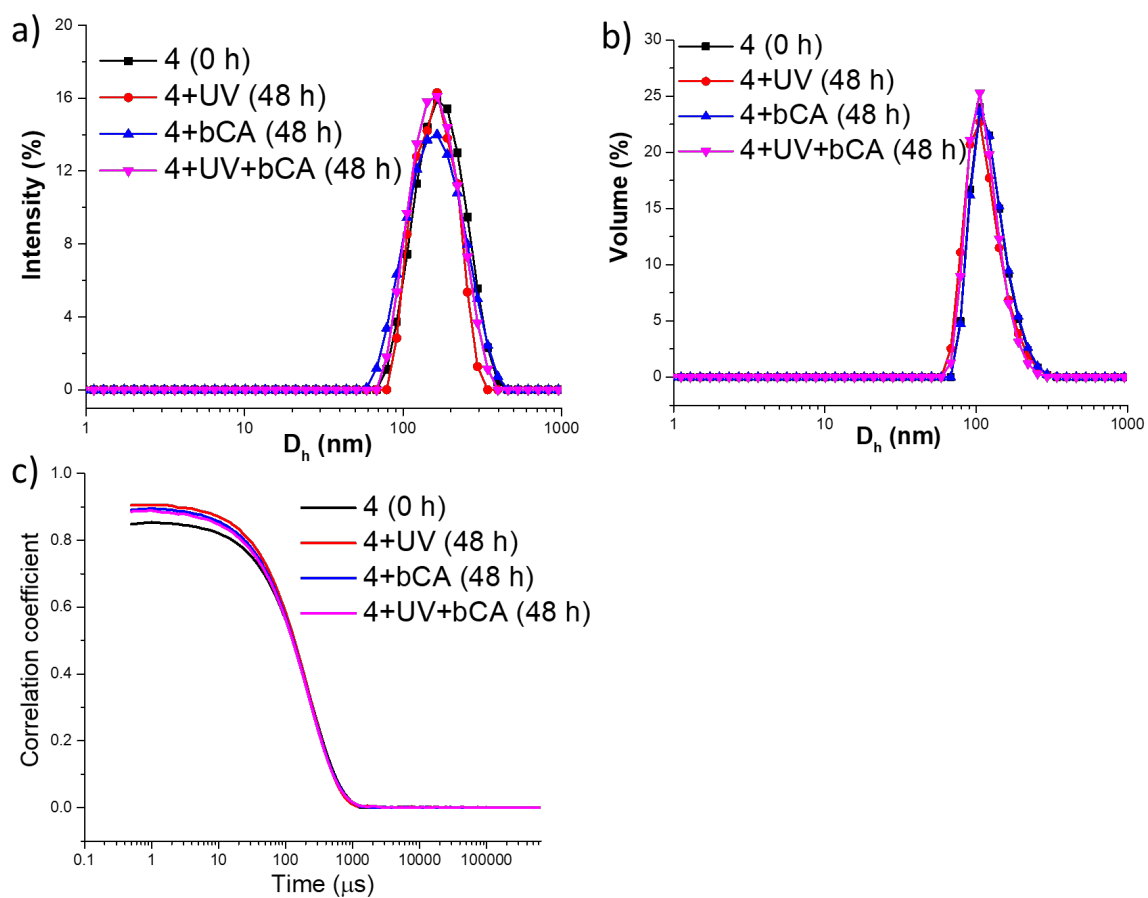
**Figure S8:** DLS profile of **3** in aqueous solution in presence of UV, bCA, UV+bCA (a) number distribution, (b) volume distribution, (c) intensity distribution, (d) auto-correlation curve.



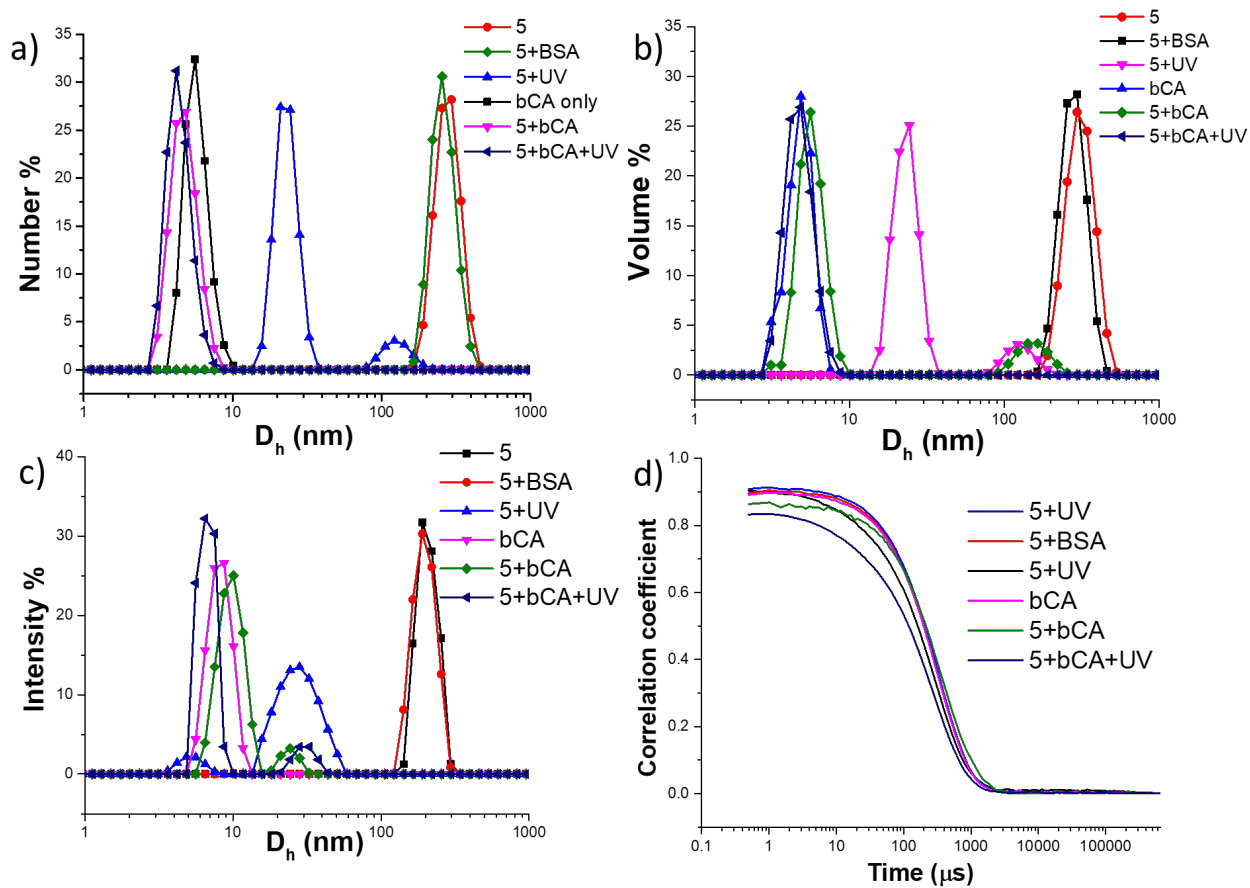
**Figure S9:** Absorbance of Dil in nanoassembly **3** in two days.



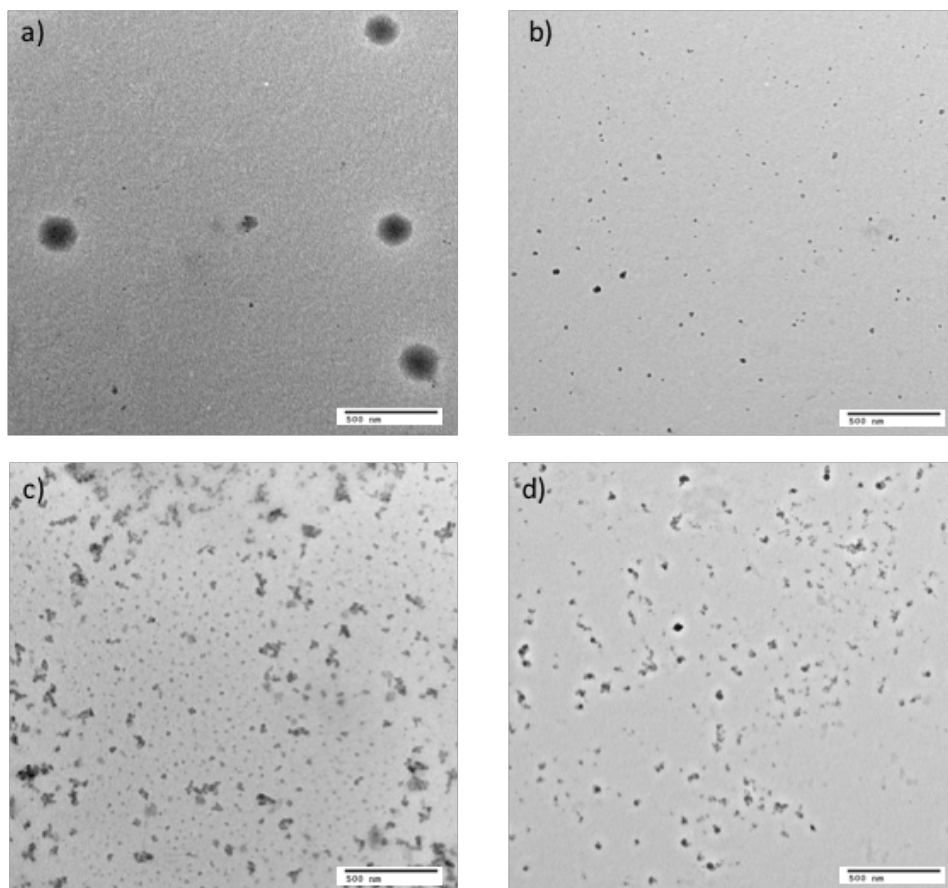
**Figure S10:** Absorbance of Dil from 50  $\mu$ M solution of **3** in response to a) UV; b) bCA; c) UV+bCA; d) UV+BSA.



**Figure S11:** DLS profile of **4** in aqueous solution in presence of UV, bCA, UV+bCA (a) number distribution, (b) volume distribution, (c) intensity distribution, (d) auto-correlation curve.

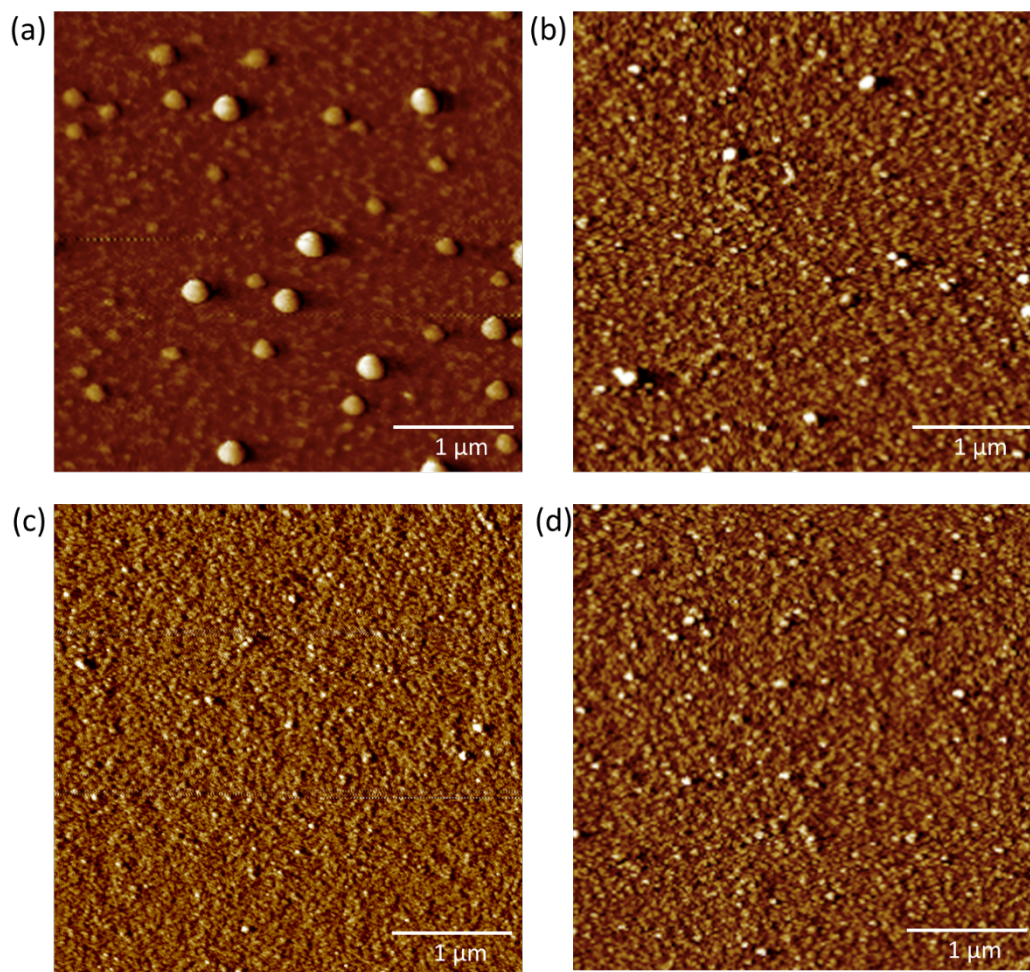


**Figure S12:** DLS profile of **5** in aqueous solution in presence of UV, bCA, UV+bCA (a) number distribution, (b) volume distribution, (c) intensity distribution, (d) auto-correlation curve.

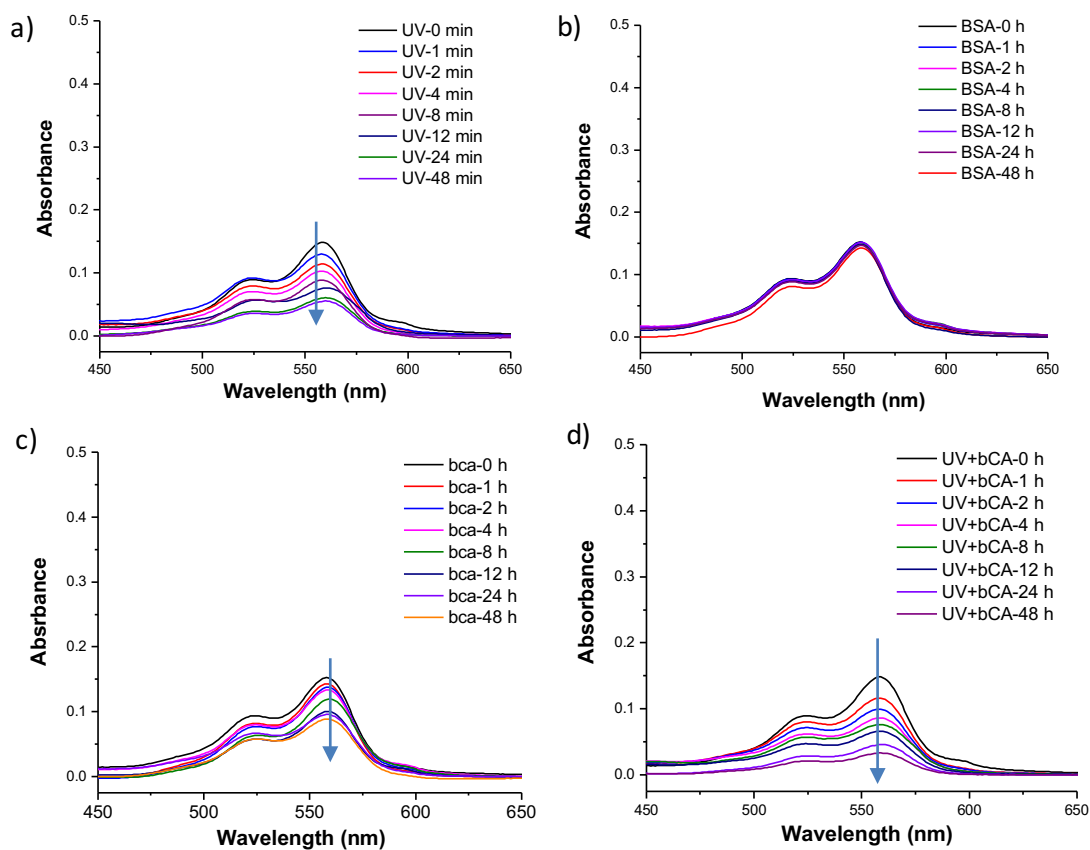


**Figure S13:** TEM images (scale bar: 500 nm) of **5** (50 μM) supramolecular micellar structures in aqueous solution in presence of (a) no inputs, (b) UV light, (c) bCA, (d) bCA and UV light.

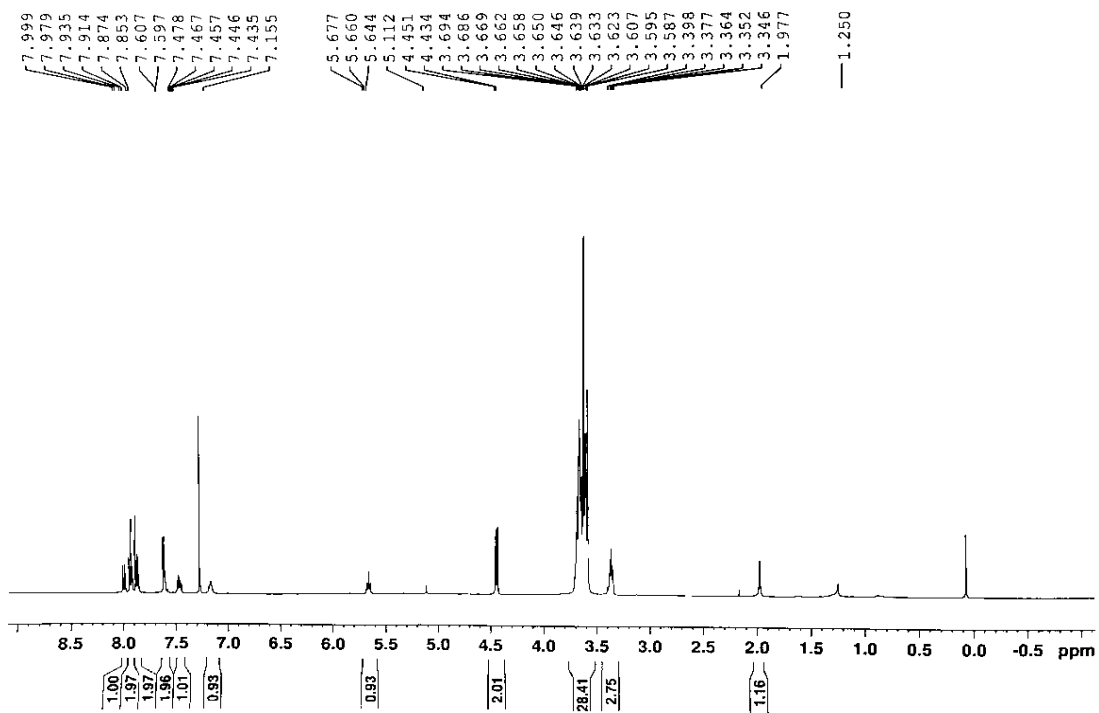
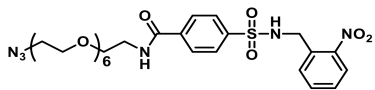
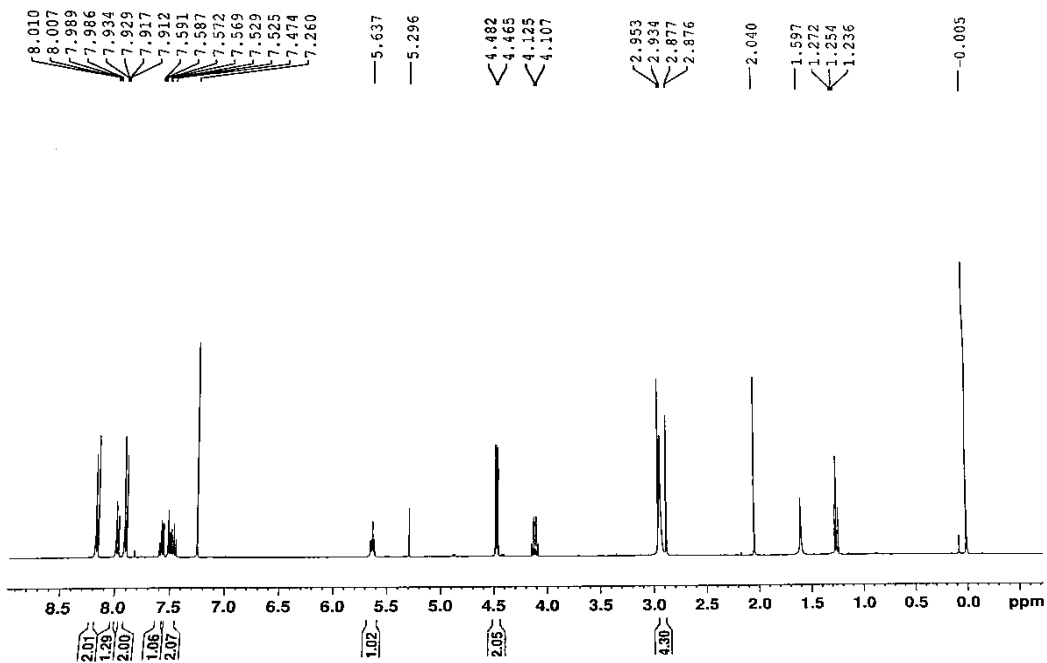
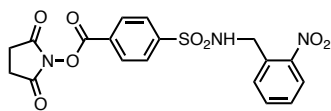


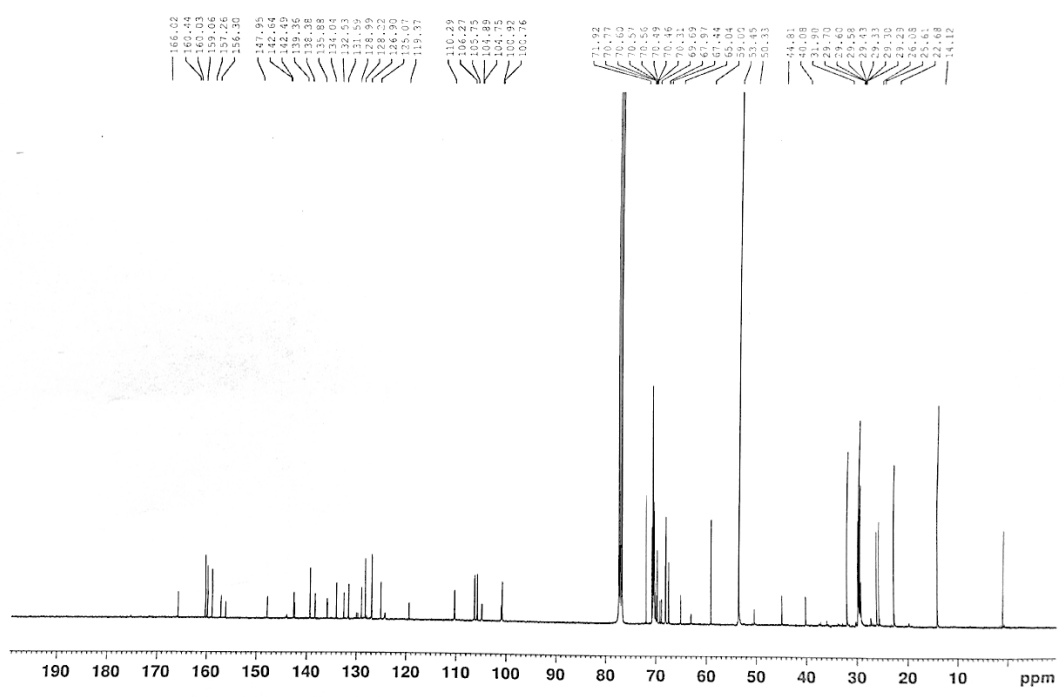
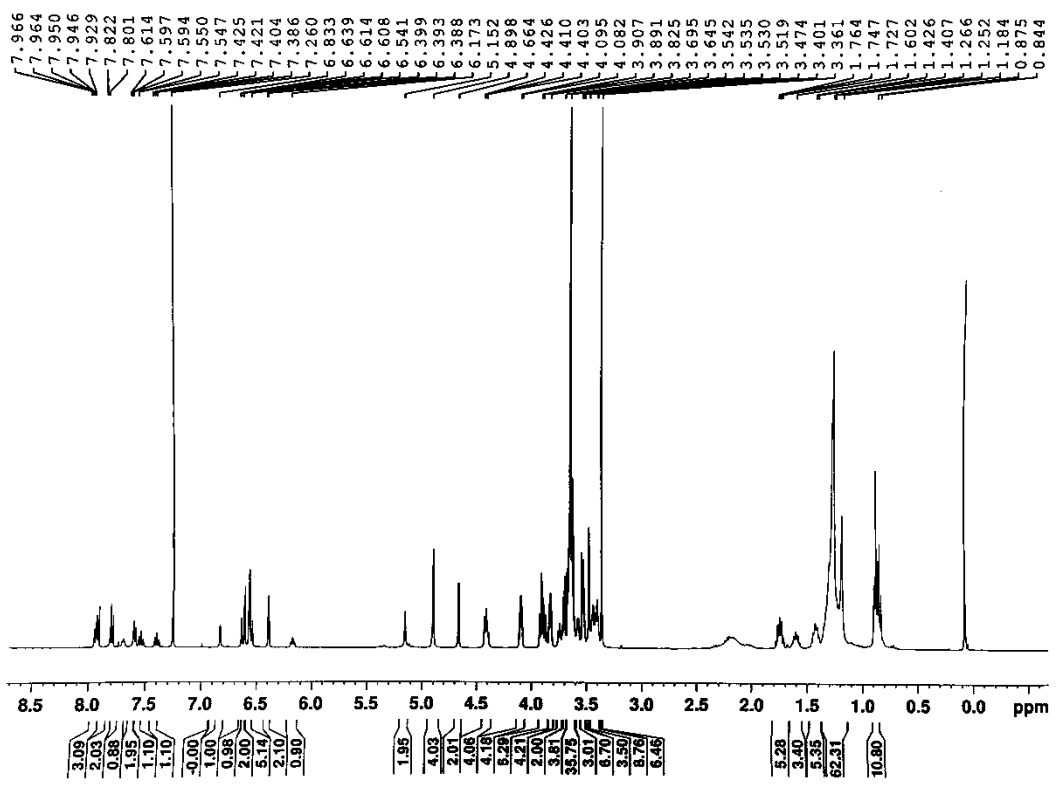
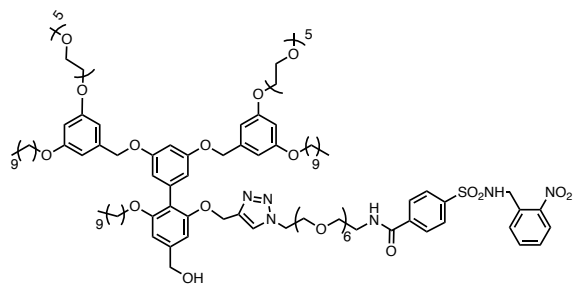


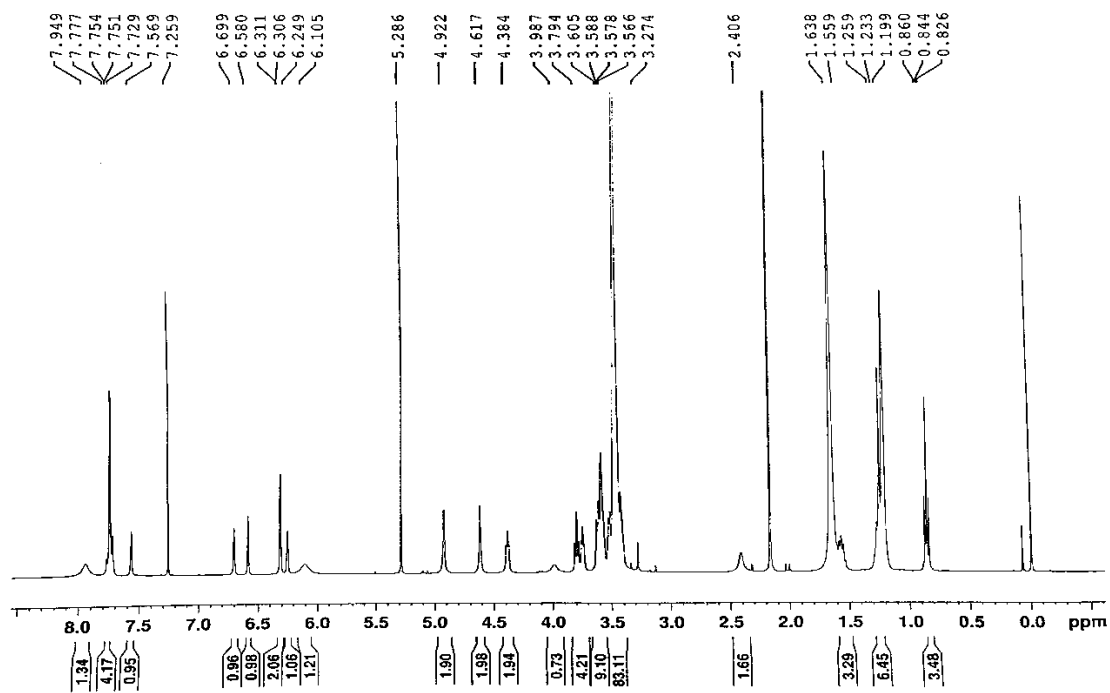
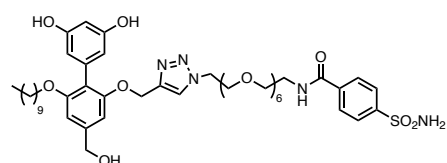
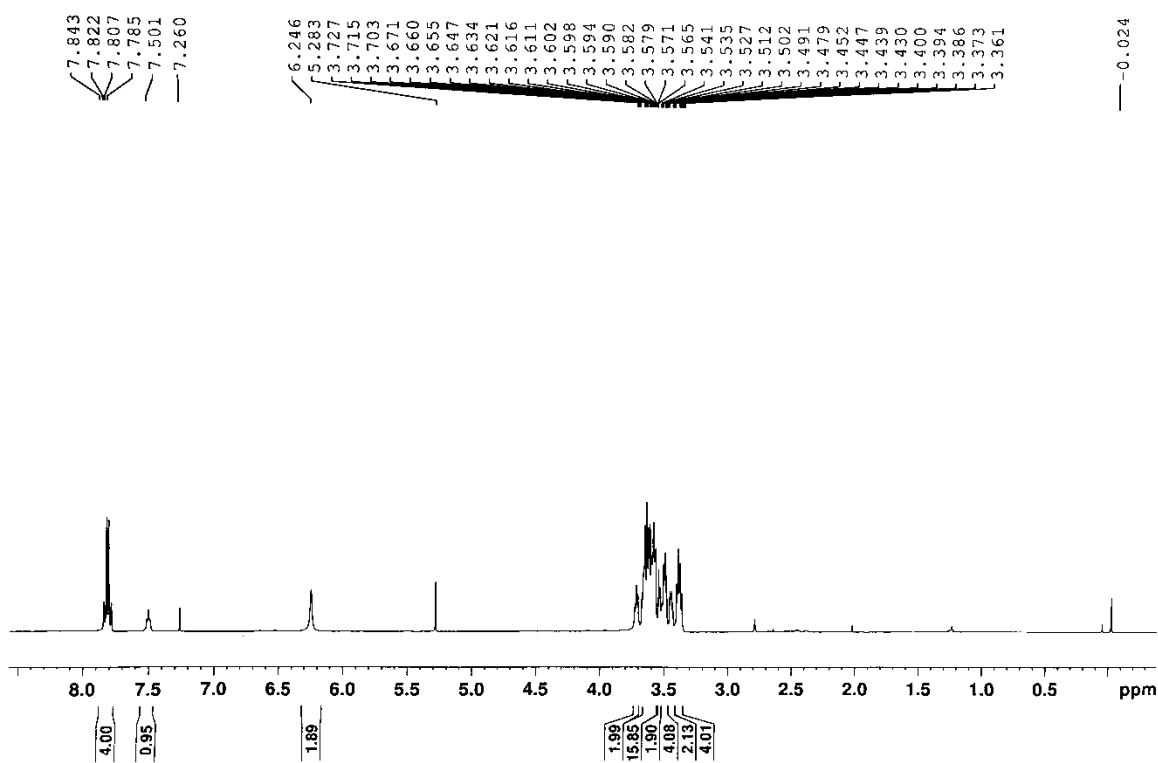
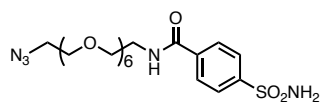
**Figure S14:** AFM images of **5** (50  $\mu\text{M}$ ) in aqueous solution in presence of (a) no inputs, (b) UV light, (c) bCA, (d) bCA and UV light.



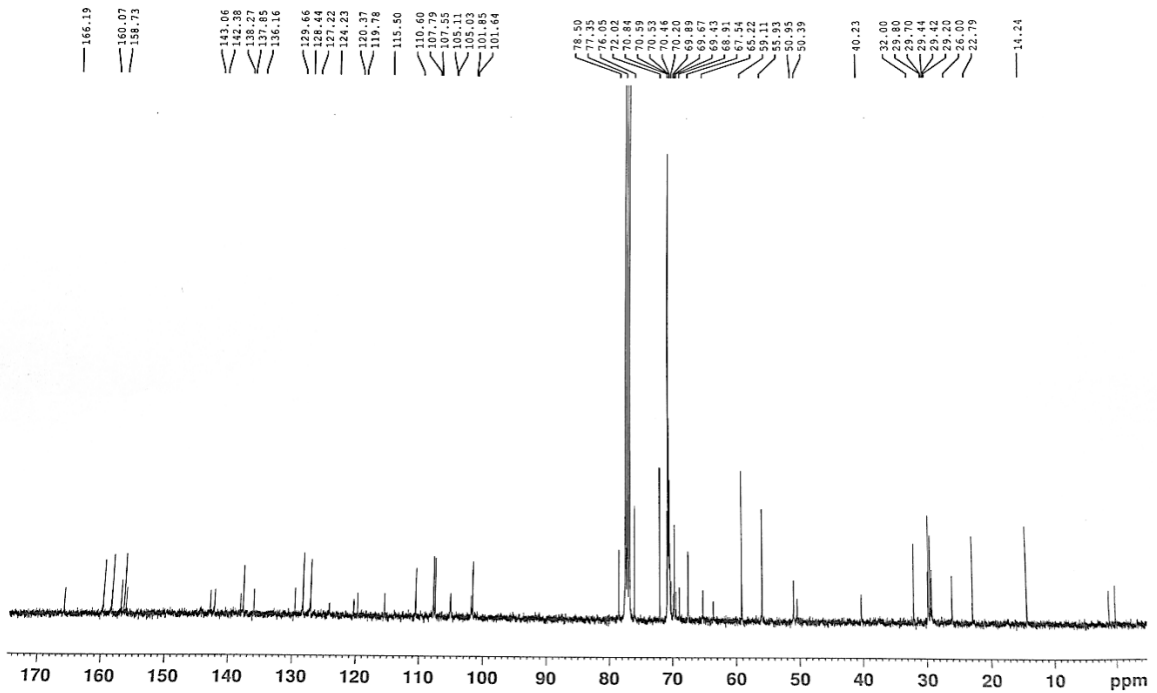
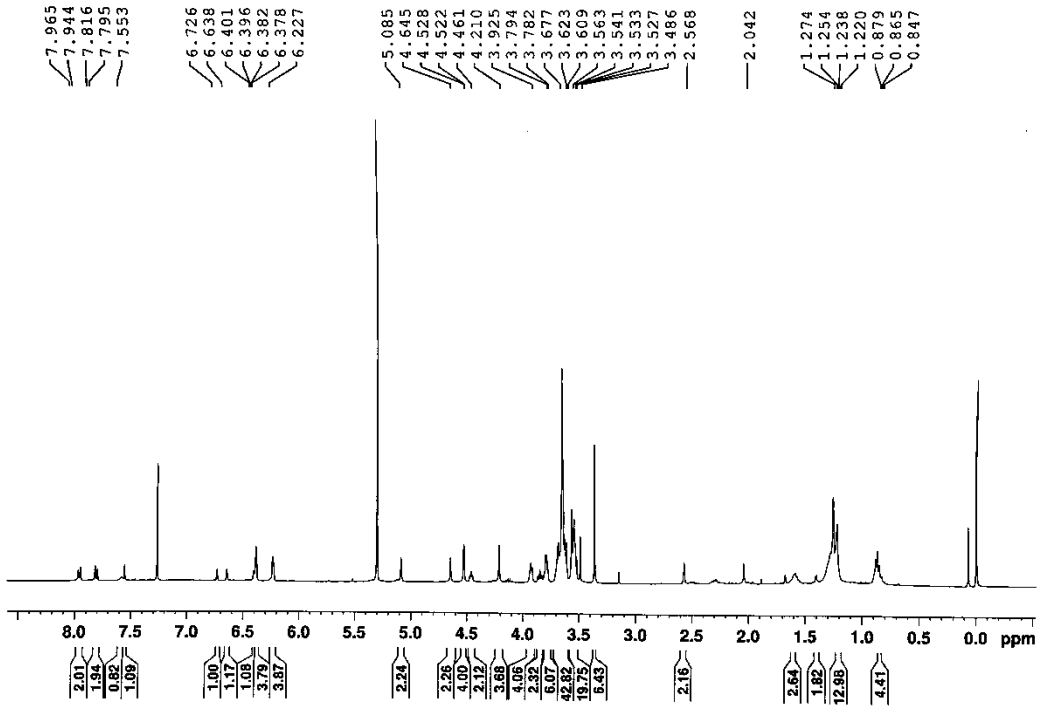
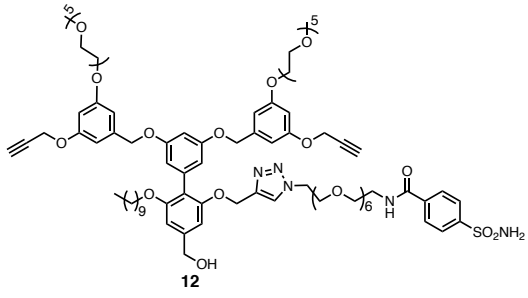
**Figure S15:** Absorbance of Dil from 50  $\mu\text{M}$  solution of **5** in response to a) UV; b) BSA; c) bCA; d) UV+bCA.

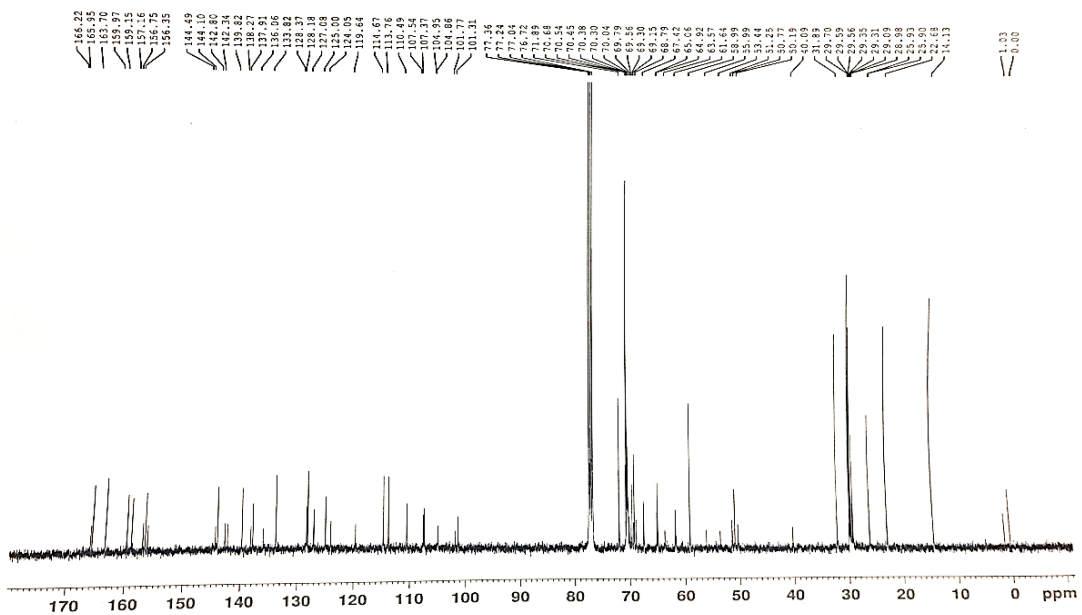
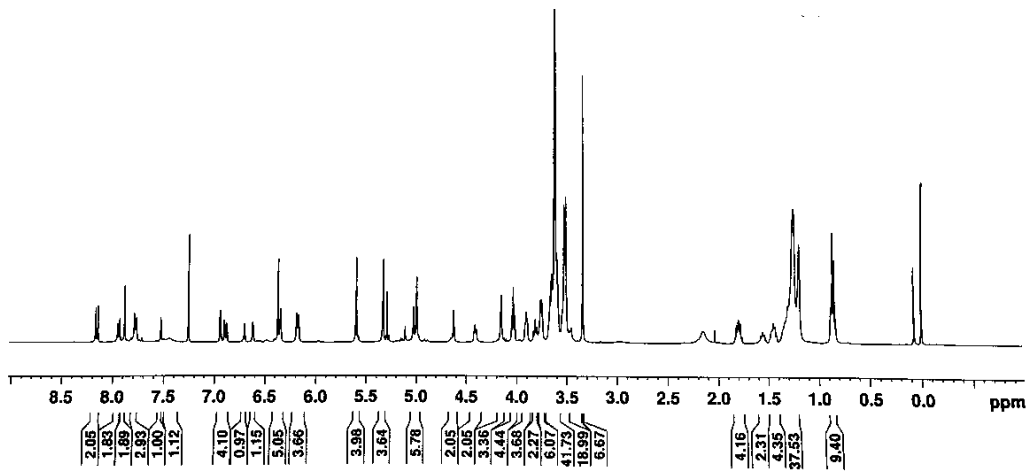
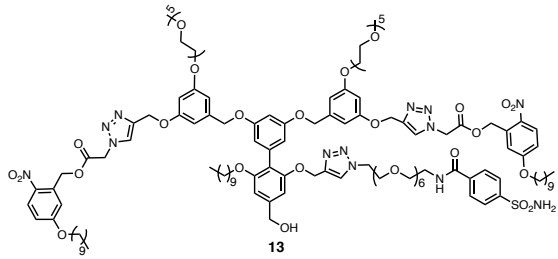


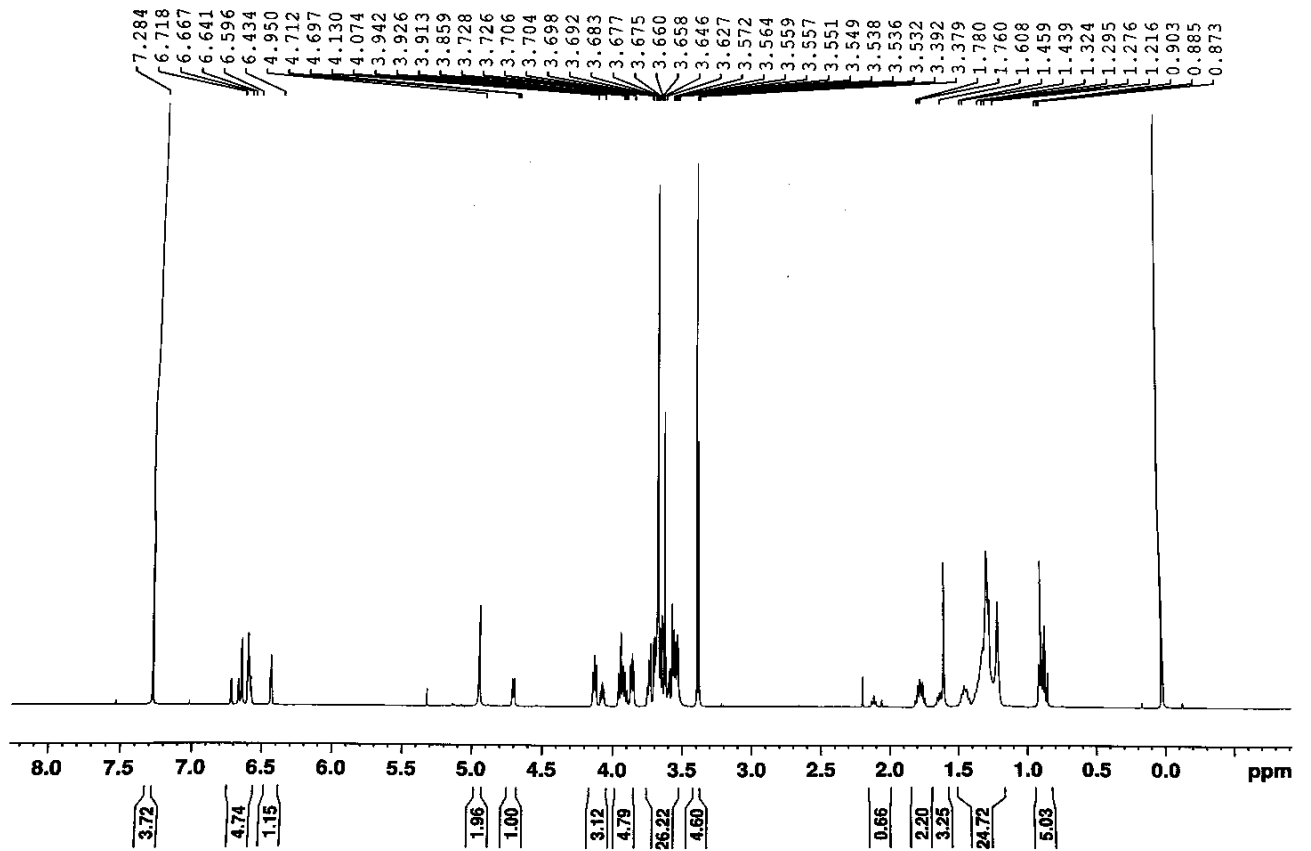
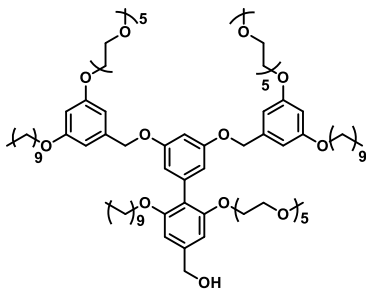




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S2) Yesilyurt, V., Ramireddy, R., Thayumanavan, S. *Angewandte Chemie International Edition*, 2011, *50*(13), 3038-3042.

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