Supporting information for

Reversible covalent locking of a supramolecular hydrogel via UV-controlled anthracene dimerization

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Experimental section

Materials

All chemicals and solvents were commercially available and used as received unless otherwise stated. Dichloromethane (DCM), *N,N*-dimethylacetamide (DMA), THF, methanol, $CDCl_3$, hexane were obtained from Sigma Aldrich. DCM and THF was purified over aluminum oxide by means of a solvent purification system from J.C. Meyer when it was use as reaction solvent. Milli-Q Water (18.2 MΩ/cm) was generated using a Millipore Milli-Q academic water purification system. 2-anthracenecarboxylic acid, *N*-acryloylmorpholine and γ-cyclodextrin were obtained from Tokyo Chemical Industry (TCI). 2-(2-Aminoethoxy)ethanol (98%), Di-*tert*-butyldicarbonate (99%), 2-dimethylaminoethanol, 2-bromoethanol, trifluoroacetic acid (TFA, 99%) and pentafluorophenol were purchased from Sigma-Aldrich. Azobisisobutyronitrile (AIBN, 98%, Sigma-Aldrich) was recrystallized from MeOH (2x) and stored in the freezer. Methyl-2-(*n*-butyltrithiocarbonyl)propanoate (MBTTCP) was prepared according to the established procedures.[1] Cucurbit[8]urils (CB[8]) was synthesized according to a literature procedure and was kindly provided by Prof. Werner Nau.[2]

Analytical techniques

^{1}H and ^{13}C spectra were acquired on a Bruker Avance 400 MHz spectrometer. ^{19}F NMR spectra were recorded on a Bruker Avance 500 MHz spectrometer. Samples were dissolved in $CDCl_3$ or CD_3OD. Chemical shifts are expressed in ppm by comparison with the signal of TMS used as an internal standard.

Gas chromatography (GC) was performed on a 7890A from Agilent Technologies with an Agilent J&W Advanced Capillary GC column (30 m, 0.320 mm and 0.25 µm). Injections were performed with an Agilent Technologies 7693 auto sampler. Detection was done with a FID detector. Injector and detector temperatures were kept constant at 250 and 280 °C, respectively. The column was initially

set at 50 °C, followed by two heating stages: from 50 °C to 100 °C with a rate of 20 °C/min and from 100 °C to 300 °C with a rate of 40 °C/min. and then held at this temperature for 0.5 minutes. Conversion was determined based on the integration of monomer peaks using DMA as internal standard.

Size exclusion chromatography (SEC) was performed on an Agilent 1260-series HPLC system equipped with a 1260 online degasser, a 1260 ISO-Pump, a 1260 automatic liquid sampler, a thermostatted column compartment, a 1260 diode array detector (DAD) and a 1260 refractive index detector (RID). Analyses were performed on a PPS Gram30 column in series with a PPS Gram 1000 column at 50 °C. DMA containing 50 mM of LiCl was used as an eluent at a flow rate of 0.6 mL/min. The SEC traces were analysed using the Agilent Chem station software with the GPC add on. Molar mass and PDI values were calculated against PMMA standards.

Fluorescence measurement were carried out on a Cary Eclipse fluorescence spectrophotometer (Agilent Technologies) equipped with a Varian Cary Temperature Controller. The emission spectra resulting from excitation by a 428.5 nm laser were monitored from 500 -700 nm, and the slit width was kept at 5 nm during the measurements.

Rheology was studied using an Anton Paar MCR 302 rheometer fitted with a water bath set to 25 °C. Time sweep measurements were carried out using a 25 mm parallel-plate geometry with a gap of 0.5 mm.

Job plots (continuous variation method)

The stoichiometry of the self-assembly was determined *via* Job's method of continuous variation.[3] A stock solution was prepared for each complementary recognition motif in Milli-Q water in a 5 mL round bottom flask. The appropriate amount from the stock solution was transferred to the UV-Visible cuvette or fluorescence cuvette in which the total concentration of the recognition motifs was kept constant at 50 µM. The molar fraction of the motifs was varied between 0 and 1. The changes in absorption intensity were multiplied by the molar fraction and plotted *vs*. molar fraction to construct the Job plot.

UV-Vis spectrophotometric titration experiment

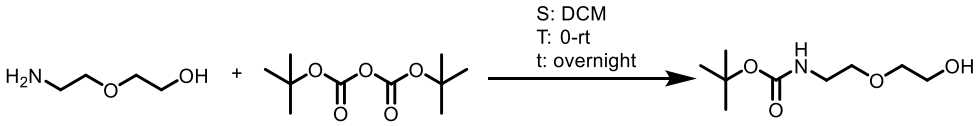
UV-Visible titration was performed by adding solutions containing the host (γ-CD or CB[8]) to a solution of the guest (**1a** or **2a**) in a 1 cm path quartz cuvette by using microliter syringes. In all cases the guest was present in the host solution at the same concentration as that in the cuvette to avoid dilution effects. Mili-Q water (18.2 mΩ/cm) was used as solvent for UV-Visible titration. UV-Visible scanning conditions were as follows: Scanning rate =300 nm/min, bandwidth = 0.5 nm, response time = 0.1 s, accumulations = 1 scan.

Photochemical reactions

Photodimerization of anthracene occurred in a Metalight Classic from Primotec equipped with 12 double centered at 365 nm UV lamps of 9 W each; the cycloreversion was performed in a Metalight Classic from Primotec equipped with 12 double centered at 254 nm UV lamps of 9 W each.

Synthesis and characterizations

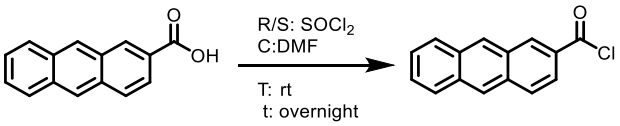
*tert-butyl (2-(2-hydroxylethoxy) ethylcarbamate (**1b**)*



1b

To a solution of 2-(2-aminoethoxy) ethanol (6.0 g, 56.76 mmol) in anhydrous DCM (75 mL) was added di-*tert*-butyldicarbonate (13.6 g, 62.44 mmol) at 0 °C. The reaction solution was warmed to room temperature and stirred overnight. The reaction solution was washed with H_2O (20 mL*4) and dried with anhydrous $MgSO_4$, filtered. The product was given after removing solvent under vacuum as colorless oil (11.05 g, 94.9%). ^{1}H NMR: (400 MHz, $CDCl_3$) δ: 5.04 (br, 1H), 3.76-3.68 (m, 2H), 3.61-3.50 (m, 4H), 3.37-3.25 (m, 2H), 1.43 (s, 9H). ^{13}C NMR: (100 MHz, $CDCl_3$, δ): 156.32, 79.41, 72.37, 70.37, 61.62, 40.42, 28.48. HRMS (ESI, m/z): $[M+Na]^+$ calcd for $C_9H_{19}NNaO_4$, 228.1212; found 228.1207.

2-Anthracenecarboxyl chloride



To a solution of 2-anthracenecarboxylic acid (4 g, 18 mml) in 60 mL $SOCl_2$ was added one drop of DMF. The solution was stirring 48 h under anhydrous condition at room temperature and the solvent was removed under reduced pressure. The residual amount of $SOCl_2$ was removed as an azeotrope with toluene (50 mL*2). Pure product was obtained as fine yellow powder in quantitative yields. ^{1}H NMR: (400 MHz, $CDCl_3$) δ: 8.98 (s, 1H, #1), 8.65 (s, 1H, #9), 8.47 (s, 1H, #10), 8.09-8.04 (m, 3H, #4,5,8), 7.97-7.94 (m, 1H, #3), 7.62-7.54 (m, 2H, #6,7). ^{13}C NMR: (100 MHz, $CDCl_3$, δ): 168.41, 137.18, 134.17, 133.07, 132.46, 130.26, 130.07, 129.36, 128.83, 128.40, 127.67, 126.60, 123.65.

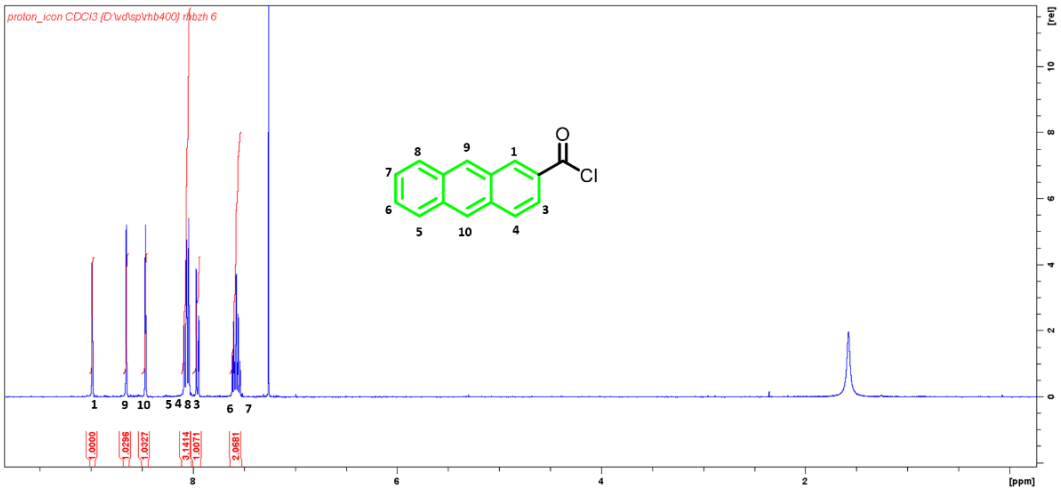
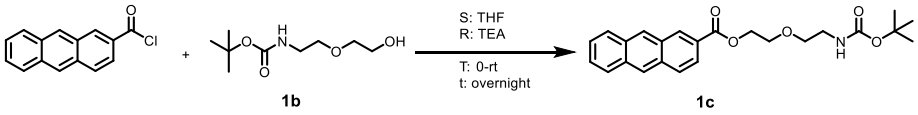


Figure S1. H-NMR of 2-Anthracenecarboxyl chloride in $CDCl_3$.

*2-[2-(tert-Butoxycarbonylamino)ethoxy]ethyl-2-anthracenecarboxylate (**1c**)*



To the solution of tert-butyl (2-(2-hydroxylethoxy)ethylcarbamate (3.6 g, 17.5 mmol) and Et_3N (2.4 mL, 17.5 mmol) in dry THF (50 mL), 2-Anthracenecarboxyl chloride (2 g, 8.3 mmol) in 30 mL dry THF was added dropwise. This mixture was stirred 24 hours at room temperature. The solvent was removed under reduced pressure. The residue was dissolved with DCM, then the solution was washed with saturated $NaHCO_3$ aqueous solution (3x), brine (1x) and water (1x). The given solution was dried with $MgSO_4$ and filtered. The crude product was concentrated and purified by silica chromatography (EtOAc:DCM=1:10 by volume). (2.8 g, 82.8%). ^{1}H NMR: (400 MHz, $CDCl_3$) δ: 8.84 (s, 1H, #1), 8.59 (s, 1H, #9), 8.47 (s, 1H, #10), 8.06-7.97 (m, 4H, #3,4,5,8), 7.57-7.49 (m, 2H, #6,7), 4.95 (br, 1H, NH), 4.56 (t, 2H, -C(O)OCH_2-), 3.87 (t, 2H, -C(O)OCH_2CH_2-), 3.64 (t, 2H, -C(O)NHCH_2CH_2-), 3.37 (t, 2H, -C(O)NHCH_2-), 1.42 (s, 9H, -C(CH_3)$_3$. ^{13}C NMR: (100 MHz, $CDCl_3$, δ): 166.89, 133.27, 132.82, 132.60, 132.14, 130.48, 128.90, 128.63, 128.60, 128.32, 126.92, 126.74, 126.37, 126.04, 124.18, 73.62, 69.22, 64.38, 41.97.

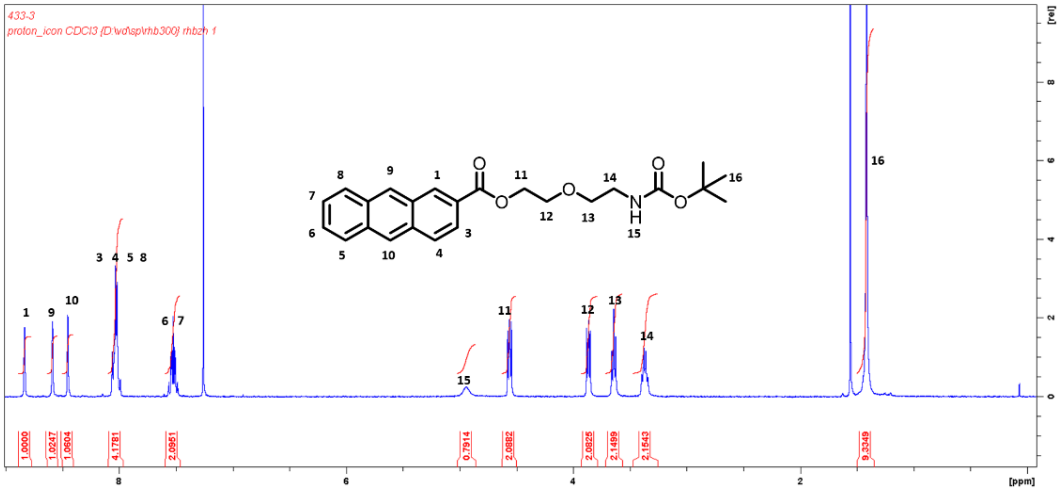
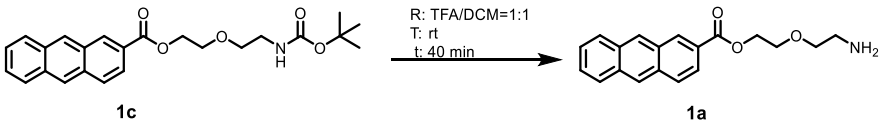


Figure S2. H-NMR of 2-[2-(tert-Butoxycarbonylamino)ethoxy]ethyl-2-anthracenecarboxylate in $CDCl_3$.

*2-(2-aminoethoxy)ethyl-2-anthracenecarboxylate (**1a**)*



1c **1a**

2-[2-(tert-Butoxycarbonylamino)ethoxy]ethyl-2-anthracenecarboxylate (2.7 g, 6.6 mmol) was dissolved in 30 mL of a 1:1 (vol/vol) solution of TFA in CH_2Cl_2. This mixture was stirred for 30 min at room temperature. The solvent was removed under reduced pressure. The residue was taken up by 50 mL CH_2Cl_2 followed by washing with saturated aqueous $NaHCO_3$ solution and water. The organic phase was dried with Na_2SO_4 and filtered. The result solution was concentrated and subjected to silica column chromatography (methanol (1 M NH_3) / EtOAc =1:20). The fraction containing the product was collected, solvents were removed under reduced pressure and the product was obtained as brown solid (1.95 g, 95.6 %). ^{1}H NMR: (400 MHz, $CDCl_3$) δ: 8.84 (s, 1H, #1), 8.59 (s, 1H, #9), 8.47 (s, 1H, #10), 8.06-7.97 (m, 4H, #3,4,5,8), 7.57-7.49 (m, 2H, #6,7), 4.58 (t, 2H, -C(O)OC<u>H$_2$</u>-), 3.88 (t, 2H, -C(O)OCH$_2$C<u>H$_2$</u>-), 3.61 (t, 2H, NH$_2$CH$_2$C<u>H$_2$</u>-), 2.92 (t, 2H, NH$_2$C<u>H$_2$</u>-). ^{13}C NMR: (100 MHz, $CDCl_3$, δ): 166.89, 133.27, 132.82, 132.60, 132.14, 130.48, 128.90, 128.63, 128.60, 128.32, 126.92, 126.74, 126.37, 126.04, 124.18, 73.62, 69.22, 64.37, 41.97.

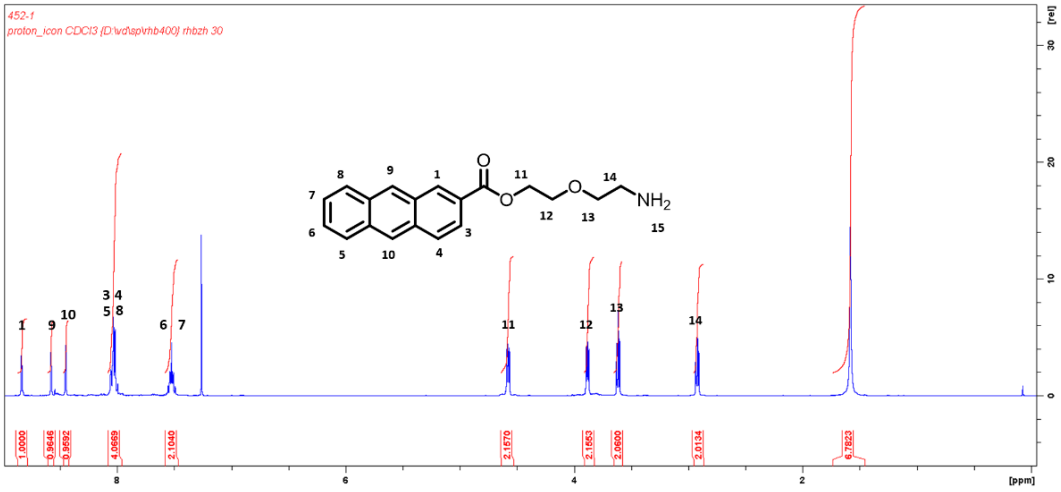
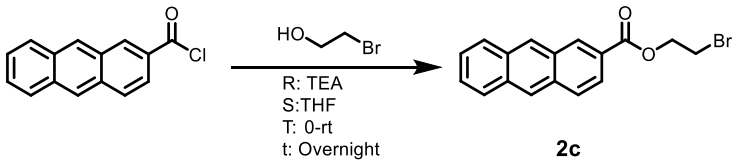


Figure S3. H-NMR of 2-(2-aminoethoxy)ethyl-2-anthracenecarboxylate in $CDCl_3$.

*2-bromoethyl-2-anthracenecarboxylate (**2c**)*



2c

To the solution of 2-bromoethanol (2.04 g, 16.37 mmol) and Et_3N (1.5 mL, 10.9 mmol) in dry THF (40 mL), 2-Anthracenecarboxyl chloride (1.31 g, 5.46 mmol) in 20 mL dry THF was added dropwise. This mixture was stirred 24 hours at room temperature. The solvent was removed under reduced pressure. The residue was dissolved with DCM, then the solution was washed with saturated $NaHCO_3$ aqueous solution (3x), brine (1x) and water (1x). The given solution was dried with $MgSO_4$ and filtered. The crude product was concentrated and purified by silica chromatography (petroleum:EtOAc=10:1 by volume). (1.5 g, 83.6%). ^{1}H NMR: (400 MHz, $CDCl_3$) δ: 8.85 (s, 1H, #1), 8.59 (s, 1H, #9), 8.46 (s, 1H, #10), 8.06-7.97 (m, 4H, #3,4,5,8), 7.57-7.49 (m, 2H, #6,7), 4.72 (t, 2H, -$C\underline{H_2}CH_2Br$), 3.72 (t, 2H, -$C\underline{H_2}Br$). ^{13}C NMR: (100 MHz, $CDCl_3$, δ): 166.41, 133.37, 132.87, 132.19, 130.45, 129.01, 128.76, 128.63, 128.34, 126.84, 126.42, 126.11, 124.07, 64.53, 29.03. ESI-MS (m/z): $[M+H]^+$ calculated for $C_{17}H_{14}BrO_2^+$: 329.01; found: 329.03.

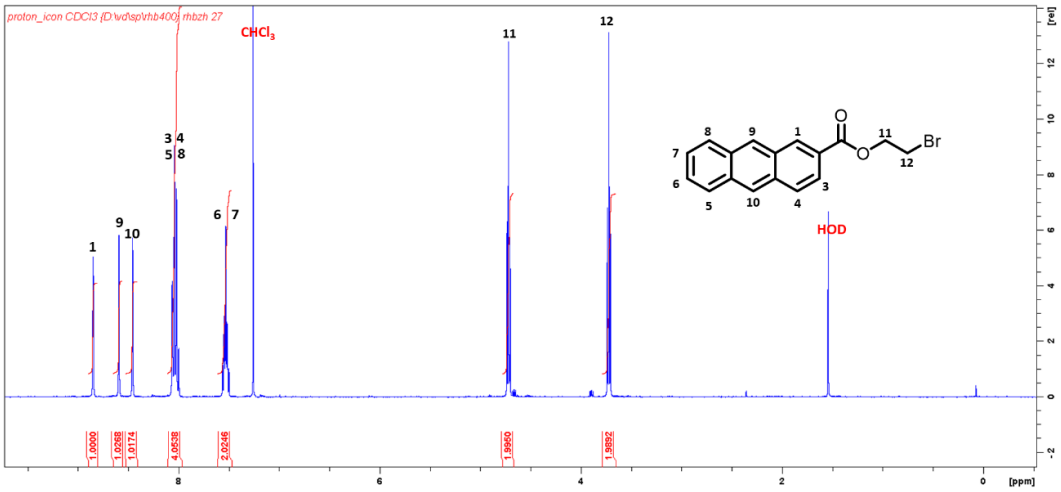
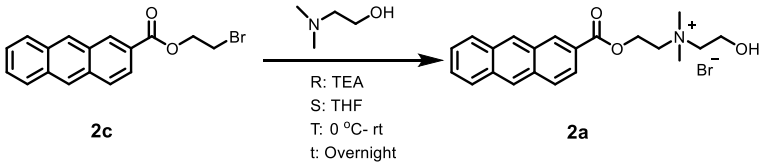


Figure S4. H-NMR of 2-bromoethyl-2-anthracenecarboxylate in $CDCl_3$.

*2-((anthracene-2-carbonyl)oxy)-N-(2-hydroxyethyl)-N, N-dimethylethan-1-aminium bromide (**2a**)*



2c **2a**

Mix the 2-bromoethyl-2-anthracenecarboxylate (0.5 g, 1.52 mmol) and 2-Dimethylaminoethanol (764 µL, 7.60 mmol) in 30 mL acetonitrile. The reaction mixture was heated to reflux overnight. A yellow solid was precipitated during this period. The precipitation was filtered off and washed with DCM. After drying under reduced pressure, the pure product (**2a**) was obtained as yellow powder. (yield 0.62 g, 97.6%). ^{1}H NMR: (400 MHz, CD_3OD, ppm) δ: 8.89 (s, 1H, #1), 8.70 (s, 1H, #9), 8.56 (s, 1H, #10), 8.16-8.08 (m, 3H, #4,5,8), 8.02-7.96 (m, 1H, #3), 7.61-7.52 (m, 2H, #6,7), 4.91 (m, 2H, -C(O)OC$\underline{H_2}$-), 4.12-4.06 (m, 2H, -NC$\underline{H_2}CH_2OH$), 4.05-4.03 (m, 2H, -C(O)OC$H_2C\underline{H_2}$-), 3.72-3.69 (m, 2H, -$\underline{CH_2}OH$), 3.38 (s, 6H, -N($\underline{CH_3}$)$_2$). ^{13}C NMR: (100 MHz, CD_3OD, δ): 167.21, 134.88, 134.12, 133.83,

133.67, 131.63, 130.00, 129.96, 129.50, 129.28, 127.99, 127.41, 127.27, 127.20, 124.53, 67.73, 65.23, 59.60, 56.91, 53.07. ESI-MS (m/z): $[M\text{-}Br^-]^+$ calculated for $C_{21}H_{24}NO_3^+$: 338.17; found: 338.10.

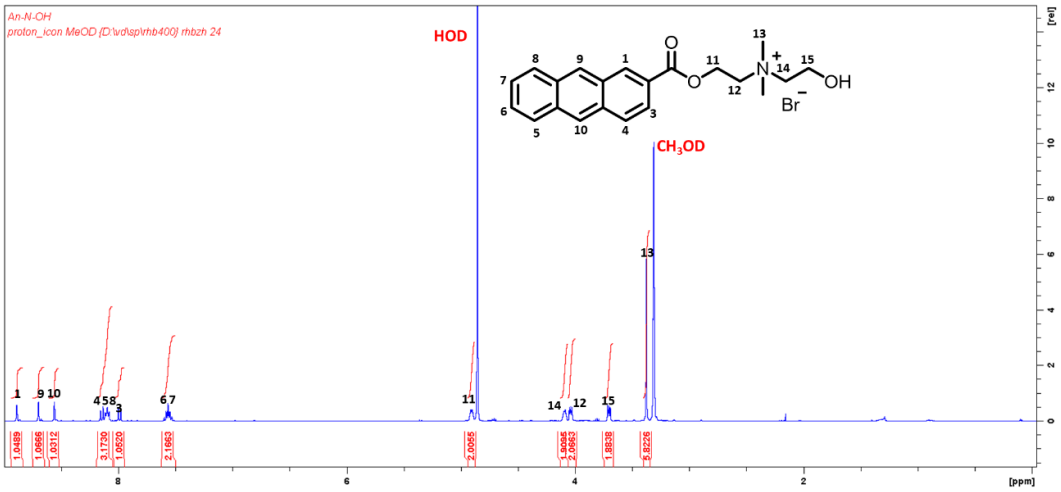


Figure S5. H-NMR of 2-((anthracene-2-carbonyl)oxy)-N-(2-hydroxyethyl)-N, N-dimethylethan-1-aminium bromide in $CDCl_3$.

Pentafluorophenyl acrylate

Pentafluorophenol (9.0 g, 48.90 mmol) and triethylamine (7.5 mL, 53.79 mmol) were dissolved in 250 mL dry DCM and cooled to 0 °C. To this solution, acryloyl chloride (4.4 mL, 53.79) in 100 mL dry DCM was added dropwise, and the mixture was stirred and let warm to room temperature overnight. The product was obtained after washing the organic phase with water (200 x 3). 9.59 g product was obtained by drying in oven (yield, 82%). ^{1}H NMR: (400 MHz, $CDCl_3$, ppm) δ: 6.72 (dd, 1H, -CHCHC(O)-, cis position with respect to carbonyl group), 6.37 (dd, 1H, CH_2C<u>H</u>-), 6.18 (dd, 1H, -<u>CH</u>CHC(O)-, *trans*-position with respect to carbonyl group). ^{13}C NMR: (100 MHz, $CDCl_3$, ppm) δ: 161.82, 142.59, 140.95, 140.04, 139.32, 138.42, 136.85, 135.64, 125.49. ^{19}F NMR: (470 MHz, $CDCl_3$, ppm) δ: -152.61 (m, 2F, ortho), -158.00 (t, 1F, para), -162.37 (m, 2F, meta). GC was measured for purification (>99%).

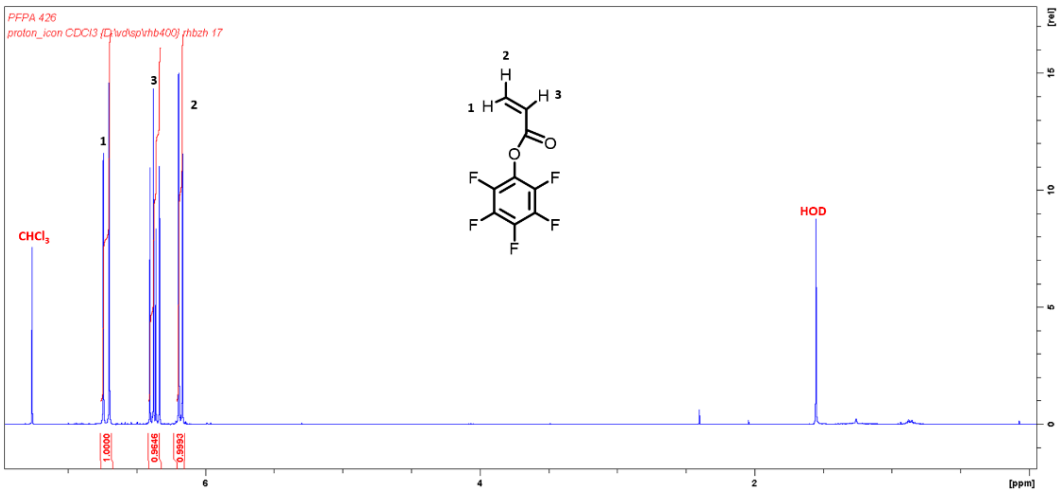


Figure S6. H-NMR of Pentafluorophenyl acrylate in $CDCl_3$.

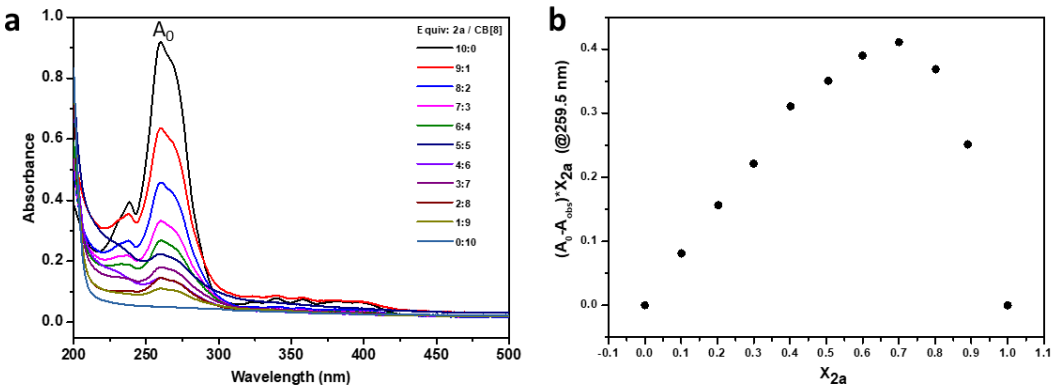
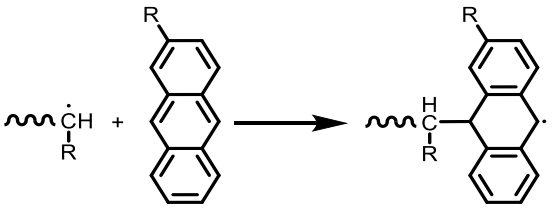


Figure S7. a UV-Vis spectra of the aqueous solution of **2a** and CB[8] at different molar ratio of the two moieties at 25 ^{o}C, in which the total concentration was kept constant at 30 μM; b). Job's plot of **2a** and CB[8], where the absorbance at 259.5 nm was plotted against the molar fraction of **2a**.



Scheme S1 Schematic representation of 2-substituted anthracene as radical trap to terminate the growing polymer

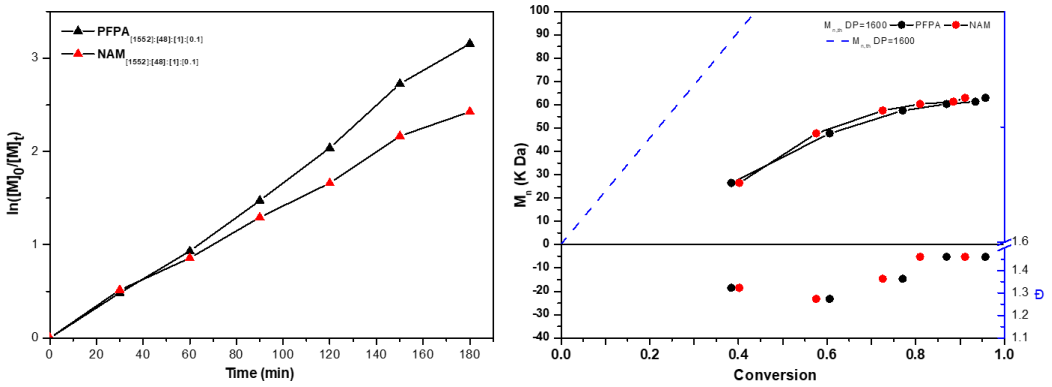


Figure S8. The kinetic data for the copolymerization of PNAM-PFPA.

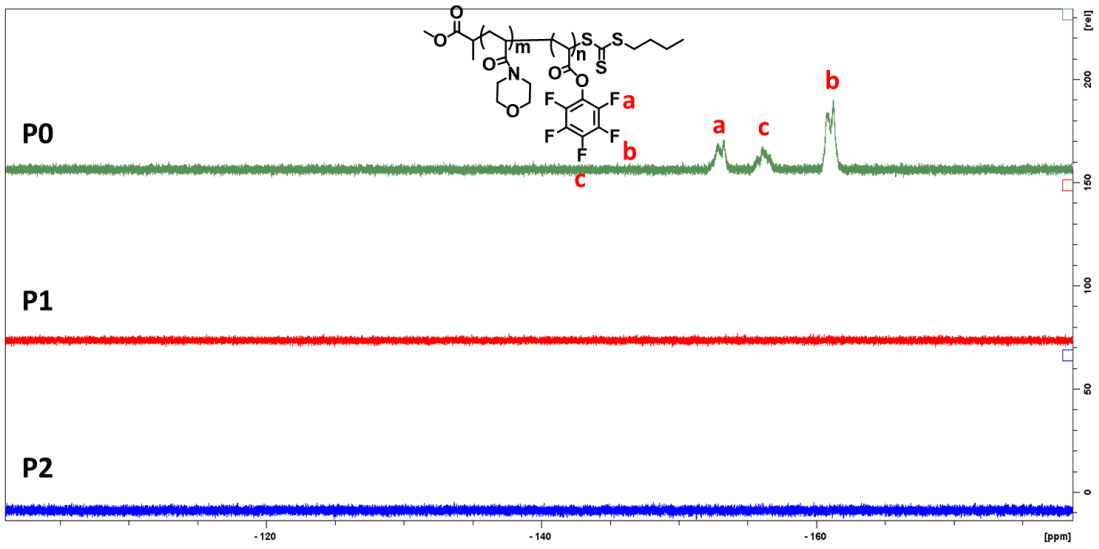


Figure S9. ^{19}F NMR spectra of **P0**, **P1** and **P2** in $CDCl_3$.

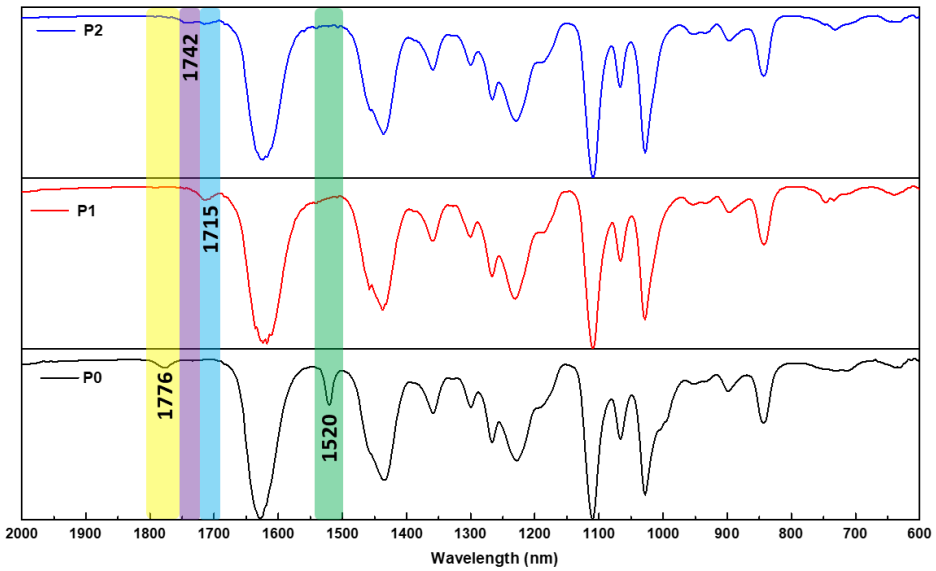


Figure S10. FT-IR spectra of the PNAM-PFPA precursor **P0** (bottom), the **P1** (middle) and **P2** (top).

Table S1 Summary of the gelation study. (---: CB[8] is insoluble in water; **/**: the system was not studied)

Polymer/Host	5%	10%	15%
P1/γ- CD	sol	sol	gel
P1/CB[8]	---	---	---
P2/γ- CD	sol	/	/
P2/CB[8]	gel	/	/

References

1. Urbani, C. N.; Monteiro, M. J., Nanoreactors for Aqueous RAFT-Mediated Polymerizations. *Macromolecules* **2009,** *42* (12), 3884-3886.

2. Kim, J.; Jung, I.-S.; Kim, S.-Y.; Lee, E.; Kang, J.-K.; Sakamoto, S.; Yamaguchi, K.; Kim, K., New Cucurbituril Homologues: Syntheses, Isolation, Characterization, and X-ray Crystal Structures of Cucurbit[n]uril (n = 5, 7, and 8). *J. Am. Chem. Soc.* **2000,** *122* (3), 540-541.

3. Renny, J. S.; Tomasevich, L. L.; Tallmadge, E. H.; Collum, D. B., Method of continuous variations: applications of job plots to the study of molecular associations in organometallic chemistry. *Angew. Chem. Int. Ed.* **2013,** *52* (46), 11998-2013.