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Supporting Information of

Fixable Supramolecular Cyclic Polymer based on Cucurbit[8]uril-stabilized π-π Interaction

Zhongwei Ji[a], Yipeng Li[b], Yu Ding[b], Guosong Chen[a], Ming Jiang[a]*

[a]State Key Laboratory of Molecular Engineering of Polymers, and Department of Macromolecular Science, Fudan University, Shanghai, 200433 China

[b]Department of Physiology and Biophysics, School of Life Sciences, Fudan University, Shanghai 200438, China

Experimental Section

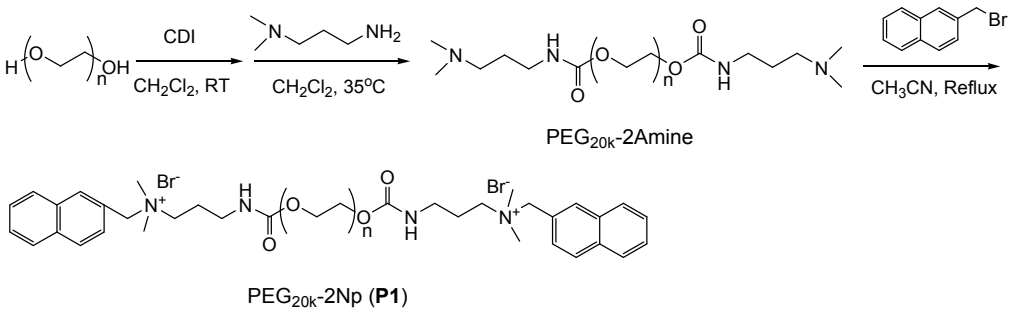
Materials. 1,1'-carbonyldiimidazole (CDI), poly(ethylene glycol) (PEG, M_n=20000), trimethylamine (3.2 M in methanol), propagyl bromide (80 wt% solution in toluene), 2-Aminoanthraquinone, 2-(bromomethyl)naphthalene, 3-dimethylaminopropylamine, were purchased from J&K Scientific Ltd. Zn powder, ammonium hydroxide (NH_4OH), 37% aqueous paraformalde, methanesulfonyl chloride, acetic acid, diethyl ether, sodium chloride (NaCl), potassium hydroxide (KOH), magnesium sulfate ($MgSO_4$), acetonitrile (CH_3CN), acetone, triethylamine, chloroform (CH_3Cl), copper sulfate ($CuSO_4$), sodium ascorbate were supplied by Sinopharm Chemical Reagent Co. Silver nitrate ($AgNO_3$), sodium cyanoborohydride, sodium azide (NaN_3) were purchased from Energy Chemical. N,N-dimethylformamide (DMF) and dichloromethane (DCM) were dried by calcium hydride and distilled before use. Cucurbit[8]uril was prepared following reported procedure[1]. Unless specially mentioned, all other chemicals were used as received.

Characterizations. ^{1}H NMR spectra were recorded with a Bruker DMX400 spectrometer. MALDI-TOF MS experiments were performed on AB Sciex 5800 from the Applied Biosystems (USA). Gel permeation chromatography (GPC) analysis was carried out with a Waters Breeze 1525 GPC analysis system with two TSK-gel column, using DMF with 0.5 M LiBr as eluents at the flow rate of 1 mL/min at 80 ºC. PEO calibration kit (purchased from TOSOH) was used as the calibration standard. The ITC experiments were carried out on a MicroCal VP-ITC system at 25.00 ± 0.01 ºC. Experimental titration curves were analyzed with the Origin LLC ITC 7.0 program. UV-vis spectra were recorded in a conventional quartz cell (light path 10 mm) on a spectrophotometer (Shimadzu UV-2550) equipped with a temperature controller. All Fourier transform infrared (FT-IR) spectra were recorded with 64 scans in the range 4000-400 cm^{-1} on a Nicolet Nexus 470 spectrometer with a resolution of 4 cm^{-1}. Dynamic light scattering studies were conducted by ALV/5000E laser light scattering (LLS) spectrometer at scattering angle of 90° (or 45°) for 0.5-1 h, depending on the concentration of polymer. CONTIN analysis was used for the

extraction of R_h data. Samples were filtered through 220 nm PVDF filters and stand overnight before test.

Viscometry. Viscosities were measured in an Ubbelohde semi-micro dilution viscometer immersed in a thermostatic water bath (± 0.01 °C) with a 0.63 mm inner diameter capillary (ZONWON IVS300). Samples were filtered over 450 nm PVDF filters and stand at 20 °C for 20 min before test. Flowing time was recorded by a laser timer automatically. Every sample was tested at least three times and the error was kept less than 0.05 sec.

Photoirradiation of CB[8]+P2 in aqueous solution. The aqueous solution of CB[8]+**P2** was sealed in a pyrex round-bottom flask, purged with N_2 for 30 min and irradiated by a UV radiometer (365nm, 500 W, Beijing Changtuo Technology Co. Ltd). The UV-lamps were "pre-warmed" for 10 min prior to any experiments. During irradiation, the solution gradually became non-fluorescent and turned into yellow. The process was followed by UV-vis absorption spectrum.



Scheme S1. Synthetic procedure of Np end-functionalized PEG_{20K} (**P1**).

Synthesis of PEG_{20k}-2Amine. In a 100 mL round-bottom flask fitted with a funnel, CDI (1.3 g, 8.0 mmol) was dissolved in 10 mL of anhydrous DCM. The dehydrated PEG_{20k} (8 g, 0.4 mmol) was dissolved in 50 mL of anhydrous DCM and added dropwise to the CDI solution with stirring in N_2 environment. The mixture was stirred at room temperature for 24 h. After that, most solvent was removed under reduced pressure and the resulting mixture was precipitated in diethyl ether. The precipitate was centrifuged and used for next reaction without further purification.

The activated PEG_{20k}-2CDI was re-dissolved in 50 mL DCM, added dropwise to a 10 mL DCM solution of 3-dimethylaminopropylamine with stirring in N_2 atmosphere. The mixture was stirred at 35 ^oC for 24 h. After cooled to room temperature, most solvent was removed under vacuum and the residue was precipitated in diethyl ether. The precipitate was collected by filtration and obtained as a white powder (7.7g, 96%). ^1H NMR (400 MHz, $CDCl_3$) δ 4.23-4.12 (t, 4H), 3.76 – 3.48 (m, 1904H), 3.20 (q, 4H), 2.75 (t, 4H), 2.18 (s, 12H), 1.68 – 1.56 (m, 4H).

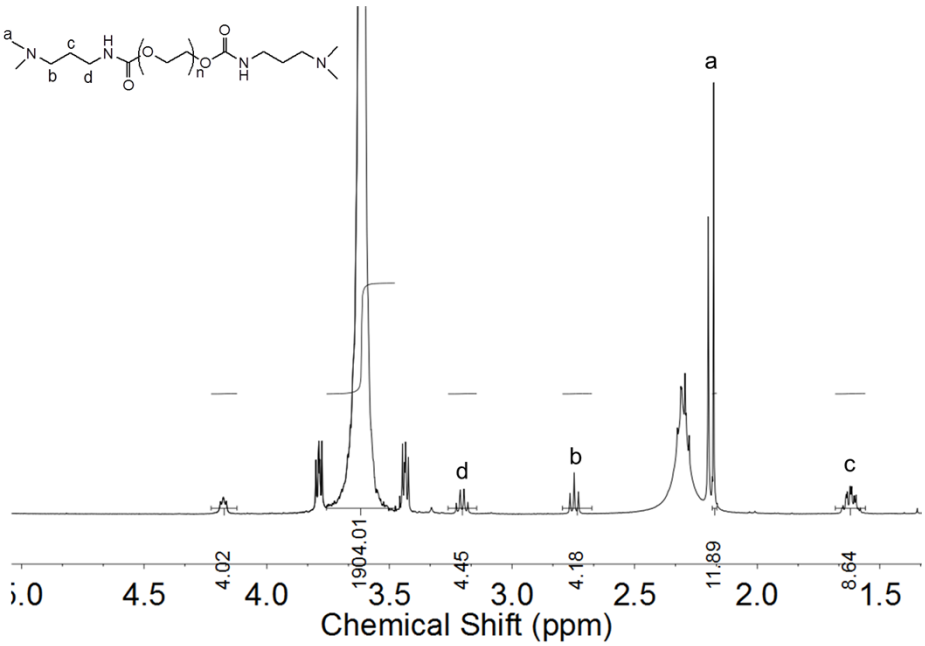


Fig. S1 ^1H NMR spectrum of PEG_{20K}-2Amine

Synthesis of PEG_{20k}-2Np (**P1**) PEG_{20k}-2Amine (2 g, 0.1 mmol) and 2-(bromomethyl)naphthalene (0.22 g, 1mmol) were dissolved in 50 mL CH_3CN in a 100 mL round-bottom flask. The mixture was heated to reflux for 24 h. After cooled to room temperature, the reaction solution was concentrated under vacuum and precipitated into diethyl ether. The precipitate was collected by filtration, which was further purified in a dialysis membrane with a molecular weight cut-off of 3 kDa against water for 3 days. Then the aqueous solution was freeze-dried to get a white powder (1.23 g, 61%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 2H), 8.02 – 7.78 (m,

6H), 7.73 – 7.45 (m, 6H), 5.00 (s, 4H), 4.17 (s, 4H), 3.62 (m, 2072H), 3.33 (q, 4H), 3.25 (s, 12H).

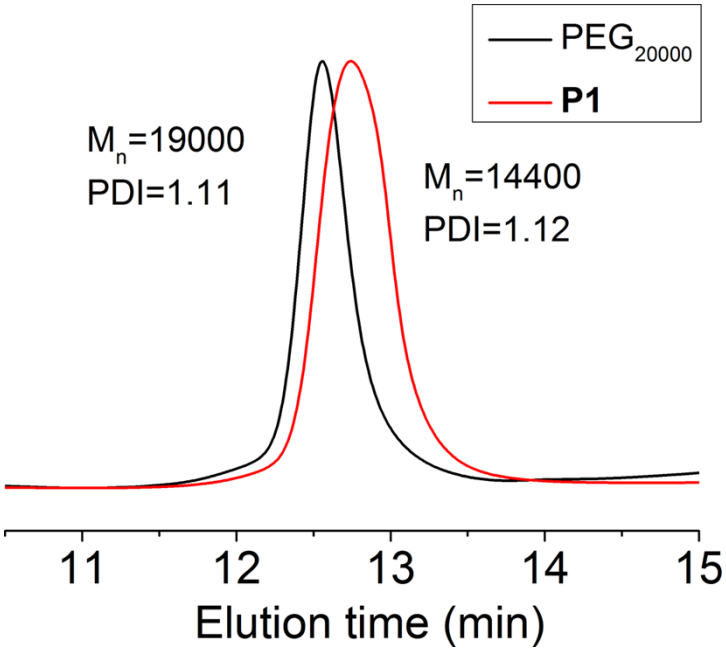


Fig. S2 GPC of PEG_{20000} and **P1**.

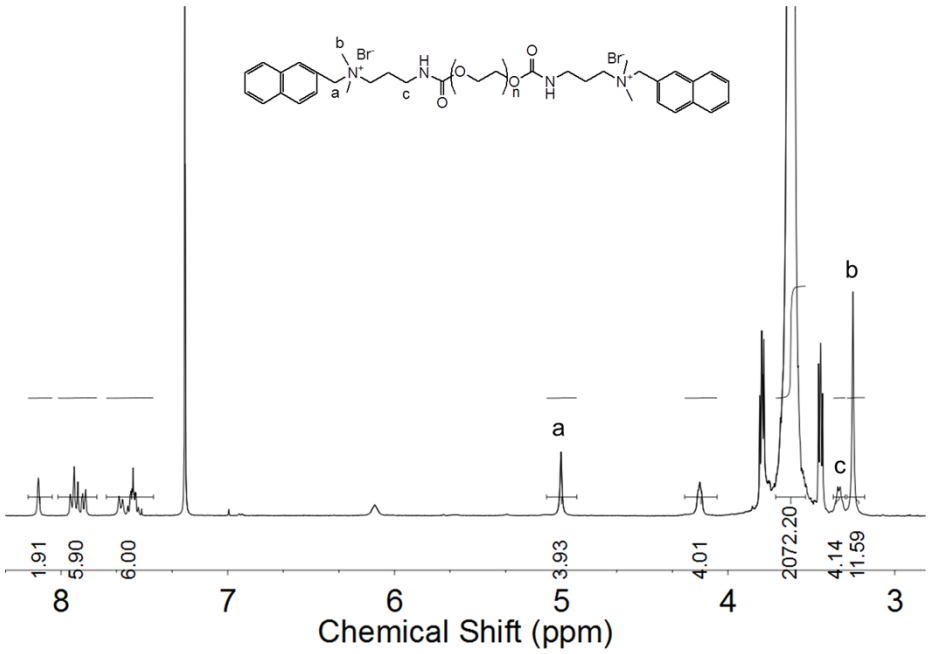


Fig. S3 ^{1}H NMR spectrum of PEG_{20K}-2Np (**P1**).

Synthesis of M1 2-(Bromomethyl)naphthalene (1 g, 4.5 mmol) was reacted with excess trimethylamine (7 mL, 3.2 M in methanol) in CH_3CN at 80 °C overnight. After cooled to room temperature, the mixture was precipitated in diethyl ether and filtrated to give a white powder (1.23 g, 98%). ^{1}H NMR (400 MHz, D_2O) δ 8.02 (m, 4H), 7.71 – 7.61 (m, 2H), 7.58 (dd, 1H), 4.62 (s, 2H), 3.12 (s, 9H). MALDI-TOF MS: $(C_{14}H_{15}N)^+$: 200.2 (Calculated: 200.14).

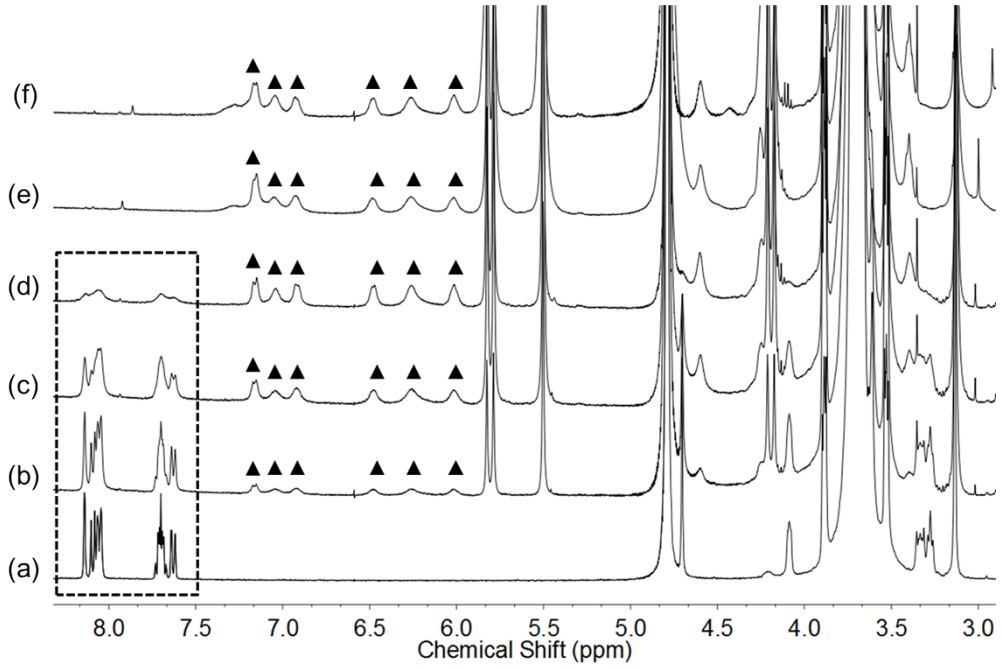


Fig. S4 ^{1}H NMR (D_2O) of (a) **P1**,(b) **P1** + CB[8] (1 : 0.25), (c) **P1** + CB[8] (1 : 0.5), (d) **P1** + CB[8] (1 : 0.75), (e) **P1** + CB[8] (1 : 1), and (f) **P1** + CB[8] (1 : 1.2). The concentration of **P1** was 0.5 mM. Peak in the dashed box is belonging to free Np groups, while triangle shows the peak belonging to CB[8]-encapsulated Np groups.

Successive addition of CB[8] into an aqueous solution of **P1** resulted in a decrease of the intensities of the peaks corresponding to free Np and growth of a new set of signals which were assigned to CB[8]-encapsulated Np. The peaks of free Np disappeared when the molar ratio of **P1** and CB[8] reached 1 : 1 and further addition of CB[8] didn't cause more difference, indicating a 2:1 binding between Np and CB[8].

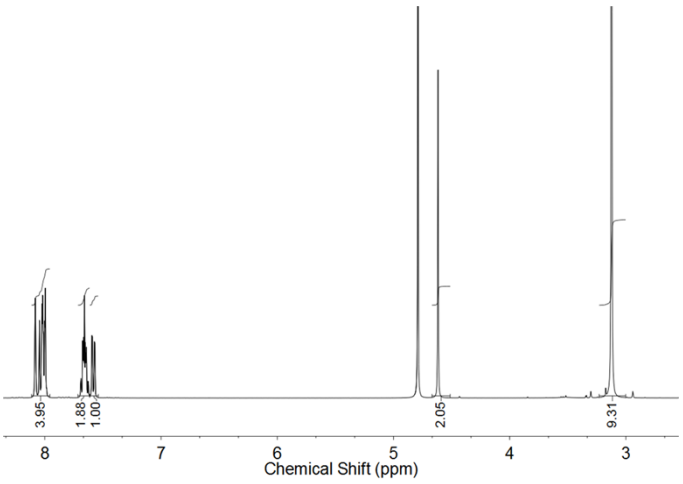


Fig. S5 ^{1}H NMR spectrum of **M1**.

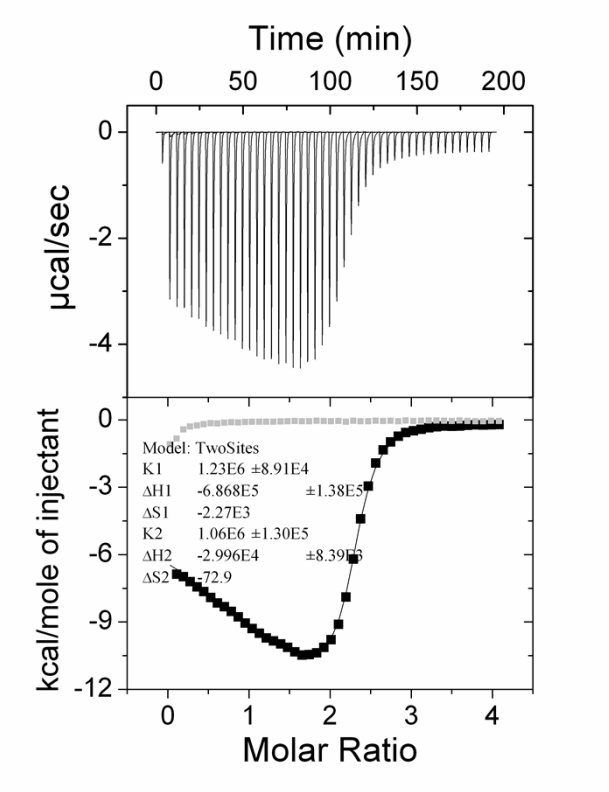


Fig. S6 ITC data for the titration of CB[8] (0.1 mM) with **M1** (2.0 mM) in aqueous solution at 25 °C.

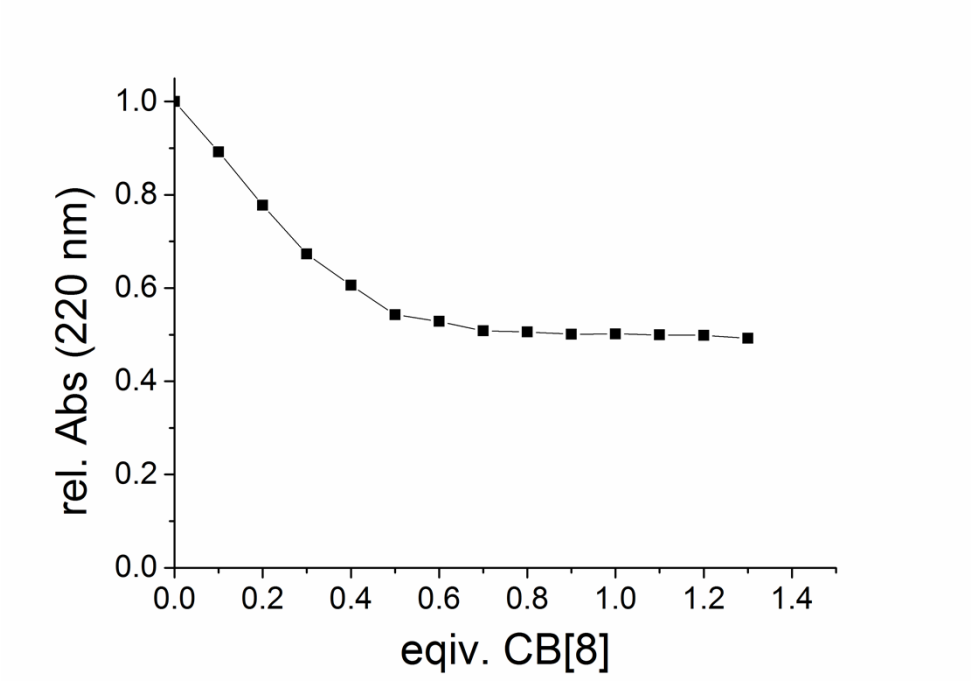


Fig. S7 UV/vis spectra for the titration of **P1** (0.25 mg/mL in water) with CB[8].

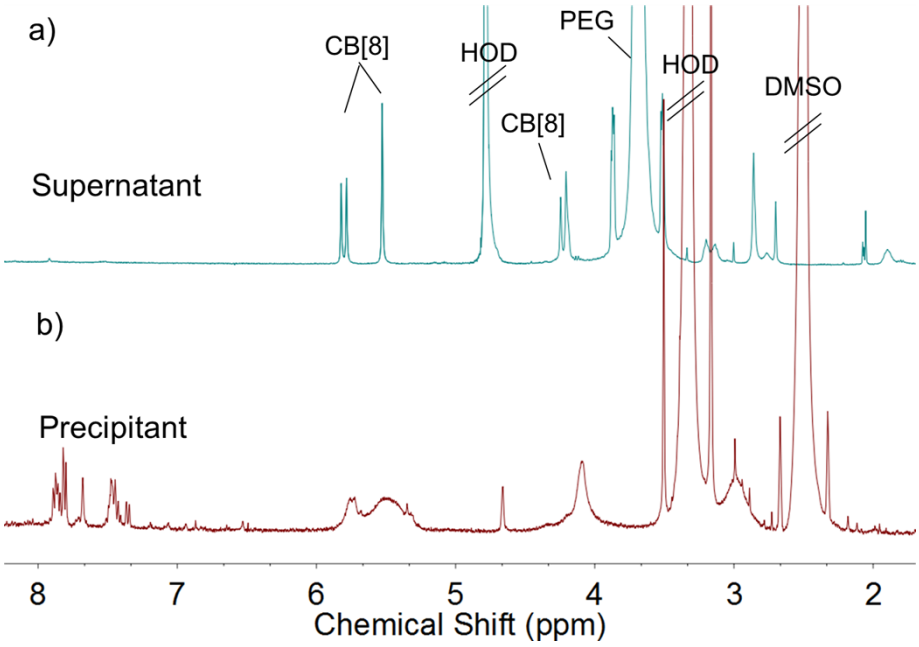
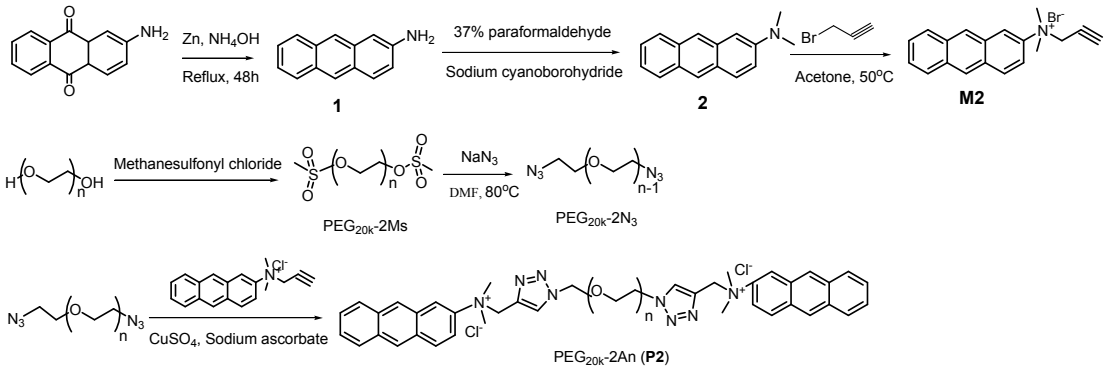


Fig. S8 ^{1}H NMR of CB[8]+**P1** after photo-irradiation for 0.5 h at >280 nm. (a) Supernatant in D_2O. (b) Precipitant in DMSO-d_6.



Scheme S2. Synthetic procedure of An end-functionalized PEG_{20K} (**P2**).

Synthesis of 1. 2-Amino anthraquinone (4 g, 17.9 mmol), zinc (0.436 mol, 28.5 g) and NH_4OH (350 mL) were mixed and refluxed for 48 h. The reaction mixture was cooled to r.t. and neutralized with aqueous HCl (6 M). The residue was filtered and washed with water. The crude product was purified by column chromatography, generating the desired product as a light yellow solid (2.4 g, 70%). ^{1}H NMR (400 MHz, DMSO) δ 8.27 (s, 1H), 8.02 (s, 1H), 7.94 – 7.75 (m, 3H), 7.32 (m, 2H), 7.04 (dd, 1H), 6.92 – 6.83 (m, 1H).

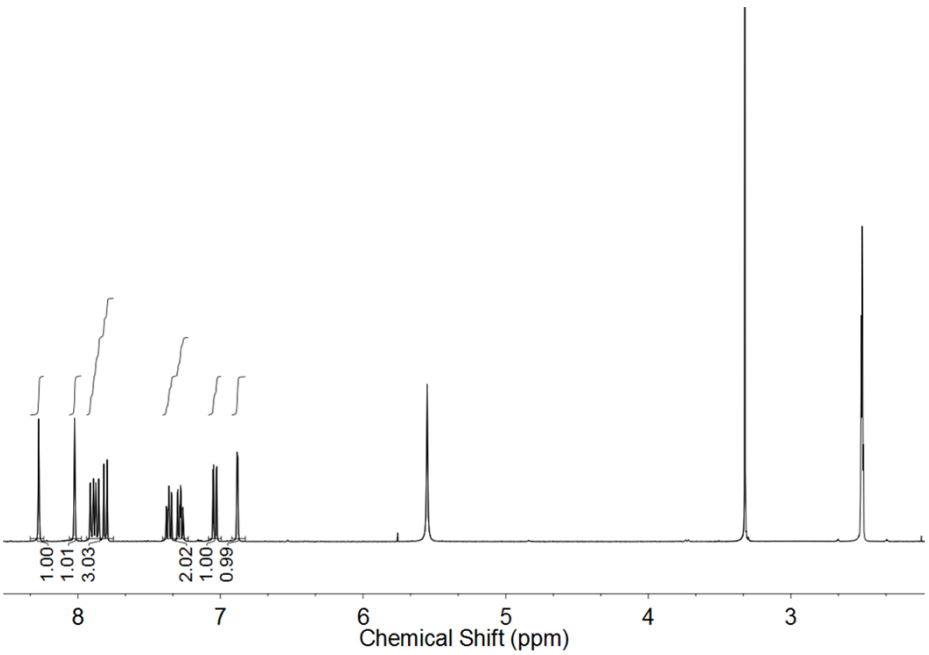


Fig. S9 ^{1}H NMR spectrum of **1**.

Synthesis of 2. 2 was synthesized according to the procedure described in the

literature[2]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 8.17 (s, 1H), 7.90 (t, 3H), 7.41 – 7.27 (m, 3H), 6.99 (t, 1H), 3.10 (s, 6H).

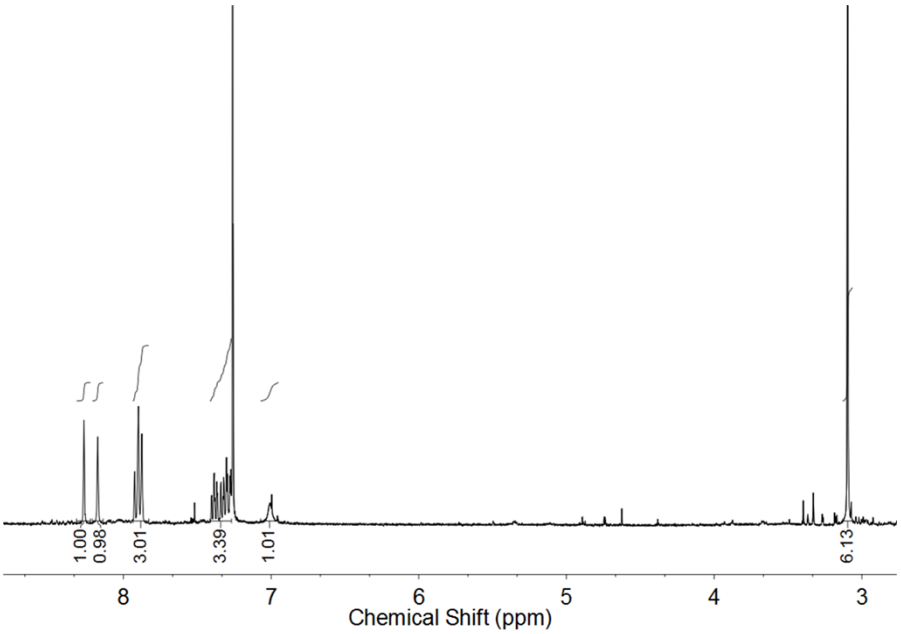


Fig. S10 ^{1}H NMR spectrum of **2.**

Synthesis of M2. To a solution of *N*,*N*'-dimethylanthracen-2-amine (1 g, 5 mmol) in 50 mL acetone was added propagyl bromide (2.5 mL, 80 wt% solution in toluene, 25 mmol) and the reaction mixture was stirred at 50^{o}C for 24 h. The resulting precipitate was collected by suction filtration and washed with diethyl ether to yield the product as a yellow solid (1 g, 60%). ^{1}H NMR (400 MHz, d^6-DMSO) δ 8.79 (s, 1H), 8.75 (s, 1H), 8.68 (d, 1H), 8.40 (d, 1H), 8.19 (m, 2H), 8.07 (dd, 1H), 7.69 – 7.59 (m, 2H), 5.10 (d, 2H), 3.86 (t, 1H), 3.77 (d, 6H).

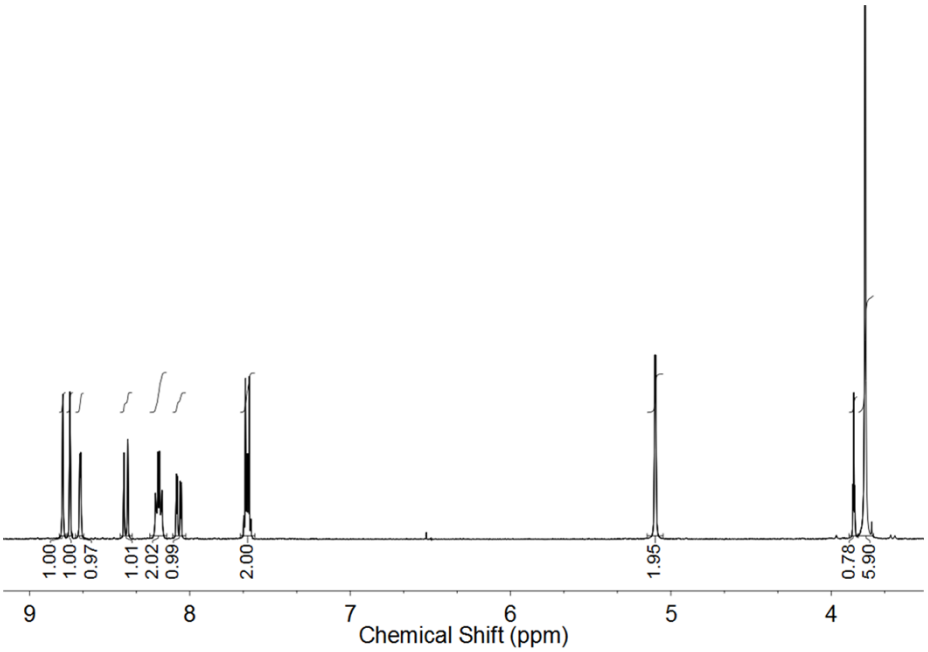


Fig. S11 ^{1}H NMR spectrum of **3.**

Synthesis of PEG_{20k}-2Ms. To a 60 mL DCM solution of PEG_{20k} (8 g, 0.4 mmol), anhydrous triethylamine (0.34 mL, 2.4 mmol), methanesulfonyl chloride (0.186 mL, 2.4 mmol) in 20 mL anhydrous DCM was added dropwise. The mixture was stirred at room temperature for 24 h. Then, the solution was concentrated under reduced pressure and precipitated into diethyl ether. The precipitate was collected through filtration, dried under vacuum and used for the next step without further purification (7.8 g, 98%).

Synthesis of PEG_{20k}-$2N_3$. Sodium azide (0.26 g, 4 mmol), PEG_{20k}-2Ms (7.8g, 0.39 mmol) were dissolved in 60 mL DMF. The mixture was put under nitrogen and constant stirred in a hot water bath at 80°C for 24 h. After removing DMF under reduced pressure, 100 mL of DCM was added and the resulting solution was washed three times with 50 mL of H_2O. The organic phase was dried over $MgSO_4$ and the solvent was removed under reduced pressure to give a white powder (4.7 g, 60%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.6 (t, 4H), 3.51 (s, 1805H), 3.38 (t, 4H).

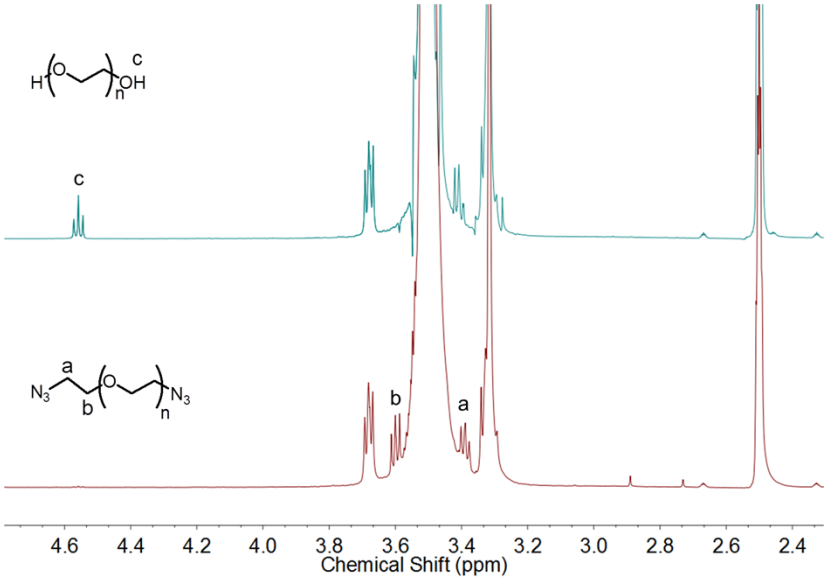


Fig. S12 ^{1}H NMR spectrum of PEG_{20k}-$2N_3$ and PEG_{20k}.

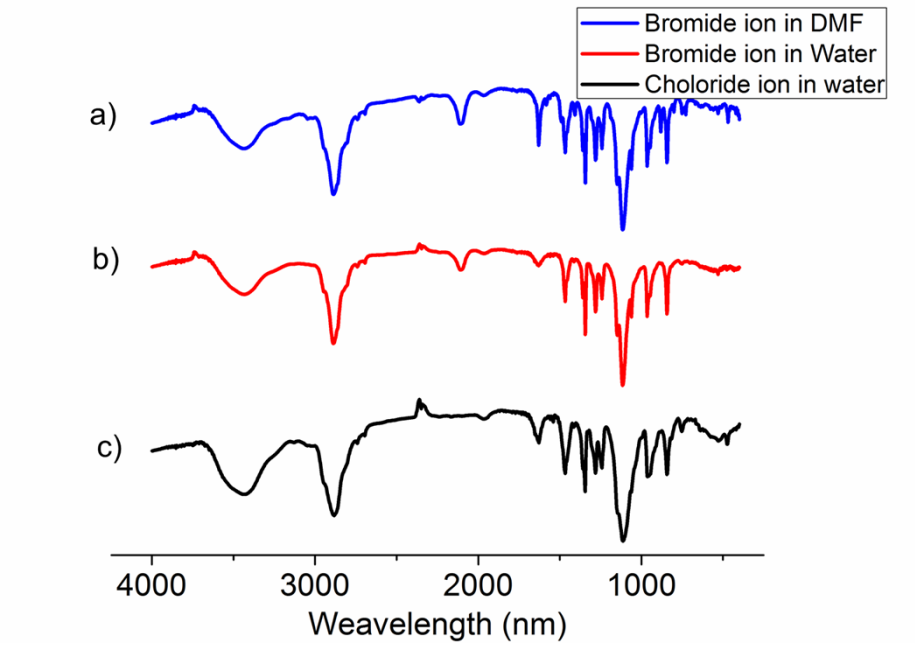


Fig. S13 FT-IR of PEG_{2K}-$2N_3$ after react with **M2** for 24 h: a) Br^-, DMF; b) Br^-, H_2O; c) Cl^-, H_2O.

Synthesis of PEG_{20k}-2An (**P2**)[2]. Counterion exchange to chloride was achieved through vigorous stirring of an aqueous solution (120 mL) of *N*,*N*-dimethyl-*N*-(prop-2-yn-1-yl)anthracen-2-aminium bromide **M2** (0.34 g, 1 mmol) over freshly precipitated silver chloride (25 equiv. per bromide counter ion) overnight. The silver salt was filtered off and the filter cake was washed with water for several times. The combined aqueous solution was concentrated to about 80 mL and used for the next step.

PEG_{20k}-$2N_3$ (2 g, 0.1 mmol) was dissolved into the above aqueous solution of **M2** and degassed with nitrogen for 30 min. To this solution was added a degassed and slightly sonicated solution of $CuSO_4$ (16 mg, 0.1 mmol) and sodium ascorbate (57 mg, 0.3 mmol) in 5 mL water. The resulting mixture was stirred at 30 ^oC for 24 h under light protection. After cooled to room temperature, the solution was extracted with $CHCl_3$ (3 times 200 mL) and the combined organic fractions were washed with an aqueous EDTA (20 equiv. to Cu) solution followed by a washing step with brine and with water. The organic phase was dried over magnesium sulfate and filtered. The solvent was removed under reduced pressure and the solid was redissolved in a minimal amount of DCM, precipitated into diethyl ether. The product was obtained as a light yellow powder (1.6 g, 80%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, 4H), 8.61 (d, 4H), 8.52 (dd, 2H), 8.40 (d, 2H), 8.16 (dd, 4H), 7.68 (m, 4H), 5.85 (s, 4H), 4.56 (t, 4H), 3.75 (s, 1972H).

The obtained light yellow solid was redissolved in a minimum amount of water and filtered through a 220 nm membrane. Then the aqueous solution was loaded to a 5 mL HiTrap SP FF column equilibrated with cation exchange buffer A (H_2O), eluted with a linear 0-0.5 M NaCl gradient by automatically mixing cation exchange buffer A and buffer B (0.5 M NaCl). The collected eluent was dialyzed against water under light protection for 3 d to remove NaCl.

Click reaction in DMF was performed at 50 ^oC with similar procedure. And **M2** was used without counterion exchange.

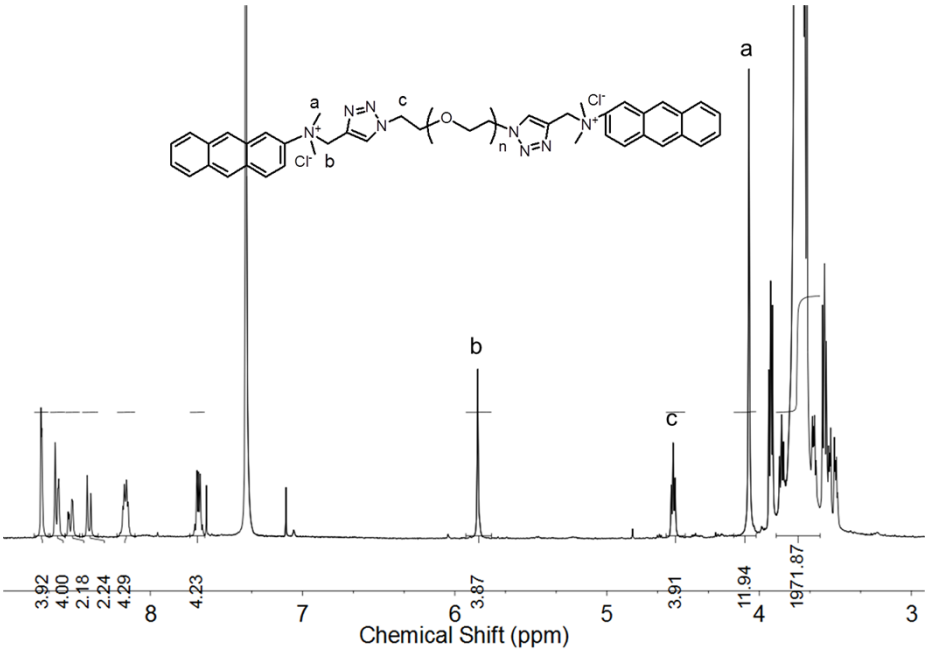


Fig. S14 ^{1}H NMR spectrum of PEG_{20K}-2An (**P2**).

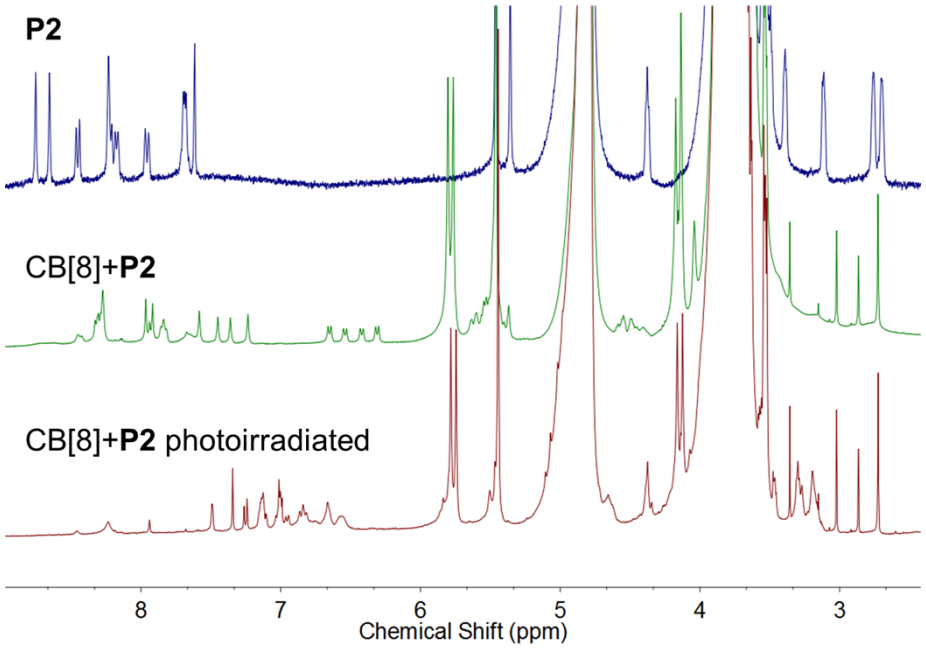


Fig. S15 ^{1}H NMR spectra (D_2O, 0.5 mM) of **P2**, CB[8]+ **P2** and CB[8]+ **P2** after photo-irradiation for 30 min.

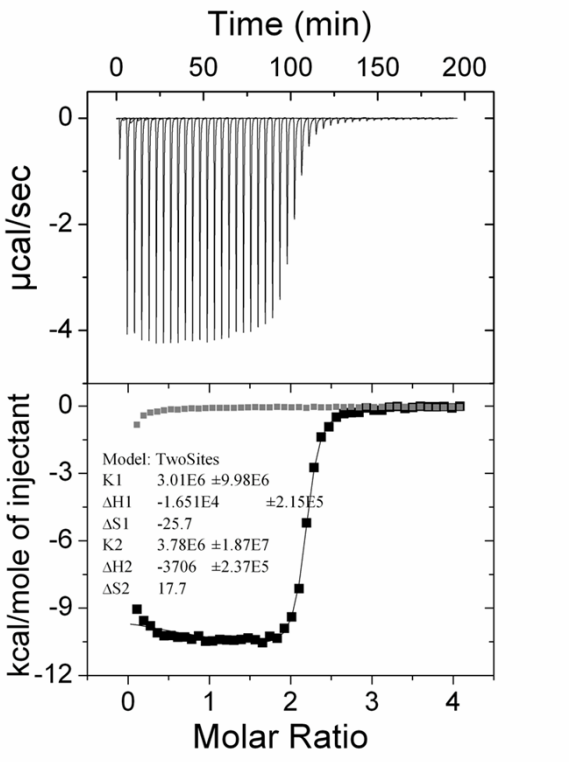


Fig. S16 ITC data for the titration of CB[8] (0.1 mM) with **M2** (2.0 mM) in aqueous solution at 25 °C.

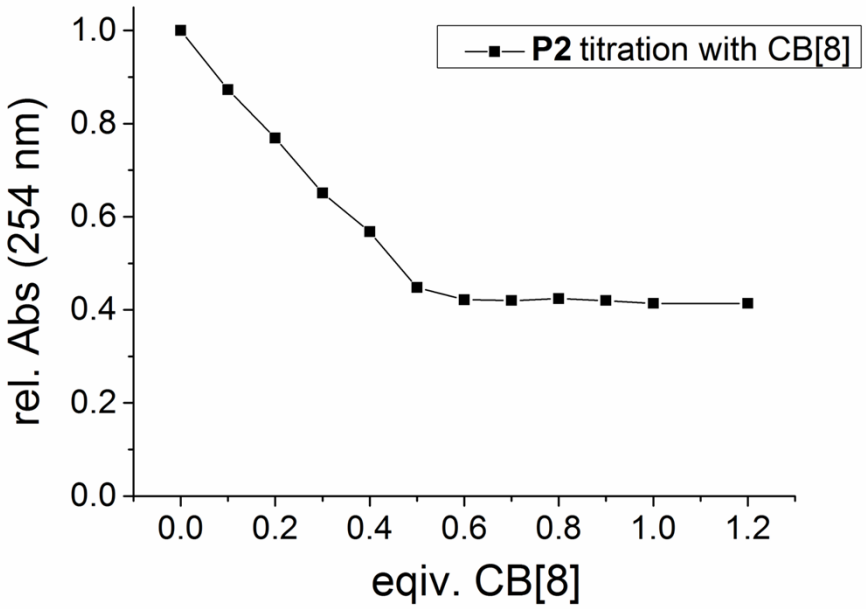


Fig. S17 UV/vis spectra for the titration of **P2** (0.25 mg/mL in water) with CB[8].

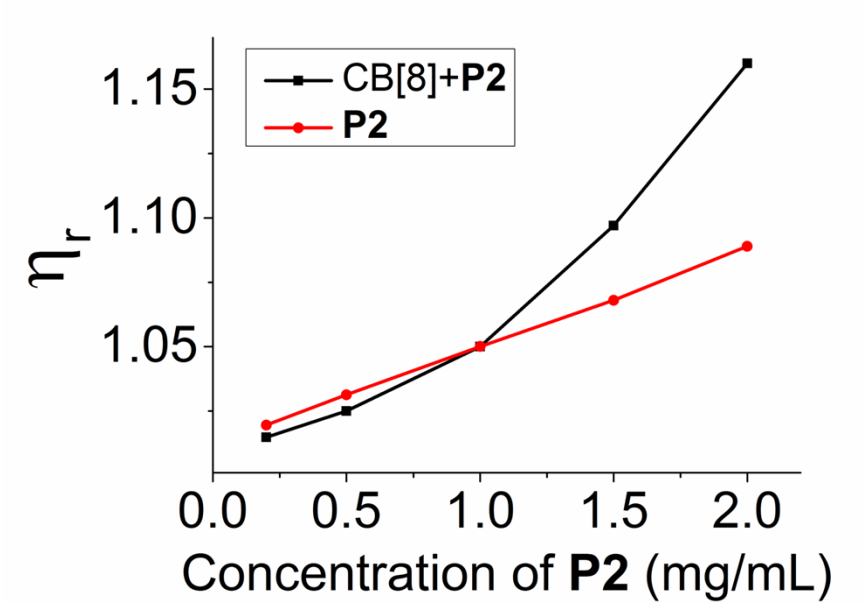


Fig. S18 Relative viscosity of CB[8]+**P2** and **P2** alone at different concentrations.

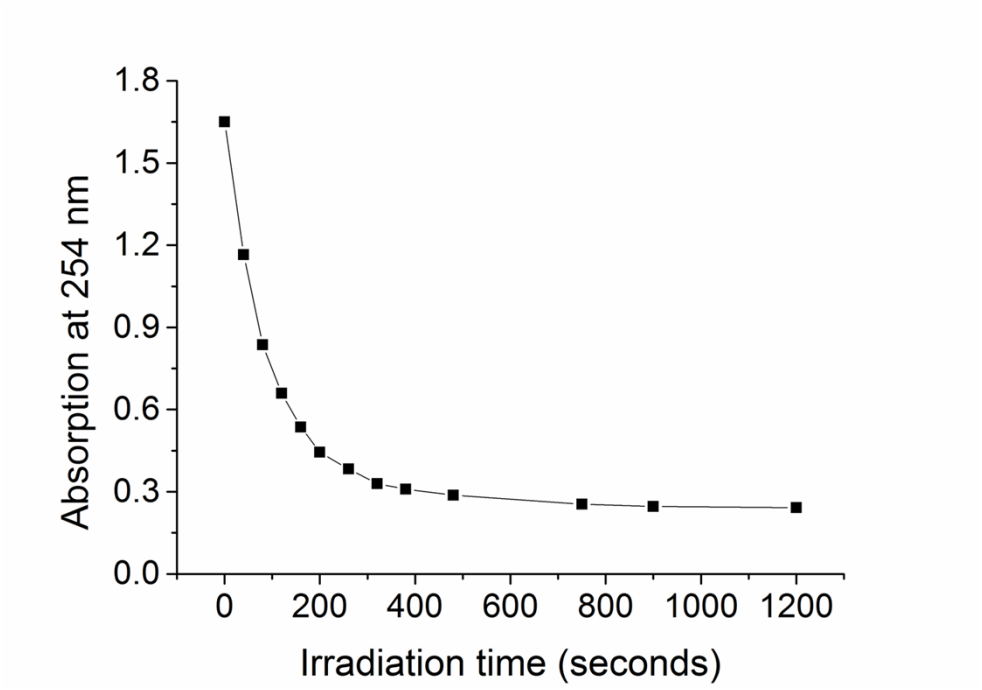


Fig. S19 UV/vis spectra for CB[8]+**P2** (0.25 mg/mL in water) upon photo-irradiation (365 nm).

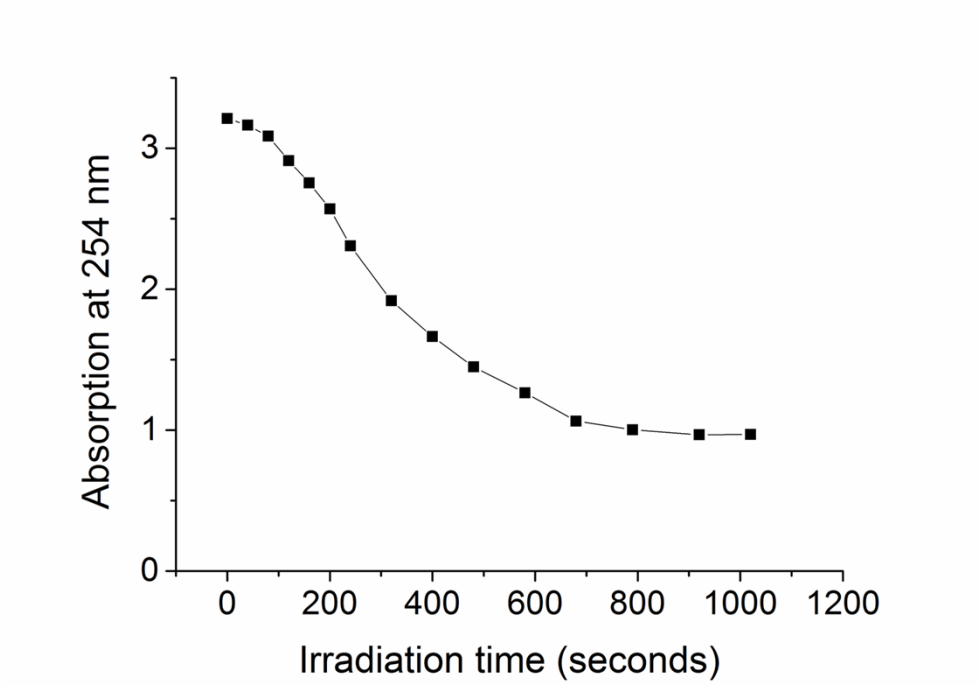


Fig. S20 UV/vis spectra for **P2** (0.25 mg/mL in water) upon photo-irradiation (365 nm)

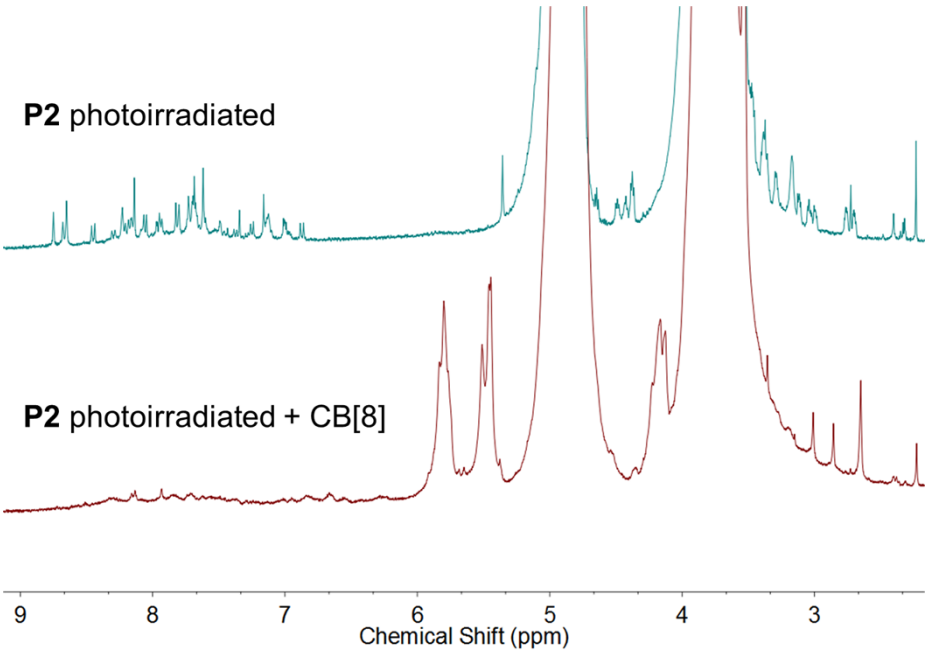


Fig. S21 ^{1}H NMR spectra (D_2O, 0.5 mM) of **P2** after photo-irradiation for 30 min and subsequent addition of CB[8].

Reference

(1) J. Kim, I. S. Jung, S. Y. Kim, E. Lee, J. K. Kang, S. Sakamoto, K. Yamaguchi

and K. Kim, *J. Am. Chem. Soc.*, 2000, **122**, 540.

(2) F. Biedermann, I. Ross and O. A. Scherman, *Polym. Chem.*, 2014, **5**, 5375.