Electronic Supplementary Material (ESI) for Polymer Chemistry.

Host-Guest Accelerated Photodimerisation of Anthracene-labeled Macromolecules in Water

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S.1 Materials and methods

All starting materials were purchased from Alfa Aesar and Sigma Aldrich and used as received unless stated otherwise. CB[8] was prepared according to literature procedure (J. Kim, I.S. Jung, S.Y. Kim, E. Lee, J.K. Kang, S. Sakamoto, K. Yamaguchi, K. Kim, *J. Am. Chem. Soc.* **2000**, *122*, 540-541). N_3-PEG was synthesised in analogy to literature procedures, see for example (S. Zalipsky, Bioconjugate Chem. 1995, 6, 150-165) and reference therein. ^{1}H and ^{13}C NMR spectra were recorded on an Avance 500 BB-ATM (500 MHz) spectrometer, UV/visible spectra on a Varian Cary 4000 UV-Vis spectrophotometer and fluorescence spectra were recorded on a Cary Eclipse spectrofluorometer. Gel permeation chromatography (GPC) was carried out in water on a Shodex glucose column with a Shimadzu SPD-M20A prominence diode array detector. Samples were filtered over 0.2 mm PVDF filters before injection using a 0.6 mL / min flow rate. Rheological characterisation was performed using an Discovery HR-2 hybdrid rheometer from TA instruments fitted with a water bath set to 25 °C. Strain sweep measurements were performed at a frequency of 10 rad/s. Frequency sweep measurements were performed at a 5% strain amplitude. All measurements were performed using a 20 mm parallel plate geometry and analyzed using TA Instruments TA Orchestrator software. Hydroxyethyl cellulose (HEC) was purchased from Aldrich and dried overnight in a vacuum oven at 105 °C.

S.1.1 Determination of solution binding constants by ITC

Titration experiments were carried out on a VIP-ITC from Microcal Inc., at 25°C in deionised water (Millipore, 18.2 MΩ·cm). The binding equilibria were studied using a cellular CB[8] concentration of typically of 0.04 mM to which the 0.5-1.0 mM solution of **1** was titrated. Typically 20-30 consecutive injections of 2.4 μL each were used. The first data point was removed from the data set prior to curve fitting. The data was analyzed utilising the Origin 7.0 software package.

S.1.2 Photochemical reactions

Photoirradiation experiments were performed in a UV-box from Luzchem equipped with 10 UVA light bulbs from Hitachi (8 W, centered around 350 nm). The UV-lamps were "pre-warmed" for 15 min prior to any experiments. A Spectrosil quartz cuvette (170-2,700 nm spectral range, 3.5 mL volume, 10 mm pathlength) equipped with a magnetic stir bar, a screw-cap lid and 3 mL of an aqueous solution of the analyte (typically 10 μM concentration) was placed in the middle of the chamber and irradiated under vigorous stirring for a defined

time. Care was taken that in each case the positioning and orientation of the cuvette is similar. The smallest irradiation time increment was chosen to be 15 s to keep manual time stopping errors to a minimum. UV/Vis and fluorescence spectra were taken by transferring the cuvette into the spectrometer, making sure that an identical orientation and positioning of the cuvette was kept for each measurement. Unless mentioned otherwise, the solutions were aerated. The reproducibility of the kinetics was confirmed by carrying out multiple runs.

S.1.3 Regioisomers formed by the photoreaction

The photodimerization experiments in the presence and absence of CB[8] were carried out in H_2O, followed by removal of the solvent through lyophilization. The sample prepared in the *absence* of CB[8] was then directly redissolved in d^6-DMSO and analysed by NMR experiments. The sample prepared in the *presence* of CB[8] was uptaken in acetonitrile, which decomplexes the dimerised anthracene species from the CB[8] host, and then CB[8] was removed by filtration (CB[*n*] macrocycles are fully insoluble in organic solvents). The solvent was removed under reduced pressure, and the sample was uptaken in d^6-DMSO and analysed by NMR experiments, which confirmed that CB[8] had been fully removed. From the ^{1}H and ^{13}C NMR spectra of the photodimerization products in comparison to the starting material **1a**, it is clear that a [4+4]-type photoreaction of the anthracene moieties occurred, *e.g.* the 9- and 10-anthryl protons and carbons shifted upfield into the aliphatic peak region upon photoirradiation (Fig. S14). In principle, four different regioisomers, depicted in Fig. S5, could result as racemic mixtures upon dimerisation of **1a**. Analysis of the ^{1}H and ^{13}C NMR spectra (Fig. S14) revealed that an approximately equimolar mixture of two regioisomers was formed in presence of CB[8], whereas in the absence of host all four regioisomers, unreacted starting material and possibly some other side products were present. The attempted structural assignment of such products by NOESY and COSY NMR was inconclusive, however, it is reasonable to assume that the NMR peaks of the -N(CH_3)$_3$ groups are more downfield shifted for the *head-to-head* than for the *head-to-tail* dimers on account of charge accumulation on one face of the molecule, see Fig. S5. Under this premise, it follows from a comparison of all NMR spectra that predominately the *head-to-tail* dimers were produced for the CB[8] mediated photodimerisation (tail-to-tail dimers could not be observed by ^{1}H NMR, *e.g.* their fraction is below 5-10%), whereas in the absence of the templating host the reaction was much less selective. This conclusion is also supported by ^{1}H NMR spectra in D_2O in the presence of CB[8], where CB[8] has been added prior (Fig. 2 in the main text) and after the photoirradiation (Fig. S13); a significant larger number of peaks assignable to the regioisomeric photodimers were observed for the sample where photoirradiation was carried out in the absence of CB[8]. A possible explanation for the presence of all possible regioisomeric photodimers in the absence of templating CB[8] is the high reactivity of photoexcited **1a** that reacts upon diffusional encounter with another equivalent of **1a** relatively irrespective to the molecular orientation of encounter. In contrast, the templating effect of the CB[8] macrocycle preselects a *head-to-tail* arrangement of two **1a** molecules in the host cavity on account of minimised **1a**-**1a** charge repulsion. Subsequent photoexcitation and photodimerization therefore biases the product mixture to *head-to-tail* photodimers.

S.1.4 Synthesis of N,N-dimethylanthracen-2-amine

N,N-dimethylanthracen-2-amine was obtained via reductive amination from 2-amino-anthracene in analogy to literature procedures: R. Borch, A. Hassid, *J. Org. Chem*, **1972**, 1673-1674: To a stirred slurry of 2-amino-anthracene (1.0 g, 5 mmol) and 4 mL (50 mmol) of 37% aqueous paraformaldehyde in 100 mL acetonitrile, cooled in an ice bath, was added 950 mg (15 mmol) of sodium cyanoborohydride. Glacial acetic acid (0.5 mL) was added over 10 min, the reaction mixture was warmed to room temperature and the reaction was stirred for 2 h. An additional 0.5 mL of glacial acetic acid was added, and stirring was continued for another 1 h. The reaction mixture was poured into 150 mL of diethyl ether and then washed with three 20-ml portions of 1 *N* KOH and one 20-mL portion of brine. The ether solution was dried over magnesium sulfate and the solvent

was evaporated under reduced pressure to yield the title compound in 95% yield. The crude material was of sufficient purity (>90% by NMR) for the following steps and not further purified.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27 (s, 1H), 8.19 (s, H), 7.93-7.88 (m, 3H), 7.40-7.31 (m, 3H) 3.11 (s, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 133.25, 132.33, 129.58, 129.04, 128.13, 127.37, 126.88, 125.77, 125.10, 123.51, 122.87, 118.27,52.68 ppm. HRMS: m/z calcd for $[M+H]^+$ 222.1278, found 222.1271 Da.

S.1.5 Synthesis of N,N,N-trimethylanthracen-2-aminium chloride (1a)

To a solution of N,N-dimethylanthracen-2-amine (0.1 g, 0.5 mmol) in 20 mL acetone was added methyl iodide (0.2 ml, 2.5 mmol) and the reaction mixture was stirred under light protection for 7 days at room temperature. The resulting precipitate was collected by suction filtration and washed with diethyl ether to yield the NMR-pure product as its iodide salt. Counterion exchange to chloride was achieved through stirring and sonicating of an aqueous solution (ca 20 mL) of the product over freshly precipitated silver chloride (20 equiv. per iodide counter ion) for several hours. The silver salt was filtered off and the filter cake was washed with water. The combined aqueous solution was freeze dried to yield the title compound as a off-white solid (74 mg, 60%).

^{1}H NMR (400 MHz, d^6-DMSO): δ = 8.79 (s, 1H), 8.74 (s, 1H), 8.66 (d, 1H, 2.5 Hz) 8.38 (d, 1H, 10.2 Hz), 8.18 (mc, 2H), 8.12 (dd, 1H, 2.7 Hz, 9.5 Hz), 7.63 (mc, 2H), 3.75 (s, 9H) ppm. ^{13}C NMR (126 MHz, d^6-DMSO): δ = 143.40, 132.14, 131.81, 130.90, 129.58, 129.22, 128.07, 128.01, 127.87, 126.66, 126.52, 126.26, 119.21, 117.46, 55.90 ppm. HRMS: m/z calcd for $[M]^+$ 236.1434, found 236.1427 Da.

S.1.6 Synthesis of N,N-dimethyl-N-(prop-2-yn-1-yl)anthracen-2-aminium chloride

To a solution of N,N-dimethylanthracen-2-amine (0.1 g, 0.5 mmol) in 20 mL acetone was added propagyl bromide (0.25 ml, 80 wt% solution in toluene, 2.5 mmol) and the reaction mixture was stirred under light protection for 7 days at room temperature. The resulting precipitate was collected by suction filtration and washed with diethyl ether to yield the NMR-pure product as its bromide salt. Counterion exchange to chloride was achieved through stirring and sonicating of an aqueous solution (ca 20 mL) of the product over freshly precipitated silver chloride (20 equiv. per bromide counter ion) for several hours. The silver salt was filtered off and the filter cake was washed with water. The combined aqueous solution was freeze dried to yield the title compound as a yellowish solid (71 mg, 58%).

^{1}H NMR (400 MHz, d^6-DMSO): δ = 8.79 (s, 1H), 8.74 (s, 1H), 8.68 (d, 1H, 2.5 Hz), 8.39 (dd, 1H, 9.7 Hz, 2.7 Hz), 8.21-8.17 (m, 2H), 8.07 (dd, 1H, 9.7 Hz, 2.7 Hz), 7.63 (mc, 2H) 5.09 (d, 2H, 2.5 Hz), 3.86 (t, 1H, 2.5 Hz) 3.78 (s, 4H) ppm. ^{13}C NMR (126 MHz, d^6-DMSO): δ = 140.87, 132.07, 131.66, 130.87, 129.45, 128.92, 127.90, 127.86, 127.79, 126.60, 126.42, 126.16, 120.67, 117.16, 82.67, 72.39, 57.44, 53.11. ppm HRMS: m/z calcd for $[M]^+$ 260.1434, found 260.1428 Da. FTIR: $\tilde{\nu}$ = 3143 (H-C≡C), 2120 (-C≡C-) cm^{-1}.

S.1.7 Synthesis of 1b

Azido functionalised poly(ethylene glycol) monomethyl ether, N_3-PEG-OMe, 2,000 g/mol, (200 mg, 0.08 mmol) and N,N-dimethyl-N-(prop-2-yn-1-yl)anthracen-2-aminium chloride (34 mg, 0.12 mmol) were dissolved under light protection in 20 mL water and degassed with nitrogen. To this solution was added a degassed and for 5 min sonicated solution of $CuSO_4$ (1.5 mg, 0.001 mmol) and sodium ascorbate (1.8 mg, 0.001 mmol) in 5 mL water. The resulting mixture was stirred at room temperature for 24 h under light protection. The aqueous solution was extracted with $CHCl_3$ (3 times 50 mL) and the combined organic fractions were washed with an aqueous EDTA solution followed by a washing step with brine and with water. All work-up steps should be performed under light protection. 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 (approx 5 mL). Precipitation of the product occurred upon addition of 100 mL of diethylether. The product was kept at

–4 °C overnight in the freezer and collected by suction filtration. Overnight drying in the vacuum oven at 30 °C yielded the title compound in 80% yield as brown-yellow solid.

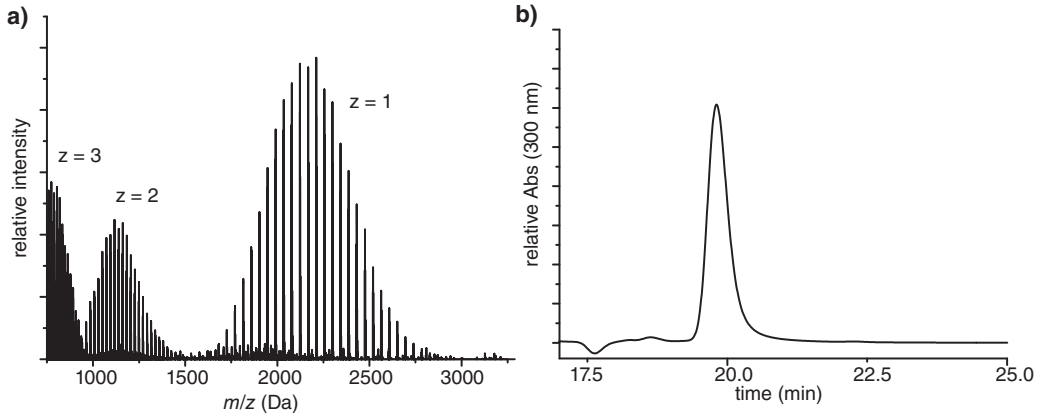

Figure S1: a) ESI-MS spectra of **1b** in acetonitrile. b) GPC elution curve for **1b** in THF.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.59 (s, 1H), 8.54 (s, 1H), 8.50 (s, 1H), 8.48 (d, 1H, 2.3 Hz), 8.37 (dd, 1H, 9.5 Hz, 2.6 Hz), 8.27 (d, 1H, 9.5 Hz), 8.06-8.02 (m, 2H), 7.56 (mc, 2H) 4.43 (t, 2H, 5.1 Hz), 4.42 (s, 6H), 3.96-3.35 (PEG-backbone) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 144.43, 141.69, 135.73, 133.07, 132.60, 132.22, 130.09, 129.69, 129.41, 128.50, 128.24, 128.21, 127.00, 126.80, 126.68, 124.10, 120.44, 117.50, 72.00-70.00 (PEG-backbone), 68.90, 63.91, 59.03, 53.85, 50.43, 36.30, 31.91, 30.02, 29.64, 29.35, 22.68, 14.12 ppm. HRMS: see Fig. S1a. FTIR: N_3 stretch is absent, suggesting that the azido-groups of N_3-PEG were fully consumed. GPC: See Fig. S1b.

S.1.8 Synthesis of N_3-HEC

Hydroxyethyl cellulose, (2.0 g, Mw = 700,000 g/mol) was dissolved in 150 mL N-Methyl-2-pyrrolidone (NMP) at 110 °C under stirring. The solution was allowed to cool to room temperature and 1-chloro-3-isocyanatopropane (0.1 mL) and of one drop of dibutyl tin dilaurate (TDL) were added. The reaction was stirred for 24 h at room temperature and then sodium azide (0.1 g) was added. The reaction mixture was heated to 80 °C and stirred for another 24 h. Upon cooling to room temperature and addition of ten parts acetone, the polymer precipitated and was collected by suction filtration. The solid was redissolved in a minimal amount of water and reprecipitated from acetone. The filter cake was washed with copious amounts of acetone and dried in the vacuum oven at 40 °C overnight to yield the title compound in 90% yield.

^{1}H NMR: see Fig. S2a. FTIR: $\tilde{\nu}$ = 2103 cm^{-1} (-N_3), Fig. S2b.

S.1.9 Synthesis of 1c

Azido functionalised hydroxyethyl cellulose, N_3-HEC, (0.2 g, Mw = 700,000 g/mol) and N,N-dimethyl-N-(prop-2-yn-1-yl)anthracen-2-aminium chloride (40 mg) were dissolved under light protection in 200 mL water and degassed with nitrogen. To this solution was as added a degassed and for 5 min sonicated solution of $CuSO_4$ (1.5 mg, 0.001 mmol) and sodium ascorbate (1.8 mg, 0.001 mmol) in 5 mL water. The resulting mixture was stirred at room temperature for 24 h under light protection. The solvent was reduced to approx 25 mL under reduced pressure and ten parts of acetone were added. All work-up steps should be performed under light protection. The precipitate formed was collected by suction filtration and washed with acetone. The solid was redissolved in a minimal amount of water and dialysed (regenerated cellulose membrane from Spectrum Labs with Mw(cutoff) = 3500 Da) against a 0.1% brine solution and then against water for 48 h in the darkness. After

freeze drying, the title compound was obtained in 85% yield as fluffy yellowish solid. From the absorbance at 254 nm of a 60 μg/mL stock solution, a polymer loading of approx. 80 μmol of the anthracene side chains per gram of polymer was calculated which equals approx. 30 mg of the anthracene moiety per gram of polymer.

^{1}H NMR: see Fig. S2a. FTIR: N_3 stretch is absent, suggesting that the azido-groups of N_3-HEC were fully consumed (Fig. S2b). GPC: See Fig. S3

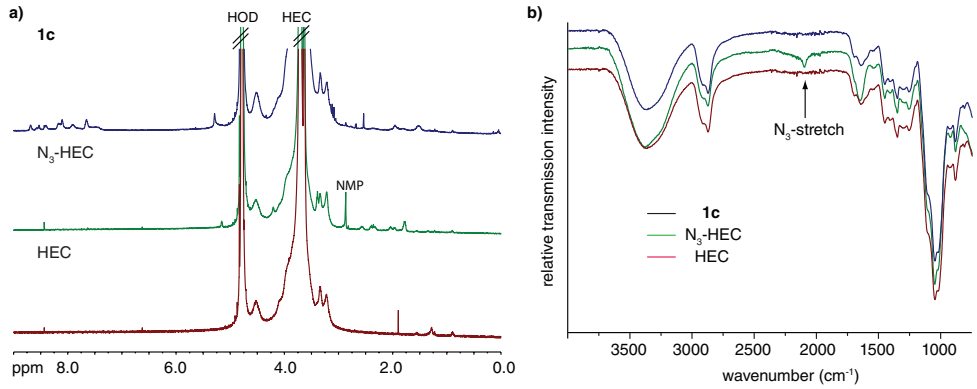

Figure S2: a) ^{1}H NMR (D_2O) spectra and b) FTIR spectra of commercial HEC (700,000 g/mol), N_3-HEC and **1c**.

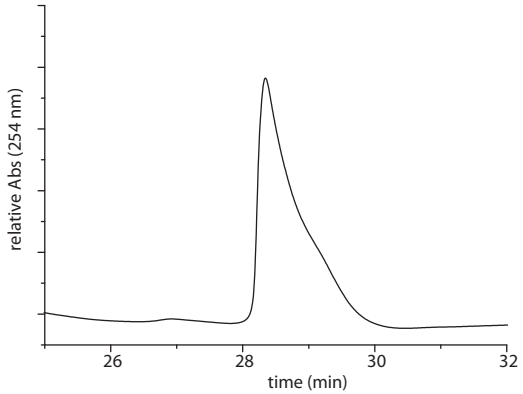

Figure S3: GPC elution curve for **1c** in water.

S.2 Supporting Tables

Table S1: Thermodynamic data for the binding of compounds **1a** and **1b** with CB[7] and CB[8]. [a] Mean values and estimated errors at 25 °C in water, pH 7.0. [b] K_a(ternary) = $K_a(1)\times K_a(2)$. Note that K_a(ternary) can be obtained with higher accuracy from the measured isotherms than the individual binding constants $K_a(1)$ and $K_a(2)$, see the discussion in L. M. Heitmann, A. B. Taylor, P. J. Hart, A. R. Urbach, *J. Am. Chem. Soc.* **2006**, 128, 12574 for further details. [c] Total enthalpy contribution to ternary complex formation measured by ITC. [d] Total entropy contribution to ternary complex formation calculated from K_a(ternary) and ΔH(ternary) values.

	$K_a(1)$ $(M^{-1})^{[a]}$	$K_a(2)$ $(M^{-1})^{[a]}$	K_a(ternary) $(M^{-2})^{[b]}$	ΔH(ternary) (kJ/mol)$^{[c]}$	$-T\Delta S$(ternary) (kJ/mol)$^{[d]}$
CB[7] + **1a**	$(4.1\pm0.5)\times10^5$	–	–	–18.1±1.0	–14.0±1.5
CB[8] + **1a**	$(4\pm1)\times10^4$	$(2\pm1)\times10^7$	$(1\pm0.5)\times10^{12}$	–81±4	13±2
CB[7] + **1b**	$(8.0\pm1.0)\times10^3$	–	–	n.a.	n.a.
CB[8] + **1b**	$(8\pm1)\times10^4$	$(3\pm1)\times10^5$	$(2.1\pm1.0)\times10^{10}$	–94±5	35±5

S.3 Supporting Figures

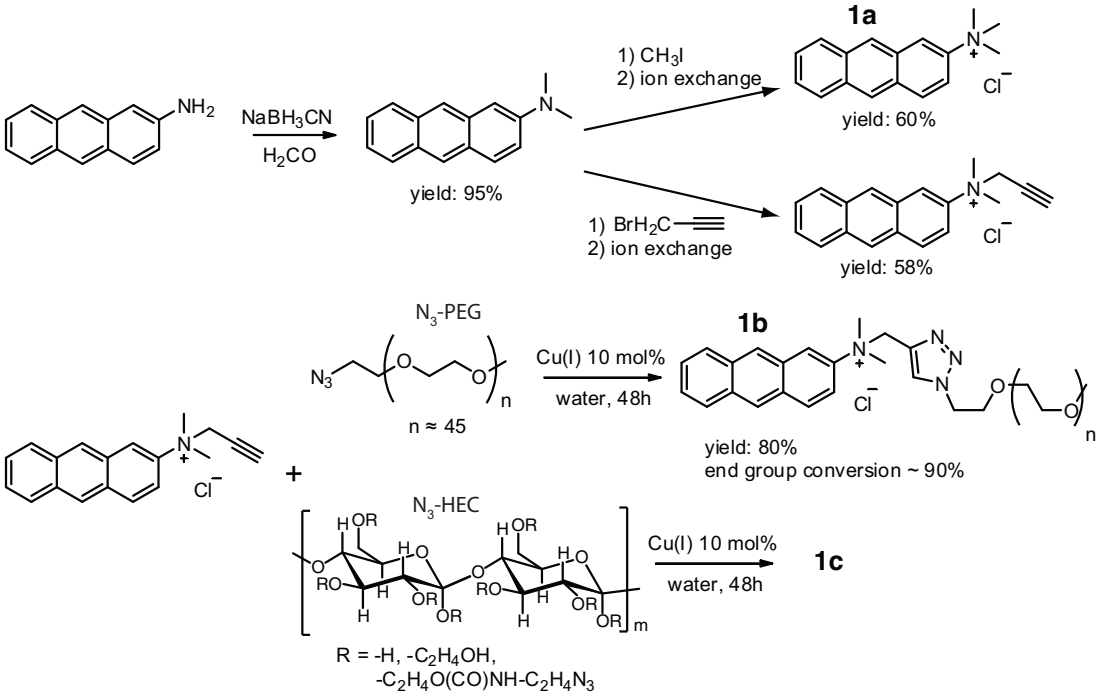

Figure S4: Synthetic pathway towards **1a**, **1b** and **1c**.

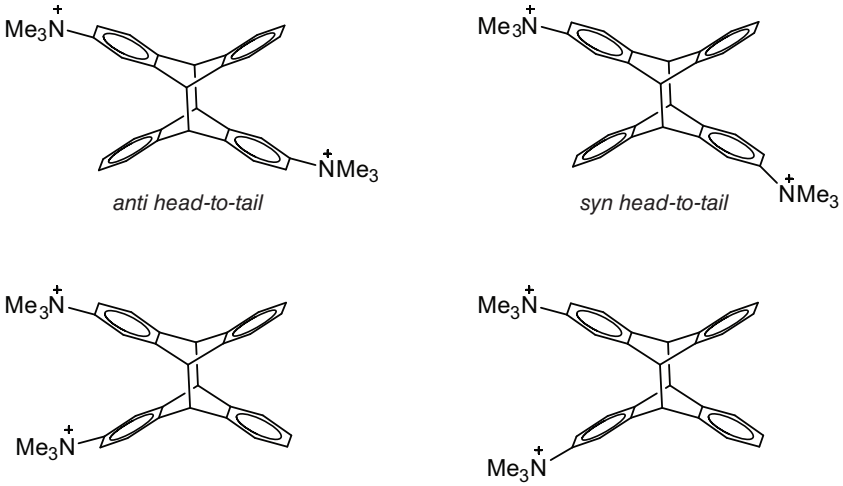

Figure S5: Possible regioisomeric products of the dimerisation reaction of **1a**.

S.3.1 Host-guest complexation and photodimerisation of small molecule anthracene 1a

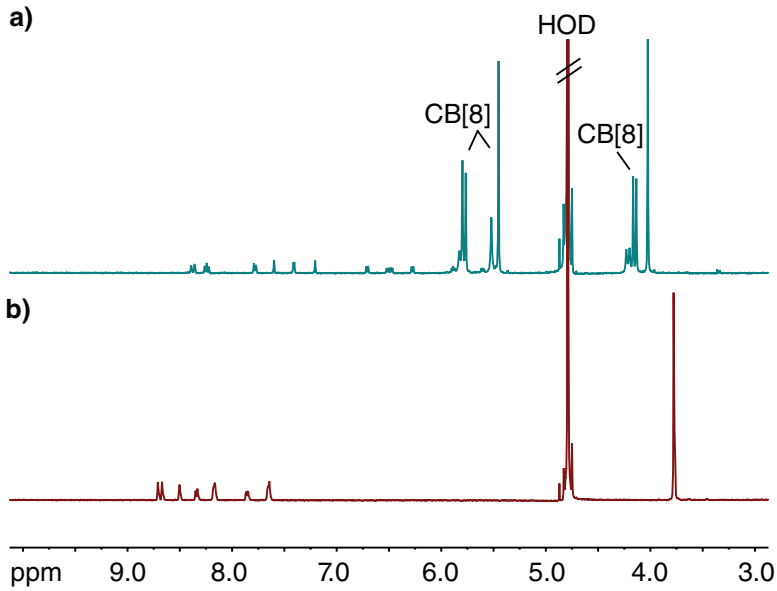

Figure S6: ^{1}H NMR spectra (D_2O) of **1a** (0.5 mM) in a) the presence of 0.5 equiv. of CB[8] and b) absence of the host.

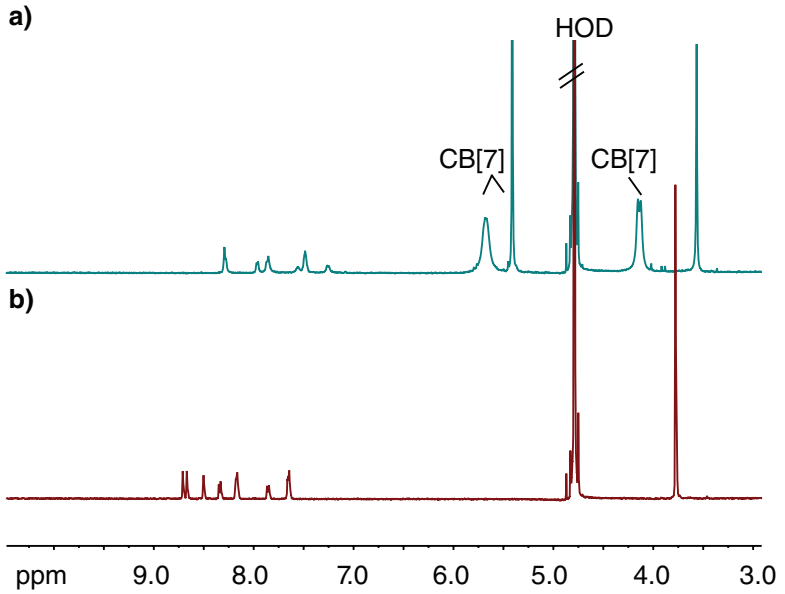

Figure S7: ^{1}H NMR spectra (D_2O) of **1a** (0.5 mM) in a) the presence of 1 equiv. of CB[7] and b) absence of the host.

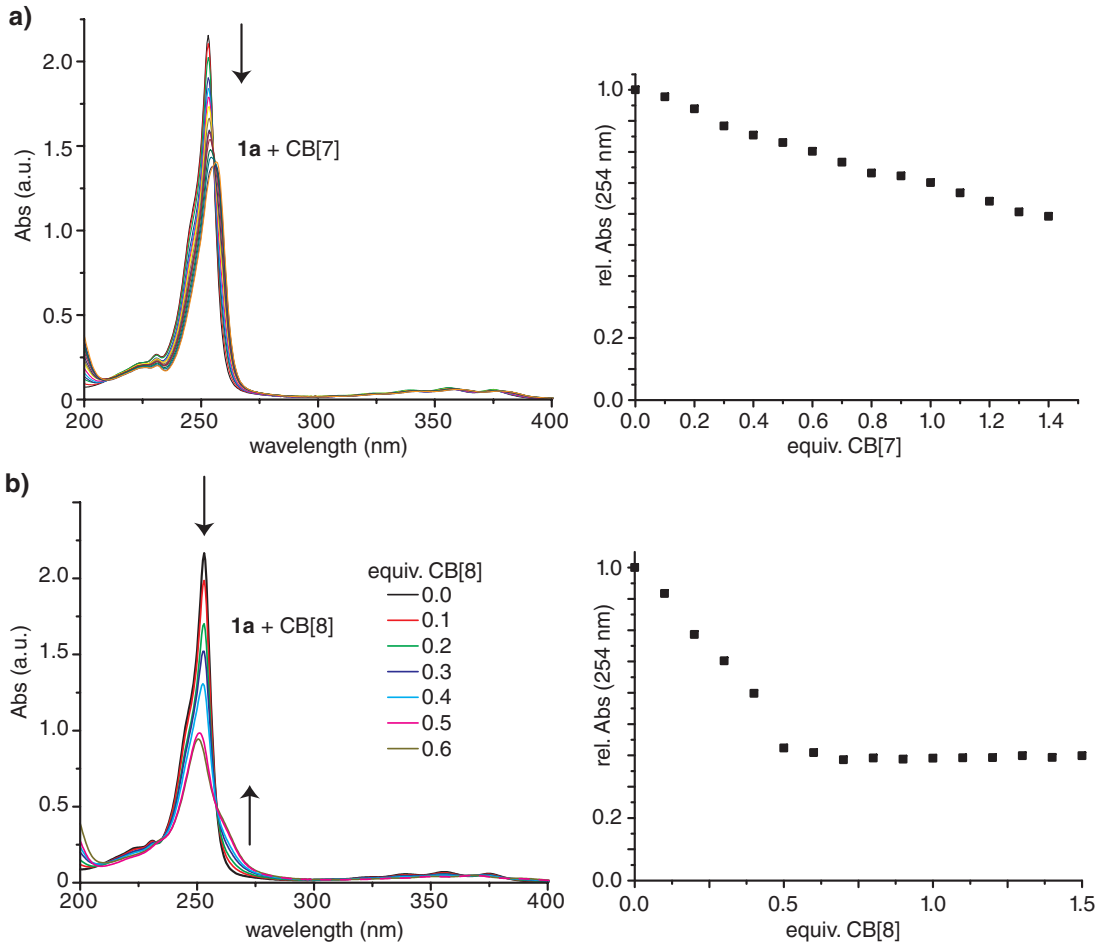

Figure S8: UV/vis spectra for the titration of **1a** (10 μM in water) with a) CB[7] and b) CB[8].

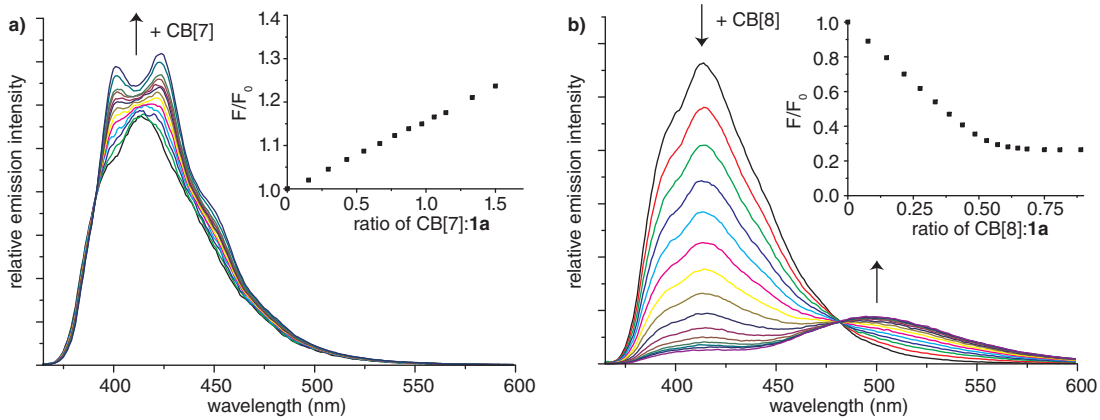

Figure S9: Emission spectra (356 nm excitation) for the titration of **1a** (10 μM in water) with a) CB[7] and b) CB[8]. The inset shows the normalised total fluorescence as a function of the ratio of CB[*n*] to **1a**.

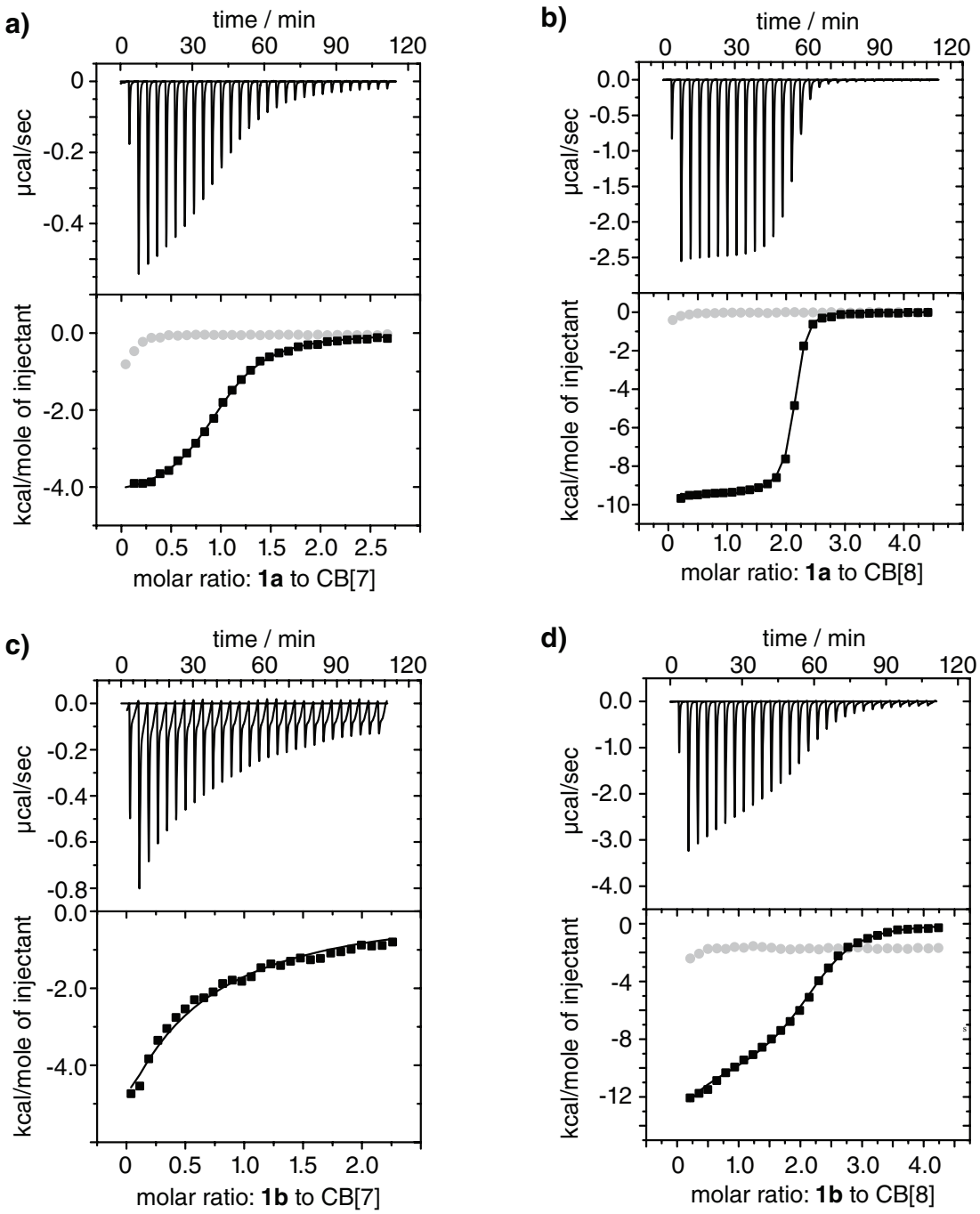

Figure S10: Representative isotherms for titration of a solution of **1a** or **1b** (0.5 - 1.0 mM) into an aqueous solution of CB[7] or CB[8] (40 μM) at 25 °C. Integrated heats are shown as black squares, which were corrected for the heat of dilution (grey circles) prior to fitting of the isotherms to a 1:1 binding model in the case of CB[7] or a stepwise binding model in the case of CB[8].

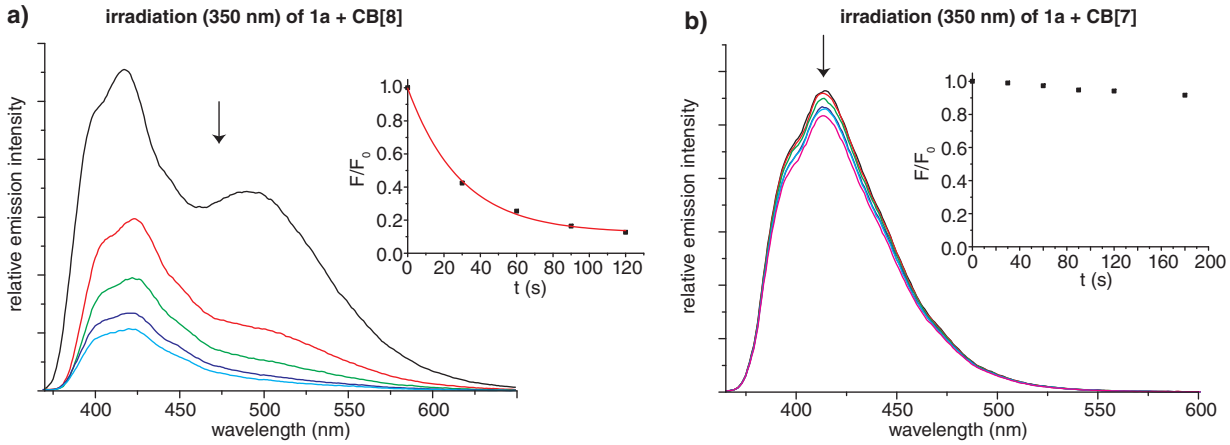

Figure S11: Emission spectra (356 nm excitation) upon photoirradiation (350 nm) of **1a** (10 μM in water) in the presence of a) 0.5 equiv. of CB[8] and b) 1 equiv. of CB[7]. The inset shows the normalised total fluorescence as a function of the irradiation time. The solid red line shows the best monoexponential fit of the kinetic data.

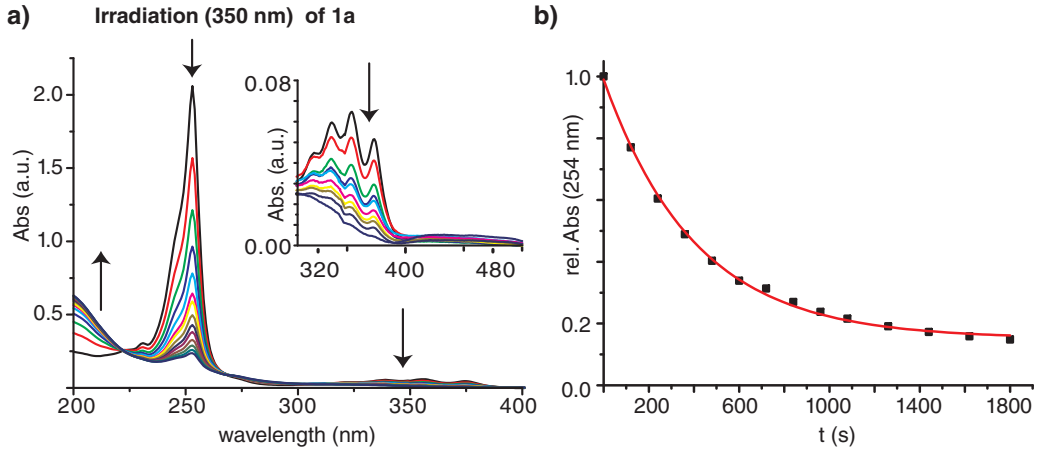

Figure S12: a) UV/vis spectra for **1a** (10 μM in water) upon photoirradiation (350 nm). b) Normalised absorbance at 254 nm as a function of irradiation time. The solid red line shows the best monoexponential fit of the kinetic data.

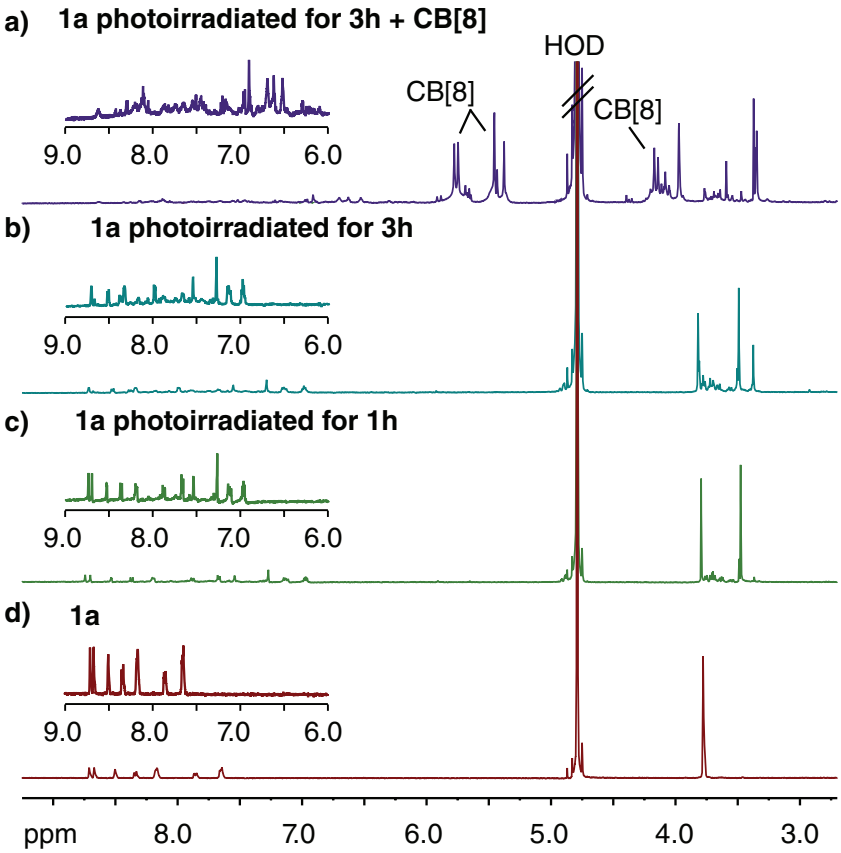

Figure S13: a) ^{1}H NMR spectra (D_2O) of **1a** (0.5 mM) after photoirradiation for 3 h and subsequent addition of 0.5 equiv. of CB[8]. b) ^{1}H NMR spectra (D_2O) of **1a** (0.5 mM) after photoirradiation for 3 h. c) ^{1}H NMR spectra (D_2O) of **1a** (0.5 mM) after photoirradiation for 1 h. d) ^{1}H NMR spectra (D_2O) of **1a** (0.5 mM) prior to photoirradiation. The insets show the enlarged aromatic peak region.

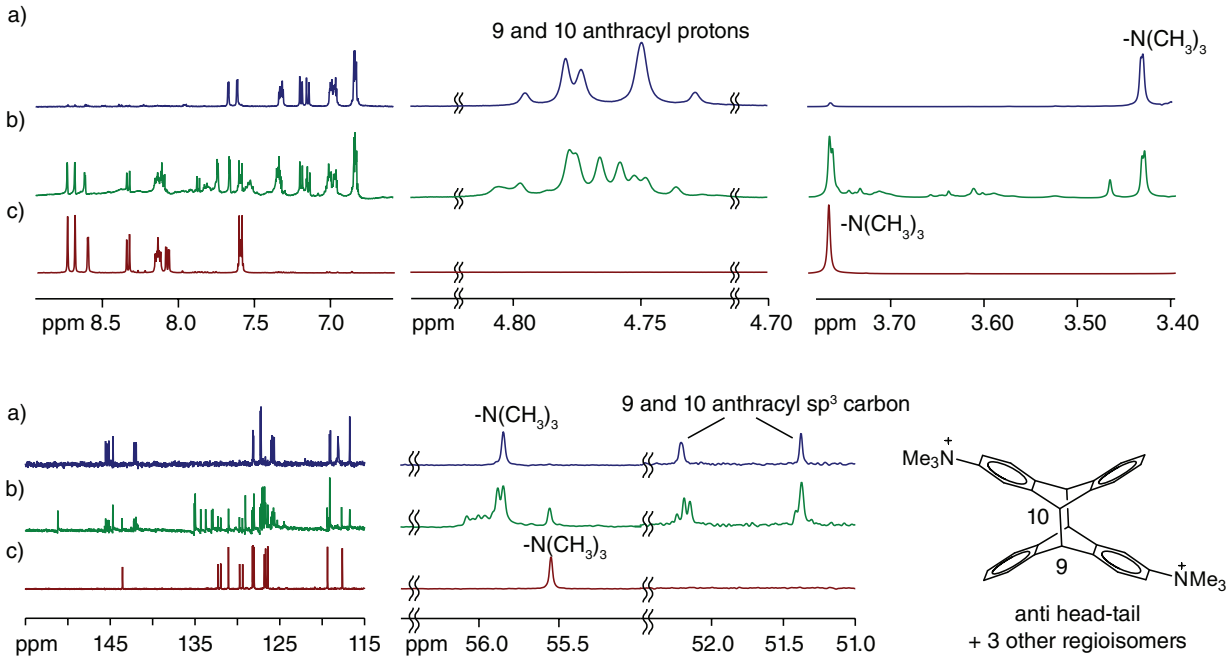

Figure S14: Top ^{1}H and bottom ^{13}C NMR spectra (d^6-DMSO) of a) anthracene-dimer that was prepared via photoirradiation (15 min) of a CB[8]·**1a**$_2$ aqueous solution, followed by freeze drying and extraction of the photodimer with acetonitrile, b) a product mixture that was prepared via photoirradiation (3 h) of a **1a** aqueous solution, followed by freeze drying, c) reference spectra for **1a**.

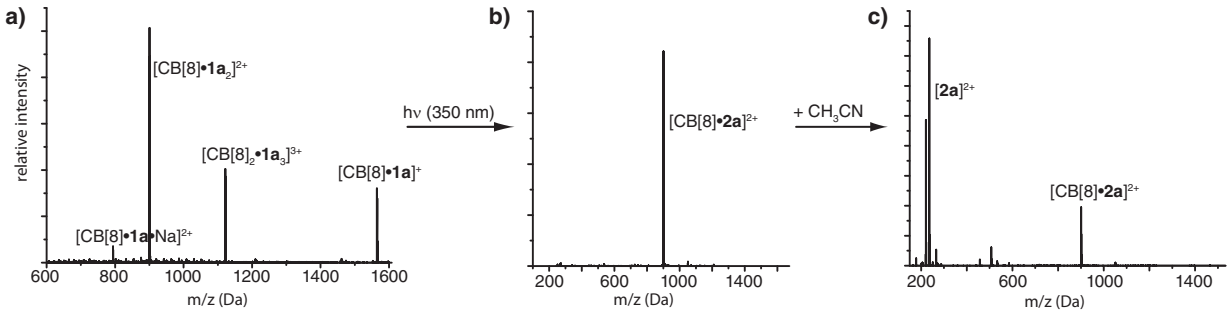

Figure S15: ESI-MS spectra of a 1:2 solution of CB[8] and **1a** in water a) prior to and b) after photoirradiation for 15 min. c) Acetonitrile was added to the photoirradiated mixture to decomplex the ternary CB[8] complex and the ESI-MS spectrum was measured. Absolute charges were assigned through analysis of the isotopic pattern.

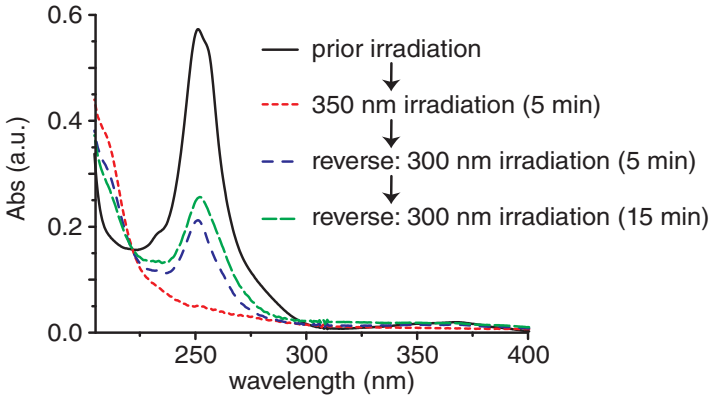

Figure S16: UV/vis spectra for **1a** (10 μM in water) in the presence of 0.5 equiv. CB[8] upon photoirradiation (350 nm) and subsequent irradiation with a 300 nm light source to reverse the photodimerization.

S.3.2 Host-guest complexation and photodimerisation of anthracene-labeled PEG-polymer 1b

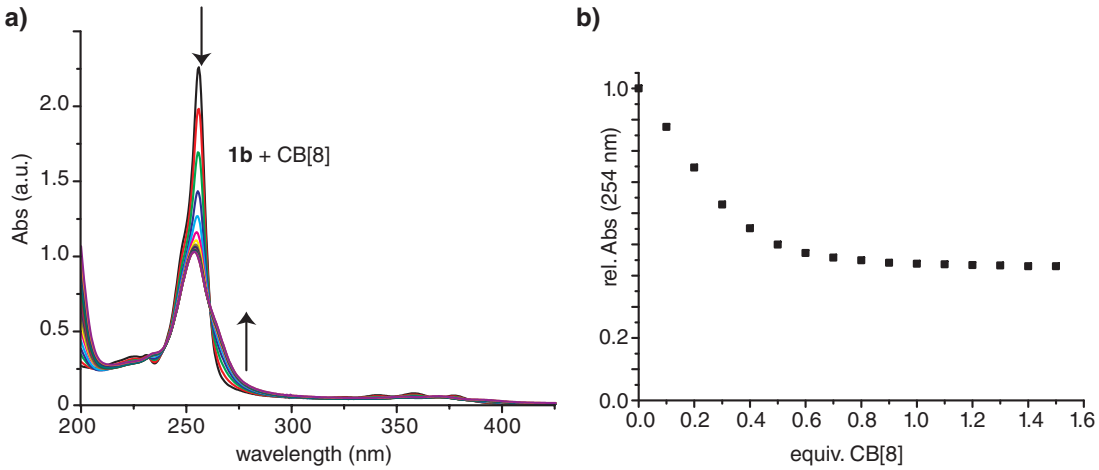

Figure S17: a) UV/vis spectra for the titration of **1b** (10 μM in water) with CB[8]. b)Normalised absorbance at 254 nm as a function of the CB[8] equivalents.

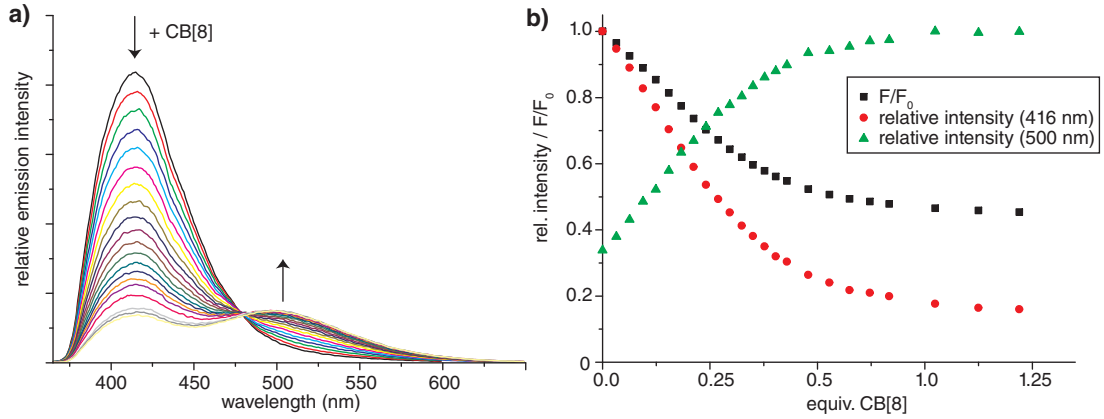

Figure S18: a) Emission spectra (356 nm excitation) for the titration of **1b** (10 μM in water) with CB[8]. b) Normalised total fluorescence and intensities at 416 nm (emission of monomeric **1b**) and 500 nm (excimer emission of **1b**) as a function of the added CB[8] equivalents.

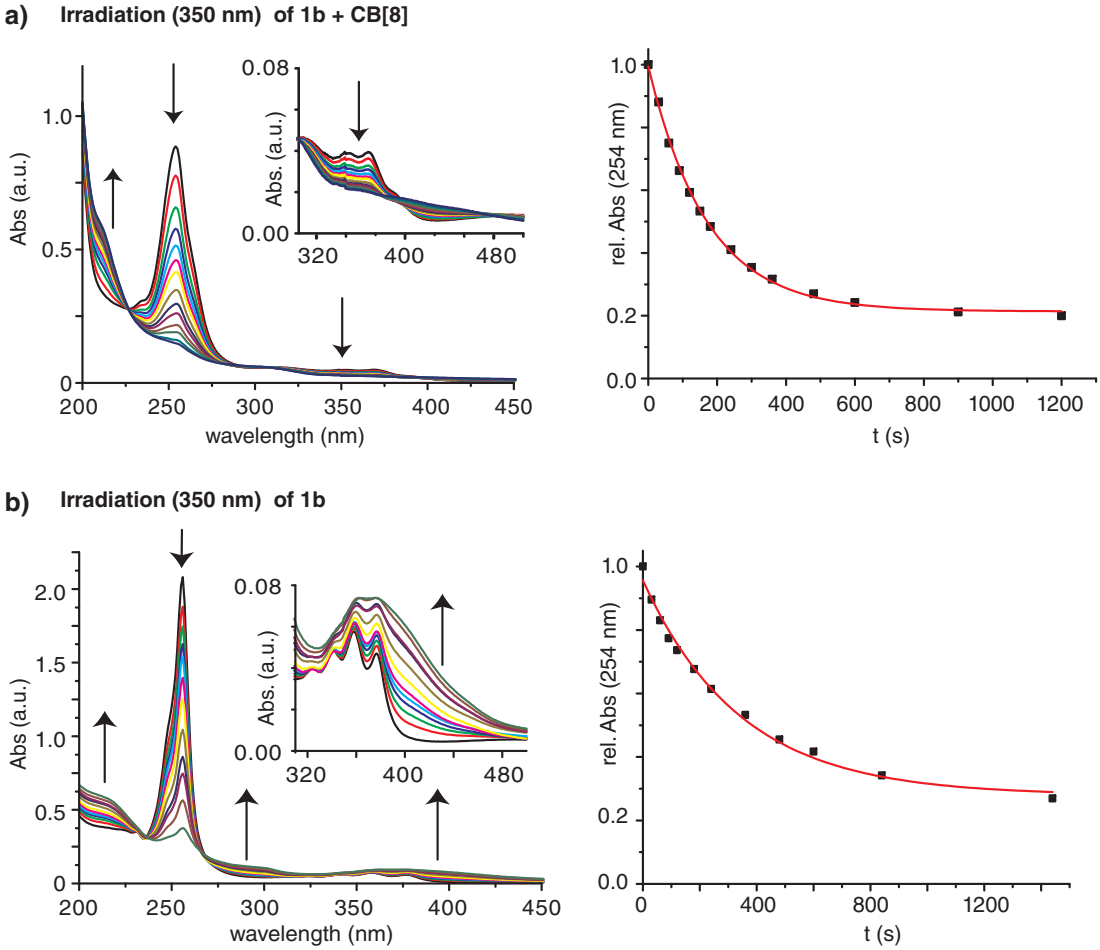

Figure S19: UV/vis spectra for **1b** (10 μM in water) upon photoirradiation (350 nm) in a) the presence of 0.5 equiv. CB[8] and b) in the absence of the host. The plot on the right shows the normalised absorbance at 254 nm as a function of irradiation time. The solid red line shows the best monoexponential fit of the kinetic data.

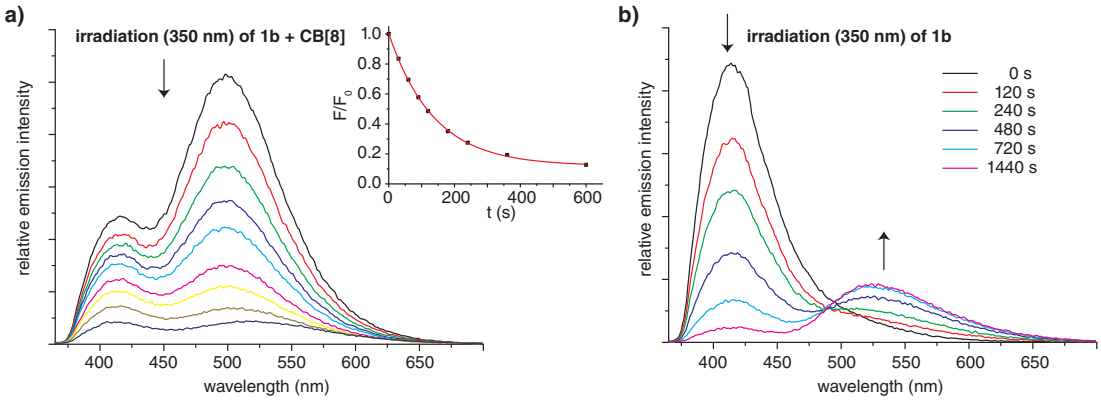

Figure S20: Emission spectra (356 nm excitation) upon photoirradiation (350 nm) of **1b** (10 μM in water) in a) the presence of 0.5 equiv. of CB[8] and b) the absence of the host. The inset shows the normalised total fluorescence as a function of the irradiation time. The solid red line shows the best monoexponential fit of the kinetic data.

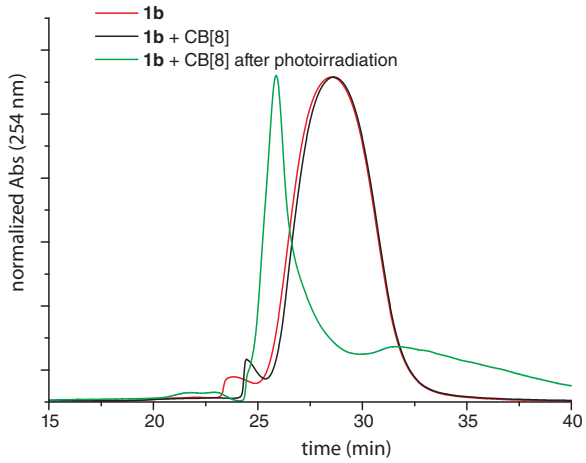

Figure S21: GPC elution curves (eluent: H_2O) for **1b** upon addition of CB[8] and subsequent photoirradiation. The broad peak-shape is likely on account of aggregation in water and sticking to the GPC column.

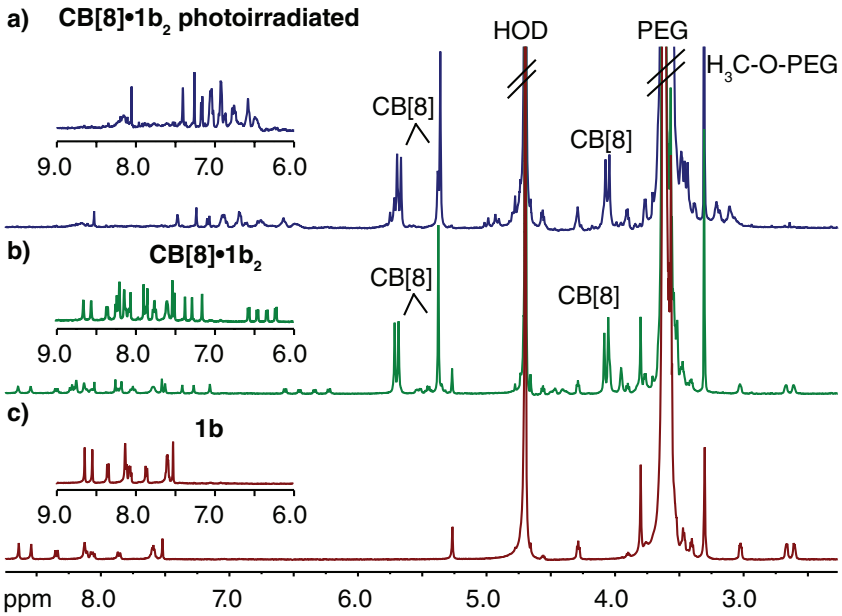

Figure S22: ^{1}H NMR spectra (D_2O) of **1b** (0.5 mM) in the presence of 0.5 equiv CB[8] a) after photoirradiation for 30 min and b) prior to photoirradiation. c)^{1}H NMR spectra (D_2O) of **1b** (0.5 mM) in the absence of the host. The insets show the enlarged aromatic peak region.

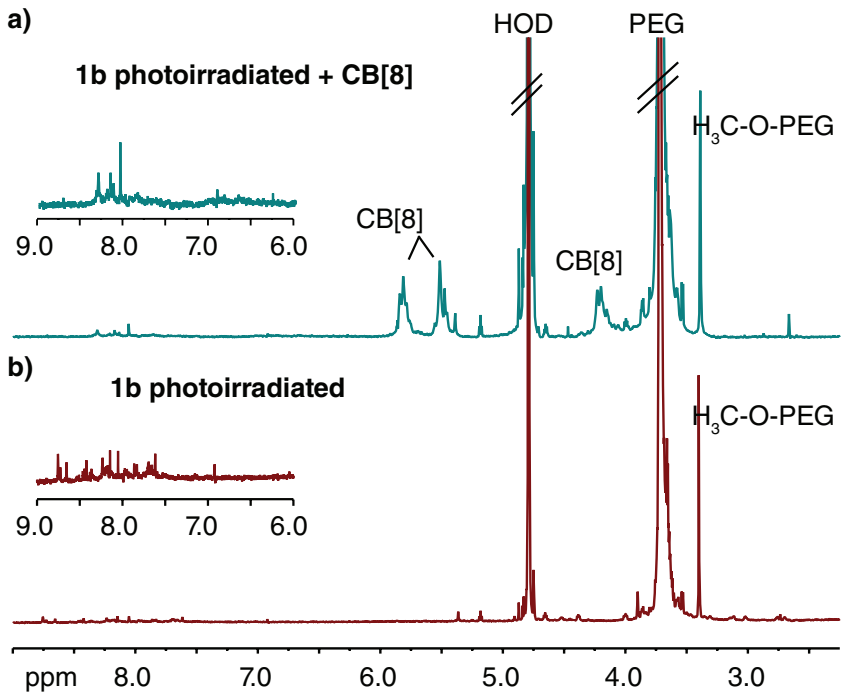

Figure S23: a) ^{1}H NMR spectra (D_2O) of **1b** (0.5 mM) after photoirradiation for 30 min and subsequent addition of 0.5 equiv. of CB[8]. b) ^{1}H NMR spectra (D_2O) of **1b** (0.5 mM) after photoirradiation for 30 min. The insets show the enlarged aromatic peak region.

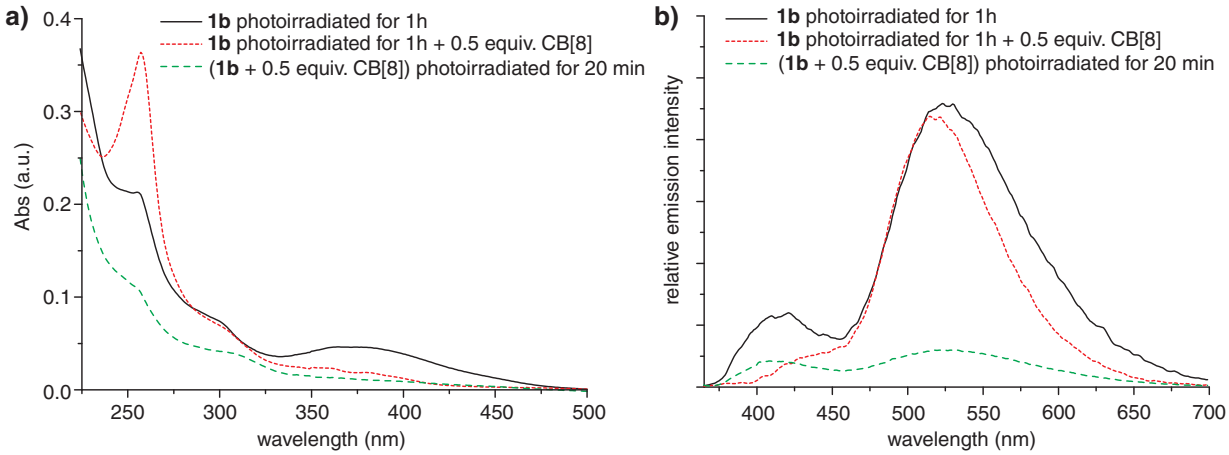

Figure S24: a) UV/vis and b) Emission spectra (356 nm excitation) of photoirradiated **1b** (10 μM in water) prior to (solid black line) and after (dashed red line) addition of 0.5 equiv. of CB[8] in comparison to the spectra obtained after photoirradiation of **1b** in the presence of CB[8] (dashed green line).

S.3.3 Gel-formation and photochemical crosslinking of 1c and CB[8].

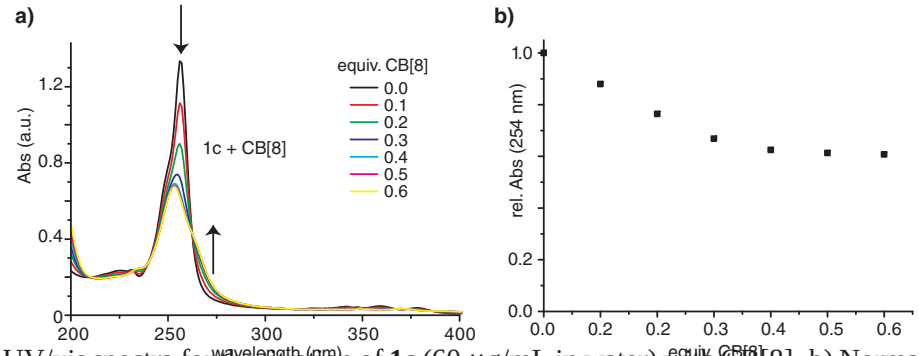

Figure S25: a) UV/vis spectra for the titration of **1c** (60 μg/mL in water) with CB[8]. b) Normalised absorbance at 254 nm as a function of the CB[8] equivalents.

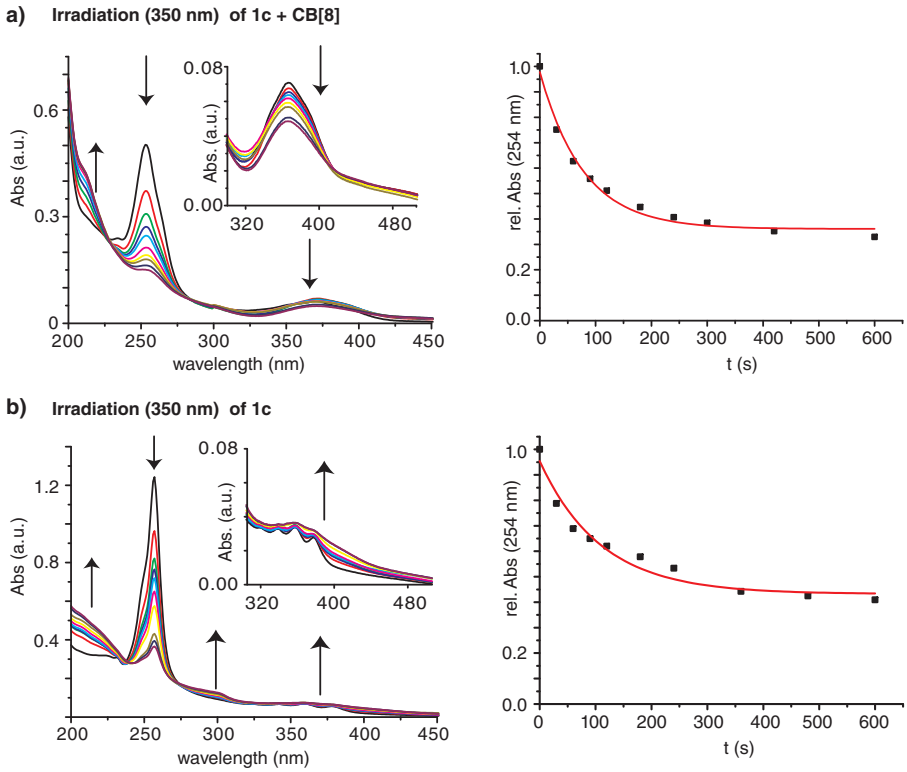

Figure S26: UV/vis spectra for **1c** (60 μg/mL in water) upon photoirradiation (350 nm) in a) the presence of 0.5 equiv. CB[8] and b) in the absence of the host. The plot on the right shows the normalised absorbance at 254 nm as a function of irradiation time. The solid red line shows the best monoexponential fit of the kinetic data.

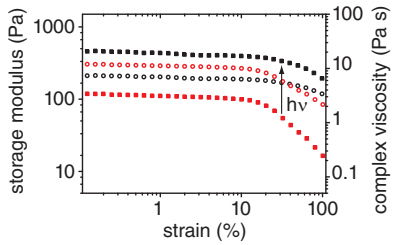

Figure S27: Oscillatory rheological analysis at 20 °C of the hydrogel formed upon addition of CB[8] to a 1.0 wt% solution of **1c** in water. Storage modulus and complex viscosity obtained from a strain-amplitude sweep performed at 10 rad s^{-1}. Changes upon UV-light exposure (15 min) are indicated by an arrow. Squares refer to the left axis and circles to the right axis. Red-symbols: prior to photoirradiation, black symbols: after photoirradiation.

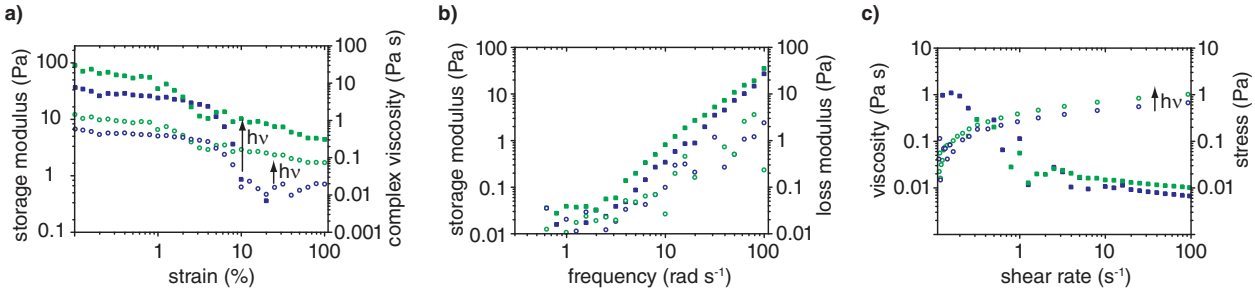

Figure S28: Rheological analysis at 20 °C of a 1.0 wt% solution of **1c** in water. Changes upon UV-light exposure (15 min) are indicated by an arrow. Squares refer to the left axis and circles to the right axis. Blue-symbols: prior to photoirradiation, green symbols: after photoirradiation. a) Storage modulus and complex viscosity obtained from a strain-amplitude sweep performed at 10 rad s^{-1}. b) Storage and loss moduli obtained from a frequency sweep performed at 5% strain. e) Steady-shear rheological measurements.

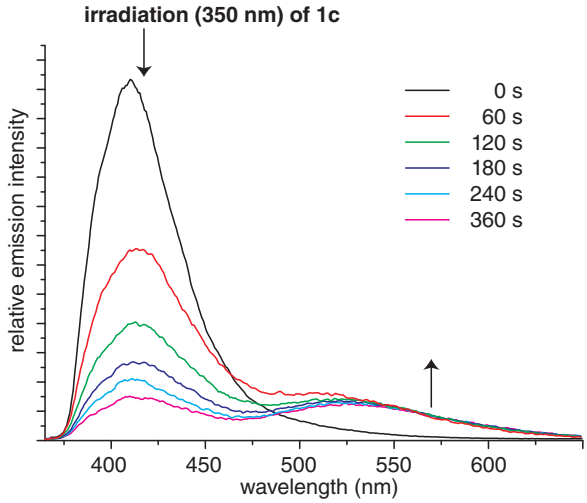

Figure S29: Emission spectra (356 nm excitation) upon photoirradiation (350 nm) of **1c** (60 μg/mL in water) in the absence of the host.