Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information (ESI)

A supramolecular keypad lock

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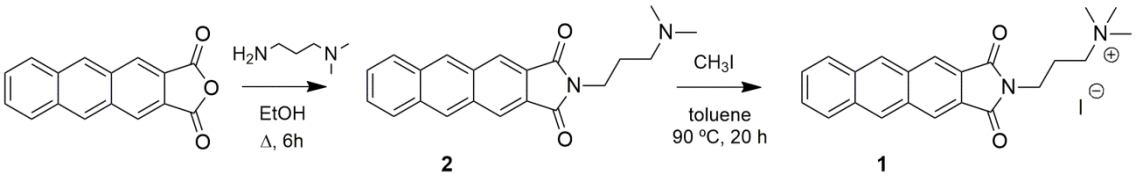
Materials

3-(*N*,*N*-Dimethylamino)-1-propylamine (99%), iodomethane (≥99%), 1-adamantylamine (97%), and cucurbit[8]uril were purchased from Sigma Aldrich. 2,3-Anthracenedicarboxylic anhydride (> 90%) was supplied by Tokyo Chemical Industry CO., Ltd (TCI). All compounds were used as received. Cucurbit[7]uril was prepared according to a published procedure.[1]

Synthesis of Dye 1



Scheme S1. Synthesis of dye **1**.

Synthesis of 2. A solution of 2,3-anthracenedicarboxylic anhydride (100 mg, 0.40 mmol) and 3-(*N*,*N*-dimethylamino)-1-propylamine (61.7 mg, 0.60 mmol) in 4 mL ethanol was heated to reflux for 6 h. The resulting solution was concentrated to dryness and the residue was re-dissolved in chloroform (10 mL). The organic layer was washed with water (4 × 10 mL), dried with anhydrous Na_2SO_4, and then the solvent was evaporated to yield the NMR-pure product **2** as light yellow solid (108 mg, 0.32 mmol) in a yield of 80%.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.87–1.95 (m, 2H), 2.23 (s, 6H), 2.39 (t, J = 7.2 Hz, 2H), 3.83 (t, J = 7.6 Hz, 2H), 7.60–7.65 (m, 2H), 8.05–8.11 (m, 2H), 8.50 (s, 2H), 8.63 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 26.7, 36.8, 45.5, 57.2, 125.9, 126.9, 127.6, 128.6, 130.2, 132.1, 133.4, 168.0 ppm.

Synthesis of 1. To solution of **2** (100 mg, 0.30 mmol) in toluene (4 mL) dry iodomethane (213.5 mg, 1.50 mmol) was added under stirring and the mixture was then heated under exclusion of light at 90 °C for 20 h. After removal of all volatiles, dye **1** was obtained as light yellow solid (124 mg, 0.26 mmol) in 87% yield.

^{1}H NMR [$(CD_3)_2SO$, 400 MHz] δ 2.05–2.17 (m, 2H), 3.04 (s, 9H), 3.38–3.45 (m, 2H), 3.75 (t, J = 6.4 Hz, 2H), 7.68–7.73 (m, 2H), 8.18–8.23 (m, 2H), 8.70 (s, 2H), 8.95 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 22.0, 34.9, 52.2, 63.0, 125.6, 126.6, 127.7, 128.4, 130.1, 131.6, 132.7, 167.4 ppm. MS (ESI) m/z calcd M^+: 347.1754; found: 347.1751.

Methods

General. All measurements and photoreactions were performed with freshly prepared air-equilibrated aqueous solutions at room temperature. The pH of the solutions was adjusted to pH 7 by the addition of sodium hydroxide and controlled during the titration experiments with a pH meter (model HI221, HANNA Instruments). NMR measurements were done on an Agilent 400 MHz spectrometer.

Photophysical Measurements. All photophysical measurements were done in quartz cuvettes with 1 cm optical path length. The UV/vis absorption spectra were recorded with a UV-1603 spectrophotometer from Shimadzu. Steady-state fluorescence measurements were recorded on a Cary Eclipse fluorimeter from Varian. The fluorescence quantum yield was determined by employing quinine sulfate in 0.05 M H_2SO_4 as standard (Φ_f = 0.55).[2, 3] Time-resolved fluorescence measurements were performed with a time-correlated single-photon-counting setup from Edinburgh Instruments (FLS 920) using a picosecond pulsed diode laser EPL-445 (λ_{exc} = 442.2 nm,

pulse width 78.3 ps) as excitation source. The deconvolution analysis of the decay curve yielded the corresponding fluorescence lifetime.

Irradiations. A 150 W Xenon Lamp (Oriel GmbH & Co. KG) was used as light source for the photodimerization of **1**. The irradiation light was passed through a 395-nm optical cut-off filter. For the cycloreversion of the photodimer a hand-held UV lamp with output at 254 nm (VL-4.LC, 4 W) was used.

Complexation Studies. The titration experiments were done by administering aliquots of stock solutions of the cucurbituril macrocycles (CB7 or CB8) to solutions containing the guest dye **1**. The water content of the samples of the organic macrocycles was determined according to published procedures.[4] The excitation wavelength in the fluorescence titration was chosen to coincide with an isosbestic point of the UV/vis absorption titration. The fitting of the titration curves was done with a 1:1 or 1:2 complexation model, as described in the literature.[5, 6] The Job plot was obtained for a constant total (host and guest) concentration of 20 μM.

Liquid Chromatography with Diode-Array and Mass-Spectrometric Detection. The chromatographic separation was achieved using an Hamilton PRP-1 reversed phase column (15.0 cm length, 2.1 mm internal diameter, 5 μm particle diameter), stabilized at 25 °C. The mobile phase consisted of water (H_2O) and acetonitrile (MeCN), both with 0.1% of formic acid at 0.4 mL/min flow. Two gradient programs were used. In the first program the mobile phase started with 95% of H_2O and 5% of MeCN and then changed to 0% of H_2O and 100% of MeCN within 10 minutes. This composition was kept for 4 minutes and then the initial composition was recovered within 0.5 minutes and stabilized for additional 5 minutes before the next run. In the second program the mobile phase started with 95% of H_2O and 5% of MeCN, was changed to 70% of H_2O and 30% of MeCN within 25 minutes and then to 0% of H_2O and 100% of MeCN

within 5 minutes. This composition was kept for 4 minutes, then the initial composition was recovered within 0.5 minutes, and finally stabilized for additional 5 minutes before the next run.

The LC-MS system is an Agilent Technologies 1200 Series LC, equipped with a photodiode array detector (DAD) and coupled to a Bruker Daltonics HCT ultra (ion trap). The UV/Vis absorption spectra of the separated products were obtained using the DAD. LC-DAD traces were acquired at 300 nm. The parameters of the electrospray-ionization mass spectrometry detection were set as follows: polarity, positive; capillary voltage, –4.0 kV; capillary exit voltage, 180 V; skimmer voltage, 60 V; temperature of drying gas, 330 ºC; nebulizer gas pressure, 40 psi; drying gas flow, 8 L/min.

Detection of Host-Guest Complexes in the Gas Phase. The mass spectrometric experiments to identify the **1•1•**CB8 complex were performed with a Bruker Daltonics HCT ultra mass spectrometer (ion trap), equipped with an electrospray ionization source (Agilent) that utilized a nickel-coated glass capillary with an inner diameter of 0.6 mm. The ions were continuously generated by infusing the aqueous solution sample into the source with a syringe pump (KdScientific, model 781100, USA) at a flow rate of 4 μL/min. The parameters used to detect host-guest complexes in the gas phase were typically as follows: polarity, positive; capillary voltage, –4.0 kV; capillary exit voltage, 20 V; skimmer voltage, 100 V; temperature of drying gas, 300 ºC; nebulizer gas pressure, 20 psi; drying gas flow, 5 L/min.

Electrospray Ionization Mass Spectrometry of the 1•1•CB8 Complex

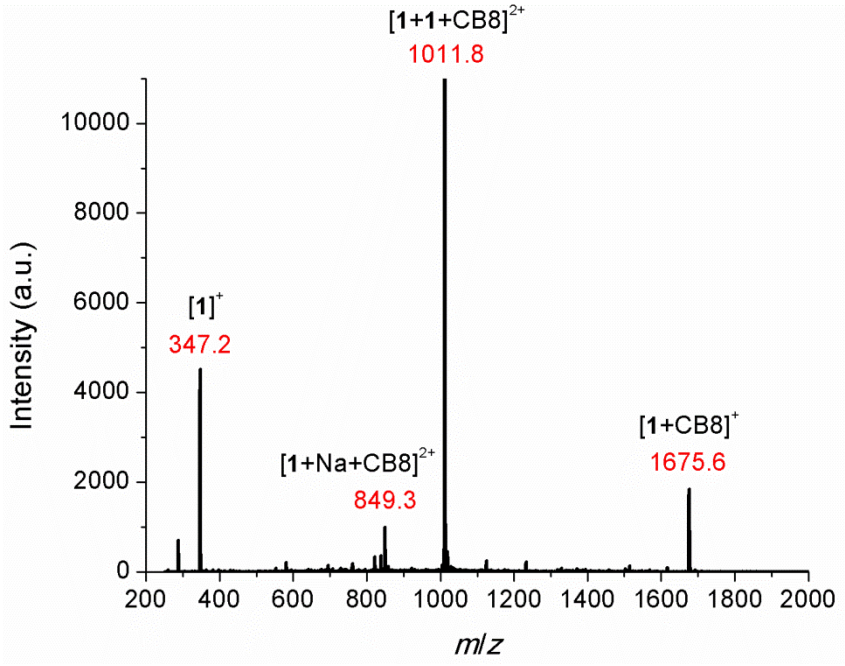


Figure S1. Electrospray ionization mass spectrum of a mixture of **1** (30 μM) and CB8 (15 μM) in neutral water.

Absorption Titration of 1 with CB8

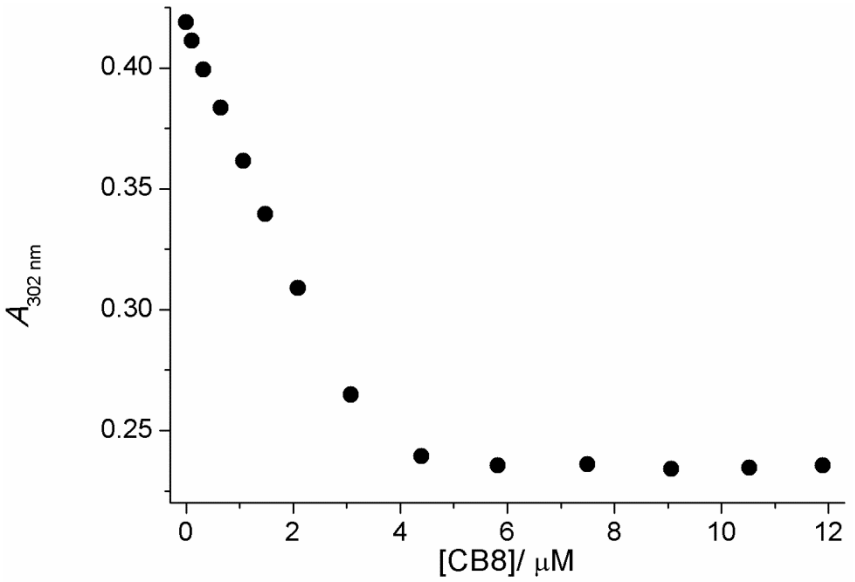


Figure S2. UV/vis absorption titration of **1** (10 μM) with CB8 in pH-neutral water.

Job's Plot

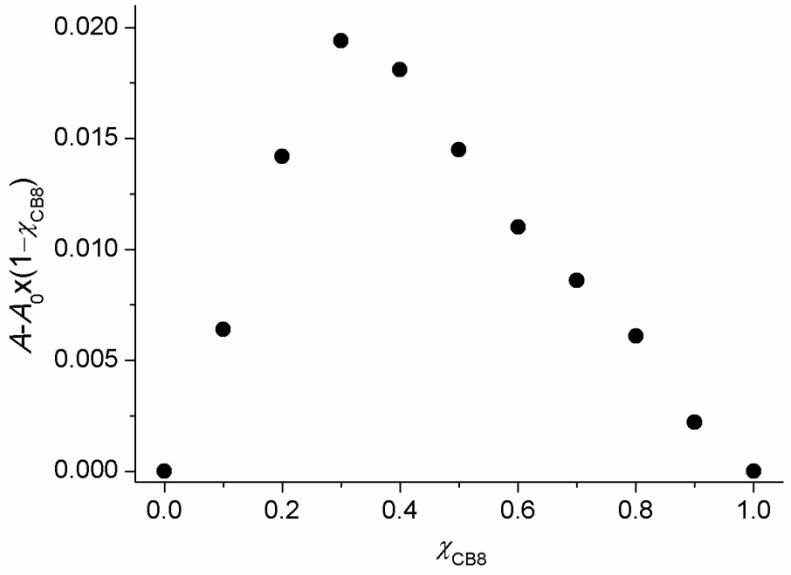


Figure S3. Job's plot for the complexation of **1** by CB8; the total concentration of both components was fixed at 20 μM.

Reversible Photoswitching

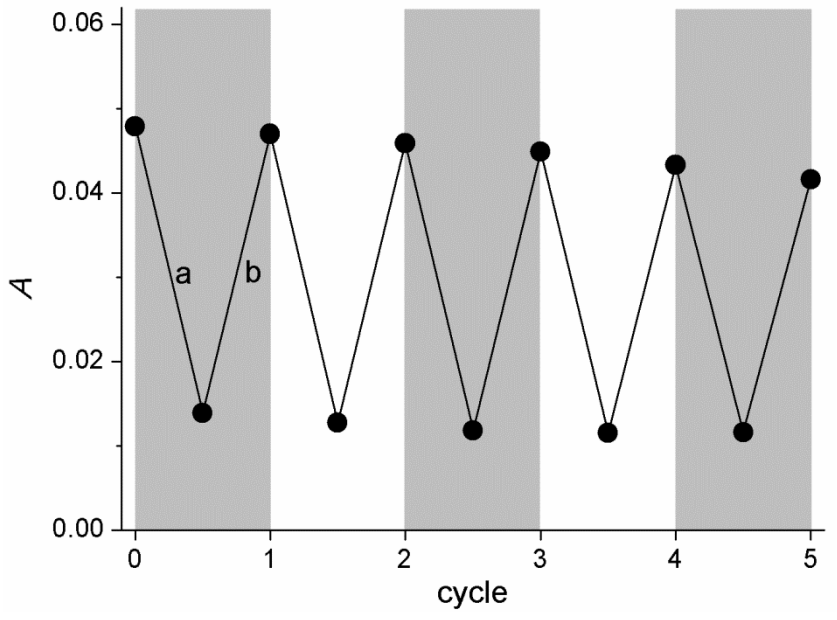


Figure S4. Reversible photoswitching of **1** (10 μM) in the presence of 0.5 equiv. of CB8 monitored at 418 nm; a: 20 min irradiation at > 395 nm; b: 20 s irradiation at 254 nm.

Recycling

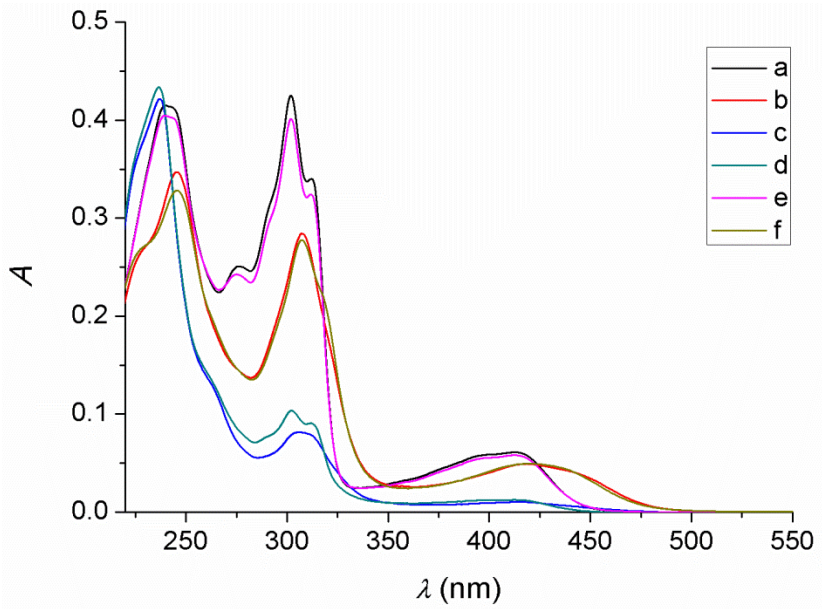


Figure S5. UV/vis absorption changes for the recycling of the supramolecular keypad lock. a: 10 μM **1**; b: after addition of CB8 (5 μM) to solution a; c: after irradiation of solution b at >395 nm for 45 min; d: after addition of 1-aminoadamantane (20 μM) to solution c; e: after irradiation of solution d at 254 nm for 30 s; f: after addition of CB7 (35 μM) to solution e. Note that the spectra corresponding to the cases b and f are hardly distinguishable.

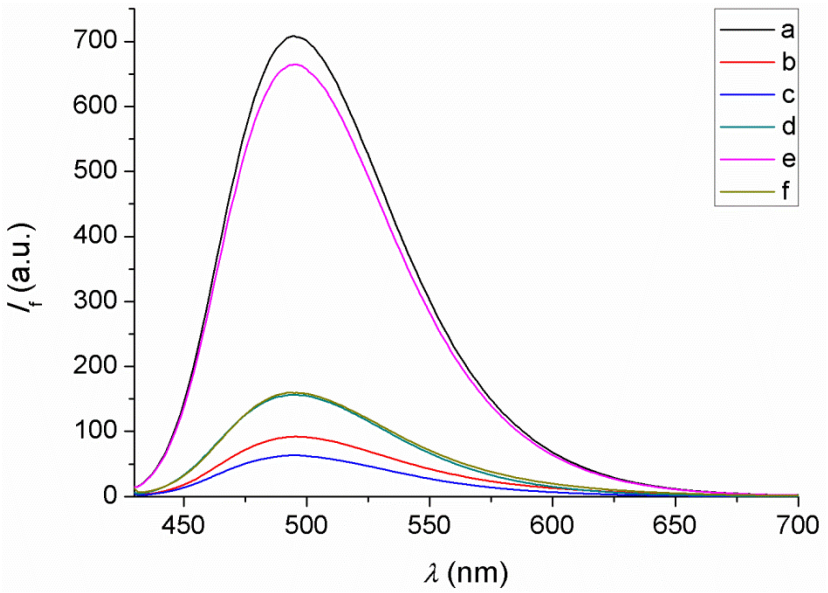


Figure S6. Fluorescence changes for the recycling of the supramolecular keypad lock. a: 10 μM **1**; b: after addition of CB8 (5 μM) to solution a; c: after irradiation of solution b at >395 nm for 45 min; d: after addition of 1-aminoadamantane (20 μM) to solution c; e: after irradiation of solution d at 254 nm for 30 s; f: after addition of CB7 (35 μM) to solution e. Note that the spectra corresponding to the cases d and f are hardly distinguishable.

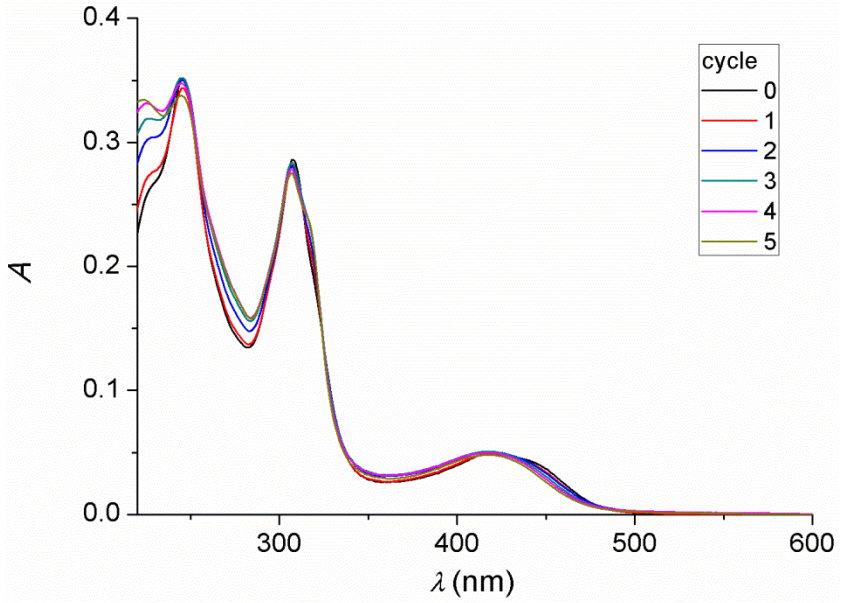


Figure S7. Absorption spectra after the final addition of CB7 for several cycles corresponding to the sequences c)-f) shown in Figure S5.

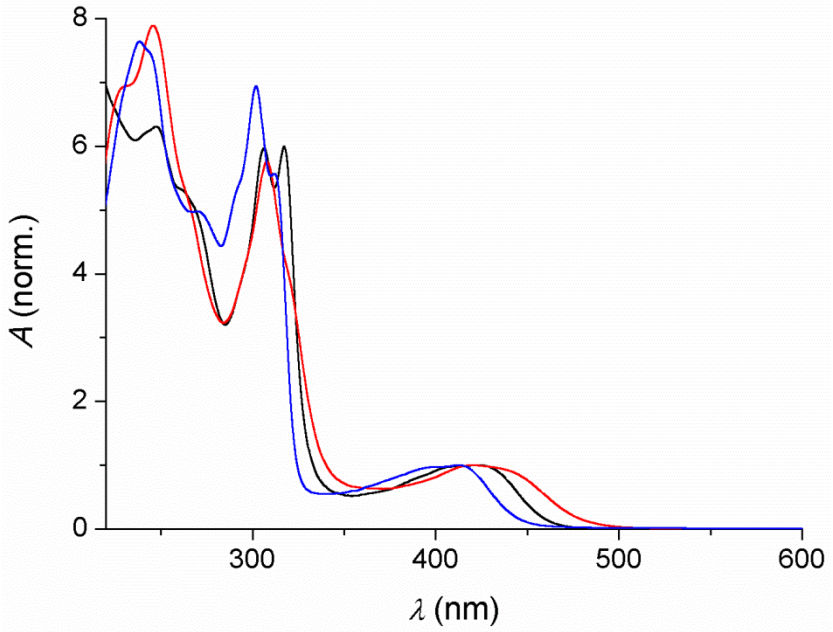


Figure S8. Comparison of the UV/vis absorption spectra of dye **1** (blue line), the complex **1**•CB7 (black line), and the complex **1**•**1**•CB8 (red line).

Observations about the recycling process: As can be seen in Figure S7 the recycling process can be repeated several times (tested for 5 cycles in this work). It has to be taken into consideration that the self-sorting process on addition of CB7 involves a multicomponent mixture with several coupled equilibria, and that CB7 and 1-aminoadamantane are used in excess. Thus, these chemicals accumulate over the various cycles. From a comparison with Figure S8 it can be seen that the characteristic spectral fingerprint of the **1**•**1**•CB8 complex is obtained after completion of each cycle. For the encountered intricate multi-equilibrium situation the reproducibility is very good. However, a loss of ca. 30% of the dye **1** available for recycling is noted over the 5 cycles. This could be probably further improved by optimizing the concentrations of the 4 components (dye **1**, 1-aminoadamantane, CB7, and CB8).

Liquid Chromatography

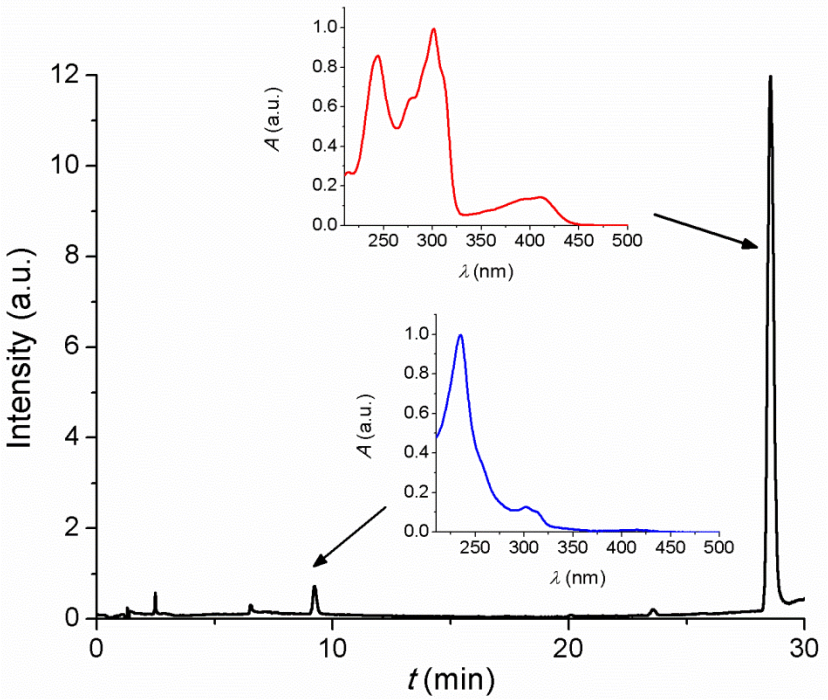


Figure S9. LC-DAD chromatogram (observed at 300 nm) after partial photodimerization of **1** in the presence of 0.5 equiv. of CB8 by irradiation at >395 nm. The insets show the UV/vis absorption spectra of **1** (red) and the photodimer $\mathbf{1}_2$ (blue), as detected by the DAD.

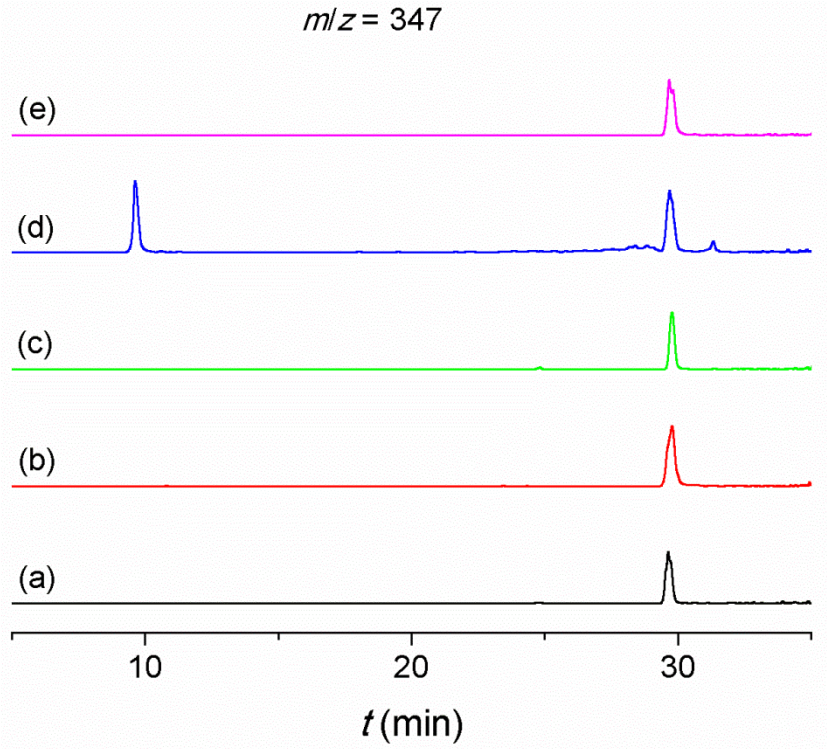


Figure S10. Single ion LC-MS traces at *m*/*z* 347 of (a) the non-complexed dye **1**, (b) the dye in presence of CB8, (c) after irradiation of the non-complexed dye **1** at >395 nm, (d) after partial photodimerization by irradiation of the complex at >395 nm, (e) after cycloreversion of the complexed dimer by irradiation at 254 nm. The concentrations were adjusted to [**1**] = 30 μM and [CB8] = 15 μM (whenever present). All solutions were prepared in pH-neutral water. Note that the host-guest complexes do not withstand to the chromatographic separation; only the guests are observed.

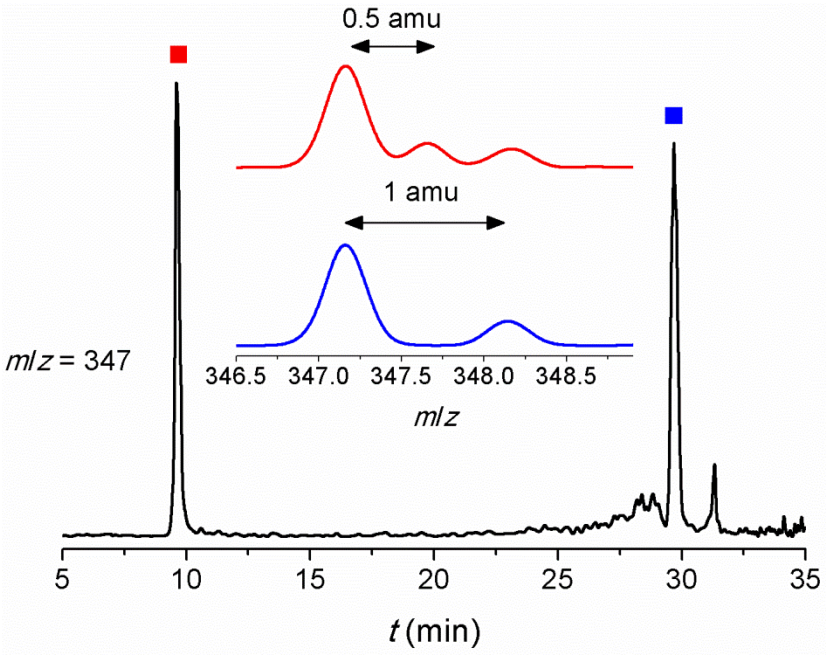


Figure S11. Single ion LC-MS trace at *m*/*z* 347 observed after irradiation of **1** (30 μM) in presence of CB8 (15 μM). The photoreaction was not completed to demonstrate the signals of both the monomer dye and the photodimer. The color-coded inset graphs show the molecular ion peak and the isotope pattern spacing (blue: dye **1**, red: photodimer $\mathbf{1}_2$). Note that the host-guest complexes do not withstand to the chromatographic separation; only the guests are observed.

NMR Study of Complexation and Photoreactions

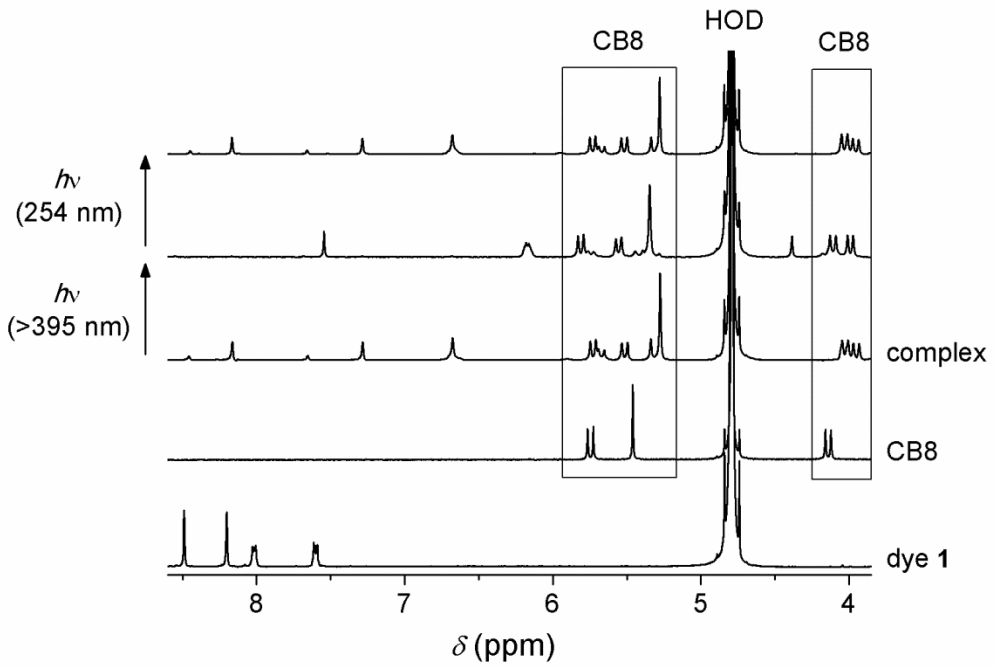
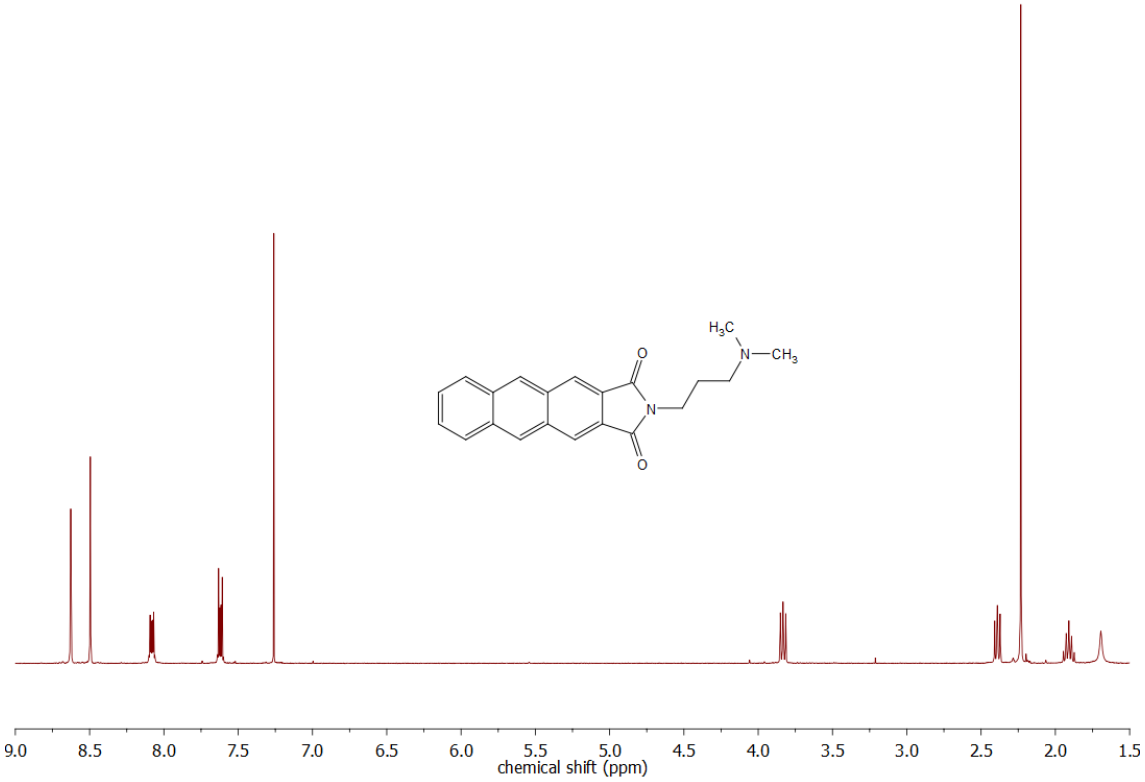
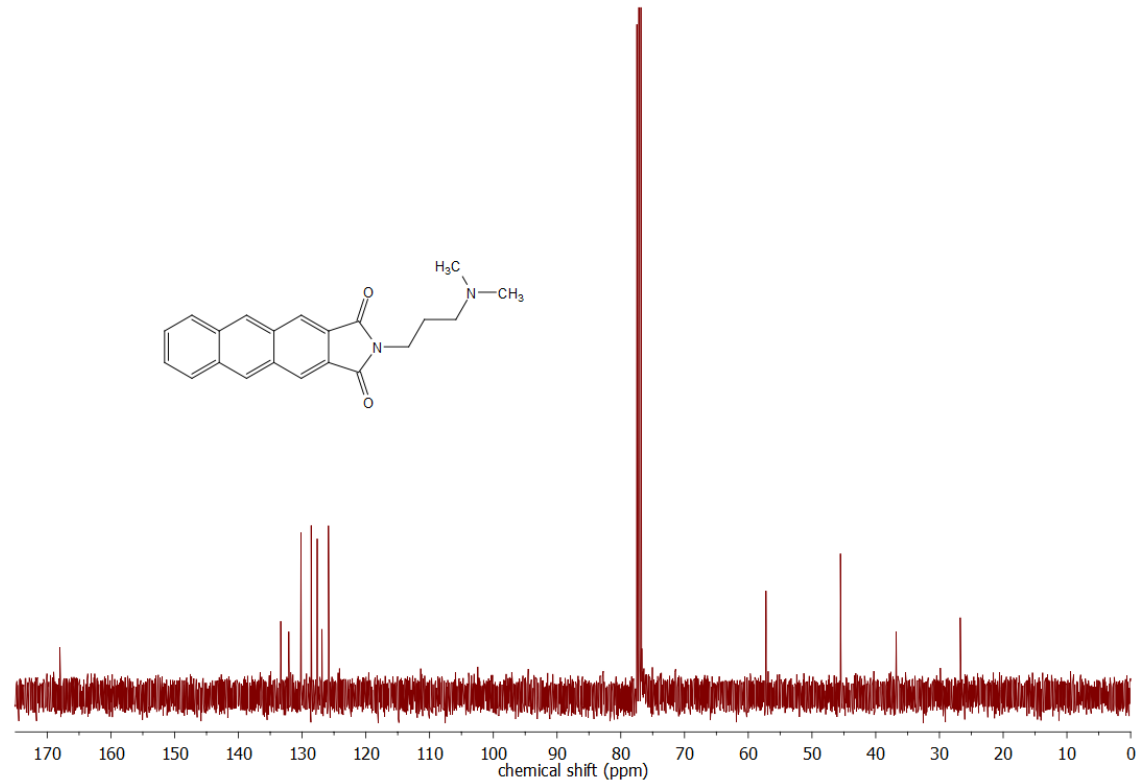


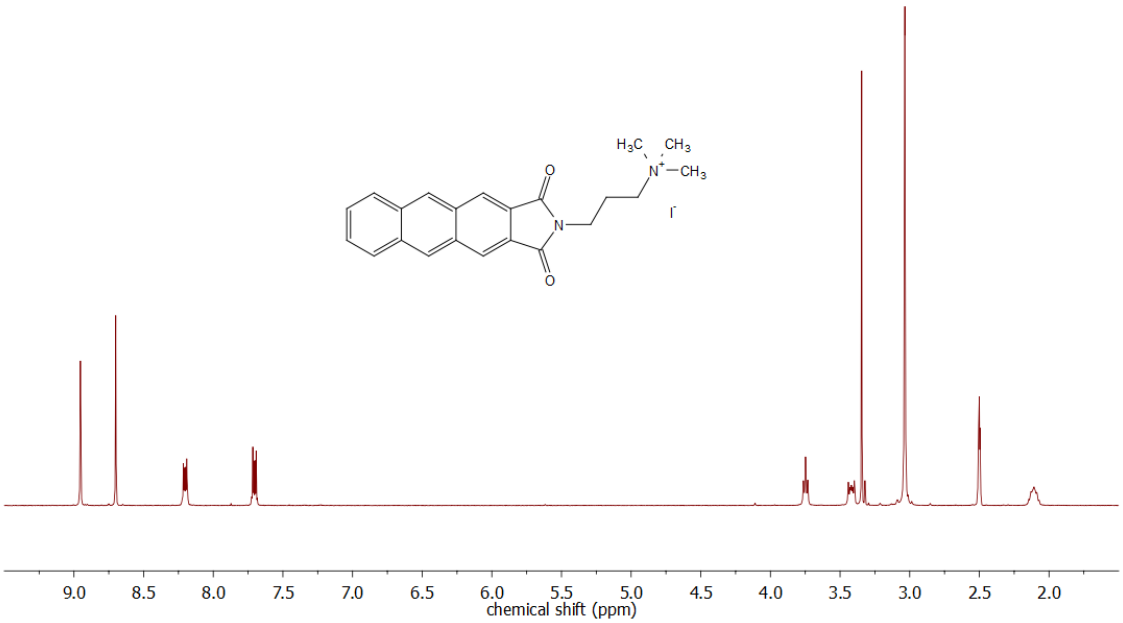
Figure S12. Partial ^{1}H NMR spectra (in D_2O) of dye **1**, CB8, the mixture of **1** (250 μM) and CB8 (125 μM), the irradiated (>395 nm for 45 min) mixture, and the mixture after cycloreversion (irradiation at 254 nm for 4 min of the CB8-complexed photodimer that was generated previously by irradiation at >395 nm for 45 min); from bottom to top.

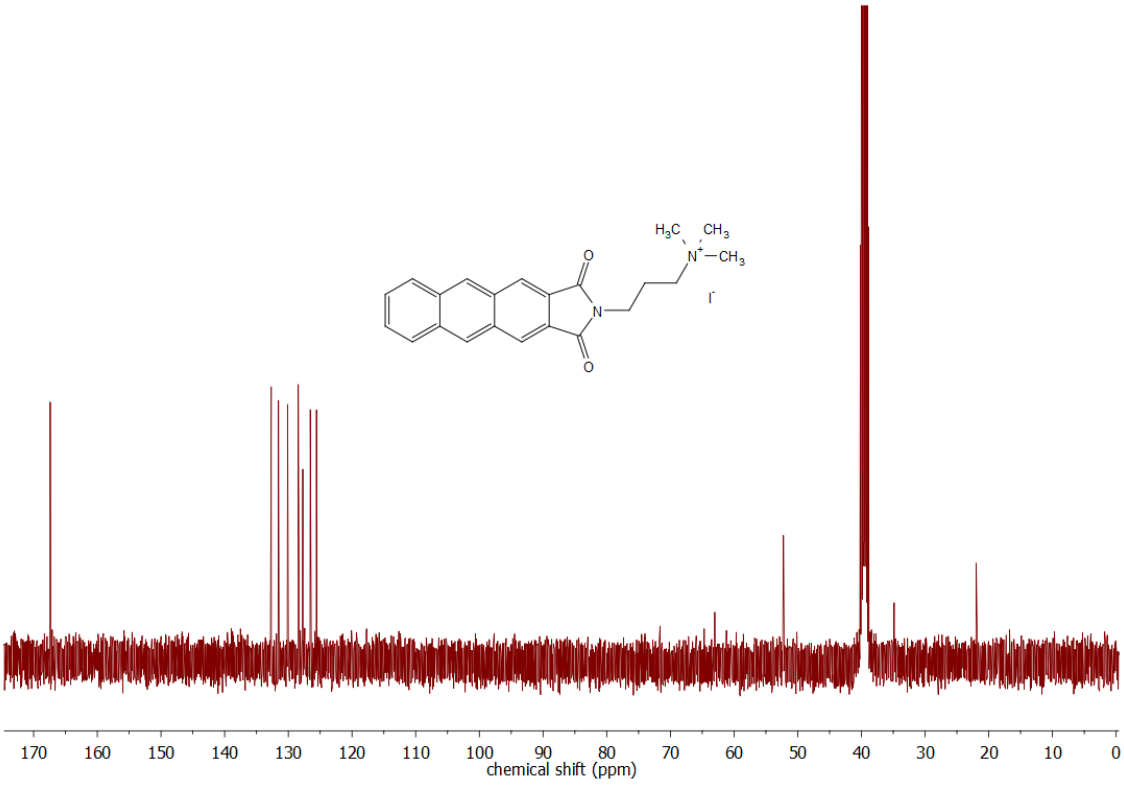
Additional notes: In the mixture of dye **1** and CB8 (third spectrum from bottom) two different complexes can be found. The major species (ca. 80%, based on integrations of the aromatic protons) is assigned to the **1•1•**CB8 complex. This was independently confirmed by mass spectrometry and Job's plot analysis (see above). The minor species (ca. 20%) is tentatively assigned to the **1•**CB8 complex that was also observed in mass spectrometry. A second observation is that for the **1•1•**CB8 complex some symmetry distortion of the portal methylene protons is noted.

NMR spectra


H3C
N
CH3
O
N
O
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
chemical shift (ppm)


H3C
N
CH3
O
N
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
chemical shift (ppm)





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3. W. H. Melhuish, *J. Phys. Chem.*, 1961, **65**, 229-235.

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