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Supporting Information

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Photochemical Control of Reversible Encapsulation**

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Experimental

Materials and General Methods: ^{1}H NMR spectra were recorded on a Bruker DRX-600 spectrometer with a 5 mm QNP probe. Proton (^{1}H) chemical shifts, reported in parts per million (ppm), were indirectly referenced to external tetramethylsilane employing resonance as an internal reference. Deuterated mesitylene was obtained from Cambridge Isotope Laboratories, Inc.

Compounds **1**, *n*-tridecane, benzoic acid, benzamide, 4,4'-dimethylbenzil, 4-ethylbenzamide, *p*-cymene, and 4,4'-dibromobenzil were purchased at reagent grade from Acros, Fluka, Fisher and Sigma-Aldrich, and used as received. Compounds **2**,[1] **3**,[2] **4**,[3] and **5**[4] were prepared according to literature procedures.

Samples of the capsular assembly **2·2** were prepared at 1.2 mM concentrations. Samples of extended assemblies were prepared at 0.6 mM concentrations. First, capsule (and glycoluril) and azo-guests were dissolved in 0.5 mL mesitylene-d_{12} at elevated temperature (160 ºC). Afterwards, the second guest was added to the solution and ^{1}H NMR spectra were recorded. After irradiation with a Blak-Ray Long Wave Ultraviolet Lamp, Model B-100 AP ^{1}H NMR spectra were recorded after which the sample was heated to 160 ºC for 2 min and ^{1}H NMR spectra were recorded again. This cycle was repeated three times for each sample.

Experimental Setup for Irradiaton

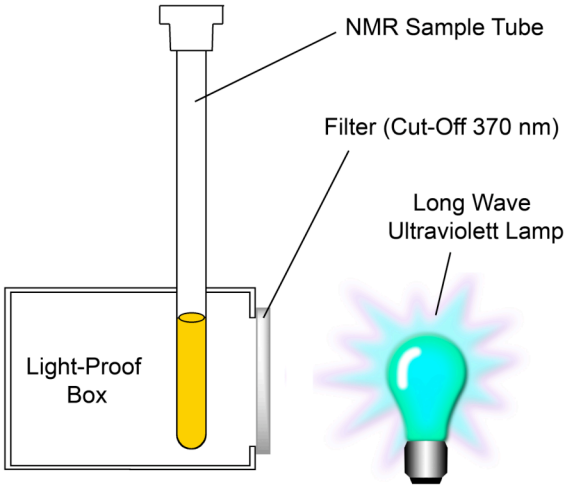

Figure 1SI: Experimental setup for irradiation. A Blak-Ray Long Wave Ultraviolet Lamp, Model B-100 AP was used as light source.

Spectra

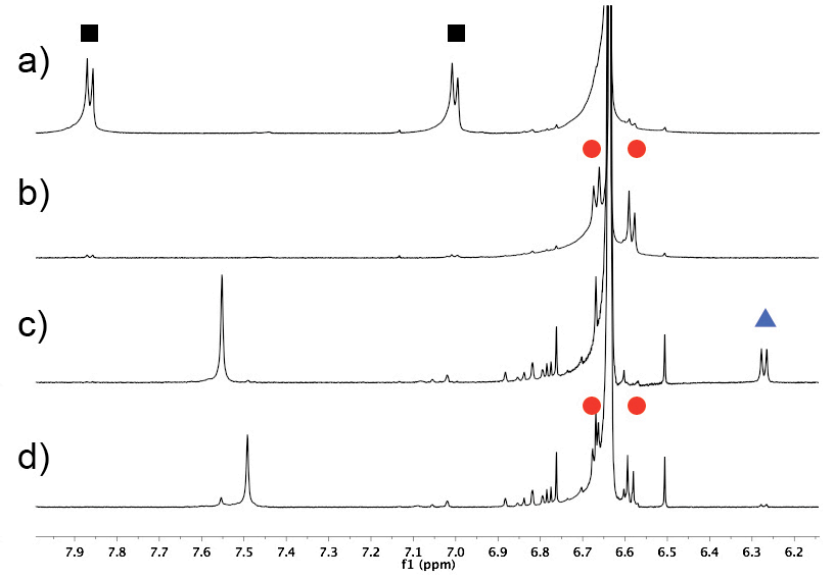

Figure 2SI: Aromatic region of ^{1}H NMR spectra (mesitylene-d_{12}, 20 ºC). a) Black squares indicate aromatic signals of free *trans*-**1**. b) Red circles indicate aromatic signals of free *cis*-**1**. c) The blue triangle indicates one aromatic signal of encapsulated *trans*-**1**. d) After irradiation with 365 nm light, the aromatic signals of free *cis*-**1** can be seen.

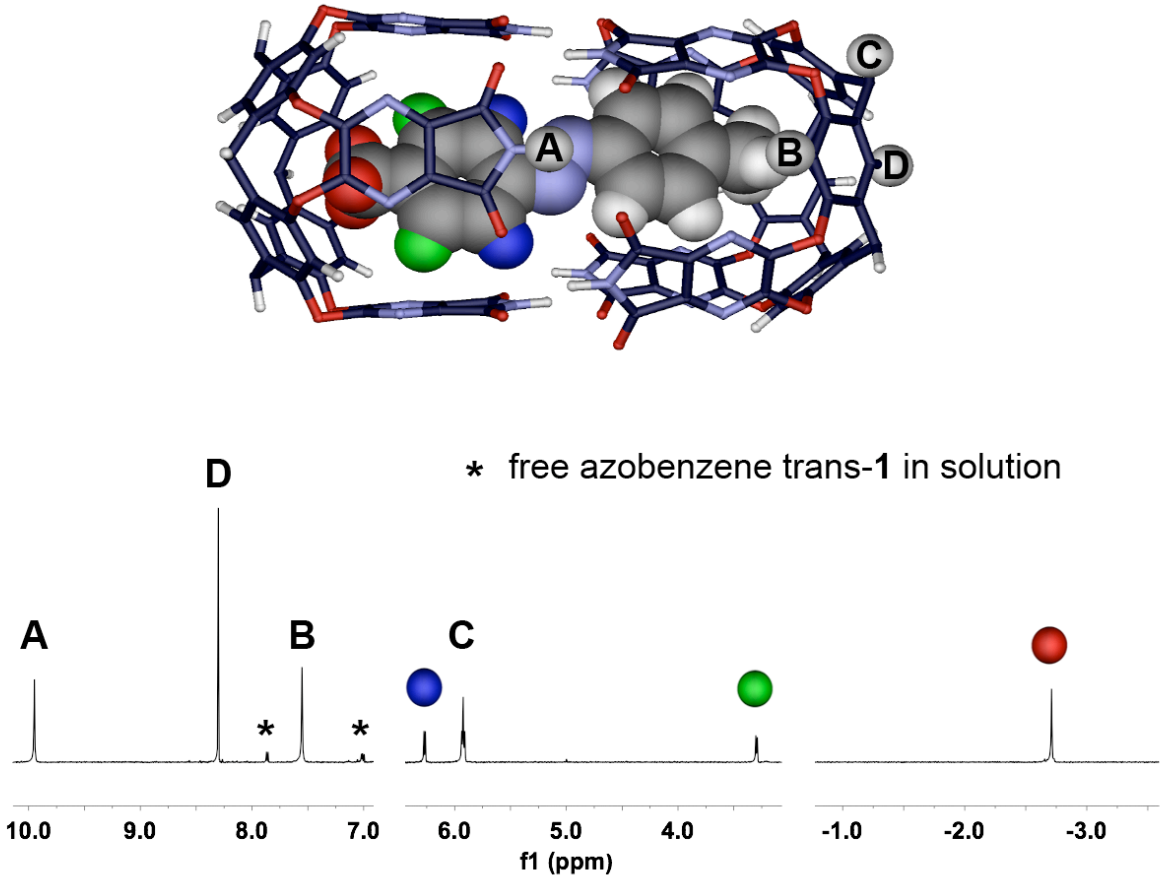

Figure 3SI: ^{1}H NMR spectrum of *trans*-**1** encapsulated in **2·2** (mesitylene-d_{12}, 20 ºC) and assignment of the signals to the structure.

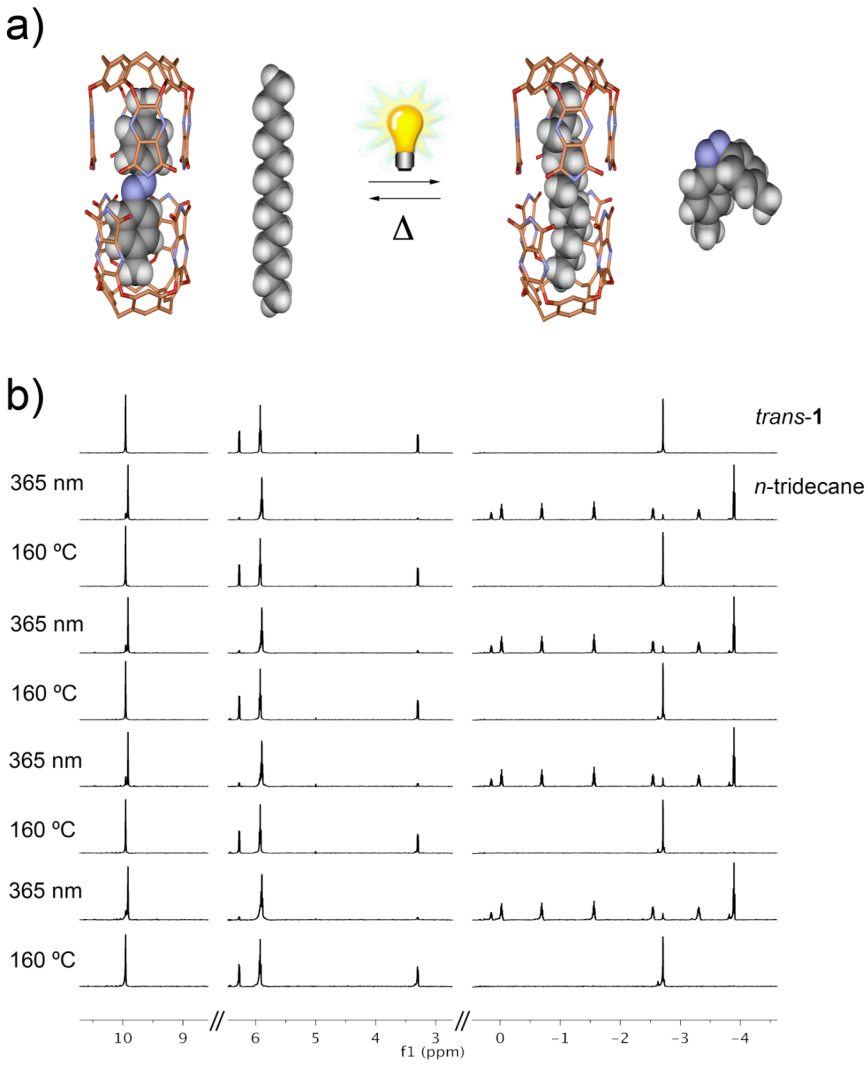

Figure 4SI: a) Light induced guest exchange of *trans*-**1** by *n*-tridecane in **2·2** (mesitylene-d_{12}, 20 ºC). Heating the sample restores the starting point. b) Indicative regions of the ^{1}H NMR spectra measured at 20 ºC in mesitylene-d_{12} are shown before irradiation (*trans*-**1** is the only guest) and after irradiation at 365 nm wavelength for 50 min at 20 ºC (*n*-tridecane is the only guest). After heating the sample to 160 ºC for 2 min, the initial state is completely restored. The cycle was repeated three times.

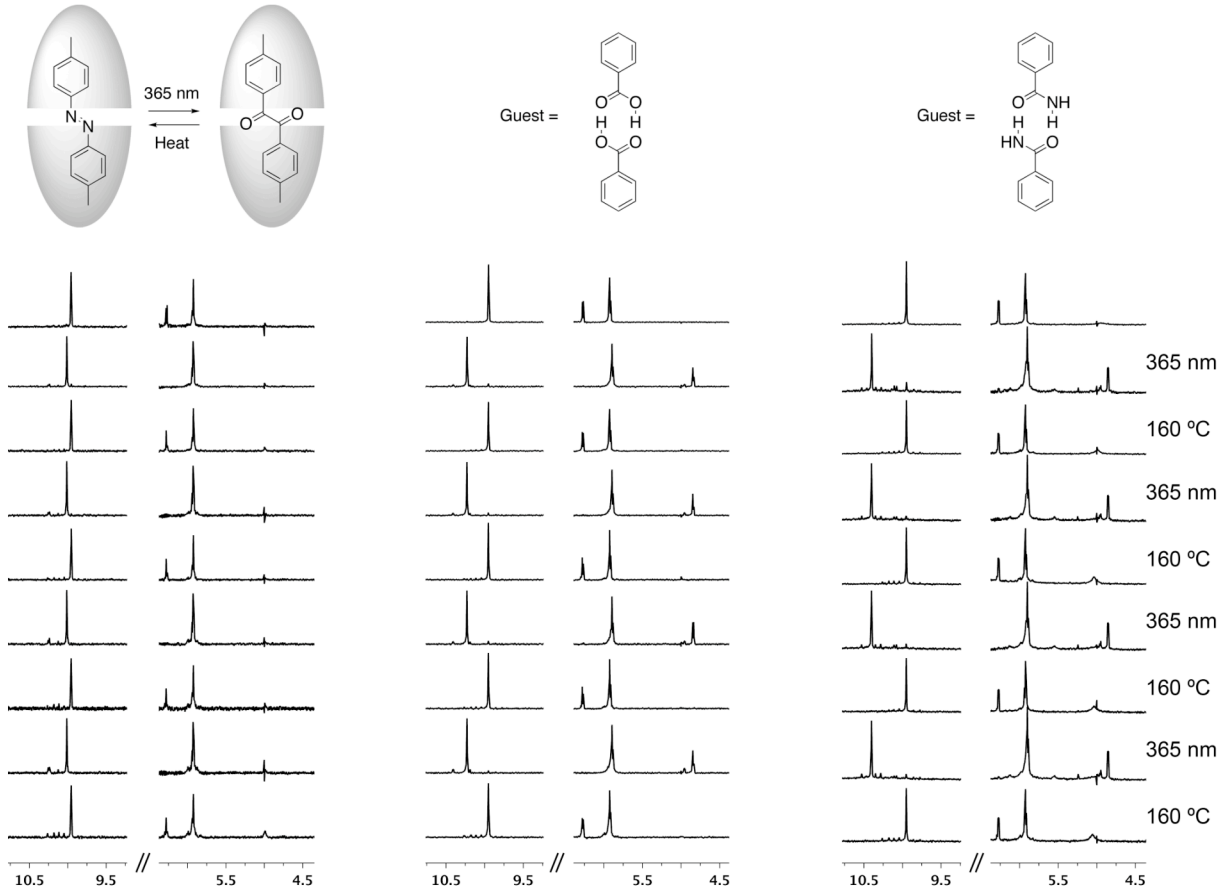

Figure 5SI: Light induced guest exchange of *trans*-**1** in **2·2** (mesitylene-d_{12}, 20 ºC) by a) 4,4'-dimethylbenzil; b) benzoic acid hydrogen bonded dimer; and c) benzamide hydrogen bonded dimer. Indicative sections of ^{1}H NMR spectra are shown before irradiation (*trans*-**1** is the only guest) and after irradiation at 365 nm wavelength for 50 min at 20 ºC. After heating the sample to 160 ºC for 2 min, the starting point is restored completely. The cycle was repeated three times in each case.

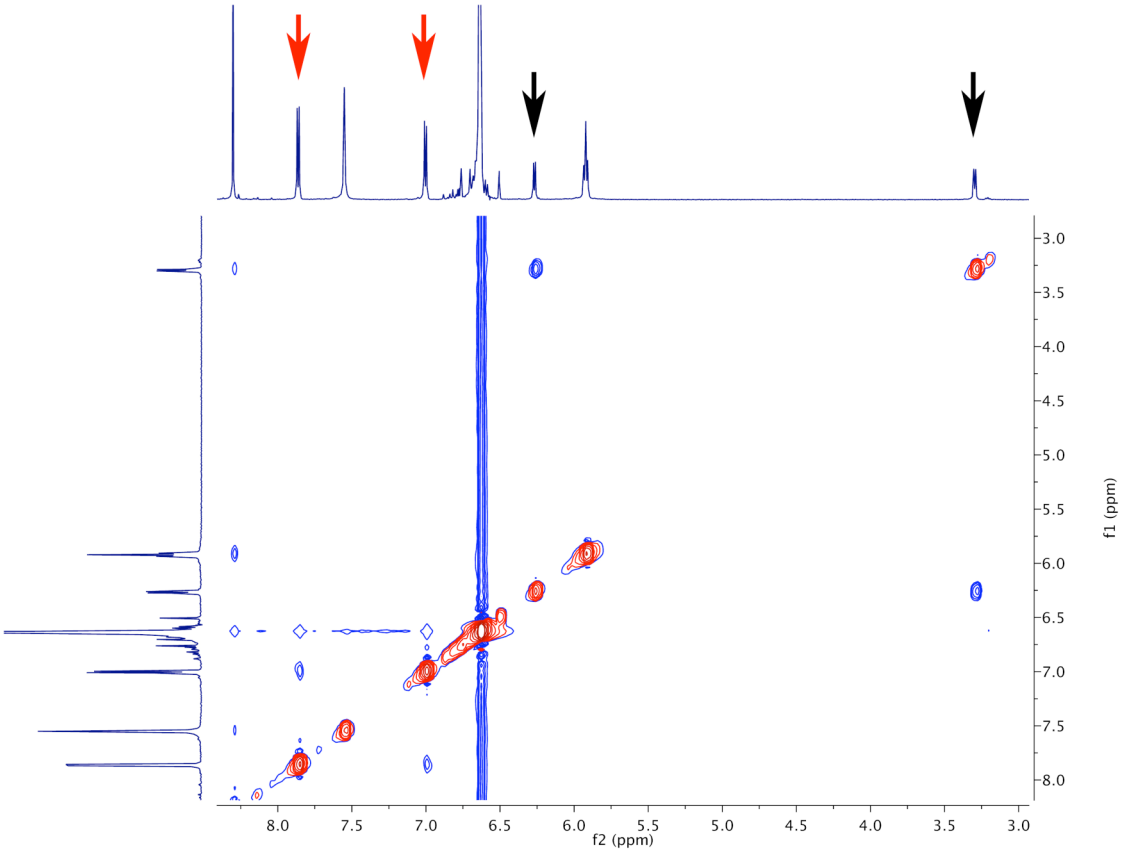

Figure 6SI: Partial ^{1}H NMR ROESY spectrum (mesitylene-d_{12}, 300 K, mixing time = 0.3 s, D1 = 1.5 s) of the host guest complex of *trans*-**1** and **2·2** in the presence of 1.5 equiv. *trans*-**1** free in solution. Red arrows assign the aromatic signals of free *trans*-**1** whereas black arrows assign the aromatic signals of encapsulated *trans*-**1**. No exchange signals between these signals can be observed as the guest exchange is slow.

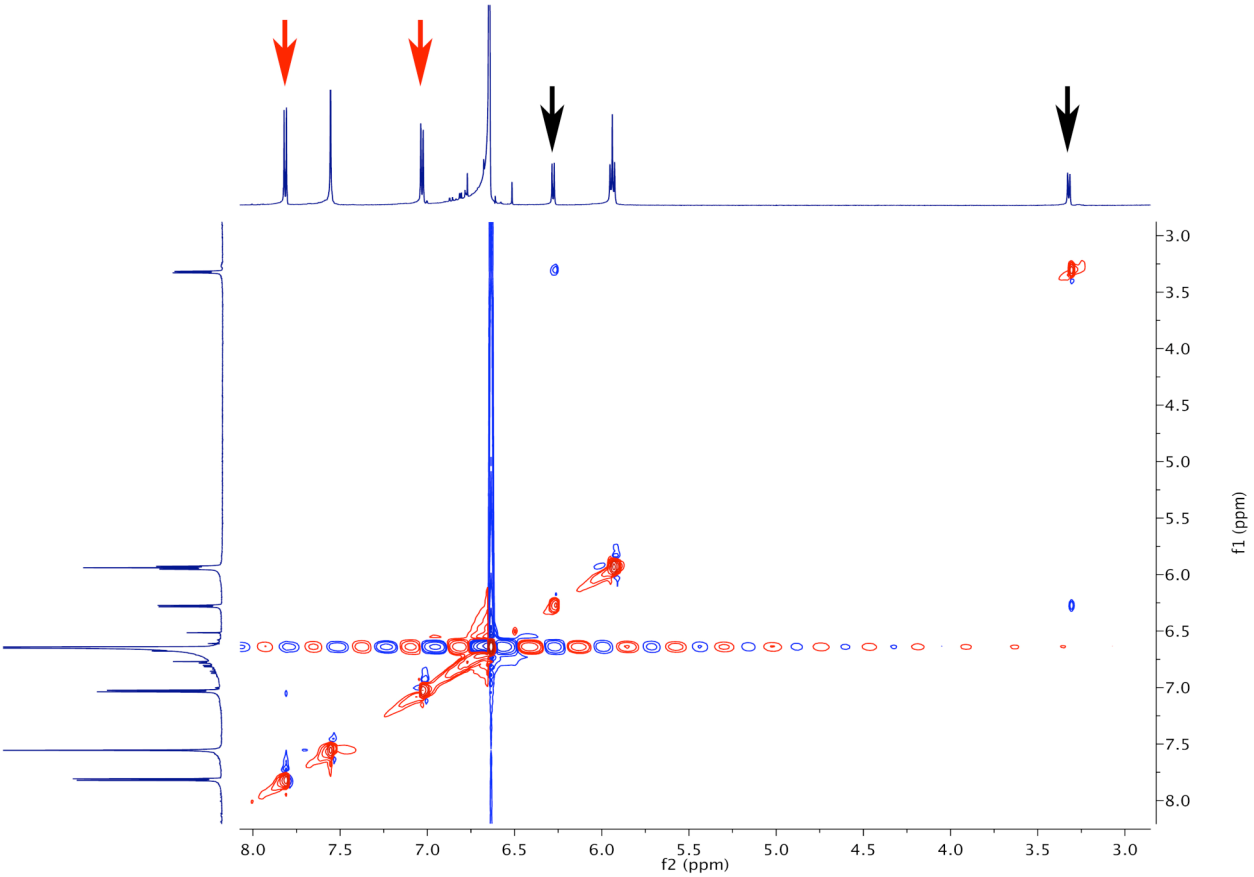

Figure 7SI: Partial ^{1}H NMR ROESY spectrum (mesitylene-d_{12}, 335 K, mixing time = 0.3 s, D1 = 1.5 s) of the host guest complex of *trans*-**1** and **2·2** in the presence of 1.5 equiv. *trans*-**1** free in solution in mesitylene-d_{12} at 335 K. Red arrows assign the aromatic signals of free *trans*-**1** whereas black arrows assign the aromatic signals of encapsulated *trans*-**1**. No exchange signals between these signals can be observed as the guest exchange is slow.

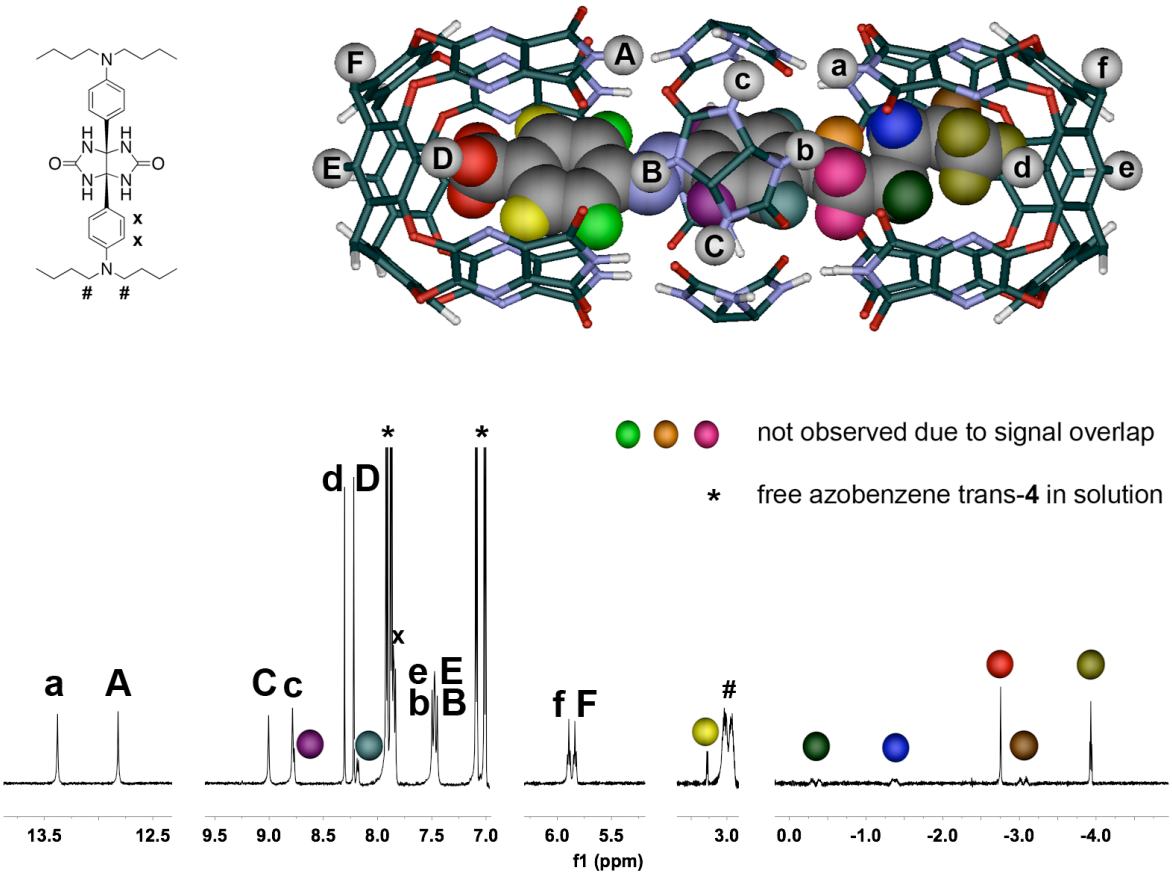

Figure 8SI: ^{1}H NMR spectrum of *trans*-**4** encapsulated in **2·3$_4$·2** (mesitylene-d_{12}, 20 ºC) and assignment of the signals to the structure.

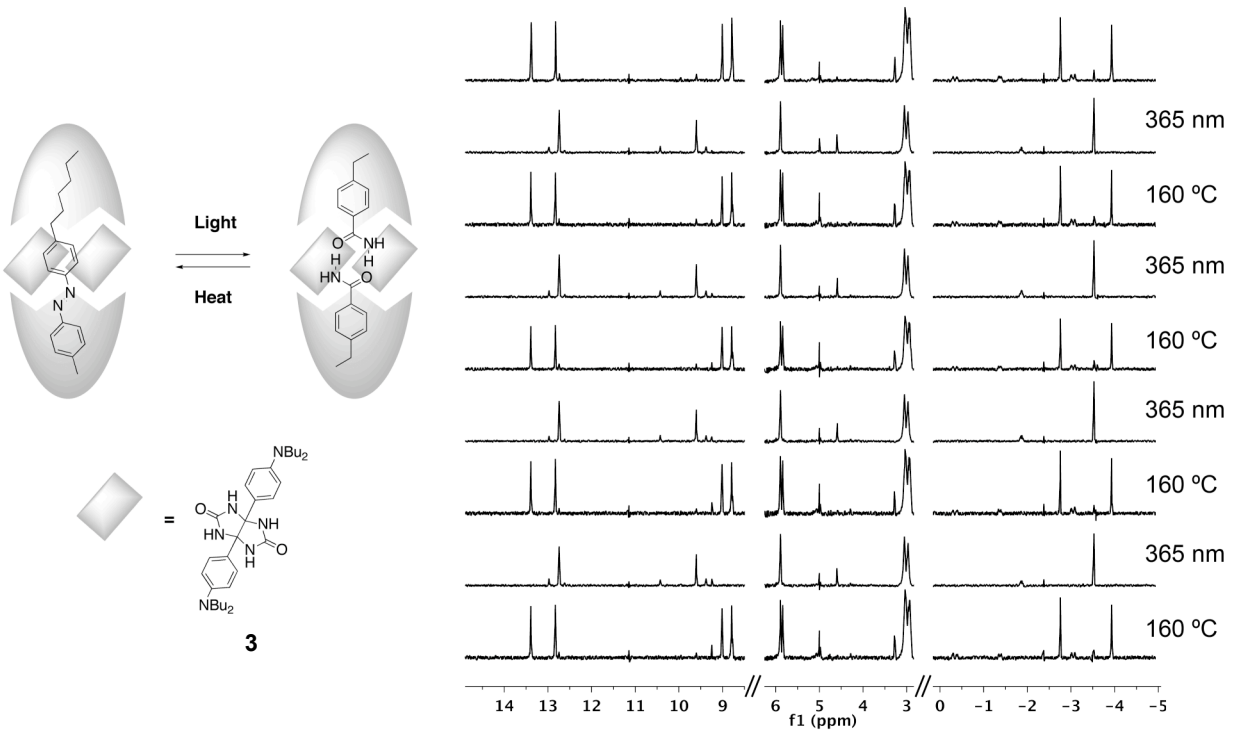

Figure 9SI: Light induced guest exchange of *trans*-**4** by 4-ethylbenzamide in **2·3$_4$·2** (mesitylene-d_{12}, 20 ºC). The ^{1}H NMR spectrum is shown before irradiation (*trans*-**4** is the only guest, top spectrum) and after irradiation at 365 nm wavelength for 50 min at 20 ºC (the homodimer of 4-ethylbenzamide is the only guest). After heating the sample to 160 ºC for 2 min, the starting point is completely restored. This cycle was repeated three times.

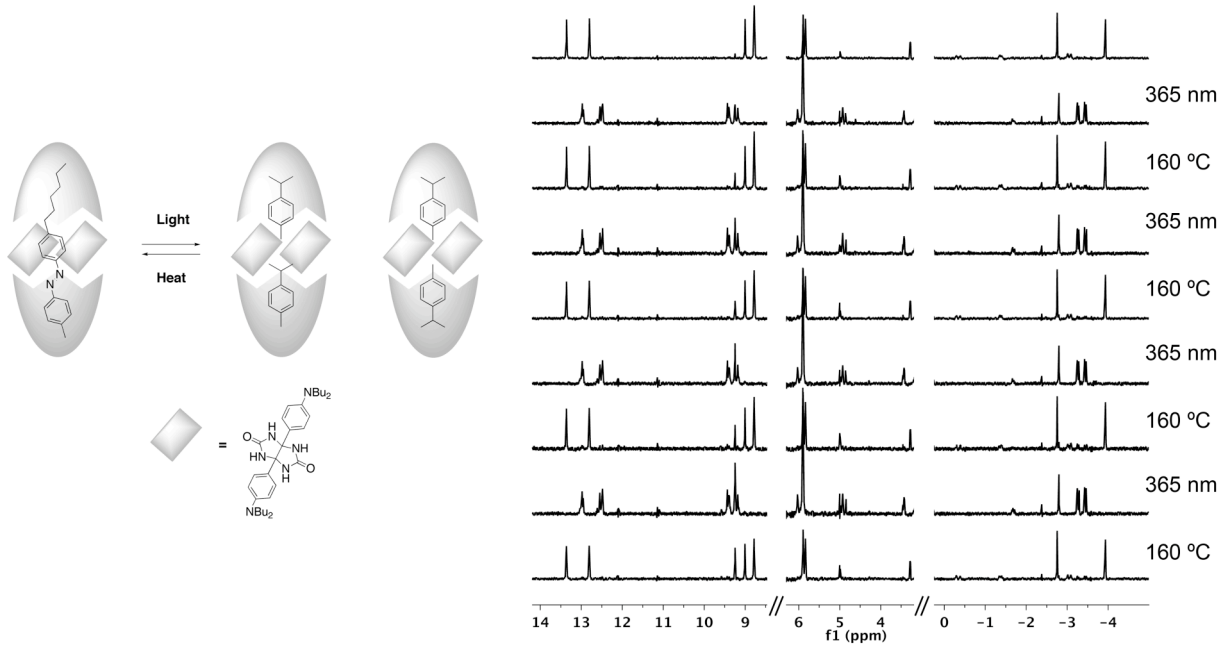

Figure 10SI: Light induced guest exchange of *trans*-**4** in **2·3$_4$·2** (mesitylene-d_{12}, 20 ºC) by *p*-cymene. The ^{1}H NMR spectrum is shown before irradiation (*trans*-**4** is the only guest) and after irradiation at 365 nm wavelength for 50 min at 20 ºC (two molecules of *p*-cymene are encapsulated in two different orientations). After heating the sample to 160 ºC for 2 min, the starting point is completely restored. This cycle was repeated three times.

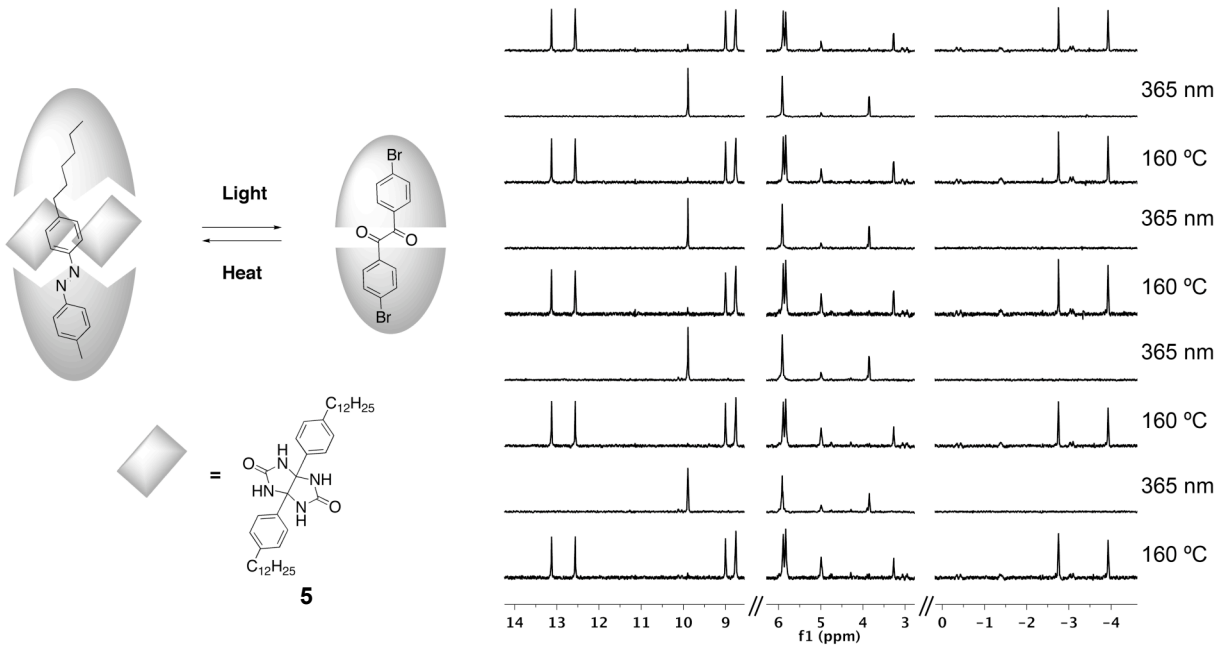

Figure 11SI: Light induced guest exchange with concomitant change of assembly (mesitylene-d_{12}, 20 ºC). The ^{1}H NMR spectrum is shown before irradiation (*trans*-**4** is the guest in the extended assembly **2·5$_4$·2**) and after irradiation at 365 nm wavelength for 50 min at 20 ºC (4,4'-dibromobenzil is the guest in the capsule **2·2**). After heating the sample to 160 ºC for 2 min, the starting point is completely restored. This cycle was repeated three times.

References

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