Electronic Supplementary Material (ESI) for Photochemical & Photobiological Science

Electronic Supporting Information

Supramolecular Control During Triplet Sensitized Geometric Isomerization of Stilbenes Encapsulated in a Water Soluble Organic Capsule

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Experimental Section

Materials and Methods: Bispyridylethylene (**8**), 4-stilbazole (**9**), 4,4'-dimethylbenzil (**10**), 9-fluorenone (**11**), and 1′-acetonaphthone (**12**), 2′-acetonaphthone (**13**), (from Sigma-Aldrich/Acros) were used as received. The host OA, *cis* and *trans* stilbene derivatives (**1**-**6**), methylstilbazolium salt (**7**) were synthesized following literature procedure.

NMR experiments: NMR studies were carried out on a Bruker 500 MHz NMR spectrometer at 25 °C. Diffusion coefficients for the capsular assemblies were determined by using gradient field in Bruker 500 MHz NMR spectrometer at 25 ^{o}C. Data were collected by using 'stebpg1s' pulse sequence, Δ = 99.9 ms, δ = 3.6 ms, pulsed field gradients were incremented linearly from 1.06 (2 % of field gradient strength) to 50.35 G/cm (95 % of field gradient strength) in 16 steps with each step consisting of 8 scans. The collected data were processed by T_1/T_2 relaxation module in the TOPSIN 2.1 software.

Phosphorescence emission experiments: Phosphorescence lifetimes were measured on an OB920 fluorometer (Edinburgh Analytical Instruments) using a pulsed microsecond xenon lamp as excitation source and multi-channel scaling for data acquisition at λ_{ex} 318 nm and λ_{em} 560 nm.

^{1}H NMR and diffusion NMR studies with guests@(OA): 600 µL of a D_2O solution of host OA (1 mM OA in 10 mM $Na_2B_4O_7$) was taken in a NMR tube and to this 0.25 equivalent increment of guest (2.5 µL of a 60 mM solution in DMSO-d_6) was added. The ^{1}H NMR experiments were carried out after shaking the NMR tube for 5 min after each addition. Completion of complexation was monitored by disappearance of the free host OA signals upon the addition of guest. Further, diffusion experiments were carried out to characterize capsular assemblies.

Sample preparation for luminescence measurements: Capsular assemblies of **10** in 1 mM concentration of OA were made separately by adding 5 µL of 60 mM solution of guest (in DMSO solution) to 0.6 mL of 1 mM OA in 10 mM borate buffer in H_2O for a 2:1 (H:G) capsular assembly. This solution was then diluted to make final guest solution of 10^{-5} M. Standard solution of quencher **7** was prepared in 10 mM borate buffer solution. In the case of *cis/trans* **1** and **3** capsular assembly was prepared by adding 5 µL of 60 mM solution of guest (in DMSO solution) to 0.6 mL of 1 mM OA in 10 mM borate buffer in H_2O. Similarly it was further diluted

appropriately with 10 mM buffer solution to have the required concentration of bound guest. The solutions were deoxygenated by purging with nitrogen or argon gas for 60 min prior to the emission studies. To this solution calculated amount of quencher solution was added to make solutions with known quencher concentrations. The bimolecular quenching rate constants were derived from the slope of the plot of quencher concentration vs. triplet state decay constant ($1/\tau$).

Sample preparation for sensitized photoisomerization: For sensitization experiments, the capsules of **(11)**$_2$@(OA)$_2$, **(12)**$_2$@(OA)$_2$ and **(13)**$_2$@(OA)$_2$ were prepared by adding 20 µL of 60 mM standard guest solution to 0.6 mL of 2 mM of OA in 20 mM of borate buffer solution and stilbenes@(OA)$_2$ were made by adding 10 µL of 60 mM standard guest solution to 0.6 mL of 2 mM of OA in 20 mM of borate buffer solution. ^{1}H NMR spectrum of this solution was recorded to confirm the formation of capsular assemblies. Then these two solutions were mixed together in equal amount and ^{1}H NMR were recorded and observed that each capsular assembly was intact in presence of the other. Selective excitation of encapsulated donors in presence of stilbenes@(OA)$_2$ was achieved with 450 W medium pressure mercury lamp using 380 nm cut off filter for **(11)**$_2$@(OA)$_2$ and 370 nm cut off filter for **(12)**$_2$@(OA)$_2$ and **(13)**$_2$@(OA)$_2$. For acceptor **7**, sensitizitaion was carried out in CD_3CN and in buffered D_2O by free donor and encapsulated donor respectively using 420 nm cut off filter.

NMR competition study with stilbene derivatives: For the competition studies with *trans* and *cis* stilbene derivatives, the complex of stilbene@(OA)$_2$ was taken in NMR tube. A solution of other isomer in DMSO-d_6 was gradually added to it and the binding behavior was monitored by ^{1}H NMR. For example, in the case of guest **1**, addition of one equivalent of *trans* derivative (with respect to one equivalent of *cis* derivative) to *cis* complex (*cis*-**1**@(OA)$_2$) resulted in complete displacement of the encapsulated *cis*-**1** within 1 h. On the other hand, the reverse experiment carried out by adding 1.5 equivalents of *cis* counterpart, to *trans*-**1**@(OA)$_2$ (with respect to one equivalent *trans*) resulted in no displacement of encapsulated *trans*-**1** from its capsular complex.

Synthesis of methylstilbazolium salt (7). In 10 mL of acetonitrile 1 g of stilbazole was dissolved and to this solution 10 equivalent of MeI was added and refluxed for 2 h. After that the solvent and excess MeI was distilled out. Product was extracted in $CHCl_3$ layer and dried over Na_2SO_4. $CHCl_3$ was distilled out to obtain pure product of *methylstilbazolium salt* with yield 875 mg.

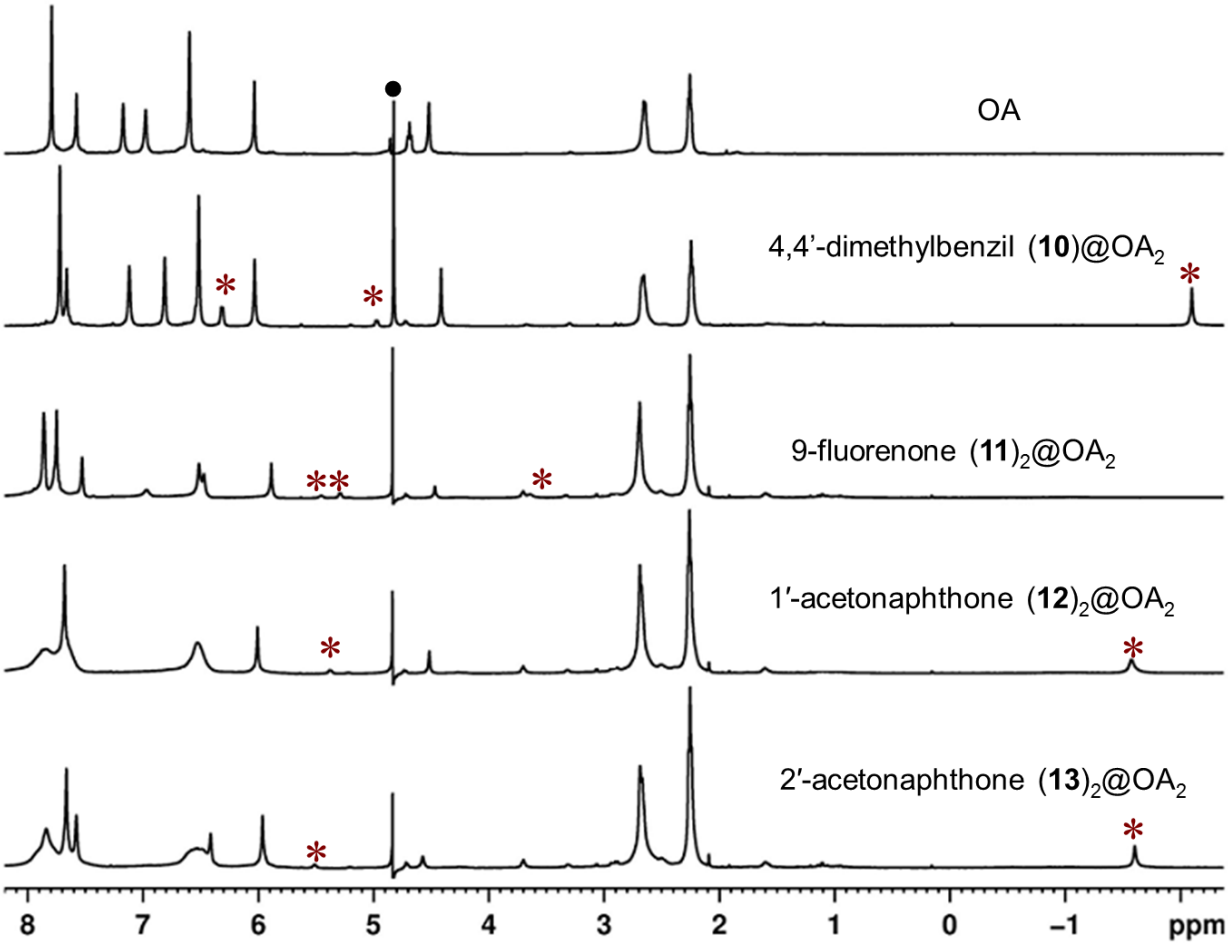

Figure S1 ^{1}H NMR spectra of capsular assemblies of donors in 10 mM borate buffer (500 MHz, [OA] = 1 mM). '∗' represents bound guest signal and '•' represents the residual proton resonances from D_2O.

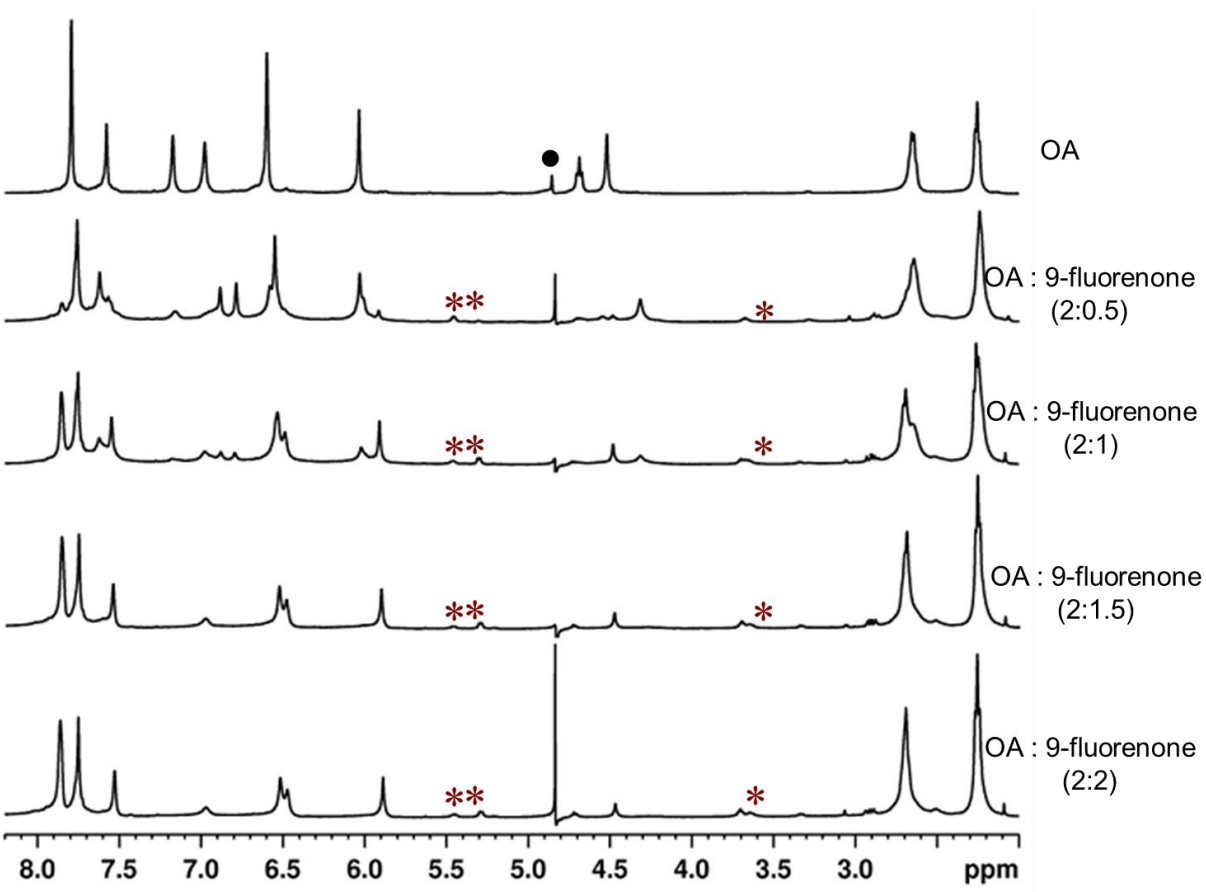

Figure S2 ^{1}H NMR titration spectra of 9-fluorenone (**11**) with OA (500 MHz, [OA] = 1 mM, buffer 10 mM). '∗' represents bound guest signal and '●' represents the residual proton resonances from D_2O.

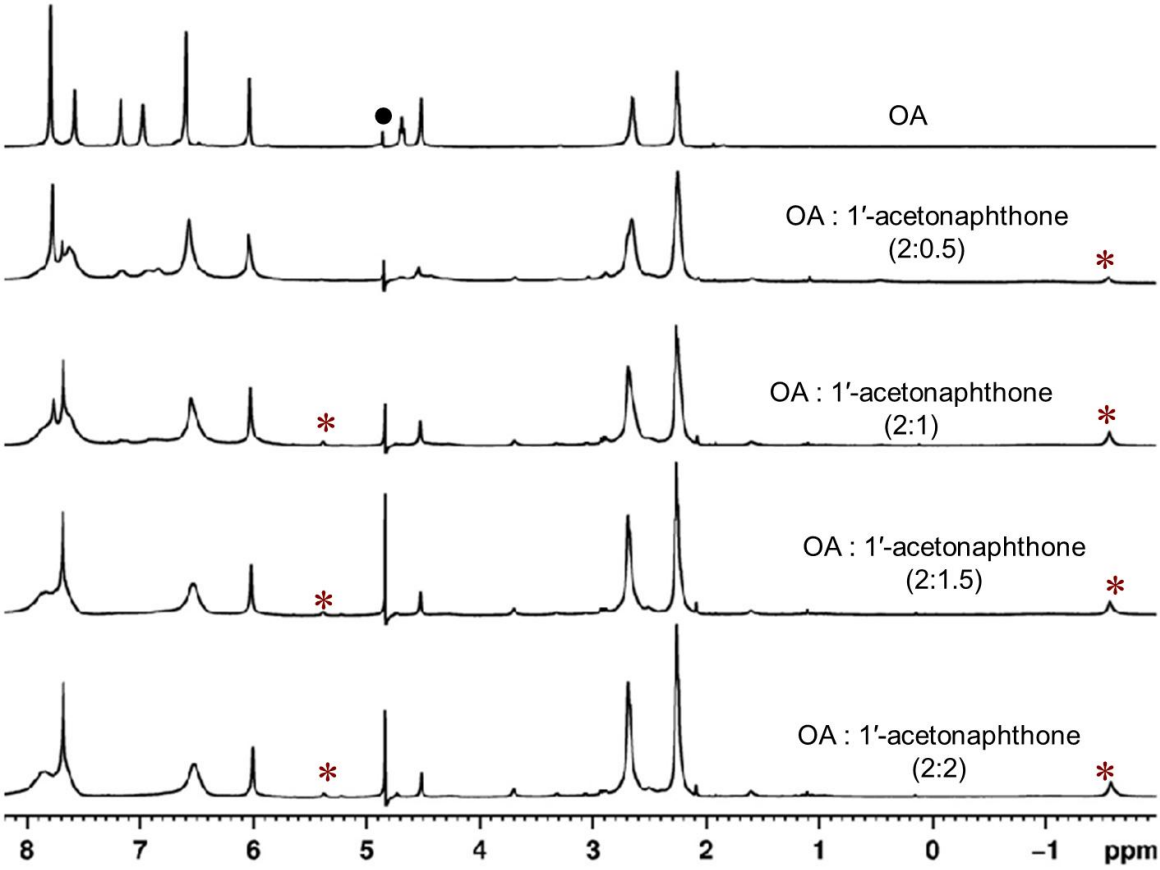

Figure S3 ^{1}H NMR titration spectra of 1′-acetonaphthone (**12**) with OA (500 MHz, [OA] = 1 mM, buffer 10 mM). '∗' represents bound guest signal and '●' represents the residual proton resonances from D_2O.

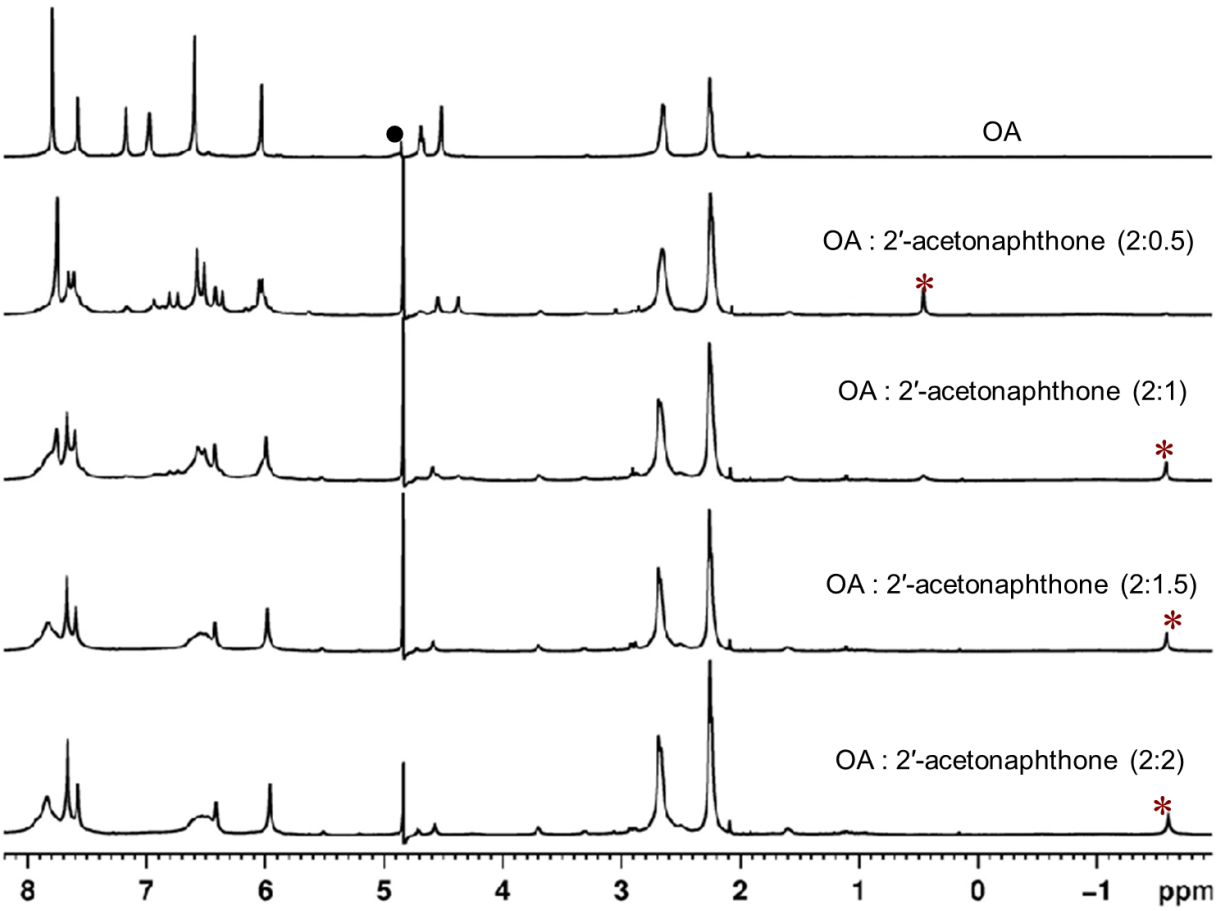

Figure S4 ^{1}H NMR titration spectra of 2′-acetonaphthone (**13**) with OA (500 MHz, [OA] = 1 mM, buffer 10 mM). '∗' represents bound guest signal and '•' represents the residual proton resonances from D_2O.

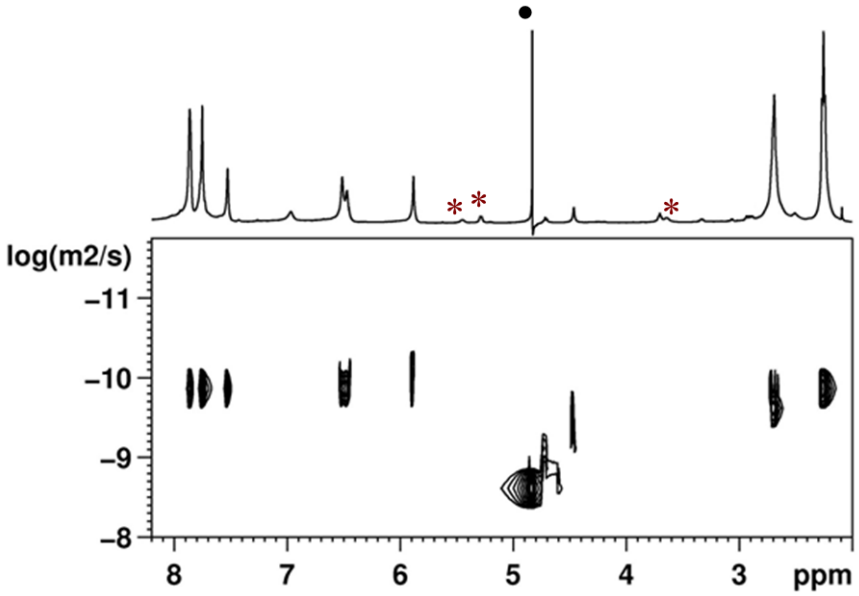

Figure S5 2D-DOSY spectra of 9-fluorenone (**11**)$_2$@ OA_2 (500 MHz, [OA] = 1 mM, buffer 10 mM). '∗' represents bound guest signal and '•' represents the residual proton resonances from D_2O.

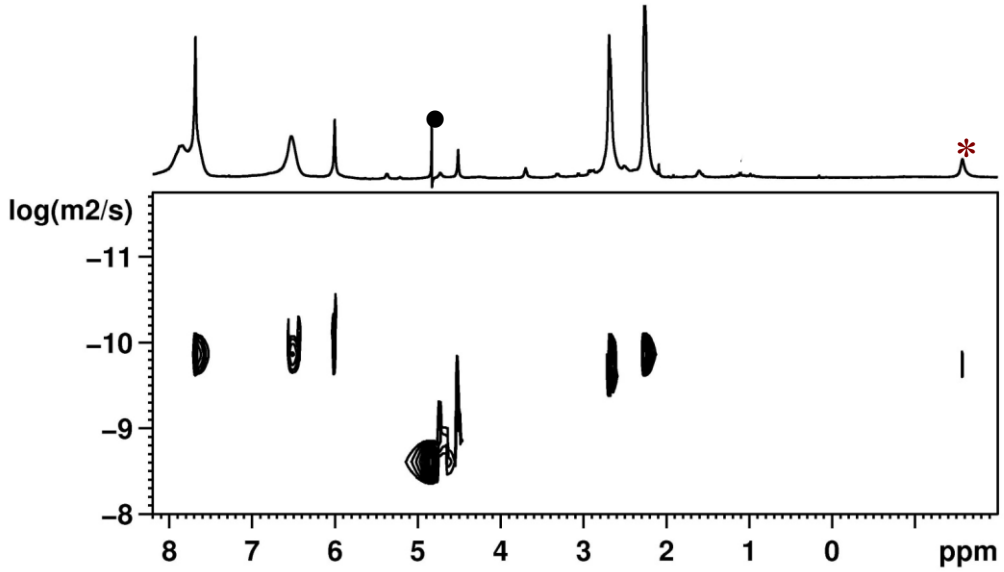

Figure S6 2D-DOSY spectra 1′-acetonaphthone (**12**)$_2$@ OA_2 (500 MHz, [OA] = 1 mM, buffer 10 mM). '∗' represents bound guest signal and '•' represents the residual proton resonances from D_2O.

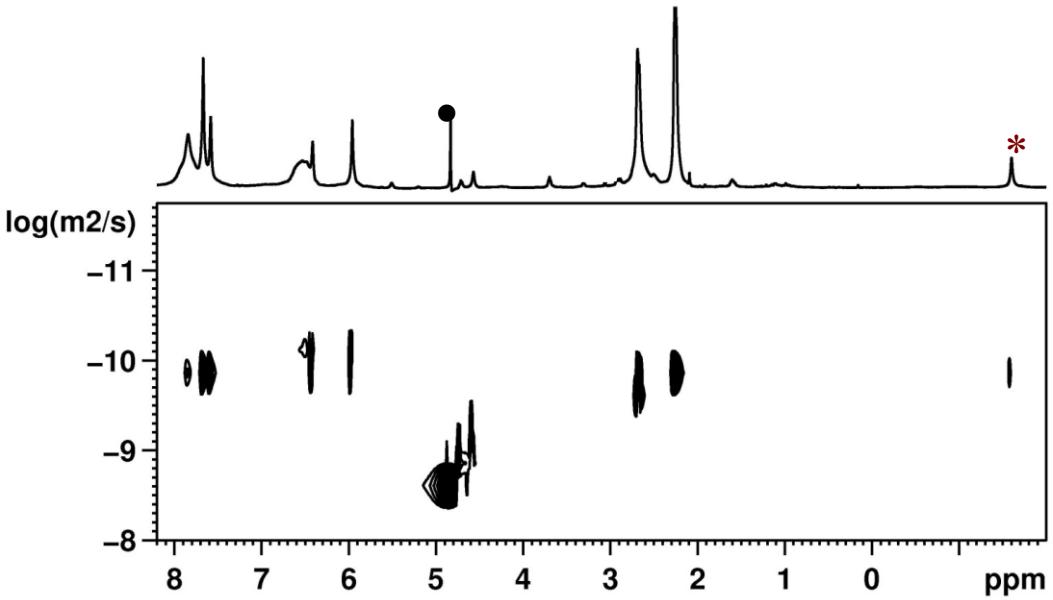

Figure S7 2D-DOSY spectra 2′-acetonaphthone (**13**)$_2$@ OA_2 (500 MHz, [OA] = 1 mM, buffer 10 mM). '∗' represents bound guest signal and '●' represents the residual proton resonances from D_2O.

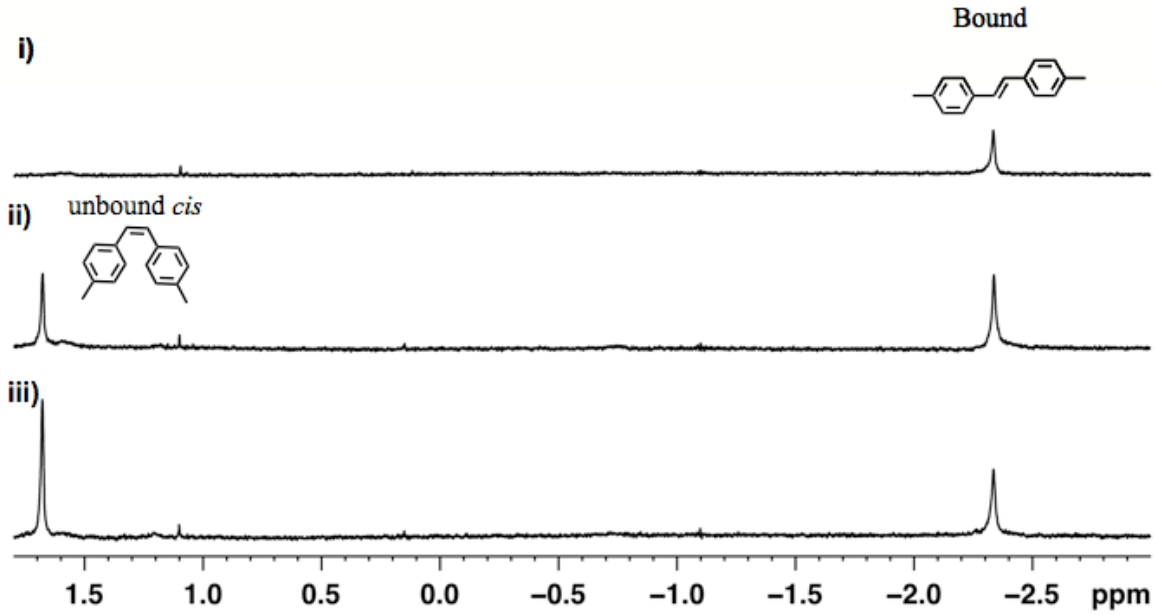

Figure S8 Partial ^{1}H NMR competition experiments between corresponding *trans* and *cis* isomers of **1** with OA, showing the formation of the capsule with the more preferred isomer in buffered D_2O (500 MHz). i) 1:2 complex of *trans*-**1** in OA. ii) Upon addition of 1 eq of *cis*-**1** to i. iii) Upon addition of 1.5 eq of *cis*-**1** to i.

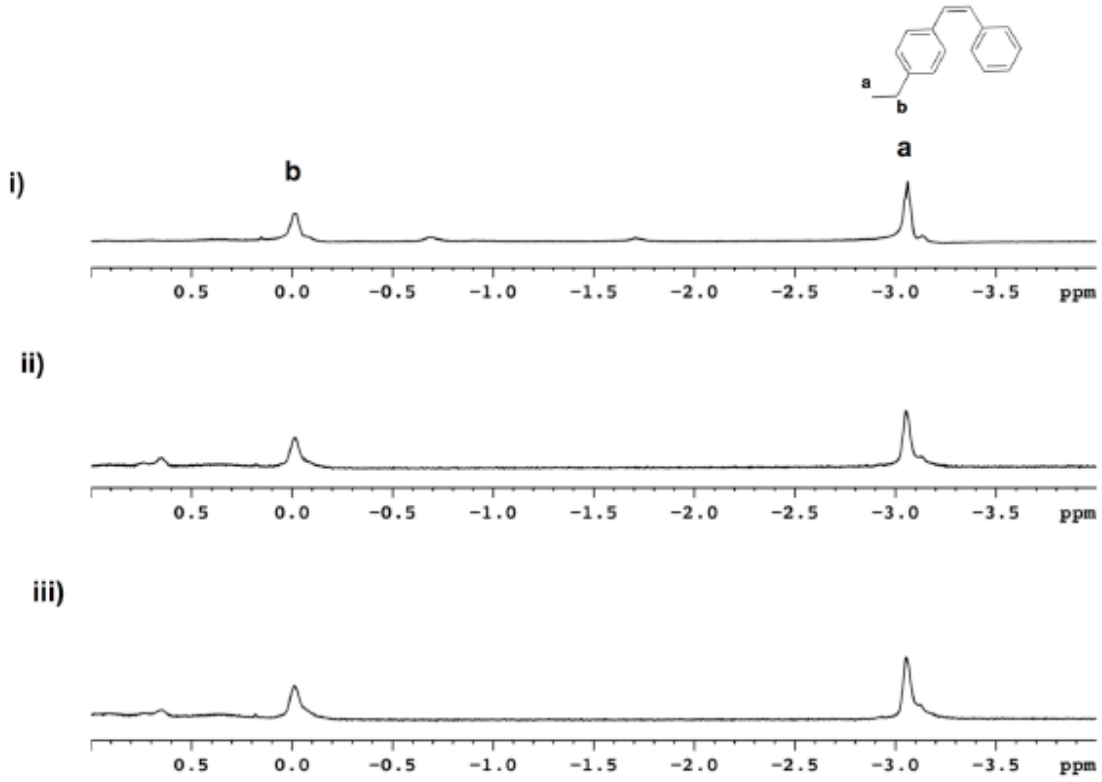

Figure S9 Partial ^{1}H NMR competition experiments between corresponding *trans* and *cis* isomers of **3** with OA, showing the formation of the capsule with the more preferred isomer in buffered D_2O (500 MHz). i) 1:2 complex of *cis*-**3** in OA. ii) Upon addition of 0.5 eq of *trans*-**3** to i. iii) Upon addition of 1.5 eq of *cis*-**3** to i.

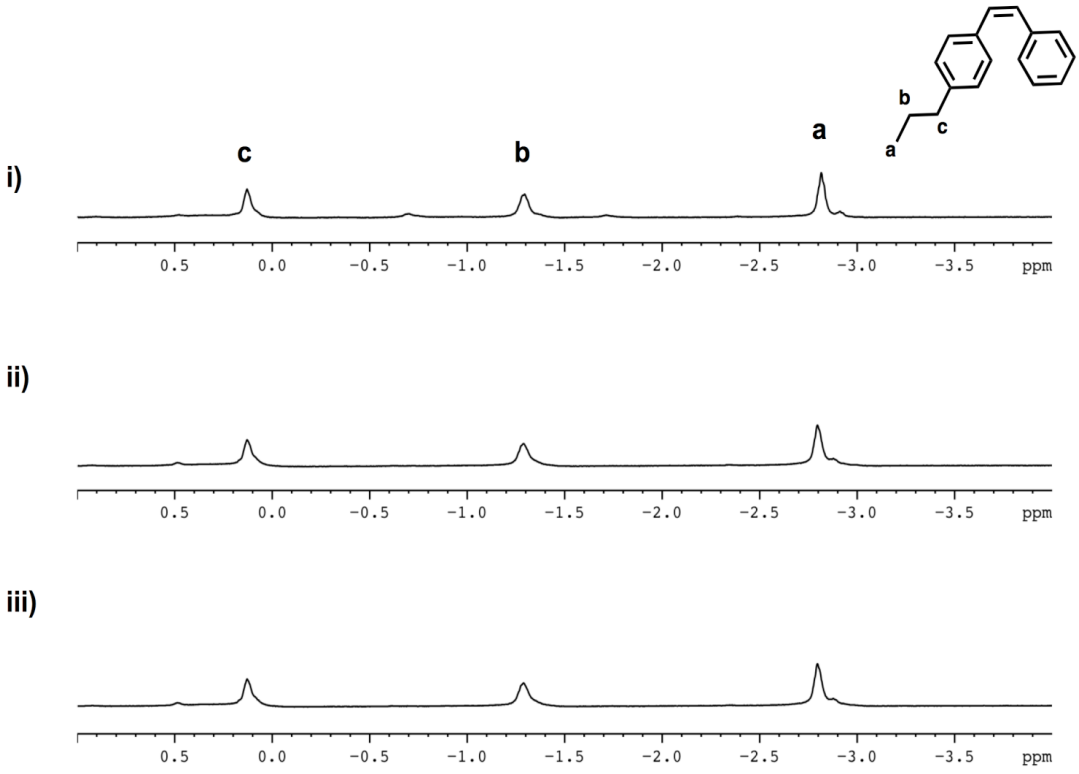

Figure S10 Partial ^{1}H NMR competition experiments between corresponding *trans* and *cis* isomers of **4** with OA, showing the formation of the capsule with the more preferred isomer in buffered D_2O (500 MHz). i) 1:2 complex of *cis*-**4** in OA. ii) Upon addition of 0.5 eq of *trans*-**4** to i. iii) Upon addition of 1.5 eq of *trans*-**4** to i.

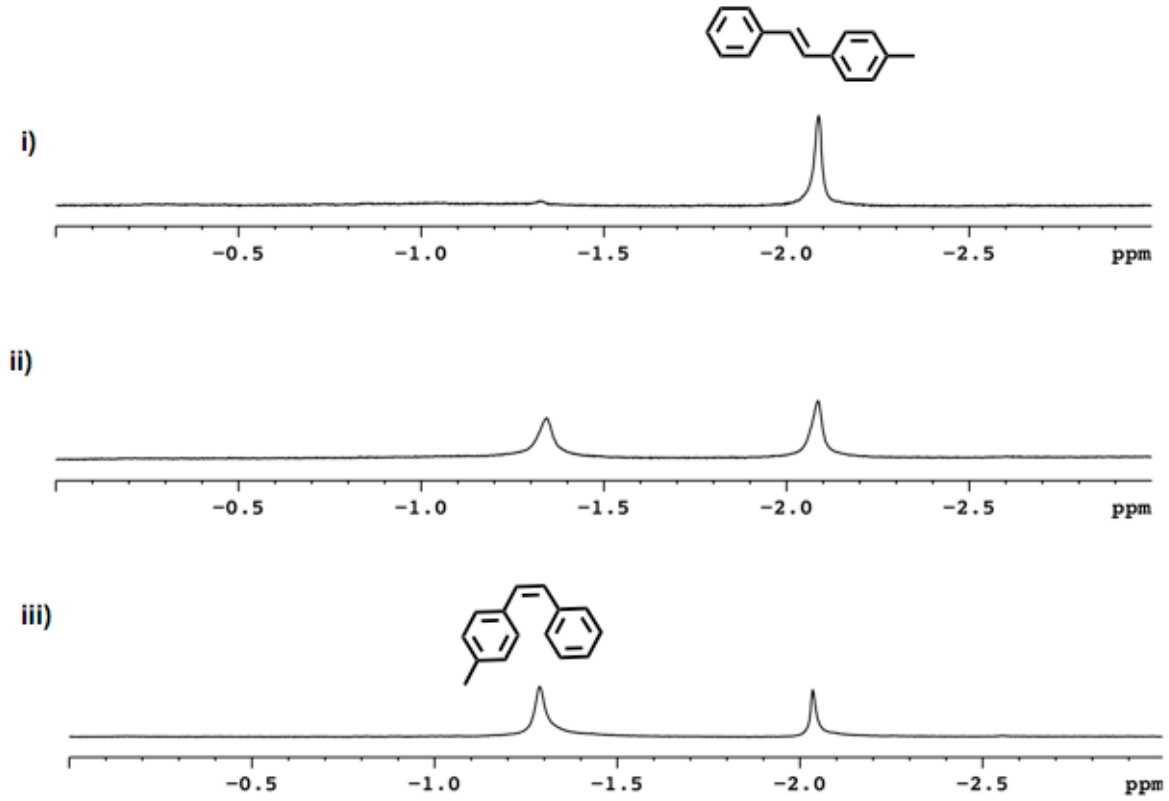

Figure S11 Partial ^{1}H NMR competition experiments between corresponding *trans* and *cis* isomers of **2** with OA, showing the formation of the capsule with the more preferred isomer in buffered D_2O (500 MHz).i) 1:2 complex of *trans*-**2** in OA. (ii) upon addition of 0.5 eq of *cis*-**2** to i.(iii) upon addition of 1.5 eq of *cis*-**2** to i.

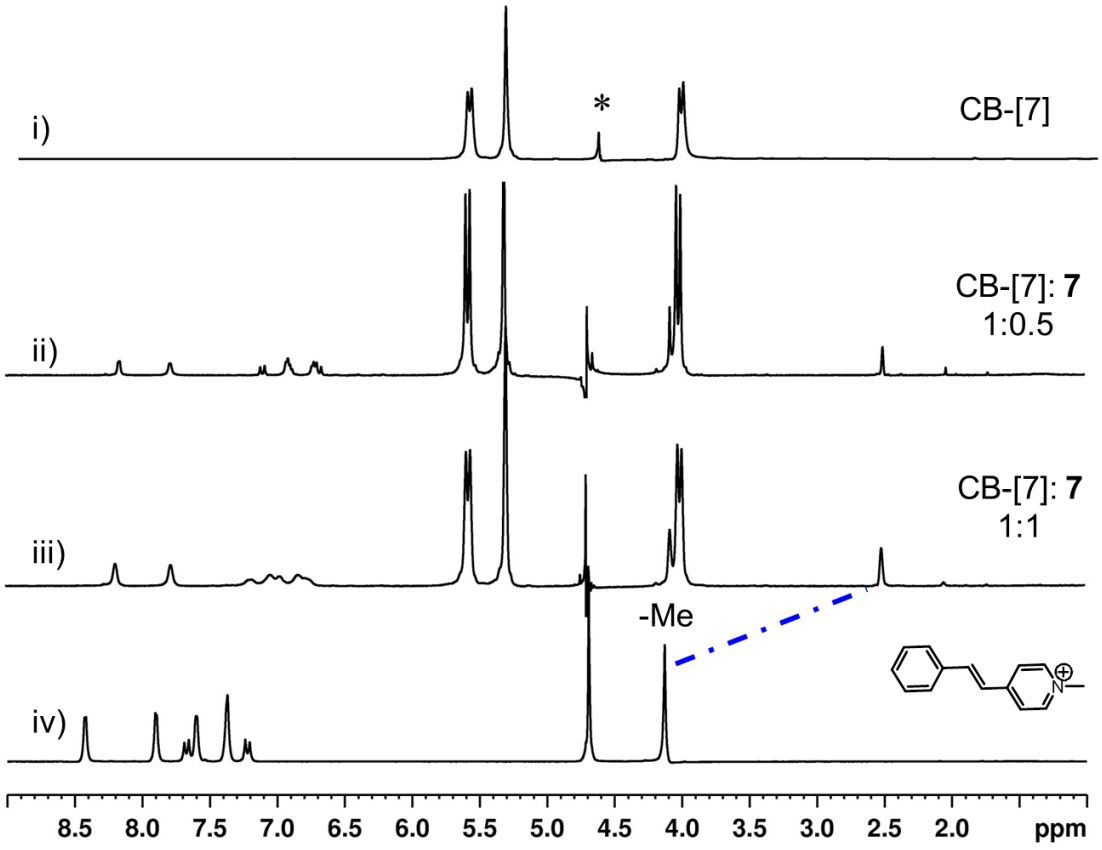

Figure S12 ^{1}H NMR of titration of CB-[7] with guest **7** in D_2O (500 MHz). i) 1 mM CB-[7] in D_2O ii) Upon addition of 0.5 eq of **7** to i. iii) Upon addition of 1 eq of **7** to i. iv) 1 mM free **7** in D_2O. '*' represents the residual proton resonances from D_2O.

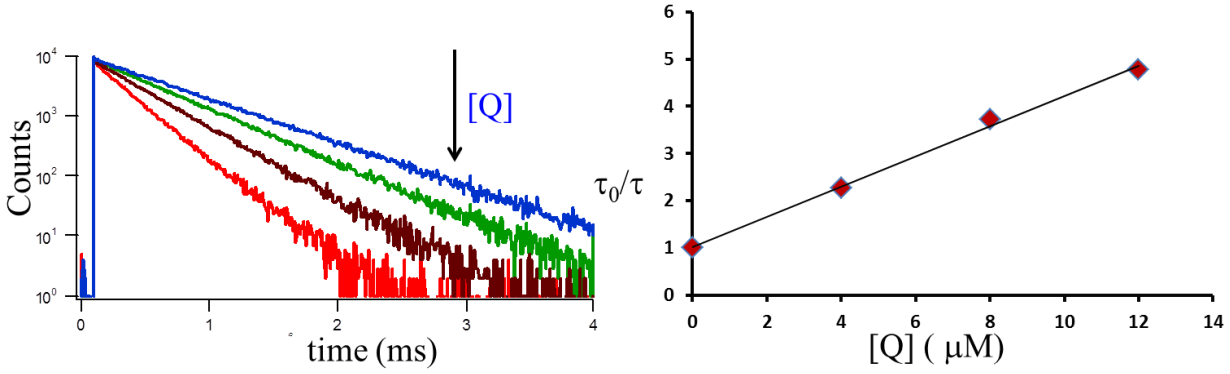

Figure S13 (left) Plot showing the quenching of triplet lifetime of **10**@OA_2 with gradual increment of concentration of **9**, (right) Stern_Volmer plot for phosphorescence quenching of **10**@OA_2 by **9** using phosphorescence lifetimes (τ_0/τ) quenching constant $k_q = (5.7\times10^8\ M^{-1}\ s^{-1})$.

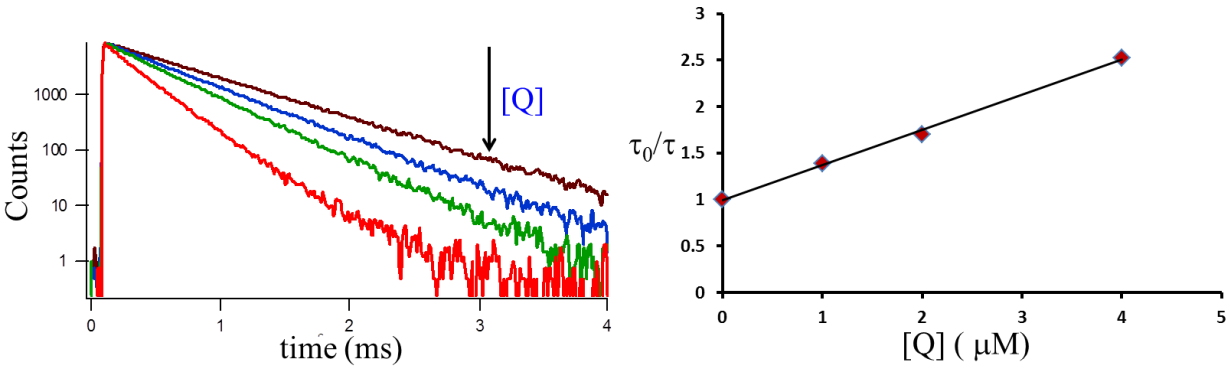

Figure S14 (left) Plot showing the quenching of triplet lifetime of 8@OA_2 with gradual increment of concentration of **8**, (right) Stern_Volmer plot for phosphorescence quenching of **10**@OA_2 by **8** using phosphorescence lifetimes (τ_0/τ) quenching constant $k_q = (6.8\times10^8\ M^{-1}\ s^{-1})$.

Table S1. Diffusion coefficients of capsular assemblies at 25 ^{o}C by pulsed field gradient NMR.

Capsular assemblies	**H:G**	**Diffusion coefficient (cm^2s^{-1})**
4,4'-Dimethylbenzil (**10**)	2:1	1.3×10^{-6}
9-fluorenone (**11**)	2:2	1.1×10^{-6}
1′-acetonaphthone (**12**)	2:2	1.1×10^{-6}
2′-acetonaphthone (**13**)	2:2	1.1×10^{-6}
OA	-	1.88×10^{-6}