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Remote Electron and Energy Transfer Sensitized Photoisomerization of Encapsulated Stilbenes

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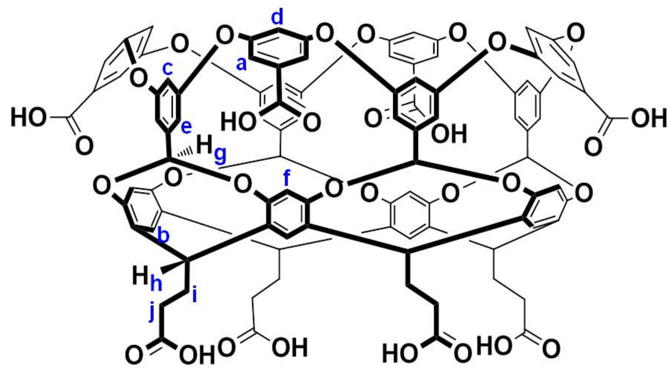
Abstract

Excited state chemistry and physics of molecules, in addition to their inherent electronic and steric features, depend on their immediate microenvironments. This study explores the influence of an organic capsule, slightly larger than the reactant molecule itself, on the excited state chemistry of the encapsulated molecule. Results presented here brings out that the confined molecule, in fact, is not isolated and can be manipulated from outside even without direct physical interaction. Examples where communication between a confined molecule and a free molecule present outside is brought about through electronic and energy transfer processes are presented. Geometric isomerization of octa acid encapsulated stilbenes induced by energy and electron transfer by cationic sensitizers that attach themselves to the anionic capsule is examined. The fact that isomerization occurs when the sensitizer present outside is excited illustrates that the reactant and sensitizer are communicating across the molecular wall of the capsule. Ability to remotely activate a confined molecule opens up new opportunities to bring about reactions of confined radical ions and triplet excited molecules generated via long distance energy and electron transfer processes.

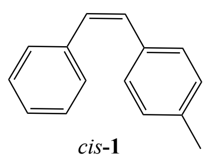
Introduction

It is a well-known fact that phototransformations of organic molecules can be brought about by direct light absorption and/or through indirect excitation via sensitization.[1-3] In the second process, a second molecule known as sensitizer absorbs the incident light and triggers energy and/or electron transfer to generate the triplet of the reactant or radical ion pairs, respectively. During the last six decades, the phenomena of triplet-triplet energy transfer and electron transfer processes have been extensively investigated and their value in chemistry, biology and materials science have been established.[1-5] During the last decade, propelled by the demand to devise 'new green synthetic methods', photochemistry, especially energy and electron transfer processes under the name of 'visible light photocatalysis' (VLPC), has witnessed a surge in activity.[6-10] For over three decades, we have been interested in manipulating photochemical reactions employing supramolecular concepts.[11-19] Envisaging that blending the concepts of supramolecular chemistry (SC)[19] and VLPC[20] would yield new opportunities in constructing organic molecules in a selective fashion, we have explored the possibility of conducting energy and electron transfer between a confined reactant molecule and a free sensitizer that is present outside the confined space. Further, ability to manipulate encapsulated molecules from outside opens up a new dimension in supramolecular photochemistry. In this context, we have recently established the occurrence of spin, energy and electron transfer between confined and free molecules through time resolved photophysical techniques.[21-30] These examples unequivocally established that communication between molecules occurs even if one of them is incarcerated in a molecular capsule. In this article, we have exploited the remote activation concept to bring about photoreactions of encapsulated molecules by activating them through energy and electron transfer sensitization from outside. In this study, the supramolecular host is a capsule made up of two molecules of a synthetic cavitand octa acid (OA),[31] the guests are stilbenes, the electron transfer sensitizer is *bis*-N-methylacridiniumnitrate (BMAN, also known as lucigenin), triplet energy transfer sensitizer is N,N,N-trimethyl-4-(phenylcarbonyl)benzenaminium iodide (4-TMABP) and the photoreaction used as the probe is the well-known geometric isomerization around C=C bond (Scheme 1).[32-34]

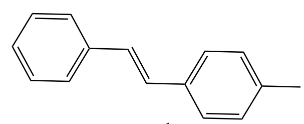
Mechanistic details of electron and energy transfer sensitized geometric isomerization of stilbenes are well documented.[32-33, 35-38] The triplet energies of *cis* and *trans*-stilbenes are closer to 57 and 49 kcal/mol respectively,[33] while oxidation potentials of these isomers are in the range of 1.75 to 2.05 eV (Ag/AgI) with *cis* ~ 0.1 eV higher than the corresponding *trans*.[32, 36] The energy transfer sensitizer 4-TMABP with triplet energy > 60 kcal/mol should be able to sensitize both isomers of stilbene while the electron transfer sensitizer with a reduction potential of - 0.3 eV (Ag/AgCl in water) and excitation energy of ~2.7 eV should be able to oxidize both isomers. Results that establish the occurrence of electron and triplet energy transfer sensitized geometric isomerization of OA encapsulated stilbenes **1**, **2** and **3** with BMAN and 4-TMABP as sensitizers are discussed in this presentation. One should note that while the triplets of stilbenes isomerize both ways (*cis* to *trans* and *trans* to *cis*),[35] the radical cations of stilbenes generated by electron transfer isomerize only one way,[36] *cis* to *trans*. Therefore, the triplet sensitization experiments with 4-TMABP were performed with both *cis* and *trans* isomers while electron transfer sensitization with BMAN was conducted only with the *cis* isomer.



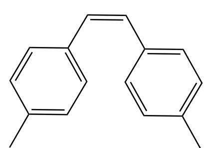
Host-Octa acid



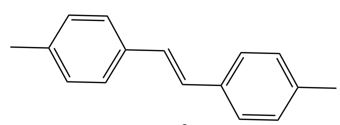
cis-**1**



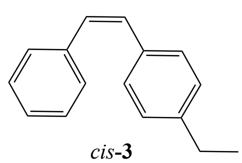
trans-**1**



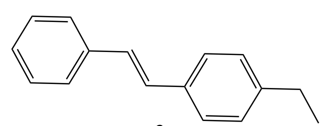
cis-**2**



trans-**2**

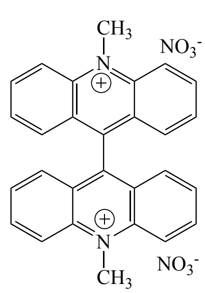


cis-**3**

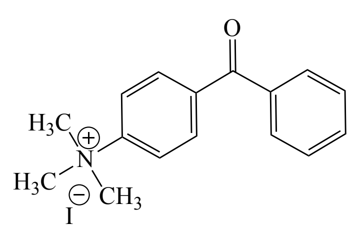


trans-**3**

Guest molecules



BMAN



4-TMABP

Scheme 1. Chemical structures of host octa acid (OA), guest stilbenes and sensitizers - N-methylacridiniumnitrate (BMAN) and N,N,N-trimethyl-4-(phenylcarbonyl) benzenaminium iodide (4-TMABP).

Experimental

General information: All commercially available chemicals were used as supplied without further purification, unless otherwise noted. ^{1}H NMR characterization, NMR titration studies and diffusion experiments were performed on Bruker Avance 500 spectrometer equipped with cryoprobe. Deuterated solvent was used as a lock and residual protonated solvent peak was used as reference. Absorption spectra were recorded on a Shimadzu UV-3150 spectrophotometer. Steady-state luminescence spectra were recorded using a FS920CDT fluorometer (Edinburgh Analytical Instruments).

Synthesis of host and guest molecules: Host octa acid (OA) was synthesized and characterized according to the reported procedure.[31] The stilbenes were synthesized according to the literature procedures.[36, 39] The bis-N-methylacridiniumnitrate was purchased from Aldrich and used as received.

Synthesis of 4-TMABP: Methyl iodide (0.93 mL, 1.5 mmol) was added dropwise to a stirred solution of 4-aminobenzophenone (10 mmol) in DMF (5 mL) at room temperature. The mixture was stirred for 24 h at 50°C. Following this, the reaction mixture was cooled to RT and diethyl ether (15 mL) was added dropwise to the solution. Resulting mixture was kept aside for 12 hour and filtered. Residue was washed with ether and dried, and crystallized at room temperature from methanol to afford 4-TMABP as a pale gray powder. Pure product (490 mg, 25%) was obtained and characterized by ^{1}H, ^{13}C NMR and Mass spectrometry.

^{1}H NMR (500 MHz, D_2O): δ 7.97 (s, 4H), 7.79 (d, 2H), 7.72 (t, 1H), 7.56 (t, 2H), 3.67 (s, 9H).

^{13}C NMR (125 MHz, D_2O): δ 198.93, 149.54, 138.68, 135.97, 134.11, 132.02, 130.37, 128.73 120.20, 56.97.

HRMS (ESI): calculated for $C_{16}H_{18}NOI^{+}$ $[M-I]^{+}$ 240.14, found 240.1394.

Complexation of guest molecules: To a D_2O (10 mM borate buffer) solution of OA (1 mM) 5 μL of 60 mM (DMSO-d_6) of guest solution was added in gradual increments. After each addition, NMR spectrum was recorded.

Identification of the location of the sensitizers: To locate the cationic sensitizers BMAN and 4-TMABP in presence of stilbene@OA_2, buffer solutions containing the capsules of *cis*-**1**@$(OA)_2$ and *trans*-**1**@$(OA)_2$ were prepared by adding 5 μL of 60 mM respective standard guest solution to 0.6 mL of 1 mM of OA in 10 mM of borate buffer solution. To this 60 μL of 20 mM of BMAN or 4-TMABP solution were added in a step wise manner. After each addition, NMR spectrum was recorded.

Irradiations: For electron transfer experiments, a solution containing *cis*-**1**@$(OA)_2$, *cis*-**2**@$(OA)_2$ and *cis*-**3**@$(OA)_2$ were prepared by adding 5 μL of 60 mM respective standard solutions to 0.6 mL of 1 mM of OA in 10 mM of borate buffer solution. To this 4 μL of 15 mM BMAN solution was added and the solution was purged with nitrogen for 20 mins. The solution was irradiated using filter (Corning CS 3-75, cut off wavelength 375 nm) and monitored over a period of time by recording ^{1}H NMR spectra. For energy transfer experiments, a solution containing *cis*-**1**@$(OA)_2$, *cis*-**2**@$(OA)_2$ and *cis*-**3**@$(OA)_2$ were prepared by adding 5 μL of 60 mM respective standard solutions to 0.6 mL of 1 mM of OA in 10 mM of borate buffer solution. To this 60 μL of 20 mM 4-TMABP solution was added and the solution irradiated using filter (Corning CS 0-51, cut off wavelength 360 nm) and monitored over a period of time by recording ^{1}H NMR spectra. Experiments with corresponding *trans*-isomers were also repeated by following a similar procedure.

Results

We have earlier reported inclusion of stilbenes within OA and their photochemistry in the confined environment of OA capsule.[39-43] This study concerns with energy and electron transfer sensitized isomerization of OA encapsulated stilbenes. Although occurrence of electron transfer across the OA capsular wall has been established through ultrafast photophysical studies,[23, 25-27] no electron transfer sensitized photoreaction of OA encapsulated molecule has been reported. Lack of clear understanding of the location of the sensitizer in the known examples of triplet sensitized isomerization of encapsulated olefins prompted us to reexamine this phenomenon.[40-41] To keep the capsule and the sensitizers closer, cationic molecules were chosen as sensitizers so that they would be electrostatically held closer to the encapsulated stilbenes by the anionic OA. To infer the location of the sensitizers, ^{1}H NMR spectra of stilbene@OA_2 capsule in the absence and presence of sensitizers were recorded. Initial experiments were focused on confirming the inclusion of stilbenes within OA and getting information on guest-host ratio.

In Figure 1, the ^{1}H NMR spectra of the two isomers of stilbene **1**-**3** in presence of OA (1:2, guest to host ratio) are displayed. Inclusion of the guest within OA is evident from the large upfield shift of the 4-alkyl group.[41] Such upfield shift is established to be a characteristic of the guest present in the cavity of OA that provides diamagnetic shielding.[44-46] Focusing on the alkyl signals, it is clear that in all three cases the signals for the *cis* and *trans* isomers appear with distinctly different chemical shifts. In the case of **3** the signals for the two isomers although closer are still distinct. This feature enabled us to follow the progress of irradiation by ^{1}H NMR.

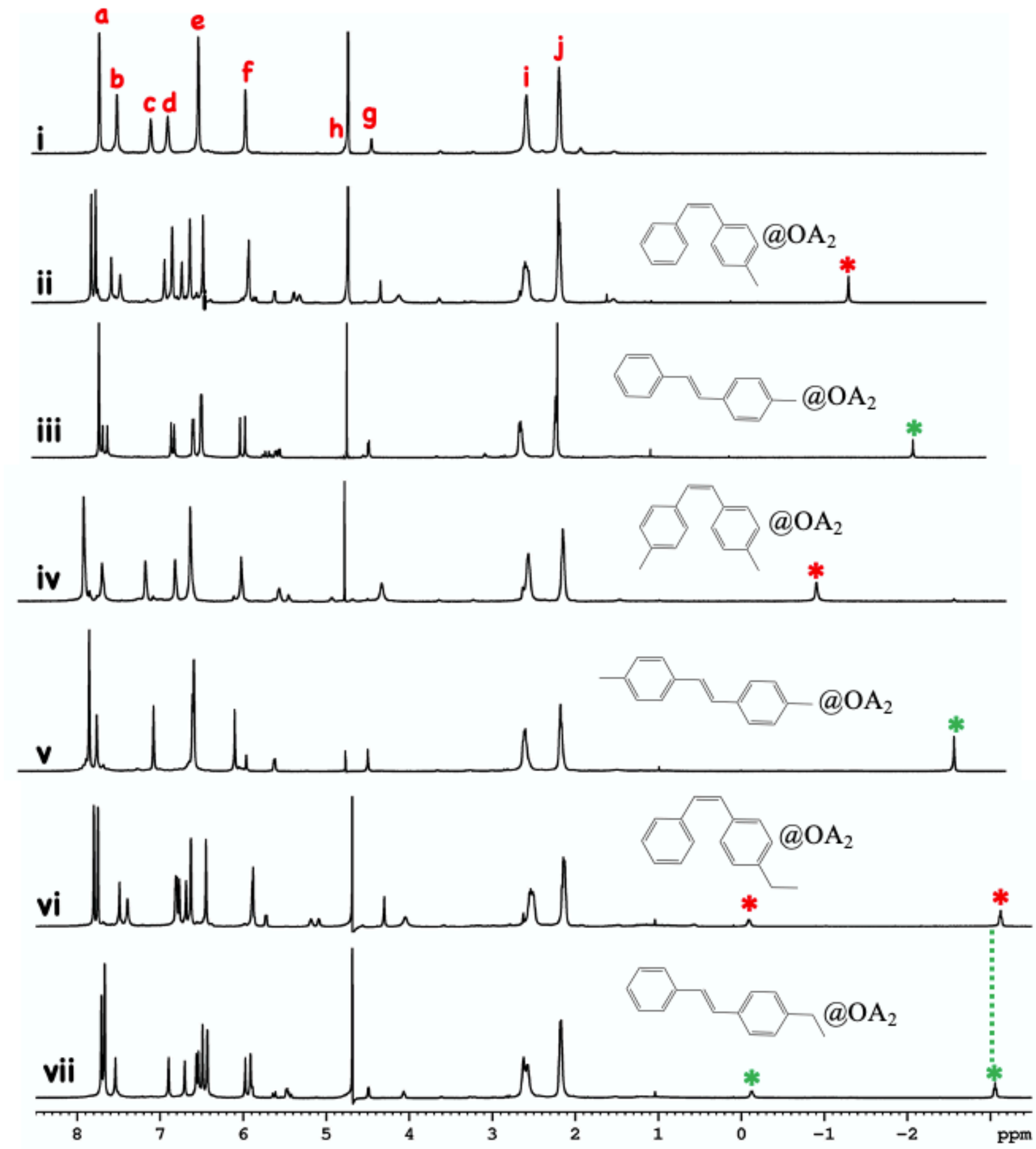


Figure 1. [1]H NMR spectra (500 MHz, D_2O) of (i) 1 mM OA in borate buffer (ii) *cis*-**1**@(OA)$_2$ (iii) *trans*-**1**@(OA)$_2$ (iv) *cis*-**2**@(OA)$_2$ (v) *trans*-**2**@(OA)$_2$ (vi) *cis*-**3**@(OA)$_2$ and (vii) *trans*-**3**@(OA)$_2$ (* & *) – represent the bound methyl protons of (*) *cis* and (*) *trans* respectively. The OA signals are identified as alphabets; see Scheme 1 for the structure of OA and the identified protons.

Based on our earlier studies we are aware that stilbenes **1-3** form 1:2 guest-host complexes.[39-40] Formation of capsular complex was further confirmed by measuring its diffusion constant by DOSY experiments. Values of diffusion constants are summarized in SI (Table S1). The values obtained for various complexes lower than that for free OA and the sensitizers, are consistent with the numbers reported in the literature for 1:2 (guest-host) complex.[44, 46]

^{1}H NMR spectra of *cis*-**1**@(OA)$_2$ in presence of BMAN and *trans*-**1**@(OA)$_2$ in presence of 4-TMABP are shown in Figures 2 and 3. Interestingly, the signals due to the guest methyl group and select hydrogens of OA are upfield shifted upon addition of the cationic sensitizers (see the green and red stars in the figure). Expanded spectrum included in each figure clearly reveals the upfield shift of the methyl signal with the increasing concentration of the cationic sensitizers. The fact that the sensitizer has a significant effect on the chemical shifts of the guest and host signals suggest that it remains closer to the host molecule. Lack of shift in the signals of the sensitizer in presence of OA suggests that the sensitizer is not included within the capsule and it is present outside in water. Based on the effect of the sensitizer on the guest chemical shift we believe that the sensitizer is associated with OA capsule as shown in Figure 4. This is also confirmed by the diffusion constant of the sensitizers in presence of the capsule. For example while BMAN and TMABP have diffusion constants of 4.35 and 5.50 x 10^{-6} cm^2/s, the termolecular complexes (stilbene@OA/sensitizer) have 1.29 and 1.88 x 10^{-6} cm^2/s respectively (Table S1 in SI). Decreased diffusion constants must be the result of the sensiztizers being attached to the capsules. The number of molecules attached to the capsule is expected to increase with the concentration which is likely to be responsible for the chemical shift dependence on the sensitizer concentration. The upfield shift in presence of cationic sensitizers, most likely, is the result of changes in the electron density of the aromatics that form the capsular wall.

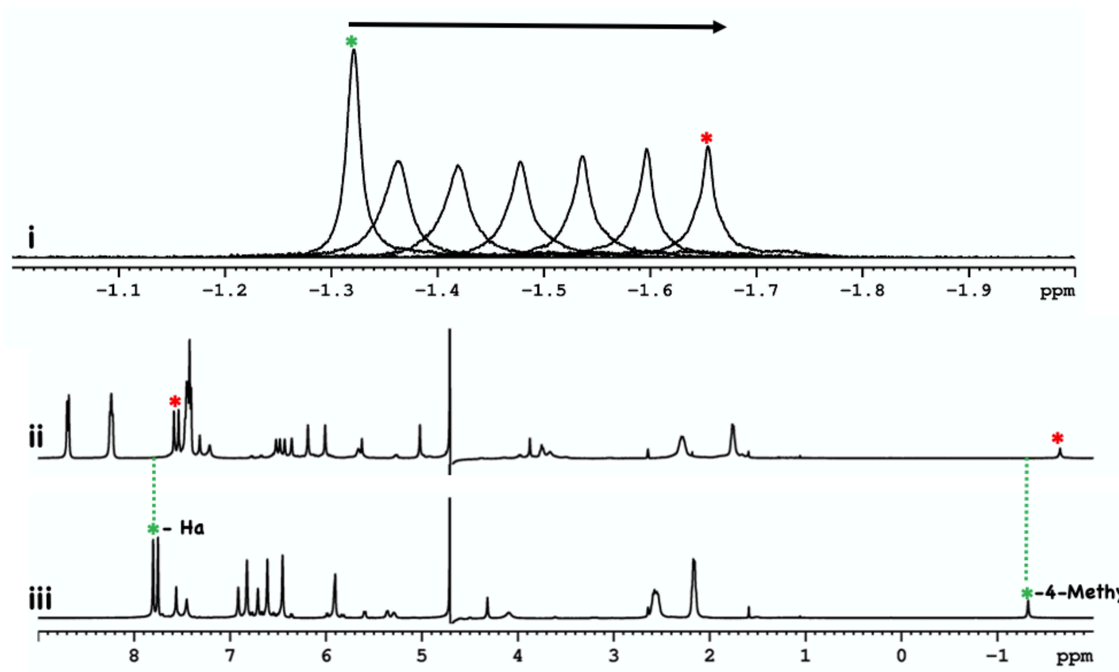


Figure 2. ^{1}H NMR spectra (500 MHz) of *cis*-**1** encapsulated within OA (1 x 10^{-3} M) in buffered D_2O in presence of BMAN. (i) NMR signal of methyl protons of *cis*-**1**@$(OA)_2$ upon slow addition of BMAN (0.33 mM to 2.0 mM) (ii) Full spectrum upon addition of 2.0 mM of BMAN to *cis*-**1**@$(OA)_2$. (iii) Full spectrum of *cis*-**1**@$(OA)_2$; no BMAN. In the above spectra (*) – indicates the signals in the absence of BMAN and (*) – indicates the signals in the presence of BMAN.

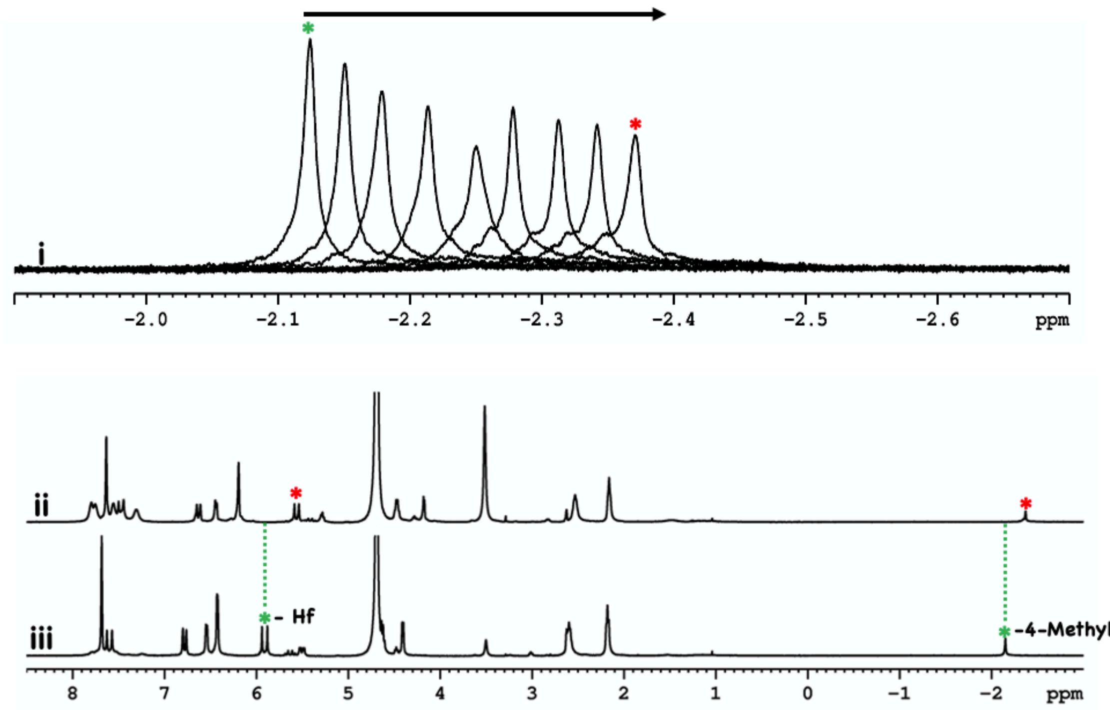


Figure 3. ^{1}H NMR spectra (500 MHz) of *trans*-**1**@(OA)$_2$ encapsulated within OA (1 x 10^{-3} M) in buffered D_2O with slow addition of (0.33 mM to 2.0 mM) (i) expanded NMR region of methyl protons of *trans*-**1**@(OA)$_2$ with slow addition of of 4-TMABP (ii) addition of 2.0 mM of 4-TMABP (iii) *trans*-**1**@(OA)$_2$ only. (*) – represents the *trans*-**1**@(OA)$_2$ and (*) – represent the *trans*-**1**@(OA)$_2$ with 4-TMABP.

^{1}H NMR spectra (500 MHz) of *trans*-**1** encapsulated within OA (1 x 10^{-3} M) in buffered D_2O in presence of 4-TMABP. (i) NMR signal of methyl protons of *trans*-**1**@(OA)$_2$ upon slow addition of 4-TMABP (0.33 mM to 2.0 mM) (ii) Full spectrum upon addition of 2.0 mM of 4-TMABP to *trans*-**1**@(OA)$_2$. (iii) Full spectrum of *trans*-**1**@(OA)$_2$; no 4-TMABP. In the above spectra (*) – indicates the signals in the absence of 4-TMABP and (*) – indicates the signals in the presence of 4-TMABP.

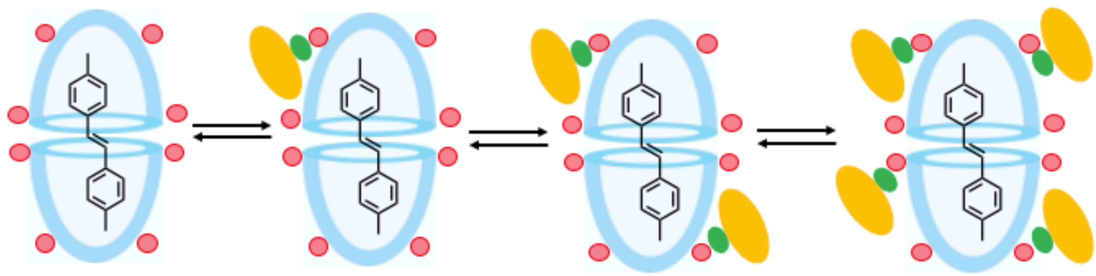


Figure 4. Graphical representation of association of the cationic sensitizer to the capsule. We believe with increasing concentration of the sensitizer the number of sensitizer molecules attached to the capsule would increase. Red circles represent COO^{-} and green ovals $(CH_3)_3N^{+}$.

Having established nature of the complexes and location of the sensitizers we proceeded to irradiate the stilbene@OA_2–sensitizer complexes in borate buffer. Control experiments showed that these solutions were stable in dark for days. Since host OA is known to act as an energy and electron transfer sensitizer[47] and stilbenes photoisomerize upon direct light absorption[35] we made sure that light is absorbed only by the sensitizer. The absorption spectra of the complex, sensitizers and the filters used are provided in Figure 5. Under our irradiation conditions (with Corning filters 0-51 and 3-75) the light is absorbed mainly by the sensitizers. Therefore, geometric isomerization reported here, we believe is mainly due to the sensitization by BMAN and 4-TMABP and not due to direct absorption by encapsulated stilbenes. To confirm this, we carried out control experiments for the stilbene complexes using the same filter but without sensitizers. Less than 15% isomerization occurred under these conditions. Results of these irradiations are included in Table 1.

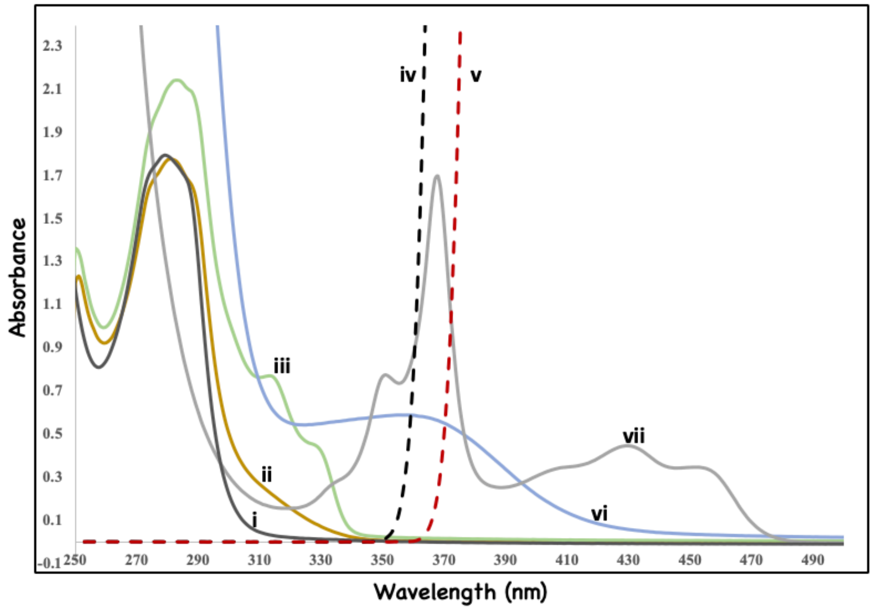


Figure 5. Absorption spectra of (i) OA ([OA] = 1 X 10^{-4} M) (ii) *cis*-**1**@$(OA)_2$ ([*cis*-**1**] = 1 X 10^{-4} M : [OA] = 2 X 10^{-4} M) (iii) *trans*-**1**@$(OA)_2$ ([*trans*-**1**] = 1 X 10^{-4} M : [OA] = 2 X 10^{-4} M) (iv) Filter 0-51(v) Filter 3-75 (vi) 4-TMABP ([4-TMABP] = 0.5 X 10^{-4} M) and (vii) BMAN ([BMAN] = 0.5 X 10^{-4} M).

We chose BMAN to test the feasibility of electron transfer sensitized isomerization across the OA wall. Sensitization with BMAN was carried out using Corning 3-75 filter (Figure 5). Prior to this study we attempted sensitization with dimethyl viologen, N-methylacridinium iodide, dimethyldiazaphenanthrenium iodide and dimethyldiazapyrenium iodide.[47] But none of them were effective in generating the *cis* radical cation. Various problems confounded the choice: absorption in the case of dimethyl viologen, poor stability in water in the case of N-methylacridinium iodide and not enough oxidizing power in the case of the last two. Therefore, BMAN with stronger oxidizing power and longer absorption seemed promising.[48-50] As seen in Table 1 it was effective as the sensitizer. Photoisomerization occurred in the time range of 4-10 hrs. ^{1}H NMR spectra of the irradiated samples of *cis*-**1**@$(OA)_2$ are shown in Figure 6. The spectra for others are provided in SI (Figure S20-S21). Clearly, the *cis* isomer gave the *trans* without any side reactions and as expected conversion was 100%. However, BMAN was found to be unstable in water upon prolonged (>5 h) irradiation.[50] But the amount of BMAN used was sufficient to function as the sensitizer.

Table 1. Product distribution upon energy and electron transfer sensitized geometric isomerization of OA encapsulated stilbenes.

Compound	Photostationary state during energy transfer sensitization with 4-TMABP [a, b, c]				Product distribution during electron transfer sensitization by BMAN[c, d, e]	
	starting isomer: 100% *cis*		starting isomer: 100% *trans*		starting isomer: 100% *cis*	
	cis	*trans*	*cis*	*trans*	*cis*	*trans*
1@(OA)$_2$[a]	50	50	49	51	10	90
1@(OA)$_2$-control[*b*]	85	15	5	95	90	10
2@(OA)$_2$ [a]	0	100	0	100	0	100
2@(OA)$_2$-control[*b*]	81	19	0	100	85	15
3@(OA)$_2$ [a]	84	16	85	15	73	27
3@(OA)$_2$-control[*b*]	96	4	14	86	100	0

a: Irradiation times for energy transfer experiments were ~72 h; numbers entered are average of 3 runs.

b: Note irradiations were done starting from pure cis and pure trans.

c: Control experiments did not use sensitizers.

d: Irradiation times for electron transfer experiments varied between 4-10 h; numbers entered are average of 3 runs.

e: Note irradiations were done starting from pure cis only

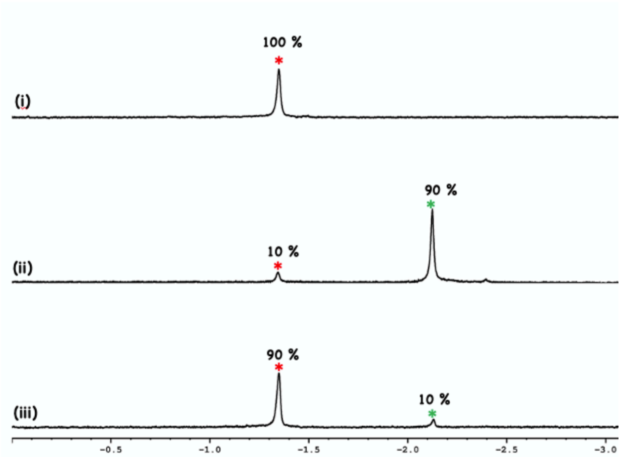


Figure 6. Partial ^{1}H NMR spectra (500 MHz) of *cis*-**1**@(OA)2 encapsulated within OA ($1x10^{-3}$ M) in buffered D_2O after added photocatalyst BMAN (i) before irradiation (ii) after 4 hour irradiation (iii) without BMAN after 24 hour irradiation (control).

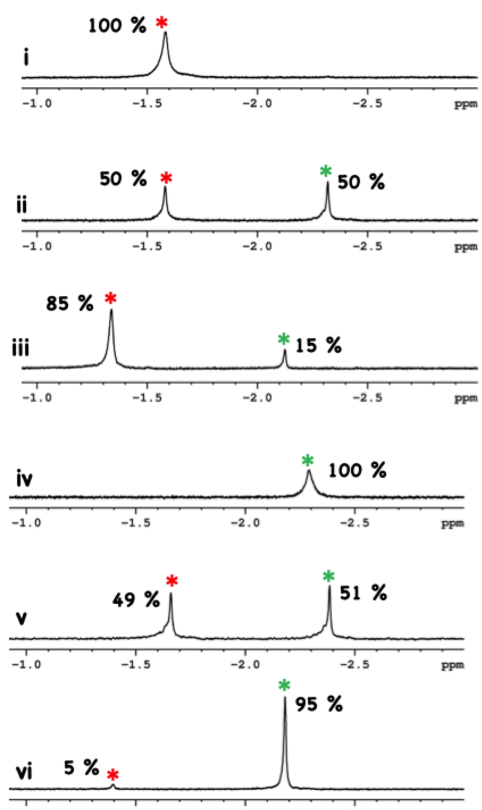


Figure 7. Partial ^{1}H NMR spectra (500 MHz) of *cis*-**1**@$(OA)_2$ and *trans*-**1**@$(OA)_2$ encapsulated within OA (1 X 10^{-3} M) in buffered D_2O after added sensitizer 4-TMABP (i & iv) initial (ii & v) after 72 hour irradiation (iii & vi) without 4-TMABP after 72 hour irradiation (control). (* & *) – represent the bound methyl protons of (*) *cis* and (*) *trans* respectively.

In the case of 4-TMABP sensitization, six samples (*cis* and *trans* isomers of **1**, **2** and **3**) along with controls were irradiated using light from 450 W medium pressure mercury lamp filtered through Corning 0-51 filter (Figure 5). The concentrations of the stilbenes (**1**, **2** and **3**) and the 4-TMABP were 0.5 mM and 2 mM respectively. Control without 4-TMABP under the same conditions was carried out. The progress of the reaction was followed by recording ^{1}H NMR and integrating the signals due to 4-alkyl group of the stilbenes. Because of the use of cut-off filters it took > 70 h to reach the photostationary state (pss). The percentage of *trans* and *cis* isomers at the pss starting from *trans* and *cis* isomers are provided in Table 1. ^{1}H NMR spectra of 4-TMABP sensitized isomerization of **1**@$(OA)_2$ are shown in Figure 7. For the other stilbenes the spectra are provided in SI (Figures S18-S19). It is important to note that isomerization was much less effective in the absence of the sensitizer (control). For example, in the case of **1**@$(OA)_2$, in the absence of the sensitizer the *cis* isomerized to 15% *trans* while upon sensitization it gave 50% *trans*. Similarly, the *trans*-**1** gave 5% *cis* by direct light absorption and 49% by sensitization. Similar observations were made with other two stilbenes **2** and **3**. These observations clearly establish that 4-TMABP functions as a sensitizer in the photoisomerizations listed in Table 1. The fact that both *cis* and *trans* isomers could be sensitized suggests certainly sensitization is not through electron transfer but energy transfer.

Discussion

Photoinduced electron transfer sensitized geometric isomerization of stilbenes has been investigated in detail by Lewis group.[36-37] Sensitization by 9-cyanoanthracene, 9,10-dicyanoanthracene, 2,6,9,10-tetracyanoanthracene and N-methylacridinium hexafluorophosphate (NMA) is demonstrated to be effective in converting *cis*-stilbenes to the corresponding *trans* isomers. First three are not water soluble and too large to fit within a OA capsule. Although N-methylacridinium salt is water soluble, prolonged irradiation resulted in its degradation. To overcome this problem we employed 9-mesityl N-methylacridinium salt.[51] Similar to NMA this also had poor stability in water. In addition to their poor stability the two were found to be ineffective in sensitizing the isomerization of the stilbenes.

Having eliminated the common electron transfer sensitizers, we used the less well known sensitizer BMAN (dimeric form of NMA) for inducing geometric isomerization of the encapsulated *cis*-stilbenes.[50] Its absorption in the visible extending up to 480 nm (2.58 eV) permitted excitation of the sensitizer without directly exciting the stilbenes. Also its reduction potential is reported to be -0.30 eV in water where the sensitizer resides under our condition. Based on Rehm-Weller equation the free energy of electron transfer from excited BMAN to *cis*-stilbene is estimated to be exothermic by ~ 0.2 eV. For the methyl substituted stilbenes the process is even more exothermic than unsubstituted stilbene. Given that the OA has a lower oxidation potential than *cis*-stilbene, it could also act as an electron donor to the excited BMAN. Based on the estimated oxidation potential of OA (~ 1.5 eV) the free energy of electron transfer from excited BMAN to OA is estimated to be exothermic by ~ 0.7 eV. As shown in Figure 8, all three, host, guest and host-guest complex namely OA, *cis*-**1** and *cis*-**1**@OA_2 quench the fluorescence of BMAN. Since OA as well as *cis*-**1** can act as quenchers, in the case of *cis*-**1** @OA_2 it is not obvious what is the quencher, OA or *cis*-**1**. We believe that both are acting as quenchers under our condition. Since the electron transfer from *cis*-stilbene to the OA radical cation is an uphill process (+ ~ 0.5 eV; oxidation potential of *cis*-stilbene and OA are 2.06 eV and ~1.5 eV respectively), we believe any reaction that we observe must be the result of direct quenching of the excited BMAN by encapsulated *cis*-stilbene.

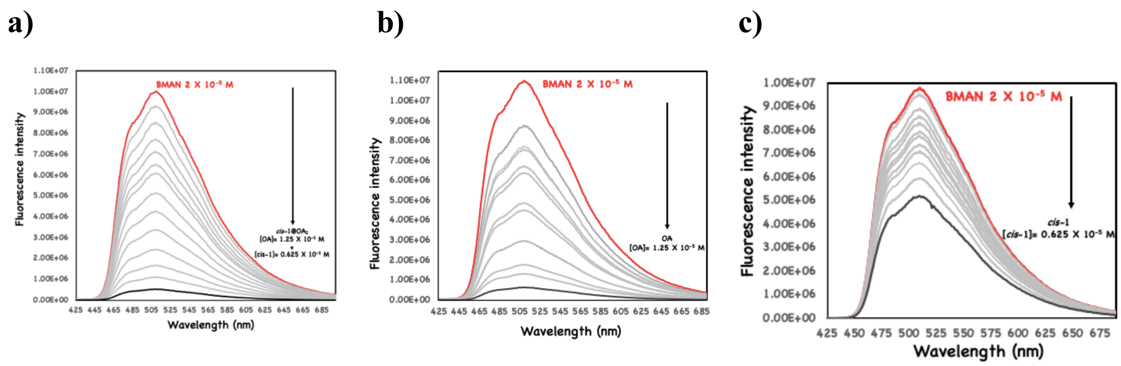


Figure 8. a) Emission spectra (λ_{exc} = 420 nm) of acceptor BMAN (red), and BMAN (black) as function of the donor (*cis*-**1**@OA_2) concentration ; ([BMAN] = 2.0 x 10^{-5} M, [*cis*-**1**]= 0 – 0.625 x 10^{-5} M + [OA]= 0 – 1.25 x 10^{-5} M in buffer/H_2O, pH = 8.7). b) Emission spectra (λ_{exc} = 420 nm) of acceptor BMAN (red), and BMAN (black) as function of the donor OA concentration ;([BMAN] = 2.0 x 10^{-5} M, [OA]= 0 – 1.25x 10^{-5} M in buffer/H_2O, pH = 8.7) **c)** Emission spectra (λ_{exc} = 420 nm) of acceptor BMAN (red), and BMAN (black) as function of the donor *cis*-**1** concentration ;([BMAN] = 2.0 x 10^{-5} M, [*cis*-**1**]= 0 – 0.625 x 10^{-5} M in buffer/H_2O, pH = 8.7)

Irradiation (> 370 nm; 450 W medium pressure mercury lamp with Corning CS 3-75) of a solution of OA encapsulated *cis*-stilbene and BMAN (0.5 mM and 0.1mM) gave the corresponding *trans* isomer quantitatively within 4 h-10 h. Under the same conditions without BMAN the isomerization was slow and 10% *trans* isomer was formed even after 24 h of irradiation. As shown in Figure 6 and Figures S20 and S21 for the three stilbenes (**1**-**3**) the isomerization is clean and no other products were formed. We believe the results support the conclusion that electron transfer from stilbene to excited BMAN does occur across the walls of the OA capsule. Clearly, photoreaction of encapsulated molecules can be initiated by molecules that stay outside the capsule. Such a possibility opens an opportunity to remote trigger photoreactions via electron transfer. While the results presented here establish the phenomenon, we are yet to find a good electron transfer sensitizer that would be stable and function in water. Unfortunately, BMAN degrades slowly in water under our irradiation conditions. This prompts us to continue our search for a better electron transfer sensitizer in the context of remote sensitization in water.

We visualized that a combination of supramolecular photochemistry[11, 19, 52] and triplet-triplet energy transfer[4] would be a valuable tool to manipulate excited state reactions. Following the remarkable discovery of triplet-triplet energy transfer in a rigid solution at 77°K by Terenin and Ermolaev,[53] the value of this process in organic photochemistry was established by Hammond and his students in the 60s.[35, 54-59] Recently, this technique has re-emerged in the context of finding new green synthetic methods to build organic molecules.[7, 10] To be effective as the triplet sensitizer under our conditions, the sensitizer must remain closer to the capsule and also should be water-soluble. However, the common well-known organic sensitizers are generally water insoluble. We overcame this problem by functionalizing the well-known sensitizer benzophenone with an ammonium group that would not only make them water soluble but also get them non-covalently attached to the anionic capsule. As evident from the ^{1}H NMR spectra in Figure 3, sensitizer 4-TMABP remains closer to the capsule in aqueous solution. The up-field shift of the ^{1}H signals of the host as well as guest with the increasing concentration of the sensitizer is a direct result of the proximity of the capsule and the sensitizer. This feature we believe will facilitate double electron transfer (collisional energy transfer) across the capsular wall.

The emission spectrum of TMABP in aqueous solution at room temperature is shown in Figure S17 in SI. Since the emission is not quenched by oxygen we believe this to be fluorescence. Based on the 0-0 band the S_1 energy of the sensitizer is estimated to be 71 kcal/mol (400 nm). Currently, we do not know the nature of the lowest excited state (nπ* or $\pi\pi$*). Independent of this, it is safe to assume the lowest triplet of 4-TMABP to be above 60 kcal/mol (benzophenone: 69 kcal/mol). With the triplet energies of *cis* and *trans*-stilbenes estimated to be 57 and 49 kcal/mol respectively, we believe that 4-TMABP would be able to sensitize both isomers. The three stilbenes chosen for investigation have unique behavior within OA. For example, within the OA capsule the three chosen olefins behave differently:[42] at the pss *cis* and *trans* isomers are present in equal amounts in **1**, *trans* rich in the case of **2**, and *cis* rich in the case of **3**. Therefore, based on the photostationary state achieved one could infer whether the reaction occurred within OA or in aqueous solution. With this background we analyze the results summarized in Table 1.

Irradiations were performed with light of wavelength >350 nm where the stilbenes do not absorb. Progress of isomerization was followed by ^{1}H NMR (Figure 7 and Figures S18 and S19 in SI). Independent of the initial isomer the same photostationary state (pss) was achieved in about 72 h. The control experiments revealed that although there is background isomerization, majority of the isomerization observed in presence of 4-TMABP is the result of sensitization. Considering the absorptions of stilbene and 4-TMABP (Figure 5), one would expect 4-TMABP to be the primary absorber under our irradiation condition. Close examination of the Table reveals, for example when **1**@$(OA)_2$ was irradiated in the absence of the sensitizer the pss contained 5 % *cis* and 95% *trans* when the starting isomer was *trans*, but the pss was 85% cis and 15% *trans* when the starting isomer was *cis*. Clearly the pss ratio is not the same starting from the two isomers. On the other hand, when [**1**@$(OA)_2$+4-TMABP] solution was irradiated the same *cis*-*trans* composition was obtained at the pss (equal amounts of *cis* and *trans*). If the isomerization is due to direct absorption the ratio would not be the same from both isomers. More importantly, in the case of **2**@$(OA)_2$ upon direct excitation about 19% of *trans* was obtained from *cis*. On the other hand, irradiation of [**2**@$(OA)_2$+4-TMABP], 100% *trans* resulted at the pss. Once again this must be the result of sensitization by 4-TMABP, not due to direct excitation. Similar analysis of the results of **3**@$(OA)_2$ supports the conclusion that 4-TMABP is able to generate the triplet of encapsulated stilbene from staying outside the capsule. In conclusion, results summarized in Table 1 suggest that the triplet-triplet energy transfer could occur across the OA wall.

Conclusions

Results presented in this study demonstrate that sensitizers remaining outside a supramolecular assembly can trigger photoreactions of guest molecules trapped within the assembly. Based on ultrafast time resolved studies we are aware that in the time scale of excited states, the OA capsule remain closed.[60] Although at longer time (300 ms) scales disassembly-assembly is likely,[61-64] in the time scale of excited states (μs to ns) the capsule is closed and the energy and electron transfer occur across the molecular wall of

OA capsule. Thus the proof of principle of the viability of remote sensitization is established and this, in our opinion offers opportunity to remotely manipulate photoreactions in a tight capsular assembly. We are in the process of identifying useful and stable sensitizers and reactions to explore the concept further.

Conflicts of interest

There are no conflicts of interest to declare.

Electronic Supplementary Information

Experimental procedures, Irradiation and analysis of products, complexation and diffusion of complexes experiments by NMR experiments, fluorescence quenching

Acknowledgement

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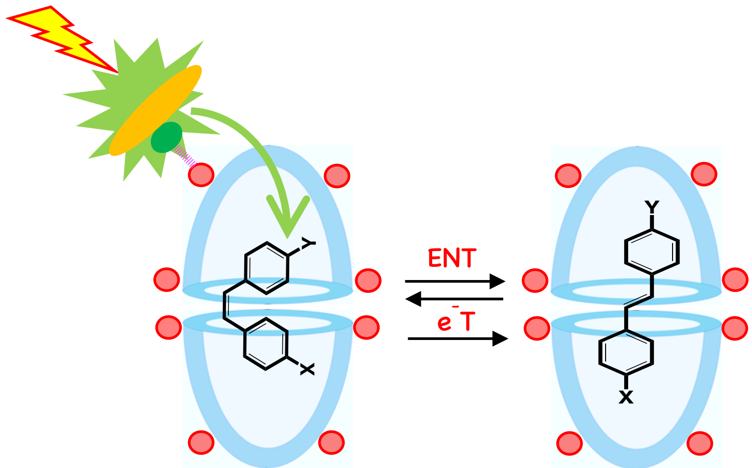
TOC Graphics



Energy and electron transfer sensitizers present outside trigger the photoisomerization of encapsulated stilbenes, thus establishing the communication between a donor and an acceptor is not arrested by a molecular wall.