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Special Issue Research Article

Reversible Photoisomerization of Norbornadiene-Quadricyclane within a Confined Capsule†

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ABSTRACT

With the desire to develop a sustainable green method to store and release solar energy *via* a chemical reaction, we have examined the well-investigated norbornadiene-quadricyclane (NBD-QC) system in water. In this context, we have employed octa acid (OA) as the host that forms a capsule in water. According to ^{1}H NMR spectra and diffusion constants, OA forms a stable 2:2 complex with both NBD and QC and 1:1:2 mixed complex in the presence of equal amounts of both NBD and QC. The photoconversion of NBD to QC within the OA capsule is clean without side reactions. In this case, OA itself acts as a triplet sensitizer. Recognizing the disadvantage of this supramolecular approach, in the future we plan to look for visible light absorbing sensitizers to perform this conversion. The reverse reaction (QC to NBD) is achieved *via* electron transfer process with methylene blue as the sensitizer. This reverse reaction is also clean, and no side products were detected. The preliminary results reported here provide "proof of principle" for combining green, sustainable and supramolecular chemistries in the context of solar energy capture and release.

INTRODUCTION

The energy-rich, structurally constrained quadricyclane (QC; Scheme 1) skeleton has fascinated chemists for over seven decades for various reasons (1,2). The frustration with early attempts at synthesizing QC skeleton by conventional methods was quashed by irradiating the corresponding norbornadiene (NBD) derivative (3–5). This success that contributed to the promising beginnings of organic photochemistry (6), interestingly, was also one of the early intramolecular photocycloaddition reactions in solution, a reaction that has become widely popular and synthetically powerful during the last decade (7–9). At the time when the importance of triplet state in organic photochemistry was being recognized, the intramolecular addition to generate the energy-rich QC became a model reaction in the hands of Hammond and co-workers in 1961 (10,11). Compared to the direct excitation reported above, triplet sensitized intramolecular [2 + 2] addition resulted in very high quantum yield (12). Thus, triplet sensitization helped bring about the reaction with light of longer wavelength and higher quantum yield (Φ = 0.05 and 0.8 for direct excitation and benzophenone sensitized, respectively) and became the sought-after method to synthesize the energy-rich QC in large quantities (13).

The ~21 kcal mole^{-1} of strain energy QC carries led the NBD-QC system to be considered as a candidate to store solar energy (14,15). Studies along this line were intensely pursued by several groups in late 1970s and 80s but interest waned with the cost-effective dye-sensitized solar cells, and other forms of energy storage devices became more affordable (16–26). Interestingly, keeping the potential usefulness of QC in solar energy applications, five decades after the initial report of QC production by triplet sensitization of NBD (10) a patent was issued for large-scale preparation QC *via* Michler's ketone sensitized synthesis from NBD in 2004 (27). After a gap of more than two decades, interest in this system has had a recent resurgence (28–39). In addition to strain another unusual property of QC that has played an important role for energy storage and release is its low oxidation potential (0.91 V *vs* SCE) in comparison to NBD (1.54 V *vs* SCE) (40). Thus, the electron transfer pathway helps to release the stored chemical energy with less electrical energy or long wavelength absorbing sensitizers with low reduction potentials (36,37,41–46). Although QC has lower triplet energy than NBD, on the triplet surface, apparently it returns to its ground state *via* a nearby conical intersection and does not cross over to NBD (12). While in the context of solar energy applications the preferred mode of energy release is by thermally activated catalytic cycles (1,2), we were attracted to the possibility of doing so *via* the electron transfer sensitization pathway using semiconductors (TiO_2 and CdS) and conventional organic and inorganic sensitizers (19,38,47). Thus, in principle, QC could be prepared from NBD by classic triplet energy transfer sensitization, and the reverse process (energy release) can be realized *via* well-investigated electron transfer sensitization.

With the aim of integrating the principles of supramolecular (48,49), green (50) and basic organic photochemistries (6), we have carried out the molecular transformation NBD to QC and the reverse process within a water-soluble organic host octa acid (OA) (51,52). In this process, we have exploited the unique properties of OA namely its ability (a) to solubilize organic molecules in water by encapsulating them by forming a capsular assembly (53,54), (b) to act as a triplet sensitizer (E_T ~ 73 kcal mole^{-1}) by

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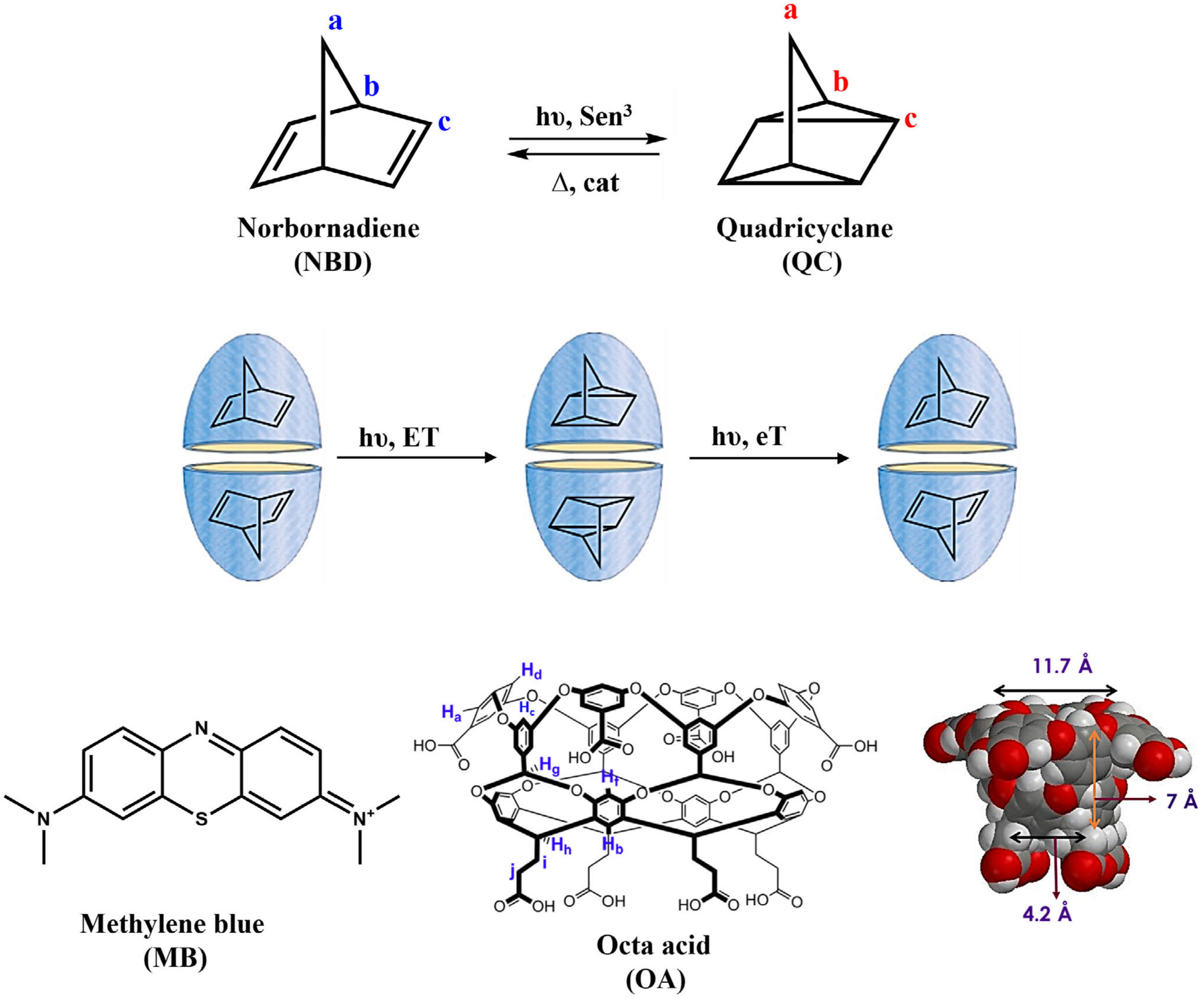


Scheme 1. Molecules used in this investigation, photoreactions considered in solution and within octa acid (OA) capsule and the structure of host OA and its internal dimensions.

absorbing light at longer wavelengths than NBD (55) and (c) to act as a mediator of electron transfer across its molecular wall (56–59). The main goals of this study are to (a) establish the feasibility of light-activated conversion of NBD to QC within the water-soluble host OA, and converting QC back to NBD with an eT sensitizer and (b) from the context of host-guest chemistry explore the feasibility of co-including more than one type of guest molecule within the OA capsule (60–64). Mindful of sustainability, developing light, especially sunlight, activated transformations in water is very attractive (5,50,65–69). Experiments were conducted with NBD and QC as guests, OA as host, water as the medium and light as reagent to address our long range of goal developing the above phototransformation as solar energy storage-release system under sustainable conditions. Aware of the limitation of the absorption range of the OA capsule we plan to explore visible light absorbing NBDs in the future. We view the current study as a proof of principle and are encouraged by its success.

MATERIALS AND METHODS

Chemicals. The host OA that has been used for the experiments is synthesized by following literature procedures. NBD, QC and methylene blue (MB) were purchased from Sigma-Aldrich.

General procedure for the complexation of host and guest analyzed by NMR. A solution of 1 mM OA along with 10 mM of sodium tetraborate buffer in 600 μL D_2O was taken in an NMR tube to which 60 mM guest solution made in DMSO-d_6 was added in a stepwise manner. After each addition, the NMR tube was shaken vigorously to achieve complexation and the resultant NMR was taken in 500 MHz NMR at room temperature. The 2:2 (guest: host) complex was attained by adding 10 μL of 60 mM guest solution into the 600 μL D_2O containing 1 mM OA and 10 mM buffer. The completion of complexation can be confirmed by the disappearance of un-complexed OA peaks and appearance of encapsulated guest peaks.

General procedure for the competitive studies conducted for host and guest molecules. A solution of 1 mM OA along with 10 mM of sodium tetraborate buffer in 600 μL D_2O was taken in an NMR tube to which 60 mM guest solution made in DMSO-d_6 was added. After the addition, the NMR tube was shaken strongly to achieve complexation, and the resultant NMR was taken in 500 MHz at room temperature. Once the complexation is achieved, other guest (competitive guest) molecule was added into the NMR tube in a stepwise manner. After each addition, the NMR tube was shaken vigorously and the corresponding NMR was recorded.

General procedure for the irradiation experiment probed by NMR for $NBD_2@OA_2$ *irradiation.* A complexed solution of guest and OA (2:2) was prepared in an NMR tube and was irradiated for up to 6 h 30 min. Irradiation was conducted by using Rayonet reactor and excited at 300 nm. NMR was taken periodically, and the observed changes in the guest-host peak were analyzed.

General procedure for the irradiation of NBD in D_2O *analyzed by NMR.* A solution of 5 mM NBD in 600 µL D_2O was taken in a quartz NMR tube by adding 120 mM guest solution made in DMSO-d_6. Irradiation was conducted by using Rayonet reactor and excited at 254 nm. NMR was taken periodically and the observed changes in the guest peak were analyzed.

General procedure for the irradiation experiment probed by NMR for $QC_2@OA_2$ *irradiation.* A complexed solution of QC and OA (2:2) was prepared in an NMR tube, and the solution was purged with nitrogen for 20 min. Afterward, 0.1 mM of MB was added and the solution was again purged for 10 min. After purging, corresponding NMR was taken, and then, the solution was irradiated with 410 nm filter in the Mercury 450 W pyrex chamber. NMR was taken at variable time intervals during irradiation to monitor the progress of the reaction.

RESULTS

To establish inclusion of guests NBD and QC within OA experiments on characterization of the structure of the complex, photochemical formation of QC from NBD within OA capsule, checking if NBD could be regenerated *via* eT sensitization of encapsulated QC and the relative preference for inclusion of NBD and QC were carried out. Complexation of the host with NBD/QC was achieved by stirring known amounts of the guest and the host in D_2O-borate buffer solution (70). For titration experiments, the guest was added gradually to OA in D_2O-borate buffer and the ^1H NMR spectrum was recorded after each addition and sonication for 5 min. These spectra are provided in Figures S2 and S6. In Fig. 1, the ^1H NMR spectra of 2:2 complexes of NBD and QC with OA as well as pure guests and host are provided. Complexation of NBD and QC with OA was suggested by the well-established, large up-field shift of the guest signals upon inclusion within OA (53,71,72). Significant, but not large changes in select host signals are also evident; only two host hydrogen signals were affected upon inclusion of the guest molecules. From the NMR titration experiments (Figures S2 and S6), the stoichiometries of the NBD-OA and QC-OA complexes were determined to be 2:2 suggesting the complex to be a closed capsule; *that is* two molecules of the guest are included within a capsule formed by two molecules of OA cavitand. This is further confirmed by the diffusion constants determined for NBD and QC complexes to be 1.11×10^{-10} m^2 s^{-1} and 1.26×10^{-10} m^2 s^{-1}, respectively (Figures S3 and S7). These values are consistent with the numbers reported for capsules in the literature (53,54,72). Thus, the above NMR data supported the conclusion that the chemistry described here occurred within a molecular-sized capsule in water known to be dry and nonpolar.

The 2:2 NBD:OA complexes in D_2O-borate buffer solution in a Pyrex NMR tube were irradiated with light of 300 ± 50 nm wavelength using a Rayonet photo-reactor fitted with RPR-3000 Å lamps. The sequential ^1H NMR spectra recorded during the irradiation are collected in Figure S9A,B. From the select ^1H NMR spectra from Figure S9A of irradiated samples provided in Fig. 2, it is clear that conversion up to 90% from NBD to QC occurred within 6.5 h. Continued irradiation for 36 h did not result in any further changes (Figure S11). It should be noted that irradiation (254 ± 40 nm; RPR-2536 Å lamp) of NBD alone in water does yield QC (Figure S16) (3). However, it does not give any products under the conditions used for $NBD_2@OA_2$ mentioned above (RPR-3000 Å lamps) (Figure S15). This suggests OA not only helps to solubilize NBD in water but also sensitizes the formation of QC. From complexation experiments, distinct signals due to the capsules containing 2 NBD and 2 QC molecules are readily identified in Fig. 2b. At the intermediate stage of irradiation, additional four new signals appear that are assigned to guests present in capsules containing one NBD and one QC molecule (for details see Discussion section). This allowed us to keep track of the number of capsules doubly occupied by NBD or QC ($NBD_2@OA_2$ or $QC_2@OA_2$) and with both NBD and QC (NBD-QC@OA_2) with respect to irradiation time. The data thus obtained are provided in tabular and graphic forms (Fig. 3).

Having established that direct excitation of $NBD_2@OA_2$ complex yields QC, we proceeded to experiment with the feasibility of converting QC back to NBD. Triplet sensitization is not a feasible option as the QC's triplet energy although lower is known to predominantly return to the QC in the ground state without crossing to the NBD surface (12). The lower oxidation potential of QC (QC ~ 0.91 V; NBD ~ 1.56 V, SCE) on the other hand is known to favor electron transfer sensitized retro-cycloaddition to regenerate NBD (19,40,42,43,47). MB (reduction potential: −0.47 V, SCE; absorption maximum; 664 nm; E_T: 1.5 eV) was used as the electron transfer sensitizer in this study to establish occurrence of this process (73). This positively charged sensitizer is expected to stay closer to the walls of the OA capsule (74). Irradiation ($\lambda > 410$ nm) of a D_2O-borate buffer solution of MB and $QC_2@OA_2$ resulted in quantitative conversion of QC to NBD (Fig. 4). Degradation of MB over time needed its replenishment (42–44).

DISCUSSION

Large up-field shifts of included NBD and QC hydrogens observed in ^1H NMR spectra (Fig. 1) and the measured diffusion constants (Figures S3 and S7) suggest the formation of 2:2 OA-guest (NBD or QC) capsular complexes. The large up-field shift of the $CH_{2(a)}$ hydrogens of both NBD and QC suggests that the two molecules are included within OA such that the cyclopentyl ring CH_2 is located at the narrower end of the capsule leaving the broader cyclohexyl part placed in the middle part of the capsule (see Scheme 1 for a cartoon representation). Identical chemical shifts of the CH_2 of included NBD and QC suggest that both molecules occupy similar space within OA. As far as host OA is concerned, the guest has an effect on only one hydrogen H_c as indicated with an arrow in Fig. 1. Interestingly, its position switches to the left or the right of the H_e signal of OA (δ 6.5) depending on the nature of the guest (NBD or QC). The changes in the chemical shifts of the guests and the host hydrogens upon inclusion of NBD and QC help follow the progress of the photoreaction *in situ* without the need for extracting the guests from the host.

Having established the nature of the host-NBD complex, we irradiated $NBD_2@OA_2$ taken in Pyrex NMR tube with light of λ 300 ± 50 nm. Progress of the reaction was followed by NMR.

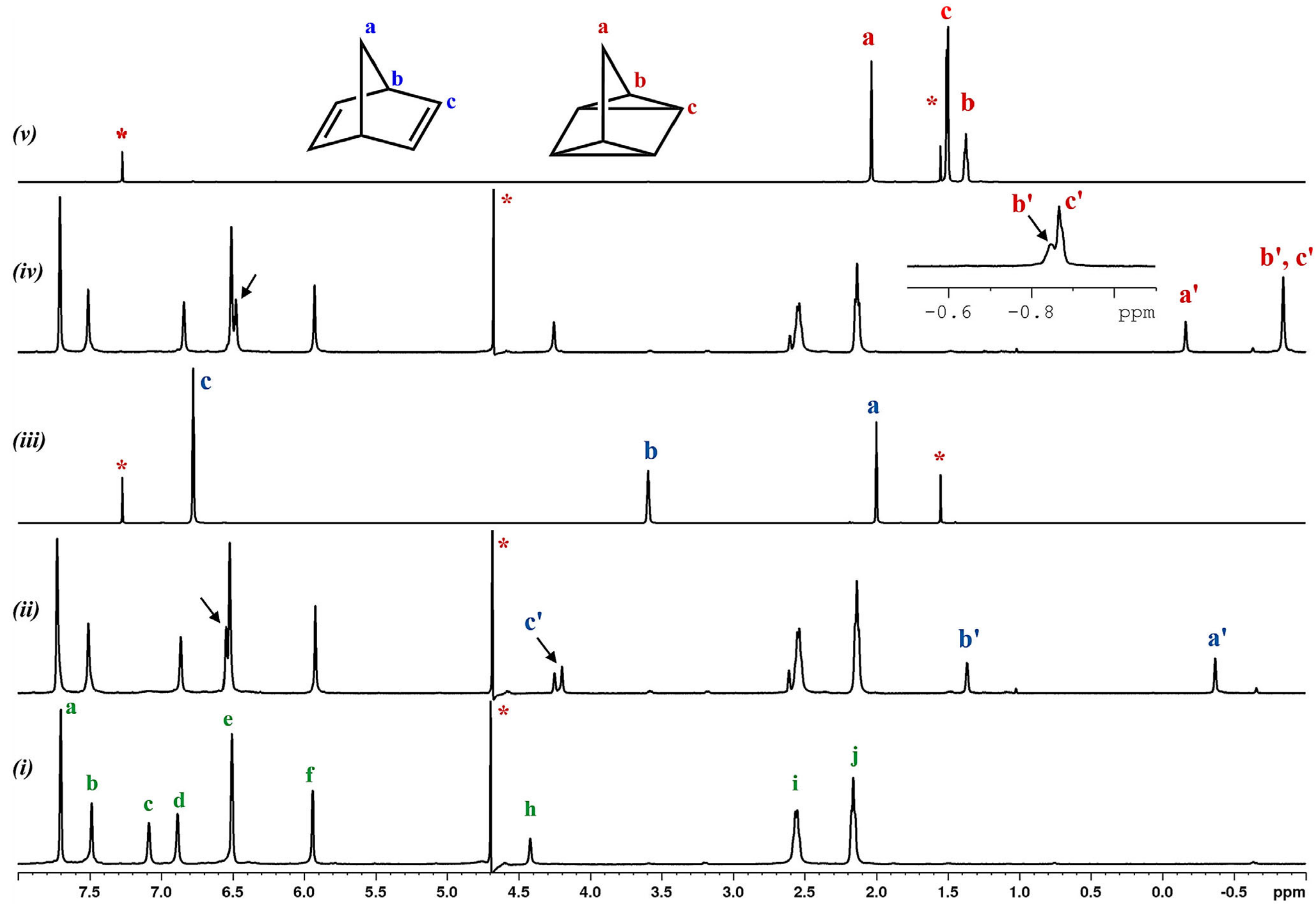


Figure 1. ^{1}H NMR spectra (500 MHz) of (i) octa acid at 1 mM in 10 mM sodium tetraborate buffer/D_2O (ii) $NBD_2@OA_2$ host-guest complex; ([NBD] = 1 mM, [OA] = 1 mM in $Na_2B_4O_7$ buffer/D_2O), (iii) NBD in $CDCl_3$ (iv) $QC_2@OA_2$ host-guest complex; ([QC] = 1 mM, [OA] = 1 mM in $Na_2B_4O_7$ buffer/D_2O), inset is $QC_2@OA_2$ at 3.4 deg C and (v) QC in $CDCl_3$. The signals marked a-c in blue and red represent free NBD and QC, respectively, and the peaks labeled from a' and c' indicate bound guest protons. The * represents solvent residuals. Letters in (i) indicate the hydrogens in the host octa acid - See Scheme 1.

The spectra with time of irradiation are displayed in Figure S9 with select ones in Fig. 2. Comparison of the spectra in Figs. 1 and 2 confirms near quantitative (90%) formation of QC without any side reactions. Quantitative conversion of NBD to QC could not be achieved under our conditions of irradiation. The triplet energies of both NBD and QC are known to be lower than that of OA (12). Thus, in principle both NBD and QC can be sensitized by OA and a photostationary would be expected based on the decay ratios of the excited intermediate to NBD and QC. The lack of isomerization of QC to NBD is, however, attributed to the tilting of the energy surface toward QC (12). However, continued presence of <10% of NBD even after 24 h of irradiation suggests that the proposed tilting does not fully block the decay of the excited intermediate toward NBD (10,11). Further work is needed to carefully assess the photostationary state composition of NBD and QC with respect to triplet energies of the sensitizers. As shown in Figure S17, absorptions of NBD and QC are masked by that of OA. Also, compared to OA the absorbance of NBD and QC is an order of magnitude smaller in the region of overlap. Therefore, based on the absorption spectra of NBD, QC and OA the last one (the host OA) would be expected to absorb all the incident light (300 ± 50 nm). It is known that OA upon excitation reaches the triplet (T_1) *via* S_1 with a high quantum yield (55). With these photophysical features, one would expect OA with the triplet energy of ~73 kcal to act not only as a host for NBD but also as an energy donor. Thus, it is clear that conversion of NBD to QC can be achieved within OA capsule without any additional triplet sensitizer. It is important to note that in spite of the proximity of the two NBD molecules within a small, confined space no intermolecular [2 + 2] dimerization occurred.

Having established the feasibility of quantitative photochemical conversion of NBD to QC within OA, we were curious if the two NBD molecules within the capsule react simultaneously or sequentially. ^{1}H NMR helped probe this photoprocess. As shown in Fig. 2, chemical shifts of H_a hydrogens of both NBD and QC within OA capsule were different depending on its neighbor. In the region δ 0 to −0.5, there are three distinct signals corresponding to $NBD_2@OA_2$, $QC_2@OA_2$ and NBD-QC@OA_2. Integration of these signals provided the ratio of the three types of capsules present at a given time. From the plot shown in Fig. 3 and Figure S10, it is clear that the photoisomerization follows two pathways simultaneously. In one case, both NBD molecules are converted to QC ($QC_2@OA_2$), and in

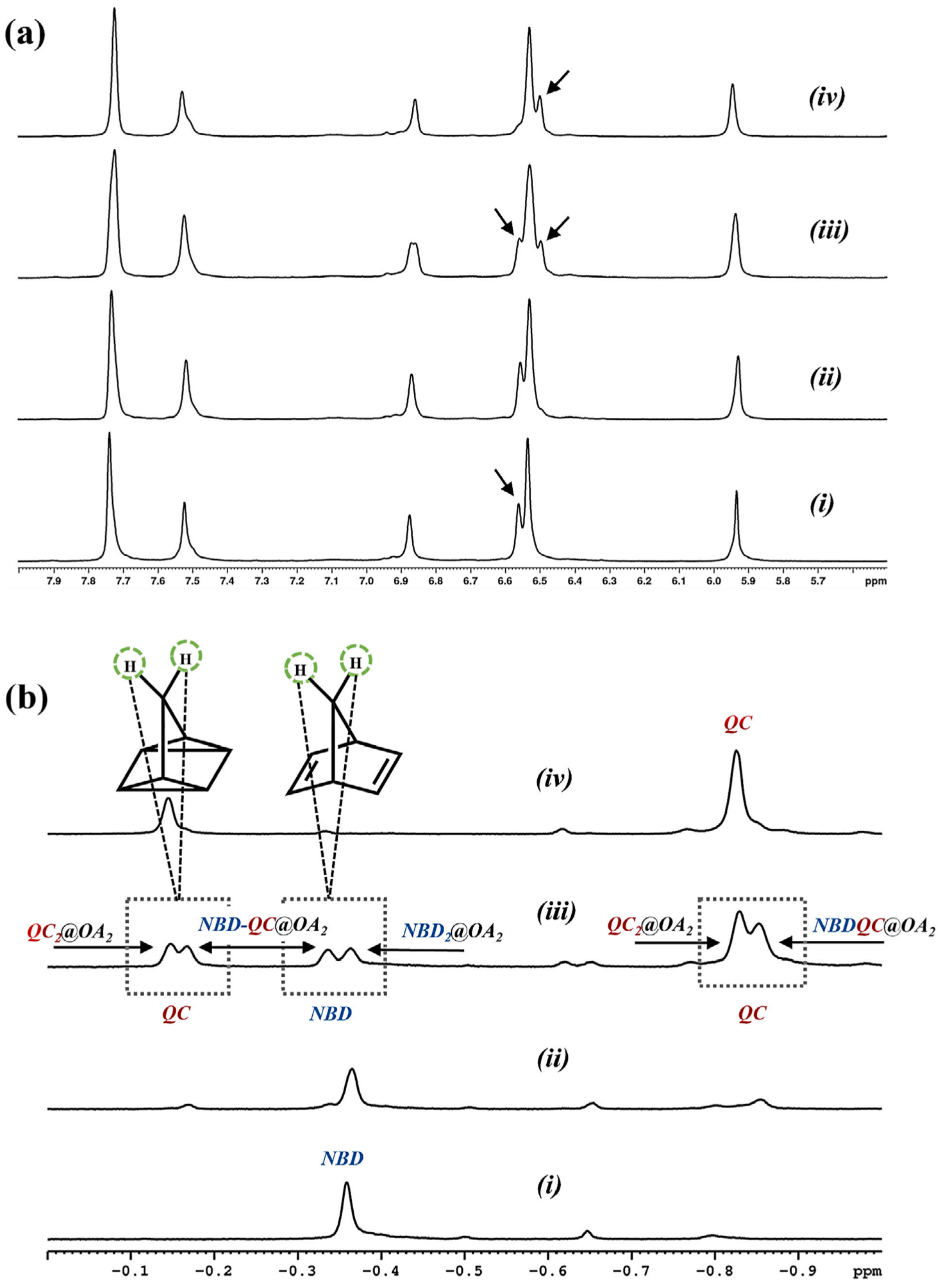
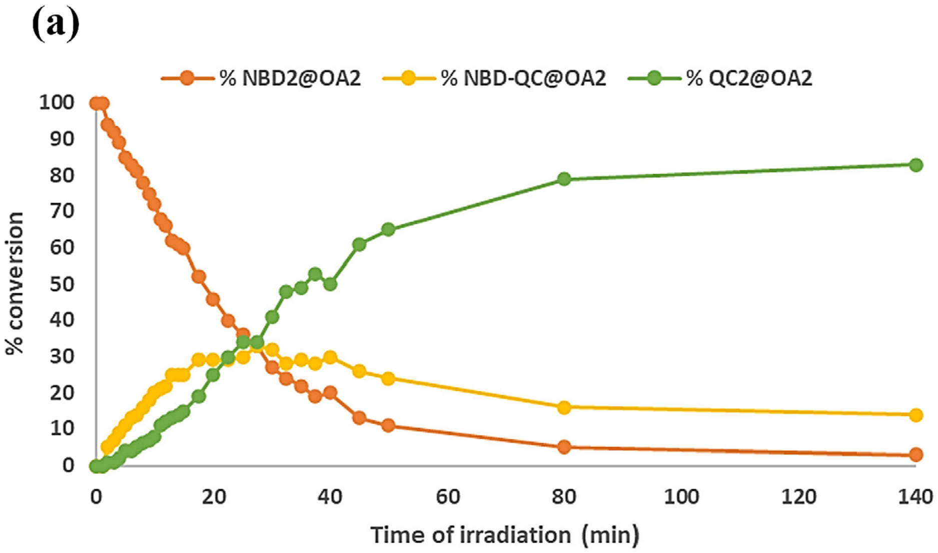


Figure 2. Partial ^{1}H NMR spectra of samples irradiated to various times. (a) Aromatic signals of $NBD_2@OA_2$ complex at (i) 0 min, (ii) 4 min, (iii) 28 min, and (iv) 6 h 30 min irradiation time; (b) aliphatic signals of $NBD_2@OA_2$ complex at (i) 0 min, (ii) 4 min, (iii) 27.5 min and (iv) 6 h 30 min irradiation time.

the other one, NBD molecule is converted to QC (NBD-$QC@OA_2$). Even at the early stages of irradiation, there are three types of capsules (reactant $NBD_2@OA_2$ and products $QC_2@OA_2$ and NBD-$QC@OA_2$). As expected, of the two molecules present in a capsule one NBD reacts more efficiently than both NBD molecules leading to the predominance of the capsule containing one NBD and one QC molecule at any stage of irradiation. The presence of small amounts of capsules containing two QC molecules even within 3 min of irradiation suggests that OA can simultaneously activate both NBD molecules included within a capsule. This likely happens from the ability of each OA capsule to capture more than one photon at the same time. Likelihood of this happening is facilitated by the presence of eight $PhCOO^-$ chromophoric groups at the periphery of the capsule. From the discussion above, it is clear that the isomerization is not necessarily a stepwise process. Both processes occur simultaneously, and the probability of two photons being absorbed by a single capsule although small is not zero. Had the conversion been a sequential process conversion of two NBD to two QC will go through a build-up of NBD-$QC@OA_2$ capsules. Such is not evident in the conversion *vs* time plot shown in Figure S10.

The reverse exothermic reaction (QC to NBD) should proceed with little energy of activation for the system to be competitive.



(b)

Time (min)	% $NBD_2@OA_2$	% NBD-QC@OA_2	% $QC_2@OA_2$
0	100	0	0
2	94	5	1
4	89	9	2
6	83	13	4
8	78	16	6
10	72	20	8

Figure 3. Monitoring the progress of the NBD-QC conversion with time of irradiation by ^1H NMR. (a) Plot of percentage conversion of $NBD_2@OA_2$ (1 mM OA, 1 mM NBD in $Na_2B_4O_7$ buffer/D_2O) complex upon irradiation to various times, (b) Table representing the percentages of $NBD_2@OA_2$ to NBD-QC@OA_2 and $QC_2@OA_2$ complexes at various times of irradiation.

Such lower activation energy for QC to NBD is possible where QC is present as a radical cation. We were curious if this feature could be experimented in OA-encapsulated QC. Employing the established electron transfer across the OA wall between an encapsulated guest (56–58,75,76), water-soluble cationic MB was used as the sensitizer to induce QC to NBD conversion (73). Reported conversion of QC to NBD in solution with MB prompted its choice (42,43). Based on the reduction potential and triplet energy of MB and oxidation potential of QC, the electron transfer from QC to MB triplet is expected to be exothermic by −0.48 eV. Irradiation (>400 nm) of D_2O borate buffer solution containing MB and $QC_2@OA_2$ mixture yielded NBD quantitatively in 42 h (Fig. 4). The long irradiation time is due to photodegradation of the dye with time. Increasing the dye concentration to avoid constant replenishment could not be practiced due to the fact that MB aggregates at higher concentrations, and these aggregates do not serve as energy and electron transfer sensitizers. Therefore, we had to maintain the dye concentrations in mM range (0.1 mM) during the irradiation. Also, similar to NBD-QC conversion the reversal proceeded one molecule at a time (Fig. 4b iii). Thus, QC to NBD conversion could be achieved by visible light photocatalysis using MB as the sensitizer. With this established proof of principle, we are confident that we will be able to find a better electron transfer sensitizer than MB in the future.

The final aspect of this study dealt with probing the complexation behavior of NBD and QC in presence of each other. This also helps to develop the OA-mediated conversion of NBD to QC as a photocatalytic one. Fig. 5 provides the ^1H NMR spectra of NBD, QC and OA taken under different ratios of the two guests (for more spectra see Figures S12 and S13). In Fig. 6, the percentages of three types of cages upon gradual addition and equilibration of the mixture with varying amounts of QC and NBD and fixed amount of OA (1 mM) estimated

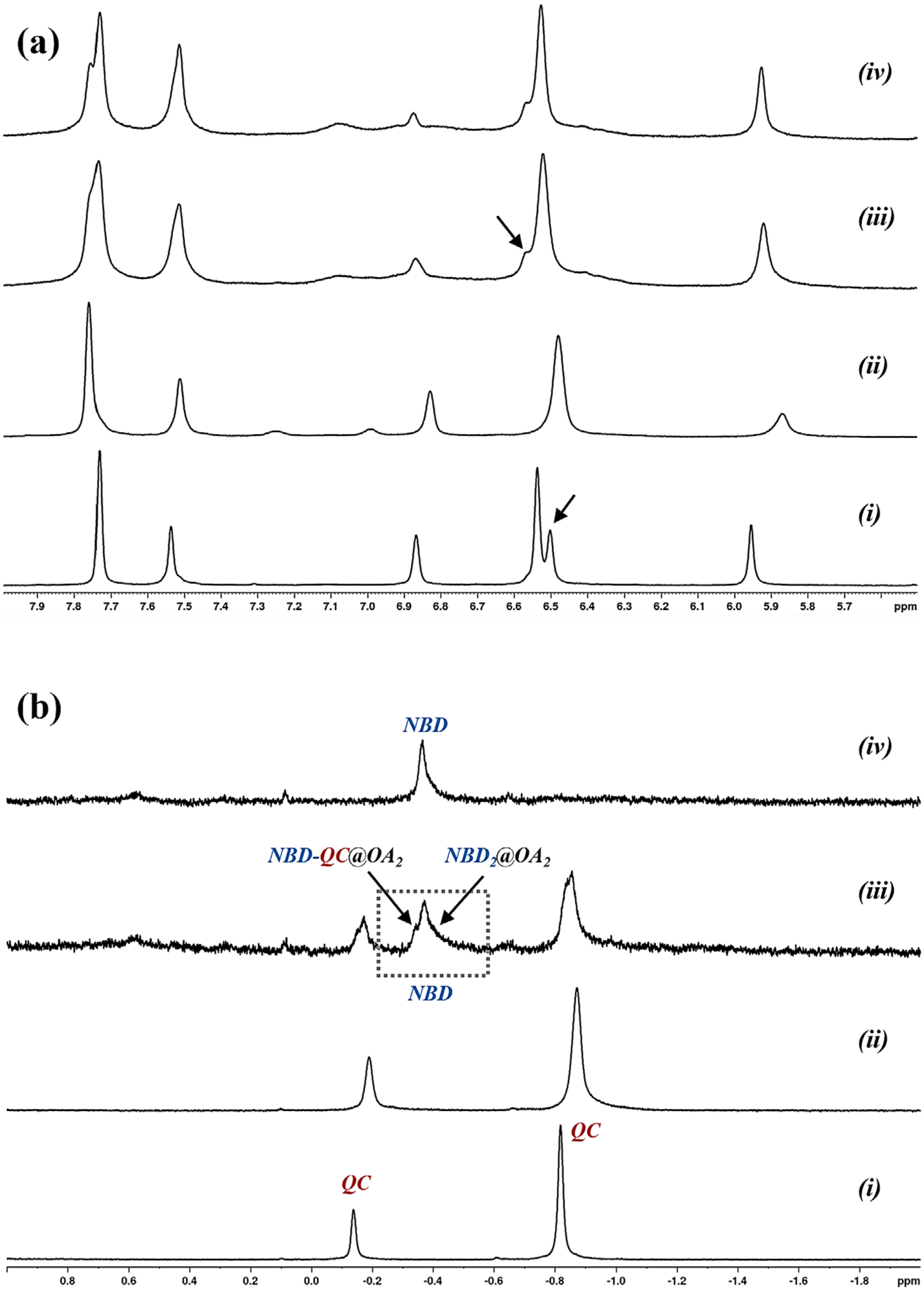


Figure 4. Partial ^{1}H NMR spectra of 1 mM OA and 10 mM sodium borate of QC_2@OA_2 complex and methylene blue irradiated to various times. (a) Aromatic part and (b) aliphatic part. (i) Each spectrum represents the QC_2@OA_2 complex without MB. The rest corresponds to the irradiated QC_2@OA_2 complex in presence of MB; (ii) 0 min, (iii) 22 h and (iv) 42 h.

from the ^{1}H NMR spectra are plotted. For example, to QC_2@OA_2 in solution 0.25–10 equivalents of NBD was added, and the percentages of the three types of capsules were estimated from the ^{1}H NMR spectra. The plots in Fig. 6 show NBD gradually replacing QC and at the maximum used amount (10 eq.); the replacement is complete to show only NBD_2@OA_2 signals. Similar observation was made with QC displacing NBD to result in QC_2@OA_2. With equal amounts of QC and NBD, all three types of capsules (NBD_2@OA_2, QC_2@OA_2 and NBD-QC@OA_2) were obtained in 1:1:1 ratio suggesting no preference by OA for QC or NBD. Equal amounts of all three types of capsules were obtained on stirring 1:1:1 mixture of QC, NBD and OA (Fig. 7). This behavior differs from the stronger binding behavior of *trans*- and *cis*-4,4′-dimethylstilbenes and azobenzenes (77,78) where OA binds strongly to one than the other isomer (64,79,80). Thus, the preferential binding of OA to one between two stereoisomers is not seen with structural isomers, at least with those we have tested. Other weaker forces than van der Walls clearly have a role in the inclusion of guests within OA capsule.

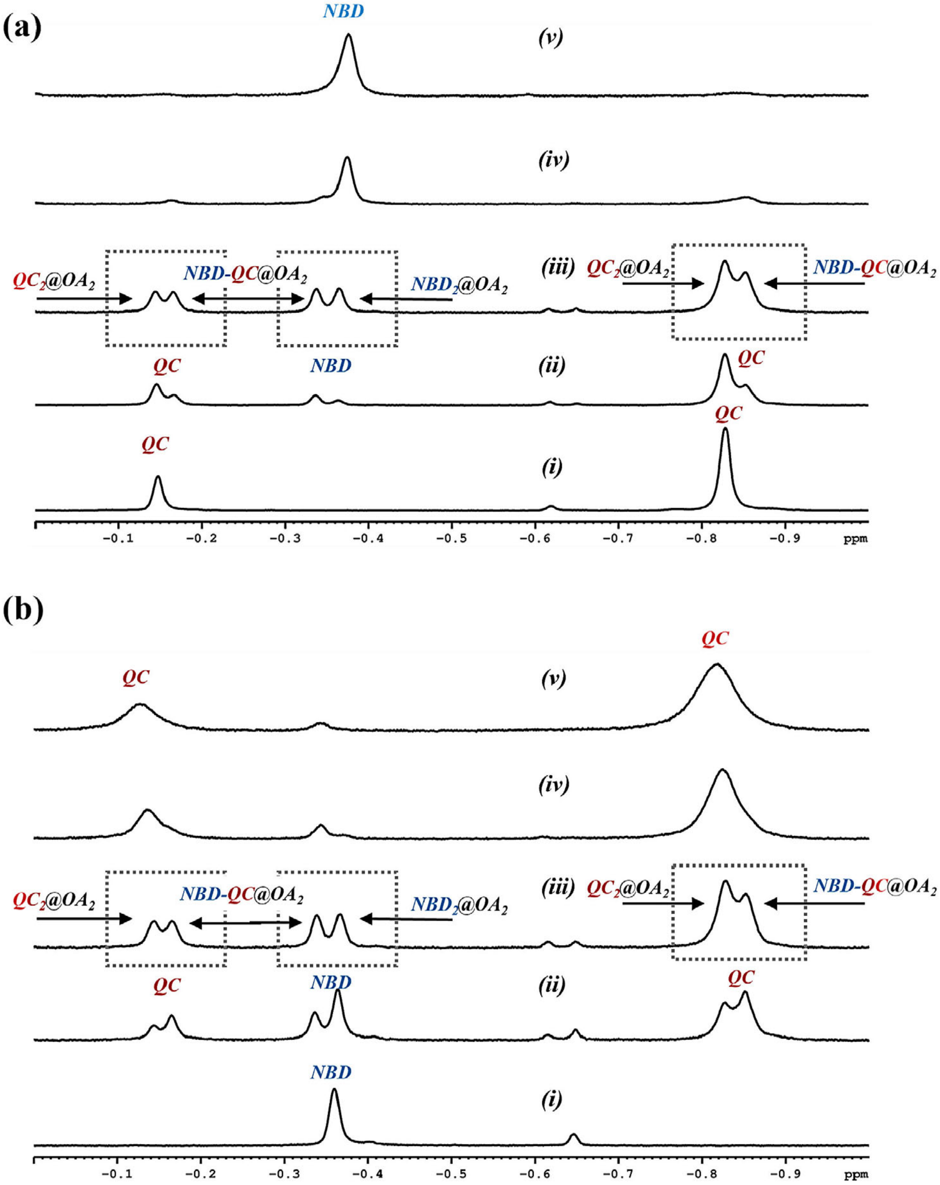
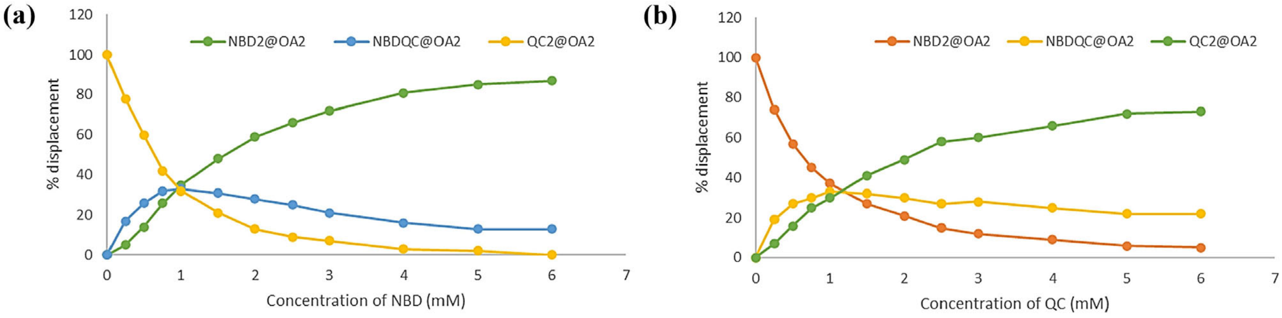


Figure 5. Monitoring the displacement of one guest by the other. ^{1}H NMR spectra (500 MHz) of 1 mM OA, 1 mM QC, 1 mM of NBD and 10 mM sodium borate) in D_2O. (a) Displacement of QC by NBD (i) Aliphatic part of $QC_2@OA_2$ complex and $QC_2@OA_2$ complex after the addition of (ii) 0.5 eq of NBD, (iii) 1 eq of NBD, (iv) 5 eq of NBD and (v) 10 eq of NBD. (b) Displacement of NBD by QC. Aliphatic expansion ^{1}H NMR spectra (i) $NBD_2@OA_2$ complex and $NBD_2@OA_2$ complex after the addition of (ii) 0.5 eq of QC, (iii) 1 eq of QC, (iv) 5 eq of QC and (v) 10 eq of QC.

Another interesting observation is the formation of 1:1:1 ratio of three types of capsules. Based on the photochemistry of unsymmetrical dibenzyl ketones where CO loss leads to two radicals A and B (reactant: ACOB; product: AA, AB and BB; ratio 1:2:1) in solution, we expected the ratio of the three types of capsules would be 1:2:1 (81). The visualized sequence of inclusion of NBD and QC within OA is shown in Fig. 8. When the capsule remained completely closed during the entire time, no equilibrium would be expected at stage II of inclusion and the ratio would be 1:2:1. However, a 1:1:1 final ratio would be expected with capsule dynamic and equilibrating as recorded in Fig. 7. This study once again demonstrates that the OA capsule is dynamic and the time scale of disassembling-assembling depends on the guest.



(c)

Concentration of NBD (mM)	% $NBD_2@OA_2$	% $NBD\text{-}QC@OA_2$	% $QC_2@OA_2$
0	0	0	100
0.25	5	17	78
0.5	14	26	60
0.75	26	32	42
1	35	33	32
5	85	13	2
10	98	2	0

(d)

Concentration of QC (mM)	% $NBD_2@OA_2$	% $NBD\text{-}QC@OA_2$	% $QC_2@OA_2$
0	100	0	0
0.25	74	19	7
0.5	57	27	16
0.75	45	30	25
1	37	33	30
5	6	22	72
10	88	12	0

Figure 6. Plots of percentage displacement of (a) QC from $QC_2@OA_2$ and (b) NBD from $NBD_2@OA_2$ ([OA] = [NBD] = [QC] = 1 mM in $Na_2B_4O_7$ buffer/D_2O) complex with variable addition of competitive guests NBD and QC. (c) and (d) Table lists the % of three types of complexes under various conditions.

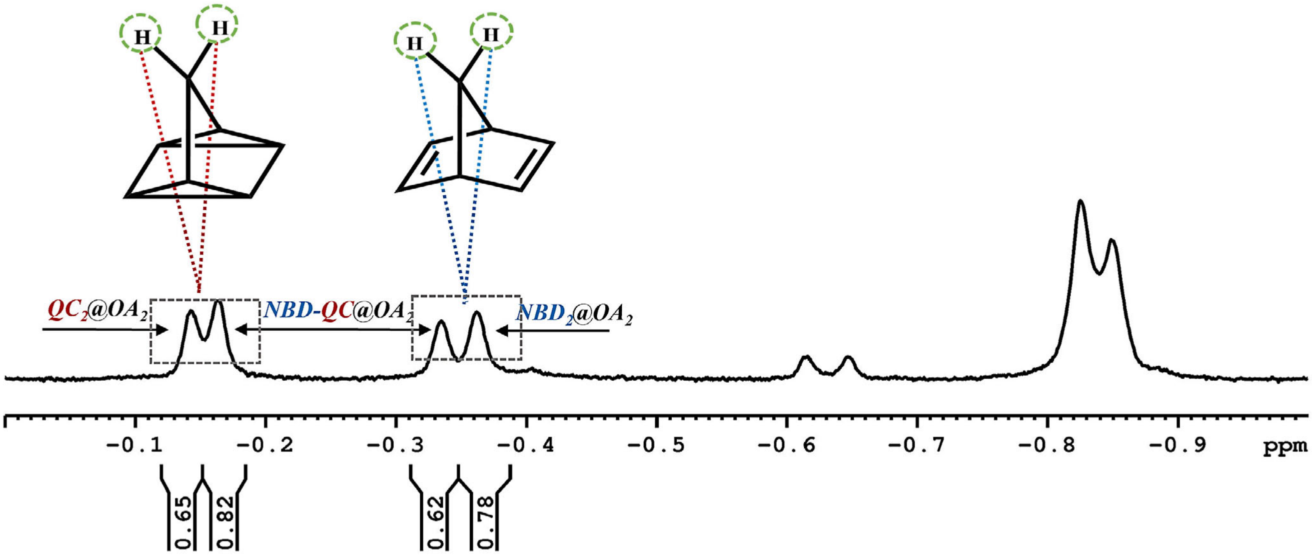


Figure 7. Partial ^1H NMR spectrum of (500 MHz in D_2O, 10 mM sodium borate buffer) 1 mM OA solution containing 1 mM of NBD and 1 mM QC; complexation was done by stirring all three in sodium borate buffer simultaneously. The two sets of integrated peaks correspond to labeled hydrogens of NBD and QC.

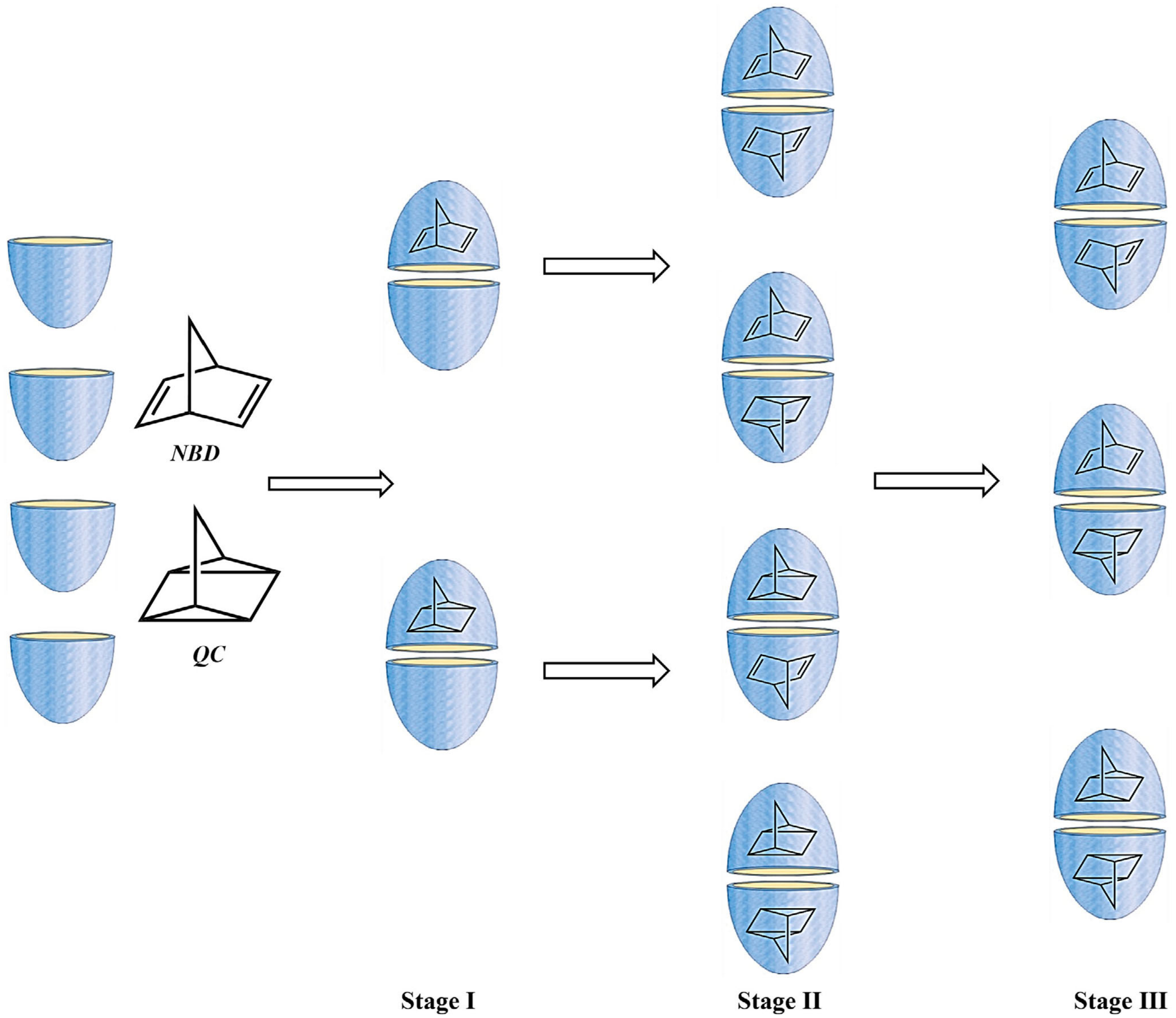


Figure 8. Pictorial representation of three types of complex formation in the ratio of 1:2:1 ($NBD_2@OA_2$: NBD-$QC@OA_2$:$QC_2@OA_2$) upon equal addition of guest molecules into the OA solution.

CONCLUSION

The goal of establishing the feasibility of converting NBD to energy-rich QC within a confined space has been achieved. In the process, host OA not only served as a confining reaction vessel but also as triplet sensitizer. This allowed the transformation to be performed at wavelengths longer than 300 nm where the NBD does not absorb. The transformation is nearly quantitative, and the product QC remained within the OA capsule solubilized in water. Importantly, the OA confined QC can be converted back to NBD to release the stored energy *via* electron transfer sensitization using visible light absorbing sensitizer. Despite the adjacent positioning of the guest molecules within a single capsule, the predominant reaction is the intramolecular cycloaddition. Thus, the NBD–QC conversion within the OA capsule has the potential to be a useful system to store light energy. While the use of OA as the reaction vessel does not solve any of the limitations debated in the literature, the results obtained offer hope. Further studies with modified NBDs are needed to fully exploit the features of supramolecular chemistry as well as recent advances in NBD-QC research in realizing the goal of storing and releasing sunlight under sustainable green conditions. The preliminary results reported here provide “proof of principle” for combining green, sustainable and supramolecular chemistries in the context of solar energy capture and release.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article:

Figure S1. ^{1}H NMR (400 MHz in $CDCl_3$ at 25°C) of Norbornadiene (NBD). Peaks labeled as a, b and c represent the protons of NBD and * represents solvent residual.

Figure S2. ^{1}H NMR spectra (500 MHz) D_2O solution containing 1 mM of OA and varying amounts of NBD. (i) Octa acid alone and octa acid with (ii) 0.25 eq, (iii) 0.5 eq and (iv) 1 eq of norbornadiene (NBD). The signals marked a, b and c in the top spectrum represent the encapsulated NBD protons.

Figure S3. 2D DOSY spectrum (400 MHz in D_2O) of $NBD_2@OA_2$ complex (1 mM OA, 1 mM NBD and 10 mM borate buffer) in borate buffer solution. Measured diffusion constant for $NBD_2@OA_2$: 1.11×10^{-10} m^2 s^{-1}.

Figure S4. COSY NMR correlations (500 MHz in D_2O) of $NBD_2@OA_2$ complex (1 mM OA, 1 mM NBD and 10 mM borate buffer). Complexed octa acid peaks are labeled from a-j (green) and the encapsulated guest peaks are labeled as a, b and c (blue).

Figure S5. ^{1}H NMR (400 MHz in $CDCl_3$ at 25°C) of quadricyclane (QC). Peaks labeled as a, b and c represent the protons of QC and * represents solvent residual.

Figure S6. ^{1}H NMR spectra (500 MHz in D_2O 1 mM OA and 10 mM sodium borate at 25 deg) upon addition of QC into OA solution. (i) Octa acid alone and octa acid with (ii) 0.25 eq, (iii) 0.5 eq, and (iv) 1 eq of QC. The signals marked as a, b and c in the top spectrum represents the protons of encapsulated QC.

Figure S7. 2D DOSY spectra (400 MHz) 1 mM OA, 1 mM QC and 10 mM borate buffer in D_2O. Measured diffusion constant for $QC_2@OA_2$ complex: 1.26×10^{-10} m^2 s^{-1}.

Figure S8. COSY NMR correlations (500 MHz) of $QC_2@OA_2$ complex in D_2O. Complexed octa acid peaks are labeled from a-j (green) and the encapsulated guest peaks are labeled as a, b and c (red).

Figure S9. (A) ^{1}H NMR spectra (500 MHz in D_2O) of $NBD_2@OA_2$ complex (1 mM OA, 1 mM NBD and 10 mM sodium borate) at various times of irradiation (300 nm): 0 min, 2 min, 4 min, 6 min, 8 min, 10 min, 11 min, 13 min, 17.5 min, 20 min, 22.5 min, 30 min, 35 min, 45 min and 3 h 20 min. (B) ^{1}H NMR spectra of the aliphatic region (500 MHz in D_2O) of $NBD_2@OA_2$ complex (1 mM OA, 1 mM NBD and 10 mM sodium borate) at various times of irradiation (300 nm): 0 min, 2 min, 4 min, 6 min, 8 min, 10 min, 11 min, 13 min, 17.5 min, 20 min, 22.5 min, 30 min, 35 min, 45 min and 3 h 20 min.

Figure S10. Plot of percentage conversion of $NBD_2@OA_2$ complex upon irradiation (300 nm) up to 10 min.

Figure S11. ^{1}H NMR spectrum of (500 MHz in D_2O) of 1 mM $NBD_2@OA_2$ solution (i) before and (ii) after 36 h of irradiation. The complexed solution was irradiated for longer duration to check the completion of the reaction and found out that NBD to QC conversion is only ~90%. The irradiation was carried out in the Rayonet reactor with $\lambda = 300 \pm 50$ nm light.

Figure S12. (A) ^{1}H NMR spectra (500 MHz in D_2O 1 mM OA, 1 mM QC) of $QC_2@OA_2$ complex with the addition of 0.25 eq, 0.5 eq, 0.75 eq, 1 eq, 1.5 eq, 2 eq, 2.5 eq, 3 eq, 4 eq, 5 eq, 6 eq, 8 eq and 10 eq NBD. (B) ^{1}H NMR spectra, aliphatic region, (500 MHz in D_2O 1 mM OA, 1 mM QC) of $QC_2@OA_2$ complex with the addition of 0.25 eq, 0.5 eq, 0.75 eq, 1 eq, 1.5 eq, 2 eq, 2.5 eq, 3 eq, 4 eq, 5 eq, 6 eq, 8 eq and 10 eq of NBD.

Figure S13. (A) ^{1}H NMR spectra (500 MHz in D_2O 1 mM OA, 1 mM NBD) of $NBD_2@OA_2$ complex upon addition of 0.25 eq, 0.5 eq, 0.75 eq, 1 eq, 1.5 eq, 2 eq, 2.5 eq, 3 eq, 4 eq, 5 eq, 6 eq, 7 eq, 8 eq and 10 eq. QC. (B) ^{1}H NMR spectra, aliphatic region (500 MHz in D_2O 1 mM OA, 1 mM NBD) of $NBD_2@OA_2$ complex and $NBD_2@OA_2$ complex with the addition of 0.25 eq, 0.5 eq, 0.75 eq, 1 eq, 1.5 eq, 2 eq, 2.5 eq, 3 eq, 4 eq, 5 eq, 6 eq, 7 eq, 8 eq and 10 eq. QC.

Figure S14. ^{1}H NMR spectrum of (500 MHz in D_2O, 10 mM sodium borate buffer) 1 mM OA solution containing 1 mM of NBD and 1 mM QC that has been added simultaneously.

Figure S15. Irradiation (300 nm) ^{1}H NMR spectrum of (500 MHz in D_2O) 5 mM NBD solution (i) before and after (ii) 36 h of irradiation. Signals marked a-c represents the protons of NBD and * represents solvent residual. No reaction observed under this condition. No reaction under the condition used for OA complex irradiation (300 nm). Control experiment to establish the need of OA to photoisomerize NBD to QC.

Figure S16. Irradiation (254 nm) of NBD in water: ^{1}H NMR spectra of (500 MHz in D_2O) 5 mM NBD in aqueous solution (i) before irradiation and after (ii) 35 min, (iii) 2 h, (iv) 3 h, (v) 5 h, (vi) 7 h, (vii) 9 h of irradiation. Signals marked a-c in blue and red represents the protons of NBD and QC, respectively. * represents DMSO solvent residual. The sample containing quartz NMR tube was irradiated at 254 nm using Rayonet irradiation chamber. NBD does react in water when irradiated at 254 nm.

Figure S17. UV spectrum of free host (OA = 0.1 mM), free guests (NBD & QC = 0.5 mM), 2:2 complexes ($NBD_2@OA_2$ & $QC_2@OA_{2,}$ NBD = QC = OA = 0.1 mM) and mixed complex ($NBDQC@OA_{2,}$ NBD = QC = 0.05 mM, OA = 0.1 mM). Inset is the absorbance spectrum of guest molecules (NBD & QC) alone in water.

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