

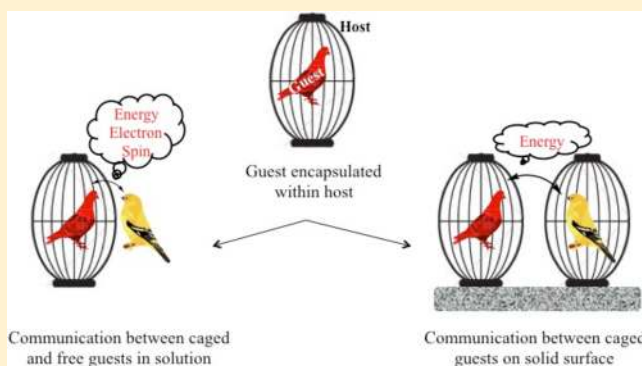
Supramolecular Photochemistry in Solution and on Surfaces: Encapsulation and Dynamics of Guest Molecules and Communication between Encapsulated and Free Molecules

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ABSTRACT: Supramolecular assemblies that help to pre-organize reactant molecules have played an important role in the development of concepts related to the control of excited-state processes. This has led to a persistent search for newer supramolecular systems (hosts), and this review briefly presents our work with octa acid (OA) to a host to control excited-state processes of organic molecules. Octa acid, a water-soluble host, forms 1:1, 2:1, and 2:2 (host–guest) complexes with various organic molecules. A majority of the guest molecules are enclosed within a capsule made up of two molecules of OA whereas OA by itself remains as a monomer or aggregates. Luminescence and ¹H NMR spectroscopy help to characterize the structure and dynamics of these host–guest complexes. The guest molecule as well as the host–guest complex as a whole undergoes various types of motion, suggesting that the guests possess freedom inside the confined space of the octa acid capsule. In addition, the confined guests are not isolated but are able to communicate (energy, electron, and spin) with molecules present closer to the capsule. The host–guest complexes are stable even on solid surfaces such as silica, clay, α -Zr phosphate, TiO₂, and gold nanoparticles. This opens up new opportunities to explore the interaction between confined guests and active surfaces of TiO₂ and gold nanoparticles. In addition, this allows the possibility of performing energy and electron transfer between organic molecules that do not adsorb on inert surfaces of silica, clay, or α -Zr phosphate. The results summarized here, in addition to providing a fundamental understanding of the behavior of molecules in a confined space provided by the host OA, are likely to have a long-range effect on the capture and release of solar energy.



I. INTRODUCTION

Chemical reactions, activated by heat or light and carried out in conventional media such as organic solvents and water, differ drastically from those occurring in biological assemblies.¹ Biological systems have thus sparked interest in new supramolecular structures that would mimic them and solubilize organic molecules in an aqueous environment.² In this context, during the last 50 years a number of less complex organized assemblies have been explored as biological mimics. Among these, micelles, cyclodextrins, calixarenes, calixarene-based cavitands, cucurbiturils, organometallic-based hosts, dendrimers, and polymers have received considerable attention.^{3–7} The size, shape, and nature of the reaction cavity of these hosts vary. For a reaction to be selective, the cavity space should be neither too small nor too large. In smaller spaces the host–guest fit would be too tight and the guest would not be able to undergo shape changes, whereas excessive space will result in an environment very similar to an isotropic solvent medium.^{8,9} Thus, the required judicious choice of a supramolecular assembly crucial to realizing the desired influence on a reaction has fueled an incessant search for new hosts.

This Feature Article outlines our effort in exploring a new synthetic host known as octa acid (OA) as a reaction container in water. The moniker octa acid for this water-soluble cavitand refers to the eight COOH groups, four at the top and four at the bottom, whose synthesis and complexation properties were reported by Gibb and coworkers.^{10,11} As illustrated in Figure 1, the features of the OA resemble those of cyclodextrins (CD), cucurbiturils (CB), and calixarenes (CA).^{12–15} In the first part of the review our results on the complexation behavior of OA and the structure and dynamics of the host–guest complexes are highlighted. The second part of the review deals with communication between an OA incarcerated guest and a free molecule in solution, highlighting the feasibility of energy, electron, and spin transfer across a molecular barrier in solution. The third part of the review highlights our preliminary studies on energy- and electron-transfer processes between encapsulated OA and free molecules aligned on surfaces. Readers are directed to the various reports on supramolecular

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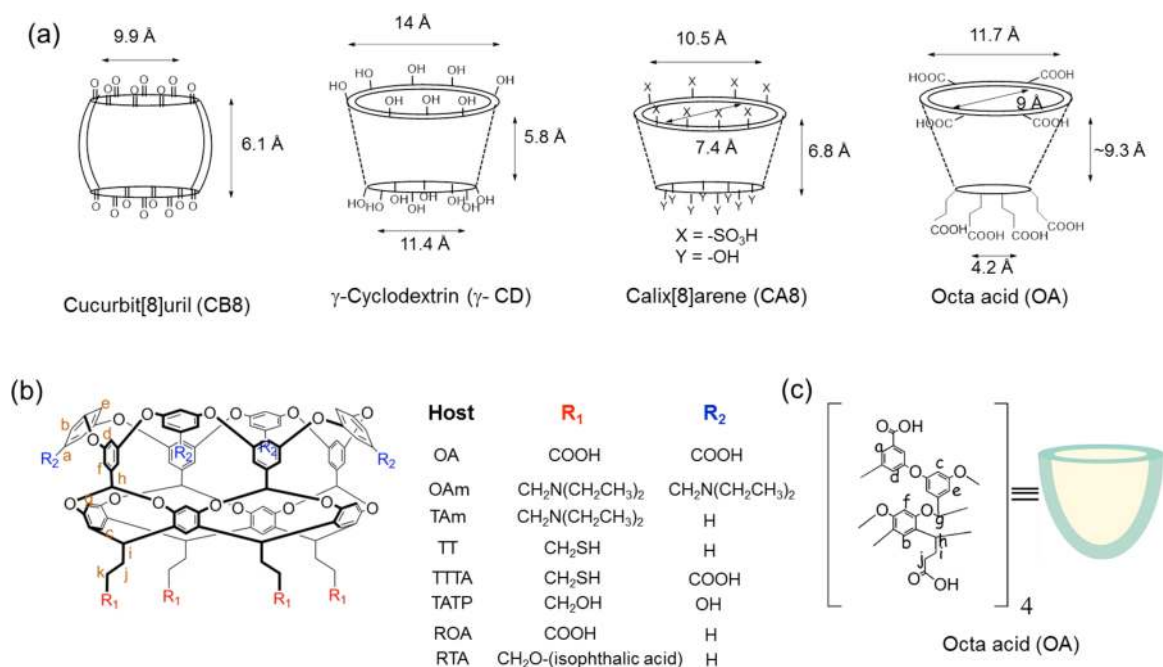


Figure 1. (a) Schematic representation of different hosts, (b) chemical structure of various synthesized hosts employed in this study, and (c) the structure of the four repeating panels of octa acid (OA), where the hydrogens in OA are labeled a–j. The cavitand representation used in this study is shown in green color as a cup.

photochemistry in the literature for work from other groups that have helped us tremendously to plan and execute our research and make this review possible.^{7,16–32}

II. OCTA ACID AS A REACTION VESSEL (CONTAINER, CAVITY)

Though not water-soluble under neutral conditions, OA will become soluble under slightly alkaline conditions (borate buffer, pH ~9). The aggregation of OA molecules (in aqueous solution) normally occurring at concentrations above 2 mM does not happen even at a 5 mM concentration in the presence of a guest such as 4,4'-dimethylbenzophenone.³³ Clear differences are noticeable between aggregated and free OA in ¹H NMR spectra (broad vs sharp peaks). Although the dimensions of both rims and the top and bottom of CD, CA, and CB are very similar, those of OA are different: the bottom rim is narrower (diameter 4.2 Å), and the top rim is wider (diameter 11.7 Å) (Figure 1). As a result OA presents only one entrance (wider top) for guest molecules; even oxygen cannot enter from the bottom rim.

Depending on the guest, OA forms a 1:1 (host–guest) cavitandplex, or a 2:1 or 2:2 capsuleplex (structures in Figure 2a).³³ As outlined in Figure 2 a guest molecule with a hydrophilic head and hydrophobic body forms a 1:1 cavitandplex whereas a guest with no hydrophilic head or tail forms only a 2:1 or 2:2 capsuleplex. In the case of adamantane, the guest being hydrophobic with no hydrophilic groups apparently prefers a closed capsuleplex rather than an open cavitandplex. A cavitandplex is a partially open complex in which a part of the guest molecule remains exposed to water while in a capsuleplex formed through the self-assembly of two OA molecules the guest is totally protected from water. It has been inferred by employing probes such as pyrene, pyrenealdehyde, 2-acetylanthracene, and coumarin-1 that the interior polarity of a capsuleplex is akin to benzene's.³⁴ Thus,

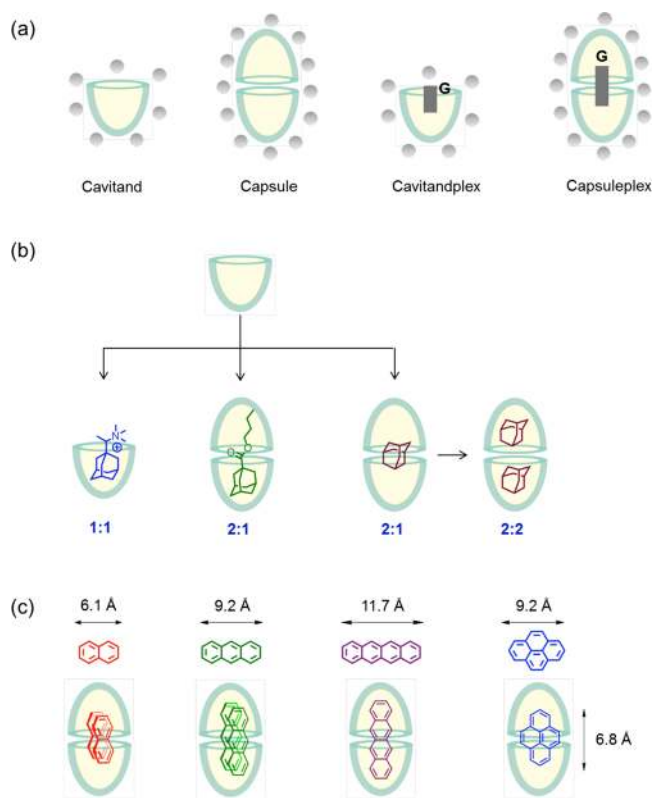


Figure 2. (a) Schematic representation of OA (green) and OA–guest complexes in water (gray spheres); examples of host–guest complexes with OA depending upon the variation of (b) the structure and (c) the size of guest molecules. Note that OA does not form a capsule in the absence of a guest.

the capsuleplex, though in water, provides a truly hydrophobic environment to the included guests.

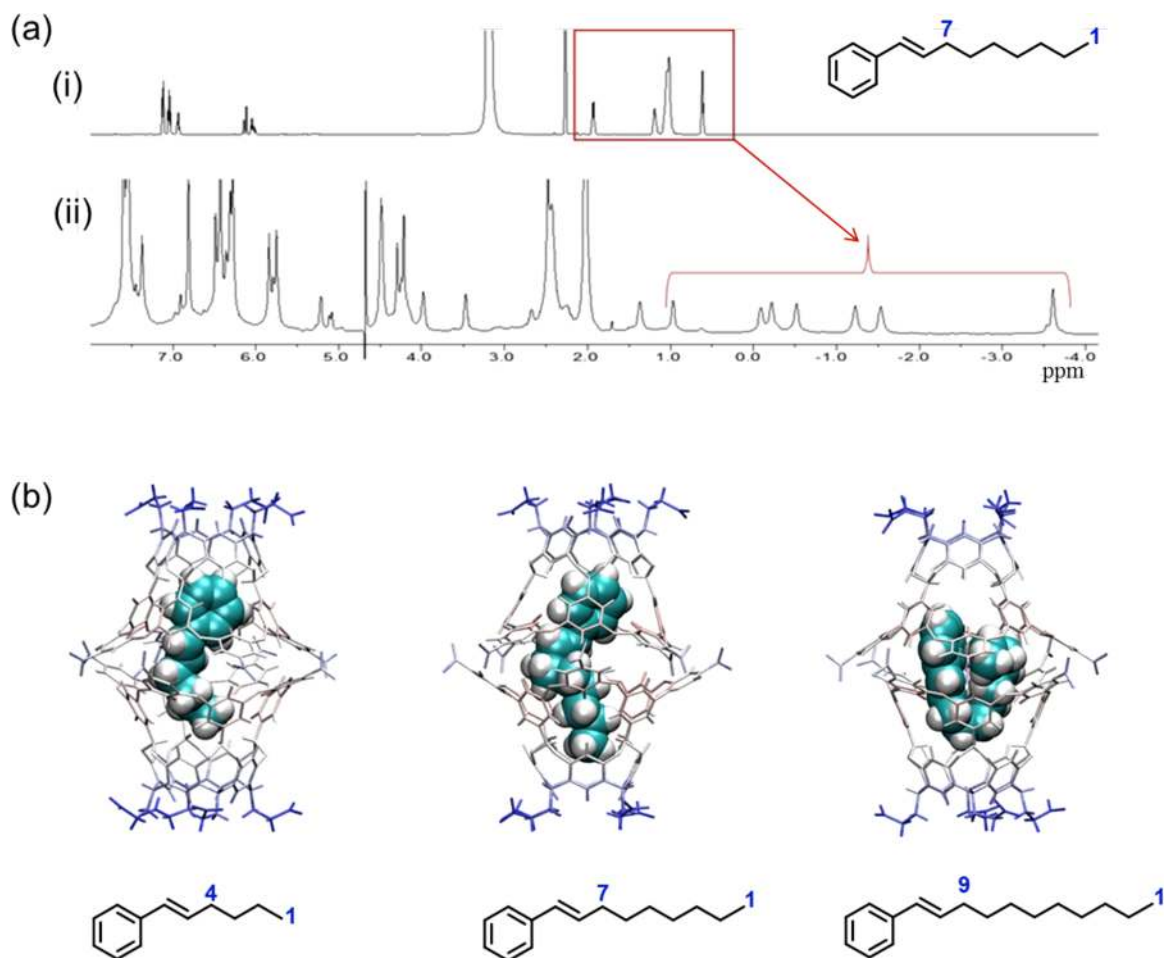


Figure 3. (a) ¹H NMR spectra (500 MHz, D₂O) of (i) β-*trans*-heptyl styrene and (ii) a 2:1 (host-guest) complex of β-*trans*-heptyl styrene with OA. (b) The most representative structures obtained from MD simulation (GROMACS, OPLS-AA force field) showing the orientation of three alkyl styrenes inside the OA capsule.

Both the cavitandplex and capsuleplex may accommodate one or two guest molecules within the cavity. Studies with a large number of molecules have shown that small organic molecules with a polar ionic headgroup (e.g., COO⁻ or N⁺R₃) would prefer to form a cavitandplex whereas nonpolar molecules, depending on their size, would form either a 2:1 or a 2:2 capsuleplexes (host-guest) (Figure 2b).³³ That a slight variation in guest structure could alter the nature and stoichiometry of the complex and the size of molecules that would fit within the OA capsule is evident from Figure 2b,c, respectively. For example, two molecules each of naphthalene and anthracene or one molecule each of tetracene and pyrene could be accommodated, but an aromatic molecule longer than tetracene or bulkier than pyrene would not fit within an OA capsule. A large number of studies involving ¹H NMR, isothermal calorimetry, fluorescence spectroscopy, and photo-reactions with a wide variety of molecules have firmly established the value of OA as a reaction container.

The inclusion of guests within OA is readily deduced from the upfield shift of guest protons because of diamagnetic shielding by the aromatic interior walls of the OA capsule in the ¹H NMR spectra (Figure 3a).^{33,35,36} Additionally, NMR data provide information on the nature of the complex and location of the guest within the OA capsule: e.g., DOSY NMR data on whether the host-guest complex is a capsuleplex or cavitandplex and 2D-NMR (NOESY and ROSEY) regarding

the location of guest molecules within the capsule. Molecular dynamics (MD) simulations provide details on the conformation adopted by the included guests.³⁷ For example, the likelihood of guest molecules adopting a high-energy conformation within a capsule as predicted by MD simulation of three alkyl styrenes of different lengths and supported by ¹H NMR spectra are presented in Figure 3b. With the length increasing from ~10 to 16 Å, the guest molecule prefers a higher-energy folded conformation. Alkyl styrenes in solution, independent of the alkyl chain length, prefer a fully extended conformation. Thus, the OA capsule's ability to place molecules in conformations different from that in solution unravels opportunities to explore specific conformer chemistry not accessible in solution.

The above observations are summarized as follows: (a) Hydrophobic organic molecules can be solubilized in water with the water-soluble host, octa acid. (b) OA forms two types of complexes with a guest: cavitandplex where the guest is partially exposed to water and capsuleplex where the guest is fully protected from water. (c) Capsuleplex, the most common type, can accommodate either one or two guest molecules within its cavity. (d) The conformation of a guest molecule within a capsule does not need to be the same as in solution.

III. DYNAMICS OF OA HOST–GUEST ASSEMBLY

The environment around guest molecules with limited freedom within the capsule is neither like a crystal's nor like an isotropic solution's. As restricted motions of a molecule get translated into selectivity in excited-state processes, an understanding of the dynamics of the guest, the host, and the host–guest complex as a whole is essential to making predictions. In this section we present our observations on the dynamics of OA–guest complexes based on ^1H NMR and luminescence experiments.^{33,38,39} The enclosed guest cannot escape the OA capsule and diffuse out unless the capsule is disassembled. Although the translational motion of the guest is intimately coupled with the host and is arrested in OA, rotation is still possible. Figure 4 illustrates two possible, representative rotational motions of the guest, namely, rotation along its long axis (4b) or tumbling by rotating along the short axis (4c).

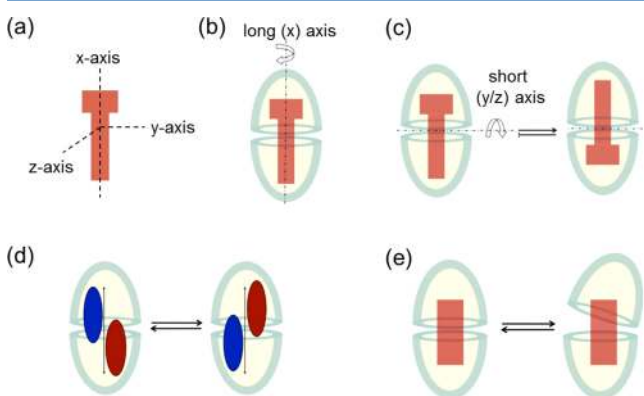


Figure 4. Cartoon representations of (a) the three axes of the guest, (b–d) various motions of guests inside the capsule, and (e) capsule opening and closing.

The occurrence of rotational motions of the guest within a cavity can be monitored by the changes in the ^1H NMR spectral pattern of OA. The OA molecule made up of four identical panels has 4-fold symmetry and contains 10 sets of chemically nonequivalent hydrogens, giving a maximum of 10 NMR signals in the region of δ 2 to 8 ppm (Figure 5a). If an unsymmetrical guest molecule remains stationary along the long axis of the capsule, the 4-fold symmetry of OA would be lost because each of the four OA panels would become magnetically nonequivalent. These nonequivalent OA panels would result in a complex ^1H NMR spectrum containing more than 10 signals for the host protons. None of the capsuleplexes we investigated distinguished the four panels of the OA molecule, suggesting that most molecules freely rotated along the long axis within the capsule (Figure 4b).

4-Methylstilbene, 4,4'-dimethylstilbene (Figure 5a), nonyl benzene, and heptyl styrene (Figure 5b) are examples of the tumbling motion along the short axis (Figure 4c).³⁷ Both guest molecules form a capsule from two molecules of OA and one guest molecule (2:1 host–guest capsuleplexes). When the guest is symmetrical (with respect to the short axis) like 4,4'-dimethylstilbene, the capsule as a whole is symmetrical (top and bottom halves of the capsule are identical) and displays only one set of signals for the top and bottom halves in the ^1H NMR spectrum (Figure 5a, spectrum ii). When OA includes an unsymmetrical guest such as 4-methylstilbene, the unsymmetrical capsuleplex entity will become symmetrical only when

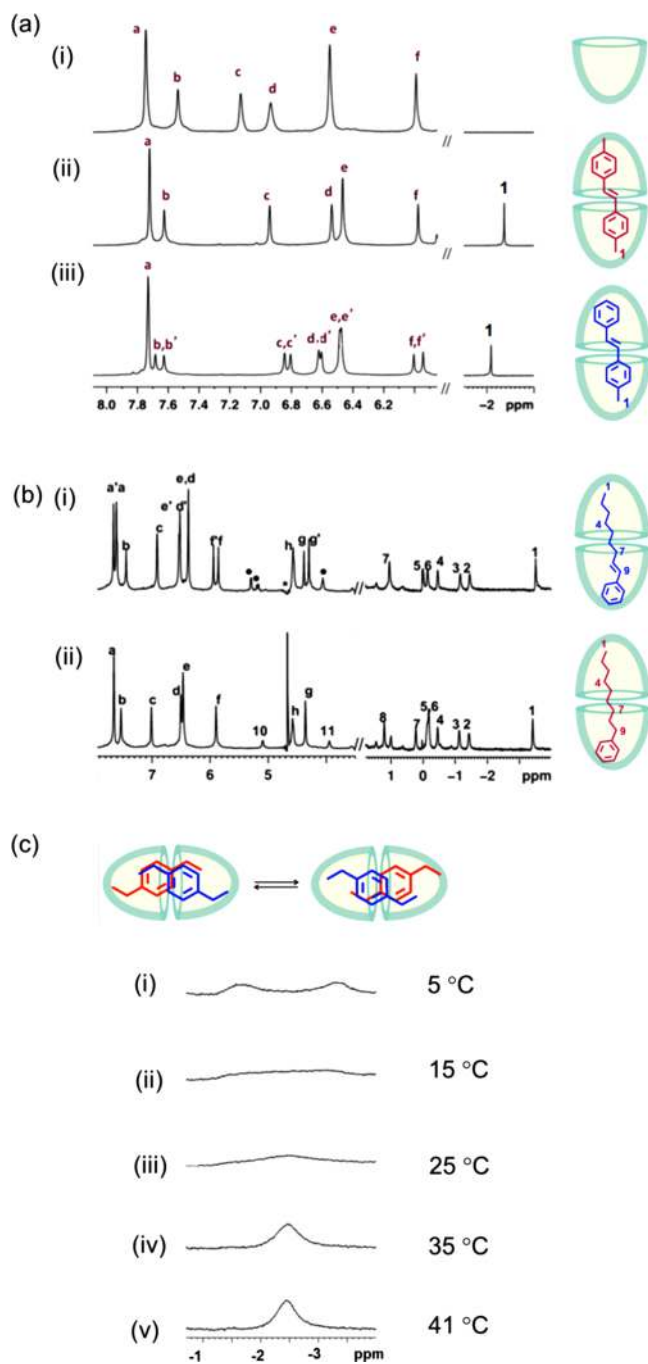


Figure 5. Partial ^1H NMR spectra (500 MHz, D_2O) of (a) (i) OA, (ii) 4,4'-dimethylstilbene@OA₂, and (iii) 4-methylstilbene@OA₂ and (b) (i) heptylstyrene@OA₂ and (ii) nonylbenzene@OA₂; ([OA] = 1 mM and [guest] = 0.5 mM in 10 mM sodium tetraborate buffer. Aromatic resonances of the host are labeled from a to f (see Figure 1c for assignments), and encapsulated guest protons are marked with numbers; (c) (i)–(v) CH_3 proton signal of 1,4-diethylbenzene@OA₂ at different temperatures.

the guest rotates freely along this axis, making the top and bottom halves equivalent. As seen in Figure 5a (spectrum iii), the many split host peaks (b, c, d, f) indicate that 4-methylstilbene does not rotate/tumble along the short axis on the NMR time scale. Its rotation along the short axis would have made the two halves magnetically equivalent to result in a single set of similar signals to that obtained for the 4,4'-dimethylstilbene-OA complex. Unlike in isotropic solution, the

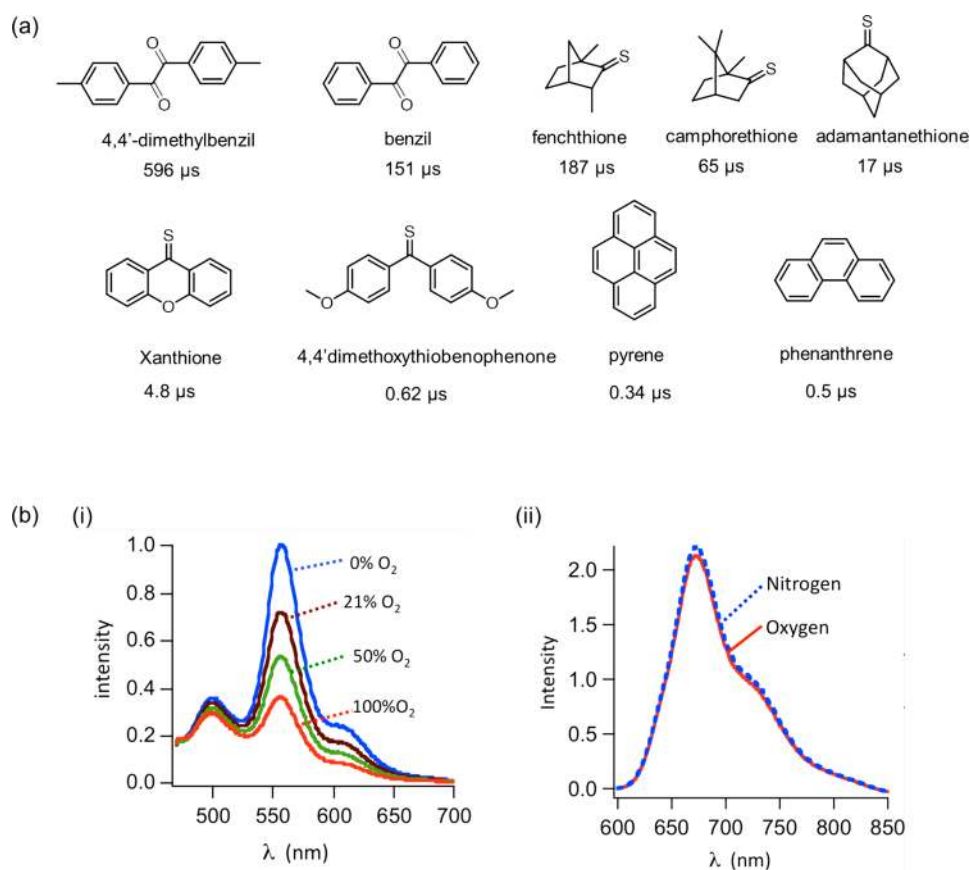


Figure 6. (a) Structure and triplet-state lifetimes (under deoxygenated conditions) of the guests used in the oxygen quenching study. (b) (i) Steady-state emission spectra of benzil@OA₂ in aqueous solution saturated with various oxygen–nitrogen mixtures, $\lambda_{\text{ex}} = 308 \text{ nm}$ and (ii) steady-state phosphorescence spectra of xanthione@OA₂ in oxygen and nitrogen-saturated aqueous solution, $\lambda_{\text{ex}} = 400 \text{ nm}$.

feasibility of rotation along the short axis within the confined capsular space depends on the structure, size, and flexibility of the molecule. Guests nonylbenzene and heptylstyrene, molecules of the same length, show two different ¹H NMR spectra (Figure 5b): although the former presents a spectrum resembling that of 4,4'-dimethylstilbene, the latter resembles that of 4-methylstilbene. This difference can be attributed to the rotation of nonylbenzene along the short axis, resulting in equivalent top and bottom halves of the capsule. The two halves remaining nonequivalent in the case of heptylstyrene and suggestive of the absence of rotation or tumbling probably arises from the rigidity introduced by the C=C bond.

The above examples dealt with 2:1 host–guest complexes where there is only one guest molecule within a capsule. In addition to the rotational motions mentioned above, in a 2:2 complex where there are two guest molecules within a capsule, the guest molecules could slide against each other as shown in Figure 4d.^{33,40} As would be expected, this motion depends on the structure of the guest. The sliding motion could be inferred by recording ¹H NMR spectra at various temperatures. For example, whereas 1,4-diethylbenzene and naphthalene were found to slide in a capsule at room temperature, encapsulated anthracene molecules were stationary. In the NMR spectra provided in Figure 5c, the methyl signals of 1,4-diethylbenzene appear at $\delta \approx -2.5 \text{ ppm}$ because of the diamagnetic shielding by the OA cavity. Whereas a single signal for both methyl groups was recorded at 35 °C, two independent signals were detected at 5 °C. This suggested that above room temperature the two 1,4-diethylbenzene molecules underwent a fast (on the

NMR time scale) sliding motion, making the two methyl groups equivalent whereas at low temperature the motion is absent or slow to make the two methyl groups nonequivalent (one methyl is above and the other is away from the phenyl group; see Figure 5c).

The OA capsuleplexes in general are weakly held together in aqueous solution. It is not obvious whether the capsuleplex would remain closed at all times or would open and close or totally disassemble and reassemble periodically (Figure 4e). To address this question, the excited states of a series of encapsulated molecules whose lifetimes vary between 0.05 to 922 μs were quenched with oxygen.³⁹ Because oxygen cannot enter the capsule from the narrower end, the required physical contact between the excited molecule and oxygen can happen only if the capsule opens, at least partially at the wider rim. The list of molecules investigated, the nature of the host–guest complexes formed, and the lifetime of the emissive states are provided in Figure 6a. All molecules were quenched by oxygen in solution, as expected, with near diffusion-limited rate constants. However, when encapsulated within the OA capsule, the guest molecules showed quenching that was at least 3 orders slower than the diffusion limit. Only molecules whose excited-state lifetimes were longer than 15 μs were quenched by oxygen, and those with a lifetime of shorter than 5 μs remained unquenched. (See Figure 6b for the phosphorescence quenching of benzil and xanthione.) Detailed analysis of the quenching kinetics revealed that the OA capsuleplex is dynamic and the capsule partially opens and closes on the microsecond time scale. On the basis of these studies, it became apparent

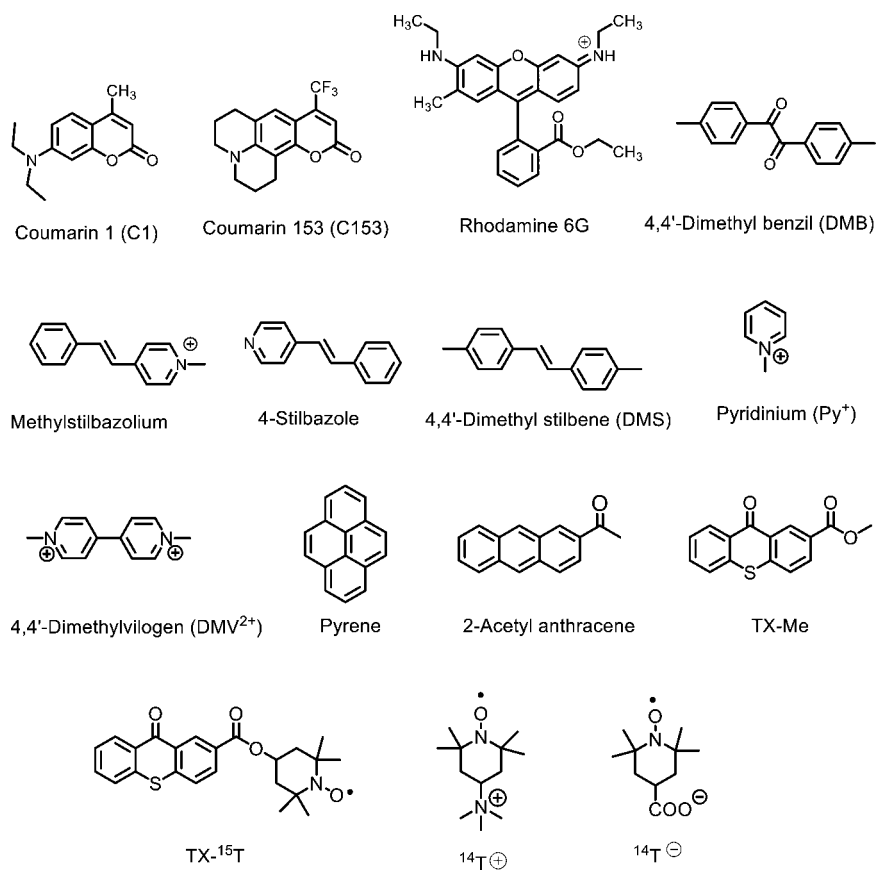


Figure 7. Chemical structures of the guests discussed in sections IV and V.

that any molecule with an excited-state lifetime shorter than 5 μ s would not be in contact with oxygen because the capsule would remain closed on that time scale. Studies by Bohne and Gibb have established that it takes much longer (~ 3 s) for the OA–pyrene capsuleplex to completely disassemble and reassemble.⁴¹ Thus, the NMR and photophysical studies have established that the capsuleplex is dynamic and the guest within the capsule and the complex as a whole undergo various types of motions (Figure 4).

IV. ENERGY, ELECTRON, AND SPIN TRANSFER BETWEEN CONFINED AND FREE MOLECULES

Communication between molecules is an important facet of excited-state chemistry. A logical question arising from the incarceration of a molecule is whether the intermolecular communication and its manner and rate can be altered. The results summarized below demonstrate that communication between an incarcerated and a free molecule does take place but at a rate different from that between free molecules in solution. This part of the review highlights communication through energy, electron, and spin transfer between a molecule confined within an OA capsule and a free molecule outside the capsule. Previously, energy transfer (triplet–triplet) and electron transfer between Cram’s hemicarcerand-included guest and free acceptors have been reported.^{42–48} During triplet–triplet energy transfer the walls of the hemicarcerand were reported to allow only weak electronic coupling between the excited donor and the acceptor. Similarly, during electron transfer between the hemicarcerand-included excited triplet guest and neutral donors the rate constants were found to be 2 to 5 orders of magnitude slower. However, a higher quenching

rate constant for the triplet of Zn-substituted cytochrome C (ZnCC) by a negatively charged hemicarcerand-encapsulated donor or acceptor in water compared to that by free donors or acceptors was noted. This was attributed to the electrostatic interaction between ZnCC and the encapsulated quencher.⁴⁴

Given the importance of energy and electron transfer in the capture and storage of solar energy, it is important to understand the feasibility and extent of energy and electron transfer involving molecules incarcerated in OA capsules.^{49–51} To assess the importance of Coulombic attraction between a negatively charged capsule that contains the donor and an acceptor during energy and electron transfer, two types of acceptor molecules were examined: positively charged ones that would be attracted to the walls of the capsule and neutral ones that would stay free in solution. The difference in the lifetime of the quadruple molecular complex (a donor, two OA cavitands, and an acceptor) involving a neutral or a positively charged acceptor should have a significant impact on the rate constants for energy and electron transfer. Strong association of the positively charged acceptor to the negatively charged external wall of the OA capsule is likely to compensate for the weaker electronic coupling between the excited donor and the acceptor. To test this thought as well as to probe the occurrence of energy and electron transfer, two types of acceptors—charged and neutral whose structures are provided in Figure 7—were examined.

Inclusion of neutral donors within the OA capsule was confirmed through ¹H NMR (section II). Although all of the donor molecules were neutral and incarcerated within the OA capsule, the acceptors were either neutral or positively charged. DOSY NMR provided information regarding the association

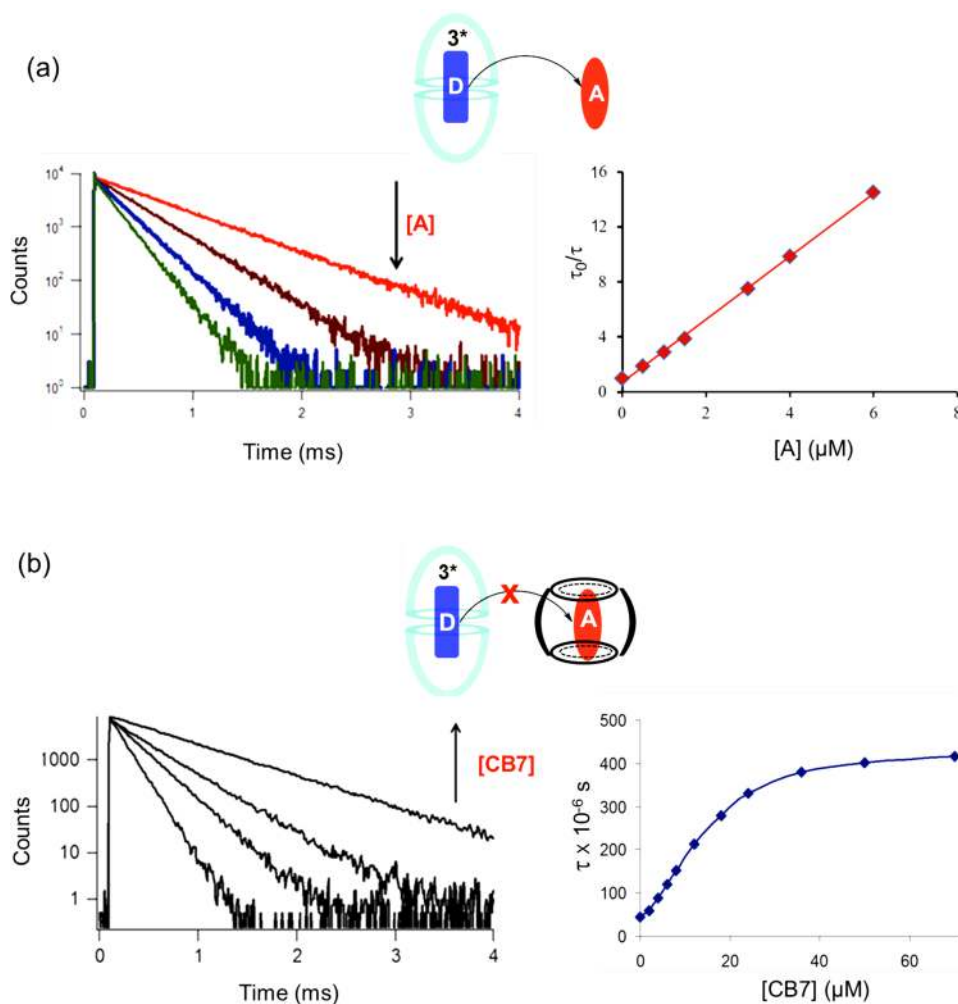


Figure 8. Phosphorescence decay traces of 4,4'-dimethyl benzil@OA₂ in the presence of (a) methylstilbazolium and (b) methylstilbazolium@CB7. Donor 4,4'-dimethyl benzil and acceptor methylstilbazolium are assigned as D and A, respectively. (a) The triplet lifetime of 4,4'-dimethyl benzil@OA₂ was quenched with an increasing concentration of A, $[A] = 0$ to 6×10^{-6} M. The Stern–Volmer plot is shown on the right. (b) The quenched triplet lifetime (τ) was gradually recovered with increasing concentration of CB7, $[CB7] = 0$ to 7×10^{-5} M, as shown on the right.

(or absence of it) of the acceptor to the capsule. All neutral acceptors had higher diffusion constants than the capsule whereas the positively charged acceptors had the same diffusion constant as the capsule, suggesting intimate association of the positively charged acceptor with the capsule.⁴⁰ The creative use of secondary host cucurbit[7]uril (CB7) helped ascertain the association of the cationic acceptors to the negatively charged OA capsule. The well-known property of CB7 to bind cationic species was used to remove the cationic acceptors from the anionic walls of the OA capsule selectively. Such a separation arrested the energy-, electron-, and spin-transfer processes, confirming the importance of Coulombic attraction between the donor-encapsulated OA and the acceptor for fast energy and electron transfer.

IV.1. Energy Transfer. Although singlet–singlet energy transfer (S–S energy transfer) proceeds by both collisional (Dexter-type) and resonance (Forster-type) mechanisms, triplet–triplet energy transfer (T–T energy transfer) occurs mainly by a collisional process.¹ The curtailing of collisions between the donor and the neutral acceptor molecules through the incarceration of one of them is likely to reduce the rates of T–T and S–S energy transfer by the Dexter process. However, it is not obvious what would be the consequence of T–T and

S–S energy transfer if the acceptor, a positively charged species, would adhere to the negatively charged capsule through Coulombic interaction. It is likely that both types of energy transfer would be enhanced if a cationic acceptor remained attached to the walls of the capsule, which would eliminate the need for diffusion prior to energy transfer.

To examine the S–S energy transfer, neutral coumarin 153 (donor) and positively charged rhodamine 6G (acceptor) were chosen (Figure 7).⁵² The positive charge of rhodamine 6G would locate it adjacent to the external walls of the OA capsule. The observed fluorescence from rhodamine 6G upon excitation of the encapsulated coumarin indicated energy transfer. The occurrence of energy transfer was confirmed by the observation of a rise in the rhodamine 6G emission intensity over time upon coumarin excitation. The rise time of the rhodamine 6G emission was surprisingly short (1 ps), which is much shorter than when both donor and acceptor molecules are free in isotropic solution. This suggested that the preassociation of the donor–acceptor complex with the help of the anionic capsule had helped the S–S energy transfer. The R_{DA} distance estimated to be 13 ± 1 Å, based on the rise time, is consistent with the donor–acceptor pair being in close proximity across the wall of the OA capsule. Encapsulation could be a route to

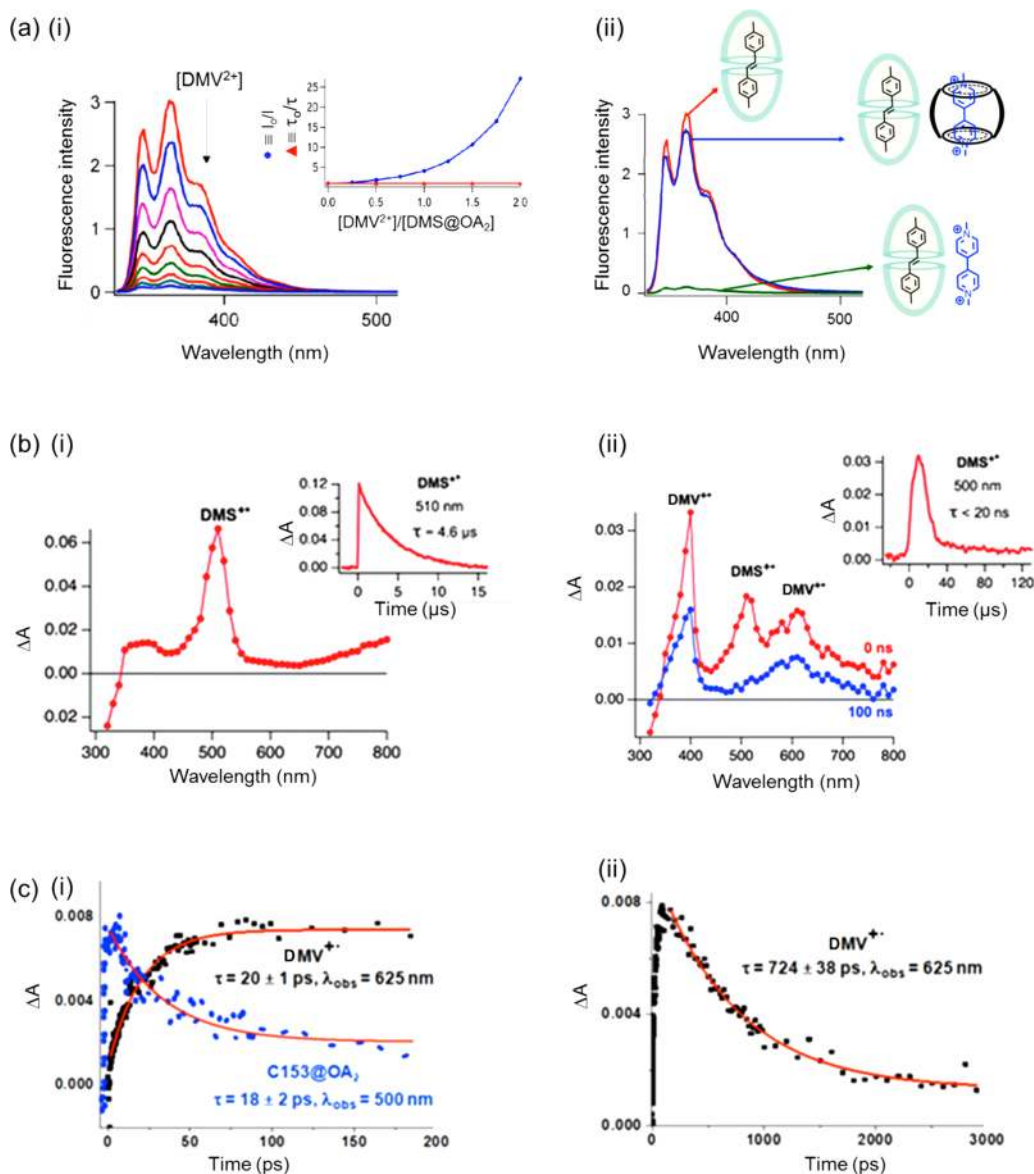


Figure 9. (a) (i) Fluorescence quenching titration spectra of DMS@OA₂ with DMV²⁺. Inset: Stern–Volmer plot. (ii) Fluorescence spectra of DMS@OA₂ in the absence and presence of DMV²⁺ and CB7. [DMS] = 1.25 × 10⁻⁵ M and [OA] = [DMV²⁺] = [CB7] = 2.5 × 10⁻⁵ M in 10 mM sodium tetraborate buffer; λ_{ex} = 320 nm, λ_{em} = 365 nm. (b) Transient absorption spectra after laser excitation (308 nm, 15 ns pulse width) of DMS@OA₂ in the presence of (i) Py⁺ and (ii) DMV²⁺. Inset: kinetic traces. [DMS] = 1.25 × 10⁻⁵ M, [OA] = 2.5 × 10⁻⁵ M, and [Py⁺] = 31.25 × 10⁻⁵ M and [DMV²⁺] = 2.5 × 10⁻⁵ M in 10 mM sodium tetraborate buffer. (c) Kinetics of formation and decay of photoexcited C153 (blue) observed at 500 nm and the rise of DMV^{•+} (black) observed at 625 nm. [DMV²⁺] = 6 × 10⁻⁴ M, [C153] = 6 × 10⁻⁵ M, and [OA] = 4 × 10⁻⁴ M in 10 mM sodium tetraborate buffer. λ_{ex} = 390 nm and pulse width = 150 fs.

enhancing the ET efficiency, especially between a neutral and an ionic acceptor.

To examine T–T energy transfer, we used 4,4′-dimethylbenzil as the donor and (A) ionic methylstilbazolium chloride and (B) neutral 4-stilbazole (Figure 7) as acceptors.⁵³ The gradual decrease in both the emission intensity and the lifetime of incarcerated donor 4,4′-dimethylbenzil upon addition of either acceptor molecule was suggestive of a dynamic process in the energy transfer (Figure 8a). The rate constants for the two types of acceptors (ionic and neutral) differing by 1 order of magnitude (methylstilbazolium chloride, 3.1 × 10⁹ M⁻¹ s⁻¹; 4-stilbazole, 0.57 × 10⁹ M⁻¹ s⁻¹) brought out the role of Coulombic attraction between the encapsulated donor and the cationic acceptor. As indicated above, in the case of methylstilbazolium chloride, the addition of a secondary host,

CB7, resulted in decreased quenching (Figure 8b). The donor regaining its lifetime when CB7 was added to the solution is compatible with the model requiring the acceptor to be closer to the capsule for energy transfer to be efficient. Consistent with this reasoning, as mentioned above with neutral 4-stilbazole, the energy transfer occurred with a lower rate constant.

The above studies suggest that (a) both S–S and T–T energy transfer between an encapsulated donor and a free acceptor can take place. (b) The rate constants for these are faster when the acceptor is held near the donor through Coulombic interaction with the anionic carboxylate groups of OA. (c) In this context, the capsule could be visualized as a rigid solvent separating the donor and acceptor molecules.

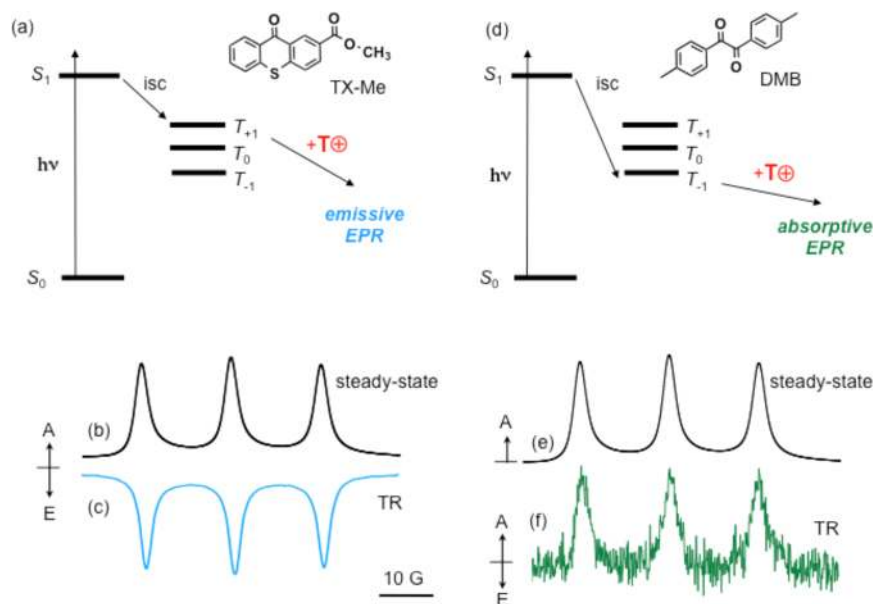


Figure 10. State energy diagram for triplet sublevel selective intersystem crossing generating spin-polarized triplet states (a, d). Steady-state EPR (b, e; integrated form) and TR-EPR (c, f) spectra of OA-encapsulated TX-Me (b, c) and DMB (e, f) in the presence of $^{14}\text{T}^\oplus$ recorded 300–500 ns (c) or 100–300 ns (f) after pulsed laser excitation at 355 nm (c) or 308 nm (f) in deoxygenated aqueous buffer solutions at room temperature. $[\text{TX-Me}] = 0.5 \text{ mM}$, $[\text{OA}] = 1 \text{ mM}$, $[\text{ $^{14}\text{T}^\oplus$ }] = 10 \text{ mM}$, 10 mM borate buffer, pH 9.

IV.2. Electron Transfer. Employing OA-encapsulated 4,4'-dimethyl stilbene (DMS) and coumarin 153 (C153) as donors and free pyridinium (Py^+) and 4,4'-dimethylviologen (DMV^{2+}) as acceptors, the feasibility of electron transfer between an OA-incarcerated donor and a free acceptor was established (for guest structures, see Figure 7).^{40,54} The interaction between these excited donors and the acceptors were ascertained by quenching the fluorescence of the donors with Py^+ and DMV^{2+} (Figure 9a(i)). That electron transfer led to the quenching of excited states of DMS by DMV^{2+} was deduced from the transient absorption spectra of $\text{DMS}^{+\circ}$ and $\text{DMV}^{+\circ}$ (Figure 9b). The necessity for cationic quenchers Py^+ and DMV^{2+} to be close to the capsule became evident upon addition of a secondary host. Upon addition of CB7, which is well known to complex DMV^{2+} , the quenched fluorescence of DMS was fully recovered (Figure 9a(ii)). In the case of the DMS system, because the time constant for forward electron transfer was within the time resolution of our nanosecond laser flash photolysis instrument, no useful data could be obtained. However, the back electron transfer rate could be measured by monitoring the decay of $\text{DMS}^{+\circ}$ and the recovery of DMS and was found to be $4.6 \mu\text{s}$ and $<20 \text{ ns}$ for Py° and $\text{DMV}^{+\circ}$, respectively. The above observations unequivocally established that the capsular wall did not prohibit the forward electron transfer between a donor and a cationic acceptor. However, interestingly, the rates of back-electron transfer were influenced by the capsular wall to different extents. Unlike the case of DMS-DMV^{2+} , the reduced rate of back electron transfer in the case of the DMS-Py^+ system is not unexpected because the neutral Py° , the product of electron transfer, would not be attached to the capsule.

The rate of forward electron transfer was measured for the C153– DMV^{2+} pair by femtosecond ($\lambda_{\text{ex}} = 390 \text{ nm}$) transient absorption measurements. The formation of $\text{DMV}^{+\circ}$ ($\tau = 20 \pm 1 \text{ ps}$) coincided with the decay of excited C153 ($\tau = 18 \pm 2 \text{ ps}$) (Figure 9c), a value in sharp contrast to the time constant of electron transfer in isotropic solution (30% acetonitrile in

water) in the absence of OA ($\tau = 630 \pm 50 \text{ ps}$). Thus, it is clear that the capsule facilitated electron transfer in this donor–acceptor pair. The $\text{DMV}^{+\circ}$ absorption decayed single-exponentially ($\tau = 724 \pm 38 \text{ ps}$), indicating that charge recombination between the donor and acceptor moieties in the presence of OA occurred within 1 ns. Thus, both forward and backward electron transfer are faster in the presence of OA.

The above studies with DMS and C153 as donors and Py^+ and DMV^{2+} as acceptors have established the following: (a) Electron transfer across the molecular walls of the OA capsule is faster than that without the OA capsule. (b) There is a strong electronic coupling among the encapsulated excited neutral donor, the Coulombically held cationic acceptor, and the host. The knowledge gained from this study could be useful in devising systems to separate and store charges generated by light absorption.

Energy- and electron-transfer studies summarized here have established that the OA capsule facilitated such processes when one of the two (donor or acceptor) is a cationic species. In the absence of anionic OA, capsule electron transfer and energy transfer cannot be conducted in water. The OA capsule, besides solubilizing the insoluble donor in water, brought the cationic acceptor closer to the neutral donor through Coulombic interaction. These features of this supramolecular system expand the list of molecules that could be used to perform energy and electron transfer in an aqueous medium. It is therefore obvious that a cationic capsule (see a later section) could facilitate energy and electron transfer between a neutral guest and anionic acceptors.

IV.3. Electron Spin Transfer. Intersystem crossing from the singlet excited state to the triplet state occurs in most cases selectively to one of the three spin levels of the triplet states, which generates a spin-polarized triplet state (Figure 10a,d). At room temperature these spin-polarized triplet states are rapidly equilibrated to the Boltzmann distribution (within several nanoseconds for ketones). However, if these spin-polarized triplet states encounter a radical, then the electron spin

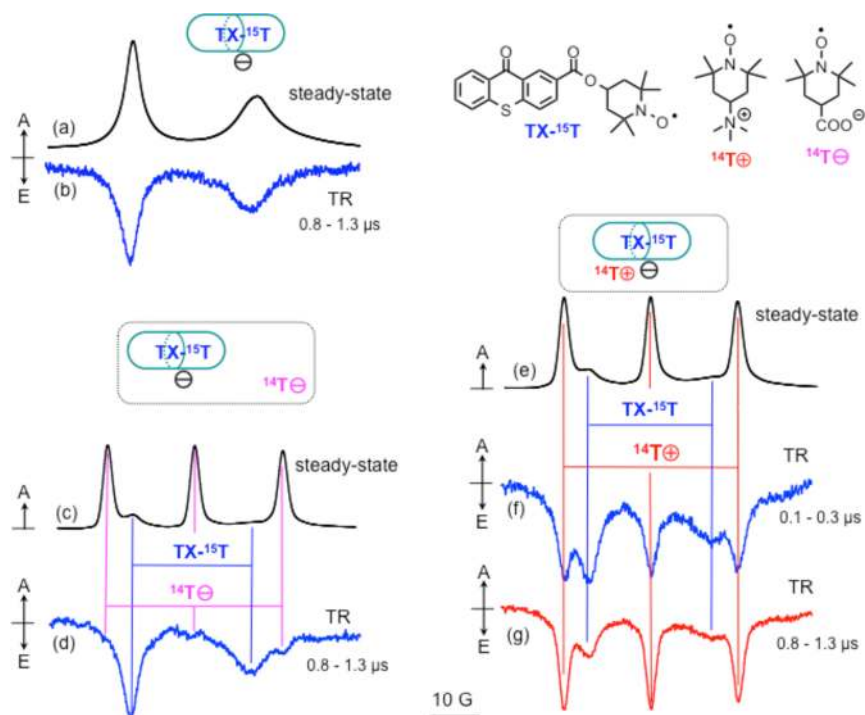


Figure 11. Steady-state EPR (a, c, e; integrated form) and TR-EPR (b, d, f, g) spectra of OA-encapsulated TX-¹⁵T in the absence (a, b) and presence of ¹⁴T[⊖] (c, d) or ¹⁴T[⊕] (e, f, g) recorded at different time windows after pulsed laser excitation at (355 nm, 5 ns pulse width) in deoxygenated aqueous buffer solutions at room temperature. [TX-¹⁵T] = 0.5 mM; [OA] = 1 mM, [¹⁴T[⊕]] = 1 mM, [¹⁴T[⊖]] = 1 mM, 10 mM borate buffer, pH 9.

polarization is transferred to the radical in this triplet quenching process. As a result, spin-polarized radicals are generated, which are observable by time-resolved electron paramagnetic resonance (TR-EPR) spectroscopy. In this section we summarize our findings of how the encapsulation of spin-polarized states (triplet states or radicals) inside OA affects the communication and spin polarization transfer to a stable radical (nitroxide) outside the capsule. The strength of interaction of the nitroxide with the encapsulated donor was manipulated by the use of cationic and anionic nitroxides as well as by selectively including the nitroxide within the cavity of a secondary host, CB8.

Thioxanthone derivatives TX-Me and 4,4'-dimethyl benzil (DMB) form 2:1 host-guest complexes with OA. The photoexcitation of these complexes generates singlet excited ketones that rapidly intersystem cross to the triplet states. It is known that the initially generated triplet states of DMB, an aromatic 1,2-diketone, have absorptive spin polarization (Figure 10d), whereas TX-Me, similar to most aromatic ketones, generates emissive spin-polarized triplet states during intersystem crossing (Figure 10a).⁵⁵ The interaction of these encapsulated spin-polarized triplet states with a positively charged nitroxide, ¹⁴T[⊕] (structure shown in Figure 11), was investigated by TR-EPR.⁵⁶ Figure 10 shows the steady-state and TR-EPR spectra of ¹⁴T[⊕] in the presence of the capsuleplex. In the case of encapsulated TX-Me an emissive spin-polarized EPR was observed (Figure 10c), and in case of encapsulated DMB an absorptive spin-polarized EPR (Figure 10f) was observed after pulsed laser excitation. The oppositely polarized EPR signals generated from the two different encapsulated ketones clearly show that spin polarization of a polarized triplet state can be transferred through the walls of the OA capsule to a radical (nitroxide) located outside the capsuleplex.

Steady-state EPR and ¹H NMR confirmed that positively charged ¹⁴T[⊕] has a strong affinity for negatively charged OA.⁵⁷ Utilizing the ability of nitroxides to induce relaxation in ¹H NMR, we determined the preferred binding site of ¹⁴T[⊕] on the surface of the OA capsuleplex.⁵⁷ ¹⁴T[⊕] had a major influence on the proton relaxation present at the wider rim of the OA cavitand. Its effect on all other OA protons was smaller, suggesting that ¹⁴T[⊕] stays closer to the middle region of the capsuleplex.

If a negatively charged nitroxide (¹⁴T[⊖]) is used instead of ¹⁴T[⊕] in TR-EPR experiments, then no detectable spin-polarized EPR signal was observable after the photoexcitation of encapsulated TX-Me.⁵⁶ The absence of a spin-polarized signal is consistent with inefficient triplet quenching caused by the electrostatic repulsion of the negatively charged nitroxide from the negatively charged capsule.

In the above experiments electron spin polarization transfer was demonstrated from an encapsulated spin-polarized triplet state to a stable radical (nitroxide), generating a spin-polarized doublet state. In the following section, we show that an encapsulated radical can communicate with another radical outside the OA capsule by electron spin polarization transfer. To be able to distinguish between the encapsulated and free nitroxide by EPR, isotope labeling was employed. A thioxanthone derivative that was covalently linked to a ¹⁵N-labeled nitroxide (TX-¹⁵T) forms a 2:1 capsuleplex with OA and shows a two-line EPR spectrum (Figure 11a). The ¹⁴N-labeled free nitroxide (¹⁴T[⊕]) gives a three-line EPR spectrum as shown above (Figure 10b). Because of the negligible overlap of the two-line and three-line EPR spectra, the simultaneous observation of both nitroxides by EPR spectroscopy can be achieved.

The photoexcitation of OA-encapsulated TX-¹⁵T with laser pulses gave an emissive spin-polarized TR-EPR spectrum

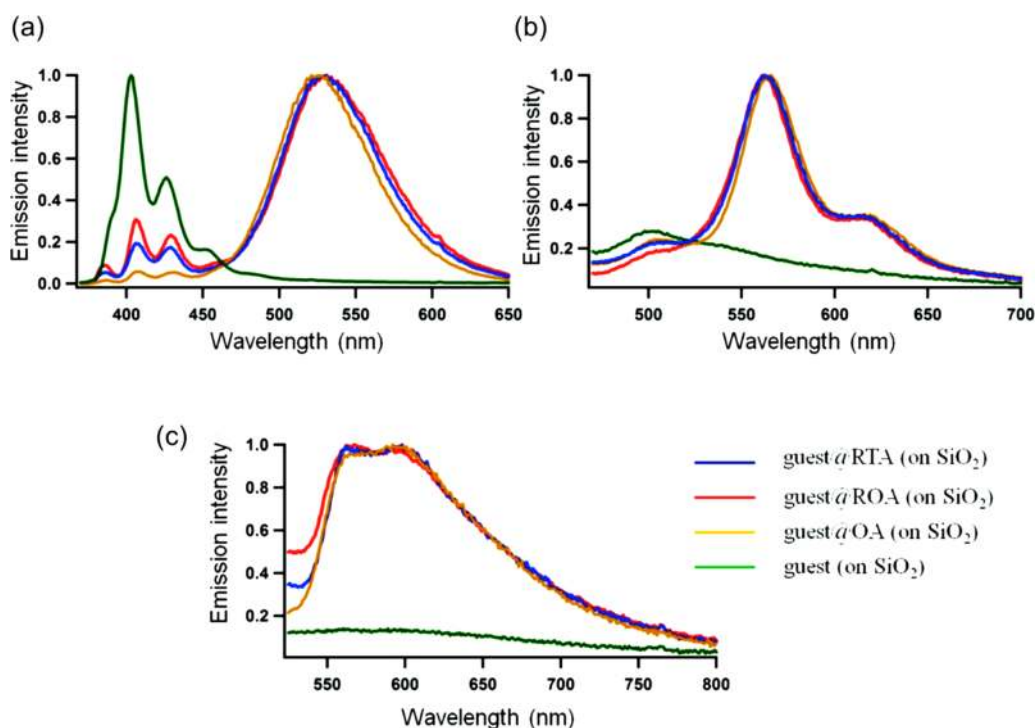


Figure 12. Emission spectra of (a) anthracene ($\lambda_{\text{ex}} = 350$ nm), (b) 4,4'-dimethyl benzil ($\lambda_{\text{ex}} = 310$ nm), and (c) camphorothione ($\lambda_{\text{ex}} = 254$ nm) alone and as complexes with hosts OA, RTA, and ROA adsorbed on silica.

(Figure 11b) that is caused by the rapid quenching of thioxanthone triplet states by the covalently linked nitroxide (within several nanoseconds as confirmed by transient absorption spectroscopy).⁵⁸ The addition of the positively charged $^{14}\text{T}^{\oplus}$ to the solution containing encapsulated TX-¹⁵T generated very different TR-EPR spectra. In an earlier detection time window (0.1–0.3 μs after the laser pulse), the two-line signal of the incarcerated TX-¹⁵T is more significant (Figure 11f), whereas in a later time window (0.8–1.3 μs) the three-line signal of $^{14}\text{T}^{\oplus}$ is dominant (Figure 11g). This spectral change in the dominance of the two-line signal (TX-¹⁵T) to the three-line signal ($^{14}\text{T}^{\oplus}$) is a strong indication of spin-polarization transfer from the incarcerated nitroxide to the nitroxide outside the capsule. The spin–spin interaction of the internal nitroxide with the external nitroxide is also reflected in the decrease in the spin-polarization lifetime of the internal nitroxide from 1.7 μs in the absence to 0.76 μs in the presence of $^{14}\text{T}^{\oplus}$.⁵⁸ Furthermore, the spin–spin exchange interaction between encapsulated nitroxides and external nitroxides ($^{14}\text{T}^{\oplus}$) causes EPR line broadening that is observable by steady-state EPR spectroscopy.⁵⁹

TR-EPR experiments using negatively charged $^{14}\text{T}^{\ominus}$ instead of $^{14}\text{T}^{\oplus}$ showed almost exclusively the two-line spectrum of spin-polarized TX-¹⁵T (Figure 11d), although in the steady-state EPR spectrum the three-line spectrum of $^{14}\text{T}^{\ominus}$ is dominant (Figure 11c).⁵⁸ The absence of a detectable three-line signal in the TR-EPR experiments demonstrates that the electron spin sublevel population of $^{14}\text{T}^{\ominus}$ remains in the Boltzmann distribution and does not interact with the incarcerated spin-polarized nitroxides of TX-¹⁵T. Similar to other systems shown above, the electrostatic repulsion of negatively charged $^{14}\text{T}^{\ominus}$ by negatively charged OA prevents spin-polarization transfer.

Spin-polarization transfer from incarcerated TX-¹⁵T to $^{14}\text{T}^{\oplus}$ can also be prevented by the introduction of a secondary host,

CB8, which is known to form inclusion complexes with nitroxides.⁶⁰ TR-EPR experiments of encapsulated TX-¹⁵T and $^{14}\text{T}^{\oplus}$ in the presence of CB8 showed exclusively the two-line spectrum of spin-polarized TX-¹⁵T.⁵⁸ The absence of a detectable three-line component from $^{14}\text{T}^{\oplus}$ demonstrates that the supramolecular entrapment of the nitroxide is an efficient tool for manipulating spin–spin interactions.

The above TR-EPR studies have established that (a) the electron spin polarization of an incarcerated nitroxide or triplet state can be transferred through the walls of the carcerand (OA) to a nitroxide outside and (b) spin polarization transfer can be controlled by supramolecular factors such as Coulombic attraction or repulsion and secondary hosts that trap external nitroxides.

V. SUPRAMOLECULAR SURFACE PHOTOCHEMISTRY: ELECTRON AND ENERGY TRANSFER INVOLVING CAPSULAR ASSEMBLIES ON SURFACES

With a knowledge of structure, dynamics, and excited-state properties of capsular assemblies in aqueous solution, it seemed appropriate to expand the realm of supramolecular photochemistry by organizing them on a surface. Hoping that organizing supramolecular assemblies on ordered surfaces would open a new dimension in supramolecular photochemistry, we sought answers to the following questions: (a) Can the capsules containing guests from an aqueous solution be transported to a solid surface? (b) Would the capsules be stable in the absence of water on solid surfaces, and if so (c) would their unique photophysical and photochemical properties be preserved? (d) Would the encapsulated guests communicate with active surfaces such as TiO_2 and gold nanoparticles? (e) Would it be possible to organize two capsules with different guests on a surface and perform energy and electron transfer

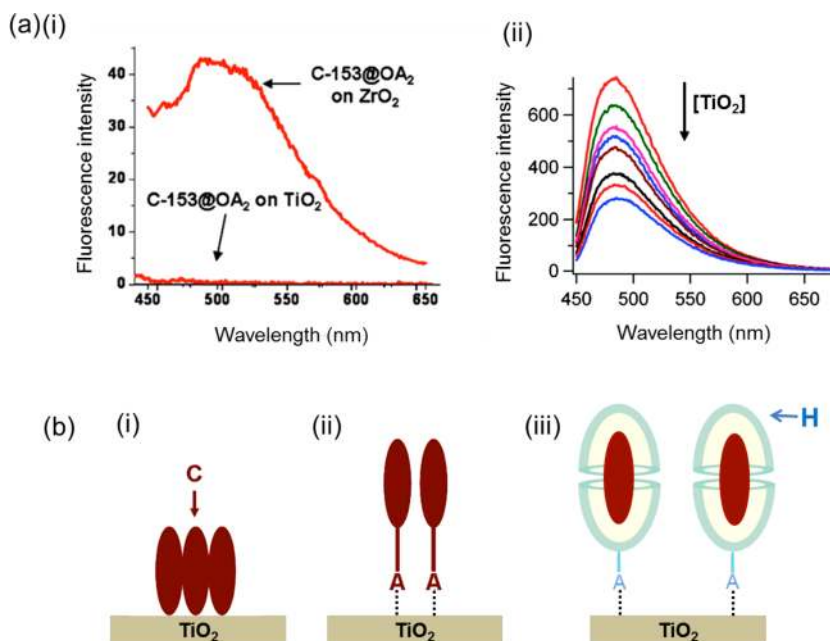


Figure 13. (a) Fluorescence spectra of (i) C153@OA₂ on TiO₂ and the ZrO₂ film, $\lambda_{\text{ex}} = 420$ nm; (ii) titration of C153@OA₂ with TiO₂ solution; $\lambda_{\text{ex}} = 440$ nm, $[\text{C153}] = 1.5 \times 10^{-5}$ M, $[\text{OA}] = 1 \times 10^{-4}$ M in water. (b) Schematic illustration of the chromophore (i) aggregated, (ii) directly bound through a linker-anchor group, and (iii) the chromophore@host bound through the host to metal oxide semiconductor surfaces. C, chromophore; H, host; and A, anchoring group.

between them? The results of these preliminary experiments are briefly summarized below.

Silica and α -zirconium phosphate (α -ZrP) were chosen as potential inert surfaces for examining the stability of capsules and TiO₂ and gold nanoparticles (AuNP) to probe the communication between encapsulated guests and active surfaces. These materials' different surface properties necessitated the modification of the functional groups of the octa acid to enable the OA capsules to adsorb strongly onto either surface. For example, for use with AuNP, either the four COOH groups on the narrower end of OA were replaced with SH (tetraacid tetrathiol, TTTA) or all COOH were removed and replaced with only four SH at the narrower bottom (tetra thiol, TT). Similarly, octaamine (OAm) was prepared by replacing all COOH groups of OA with NH₃⁺ or NMe₃⁺ to enable adsorption onto the negatively charged interlayers of α -ZrP or on the surfaces of saponite clay.⁶¹ See Figure 1b for structures and acronyms of various functionalized cavitants used. To examine the stability of capsules on silica and α -ZrP surfaces, after ensuring the formation of OA or OAm capsuleplexes (by their photophysical properties), we stirred them with silica or α -ZrP surfaces and dried them. The capsules thus prepared were presumed to be stable if their photophysical properties were the same as those of the capsules in aqueous solution. The stability of capsules on surfaces were examined with guest molecules such as anthracene, pyrene, coumarin-1, 4,4'-dimethylbenzil, and thiones (adamantanethione, fenchthione, and camphorthione) (Figure 12) that exhibit differential emissive behavior in the presence of OA.^{36,39,62} For example, within OA, anthracene shows excimer emission, pyrene shows only monomer emission with a ratio of the vibrational fine structure (I_1/I_3) of 0.92 (indicating that pyrene resides in a nonpolar environment), coumarin-1 fluoresces with a maximum at 412 nm, and 4,4'-dimethylbenzil and thiones phosphoresce. However, in isotropic solution anthracene shows only monomer emission, pyrene shows excimer emission

at higher concentrations, coumarin-1 fluoresces with a maximum at 467 nm, and 4,4'-dimethylbenzil and thiones do not phosphoresce.

V.1. Silica Surface. Capsuleplexes with guest molecules of adamantanethione, 4,4'-dimethyl benzil, and anthracene in OA were transferred onto the silica surface as detailed above. The observation of phosphorescence in the case of the former two molecules and the expected excimer emission in the case of anthracene ensured that the capsules were intact on the dry silica surface (Figure 12).⁶³ The lack of emissions when adsorbed without OA confirmed the need for the capsular assembly to prompt the unique emissive behavior. The ability to transfer capsular assemblies from aqueous solution to a solid surface opened up opportunities to explore their properties on other surfaces.

V.2. Interlayers of α -ZrP. The negatively charged surfaces of α -ZrP are present between two layers. Although neutral organic molecules have little or no tendency to adsorb directly onto α -ZrP surfaces, exfoliated α -ZrP is generally used to bind large cationic organic molecules. Thus, α -ZrP seemed to be an ideal system to test whether the supramolecular approach would facilitate the intercalation of neutral molecules into the anionic galleries of α -ZrP.⁶⁴ Positively charged OAm cavitants had to be used to encapsulate and transport neutral guests into the anionic internal surfaces of α -ZrP. In the case of 4,4'-dimethylbenzil, camphorthione, and 4,4'-dimethylstilbene as guests, stirring the guest-encapsulated OAm capsules with exfoliated α -ZrP nanosheets resulted in intercalation of the host-guest assembly as a whole and resulted in phosphorescence from the former two and fluorescence from the third.⁶⁵ This emissive behavior as well as powder XRD suggested the stability of the OAm capsules on the surfaces of α -ZrP. The limitation of the capsular stability in α -ZrP became apparent when the OAm capsules of pyrene and coumarin-1 were studied. The appearance of both monomer (I_1/I_3 of 1.32) and excimer emission upon intercalation of OAm-encapsulated

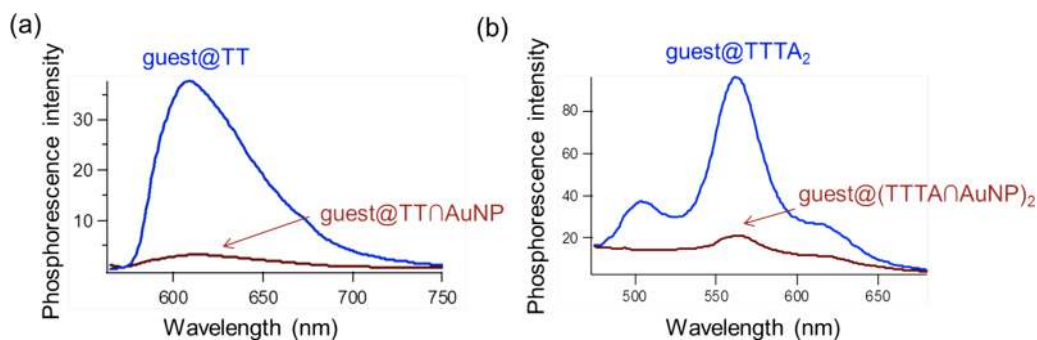


Figure 14. Phosphorescence spectra of (a) adamantanethione@TT (blue) and adamantanethione@TT∩AuNP (brown) (in DMSO, [guest] = 10⁻⁴ M, host/guest = 1:1), λ_{ex} 254 nm and (b) 4,4'-dimethyl benzil@TTTA₂ (blue) and 4,4'-dimethyl benzil@(TTTA∩AuNP)₂ (brown) (in 20 mM NaOH/H₂O, [4,4'-dimethyl benzil] = 10⁻⁴ M, host/guest = 2:1), λ_{ex} 320 nm.

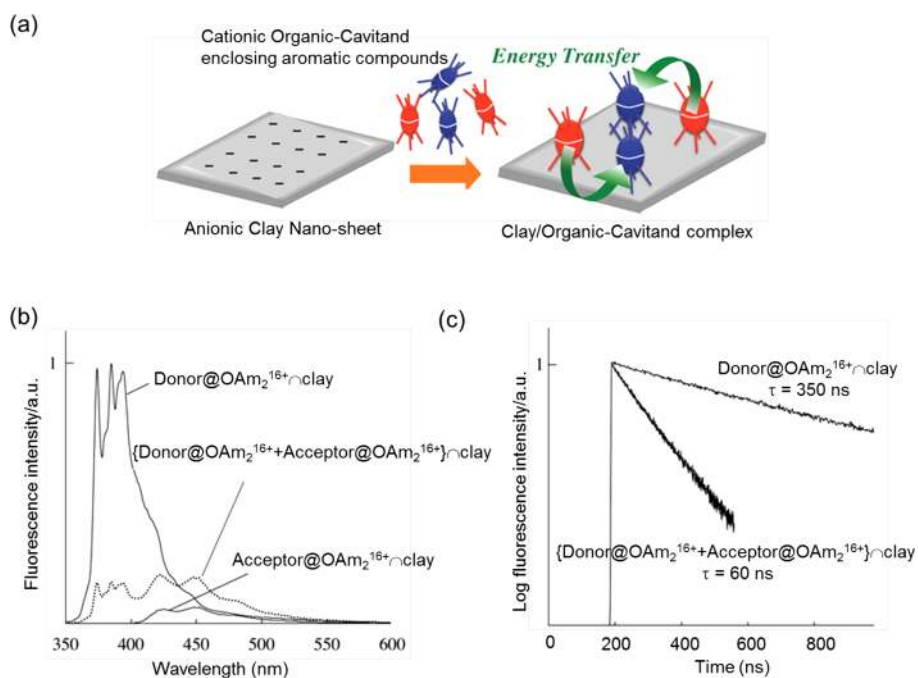


Figure 15. (a) Schematic representation of the arrangement of the donor–acceptor encapsulated within OAM on saponite and (b) fluorescence spectra for the pyrene@OAm₂¹⁶⁺ + 2-acetyl anthracene@OAm₂¹⁶⁺∩clay complex and respective pyrene@OAm₂¹⁶⁺∩clay and 2-acetyl anthracene@OAm₂¹⁶⁺∩clay complexes and (c) fluorescence decays for pyrene@OAm₂¹⁶⁺∩clay and pyrene@OAm₂¹⁶⁺ + 2-acetyl anthracene@OAm₂¹⁶⁺∩clay. Donor (pyrene) excitation at 335 nm, emission at 360 nm. The loading levels were set at 400% vs the CEC of the clay for all samples. [pyrene@OAm₂¹⁶⁺] = [2-acetyl anthracene@OAm₂¹⁶⁺] = 5.0 × 10⁻⁷ M.

pyrene within α -ZrP that showed only monomer emission with an I_1/I_3 of 0.92 before the intercalation suggested that pyrene@OAm₂ is not stable in the galleries of α -ZrP. Similarly, the fluorescence of coumarin-1@OAm₂ incubated with α -ZrP that appeared at 467 nm instead of at 412 nm before intercalation suggested an unstable capsule in the interlayers of α -ZrP. Thus, unlike on the silica surface in the interlayers of α -ZrP, not all capsules are stable. Further experiments are needed to understand fully why some capsules enter the galleries intact and others disassemble.

V.3. TiO₂ Surface. The use of organic molecules as electron donors on the TiO₂ surface is limited by their tendency to aggregate and degrade upon exposure to light and far outweighs their easy access and the fine-tuning of their absorption characteristics through innumerable modifications. Fast interfacial ion–radical recombination due to the proximity between the adsorbed organic dye molecules and TiO₂ surface contributed to the low efficiency of dye-sensitized solar cells.

The typical strategy of attachment of the organic dyes to the TiO₂ surface involving acidic groups (e.g., COOH, SO₃H, and P(O)(OH)₂) precludes the use of robust aromatic molecules lacking functional groups as electron donors on the surface of TiO₂.⁴⁹ On the basis of the above results with OA/OAm capsules on silica and α -ZrP surfaces and believing that it might be possible to overcome many of the above problems with the help of these capsules, we embarked on a study of excited-state behavior of C153@OA₂ anchored on the TiO₂ surface.⁶⁶

The emission spectra of C153@OA₂ upon addition of suspensions of TiO₂ and as adsorbed on TiO₂ films are shown in Figure 13a. The following points should be noted from Figure 13a: The emission from C153 was quenched when C153@OA₂ was adsorbed on the TiO₂ film as opposed to the gradual reduction in the fluorescence intensity on addition of a TiO₂ suspension to C153@OA₂, which was not accompanied by a change in the excited-state lifetime. The above observations are consistent with the conclusion that electron

transfer from excited C153 to TiO_2 takes place when the latter is present as a film or as a suspension. The lifetime independence of the process suggested that the electron transfer was faster than $10^9 \text{ M}^{-1} \text{ s}^{-1}$ (static quenching within the time resolution of the nanosecond single-photon counter). The advantages of a dye included in a capsule over a free dye are illustrated in a cartoon fashion in Figure 13b. The use of OA capsules as carriers of dyes should allow easy exchange of the donor dye and eliminate the need for functionalizing individual dye molecules. Encapsulation of the dye should prevent aggregation of the dyes on the surface of TiO_2 and slow the back electron transfer process. The future of this approach appears to be promising.

V.4. Gold Nanoparticle Surface. In spite of the considerable attention metal nanoparticles have received during the last three decades, the consequence of interaction between excited organic molecules and metal nanoparticles has received only sporadic attention to our knowledge. The inability to adsorb organic molecules directly on detergent-stabilized metal nanoparticles probably contributed to this status quo. Having made progress in adsorbing capsular assemblies containing neutral molecules on silica, $\alpha\text{-ZrP}$, and TiO_2 surfaces, we proceeded to functionalize the surfaces of AuNP with capsular assemblies and examine their influence on the photophysics of encapsulated organic molecules.⁶⁷

The TT cavitand (see Figure 1b for structures) functionalized AuNP's were stirred with the guest adamantaneethione in DMSO, and the cavitand TTTA-functionalized AuNP's were stirred with 4,4'-dimethylbenzil in basic aqueous solution. The phosphorescence spectra of the two guests included within TT, TTTA, TT \cap AuNP, and TTTA \cap AuNP are shown in Figure 14a,b. Note the quenched phosphorescence within the latter two. The phosphorescence from the two guests was quenched by AuNP. Though the exact mechanism is not evident, at this stage it could involve spin transfer through the heavy atom effect, energy transfer, or electron transfer.

V.5. Clay Surface. A clay surface was examined to explore the feasibility of S–S energy transfer between two different encapsulated guests assembled on a solid surface.⁶⁸ Saponite, a clay material arranged as nanostructured flat sheets with regular negative charges on the surface,⁶⁹ was exfoliated into single sheets having optical transparency in the visible region. Protonated OAm was used to align neutral molecules on a negatively charged saponite surface. OAm-encapsulated 2-acetyl anthracene (acceptor) and OAm-encapsulated pyrene (donor) were adsorbed on exfoliated saponite by stirring the two together and filtering through a PTFE membrane. Because there is no specific attraction between the capsules, the donor- and acceptor-containing capsules should be randomly adsorbed on the saponite surface. The capsular content will have no influence on the arrangement of capsules on the clay surface. A schematic representation of the arrangement of this donor–acceptor pair is provided in Figure 15a.

Importantly, the excitation of pyrene@OAm₂ resulted in fluorescence from 2-acetyl anthracene@OAm₂ (Figure 15b) with a concomitant lifetime decrease for pyrene@OAm₂ (Figure 15c) unequivocally establishing S–S energy transfer from pyrene to 2-acetyl anthracene. This is important because the two molecules cannot be adsorbed on the saponite surface on their own. The rate constant for S–S energy transfer and R_0 were calculated to be $1.4 \times 10^7 \text{ s}^{-1}$ (pseudounimolecular) and 31 Å. The above system has established that donor and acceptor molecules lacking affinity for a clay surface could be

aligned with the help of a cationic capsule for S–S energy transfer to occur between the encapsulated pair. This ability thus expands the types of molecules that could serve as candidates for efficient energy-harvest-transfer systems on solid surfaces.

VI. PERSPECTIVES

In this Feature Article we have summarized the value of exploring new water-soluble cavitands to modify the excited-state chemistry of organic guest molecules in water. The features of new host octa acid highlighted in this article are distinctly different from those of the more well known supramolecular assemblies such as micelles, cyclodextrins, and cucurbiturils. The capsular assemblies preferentially formed by OA as opposed to open cavitand assemblies formed by cyclodextrins, cucurbiturils, calixarenes, resorcinarenes, and Pd nanocages provide a truly hydrophobic environment to organic guests in an aqueous environment. Expectedly, depending on the structure of the guest, OA forms either 2:1 or 2:2 capsuleplexes. The guest molecules, depending on their size, shape, and structure, undergo different types of motions, with freedom intermediary between that in crystals and that in isotropic solution within the capsule. The restricted mobility is translated into product selectivity, an aspect not discussed in this article. The OA complexes amenable to NMR and photophysical studies as well as molecular dynamics simulations provide valuable information on the structure and mobility of guests within OA capsules.

The readily achievable functional modification of OA aids the organization of the capsular assemblies on various surfaces, expanding supramolecular photochemistry from solution to solid surfaces. The ability of the cross communication of molecules confined within OA and in the exterior media through electron, energy, and spin transfer opens up opportunities to explore the use of encapsulated donors/acceptors in the context of solar energy capture and storage. The future of OA relies on synthesizing new hosts with different internal dimensions and establishing their value as a catalytic nanoreaction container with clever integration into materials chemistry, where metal nanoparticles continue to play an important role. The capsules' value as a drug-delivery vehicle, which is yet to be established, will open avenues to transporting drugs/loads to desired sites for release on capsular disassembly as needed, which will expand its foray into medicinal chemistry and other applications. The vast potential of capsular assemblies is yet to be fully explored.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Turro, N. J.; Ramamurthy, V.; Scaiano, J. C. *Modern Molecular Photochemistry of Organic Molecules*; University Science Books: Sausalito, CA, 2010.
- (2) Lehn, J.-M. *Supramolecular Chemistry: Concepts and Perspectives*; VCH: New York, 1995.
- (3) Ramamurthy, V. Organic Photochemistry in Organized Media. *Tetrahedron* **1986**, *42*, 5753–5839.
- (4) *Photochemistry in Organized and Constrained Media*; Ramamurthy, V., Ed.; Wiley-VCH: New York, 1991.
- (5) *Supramolecular Photochemistry*; Ramamurthy, V., Inoue, Y., Eds.; John Wiley: Hoboken, NJ, 2011.
- (6) Kalyanasundaram, K. *Photochemistry in Microheterogeneous Systems*; Academic Press: New York, 1987.
- (7) Whitten, D. G.; Russell, J. C.; Schmehl, R. H. Photochemical reactions in organized assemblies. Part 25. Environmental effects on

reactions occurring in micelles, vesicles, films, and multilayer assemblies and at interfaces. *Tetrahedron* **1982**, *38*, 2455–2487.

(8) Ramamurthy, V.; Weiss, R. G.; Hammond, G. S. A Model for the Influence of Organized Media on Photochemical Reactions. In *Advances in photochemistry*, Volman, D.; Hammond, G. S.; Neckers, D. C., Eds.; John Wiley & Sons: New York, 1993; Vol. 18, pp 67–234.

(9) Weiss, R. G.; Ramamurthy, V.; Hammond, G. S. Photochemistry in Organized and Confining Media: A Model. *Acc. Chem. Res.* **1993**, *26*, 530–536.

(10) Gibb, C. L. D.; Gibb, B. C. Well-Defined, Organic Nano-environments in Water: The Hydrophobic Effect Drives a Capsular Assembly. *J. Am. Chem. Soc.* **2004**, *126*, 11408–11409.

(11) Jordan, J. H.; Gibb, B. C. Molecular Containers Assembled through the Hydrophobic Effect. *Chem. Soc. Rev.* **2015**, doi: 10.1039/C4CS00191E.

(12) Cram, D. J.; Cram, J. M. *Container Molecules and Their Guests*; Royal Society of Chemistry: Cambridge, 1997.

(13) *Comprehensive Supramolecular Chemistry, Cyclodextrins*; Szejtli, J., Osa, T., Eds.; Pergamon: Oxford, 1996; Vol. 3.

(14) Lagona, J.; Mukhopadhyay, P.; Chakrabarti, S.; Isaacs, L. The Cucurbit[n]uril Family. *Angew. Chem., Int. Ed.* **2005**, *44*, 4844–4780.

(15) Lee, J. W.; Samal, S.; Selvapalam, N.; Kim, H.-J.; Kim, K. Cucurbituril Homologues and Derivatives: New Opportunities in Supramolecular Chemistry. *Acc. Chem. Res.* **2003**, *36*, 621–630.

(16) Murase, T.; Fujita, M. Pericyclic Reactions in an Aqueous Molecular Flask. *Chem. Rec.* **2010**, *10*, 342–347.

(17) Masson, E.; Ling, X.; Joseph, R.; Mensah, L.-K.; Lu, X. Cucurbituril chemistry: a tale of supramolecular success. *RSC Adv.* **2012**, *2*, 1213–1247.

(18) Bibal, B.; Mongin, C.; Bassani, D. M. Template effects and supramolecular control of photoreactions in solution. *Chem. Soc. Rev.* **2014**, *43*, 4179–4198.

(19) Bohne, C. Supramolecular dynamics. *Chem. Soc. Rev.* **2014**, *43*, 4037–4050.

(20) Bortolus, P.; Monti, S. Photochemistry in Cyclodextrin Cavities. In *Advances in Photochemistry*; Neckers, D. C.; Volman, D. H.; Bunau, G. V., Eds.; Wiley-Interscience: New York, 1996; Vol. 21, pp 1–132.

(21) MacGillivray, L. R.; Papaefstathiou, G. S.; Friscic, T.; Hamilton, T. D.; Bucar, D.-K.; Chu, Q.; Varshney, D. B.; Georgiev, I. G. Supramolecular Control of Reactivity in the Solid State: From Templates to Ladderanes to Metal-Organic Frameworks. *Acc. Chem. Res.* **2008**, *41*, 280–291.

(22) Ramamurthy, V.; Eaton, D. F. Photochemistry and photophysics within cyclodextrin cavities. *Acc. Chem. Res.* **1988**, *21*, 300–306.

(23) Scheffer, J. R.; Garcia-Garibay, M.; Nalamasu, O. The influence of the molecular crystalline environment on organic photorearrangements. In *Organic Photochemistry*, Padwa, A., Ed.; Marcell Decker: New York, 1987; Vol. 8, pp 249–347.

(24) Shimizu, L. S.; Salpage, S. R.; Korous, A. A. Functional Materials from Self-Assembled Bis-Urea Macrocycles. *Acc. Chem. Res.* **2014**, *47*, 2116–2127.

(25) Turro, N. J. From Boiling stones to smart crystals: Supramolecular and Magnetic Isotope Control of Radical-Radical Reactions inside Zeolites. *Acc. Chem. Res.* **2000**, *33*, 637–646.

(26) Turro, N. J. Fun with Photons, Reactive Intermediates, and Friends. Skating on the Edge of the Paradigms of Physical Organic Chemistry, Organic Supramolecular Photochemistry and Spin Chemistry. *J. Org. Chem.* **2011**, *76*, 9863–9890.

(27) Turro, N. J.; Gratzel, M.; Braun, A. M. Photophysical and photochemical processes in micellar systems. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 675–696.

(28) Turro, N. J.; Kraeutler, B. Magnetic field and Magnetic Isotope effects in Organic Photochemical reactions. A novel probe of reaction mechanisms and a method for enrichment of magnetic isotopes. *Acc. Chem. Res.* **1980**, *13*, 369–377.

(29) Vallavoju, N.; Sivaguru, J. Supramolecular Photocatalysis: combining confinement and non-covalent interactions to control light initiated reactions. *Chem. Soc. Rev.* **2014**, *43*, 4084–4101.

(30) Weiss, R. G. Thermotropic liquid crystals as reaction media for mechanistic investigations. *Tetrahedron* **1988**, *44*, 3413–3475.

(31) Yang, C.; Inoue, Y. Supramolecular Photochirogenesis. *Chem. Soc. Rev.* **2014**, *43*, 4123–4143.

(32) Yoshizawa, M.; Klosterman, J. K.; Fujita, M. Functional Molecular Flasks: New Properties and Reactions within Discrete, Self-assembled Hosts. *Angew. Chem., Int. Ed.* **2009**, *48*, 3418–3438.

(33) Jayaraj, N.; Zhao, Y.; Parthasarathy, A.; Porel, M.; Liu, R. S. H.; Ramamurthy, V. Nature of Supramolecular Complexes Controlled by the Structure of the Guest Molecules: Formation of Octa Acid Based Capsuleplex and Cavitandplex. *Langmuir* **2009**, *25*, 10575–10586.

(34) Porel, M.; Jayaraj, N.; Kaanumalle, L. S.; Maddipatla, M. V. S. N.; Parthasarathy, A.; Ramamurthy, V. Cavitand Octa Acid Forms a Nonpolar Capsuleplex Dependent on the Molecular Size and Hydrophobicity of the Guest. *Langmuir* **2009**, *25*, 3473–3481.

(35) Kaanumalle, L. S.; Gibb, C. L. D.; Gibb, B. C.; Ramamurthy, V. Controlling Photochemistry with Distinct Hydrophobic Nanoenvironments. *J. Am. Chem. Soc.* **2004**, *126*, 14366–14367.

(36) Kaanumalle, L. S.; Gibb, C. L. D.; Gibb, B. C.; Ramamurthy, V. A Hydrophobic Nanocapsule Controls the Photophysics of Aromatic Molecules by Suppressing Their Favored Solution Pathways. *J. Am. Chem. Soc.* **2005**, *127*, 3674–3675.

(37) Choudhury, R.; Barman, A.; Prabhakar, R.; Ramamurthy, V. Hydrocarbons Depending on the Chain Length and Head Group Adopt Different Conformations within a Water-Soluble Nanocapsule: ¹H NMR and Molecular Dynamics Studies. *J. Phys. Chem. B* **2013**, *117*, 398–407.

(38) Kulasekharan, R.; Jayaraj, N.; Porel, M.; Choudhury, R.; Sundaresan, A. K.; Parthasarathy, A.; Ottaviani, M. F.; Jockusch, S.; Turro, N. J.; Ramamurthy, V. Guest Rotations within a Capsuleplex Probed by NMR and EPR Techniques. *Langmuir* **2010**, *26*, 6943–6953.

(39) Jayaraj, N.; Jockusch, S.; Kaanumalle, L. S.; Turro, N. J.; Ramamurthy, V. Dynamics of Capsuleplex Formed between Octacid and Organic Guest Molecules- Photophysical Techniques Reveal the Opening and Closing of Capsuleplex. *Can. J. Chem.* **2011**, *89*, 203–213.

(40) Porel, M.; Jockusch, S.; Parthasarathy, A.; Rao, V. J.; Turro, N. J.; Ramamurthy, V. Photoinduced electron transfer between a donor and an acceptor separated by a capsular wall. *Chem. Commun.* **2012**, *48*, 2710–2712.

(41) Tang, H.; de Oliveira, C. S.; Sonntag, G.; Gibb, C. L. D.; Gibb, B. C.; Bohne, C. Dynamics of a Supramolecular Capsule Assembly with Pyrene. *J. Am. Chem. Soc.* **2012**, *134*, 5544–5547.

(42) Farran, A.; Deshayes, D. K. Free Energy Dependence of Intermolecular Triplet Energy Transfer: Observation of the Inverted Region. *J. Phys. Chem.* **1996**, *100*, 3305–3307.

(43) Farran, A.; Deshayes, K.; Matthews, C.; Balanescu, I. "Through Space" Triplet Energy Transfer: Movement of electrons through the hemicarcerand skeleton. *J. Am. Chem. Soc.* **1995**, *117*, 9614–9615.

(44) Jankowska, K. I.; Pagba, C. V.; Chekler, E. L. P.; Deshayes, K.; Piotrowiak, P. Electrostatic Docking of a Supramolecular Host-Guest Assembly to Cytochrome c Probed by a Bidirectional Photoinduced Electron Transfer. *J. Am. Chem. Soc.* **2010**, *132*, 16423–16432.

(45) Parola, J. A.; Pina, F.; Ferreira, E.; Maestri, M.; Balzani, V. Photoinduced Electron- and Energy-Transfer Processes of Biacetyl Imprisoned in a Hemicarcerand. *J. Am. Chem. Soc.* **1996**, *118*, 11610–11616.

(46) Pina, F.; Parola, A. J.; Ferreira, E.; Maestri, M.; Armaroli, N.; Ballardini, R.; Balzani, V. Supramolecular Photochemistry and Photophysics. Biacetyl Imprisoned in a Hemicarcerand. *J. Phys. Chem.* **1995**, *99*, 12701–12703.

(47) Piotrowiak, P.; Deshayes, K.; Romanova, S. Z.; Pagba, C.; Hore, S.; Zordan, G.; Place, I.; Farran, A. Electron and excitation transfer in hetero-supramolecular assemblies and at molecule-nanoparticle interfaces. *Pure Appl. Chem.* **2003**, *75*, 1061–1068.

(48) Place, I.; Farran, A.; Deshayes, K.; Piotrowiak, P. Triplet Energy Transfer through the Walls of Hemicarcerands: Temperature Depend-

ence and the Role of Internal Re-organization Energy. *J. Am. Chem. Soc.* **1998**, *120*, 12626–12633.

(49) Freitag, M.; Galoppini, E. Molecular host-guest complexes: shielding of guests on semiconductor surfaces. *Energy Environ. Sci.* **2011**, *4*, 2482–2494.

(50) Hagfeldt, A.; Gratzel, M. Light - Induced Redox Reactions in Nanocrystalline Systems. *Chem. Rev.* **1995**, *9*, 49–68.

(51) Gratzel, M. Dye-sensitized solar cells. *J. Photochem. Photobiol., C* **2003**, *4*, 145–153.

(52) Gupta, S.; Adhikari, A.; Mandal, A.; Bhattacharyya, K.; Ramamurthy, V. Ultrafast singlet-singlet energy transfer between an acceptor electrostatically attached to the walls of an organic capsule and the enclosed donor. *J. Phys. Chem. C* **2011**, *115*, 9593–9600.

(53) Samanta, S. R.; Parthasarathy, A.; Ramamurthy, V. Supramolecular control during triplet sensitized geometric isomerization of stilbenes encapsulated in a water soluble organic capsule. *Photochem. Photobiol. Sci.* **2012**, *11*, 1652–1660.

(54) Porel, M.; Chuang, C.-H.; Burda, C.; Ramamurthy, V. Ultrafast Photoinduced Electron Transfer between an Incarcerated Donor and a Free Acceptor in Aqueous Solution. *J. Am. Chem. Soc.* **2012**, *134*, 14718–14721.

(55) Kawai, A.; Okutsu, T.; Obi, K. Spin Polarization Generation in the Triplet-Doublet Interaction: Hyperfine-Dependent Chemically Induced Dynamic Electron Polarization. *J. Phys. Chem.* **1991**, *95*, 9130–9134.

(56) Jockusch, S.; Porel, M.; Ramamurthy, V.; Turro, N. J. CIDEP from a Polarized Ketone Triplet State Incarcerated within a Nanocapsule to a Nitroxide in the Bulk Aqueous Solution. *J. Phys. Chem. Lett.* **2011**, *2*, 2877–2880.

(57) Porel, M.; Jockusch, S.; Ottaviani, M. F.; Turro, N. J.; Ramamurthy, V. Interaction between encapsulated excited organic molecules and free nitroxides: communication across a molecular wall. *Langmuir* **2011**, *27*, 10548–10555.

(58) Jockusch, S.; Zeika, O.; Jayaraj, N.; Ramamurthy, V.; Turro, N. J. Electron spin polarization transfer from a nitroxide incarcerated within a nanocapsule to a nitroxide in the bulk aqueous solution. *J. Phys. Chem. Lett.* **2010**, *1*, 2628–2632.

(59) Chen, J. Y. C.; Jayaraj, N.; Jockusch, S.; Ottaviani, M. F.; Ramamurthy, V.; Turro, N. J. An EPR and NMR Study of Supramolecular Effects on Paramagnetic Interaction between a Nitroxide Incarcerated within a Nanocapsule with a Nitroxide in Bulk Aqueous Media. *J. Am. Chem. Soc.* **2008**, *130*, 7206–7207.

(60) Jayaraj, N.; Porel, M.; Ottaviani, M. F.; Maddipatla, M. V. S. N.; Modelli, A.; Da Silva, J. P.; Bhogala, B. R.; Captain, B.; Jockusch, S.; Turro, N. J.; Ramamurthy, V. Self Aggregation of Supramolecules of Nitroxides@Cucurbit[8]uril Revealed by EPR Spectra. *Langmuir* **2009**, *25*, 13820–13832.

(61) Kulasekaran, R.; Ramamurthy, V. New Water-soluble Organic Capsules Are Effective in Controlling Excited State Processes of Guest Molecules. *Org. Lett.* **2011**, *13*, 5092–5095.

(62) Jayaraj, N.; Maddipatla, M. V. S. N.; Prabhakar, R.; Jockusch, S.; Turro, N. J.; Ramamurthy, V. Closed Nanocontainer Enables Thioketones to Phosphoresce at Room Temperature in Aqueous Solution. *J. Phys. Chem. B* **2010**, *114*, 14320–14328.

(63) Ramasamy, E.; Jayaraj, N.; Porel, M.; Ramamurthy, V. Excited State Chemistry of Capsular Assemblies in Aqueous Solution and on Silica Surfaces. *Langmuir* **2012**, *28*, 10–16.

(64) Kumar, C. V.; Raju, B. B. Photoactive Layered Materials: Assembly of Ions, Molecules, Metal Complexes, and Proteins. In *Molecular and Supramolecular Photochemistry*; Ramamurthy, V., Schanze, K. S., Eds.; Marcell Dekker: New York, 2001; Vol. 8, pp 505–576.

(65) Ramasamy, E.; Deshapriya, I. K.; Kulasekharan, R.; Kumar, C. V.; Ramamurthy, V. Photophysical studies of an encapsulated neutral guest intercalated into the 2- dimensional space of alpha-Zr(IV) phosphate. *Photochem. Photobiol. Sci.* **2014**, *13*, 301–309.

(66) Porel, M.; Klimczak, A.; Freitag, M.; Galoppini, E.; Ramamurthy, V. Photoinduced Electron Transfer Across a Molecular

Wall: Coumarin Dyes as Donors and Methyl viologen and TiO₂ as Acceptors. *Langmuir* **2012**, *28*, 3355–3359.

(67) Samanta, S. R.; Kulasekharan, R.; Choudhury, R.; Jagadesan, P.; Jayaraj, N.; Ramamurthy, V. Gold Nanoparticles Functionalized with Deep-Cavity Cavitands: Synthesis, Characterization, and Photo-physical Studies. *Langmuir* **2012**, *28*, 11920–11928.

(68) Ishida, Y.; Kulasekaran, R.; Shimada, T.; Takagi, S.; Ramamurthy, V. Efficient Singlet-Singlet Energy Transfer in a Novel Host-Guest Assembly Composed of an Organic Cavitand, Aromatic Molecules and Clay Nanosheet. *Langmuir* **2013**, *29*, 1748–1753.

(69) Takagi, S.; Shimada, T.; Ishida, Y.; Fujimura, T.; Masui, D.; Tachibana, H.; Eguchi, M.; Inoue, H. Size-Matching Effect on Inorganic Nanosheets: Control of Distance, Alignment, and Orientation of Molecular Adsorption as a Bottom-Up Methodology for Nanomaterials. *Langmuir* **2013**, *29*, 2108–2119.