ULTRAFAST EXCITED STATE DYNAMICS OF SPATIALLY CONFINED ORGANIC MOLECULES

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Abstract

This article highlights the role of spatial confinement in controlling the fundamental behavior of molecules. Select examples illustrate the value of using space as a tool to control and understand excited state dynamics through a combination of ultrafast spectroscopy and conventional steady state methods. Molecules of interest were confined within a closed molecular capsule, derived from a cavitand known as octa acid (OA), whose internal void space is sufficient to accommodate molecules as long as tetracene and as wide as pyrene. The free space, *i.e*. the space that is left following the occupation of the guest within the host, is shown to play a significant role in altering the behavior of guest molecules in the excited state. The results reported here suggest that in addition to weak interactions that are commonly emphasized in supramolecular chemistry, the extent of empty space (i.e. the remaining void space within the capsule) is important in controlling the excited state behavior of confined molecules on ultrafast time scales. For example, the role of free space in controlling the excited state dynamics of guest molecules is highlighted by probing the *cis-trans* isomerization of stilbenes and azobenzenes within the OA capsule. Isomerization of both types of molecule are slowed when they are confined within a small space, with encapsulated azobenzenes taking a different reaction pathway compared to that in solution upon excitation to S_2. In addition to steric constraints, confinement of reactive molecules in a small space helps to override the need for diffusion to bring the reactants together, thus enabling the measurement of processes that occur faster than the time scale for diffusion. The advantages of reducing free space and confining reactive molecules are illustrated by recording unprecedented excimer emission from anthracene and by measuring ultrafast electron transfer rates across the organic molecular wall. By monitoring the

translational motion of anthracene pairs in a restricted space it has been possible to document the pathway undertaken by excited anthracene from inception to the formation of the excimer on the excited state surface. Similarly, ultrafast electron transfer experiments pursued here have established that the process is not hindered by a molecular wall. Apparently, the electron can cross the OA capsule wall provided the donor and acceptor are in close proximity. Measurements on the ultrafast time scale provide crucial insights for each of the examples presented here, emphasizing the value of both 'space' and 'time' in controlling and understanding the dynamics of excited molecules.

Introduction

Recognizing the importance of 'time'[1-7] and 'space'[8-9] in photochemistry,[10] this article is concerned with the dynamics of confined molecules on the manifold of excited states between the time of their inception and the subsequent re-entry to the ground state (typically a few ps to a few ns timescale). Studies in organic solvents have established that the excited state dynamics of molecules are controlled not only by their inherent electronic properties but also by the properties (e.g., micro-polarity and micro-viscosity) of the environment where they reside. However, since fluid solvent molecules can accommodate changes in the size and shape of the reactant molecules, the 'space' needed for a molecule to undergo structural changes is not readily apparent when carrying out experiments in solution. Thus, space cannot be used as a tool to control photochemistry and photophysics in solution. On the other hand, excited state reactions in biological media (i.e., enzyme pockets) are selective, at least partly, due to the fact that the surroundings are relatively rigid and have the ability to control the free space around the reactant molecule. An impressive example of this behavior is the highly selective geometric isomerization of retinal within the hydrophobic pocket of the protein opsin.[11-14]

In this article, we highlight recent experiments that use a synthetic host known as octa acid (OA; see below)[15] as a closed reaction container to illustrate the importance of 'space' in controlling the excited state chemistry associated with several fundamental phenomena, including geometric isomerization, dimerization, electron transfer initiated reactions, excimer formation and heavy atom induced intersystem crossing.[16-17] Similar to the pocket of a protein,[12-14, 18-19] the OA capsule provides a rigid framework that limits the motions of atoms during a reaction. The influence of such restrictions is perhaps most evident for geometric isomerization reactions that result in a large change of molecular structure on the ultrafast time scale. For example, a study of stilbenes[20-25] and azobenzenes[23, 26-27] has revealed the difference in spatial needs for the geometric isomerization for these two systems within OA capsule based on the different mechanisms for isomerization around C=C and N=N bonds.[25-27]

The properties of 'space' and 'time' are also evident for bimolecular reactions. In solution, diffusion masks the real rates of fast photochemical process involving two molecules and thus hinders the detailed understanding of a photochemical event. Limiting the separation between two reactants by controlling the space they occupy is well utilized by nature in photosynthetic machinery to perform energy and electron transfer. In this article we illustrate

how the rate of electron transfer can be enhanced by bringing the donor and acceptor closer together with the help of an organic host. In the process we have been able to establish that electron transfer can occur across a molecular wall.[17, 28-34] A similar approach unraveled the details of anthracene excimer formation, a process that is not observed in isotropic solution.[35-36] A pair of anthracene molecules confined within the restricted volume of the capsule chooses a less space demanding pathway of excimer formation rather than dimerization, which is the preferred in isotropic solution. Restricting the space around the pair is necessary to force anthracene to choose the excimer pathway. Thus 'space' can be a valuable tool in probing excited state processes involving more than one reactant molecule.

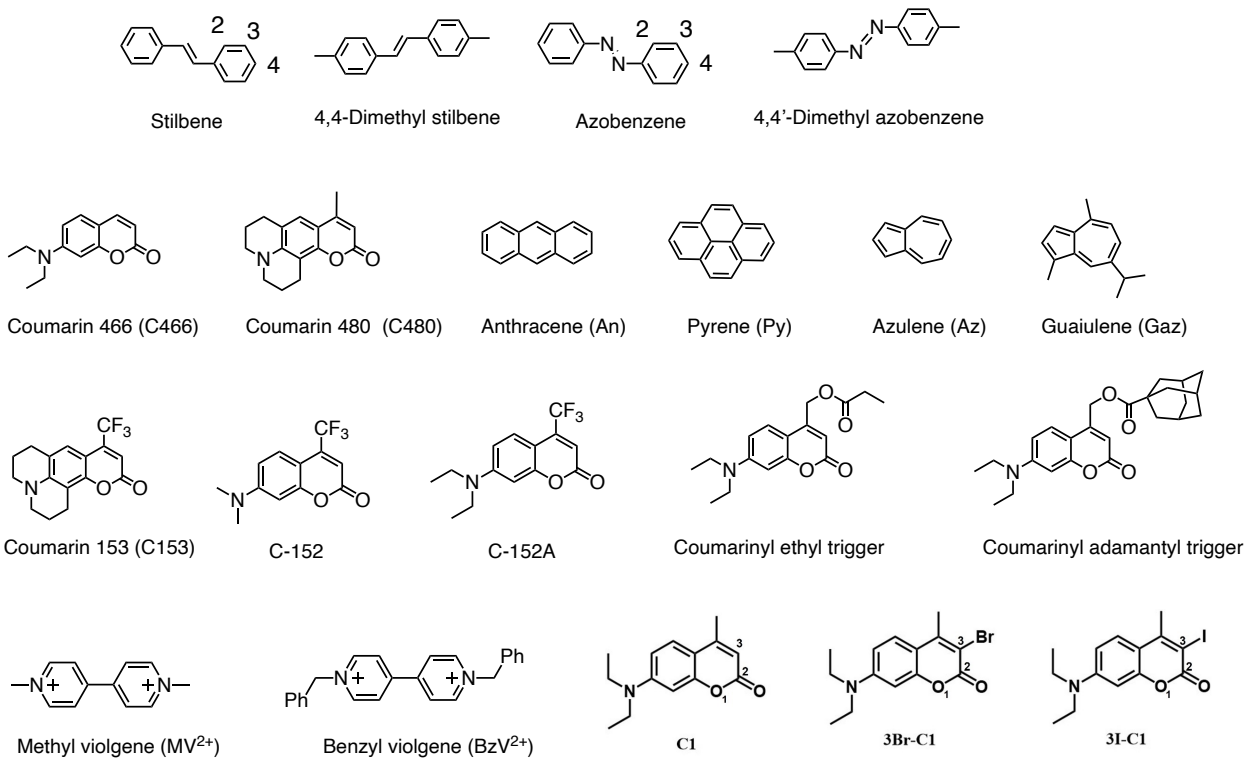
We find that time is also a valuable tool in understanding the mechanistic details of excited state processes that depend on the space around a molecule. Most organic photochemical laboratories employ steady state and nanosecond time resolved techniques to identify photoreactions and probe their mechanisms. During the last few decades with the help of ultrafast spectroscopic experiments greater insight into a number of fundamental photoreactions in solutions have been obtained.[3-5] For example, role of Woodward-Hoffmann rules in excited state electrocyclic reactions of dienes and trienes in solution and gas phase could only be obtained through ultrafast spectroscopic measurements.[37-47] Similarly, ultrafast spectroscopic experiments have played a significant role in understanding the dynamics of geometric isomerization of stilbenes[46, 48-53] and azobenzenes[54-59] in solution and retinyl systems in proteins.[13-14, 60-61] Thus a combination of steady state and ultrafast experiments has helped to gain a full understanding of dynamics of molecules on excited state surfaces. Similar to solution studies, we show in this article that probing spatially confined molecules at ultrafast time scales (femtosecond to picosecond) reveals details that cannot be gleaned at longer time scales. This has been recognized by other groups as well.[62-67] For example, the unexpected behavior of excited azobenzene and anthracene molecules in a confined space could not have been traced had we not probed them with ultrafast spectroscopic techniques. The ultrafast time scale is especially relevant for understanding the role of space, considering that the structural evolution of excited molecules occurs in the few hundred femtosecond to picosecond range. Thus, the examples discussed below highlight the importance of combining ultrafast experiments and closed confined space in understanding the excited state dynamics of molecules, as well as the

need for a collaborative approach between organic and physical chemists in solving problems in photochemistry and photophysics.

The confined space

Published results from our laboratories on ultrafast excited state dynamics of molecules enclosed within a confined capsule are highlighted in this article. The confined capsule is formed by two molecules of a synthetic host known as octa acid (OA).[15-17, 68-70] The eight COOH groups present at the periphery of OA renders it water-soluble at a slightly basic pH (borate buffer; solubility limit 10^{-3} M). Several features distinguish OA from other commonly used water-soluble hosts such as cyclodextrins (CD), cucurbiturils (CB), calixarenes (CA) and metal organic cages (*e.g.*, Pd nano-cages).[70] Unlike these hosts that form open cavitandplexes, two molecules of OA, in the presence of a guest spontaneously assemble to form a capsuleplex.[15, 71] Thus, the chemistry discussed here occurs in fully closed capsules.

The OA capsule, shown in Figure 1, can host hydrophobic molecules, including stilbenes, azobenzenes, coumarins and anthracene, the molecules of concern here (Scheme 1). Depending on the size of the guest molecule, the OA capsule can enclose one or two molecules to form host-guest (H:G) complexes of 2:1 or 2:2 ratio.[72-74] The stoichiometry and structure of the host-guest complexes are generally inferred from 1D- and 2D-NMR (DOSY, ROSY and NOSY) spectroscopy. The guest molecules are driven from water into the capsule due to hydrophobic effect and held inside through very weak C–H---π (aromatic), π---π (aromatic – aromatic) and van der Walls interactions.[75-78] The interior of the capsule is devoid of functional groups that can establish strong intermolecular interactions with the guest. Consequently, the 'free space', defined as the empty space left after the guest's occupation of the capsule, would play a crucial role in determining the mobility of encapsulated guest molecules within the capsule.[8-9]



Scheme 1. Chemical structures of the guests used in this study.

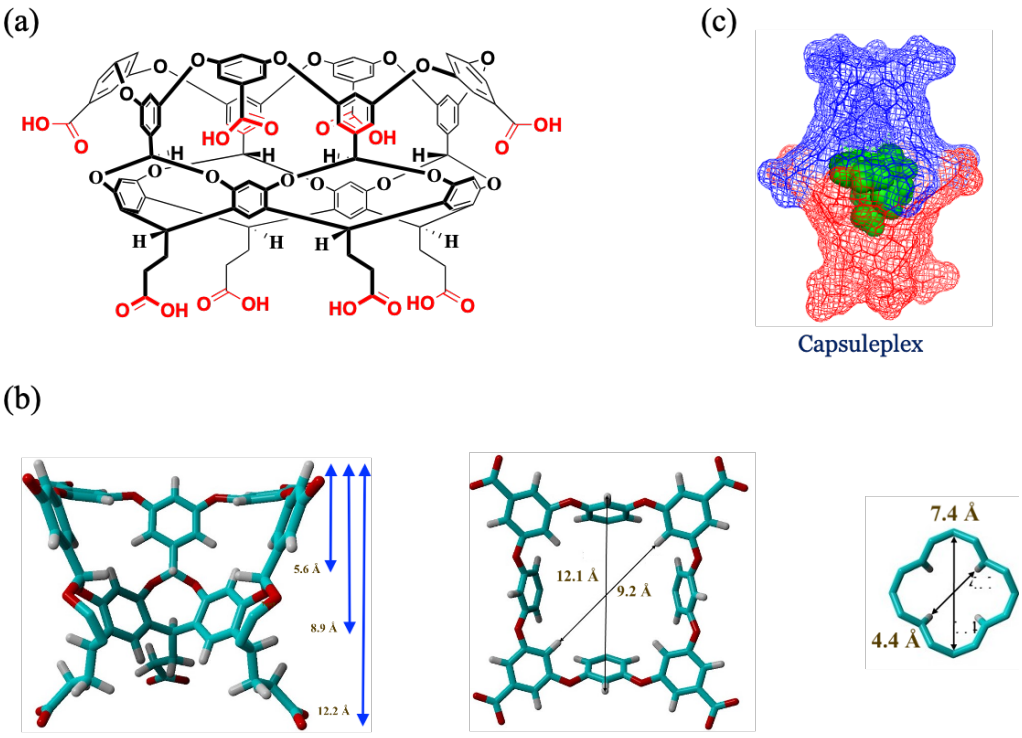


Figure 1. **(a)** Chemical structure of the host octa acid. (b) Internal dimensions of the host shown in side, top, and bottom views. (c) Capsular assembly with a guest inside.

In the context of probing the photochemistry of OA encapsulated molecules the following points are to be noted: (a) The interior of the capsule is dry even though the capsule is submerged in water.[79] The internal micro-polarity of the capsule is similar to that of benzene as revealed by fluorescence spectroscopy and corroborated by the EPR coupling constants of nitroxide probes.[80] (b) The limits for excitation and interpretation of the emission are set by the OA capsule absorbing between 220 and 300 nm and fluorescing weakly in the region 320 to 430 nm.[81] (c) Due to the OA capsule's electron donating capability from the presence of electron rich aryl ether framework, electron transfer studies should avoid donors whose oxidation potential is above ~1.5 eV.[81] (d) OA's high intersystem crossing efficiency from its multiple COO^- groups may generate triplets of guests *via* energy transfer from unintended excitation.[81] (e) Since the capsule is made up of two molecules, it is dynamic in character.[82-86] The stability of the capsule depends on the guest. The capsule's ability to remain fully closed during the time scale of photochemist's interest will depend on the size of the guest. Large guests should be avoided.

Ultrafast photoisomerization dynamics of stilbenes and azobenzenes in a restricted environment

Geometric isomerization of C=C and N=N bonds is one of the fundamental unimolecular photoreactions known to trigger various biological, chemical and physical events. The former plays an important role in biological processes such as vision (rhodopsin), energy gathering by bacteria (bacteriorhodopsin), photosensory events (PYP), phototaxis, *etc*. involving protein pockets as the reaction cavity.[11-14, 18-19, 60, 87-88] Isomerization of N=N bonds is exploited in various material science related applications involving liquid crystals, polymers, gels, *etc*. as reaction media.[89-90] While the basic mechanism of isomerization is likely to remain the same in various media including enzyme pockets, details are likely to vary between isotropic solution and the organized/confined media. With this in mind we investigated the geometric isomerization of two exemplar groups of molecules, stilbenes and azobenzenes (top row of Scheme 1) confined in the small space of the interior of the OA capsule.[20-21, 25-27] The geometric isomerization of stilbene and azobenzene has been studied in detail in solution and are established to proceed *via* different pathways, the former by torsional rotation and the later by either inversion or a combination of inversion and torsional motions. While the former sweeps a larger volume, the latter covers much less space during the isomerization process.[47, 91-93] The study of both systems within the OA capsule was undertaken to examine the role of confinement on the two related photoreactions requiring different amounts of space. Results on the parent system as well as two alkyl substituted systems (4,4'-dimethyl and 4-propyl), briefly highlighted below, suggest that the dynamics of geometric isomerization of the above molecules is significantly altered when they are confined in the small space of the OA capsule interior. For details on these and related systems, the readers are referred to original publications.[25-27]

All of the stilbenes and azobenzenes discussed here 1 form 1:2 complexes with OA (guest@OA_2) in water with a borate buffer. The influence of confinement on the photoisomerization of all six molecules (parent, 4,4'-dimethyl and 4-propyl substituted) was monitored by determining the quantum yield of *trans* to *cis* isomerization (QY), the S_1 excited state lifetime (τ) and the relative composition at photostationary state (PSSt) (Table 1). The photostationary state is a measure of the relative population of the two isomers when the composition no longer changes upon further irradiation.[94] To gather information concerning the

early stages of isomerization and to monitor the lifetime of the excited state, transient absorption spectra (TAS) were recorded with ultrafast time resolution, where the guests alone were excited. Each of these measurements confirmed that confinement leads to changes in the excited state dynamics.

Table 1. Comparison of photoisomerization (trans to cis) data in solution and within OA capsule: Stilbenes and Azobenzens[a-d]

Molecule *trans* isomers of	Photostationary state *trans* to *cis* (%)		Quantum Yield of *trans* to c*is* isomerization (%)		Lifetime of S_1 (ps)	
	Solution	Capsule	Solution	Capsule	Solution	Capsule
Stilbene	---	---	51	12	72	260
4-Methylstilbene	8:92	8:92	46	15	89	300
4-Ethylstilbene	20:82	≤ 1:99	43	18	84	289
4-Propyylstilbene	23:77	≤ 1:99	41	24	86	384
2,2'-Dimethylstilbene	9:91	15:75	57	29	124	430
3.3'-Dimethylstilbene	17:79	15:85	55	28	119	358
4,4'-Dimethylstilbene	18:76	80:20	39	6	218	670
Azobenzene	---	---	0.11	0.05	2.6	13
4-Methylazobenzene	86:14	83:17	0.10	0.10	1.8	15
4-Ethylazobenzene	90:10	77:23	0.15	0.12	2.3	21
4-Proylazobenzene	88:12	97:3	0.12	0.17	2.5	26
4,4'-Dimethylazobenzene	95:5	68:32	0.13	0.05	2.4	35
4,4'-Methylpropylazo benzene	91:9	70:30	0.13	0.03	2.6	55

a. For details please see the original publications, ref 21, 25-27.
b. Solution studies were conducted in cyclohexane in the case of stilbenes and toluene in the case of azobenzenes.
c. Lifetime, quantum yield and photostationary state data in the case of stilbenes were obtained upon excitation to S_1.
d. Lifetime, quantum yield and photostationary state data in the case of azobenzenes were obtained upon excitation to S_2.

Clear evidence of the OA capsule influencing the isomerization came from the changes in the QY for both stilbenes and azobenzenes (Table 1).[25-27] In the case of stilbenes in free solution one finds the excited molecule to partition nearly equally to *cis* and *trans* isomers; *i.e*., the QY varies between 0.39 and 0.51 for the series in Table 1. However, in the case of azobenzenes, the QY in cyclohexane is between 0.10 and 0.15, attributable to the excited *trans* returning to the ground state through a conical intersection (CoIn) that favors the *trans* side of the ground state potential. Upon comparing the QY within the OA capsule and in solution, it is clear that the isomerization of both stilbenes and azobenzenes is affected by confinement. For example the QY for stilbene decreases from 0.51 in solution to 0.12 within OA. Similar reduction was also observed in the case of azobenzene (0.11 to 0.05). The significantly lower value of the QY for both stilbene and azobenzene within the OA capsule compared to solution suggests that isomerization is impeded within the capsule independent of the isomerization mechanism (*i.e*., rotation or inversion). However, the larger reduction of the QY in the case of stilbene ($QY_{Soln}/QY_{OA} = 4.3$) than in azobenzene ($QY_{Soln}/QY_{OA} = 2.2$) probably reflects the different amount of free volume required for isomerization *via* rotation and inversion.

The fact that the capsule is able to influence the geometric isomerization of even the parent stilbene and azobenzene systems suggests that the capsular influence is not due to any specific host-guest interactions. Keeping in mind that the stilbene QY is independent of solvent polarity we attribute the above changes to the spatial effect of the capsule. However, the influence of weak interactions that are often emphasized in supramolecular chemistry becomes apparent with 4,4'-dimethyl and 4-propyl systems. One of the most dramatic examples of the influence of OA capsule is 4,4'-dimethyl stilbene, for which the QY decreased from 0.39 to 0.06 ($QY_{Soln}/QY_{OA} = 6.5$). A larger barrier for rotation in this case is attributed not only to confinement but also to the anchoring of the methyl groups to the corners of the OA capsule via C–H---π interaction between the guest and the host, which provides an additional restriction to isomerization. The less dramatic effect in the case of 4,4'-dimethyl azobenzene ($QY_{Soln}/QY_{OA} = 2.6$) is probably a consequence of the lower isomerization yield for azobenzenes even in free solution, although we note that the effect of OA on this di-substituted molecule is still stronger than the unsubstituted parent. Thus, the above examples reveal that both free space and weak interactions play a role when excited state isomerization occurs in a confined space.[8-9]

The excited state lifetimes of stilbenes and azobenzenes in cyclohexane and within the OA capsule (see Table 1) were determined from the decay of the excited state absorption (ESA) bands in the transient absorption spectra.[25-27] The lifetimes for all of the stilbenes are much longer inside OA than in cyclohexane, with the ratio τ_{OA}/τ_{soln} varying between about 3 and 4.5. The longer lifetime within the capsule implies the presence of an additional barrier between the Franck-Condon point on the excited state and the CoIn that returns the molecule to the ground state. Nearly the same level of increase in excited state lifetime for both unsubstituted parent stilbene (τ_{OA}/τ_{soln}: 3.6 times) and 4,4'-dimethyl stilbene (τ_{OA}/τ_{soln}: 3.1 times) suggests that the barrier is built up at the very early stages of isomerization and the substituent does not play a significant role at this stage. Restricted rotation and tumbling of the stilbene molecule within the OA capsule is also evident from the longer anisotropic decay time (>1 ns) compared to that in cyclohexane (< 0.2 ns), where the former represents reorientation of the entire capsuleplex (Figure 2). Given this information the interior of the OA capsule posing a barrier for torsional rotation is not surprising.

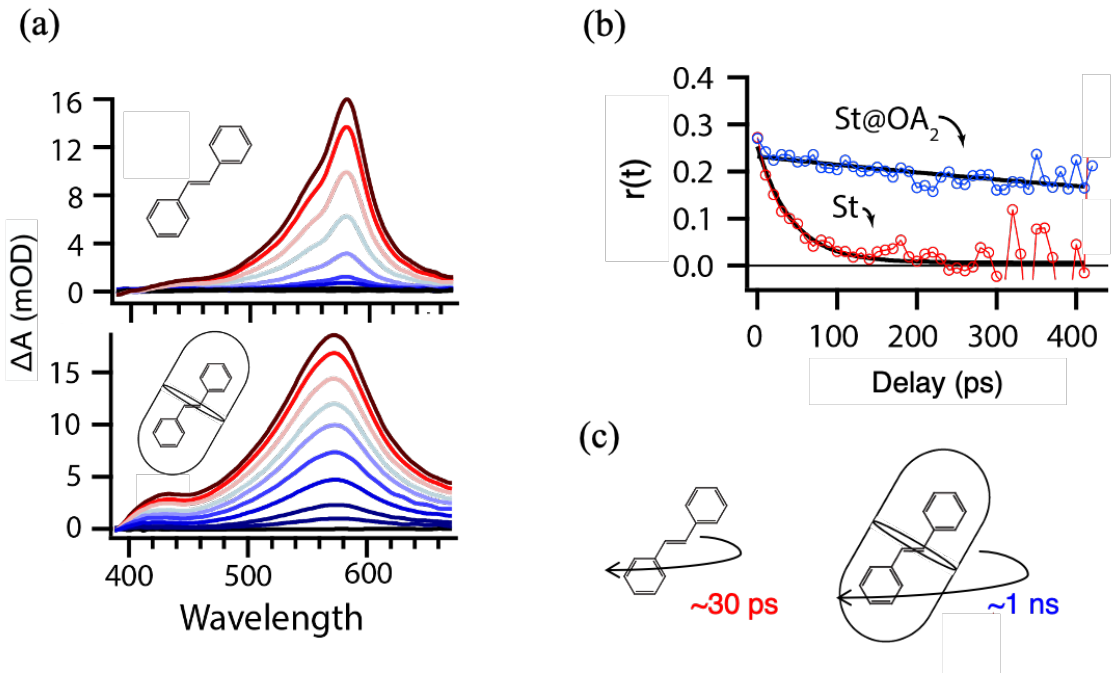


Figure 2. (a) Evolution of the transient absorption spectra following 300 nm excitation of stilbene derivatives in cyclohexane and encapsulated in aqueous OA capsule. (b) Anisotropy decay for stilbene in cyclohexane and in OA capsule. (c) Anisotropy decay times of stilbene in

cyclohexane and OA capsule. (Reprinted with permission from ref 25, Copyright 2019 American Chemical Society).

Encapsulation in OA also affects the excited state lifetimes of azobenzenes.[26] From Table 1, it is clear that the excited state lifetimes of the azobenzenes are longer within OA capsule than in cyclohexane. The longer lifetime for unsubstituted azobenzene, similar to stilbene, supports the conclusion that confinement increases the barrier for isomerization. However, the influence of confinement on the lifetime seems to be larger for azobenzene (azobenzene τ_{OA}/τ_{soln}: 5; stilbene: 3.6). Additionally, the influence of alkyl substitution is even more significant for azobenzenes. In the case of 4,4'-dimethyl and 4-propyl azobenzenes τ_{OA}/τ_{soln} were found to be 14.5 and 10.4 respectively. The large increase in these substituted azobenzenes with respect to the unsubstituted parent azobenzene suggests that the intermolecular forces between the alkyl groups and the interior of the capsule also contribute to the capsular effect on the geometric isomerization of azobenzenes. This is different from stilbenes where the alkyl groups had no special effect. Once again, the difference in mechanism of the isomerization may be responsible for such a difference.

In addition to the QY and excited-state lifetime measurements for *trans* to *cis* isomerization, the PSSt composition reveals information about the role of confinement on the reverse reaction. Combining information for the forward and reverse reactions provides a window on the dynamics through the seam of conical intersections that returns a molecule to the ground state.[95] The PSSt composition for several alkyl substituted stilbenes estimated upon steady state irradiation is valuable in this context.[24-27] The extent to which OA influences the PSSt of a given olefin depends on the location and nature of the alkyl substituent. For example, upon irradiation 4,4'-dimethyl stilbene showed a reversed PSSt composition in OA capsule favoring *trans* (*trans* to *cis*: 80 to 20) as opposed to favoring *cis* in hexane (*trans* to *cis*: 18 to 76). The difference reflects a more significant reduction of the QY for *cis* to *trans* isomerization compared with the forward reaction due to the confinement effects that favor the extended structure of the molecule in OA (i.e., due to anchoring the methyl groups in the two ends of the capsule). In contrast, the PSSt for 4-propyl stilbene consisted of 97% *cis* in OA compared with only 80% in solution due to the relaxed interaction on one end of the molecule and the ability of

the molecule to better fill the space of the cavity in the more compact *cis* geometry (Figure 3). Thus the nature of the alkyl group alters the PSSt composition from that in hexane.

Based on the available experimental evidence, the proposed potential energy surface (PES) diagram for torsional motion of stilbene in solution and within the capsule is shown in Figure 3. In this model, the reduction in QY is portrayed to be due to changes in the structure dependent topology of the CoIn. For example, destabilization of the *cis* in 4, 4'-dimethyl stilbene and the *trans* in 4-propyl stilbene within OA capsule in the ground state, as suggested by MD simulation (Figure 3), could tilt the CoIn to favor relaxation back to their corresponding isomer in the ground state. Importantly, the 'tilting' of the CoIn may depend on the structure of the cavity (*i.e.*, the relative orientation of the two host molecules), and therefore could be different depending on the initial structure of the guest molecule upon excitation. In other words, the red lines in Figure 3 might represent a snapshot for the frozen capsule geometry that could evolve on a timescale comparable to or slightly longer than the excited state lifetime of the encapsulated stilbene. At this stage we can only conclude that the characteristics of CoIn including location and dynamics are not the same within the OA capsule and in solution. More experimental results and/or excited state simulations are needed to propose a model with predictive power and fully understand how the confined space controls the excited state dynamics.

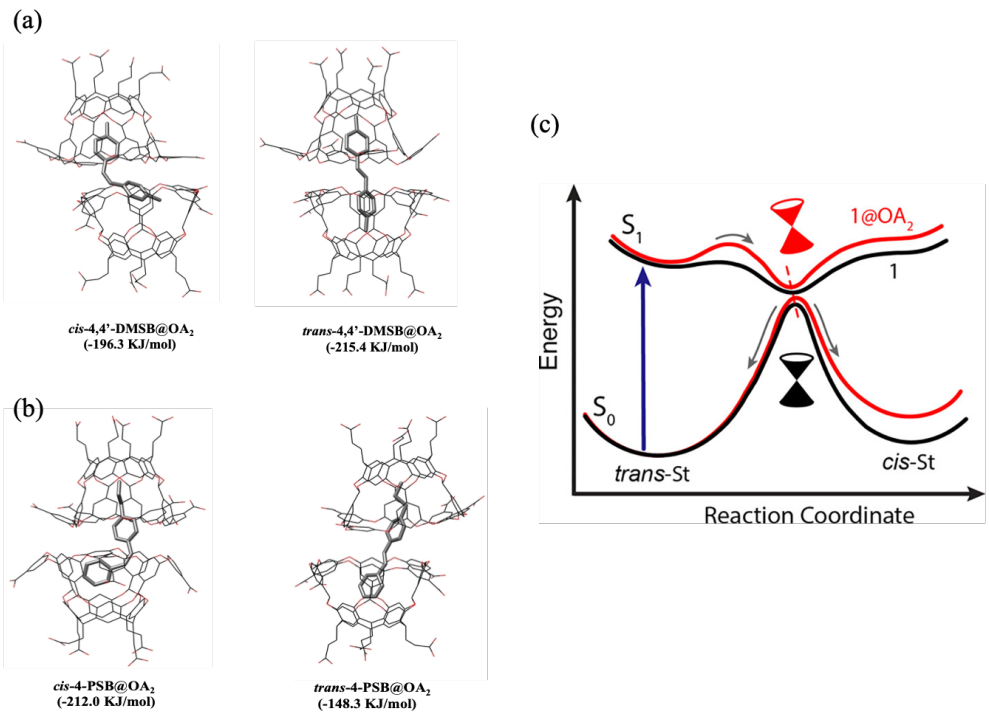


Figure 3. Most representative structures and energies of *cis* and trans *isomer* complexes within OA obtained from MD Simulations: (a) 4,4'-dimethylstilbene and (b) 4-propylstilbene. (c) Schematic diagram of the potential energy surface along the reaction coordinate for stilbene in solution (black) and in the capsule (red). Encapsulation raises the barrier for isomerization in the excited state and influences the conical intersection with the ground state. (Reprinted with permission from ref 25. Copyright 2019 American Chemical Society).

Kinetic modeling of the transient absorption spectra generated upon S_1 and S_2 excitations of azobenzene highlighted yet another unusual effect of confinement on the isomerization process involving N=N bonds.[26] Species associated spectra (SAS) representing the absorption spectra of various intermediates in the relaxation of azobenzene confirm the involvement of the same species upon excitation to S_1 at 470 nm in cyclohexane and within OA capsule (Figure 4). However, the associated time constants of the various intermediates point to a varied pathway pursued by the vibrationally excited azobenzene (S_1*) in the two media. Two paths are available in free solution, one that directly access the CoIn to the ground state and another that samples a local minimum on the excited state potential. The direct path to the CoIn is not favored in the capsule and furthermore the increased lifetime in the excited state (13.8 ps compared with 2.4 ps

in cyclohexane) indicates a deeper local minimum that inhibits the motion to the region of the CoIn. Such behavior indicates that confinement in the capsule directly affects the isomerization pathway in the excited state of azobenzene, even at early stages.

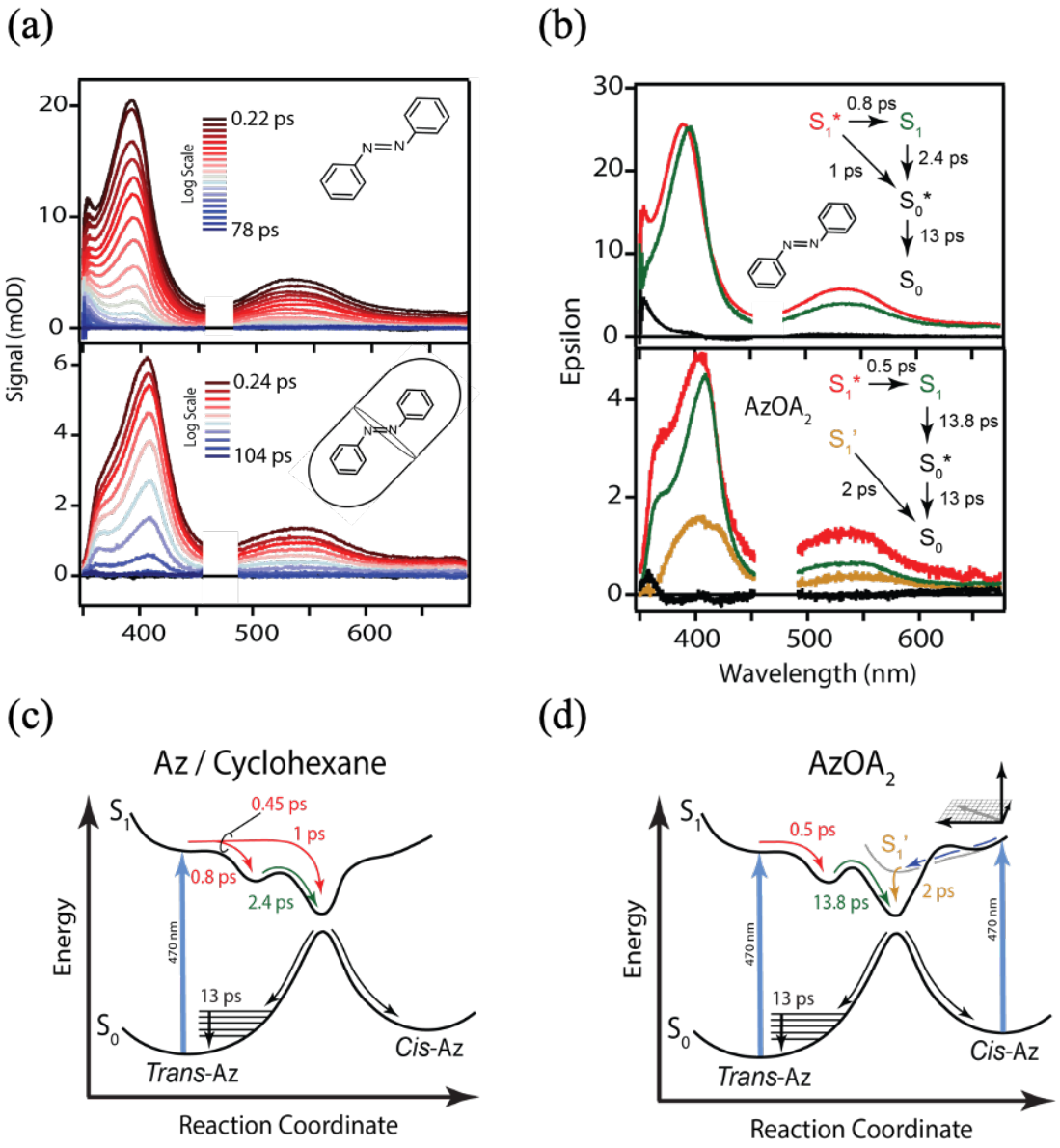


Figure 4. (a) Evolution of the TA spectra following nπ* excitation at 470 nm for *trans*-azobenzene in cyclohexane and OA capsule. (b) Species-associated spectra for nπ* excitation of *trans*-azobenzene in cyclohexane and OA capsule. The kinetic models and lifetimes from the global fits are shown in the insets. (c) Schematic diagram of the potential energy curves for

trans-azobenzene in cyclohexane and OA capsule for nπ* excitation. (Reprinted with permission from ref 26. Copyright 2020 the Royal Society of Chemistry).

Even more striking differences were observed upon excitation of azobenzene to the S_2 state at 320 nm. The species associated spectra of various intermediates in solution and within OA capsule are shown in Figure 5, along with schematic potential energy curves and observed lifetimes. Close analysis of the dynamics in the two media brings out the uniqueness of confinement on excited state processes. Several features are worth noting: (a) Initial excitation to S_2 imparts additional vibrational energy to the molecule upon rapid internal conversion to S_1 which allows the excited molecule to directly access the CoIn with the ground state despite the deeper local minimum on the S_1 potential. (b) Relaxation from the S_2 excited state results in some molecules reaching the *cis* isomer in the excited state in competition with the direct pathway to the CoIn and trapping in the *trans* geometry (330 fs), an adiabatic geometric isomerization hitherto not reported within a confined space with any system. This process is absent in cyclohexane, where the lifetime of the cis isomer is also much shorter (~100 fs compared with 2.4 ps in the capsule). Thus, within the capsule, the pathway taken by the molecule in the S_1 state with excess vibrational energy (reached upon S_2 excitation) differs from that taken by vibrationally relaxed molecules (reached upon S_1 excitation). The different behaviors can be understood in terms of confinement effects that shape the excited-state potential energy surface of encapsulated molecules and therefore influence the dynamics. Although challenging, more detailed understanding should be possible from excited-state simulations.

The above two examples have unequivocally brought out the potential of a confined space in altering the well-established reaction dynamics in solution. Overall, the steady state and ultrafast time resolved experiments have revealed that the mechanistic features of geometric isomerization via torsional and inversion motions within a confined space are not a simple extension of the solution characteristics.

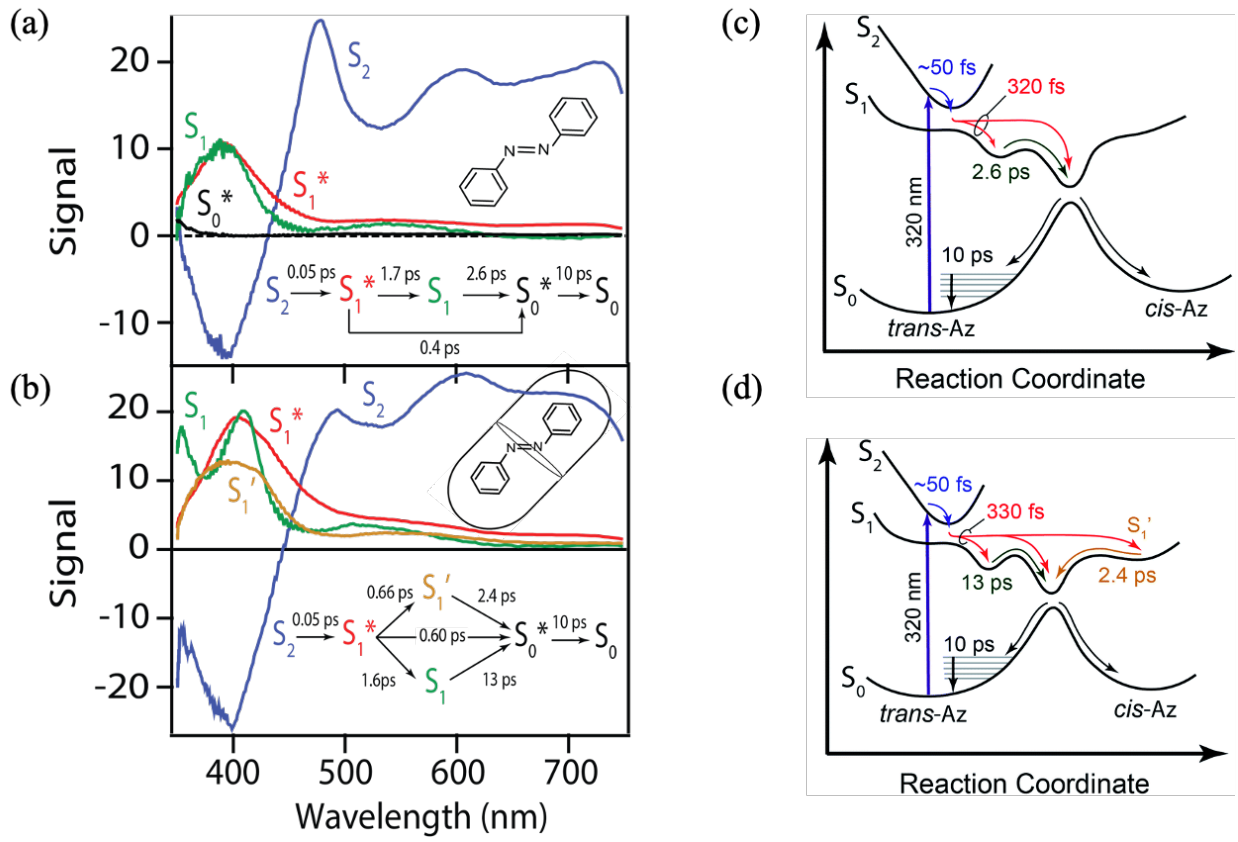


Figure 5. Species associated spectra for ππ* excitation of azobenzene in cyclohexane (a) and the OA capsule (b). The spectra are from global fits to the transient absorption spectra using the kinetic models shown in the insets. Schematic diagram of the potential energy curves for for ππ* excitation of *trans*-azobenzene in cyclohexane (c) and in the OA capsule (d). ((Reprinted with permission from ref 26. Copyright 2020 the Royal Society of Chemistry).

Ultrafast dynamics of excimer formation in a confined space

In solution the need for diffusion forbids measuring any process faster than diffusion. In this section we demonstrate that this could be overcome by performing the photochemistry in a restricted environment where reactants are pre-organized so that the diffusion is not a requirement. Under such conditions the dynamics of excited molecules are likely to be in a time scale different from that in isotropic solution. In this section, we show that information concerning translational motions of a pair of molecules along a tortuous confined path can be deciphered from ultrafast spectroscopic measurements. The example we have chosen to

illustrate this possibility is the excimer formation of anthracene (AN) that is known to photodimerize but not show excimer emission in solution at room temperature.[96-98] The tendency of the dimer size to be larger than the pair of AN suggests the possibility of suppressing the dimerization process in a 'confined container' such as OA capsule that cannot accommodate the dimer. The excimer, which contrary to the dimer does not involve a large change in volume, is not expected to be influenced by the 'confined space'. This feature should favor excimer formation over dimerization when the reaction space is restricted. Further, pre-organizing two aromatic molecules in a confined space excludes the need of diffusion before the excimer formation.

The emission of AN, sparingly soluble in water (10^{-7} M), arises from aggregates with no accompanying excimer emission. Slow addition of OA to borate buffer solution of AN replaces the aggregate emission with a broad, structureless band in the region 450 to 620 nm, with very low intensity structured emission around 400-420 nm, (Figure 6a).[35-36] The former is attributed to 2:2 host:guest complex ($AN_2@OA_2$), whose formation is confirmed by NMR. Based on excitation spectra and complexation studies, the residual weak emission in the region 400-420 nm is attributed, depending on the concentration of OA present in the solution, to either $AN@OA_2$ or uncomplexed AN in bulk. The broad emission (450 to 620 nm) as well as a long lifetime of 263 ns are similar to those previously reported for anthracene excimer generated by photocleavage of the covalent dimer in an organic glass and crystalline state at 77°.[99-101] Given the repeatedly unsuccessful attempts at excimer emission of AN in organic solvents at room temperature, the observed emission from OA encapsulated AN in aqueous solution at room temperature is remarkable. What remains is to understand how did the excimer formation occur within the confined space while in isotropic solution this does not happen?

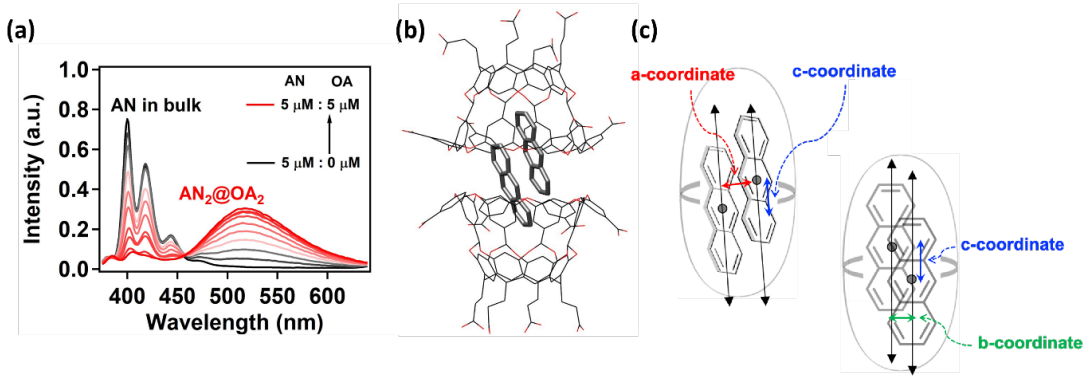


Figure 6. (a) Formation of $AN_2@OA_2$ complex (red) from bulk AN (black) upon gradual addition of octa acid (OA) studied through fluorescence upon exciting at 375 nm. (b) MD simulated slip-stacked geometry of two AN molecules within the 2:2 complex. (c) Three plausible coordinates of movements of these two AN, along the a-coordinate two AN comes closer to one another, along the b-coordinate one AN shifts along the short axis of the other AN and along the c-coordinate one AN slips along the long axis of the other AN. (Reprinted with permission from ref 36. Copyright 2021 American Chemical Society).

A slip-stacked geometry of two AN molecules within the 2:2 complex, one top of each other (at a distance of 3.26 Å) and slightly slipped along the long and short axis was deduced from both ^{1}H NMR spectra and molecular dynamics (MD) simulation (Figure 6b). This pair of AN can form an excimer with a slight adjustment of their positions upon excitation. To examine such a possibility, the AN molecule confined within OA capsule was excited at 375 nm. The low photon flux of the excitation ensures that the two AN molecules within the OA capsule are not excited simultaneously. A slow rise time (150 ps) of the excimer emission (520 nm) confirms ground state complex is not responsible for the excimer emission (Figure 7a). This is also supported by the similar rise time component (5.1-5.3 ps) recorded for methyl-viologen radical cation formation through electron transfer from the monomer ($AN@OA_2$ complex) and excimer emissions ($AN_2@OA_2$ complex) (Figure 7b and 7c). Apparently, excimer emission results from excitation of one of the two AN molecules and it's movement towards the adjacent ground state

AN. This movement provides an opportunity to closely follow the dynamics of excimer formation on the excited state surface within the confined space of OA capsule.

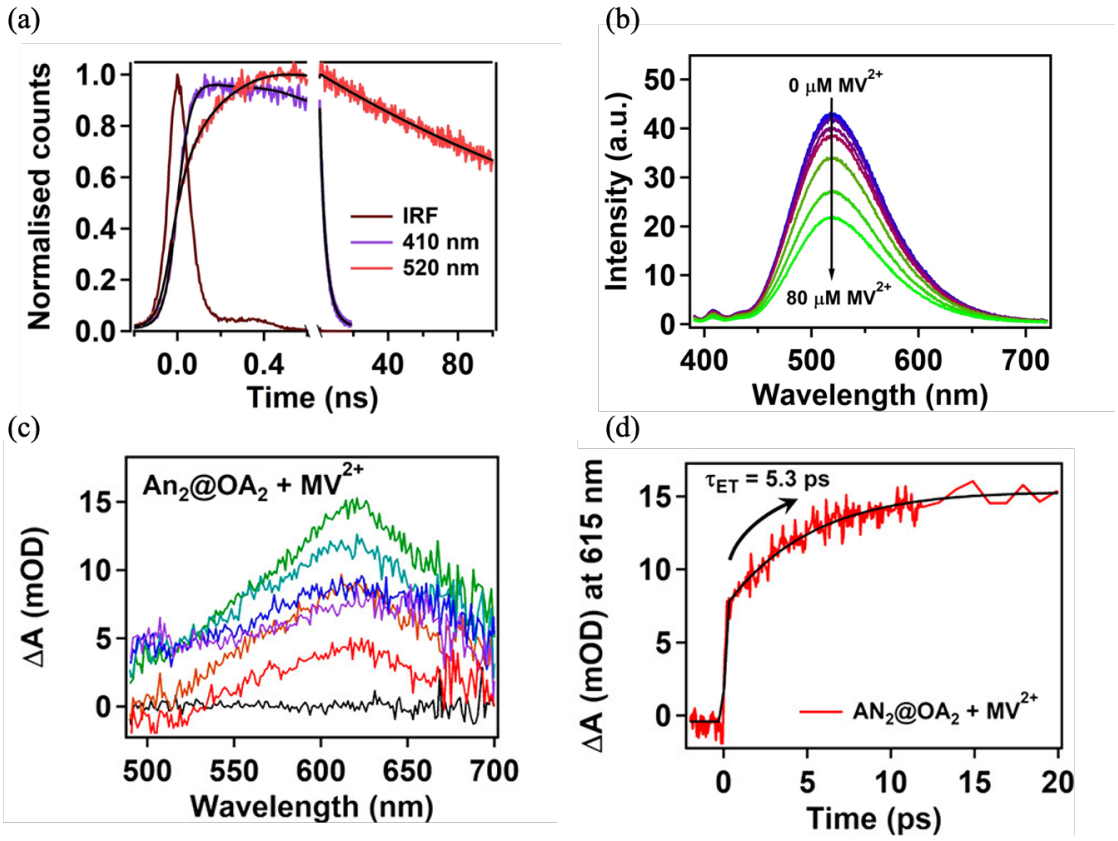


Figure 7. (a) Fluorescence transients of $AN_2@OA_2$ complex upon exciting at 375 nm. Multiexponential fitted lines to the transients are displayed in black. Fluorescence transient at 520 nm has a rise component. (b) Steady state emission spectra of $An_2@OA_2$ with increasing concentration of MV^{2+}. Spectra in the 390-430 nm region are shown as 10 times enlargements of the original data for better visualization. (c) Transient absorption spectra at some selected time delays (black: 0 ps; purple: 0.5 ps; blue: 1 ps; cyan: 5 ps; green: 20 ps; orange: 400 ps; red: 1000 ps) and (d) fitted kinetics at 615 nm for $AN_2@OA_2$, in presence of MV^{2+}. ([AN] = 100 μM and $[MV^{2+}]$ = 10 mM). Formation of positive TA band around 615 nm indicates the formation of methyl viologen radical cation ($MV^{\bullet+}$) and hence confirms the PET process for $AN_2@OA_2$. (Reprinted with permission from ref 36. Copyright 2021 American Chemical Society)

Figure 8a presents the transient emission spectra obtained in the time range 0 to 20 ns. The emission shape and maximum change with time. Immediately following the excitation, the emission is narrower and structured with a maximum at ~420 nm along with another maximum at ~460 nm. With time the intensity of the 420 nm band decreased and the structureless band moved to longer wavelength with the maximum shifting slowly towards 520 nm (excimer). The 420 nm band was not used for further analysis as it was identified to be originating from the residual AN@OA_2 or AN@bulk present in the solution. A close inspection of the structureless band revealed a red shift of emission with time, which is unusual and has not been reported during excimer formation in any media (Figure 8b). The zero-time spectrum was found at 458 nm, which is broad and structureless. It indicates that unlike in the bulk medium, AN exists in a pre-excimer type geometry inside the OA cavity, that gradually shifts towards the excimer. Evidently, the motion of the pair of molecules (AN* +AN) to attain a better geometry for excimer formation along the reaction co-ordinate within the capsule must be slow in comparison to the radiative process. Time resolved area normalized emission spectra in Figures 8c and 8d bring out yet another remarkable feature. The presence of at least two isoemissive points at 448 nm (0 to 0.1 ns window) and 487 nm (0.1 to 9 ns window) is reflective of the presence of at least three states marked M, N and O in the kinetic model presented in Figure 9a, which is also supported by the quantum chemical calculations (QM/MM-TDDFT). The time-dependent change of the ratio of the initial state (intensity of the initial peak position) and the final state (intensity of the final peak position) for each of these two steps are found to be exponential, with a time constant of 0.06 ns and 2.65 ns. Among the two, the second step is much slower, which indicates the presence of a significant barrier in its path.

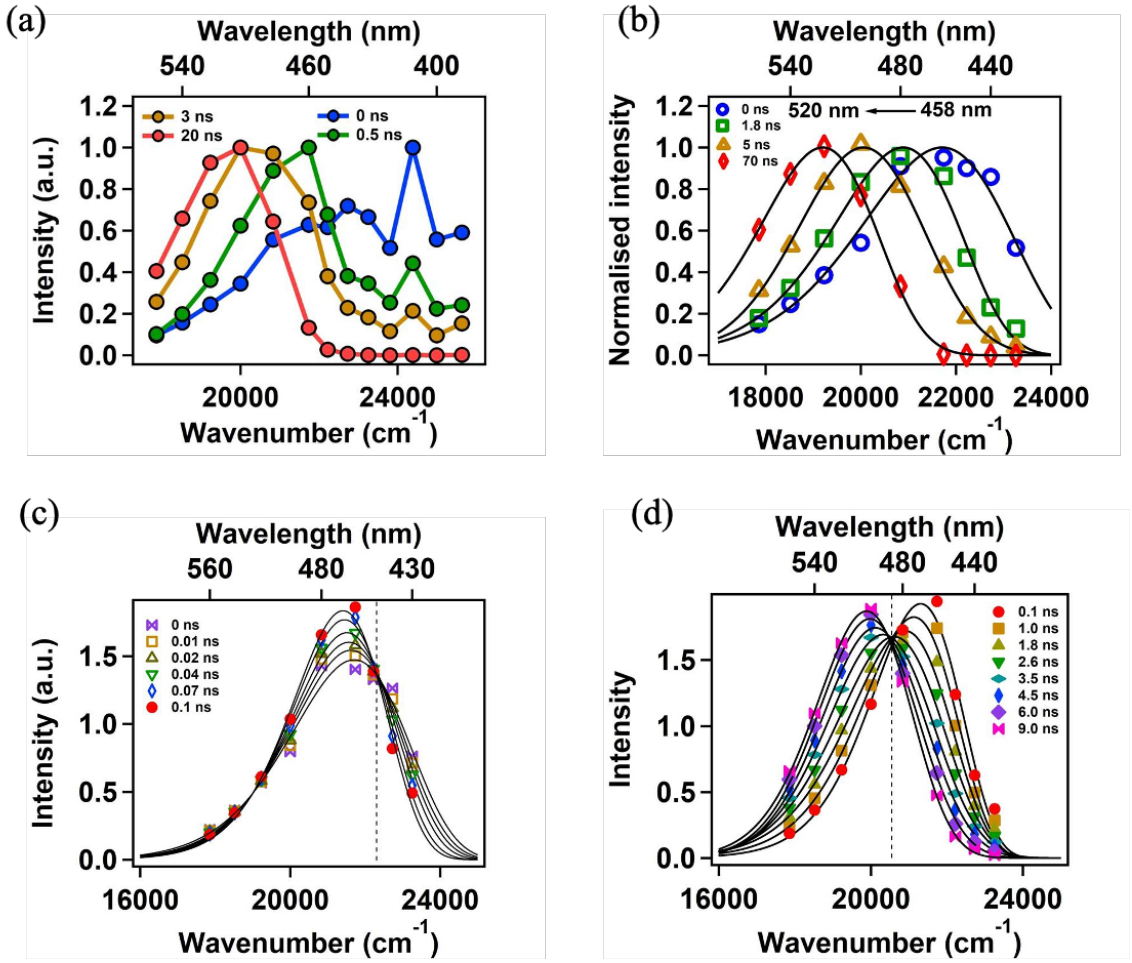


Figure 8. (a) Representative time-resolved emission spectra (TRES) (blue, 0 ns; green, 0.5 ns; yellow, 3 ns; red, 20 ns) constructed from the fitting parameters of fluorescent transients at different wavelengths along the steady-state emission spectra (390−560 nm). (b) Some representative TRES in the excimer region (blue circles, 0 ns; green squares, 1.8 ns; yellow triangles, 5 ns; red diamonds, 70 ns) fitted to a log-normal function (solid black lines). In this case the wavelength region 390−420 nm, which is mainly contributed by AN@OA_2 and free AN in bulk is excluded. Note the excimer emission shifts to longer wavelength with time. (c) and (d) TRANES showing the isoemissive points at different wavenumber at different times. Two different isoemissive points indicate that the overall process of energy relaxation occurs through two different steps. (Reprinted with permission from ref 36. Copyright 2021 American Chemical Society).

The pathway from the ground state (S_0) slip-stacked dimer to excimer mapped through QM is shown in Figure 9b. The results show that upon excitation, AN forms three types of excimers, benzene-, naphthalene- and anthracene-like of which the latter two are more stable within the OA capsule, while anthracene-like in the gas phase. As per this model, upon excitation to S_1, two molecules moves closer to the other and the pair reaches a naphthalene-like excimer by adjusting their positions along all three axes and would then reach anthracene-like excimer and emit. According to QM calculations the excimer formation within the capsule will not be as smooth as in solution and would likely involve at least one intermediate state. Results of ultrafast spectroscopic measurements described above provide an insight into the dynamics of excimer formation within the confined space of OA capsule and are consistent with QM calculations. Overall, a combination of molecular modeling, QM calculations, steady state and ultrafast time resolved experiments within the confined reaction cavity of OA have brought to light the unique features of excimer formation dynamics of aromatic molecules and established that the dynamics in a confined space is different from that in solution. The above study illustrates the power of combining 'space' and 'time' to understand the dynamics of molecules on an excited state surface.

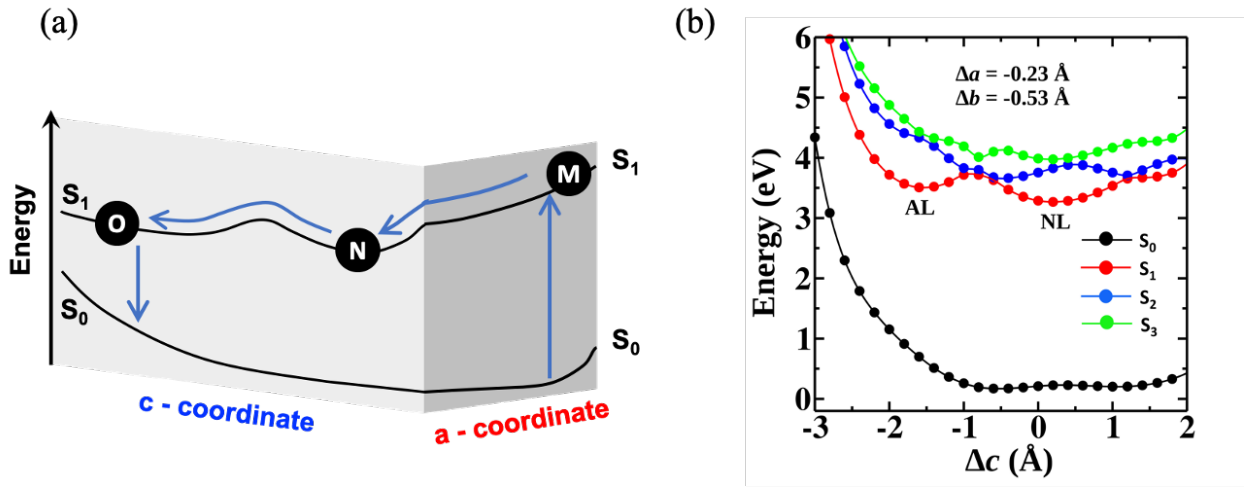


Figure 9. (a) Kinetic model based on the results of TRES, TRANES and the theoretically calculated PES (see text for expansion of abreviations). (b) Quantum mechanically calculated potential energy curve along the c coordinate with a and b assuming their minimum values on S_1

(Δa = −0.23 and Δb = −0.53) (see the original article for details). The locations of the anthracene-like (AL) and naphthalene-like (NL) excimer minima are marked. The energies and the displacements are plotted relative to their respective values in the optimized structure. (Reprinted with permission from ref 36. Copyright 2021 American Chemical Society).

Ultrafast electron transfer across the capsular wall

Of the many recent findings related to chemistry and physics within confined spaces, an important one is the occurrence of communication (electron, energy and spin transfer) between a confined donor and a free acceptor across the capsular wall.[17] Given this phenomenon is likely to have significant impact in both biological and materials sciences, it is fundamentally important to understand the process in depth. In this section our results on electron transfer across the capsular wall are discussed.[28-34, 102-103] Initial observation from steady state experiments with 4,4'-dimethyl stilbene as the donor and 4,4'-dimethyl viologen as the acceptor with OA capsule as the confined container raised a number of questions: (a) What is the role of the OA wall in this intermolecular remote electron transfer? (b) What is the rate of the process? (c) What is the mechanism? - is it by super exchange involving the capsular wall or via a tunneling process by-passing the wall? (d) Does it follow the well-established Marcus relationship? (e) Is there a strong electronic coupling (V_{el}) between the donor and acceptor molecules and how large is the reorganization energy (λ)? As discussed below these questions could only be answered through ultrafast experiments.

To answer the above questions, electron transfer between eleven donor-acceptor pairs (donors being encapsulated within hydrophobic OA capsule) listed in Scheme 1 was examined by femtosecond transient absorption spectroscopic experiments. The viologen acceptors, because of their cationic charge, stayed closer to the walls of the OA capsule decorated with eight COO^-. To have confidence in the results, it is important to note that partial opening of the capsule takes ~ 5 μs and disassembly and full reassembly takes ~ 2.7 s. The capsule is therefore fully closed with no possibility for water seeping in the < ns (see below) time required for the electron transfer. The time constants for forward transfer that is presumed to be the inverse of the rate constant of the electron transfer were measured by monitoring the rise of the viologen cation radical at 610 nm (Figure 10a,b). A plot of the rate constants of electron transfer against ΔG° values (obtained from electrochemical measurements) for the eleven pairs shown in Figure

10c displays remarkable Marcus inversion behavior suggesting the process occurring across the OA wall to follow the established model in homogeneous solution. The observed rate constants of electron transfer (Figure 10c, 3.2 x 10^{10} - 4 x 10^{11} s^{-1}), well-above the diffusion constant in aqueous solution, confirm the process to be static with no diffusion involved and consequently participation of OA wall in the electron transfer process.

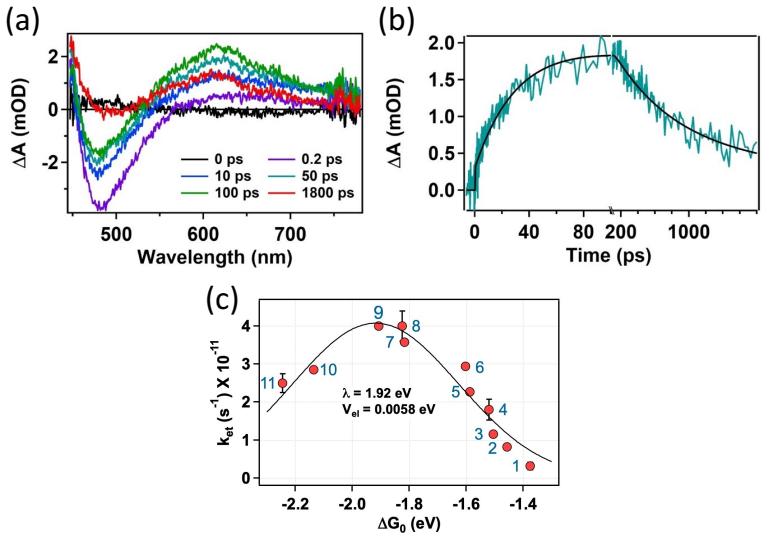


Figure 10. (a) Plot of transient absorption spectra at different time delay (in the early time stimulated emission of the C153 can be seen and with time it decreases and the absorption band at 610 nm which is due to the formation of $MV^{+\bullet}$, starts to increase). (b) Kinetic trace at 610 nm along with the fit (black solid line) for C153@OA2 in presence of 10 mM MV^{2+} (pump pulse: 400 nm, probe: 450-760 nm). (c) Plot of rate constant of electron transfer (k_{et}) obtained from transient absorption spectroscopy vs the estimated ΔG^0 for different donor/OA_2-acceptor pairs from 1-11. The pairs from 1-11 are respectively C153@OA_2 + MV^{2+}, C153@OA_2 + BzV^{2+}, Py@OA_2 + MV^{2+}, An@OA_2 + MV^{2+}, Py@OA_2 + BzV^{2+}, An@OA_2 + BzV^{2+}, C466@OA_2 + BzV^{2+}, C480@OA_2 + MV^{2+}, C480@OA_2 + BzV^{2+}, Gaz@OA_2 + MV^{2+} and Az@OA_2 + MV^{2+}. The plot was fitted with equation 1. The fitted line is displayed in black solid line. Experimental error for three representative points is also given. (Reprinted with permission from ref 34. Copyright 2020 American Chemical Society).

The Marcus relationship shown in Figure 10c provided insight into the mechanism of capsule mediated electron transfer. Using the estimated rate constants and ΔG° values in the basic equation of Marcus theory (Eq. 1), the reorganization energy (λ) and the electronic coupling matrix element (V_{el}) were calculated to be 1.918 eV and 0.0058 eV, respectively. Given the rigid environment of the OA capsular interior surrounding the donor and the expected lack of significant changes in solvation of the acceptor, still expected to be attached to the external walls of the capsule following electron transfer, the measured reorganization energy is believed to be mainly internal in nature (λ_ι). The slightly higher value of λ than the one reported for reverse electron transfer between solvent separated ion pairs in solution (equivalent to a capsular wall separated ion pair) is likely a reflection of the confinement of the donor.[104] Compared to the solvent separated ion pair, the confinement probably hinders the changes in nuclear geometry of the encapsulated donor. Thus the role of confinement is reflected in the λ value.

$$k_{et} = \frac{a}{\sqrt{\lambda}} \exp\left\{-\frac{(\Delta G^0+\lambda)^2}{b\lambda}\right\} \quad (1)$$

$$a = \frac{4\pi^2}{h}\frac{V_{el}^2}{\sqrt{4\pi k_B T}} \quad (2)$$

$$b = 4k_B T \quad (3)$$

The estimated V_{el} answers the question of whether the capsular wall participates in the electron transfer. The current supramolecular assembly could be visualized to be similar to a donor-acceptor system on a molecular 'clamp' separated by a solvent molecule.[105-108] For these systems V_{el} is reported to be in the range of 0.0035 - 0.0068 ± 0.00161 eV. The slightly enhanced value observed in the current supramolecular assembly is likely the result of the static nature of the system [donor-capsular wall-acceptor] compared to the dynamic system [donor-(C-clamp-solvent molecule)-acceptor] discussed in the literature. To conclude, ultrafast transient spectroscopic measurements has allowed us to establish the role of confinement and the capsular wall in the remote electron transfer. The results have set the stage to understanding the phenomenon by quantum chemical approach currently underway. The above experiments, where ultrafast dynamics has played a central role, have established that for electron transfer, donor and acceptor need not be adjacent and separation by another molecule will not prevent it.

Probing capsule dynamics through ultrafast spectroscopic experiments

As discussed above, the OA capsule is made up of two molecules and depending on the guest it can assemble and disassemble in various time scales (Figure 11).[82-84, 86] A fully closed capsule would be ideal to reap the full effect of the hydrophobic confined environment on the guest molecule. To gain a mechanistic understanding of an excited state phenomenon within OA capsule it is important to know whether the capsule is fully closed, partially closed or open. This is evident from the electron transfer example discussed above. As discussed below ultrafast spectroscopic experiments help us probe the time scale of the capsule stability.

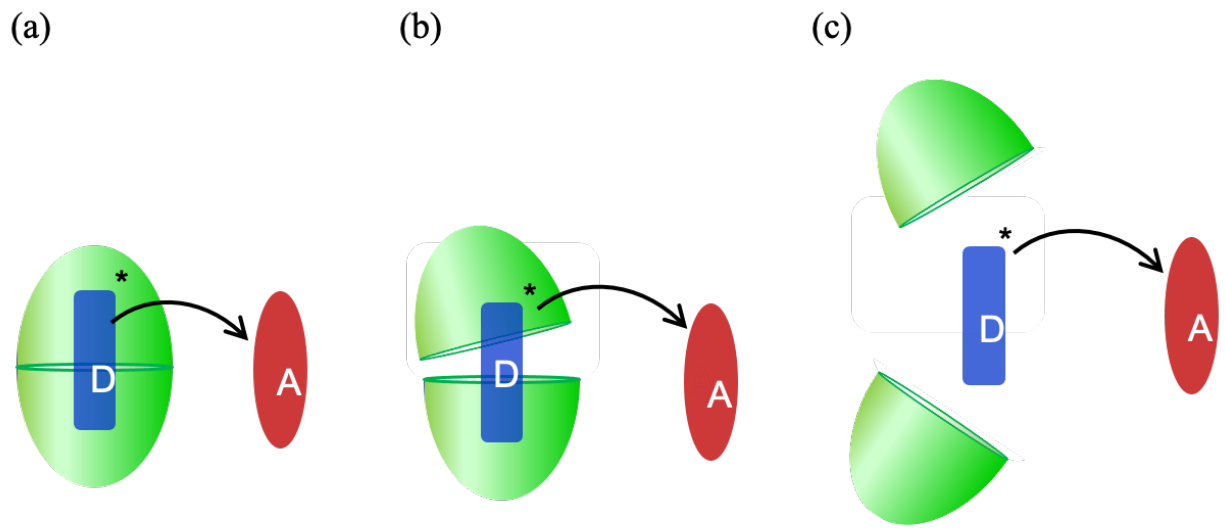


Figure 11. Closed, fully open, and partially open OA−guest complex. The time scales for fully opening and partially opening of the complex are different (~2.7 s and ~5 μs, respectively). (Reprinted with permission from ref 31. Copyright 2017 American Chemical Society).

Knowing that the capsule is made of two molecules the following questions come to mind: (a) Does it remain closed all the time or opens and closes periodically? (b) If latter, what is the time scale in which it takes place? (c) Is the rate of opening guest dependent? Through excited state quenching of the encapsulated probe molecules by oxygen, the partial opening–closing of the capsule has been established to occur in the time range of 5-17 μs. Using pyrene

as the probe the time constant for capsule to fully open is reported to be 3 sec. Thus, it is clear that the OA capsule is dynamic and equilibrates between closed and partially open structures. The question is within the time the excited state measurements are made (ns-ps) 'does the capsule remains intact without any change in its structure?'. Ultrafast solvation dynamics experiments carried out with 7-dimethylamino coumarins as probes have helped us answering this question.[109-116] In these molecules, twisting of the C–N$(CH_3)_2$ bond results in the formation of polar twisted intramolecular charge transfer (TICT) state from the non-polar Franck-Condon state (FC).[117-121] The TICT emission is expected to depend on the stabilization of the TICT state by the environment, and in ultrafast solvation dynamics experiments the solvation is probed by the time dependent fluorescence Stokes shift (TDFSS) of this TICT band. This process will work in the current case only if the capsule opens at least partially for water molecules to seep and surround the excited chromophore (coumarin) within its lifetime. We show below that this ultrafast technique has revealed that, depending on the size of the guest, the capsule opens slightly in the middle.

The MD simulated structures for two coumarins encapsulated within OA are shown in Figure 12.[111] In the first, the capsule is tightly closed and there are no water molecules around the guest as well as around the joint of the capsule. However, in the second one the capsule is slightly ajar allowing a few water molecules to remain in contact with the guest coumarins even in ground state equilibrated structures. To ascertain the consequence of the ground state structures on the capsule opening the time resolved emission spectra (TRES) were constructed for the two coumarins by recording their ultrafast fluorescence response by a combination of femtosecond fluorescence up-conversion and time correlated single photon counting method (TCSPC) (Figure 13c and e). The solvent response function was constructed from the constructed TRES. The representative decay profiles and TRES for two molecules are displayed in Figure 13. Comparison of the spectra reveal that the capsules remain intact up to 3000 ps for the coumarin that is accommodated tightly within the capsule. On the other hand, where the fit is loose, the capsule opens slightly as revealed by the change in the lifetime with respect to the monitored wavelength and observation of TDFSS. This can happen only if the capsule opens even in ps time scale. Most likely the opening is triggered by the water molecules that are already in touch with the guest coumarins. The information provided by ultrafast experiments is

exceptionally useful in interpreting the results of photochemical and photophysical experiments and planning future studies.

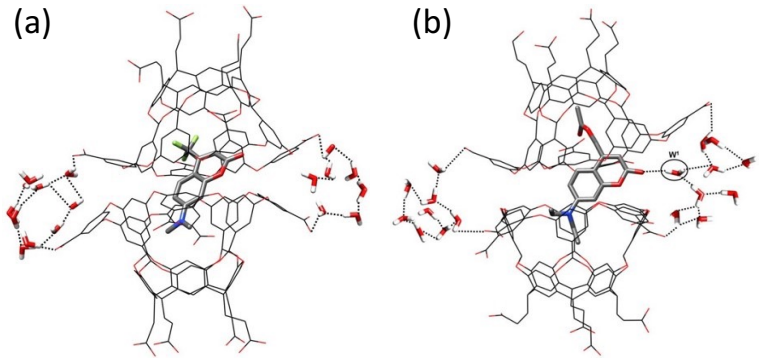


Figure 12. Molecular dynamics simulated structure for (a) coumarinal ethyl trigger@OA_2 & (b) coumarinal adanantyl trigger @OA_2, in water. Please see Scheme 1 for structures of guests. (Reprinted with permission from ref 111. Copyright 2019 American Chemical Society).

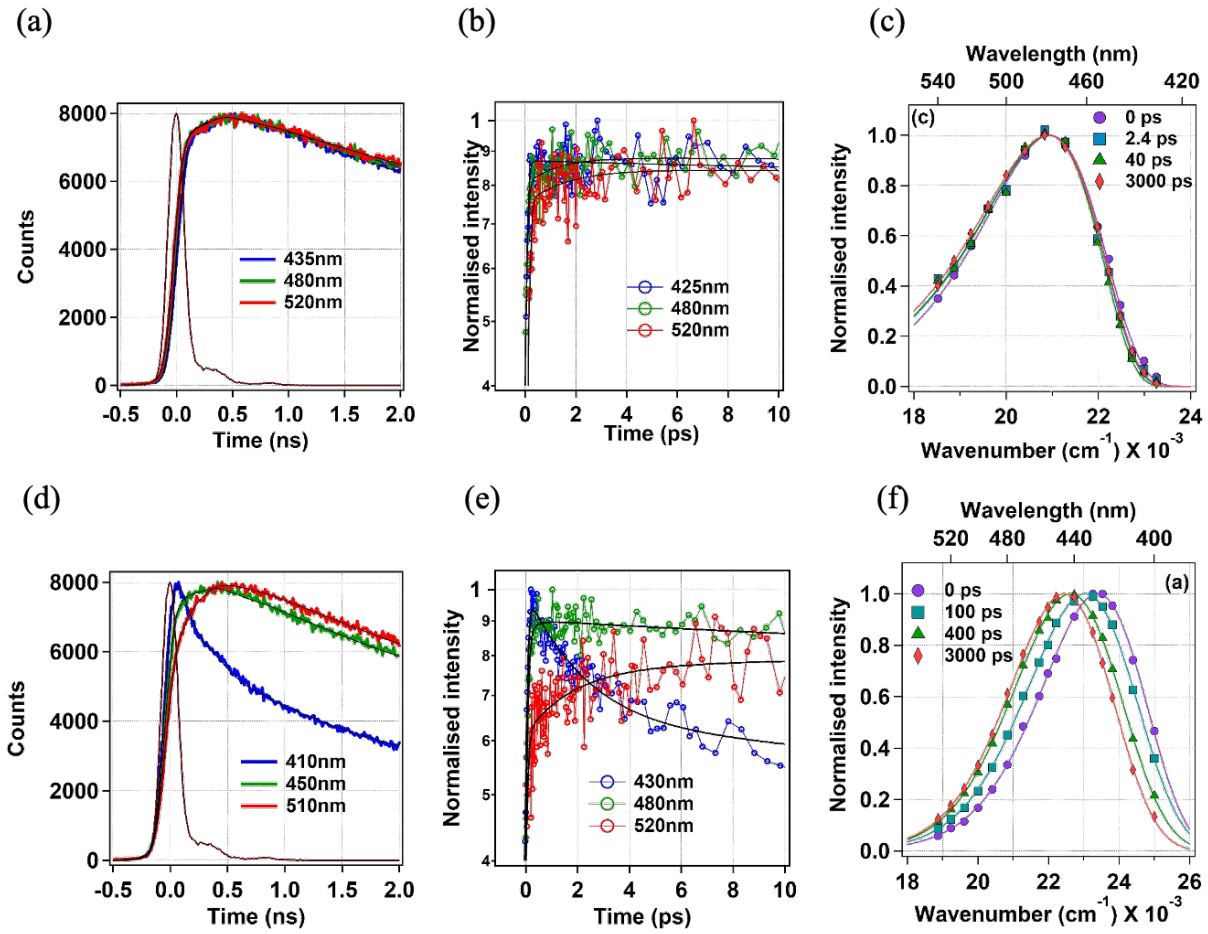


Figure 13. (a) Representative TCSPC decay profile at some selected wavelengths, (b) representative ultrafast fluorescence transients at some selected wavelengths, and (c) time-resolved emission spectra (TRES) constructed from the combination of femtosecond fluorescence up-conversion and TCSPC method for coumarinyl ethyl trigger@OA_2, (d) Representative TCSPC decay profile at some selected wavelengths, (e) representative ultrafast fluorescence transients at some selected wavelengths, and (f) time-resolved emission spectra (TRES) constructed from the combination of femtosecond fluorescence up-conversion and TCSPC method for coumarinyl adamantyl trigger @OA_2.(see Scheme 1 for triggers) (Reprinted with permission from ref 111. Copyright 2019 American Chemical Society).

Steady state and ultrafast measurements of encapsulated molecules reveal the importance of vibration-assisted intersystem crossing in halocoumarins

Based on the text book information on spin-orbit coupling one would expect the fluorescence quantum yield (ϕ_f) to decrease in the order -H, -Br and -I substitution.[10, 122-123] Contrary to this expectation the observed fluorescence trend was -H: 37.5%; -Br: 47.6 and -I: 2.6% for 3-substituted coumarin-1 (C-1).[124] To ascertain the formation of the triplet being the reason for the changes in ϕ_f, the phosphorescence of C-1 and 3-Br and 3-I substituted derivatives were attempted in solution. Expectedly, no phosphorescence was detected in solution at room temperature. In this context, the value of 'confined space of the OA capsule' in stabilizing the triplet state property became useful.[125-127] The steady state emission spectra at room temperature for the 1:2 complex 3I-C-1@OA_2 revealed a low-intensity red-shifted band, which intensifies with a decrease in the temperature, along with the normal emission band (Figure 14a,b). This new band matches with the phosphorescence of 3I-C-1 recorded at 77 K (Figure 14c), and assigned as the room temperature phosphorescence of 3I-C-1@OA_2. On the other hand, no such emission was recorded in the case of 3Br-C-1@OA_2. Consistent with this the global fitting of the TA response of both 3Br-C-1@OA_2 and 3I-C-1@OA_2 confirmed the presence of long lived component in the case of the latter and no such species in the former was detected. TA spectra of 3I-C-1@OA_2 consisted of a very short-lived stimulated emission (SE) signal and a long lived ($>$ 10 ns) broad excited state absorption (ESA) signal (Figure 15). This long-lived broad ESA signal is presumed to indicate the triplet formation in 3I-C-1. On the other hand, no such signal was observed in case of 3Br-C-1. While the lack of triplet formation in 3Br-C-1 rationalizes the enhancement of ϕ_f, with respect to C-1 the origin of this unexpected behavior is not obvious.

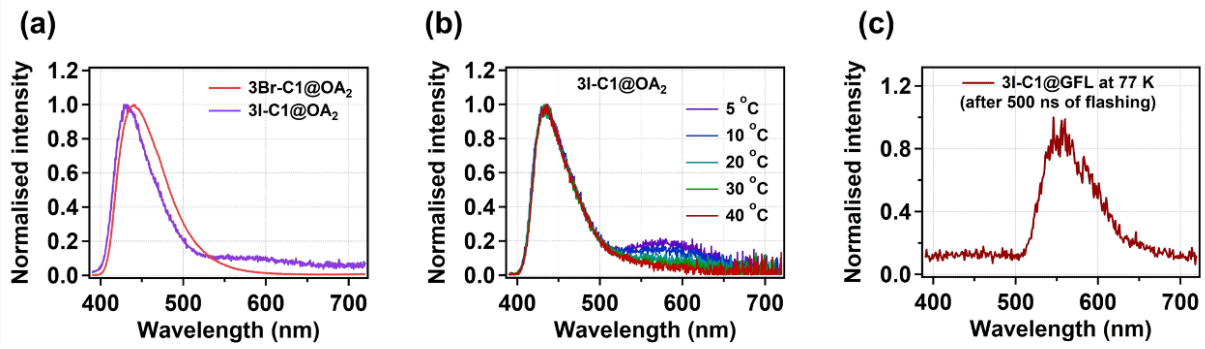


Figure 14. (a) Steady state emission of 3I-C-1@OA_2 and 3Br-C-1@OA_2 (b) temperature dependence steady state emission of 3I-C-1@OA_2 (c) Steady state emission of 3I-C-1@OA_2 compared with the phosphorescence spectra of 3I-C1 in glass forming liquid at 77 K. For 3I-C-1@OA_2, there is a weak band around 580 nm which is completely absent in case of 3/br-C-1@OA_2. This weak emission band for 3I-C-1@OA_2 intensifies with decreasing temperature. Phosphorescence spectra recorded for 3I-C-1 in glass forming liquid (Ethanol-methanol mixture) at 77 K confirms the weak band at 580 nm for 3I-C-1@OA_2 as a phosphorescence band. (Reprinted with permission from ref 124. Copyright 2022 American Chemical Society).

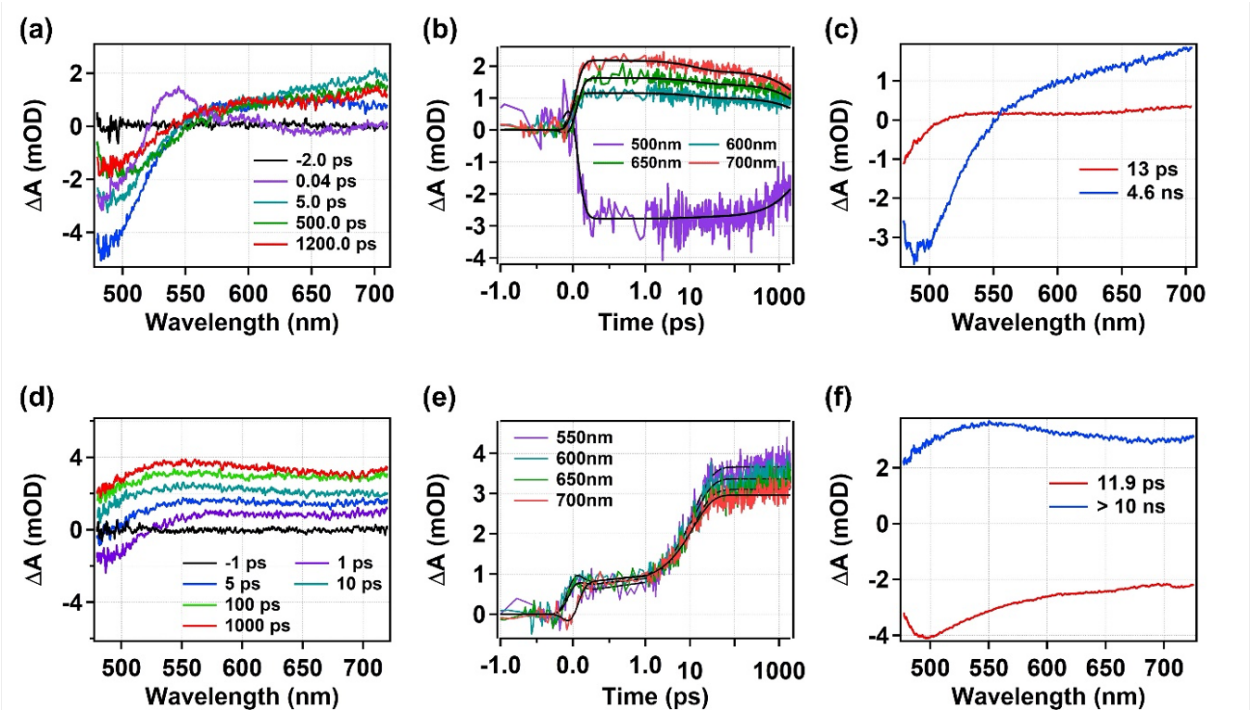


Figure 15. TA response (λex = 400 nm; probe: 470−750 nm) of 3Br-C1 and 3I-C1 inside OA cavity. (a, d) TA spectra at some representative delay times for 3Br-C1@OA_2 and 3I-C1@OA_2 respectively. For 3Br-C1@OA2, the TA spectra consists of a SE signal around 500 nm and an ESA around 600−700 nm. For 3I-C1@OA_2, the TA spectra consists entirely of a broad ESA signal throughout the probe window. (b, e) Globally fitted kinetics at some selected wavelengths

for 3Br-C1@OA_2 and 3I-C1@OA_2 respectively. For 3Br-C1@OA2, obtained time constants from global analysis are 13.0 ps and 4.6 ns. For 3I-C1@OA_2, two time constants were obtained from global analysis. One is of 11.9 ps and the other is a long time constant > 10 ns. (c, f) Corresponding decay associated spectra (DAS) obtained from global analysis for 3Br-C1@OA_2 and 3I-C1@OA2, respectively. (Reprinted with permission from ref 124. Copyright 2022 American Chemical Society)

To probe this process the potential energy curve (PEC) calculation using TDDFT along the -NEt_2 group rotation were performed for the three coumarins.[124] The calculations did not reveal any distinguishing features between the three systems suggesting that the -NEt_2 group rotation is not responsible for variations in ϕ_f. The calculated vibrational spectra for the excited states of 3I-C-1 revealed that few normal modes are in resonance for S_1, T_1 and T_2. Close inspection of the two resonating modes between S_1 and T_2 revealed that the C3-I bond vibration is much more prominent in the T_2 mode compared to the S_1 mode. This indicates that S_1 to T_2 transition might involve the C_3-I bond elongation coordinate. For other derivates, the PECs are distinctly different (Figure 16). For 3I-C-1, the S_1 and T_2 surfaces crosses with the slightest of the bond elongation and the crossing is barrierless. For 3Br-C-1 the S_1 and T_2 surfaces to cross, ~6 % of bond elongation is necessary that contains a significant energy barrier (0.11 eV). For C-1, all the electronic states were bound. Once again, a combination of steady state emission and ultrafast TA measurements of confined molecules and quantum chemical calculations have allowed us to unravel the hidden factors that play a role in the unexpected trend in heavy atom induced intersystem crossing in coumarins which is likely to be general as predicted in the vase of halo-naphthalenes.[124] The above examples illustrate the value of 'space' and 'time' in understanding the mechanism of heavy atom induced intersystem crossing of coumarins and aromatic molecules and photophysics of organic molecules in general.

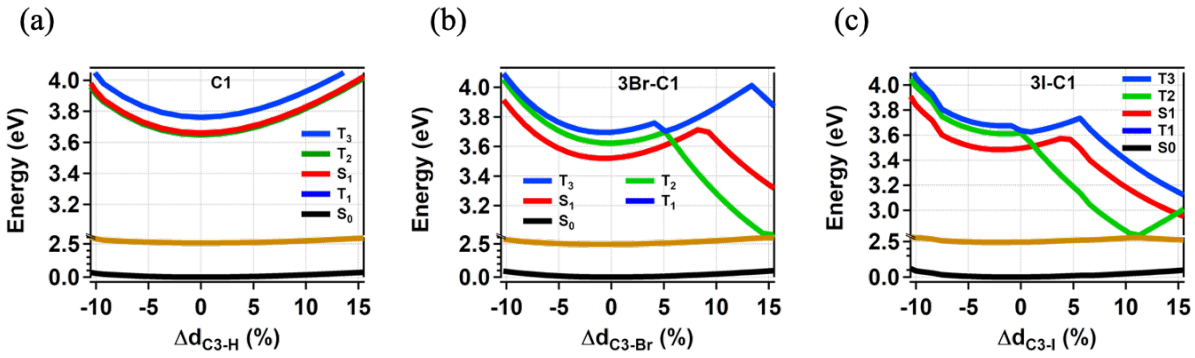


Figure 16. Potential energy curves (PEC) along the C3-X (X=H, Br, I) bond vibration coordinates of the (a) 7-diethylamino-4-methylcoumarin (C-1), (b) 3-Bromo-7-diethylamino-4-methylcoumarin (3Br-C-1), (c) 3-Iodo-7-diethylamino-4-methylcoumarin (3I-C-1). For the PEC calculations, Gaussian 09 package was used. B3LYP exchange correlation functional and 6-311++G (d,p) basis set for C, H, N, O and LANL2DZ basis set for Br and I were used for the TD-DFT calculations to determine the PECs. PE scan was done taking methanol as solvent using PCM model. DFT calculations were performed using Gaussian 09 package. $\Delta d_{C3-X}(\%)$ denotes the % change in C3-X (X= H, Br, I) bond length (d_{C3-X}). $\Delta d_{C3-X}(\%) = \left(\Delta d_{C3-X}(\text{Å})/d^{eq}_{C3-X}(\text{Å})\right) \times 100\%$. d^{eq}_{C3-X} is the equilibrium C3-X bond length in electronic ground state. (Reprinted with permission from ref 124. Copyright 2022 American Chemical Society).

Conclusions

Although confinement and control of free space are well-known strategies employed by Nature, these are yet to become routine tools in the hands of chemists in a laboratory. We believe examples such as the ones provided here confirm that space is a valuable tool that can be used to modify the behavior of molecules. The space surrounding a reactant molecule can be controlled with the help of molecular hosts of different internal volumes of nearly the same size as the reactant guest molecules. Hosts of different sizes and shapes that have become available in recent years are waiting to be explored as reaction containers.[128-132] Unlike the most popular hosts such as cyclodextrins, cucurbiturils, calixarenes, etc. that are open on more than one side, the octa acid capsule, which we have employed as the reaction container in our studies, is fully closed during the excited state lifetime of a reactant molecule. Octa acid host can enclose small

organic molecules of photochemical interest and uniquely keep them away from water molecules in which the supramolecular assembly is dissolved. Such an exclusive situation offers an unprecedented opportunity to examine the dynamics of molecules at short time scales in a highly restricted environment. Ability to control 'space' requires synthetic skills to make hosts of different sizes. To examine the dynamics of confined molecules in ultrashort time scale requires expertise in instrumentation with a physical chemistry background. We wish to draw the attention of readers to the many opportunities that exists in exploring the dynamics of excited molecules using time and space as controlling tools. In this context the value of a collaborative program involving organic and physical chemists to obtain complete picture of the behavior of excited molecules in confined spaces cannot be over emphasized.

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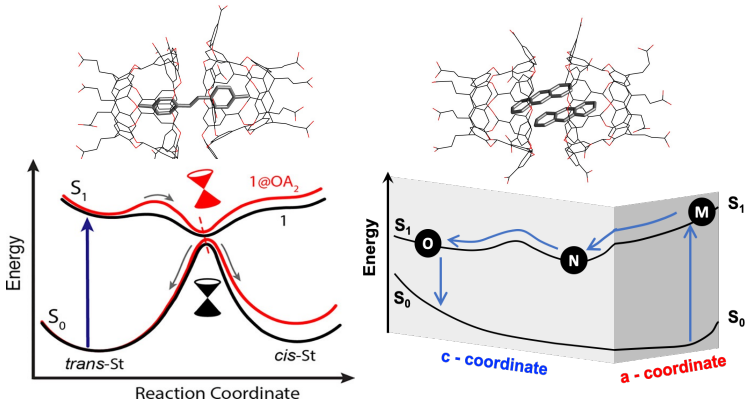
TOC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