A Study of Influence of Supramolecular Confinement on the Photochemistry of Organic Guest Molecules.

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UNIVERSITY OF MIAMI

A STUDY OF INFLUENCE OF SUPRAMOLECULAR CONFINEMENT ON THE PHOTOCHEMISTRY OF ORGANIC GUEST MOLECULES

By

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A STUDY OF INFLUENCE OF SUPRAMOLECULAR CONFINEMENT ON THE PHOTOCHEMISTRY OF ORGANIC GUEST MOLECULES

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The research work presented in this thesis is a consolidated report of experiments carried out to emphasize the superiority of supramolecular host systems in controlling the photochemical and photophysical properties of organic guest molecules. A well explored supramolecular host in our group called by its trivial name “octa acid” (OA) has been utilized in major part of this work. OA is a water soluble deep cavity cavitand having benzene like inner cavity. The ability of two OA molecules to self assemble in the presence of hydrophobic guest to form a capsule has been exploited to carry out photoreactions of various neutral organic guest molecules inside its confined space. We have synthesized two new water soluble deep cavity cavitands having same skeleton of OA. These new cavitands were found to have very similar features as that of OA in terms of their influence in controlling the photochemical and photophysical properties of various guest molecules.

Our attempt to carry out triplet sensitized photoisomerization of para-substituted stilbenes within the OA capsule using water soluble triplet sensitizers of different kind has turned out to be useful in understanding the control exerted by OA in this process. The information obtained from this study also gives some insight into the triplet energy
transfer mechanism that occurs between an incarcerated acceptor and free donor. Irradiation of OA complexes of benzonorbornadiene and dibenzobarrelene yielded only triplet products which confirm the triplet sensitizing ability of OA. Results presented in this thesis highlight the role of light in the OA capsular disassembly process by using appropriate phototriggers. In this study, a photochemical $\beta$-cleavage process centered on the $p$-substituted phenacyl group was exploited to release the acid of interest from OA capsule. The efficiency and nature of the photoproducts obtained can be altered by just changing the functional groups on the phenacyl part of the guest. Photolysis of nitrene precursors inside OA capsule produced highly reactive nitrenes and due to their restricted mobility, these nitrenes took selective path to obtain selective products. Our attempts to form host-guest complexes between hosts iTATA and TATP in their neutral form with various guests on an inert surface like SiO$_2$ were found successful in the presence of water. NMR, TEM and UV-Vis experiments on OA functionalized gold nanoparticles gave some useful information about their nature and stability.
This thesis is dedicated to my beloved parents
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Chapter 1

Introduction to Supramolecular Photochemistry
1.1. Supramolecular Chemistry.

Supramolecular assemblies are composed of several molecular entities held together by weak intermolecular interactions. Some of the reversible weak interactions like H-bonding, π-π interaction, C-H-π interaction, cation-π interaction, etc. play an important role in building the supramolecular assemblies. In the year 1987, Noble prize was awarded to Charles J. Pedersen, Jean-Marie Lehn and Donald J. Cram for their pioneering work in the field of supramolecular chemistry which established its importance to the world and infact Jean-Marie Lehn was the one who coined the term supramolecular chemistry. Following their contributions, researchers around the world have developed a wide range of supramolecular systems which are generally classified as self assembled system, mechanically interlocked system and host-guest system.

1.2. Supramolecular Self Assemblies, Interlocked Molecules and Host-Guest Complexes.

Molecular self assemblies are formed by the intermolecular weak interactions between two or more molecules to form a macro molecule.\(^1\) Here, the molecules instead of randomly aggregating, they organize themselves through explicit manipulation of molecular recognition features to obtain defined and repetitive assemblies of truly impressive architectural complexity.\(^2\) The formation of micelles and vesicles depends on the concentration of the individual units. As the concentration of the individual units reaches the critical micellar concentration (CMC) or critical vesicular concentration (CVC) they self assemble to form a supramolecular system.\(^5\) In the case of metal nanocages, metal ions interact with appropriate ligands to form a self assembled cage that can later incorporate reactive substances inside its cage.\(^6\) Mechanically interlocked
molecules are constructed by covalently linking the two end of a molecule when the other molecule’s motion is restricted completely from moving away from the loop. They interchange their structures upon introducing external stimuli like pH, redox reagents, light and electricity.\textsuperscript{10-13} These interlocked molecules like catenanes and rotaxanes are used in constructing molecular machines which are eventually used for building nanoelectronics and nanoelectromechanical devices.\textsuperscript{14,15}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{supramolecular_host_systems.png}
\caption{Various supramolecular host systems.}
\end{figure}

Host-guest interactions occurs mainly between a molecule (host) that can accommodate another molecule (guest) preferentially over other molecules in the surroundings based on the molecular recognition phenomena.\textsuperscript{16} In some cases, preorganization\textsuperscript{17} of the host molecule occurs in order to incorporate the guest molecule within its cavity. The nature of the host-guest complex formation mainly depends upon their complementarity. Few representatives from the family of host systems are cyclodextrins,\textsuperscript{18-20} calixarenes,\textsuperscript{21,22} cucurbiturils,\textsuperscript{23,24} dendrimers,\textsuperscript{25,26} micelles,\textsuperscript{27,28}
zeolites, metal-nanocages etc. Some of the classic examples of supramolecular host systems are shown in Figure 1.1.

1.3. Supramolecular Hosts as Photochemical Containers.

Photochemistry is a powerful tool in synthetic chemistry as a complementary method for achieving compounds that are difficult to obtain through thermal reaction due to high strain, low stability, and orbital symmetry reasons. Unlike thermal reactions, photoreactions deal with excited state molecules that are usually short lived but experience much lower energy barriers and exhibit high reactivities even at low temperatures. As a consequence of these features the precise control of a photoreaction is more difficult to achieve than that of thermal one. In this context supramolecular approaches to the photochemical processes enable more precise control of the orientation and conformation of substrates by utilizing non-covalent interactions in both ground and excited states.

1.3.1. Impact of Cyclodextrins on the Outcome of Photolysis of Stilbene Derivatives.

Photolysis of trans-4,4'-bis(dimethylammoniophilosphomethyl)stilbene (1.1a) in aqueous solution in the presence of β-cyclodextrin produces cis-product (1.1b), which further undergoes electrocyclization and oxidation to give the corresponding phenanthrene (1.1c). When the photolysis is carried out in the presence of γ-cyclodextrin, only [2+2]-cycloaddition products (1.2 and 1.3) are obtained (Figure 1.2). The difference reflects the formation of 1:1 host-guest inclusion complex of the stilbene with β-cyclodextrin compared with a 1:2 complex with γ-cyclodextrin.
**Figure 1.2.** Manipulation of photoproducts from the photolysis of stilbene derivative using β- and γ-cyclodextrin.

1.3.2. Selective Photodimerization of Olefins Inside Palladium Nanocage.

Fujita and co-workers carried out the photodimerization of olefins inside a palladium nanocage (PdNC) with very high selectivity. Photodimerization of acenaphthene (1.4) in solution yields both 1.5 and 1.6 in about 1:1 ratio. When the same reaction is carried out in the presence of PdNC, i.e. irradiation of acenaphthene@PdNC produces 100 % syn-dimer 1.5. Similarly, cross-photodimerization of 1.4 and 1.7 has no preference over the homo-coupling in solution, whereas when the nanocage is added 1.4 and 1.7, it exclusively incorporates one molecule of each 1.4 and 1.7 inside its cavity which upon irradiation yields about 92 % of the cross-photodimerized product 1.8, without forming any homo-dimerized (1.5 and 1.9) products (Figure 1.3).

Octa acid (OA) is a resorcinarene based cavitand synthesized by Gibb and co-workers in 2004.\textsuperscript{48,49} It is a deep cavity cavitand having eight –COOH groups, which makes it soluble in water under basic condition (pH ~ 8.7, sodium tetraborate buffer). Since OA is constructed with benzene units, the polarity of its interior cavity is very much similar to benzene which was confirmed by studying the emission pattern of various polarity probes inside OA capsule.\textsuperscript{50} Hence, it acts as a host that can accommodate hydrophobic guests that are insoluble in water. So far OA crystals are not reported; therefore, the available data on the dimensions of the OA were obtained from their molecular modeling studies. A very special quality of OA is that it has the ability of forming either 1:1 cavitandplex or 2:1 or 2:1 capsuleplex depending upon the nature and size of the guest molecule.\textsuperscript{50,51} If the guest is partially hydrophilic it forms a 1:1 complex. Neutral guests of bigger size can form 2:1 complex, whereas, small neutral guests forms
2:2 complex. Since OA is made up of benzene units, when a complex is formed between OA and a guest, the guest proton peaks get upfield shifted to a great extent due to the extraordinary shielding of the OA walls. Infact, the aliphatic peaks which normally falls in the region between 0 – 4 ppm may get shifted to the negative region (< 0 ppm) of the spectrum.$^{50-56}$

**Figure 1.4.** Various supramolecular host systems.

OA capsules are very stable but at the same time they are dynamic too.$^{57}$ The two cups of the capsule can open and close in millisecond (ms) time scale which allows any of the reactive species produced inside the capsule that is having its lifetime in this range can interact with the outside environment.$^{58}$ The guest molecule that is incarcerated within the OA capsule in a 2:1 complex is not stationary but undergoes fairly rapid rotation in nanosecond time scale along the molecular axis (x-axis) (**Figure 1.5**)$^{59}$ The extent of freedom is dependent on weak interactions that hold the guest within the container. The mobility along the y and z axes varies with the structure of guest molecule.
Figure 1.5. Pictorial representation of possible rotation of guest inside OA capsule.

OA has proved to be an excellent reaction container for various photoreactions by achieving high product selectivity which is not possible otherwise in solution\textsuperscript{52,53,55,60-62}. A remarkable asymmetric induction in photoproduct from substituted pyridones is achieved to obtain diastereomeric excess as high as 92%. This could be possible only if the chiral auxiliary group can able to get closer to the reaction center probably due to conformational control exerted by the confined space of OA capsule. In solution, the chiral auxiliary is unable to provide asymmetric induction in product, since, such a conformation is most likely not preferred because of the enforcement by confinement\textsuperscript{63}.

OA has a great influence in the photophysical properties of the included guest, for example, anthracene shows monomer emission in solution and does not show excimer emission in any solvent, and at higher concentration it dimerizes. OA forms a 2:2 complex with anthracene in water in which the two anthracene molecules are present close to each other that shows excimer emission\textsuperscript{64} upon shining with light but they are positioned in such a way that they are slided away from each other to avoid any dimer formation. This dimerization is prevented due to lack of free space within the capsule.
OA has proved to be a great supramolecular system in protecting the excited singlet and triplet states of molecules by suppressing bimolecular quenching processes.\textsuperscript{57,65} Moreover, the confined guests are not isolated but are able to communicate (energy, electron and spin) with molecules present closer to the capsule.\textsuperscript{66-73} The OA-guest complexes are found to be stable when functionalized on solid surfaces like silica,\textsuperscript{74} TiO\textsubscript{2}\textsuperscript{75} and gold nanoparticles,\textsuperscript{76} and also the guest incarcerated can communicate with the surface through the walls of OA. The aliphatic –Hg atom in OA, which is protruding inside its cavity is reactive towards any highly reactive intermediates that are produced inside the cavity like nitrenes and radicals.\textsuperscript{77,78} Thus, OA remains a great example for a versatile supramolecular system where numerous types of processes can be carried out. The research work presented in this thesis will demonstrate more features of OA.

1.5. Instruments and Techniques Used in the Projects.

1.5.1. One Dimensional $^1$H and $^{13}$C NMR.

The most important technique used in all the projects that are discussed in this thesis is NMR spectroscopy. NMR was our key tool in analyzing the identity and purity of the synthesized products to understanding the host-guest complex nature. Since, all the host systems used in our study are very rigid and having deep cavity that are constructed with walls made of benzene units, the complex formation between an organic guest molecule and host will be easily identified by the upfield shift of the guest proton peaks in their $^1$H NMR spectrum due to the high shielding of the guest’s proton by the host walls. The stoichiometry of the complex can also be determined by carrying out $^1$H NMR titration experiments. Since host-guest complexes are formed due to weak interactions,
the dynamic properties of the guest inside the host or the exchange of complexed guest with the uncomplexed guest can be studied by carrying out variable temperature NMR experiments.

1.5.2. Two Dimensional NMR.

(a) 2D Correlation Spectroscopy (COSY).

The homonuclear correlation spectroscopy (COSY) is a very important technique in identifying the spins of two nuclei that are coupled to each other in the same molecule. Thus by carrying out a COSY experiment, one can identify the atoms that are connected to each other by observing the cross peaks. The intensity of the correlation peaks are stronger for atoms that are connected very close to each other and the intensity decreases as the bond distance increases. COSY has been a very useful method in this work in order to identify the peaks corresponding to the protons of newly synthesized cavitands in NMR spectrum.

(b) 2D Nuclear Overhauser Effect Spectroscopy (NOESY).

NOESY NMR spectrum is useful in identifying the protons that are interacting through space. It is helpful in understanding the interactions of atoms within the same molecule or between different molecules which makes it one of a very important tool in studying the weak interactions in host-guest chemistry. Similar to COSY, the NOESY spectrum can be read by focusing on the cross peaks, which eventually gives an idea about the interacting atoms, thereby one can identify the structure of the host molecule, nature of the host-guest interaction and the orientation of the guest inside the host cavity.
(c) 2D Diffusion Ordered Spectroscopy (DOSY).

2D DOSY NMR is used to measure the translational diffusion of molecules in solution. Since the translational motion of molecules depends on the physical parameters such as size and shape of the molecule, temperature and viscosity of the medium, the diffusion constant value of the molecule under study also depends upon all the above factors. The Stokes-Einstein relation for determining the diffusion constant (D) for molecules is given below.

\[ D = \frac{k_B T}{6 \pi \eta R_h} \]

Where, \( k_B \) is the Boltzmann constant, \( T \) is the experimental temperature in Kelvin, \( \eta \) is the viscosity of the solvent and \( R_h \) is the hydrodynamic radius of the system under study. As we see from the equation that the diffusion constant value is inversely proportional to the hydrodynamic radius, therefore, the diffusion constant value will be lower for molecules of bigger volume. This helps in identifying the complex nature between host and guest. OA forms both capsuleplex and cavitandplex depending upon the nature of the guest, since the size of the capsuleplex is bigger than the cavitandplex, the diffusion constant value for the capsuleplex will be lesser compared to that of the cavitandplex. This is a best method to identify whether OA forms 1:1 or 2:1 (H:G) with the guest, which is very important to know prior to any further studies. In addition, it will also give an idea whether the guest molecule has formed complex with OA or remained freely in solution.
1.5.3. Gas Chromatography (GC) and GC Coupled with Mass Spectroscopy (GC-MS).

Gas chromatography is a technique used for separating a mixture of volatile organic compounds without getting disintegrated at higher temperatures. GC can be used to identify the purity of a compound and analyze the ratio of compounds in a mixture. A typical GC instrument consists of an injection port, where the sample to be analyzed is injected after dissolving in an appropriate solvent. The injected sample vaporizes and is carried through a capillary column by an inert carrier gas like helium that consists of the stationary phase which is usually a polymer coated on an inert solid support. Since each compound has different polarity, they interact with the stationary phase at different times (called ‘retention time’ of the compound), thereby they get separated. A GC-MS will have the same setup as GC and in addition, the capillary column will be attached to a mass spectrometer. Here the compounds that are separated through the GC pass through MS to get ionized and fragmented. The mass fragmentations are used to identify the mass of the product and the structure of the compound. We used GC and GC-MS to identify the photo products obtained after irradiating the guest molecules.

1.5.4. Liquid Chromatography Coupled with Mass Spectroscopy (LC-MS).

LC-MS is also a technique used for separating a mixture of compounds in order to determine their identity. LC-MS is a method that combines the operation of HPLC and mass spectroscopy. Here, the sample is first forced to pass through a column that is packed with a stationary phase using high pressure by a liquid mobile phase. The stationary phase is generally composed of silica gel with neat or mixed organic mixtures
(normal phase). The components are separated inside the column depending upon their polarity and once they get separated they pass through MS where the compounds are ionized and fragmented. Analysis of the fragmentation pattern obtained for each of the separated compounds is used for identifying the structure of the compounds.

1.5.5. Electrospray Ionization Mass Spectroscopy (ESI-MS).

Electrospray Ionization (ESI) is a mass spectrometric technique used to produce ions of the compounds under study using an electrospray in which a high voltage is applied to the solution containing the compound to create an aerosol. Since it is a soft ionization technique, it is especially used for producing ions of macromolecules whose identity cannot be determined by using the regular mass spectrometer. ESI-MS produces only very little fragmentation but produces the molecular ion peak which is useful in identifying the mass of the molecule. In our work, ESI-MS was used in identifying the molecular weight of the newly synthesized cavitands along with the OA-appended products.

1.5.6. UV-Vis Spectroscopy.

UV-Vis spectroscopy is a very important tool for understanding the electronic properties of molecules. Molecules having π-electrons or non-bonding electrons can be subjected to UV-Vis analysis. When a molecule absorbs UV-Vis radiation, the absorbed energy excites an electron into an empty, higher energy orbital. The absorbance of energy can be plotted against the wavelength to yield a UV-Vis spectrum, which gives an exact picture of where the molecules will absorb light that in turn helps in manipulating the
wavelength of light needed to carry out the photochemical or photophysical process. In our work, UV-Vis spectrum of host and guest gives an idea about where to excite the molecule in order to carry out the intended reaction. For example, in chapter-4, we wanted the host to absorb light and transfer energy to the guest inside to obtain the product without exciting the guest; hence we used a Pyrex filter that cuts off the light that the guest molecules absorb. In chapter-2, we used a cut off filter that restricts the host absorption and allows the wavelength of light required for the guest absorption; thereby we study the photophysics of only the guest. Hence it is very important to have the UV-Vis spectrum of the compound under study before proceeding towards any light induced processes.

1.5.7. Fluorescence Spectroscopy.

Molecules absorb energy upon irradiating with light and reach one of the higher vibrational levels of an excited state. Then they rapidly lose their excess of vibrational energy by collision and falls to the lowest vibrational level of the excited state. In addition, almost all molecules occupying an electronic state higher than the second undergo internal conversion and pass from the lowest vibrational level of the upper state to a higher vibrational level of a lower excited state which has the same energy. From there the molecules again lose energy until the lowest vibrational level of the first excited state is reached. From this level, they can return to any of the vibrational levels of the ground state, emitting their energy in the form of light is called fluorescence. If the molecule at its first excited state reverses its electron spin via intersystem crossing, they reach the triplet state and the emission that occurs from the triplet state is called
phosphorescence. Fluorescence spectrum gives information about the excited state properties of a molecule and as well as the nature of the medium in which the molecules is present. Hence, this technique is imperative in our studies to understand the nature of the host-guest complexes and as well as the effect of heavy metals on the electronic properties of the guest. Time resolved fluorescence spectroscopy was used to measure the lifetime of the excited state of molecules.

1.6. Scope of This Work.

The main aim of this thesis is to understand the role of supramolecular host confinement in controlling the photochemistry of organic guest molecules. **Chapter 2** discusses about the synthesis and characterization two new water soluble deep cavity cavitands called ‘inverted tetra acid tetra alcohol’ (iTATA) and ‘tetra alcohol tetra phenol’ (TATP) that are analogous to OA. Photochemistry and photophysics of various organic guest molecules were studied inside the capsules of iTATA and TATP.

**Chapter 3** gives information about the absorption and emission properties of various supramolecular baskets, along with their excited state lifetime. The emission spectrum of OA possesses some abnormality due to the presence of trace quantity of impurity. Exclusion of the emission band of the undetectable (by NMR) impurity from the original spectrum gives the emission band corresponding to OA which gives an idea about the chromophore responsible for emission in the system.

**Chapter 4** examines the triplet energy transferring property of OA to the guest molecules that are included within its cavity. Benzonorbornadiene and dibenzobarrelene,
whose photoproducts vary depending upon the type of excited state from which the reaction occurs. Hence, chosen to prove the triplet sensitizing ability of OA.

Chapter 5 deals with the studies performed to understand the energy transfer pathway between an OA encapsulated guest and a water soluble triplet sensitizer that is present outside the walls of OA. The para-substituted stilbenes (acceptor) form 2:1 complex with OA and undergo cis-trans isomerization upon triplet sensitization by donor molecules. The cis-trans product ratios obtained at the photostationary state gives an idea about the energy transfer mechanism.

Chapter 6 deals with the extensive studies done on the photoinduced disassembly of OA capsules. Different para-substituted phenacyl ester derivatives were employed in the studies. Among them, para-hydroxyphenacyl (pHP) derivative seems to be very efficient in dismantling the OA capsule, moreover, the pHP derivative was found to be following the same photo-Favorskii mechanism inside the OA capsule as it does in solution. Examining the photochemistry of para-methoxy phenacyl (pMP) derivatives demonstrated an interesting reaction with the host, yielding a para-methoxy phenacyl-OA appended product.

Chapter 7 discusses the stability of iTATA and TATP capsules on silica gel surface. In this chapter, we demonstrated the importance of water in forming host-guest complexes on silicagel surface with neutral guest, which is impossible to form otherwise. We utilized the emission properties of guest to prove the above studies.

Chapter 8 discusses the characterization of OA functionalized gold nanoparticles (AuNPs) and their stability studies. It also deals with the characterization of AuNPs
solution based on the NMR spectrum. In addition to that, quenching of various guest@OA functionalized on AuNPs were also studied.

Chapter 9 deals with the photochemistry of azido aryl ketones inside OA capsule. The azide compounds used in this work have an in-built triplet sensitizer, which upon irradiation produce triplet nitrenes. These nitrenes deliver different products when encapsulate inside OA capsule when compared to that of in solution, thereby demonstrating the effect of confinement in controlling photoreactions.
Chapter 2

New Water Soluble Cavitands that Control the Dynamics and Excited State Properties of Organic Guests
2.1. New Water Soluble Cavitands.

In the past couple of decades supramolecular chemists have striven to build various host systems to incarcerate guest molecules in order to control their dynamics and excited state properties. These efforts to confine guest molecules to mimic the functions of biological systems like enzymes have been proved to be successful.\textsuperscript{79-82} Some of the host systems like calixarenes,\textsuperscript{83} cucurbiturils, cyclodextrins, micelles, dentrimers and metal nanocages are well studied and in fact each one has their own advantages and disadvantages. For example, most of the cavitands studied are only soluble in organic solvents and water soluble hosts such as micelles, cyclodextrins, cucurbiturils, partially expose the guest to the aqueous exterior complicating the environmental effects on the ground and excited state properties of the guest.\textsuperscript{84-90}

![Figure 2.1 Structures of hosts iTATA, TATP and TATA.](image)

Following the synthesis of a water soluble hemicarcerand by Yoon and Cram, known as Crams’s octa acid,\textsuperscript{91} a few such water soluble hosts have been reported over in
the last couple of decades. Gibb. et. al. had reported one such water soluble deep cavity cavitand (OA) in the year 2004 which has been established to be an excellent reaction container to carry out photochemical reactions in a controlled manner. The exciting properties of OA prompted us to synthesis its analogs by replacing only its top and bottom acid groups with other functional groups without changing the internal features. In this chapter the synthesis, characterization of two new hosts, inverted tetra acid tetra alcohol (iTATA) and tetra acid tetra phenol (TATP) and their role in controlling the excited state properties of various organic guest molecules are discussed. The structures of two new water soluble cavitands iTATA and TATP are displayed in the Figure 2.1. In addition to this the structure of another host called tetra acid tetra alcohol (TATA) synthesized by Dr. Samanta from our group is also provided to compare its properties with OA and iTATA.

2.2. Synthesis and Characterization of iTATA.

Scheme 2.1. Synthesis of 5-ethoxymethoxy resorcinol (2f).
With the idea of replacing the –COOH groups in octa acid with –OH groups, we first synthesized a resorcinol derivative 5-ethoxymethoxy resorcinol (2f, Scheme 2.1). 1,3,5-trisacetoxy benzene (2b) was prepared from phloroglucinol (2a) by acylation reaction using acetic anhydride. The reaction of benzyl bromide with 2b in the presence of sodium hydride and water gave 1,3,5-trisbenzyloxy benzene (2c). Then 2c was
carefully converted to 3,5-bisbenzylxylophenol (2d) by bubbling hydrogen gas in the presence of Pd/C with 50 % yield. Gibb. et. al. reported the synthesis of a resorcinol derivative called 2-ethoxymethoxy resorcinol, following the same procedure we synthesized 1-ethoxymethoxy-3,5-bisbenzylxyo benzene (2e). Debenzylation of 2e in the presence of Pd/C afforded 5-ethoxymethoxy resorcinol (2f) with 45 % yield.

The benzyl footed octa bromide basket (2g) was synthesized by following the reported procedure. Compound 2h was obtained by the reacting 2g with four equivalents of 2f using the eight-fold Ullmann aryl ether reaction with the yield of 37 %. Compound 2i was obtained by deprotecting the bottom benzyl groups in 2h using H2 and Pd/C, while the top protecting groups were kept unaffected. Oxidation of 2i with KMnO4 gave 2j. Compound 2j having the labile ketal part on top of the rim was deprotected by treating with 50 % HCl solution to afford iTATA with 97 % yield.

![Figure 2.2](image)

**Figure 2.2.** 1H NMR spectrum (500 MHz, DMSO-d6) of iTATA (1 mM). ‘▲’ represents the residual proton resonance of water present in DMSO-d6 and ‘●’ represents the residual solvent proton resonance of DMSO-d6.
Unlike OA, iTATA is soluble in acetone, THF and methanol along with DMSO. It can be solubilized in sodium borate buffer (pH = 8.7) but the proton peaks in $^1$H NMR spectrum shows very broad peaks (Figure 2.3) which could be due to aggregation and the aggregation can be broken by increasing the pH to 11 by using NaOD/D$_2$O (Figure 2.4). The various proton peaks of iTATA were assigned by analyzing its 2D-NMR (NOESY and COSY) spectra (Figure 2.5, 2.6, 2.7 and 2.6). The diffusion constant for iTATA in NaOD/D$_2$O (pH = 11) at 298 °C was determined to be $1.62 \times 10^{-10}$ m$^2$/s which clearly indicates that there is no aggregation (Figure 2.9). The ESI-MS spectrum (Figure 2.10) of iTATA also supports the structure.
Figure 2.5. 2D NOESY NMR spectrum (500 MHz, mixing time 300 ms, DMSO-$d_6$) of iTATA. (▲ and ○ represent the residual solvent proton resonances from $D_2$O and DMSO-$d_6$, respectively).
Figure 2.6. 2D COSY NMR spectrum (500 MHz, DMSO-\textit{d$_6$}) of iTATA. ('▲' and '●' represent the residual solvent proton resonances from D$_2$O and DMSO-\textit{d$_6$}, respectively).
Figure 2.7. 2D NOESY NMR spectrum (500 MHz, mixing time 300 ms, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O) of iTATA. '•' represent the residual solvent proton resonances from D$_2$O.
Figure 2.8. 2D COSY NMR spectrum (500 MHz, 10 mM Na₂B₄O₇ buffer/D₂O) of iTATA. ‘•’ represent the residual solvent proton resonances from D₂O.
Figure 2.9. 2D DOSY NMR spectrum (500 MHz, NaOD/D$_2$O, 298 K) of iTATA ([iTATA] = 1 mM). The calculated diffusion constant is $1.62 \times 10^{-10}$ m$^2$/s. ‘▲’ represents the residual solvent proton resonances from D$_2$O.

Figure 2.10. ESI-MS spectrum of iTATA. (Inset: (i) theoretical and (ii) observed isotopic distribution for iTATA).
Figure 2.11. (i) Absorption and (ii) emission spectra of iTATA in THF. (iii) Absorption and (iv) emission spectra of iTATA in NaOD/D$_2$O. [iTATA] = 50 µM.
2.3. Complexation Studies of iTATA with Various Guest Molecules.

Figure 2.12. Structures of various guest molecules investigated.

The $^1$H NMR titration spectra of guests 2.1 – 2.14 with 1 mM solution of iTATA in 10 mM NaOD/D$_2$O showed that all the guest molecules form a very good complex with iTATA, which is apparent from the upfield shift of the proton peaks corresponding to the incarcerated guests due to the high shielding of iTATA benzene moieties. Except 2.1 and 2.2, all other compounds are not soluble in aqueous medium at the same millimolar concentrations that are used for complex formation, which clearly confirms the need of iTATA host that has a hydrophobic cavity in bringing the molecules as a single unit in water. Guests 2.1 and 2.2 formed 1:1 complex with iTATA due to their partial hydrophilic portion. Guests 2.3, 2.4, 2.5, 2.6, 2.7, 2.8 and 2.11 formed 1:2 guest@(iTATA)$_2$ complex, whereas guests 2.10, 2.12, 2.13 and 2.14 formed 2:2 complex.
Figure 2.13. $^1$H NMR (500 MHz, 10 mM NaOD/D$_2$O) titration spectra of 2.1 with iTATA. [iTATA] = 1 mM and [2.1] = 0 to 1 mM (“∗” indicates the iTATA incarcerated guest 2.1 proton peaks. “●” indicates the residual solvent peak of water.)
Figure 2.14. $^1$H NMR (500 MHz, 10 mM NaOD/D$_2$O) titration spectra of 2.2 with iTATA. [iTATA] = 1 mM and [2.2] = 0 to 1 mM (‘*’ indicates the iTATA incarcerated guest 2.2 proton peaks. ‘●’ indicates the residual solvent peak of water.)
Figure 2.15. $^1$H NMR (500 MHz, 10 mM NaOD/D$_2$O) titration spectra of 2.3 with iTATA. [iTATA] = 1 mM and [2.3] = 0 to 1 mM ("*" and "**" indicate the iTATA incarcerated and free guest 2.3 proton peaks, respectively. "●" indicates the residual solvent peak of water.
Figure 2.16. $^1$H NMR (500 MHz, 10 mM NaOD/D$_2$O) titration spectra of 2.4 with iTATA. [iTATA] = 1 mM and [2.4] = 0 to 0.5 mM (“*” indicates the iTATA incarcerated guest 2.4 proton peak. “●” indicates the residual solvent peak of water.)
Figure 2.17. $^1$H NMR (500 MHz, 10 mM NaOD/D$_2$O) titration spectra of 2.5 with iTATA. [iTATA] = 1 mM and [2.5] = 0 to 0.5 mM (“∗” indicates the iTATA incarcerated guest 2.5 proton peaks. “●” indicates the residual solvent peak of water.

Figure 2.18. $^1$H NMR (500 MHz, 10 mM NaOD/D$_2$O) titration spectra of 2.6 with iTATA. [iTATA] = 1 mM and [2.6] = 0 to 0.5 mM (“∗” indicates the iTATA incarcerated guest 2.6 proton peaks. “●” indicates the residual solvent peak of water.
Figure 2.19. $^1$H NMR (500 MHz, 10 mM NaOD/D$_2$O) titration spectra of 2.7 with iTATA. [iTATA] = 1 mM and [2.7] = 0 to 0.5 mM (“*” indicates the iTATA incarcerated guest 2.7 proton peaks. “●” indicates the residual solvent peak of water.

Figure 2.20. $^1$H NMR (500 MHz, 10 mM NaOD/D$_2$O) titration spectra of 2.8 with iTATA. [iTATA] = 1 mM and [2.8] = 0 to 0.5 mM (“*” indicates the iTATA incarcerated guest 2.8 proton peaks. “●” indicates the residual solvent peak of water.
Figure 2.21. $^1$H NMR (500 MHz, 10 mM NaOD/D$_2$O) titration spectra of 2.9 with iTATA. [iTATA] = 1 mM and [2.9] = 0 to 1 mM (“*” indicates the iTATA incarcerated guest 2.9 proton peaks. “●” indicates the residual solvent peak of water.
Figure 2.22. $^1$H NMR (500 MHz, 10 mM NaOD/D$_2$O) titration spectra of 2.10 with iTATA. [iTATA] = 1 mM and [2.10] = 0 to 1 mM (‘*’ indicates the iTATA incarcerated guest 2.10 proton peaks. ‘●’ indicates the residual solvent peak of water.)
**Figure 2.23.** $^1$H NMR (500 MHz, 10 mM NaOD/D$_2$O) titration spectra of 2.11 with iTATA. [iTATA] = 1 mM and [2.11] = 0 to 0.5 mM (“∗” indicates the iTATA incarcerated guest 2.11 proton peaks. “●” indicates the residual solvent peak of water.
Figure 2.24. $^1$H NMR (500 MHz, 10 mM NaOD/D$_2$O) titration spectra of 2.12 with iTATA. [iTATA] = 1 mM and [2.12] = 0 to 1 mM (“∗” indicates the iTATA incarcerated guest 2.12 proton peaks. “●” indicates the residual solvent peak of water.)
Figure 2.25. $^1$H NMR (500 MHz, 10 mM NaOD/D$_2$O) titration spectra of 2.13 with iTATA. [iTATA] = 1 mM and [2.13] = 0 to 1 mM (“*” indicates the iTATA incarcerated guest 2.13 proton peaks. “●” indicates the residual solvent peak of water.
Figure 2.26. $^1$H NMR (500 MHz, 10 mM NaOD/D$_2$O) titration spectra of 2.14 with iTATA. [iTATA] = 1 mM and [2.14] = 0 to 1 mM ("*" indicates the iTATA incarcerated guest 2.14 proton peaks. "●" indicates the residual solvent peak of water.)
Figure 2.27. 2D DOSY NMR (500 MHz, 10 mM NaOD/D₂O, 298 K) spectrum of 2.1@iTATA. [iTATA] = 1 mM and [2.1] = 1 mM (“*” indicates the iTATA incarcerated guest 2.1 proton peaks. “●” indicates the residual solvent peak of water. Diffusion constant = $1.67 \times 10^{-10}$ m²/s.
Figure 2.28. 2D DOSY NMR (500 MHz, 10 mM NaOD/D₂O, 298 K) spectrum of 2.4@iTATA₂. [iTATA] = 1 mM and [2.4] = 0.5 mM (“∗” indicates the iTATA incarcerated guest 2.4 proton peak. “●” indicates the residual solvent peak of water. Diffusion constant = $1.36 \times 10^{-10}$ m²/s.
2.4. Effect of Encapsulation on the Excited State Properties of Guests by iTATA.

2.4.1. Probing the Interior Polarity of iTATA.

Guests 2.5, 2.6 and pyrene are the three polarity probes mainly used in our group to determine the polarity of the inner cavity of hosts used. Pyrene forms good complex with OA and TATA but unfortunately it didn’t form complex with iTATA. In this respect we picked up the two coumarin dyes, coumarin-1 (2.5) and coumarin-153 (2.6) whose fluorescence quantum yield increases as the polarity of the solvent is decreased.\textsuperscript{103} Another important change that could be easily observed to detect the polarity of the environment when these dyes are used is the shift in the wavelength maximum of the emission band towards the blue region when the polarity of the medium is shifted from polar to non-polar.\textsuperscript{50,104}

![Figure 2.29. Emission spectra of 2.5 in various media.](attachment:image.png)
Figure 2.30. Fluorescence decay spectrum of $2.5@\text{iTATA}_2$, [iTATA] = 50 µM and [2.5] = 25 µM and lifetime = 3.2 ns.

Figure 2.31. Emission spectra of $2.6@\text{iTATA}_2$ in 10 mM NaOH/H$_2$O, [iTATA] = 50 µM and [2.6] = 25 µM.

Figure 2.29 illustrates that as the polarity of the medium decreased the wavelength maximum of the emission band of 2.5 shifts to the blue region and the
emission maximum obtained for 2.5 was at 413 nm in benzene which in turn matches with the emission maximum recorded for 2.5@iTATA which shows that the polarity of the interior cavity of iTATA is benzene like. The lifetime of 2.5@iTATA was determined to be 3.2 ns, Figure 2.30 shows its fluorescence decay spectrum. Furthermore, the emission maximum obtained for 2.6@iTATA is at 483 nm (Figure 2.31) which also reflects the benzene like polarity of the iTATA’s inner atmosphere. The emission maximum reported for 2.6 in water is 547 nm. These experiments also prove that iTATA’s interior atmosphere is devoid of water and it can be an excellent nano-vessel for carrying out reactions with water insoluble guests in aqueous medium.

2.4.2. Photophysics of Guest Molecules Encapsulated Inside iTATA Capsule.

Figure 2.32. Emission spectra of (2.10)2@iTATA in 10 mM NaOH/H2O, [iTATA] = 5 µM and [2.10] = 5 µM, λex = 350 nm.
Figure 2.33. Fluorescence decay spectrum of (2.10)$_2$@iTATA$_2$ in 10 mM NaOH/H$_2$O, [iTATA] = 5 µM and [2.10] = 5 µM, $\lambda_{ex} = 350$ nm.

Figure 2.34. Phosphorescence emission spectra of (2.13)$_2$@iTATA$_2$ in 10 mM NaOH/H$_2$O recorded in the presence of various oxygen concentrations, [iTATA] = 5 µM and [2.13] = 5 µM, $\lambda_{ex} = 254$ nm.
Figure 2.35. Phosphorescence decay spectrum of \((2.13)_{2@iTATA}\) in 10 mM NaOH/H₂O, [iTATA] = 5 µM and \([2.13] = 5 \mu M\), \(\lambda_{ex} = 254\) nm.

Anthracene doesn’t form an excimer in solution, whereas it forms excimer when iTATA was added, due the complementarity in their size and polarity. The excimer was formed in such a way that the two incarcerated anthracene molecules were a bit slided to avoid any dimer formation upon irradiation with light which was evident from its \(^1\)H NMR titration spectra (Figure 2.22) that have five peaks for the guest protons and a huge band with the wavelength maximum at 516 nm in the emission spectra for the excimer (Figure 2.32). The lifetime of the anthracene excimer inside iTATA capsule was determined to be 236 ns (Figure 2.33) which is very close to what was observed in the anthracene crystals and inside OA capsule. An interesting question to be answered with respect to the stability of the capsule is whether the capsules is intact at all time or does it open and close often. To study this phenomenon there were couple of thioketones having the ability to emit phosphorescence that can be quenched by oxygen were studied under OA system. The previous results with 2:2 complexes of OA and thioketones like
camphorthione (2.13) showed enhanced phosphorescence intensity when compared to that of in solution due to less exposure to oxygen and curtailment of self quenching. A clear quenching of phosphorescence when oxygen molecules were introduced in to the solution having the 2:2 complex of OA and thioketone confirmed the partial opening of the capsule in the time scale of the triplet state lifetime of the guest. Figure 2.34 illustrates the maximum intensity being observed for the deaerated (2.13)\textsubscript{2}@\textit{iTATA}\textsubscript{2} solution and when the amount of oxygen increased the phosphorescence intensity decreased that proves the partial opening and closing of the iTATA capsule. The lifetime of the incarcerated (2.13)\textsubscript{2}@\textit{iTATA}\textsubscript{2} was determined to be 69 µs (Figure 2.35).

2.4.3. Photochemistry of Guest Molecules Encapsulated Inside iTATA Capsule.

To understand the robustness of the iTATA capsules in controlling the photochemistry of guest molecules, we had chosen three guest molecules, \textit{p}-methyldibenzyl ketone (2.7), \textit{a}-methyldibenzyl ketone (2.8) and 1-methycyclohexylphenyl ketone (2.11). Photolysis of 2.7@\textit{iTATA}\textsubscript{2} resulted in the formation of only caged products and also the absence of products ‘a’ and ‘c’ (Scheme 2.3) showed that even the products that form in solution are completely restricted due to the constrains imposed by the host on the intermediates. Similarly, irradiation of 2.8@\textit{iTATA}\textsubscript{2} only produced the caged products. Moreover, a clear 100 % formation of Norrish type I product from the photolysis of 2.11@\textit{iTATA}\textsubscript{2} proved the important role of iTATA capsule in controlling the photochemistry of organic guests which may otherwise result in obtaining multiple products. The photochemistry of all the three guests was also followed by NMR (Figure 2.36 - 2.38) and the distributions of the photo
products were obtained from theirs GC and GC-MS data. These results match very well with the one obtained in OA capsules, showing that the nature of the inner cavity of iTATA is similar to OA.\textsuperscript{53,62,105}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{\textsuperscript{1}H NMR (500 MHz, 10 mM NaOD/D\textsubscript{2}O) spectra of (i) only iTATA [iTATA] = 1 mM; (ii) 2.7@iTATA\textsubscript{2} (before irradiation) and (iii) after irradiation of (ii) (λ ≥ 300 nm, 20 h). “*” indicates the iTATA incarcerated guest proton peaks. "●" represents the residual solvent peak of water.}
\end{figure}
Scheme 2.3. Reaction manifold for the photochemistry of 2.7.

Table 2.1. Product distributions upon photolysis of 2.7 inside OA and iTATA capsules.

<table>
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<th>Medium</th>
<th>b</th>
<th>f</th>
<th>g-h</th>
</tr>
</thead>
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<tr>
<td>OA (buffer)</td>
<td>44 %</td>
<td>41 %</td>
<td>15 %</td>
</tr>
<tr>
<td>iTATA (NaOH/H₂O)</td>
<td>55 %</td>
<td>31 %</td>
<td>14 %</td>
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</table>
Figure 2.37. $^1$H NMR (500 MHz, 10 mM NaOD/D$_2$O) spectra of (i) only iTATA [iTATA] = 1 mM; (ii) 2.8@iTATA$_2$ (before irradiation) and (iii) after irradiation of (ii) ($\lambda \geq 300$ nm, 1 h). “*” indicates the iTATA incarcerated guest proton peaks. · represents the residual solvent peak of water.
Scheme 2.4. Reaction manifold for the photochemistry of 2.8.

Table 2.2. Product distributions upon photolysis of 2.8 inside OA and iTATA capsules.

<table>
<thead>
<tr>
<th>Medium</th>
<th>A</th>
<th>B</th>
<th>E-H</th>
</tr>
</thead>
<tbody>
<tr>
<td>OA (buffer)</td>
<td>4 %</td>
<td>21 %</td>
<td>75 %</td>
</tr>
<tr>
<td>iTATA (NaOH/H₂O)</td>
<td>4 %</td>
<td>12 %</td>
<td>84 %</td>
</tr>
</tbody>
</table>
Figure 2.38. $^1$H NMR (500 MHz, 10 mM NaOD/D$_2$O) spectra of (i) only iTATA [$iTATA] = 1 \text{ mM}$, (ii) 2.11@iTATA$_2$ (before irradiation), (iii) after irradiation of (ii) ($\lambda \geq 300 \text{ nm, 1 h}$) and (2.14)$_2$@iTATA$_2$. “*” indicates the iTATA incarcerated guest proton peaks. "●" represents the residual solvent peak of water.
Scheme 2.5. Reaction manifold for the photochemistry of 2.11.

Table 2.3. Product distributions upon photolysis of 2.11 inside iTATA capsule.

<table>
<thead>
<tr>
<th>Medium</th>
<th>Norrish Type I product</th>
<th>Norrish Type II product</th>
</tr>
</thead>
<tbody>
<tr>
<td>iTATA (NaOH/H$_2$O)</td>
<td>100 %</td>
<td>0 %</td>
</tr>
<tr>
<td>Hexane</td>
<td>20 %</td>
<td>80 %</td>
</tr>
</tbody>
</table>
2.5. Synthesis and Characterization of TATP.

Scheme 2.6. Synthesis of host iTATA.

The synthesis of TATP involves multiple steps. Compound 2l was obtained by reacting 2g with four equivalents of 2k using the eight-fold Ullmann aryl ether reaction with the yield of 40%. TATP was obtained by deprotecting the bottom benzyl groups in 2l using H₂ and Pd/C. TATP is soluble in DMSO and NaOH/H₂O. Since there is no acid group in the bottom portal of TATP, it requires high concentration of NaOH (50 mM NaOH/H₂O for 1 mM of TATP) to completely dissolve it without any aggregation. The various proton peaks of TATP were assigned by analyzing its 2D NMR spectra (NOESY and COSY). The ESI-MS spectrum (Figure 2.43) of TATP also complied with its structure. The diffusion constant of 1 mM solution of TATP in 50 mM NaOH/H₂O was determined to be 1.70 x 10⁻¹⁰ m²/s (Figure 2.44).
Figure 2.39. $^1$H NMR spectrum (500 MHz, DMSO-$d_6$) of TATP. ‘▲’ represents the residual proton resonance of water present in DMSO-$d_6$ and ‘●’ represents the residual solvent proton resonance of DMSO-$d_6$.

Figure 2.40. $^1$H NMR spectrum (500 MHz, 50 mM NaOD/D$_2$O) of TATP. ‘●’ represents the residual solvent proton resonance of water.
Figure 2.41. 2D NOESY NMR spectrum (400 MHz, mixing time 300 ms, DMSO-$d_6$) of TATP. ‘■’ and ‘.’ represent the residual solvent proton resonances from D$_2$O and DMSO-$d_6$, respectively.
Figure 2.42. 2D COSY NMR spectrum (400 MHz, DMSO-$d_6$) of TATP. ‘■’ and ‘●’ represent the residual solvent proton resonances from D$_2$O and DMSO-$d_6$, respectively.
Figure 2.43. ESI-MS spectrum of TATP. (Inset: shows the theoretical and observed isotopic distribution for TATP).

Figure 2.44. 2D DOSY NMR spectrum (500 MHz, 50 mM NaOD/D$_2$O, 298 K) of TATP ([TATP] = 1 mM). The calculated diffusion constant is $1.70 \times 10^{-10}$ m$^2$/s. ‘●’ represents the residual solvent proton resonances from D$_2$O.
Figure 2.45. $^1$H NMR spectrum (500 MHz) of (i) 1 mM TATP in 50 mM NaOD/D$_2$O, (ii) 5 mM TATP in 100 mM NaOD/D$_2$O and (iii) 10 mM TATP in 100 mM NaOD/D$_2$O. ‘●’ represents the residual solvent proton resonance of water.
2.6. Complexation Studies of TATP with Various Guest Molecules.

Figure 2.46. $^1$H NMR (500 MHz, 50 mM NaOD/D$_2$O) titration spectra of 2.1 with TATP. [TATP] = 1 mM and [2.1] = 0 to 2 mM (‘∗’ and ‘∗’ indicate the TATP incarcerated and free guest 2.1 proton peaks. ‘●’ and ‘♦’ indicate the residual solvent peak of water and DMSO-$d_6$.}
Figure 2.47. $^1$H NMR (500 MHz, 50 mM NaOD/D$_2$O) titration spectra of 2.2 with TATP. [TATP] = 1 mM and [2.2] = 0 to 1 mM (‘∗’ indicates the TATP incarcerated guest 2.2 proton peaks. ‘●’ and ‘♦’ indicate the residual solvent peak of water and DMSO-$d_6$.}
**Figure 2.48.** $^1$H NMR (500 MHz, 50 mM NaOD/D$_2$O) titration spectra of 2.4 with TATP. [TATP] = 1 mM and [2.4] = 0 to 0.5 mM (“∗” indicates the TATP incarcerated guest 2.4 proton peaks. “●” and “♦” indicate the residual solvent peak of water and DMSO-$d_6$.}
Figure 2.49. $^1$H NMR (500 MHz, 50 mM NaOD/D$_2$O) titration spectra of 2.5 with TATP. [TATP] = 1 mM and [2.5] = 0 to 0.5 mM (‘∗’ indicates the TATP incarcerated guest 2.5 proton peaks. ‘●’ and ‘♦’ indicate the residual solvent peak of water and DMSO-$d_6$. )
Figure 2.50. $^1$H NMR (500 MHz, 50 mM NaOD/D$_2$O) titration spectra of 2.10 with TATP. [TATP] = 1 mM and [2.10] = 0 to 1 mM (‘∗’ indicates the TATP incarcerated guest 2.10 proton peaks. ‘●’ and ‘♦’ indicate the residual solvent peak of water and DMSO-$d_6$.}
Figure 2.51. $^1$H NMR (500 MHz, 50 mM NaOD/D$_2$O) titration spectra of 2.11 with TATP. [TATP] = 1 mM and [2.11] = 0 to 0.5 mM (“∗” indicates the TATP incarcerated guest 2.11 proton peaks. “●” and “♦” indicate the residual solvent peak of water and DMSO-$d_6$.)

Figure 2.52. $^1$H NMR (500 MHz, 50 mM NaOD/D$_2$O) titration spectra of 2.13 with TATP. [TATP] = 1 mM and [2.13] = 0 to 1 mM (“∗” indicates the TATP incarcerated guest 2.13 proton peaks. “●” and “♦” indicate the residual solvent peak of water and DMSO-$d_6$.)

Figure 2.53. 2D DOSY NMR (500 MHz, 50 mM NaOD/D_{2}O, 298 K) spectrum of 2.1@TATP. [TATP] = 1 mM and [2.1] = 1 mM (“*” indicates the TATP incarcerated guest 2.1 proton peaks. “●” indicates the residual solvent peak of water. Diffusion constant = 1.76 x 10^{-10} m^2/s.

The ^1H NMR titration spectra of guests 2.1, 2.2, 2.4, 2.5, 2.10, 2.11 and 2.13 (figure 2.46 – 2.53) with 1 mM solution of TATP in 50 mM NaOD/D_{2}O showed that all the guest molecules form a very good complex with TATP, which was confirmed from the upfield shift of the proton peaks corresponding to the incarcerated guests. Guests 2.1 and 2.2 formed 1:1 complex with TATP. Guests 2.4, 2.5 and 2.11 formed 1:2 guest@(TATP)₂ complexes, whereas guests 2.10 – 2.13 formed 2:2 complexes.

2.7. Photophysics of Guest Molecules Encapsulated Inside TATP Capsule.

The emission spectrum of 2.5@(TATP)₂ in Figure 2.56 displays the wavelength maximum at 410 nm indicating that the interior atmosphere of the TATP capsule is benzene like and the lifetime of 2.5@(TATP)₂ was determined to be 3.4 ns, Figure 2.57.
shows its fluorescence decay spectrum. Guest 2.10 formed 2:2 complex with TATP and showed the excimer emission band (Figure 2.58) similar to what was observed in OA and iTATA. The lifetime of 2.5@(TATP)₂ was determined to be 279 ns (Figure 2.59). The capsule opening and closing phenomena in TATP capsule was tested with guests 2.4 and 2.13. Compound 2.4 emits phosphorescence and its emission was quenched by oxygen. Encapsulation of 2.4 with TATP protects it from interacting with oxygen in solution to a greater extent but it can’t be completely overcome due to the partial opening and closing of the TATP capsule. Figure 2.54 shows the enhanced phosphorescence emission of 2.4 inside TATP capsule and its triplet lifetime was determined to be 488 µs (Figure 2.55). Likewise in the case of iTATA and OA, the phosphorescence emission intensity of 2.13 increased with the decrease in oxygen concentration in solution when it was encapsulated in TATP capsule (Figure 2.60), indicating the partial capsule opening process and the lifetime of its triplet state was determined to be 113 µs (Figure 2.61).

![Emission spectra of 2.4@(TATP)₂ in 50 mM NaOH/H₂O, [TATP] = 10 µM and [2.4] = 5 µM.](image)

*Figure 2.54. Emission spectra of 2.4@(TATP)₂ in 50 mM NaOH/H₂O, [TATP] = 10 µM and [2.4] = 5 µM.*
Figure 2.55. Fluorescence decay spectrum of 2.4@(TATP)$_2$ in 50 mM NaOH/H$_2$O. [TATP] = 10 µM and [2.4] = 5 µM and lifetime = 488 µs.

Figure 2.56. Emission spectra of 2.5@(TATP)$_2$ in 50 mM NaOH/H$_2$O, [TATP] = 10 µM and [2.5] = 5 µM.
Figure 2.57. Fluorescence decay spectrum of 2.5@(TATP)$_2$ in 50 mM NaOH/H$_2$O. 

Figure 2.58. Emission spectra of (2.10)$_2$@(TATP)$_2$ in 50 mM NaOH/H$_2$O, [TATP] = 1 mM and [2.10] = 1 mM.
Figure 2.59. Fluorescence decay spectrum of $2.10@$(TATP)$_2$ in 50 mM NaOH/H$_2$O. [TATP] = 1 mM and [2.10] = 1 mM and lifetime = 279 ns.

Figure 2.60. Phosphorescence emission spectra of $(2.13)_2@$(TATP)$_2$ in 50 mM NaOH/H$_2$O recorded in the presence of various oxygen concentrations, [TATP] = 50 µM and [2.13] = 50 µM, $\lambda_{ex} = 254$ nm.
Figure 2.61. Phosphorescence decay spectrum of \((2.13)_2@\text{TATP}_2\) in 50 mM NaOH/H\textsubscript{2}O, \([\text{TATP}] = 50 \mu\text{M}\) and \([2.13] = 50 \mu\text{M}\), \(\lambda_{\text{ex}} = 254\) nm. lifetime = 113 \(\mu\text{s}\).

Again in the case of TATP, the photolysis of \(2.11@\text{iTATA}_2\) resulted in the formation of 100 % Norrish type I products (Table 2.4) which shows the importance of a supramolecular host in controlling the overall outcome of a photochemical reaction.

![Chemical spectra](image)

**Figure 2.62.** $^1$H NMR (500 MHz, 50 mM NaOD/D$_2$O) spectra of (i) only TATP [TATP] = 1 mM, (ii) 2.11@iTATA$_2$ (before irradiation) and after irradiation of (ii) ($\lambda \geq 300$ nm, 1 h). “*” indicates the TATP incarcerated guest proton peaks. “●” and “♦” indicate the residual solvent peak of water and DMSO-$d_6$, respectively.

**Table 2.4.** Product distributions upon photolysis of 2.11 inside TATP capsule.

<table>
<thead>
<tr>
<th>Medium</th>
<th>Norrish Type I product</th>
<th>Norrish Type II product</th>
</tr>
</thead>
<tbody>
<tr>
<td>TATP (NaOH/H$_2$O)</td>
<td>100 %</td>
<td>0 %</td>
</tr>
<tr>
<td>Hexane</td>
<td>20 %</td>
<td>80 %</td>
</tr>
</tbody>
</table>

The two new hosts iTATA and TATP synthesized have a very close similarity with OA but unlike OA, iTATA is highly soluble in organic solvents like acetone, THF and methanol which extends our opportunity in crystallizing it to study more about its structural features, since the crystal structure of OA is unknown till date. In an attempt to
identify the exact –COOH units (top or bottom) that are responsible for binding and stabilizing OA-gold nanoparticles (OA∩AuNPs) in our group, Mr. Naresh had carried out the synthesis of iTATA∩AuNPs and TATA∩AuNPs. His studies revealed that only the AuNPs formed using TATA as their stabilizing agent was stable, whereas iTATA∩AuNPs remained unstable which suggested that the OA∩AuNPs are stabilized by the top –COOH units in OA. Dr. Samanta from our lab had synthesized a host called tetra thiol tetra acid (TTTA) in order to prepare TTTA∩AuNPs. TTTA∩AuNPs aggregated upon adding 2.4 and to break the aggregation she added TATP to it which did disperse the aggregates by forming 2.4@TATP-TTTA∩AuNPs hetrocapsule. Further studies on the guest@TATP-TTTA hetrocapsules were studied in detail in our lab. Thus, iTATA and TATP were very much useful in understanding some of the supramolecular and surface phenomena involved in our studies.

2.9. Experimental Section.

2.9.1. Synthetic Procedure for iTATA.

Compound 2g was synthesized by following the earlier reported procedure. Compound 2a, 2b, 2c and 2k were also reported earlier in literature.

Synthesis of 2a.

To a 0-5 °C cooled solution of phloroglucinol (5g, 0.04 mol) in pyridine added acetic anhydride (26 mL, 0.3 mol) in a dropwise manner for about 30 minutes. The mixture was stirred at room temperature for 48 h. Then the mixture was dumped on ice (500 g) and added EtOAc (100 mL) and 20% HCl solution (100 mL). The layers were
separated and the EtOAc layer was washed with water and was concentrated by rotary evaporation to yield 9.9 g (98%).

**Synthesis of 2b.**

To the solution of 2a (9 g, 0.02 mol) in DMF (60 mL) added benzyl bromide (17 mL, 0.14 mol) and sodium hydride (11.4 g, 0.03 mol) at 0-5 °C. To this mixture water (2.6 mL, 0.14 mol) was added dropwise for about 1 h and stirred at room temperature for 3 h. the reaction was quenched with water and separated between EtOAc and water. The EtOAc layer was then concentrated to get a oily liquid to which methanol was added to precipitate the product. The pale pinkish white solid was dried under high vacuum to give 9.1 g (63%).

**Synthesis of 2c.**

To a solution of 2b (9 g, 0.02 mol) in ethanol and EtOAc (1:2) mixture was added Pd/C (900 mg) and stirred for 20 minutes under N\textsubscript{2} bubbling and 30 minutes under a H\textsubscript{2} bubbling condition. The reaction mixture was then filtered and the filtrate was concentrated to get an oily liquid. The oily liquid was then passed through a silica gel column with hexane and EtOAc to isolate the product. The yield of the pale yellow solid product was 3.5 g (50%).

**Synthesis of 2d.**

To a solution of 2c (3.5 g, 0.01 mol) in THF added DIPEA (3.8 g, 0.02 mol) and chloromethyl ethyl ether (2.1 mL, 0.022 mol). The mixture was stirred at 60 °C for 48 h and the solvent was removed under reduced pressure. The residue was added CHCl\textsubscript{3} and water. The CHCl\textsubscript{3} layer was separated and washed with water and concentrated under
reduced pressure to get an oily liquid. The oily liquid was then passed through a silica gel column with hexane and EtOAc to obtain 3 g (75 %) of the product.

$^1$H-NMR (400 MHz, CDCl$_3$) δ: 1.23 (t, $J = 7.0$ Hz, 3 H), 3.72 (q, $J = 7.0$ Hz, 2 H), 5.02 (s, 4 H), 5.19 (s, 2 H), 6.31 (t, $J = 2.0$ Hz, 1H), 6.35 (d, $J = 6.0$ Hz, 2H), 7.31 – 7.46 (m, 10 H); $^{13}$C-NMR (125 MHz, CDCl$_3$) δ: 15.1, 64.3, 70.1, 93.3, 95.7, 96.1, 127.6, 128.0, 128.6, 136.8, 159.2, 160.6.

Synthesis of 2f.

To a solution of 2d (3 g, 8 mmol) in EtOAc was added Pd/C (300 mg) and stirred for 20 minutes under N$_2$ bubbling condition and 4 h under H$_2$ bubbling condition. The reaction mixture was then filtered and the filtrate was concentrated to get an oily residue. The residue was then passed through a silica gel column with hexane and EtOAc to isolate the product. The yield of the pale pinkish viscous liquid product was 660 mg (45 %).

$^1$H-NMR (400 MHz, DMSO-d$_6$) δ: 1.12 (t, $J = 6.8$ Hz, 3 H), 3.60 (q, $J = 7.0$ Hz, 2 H), 5.07 (s, 2H), 5.85 (t, $J = 1.5$ Hz, 1 H), 5.87 (d, $J = 2.0$ Hz, 2H), 9.19 (s, 2 H). $^{13}$C-NMR (125 MHz, DMSO-d$_6$) δ: 15.5, 64.6, 92.8, 95.1, 96.8, 159.2, 159.4.

Synthesis of 2h.

For 20 minutes, N$_2$ was bubbled through a suspension of 2g (1.1 g, 0.56 mmol), 2f (0.62 g, 3.36 mmol) and anhydrous K$_2$CO$_3$ (930 mg, 6.75 mmol) in pyridine (55 mL). To this CuO (540 mg, 6.75 mmol) was added and the stirring mixture was refluxed for 8 days. Then the solvent was removed under reduced pressure. The remaining solid was added CHCl$_3$ and filtered on a celite bed. The filtrate was concentrated and passed through a silica gel column and a preparative TLC using CHCl$_3$ to isolate the product. The yield was 370 mg (37 %).
\(^1\)H-NMR (500 MHz, CDCl\(_3\)) \(\delta\): 1.34 (t, \(J = 2.8 \text{ Hz}, 12 \text{ H}\)), 1.79 (m, \(J = 6.3 \text{ Hz}, 8 \text{ H}\)), 2.48 (q, \(J = 6.1 \text{ Hz}, 8 \text{ H}\)), 3.67 (t, \(J = 5.6 \text{ Hz}, 8 \text{ H}\)), 3.87 (q, \(J = 7.1 \text{ Hz}, 8 \text{ H}\)), 4.64 (s, 4 H), 4.70 (s, 8 H), 4.95 (t, \(J = 8.3 \text{ Hz}, 4 \text{ H}\)), 5.30 (s, 8 H), 6.22 (s, 4 H), 6.38 (t, \(J = 1.9 \text{ Hz}, 4 \text{ H}\)), 6.73 (d, \(J = 1.4 \text{ Hz}, 8 \text{ H}\)), 7.05 (d, \(J = 1.5 \text{ Hz}, 8 \text{ H}\)), 7.08 (t, \(J = 2.1 \text{ Hz}, 4 \text{ H}\)), 7.32 (s, 4 H); 7.55 – 7.43 (m, 20 H); 15.6, 27.3, 28.3, 36.6, 65.2, 70.0, 73.4, 93.7, 106.2, 108.2, 108.8, 109.1, 110.1, 115.6, 122.8, 128.1, 128.9, 137.2, 138.9, 139.7, 156.9, 157.6, 160.1, 161.3; \(^{13}\)C-NMR (125 MHz, CDCl\(_3\)) \(\delta\): ESI-HRMS: Calculated for C\(_{132}\)H\(_{120}\)O\(_8\)Na \([\text{M+Na}]^+\) 2176.7892, observed: 2176.7869.

**Synthesis of 2i.**

To a solution of 2h (370 mg, 0.2 mmol) in THF (100 mL) added Pd/C (185 mg). The solution was purged N\(_2\) gas for 20 minutes and H\(_2\) gas for 2 h. The reaction mixture was filtered and the filtrate was concentrated to obtain 270 mg (88 %) of the white solid product.

\(^1\)H-NMR (500 MHz, DMSO-\(d_6\)) \(\delta\): 1.17 (t, \(J = 7.0 \text{ Hz}, 12 \text{ H}\)), 1.55 (m, \(J = 6.9 \text{ Hz}, 8 \text{ H}\)), 2.55 (m, 8H), 3.62 (q, \(J = 4.6 \text{ Hz}, 8 \text{ H}\)), 3.76 (t, \(J = 7.2 \text{ Hz}, 8 \text{ H}\)), 4.58 (s, 4 H), 4.63 (t, \(J = 4.5, 4 \text{ H}\)), 4.69 (t, \(J = 8.5 \text{ Hz}, 4 \text{ H}\)), 5.47 (s, 8 H), 6.01 (s, 8 H), 6.42 (s, 4 H), 6.62 (s, 8H), 7.15 (s, 8 H), 7.19 (s, 4 H), 7.86 (s, 4 H); \(^{13}\)C-NMR (125 MHz, DMSO-\(d_6\)) \(\delta\): 15.4, 25.6, 26.5, 31.2, 36.67, 60.7, 60.8, 64.5, 67.5, 79.7, 93.2, 105.8, 109.1, 109.6, 137.0, 139.7, 155.9, 157.0, 159.5, 160.8; ESI-HRMS: Calculated for C\(_{104}\)H\(_{96}\)O\(_{28}\)Na \([\text{M+Na}]^+\) 1816.6014, observed: 1816.6008.

**Synthesis of 2j.**

To a solution of 2i (270 mg, 0.15 mmol) in DMA and tert-butanol (1:1) mixture added KMnO\(_4\) (190 mg, 1.28 mmol). The mixture was stirred at room temperature for 2 days and added 4 mL methanol and stirred for 1 h. Then filtered and the filtrate was concentrated at reduced pressure to get a solid residue. To the residue 5 % HCL solution
was added to precipitate out the product and it was filtered. The yield of the product was 130 mg (47 %).

$^1$H-NMR (500 MHz, DMSO-$d_6$) δ: 1.02 (t, $J = 6.6$ Hz, 12 H), 2.21 (t, $J = 6.8$ Hz, 8 H), 2.62 (q, $J = 6.3$ Hz, 8H), 3.62 (q, $J = 6.9$ Hz, 8 H), 4.43 (s, 4H), 4.59 (t, $J = 4$ Hz, 4 H), 5.88 (s, 4 H), 6.28 (s, 4 H), 6.48 (s, 8 H), 7.01 (s, 8 H), 7.06 (s, 4H), 7.72 (s, 4 H), 12.19 (s, 4 H); $^{13}$C-NMR (125 MHz, DMSO-$d_6$) δ: 15.4, 25.5, 30.6, 31.7, 61.3, 64.6, 93.3, 102.7, 105.8, 109.2, 109.7, 123.6, 136.5, 139.6, 152.1, 156.1, 157.0, 159.6, 160.8, 174.4; ESI-HRMS: Calculated for C$_{104}$H$_{88}$O$_{32}$Na [M+Na]$^+$ 1872.5185, observed: 1872.5109.

Synthesis of iTATA.

About 3 mL of 50 % HCl was added to a solution of 2j (130 mg, 0.07 mmol) in THF (5 mL) and stirred for 12 h at room temperature. The mixture was concentrated under reduced pressure to remove THF. The solid product precipitated was filtered and washed with water and CHCl$_3$. Further, the product was dried under high vacuum for 5 days (110 mg, yield = 97 %).

$^1$H-NMR (500 MHz, DMSO-$d_6$) δ: 2.22 (t, $J = 5.0$ Hz, 8 H), 2.64 (q, $J = 7.1$ Hz, 8 H), 4.44 (s, 4H), 4.60 (t, $J = 5.9$ Hz, 4 H), 5.89 (s, 4H), 6.04 (s, 4 H), 6.46 (s, 8 H), 6.67 (s, 8 H), 7.0 (s, 4 H), 7.73 (s, 4 H), 10.38 (s, 4H), 12.2 (s, 4 H); $^{13}$C-NMR (125 MHz, Acetone-$d_6$) δ: 25.3, 31.8, 36.4, 105.7, 106.2, 107.1, 107.8, 109.8, 114.9, 124.3, 136.7, 139.6, 156.5, 157.3, 160.3, 160.9, 173.5; ESI-HRMS: Calculated for C$_{104}$H$_{96}$O$_{28}$Na [M+Na]$^+$ 1640.3510, observed: 1640.3448.

2.9.2. Synthetic Procedure for TATP.

Synthesis of 2l.

For 20 minutes, N$_2$ was bubbled through a suspension of 2g (1 g, 0.48 mmol), 2k (0.63 g, 2.9 mmol) and anhydrous K$_2$CO$_3$ (540 mg, 3.9 mmol) in pyridine (55 mL). To this CuO (310 mg, 3.9 mmol) was added and the stirring mixture was refluxed for 8 days.
Then the solvent was removed under reduced pressure. The remaining solid was added CHCl$_3$ and filtered on a celite bed. The filtrate was concentrated and passed through a silica gel column to isolate the product in 37 % (400 mg) yield.

$^1$H-NMR (500 MHz, CDCl$_3$) $\delta$: 1.67 (quintet, $J = 6.4$ Hz, 8 H), 2.36 (q, $J = 6.7$ Hz, 8 H), 3.54 (t, $J = 5.8$ Hz, 8 H), 4.51 (s, 8 H), 4.57 (s, 4 H), 4.83 (t, $J = 8.5$ Hz, 4 H), 5.12 (s, 8 H), 6.08 (s, 4 H), 6.21 (s, 4H), 6.59 (s, 8 H), 6.83 (s, 8 H), 6.93 (s, 4 H), 7.20 (s, 4H), 7.24 - 7.46 (m, 40); $^{13}$C-NMR (125 MHz, CDCl$_3$) $\delta$: 22.8, 26.9, 27.87, 29.8, 36.2, 69.6, 70.5, 72.9, 105.8, 107.4, 107.8, 109.7, 115.4, 122.3, 127.6, 127.7, 128.3, 128.5, 128.7, 135.9, 136.7, 138.4, 139.3, 156.4, 157.2, 160.8, 161.1.

Synthesis of TATP.

Nitrogen gas was bubbled through a suspension of 2l (400 mg, mmol), Pd/C (200 mg) and THF (100 mL). Subsequently, H$_2$ gas was purged for 2 h at room temperature. The reaction mixture was filtered and the solvent was removed under reduced pressure to give the product as a white solid in 96 % (270 mg) yield.

$^1$H-NMR (500 MHz, DMSO-$d_6$) $\delta$: 1.41 (quintet, $J = 6.7$ Hz, 8 H), 2.41 (q, $J = 6.2$ Hz, 8 H), 3.49 (q, $J = 5.7$ Hz, 8 H), 4.44 (s, 4 H), 4.50 (t, $J = 5.4$ Hz, 4 H), 4.55 (t, $J = 8.5$ Hz, 4 H), 5.88 (s, 4 H), 6.04 (s, 4 H), 6.46 (s, 8H), 6.66 (d, $J = 1.8$ Hz, 8 H), 6.99 (s, 4 H), 7.73 (s, 4 H), 10.37 (s, 4H); $^{13}$C-NMR (125 MHz, CDCl$_3$) $\delta$: 26.6, 31.2, 36.8 , 60.8, 79.7, 105.6, 105.9, 107.4, 108.1, 109.7, 114.4 ,137.1, 139.5, 155.9, 157.1, 160.6, 160.8, 161.3.

2.9.3. General Procedure for Complexation, Photophysical and Photochemical Studies.

General protocol for binding studies by NMR.

All $^1$H NMR spectra were recorded using Bruker 400/500 MHz NMR at 25 °C. 0.6 mL of 1 mM iTATA solution in 10 mM NaOD/D$_2$O (pH=11) (1 mM TATP solution
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in 50 mM NaOD/D$_2$O) was prepared. 60 mM guest solutions were prepared in DMSO-$d_6$. All titrations were done by adding aliquots of 2.5 $\mu$L of the guest solution to the host solution and mixing it by shaking by hand or sonication. Diffusion constant measurements were made using Bruker 500 MHz NMR at 25 °C and the data were collected by using ‘stebpgp1s’ pulse sequence (16 scans) and processed by $T1/T2$ relaxation module in the TopSpin 2.1 software.

**General protocol for emission studies.**

Stock solution of iTATA (1 mM) was made in 10 mM NaOD/D$_2$O (pH≈11) (1 mM TATP solution in 50 mM NaOD/D$_2$O). Stock solutions of guest molecules (60 mM) were prepared in DMSO-$d_6$. Appropriate amount of the guest solution was added to the host solution to make the host@guest complex. The complex solutions were diluted according to the required concentration. All samples were bubbled with N$_2$ for 20 minutes before the experiment. If needed air, 50 % O$_2$ and 100 % O$_2$ were also bubbled for 20 minutes before the experiment. Emission spectra were recorded using an Edinburgh FC900 spectrofluorometer equipped with a xenon lamp. Fluorescence/phosphorescence lifetime measurements were made using an Edinburgh single photon counter, fitted with a hydrogen arc lamp. Spectral plots were generated using Igor Pro software.

**General protocol for photolysis.**

0.6 mL of 1 mM iTATA solution in 10 mM NaOD/D$_2$O (pH≈11) (1 mM TATP solution in 50 mM NaOD/D$_2$O) was prepared. 60 mM guest solutions were prepared in DMSO-$d_6$. The guest solutions were added to the host solutions accordingly and mixed
by shaking by hand or by sonication. The solutions were then bubbled with N₂ for 20 min and were irradiated under 450 W mercury vapor lamp with a pyrex jacket. The progress of the reactions was monitored by recording the NMR spectrum at different time intervals. The reactions were stopped once the starting guest’s proton peaks were completely disappeared and the photoproducts were extracted using CHCl₃. The extracted solutions were injected in GC and GC-MS to analyze the identity and distribution ratio of the products.
Chapter 3

Exploring the Absorption and Emission Properties of Various Supramolecular Baskets
3.1. Overview.

Supramolecular cavitands are a great system to study the photochemistry and photophysics of various organic molecules due to their ability in confining molecules from bulk solution and as well as from rest of the other reactants to carry out a single molecule per container like operation. In addition, most supramolecules are inert, therefore they don’t interact with the excited state properties of guest. Though many of them are passive under usual photoreaction conditions, host molecules that possess active chromophores can’t be considered inert. Few examples of supramolecular host-guest systems that are engaged in energy transfer processes were found in literature.\textsuperscript{107-112} Hence, it is very important to study the absorption and emission properties of the supramolecular hosts that are utilized to incarcerate photoactive molecules.

3.2. Absorption and Emission Properties of OA.

\textbf{Figure 3.1.} Structure of octa acid.

Since, majority of the host systems that we used in our studies are constructed with benzene and alkylbenzenes units, we were interested in recording the absorption and emission spectra of various supramolecular baskets. At the outset, we were really
curious in understanding the emission spectrum of OA, a host system that we used very extensively in our lab. Figure 3.2 shows the absorption spectra OA recorded at different concentrations which indicate that the OA has its absorption range till 300 nm. The emission spectrum OA has two emission maximum (Figure 3.3 (‘a’ and ‘b’)) and the intensity of peak ‘b’ varies for each batch synthesized. This suggests that peak ‘b’ could be the emission from an impurity that would have carried together with OA during its synthesis. In order to present only the peak corresponding to OA, we recorded the emission spectra of OA at different excitation wavelength (Figure 3.4) and as we increased the excitation wavelength towards a higher value (330 nm), the intensity of peak ‘a’ slowly diminished and completely disappeared when excited at 310 nm, since OA does not absorb after that but peak ‘b’ still persisted. The emission spectrum containing only peak ‘b’ was normalized and subtracted from the normalized original OA spectrum to obtain the emission band of only OA (Figure 3.5b) which looked very close to the emission band of 3,5-dimethoxy benzoic acid (Figure 3.5a). Since the top portal of OA has 3,5-dimethoxy benzoic acid like moiety, it could be well interpreted from the data available that the major emission from OA should be from the top part of it.

Figure 3.2. Absorption spectra of OA in 10 mM Na₂B₄O₇ buffer/D₂O.
Figure 3.3. Emission spectrum of OA in 10 mM Na$_2$B$_4$O$_7$ buffer/H$_2$O, [OA] = 50 µM.

Figure 3.4. Emission spectra of OA recorded at different excitation wavelength in 10 mM Na$_2$B$_4$O$_7$ buffer/H$_2$O, [OA] = 50 µM.
Figure 3.5. Normalized emission spectra of (a) 3,5-dimethoxybenzoic acid and (b) OA (impurity emission subtracted) in 10 mM Na$_2$B$_4$O$_7$ buffer/H$_2$O.
3.3. Absorption and Emission Properties of Various Host and Their Synthetic Intermediates.

Figure 3.6. Structures of various hosts and their synthetic intermediates.
Figure 3.7. Structures of various hosts and their synthetic intermediates.
Figure 3.8. Absorption spectra of BFOB, EMPCBFB, EMPCTA and EMPCPFB in DMSO-d$_6$.

Figure 3.9. Absorption spectra of octa acid, octol and iTATA in DMSO-d$_6$, and octa amine in CHCl$_3$. 
Figure 3.10. Absorption spectra of RCBFB, RCPFB and row A in DMSO-d₆, and tetra amine in CHCl₃.

Figure 3.11. Emission spectra of BFOB, EMPCBFB, EMPCTA and EMPCPFB in DMSO-d₆.
Figure 3.12. Emission spectra of octa acid, octol and iTATA in DMSO-d$_6$, and octa amine in CHCl$_3$.

Figure 3.13. Emission spectra of RCBFB, RCPFB and row A in DMSO-d$_6$, and tetra amine in CHCl$_3$. 
Figure 3.14. Fluorescence decay spectra of BFOB, EMPCBFB, EMPCTA and EMPCPFB in DMSO-$d_6$.

Figure 3.15. Fluorescence decay spectra of octa acid, octol and iTATA in DMSO-$d_6$, and octa amine in CHCl$_3$. 
Figure 3.16. Fluorescence decay spectra of RCBFB, RCPFB and row A in DMSO-d$_6$, and tetra amine in CHCl$_3$.

The absorption spectra of various host having OA like basket have their absorption band extending till about 300 nm (Figure 3.8, 3.9 and 3.10). Emission spectra recorded for the baskets indicate that OA, tetra amine, EMPCTA and EMPCPFB showed very weak fluorescence, whereas other baskets showed good intense fluorescence. None of the host showed phosphorescence at room temperature. The excited state lifetime of all the supramolecular baskets were determined to be between 0.2 – 5 ns. Thus our attempt to understand the absorption and emission properties of various cavitands gave a good idea of their excited state behavior. The absence of phosphorescence from these molecules suggests that either they don’t inter system cross to produce their triplet state or their triplet state decay to the ground state via a non-radiative process.
3.4. Experimental Section.

Materials and methods.

All the cavitands used for the studies were synthesized by following the literature procedure.

General protocol for absorption, emission and lifetime decay studies.

The solution containing various cavitands were prepared by dissolving the sample in either DMSO-$d_6$ or CHCl$_3$, depending on their solubility to obtain the concentration of the solution about 1 mM. The solutions were further diluted to obtain the solution concentration to be 50 µM. The samples were filled in a quartz cuvette to record the absorption spectra. Emission spectra were recorded using an Edinburgh FC900 spectrofluorometer equipped with a xenon lamp for the same solutions. The solutions were further bubbled with N$_2$ for 20 minutes and again recorded the emission spectra in order to see if there was any phosphorescence. Fluorescence lifetime measurements were made using an Edinburgh single photon counter, fitted with a hydrogen arc lamp. Spectral plots were generated using Igor Pro software.
Chapter 4
Photochemical Reaction Containers as Energy Transfer Agents
4.1. Overview.

One of a very important operation that sustains and evolves life in earth is the energy transfer process. Right from the naturally occurring photosynthetic process in plants to manmade solar cells involve energy transfer phenomenon.\textsuperscript{113-123} Energy transfer can occur nonradiatively via two types of mechanisms, (i) FRET (Forster resonance energy transfer) and (ii) Dexter energy transfer. FRET occurs when an excited donor molecule transfers energy to the acceptor molecule which is in ground state by dipole-dipole coupling. For FRET to occur the donor and acceptor molecules are not necessary to remain at a close proximity. FRET results in a reduction in the fluorescence intensity and the fluorescence lifetime of the donor, and an increase in the fluorescence intensity of the acceptor. The efficiency of FRET depends upon the inverse sixth power of the distance between the donor and acceptor molecules, so it can be applied as a “spectroscopic ruler” in the molecular range 1–10 nm.\textsuperscript{124} Using donor or acceptor labeled antibodies, FRET can be used to determine both inter- and intra-molecular distances of cell surface proteins. With the help of FRET, molecular dimensions can be measured in living cells, providing information inaccessible with other approaches such as electron microscopy. In Dexter energy transfer process the excited donor molecule exchanges electron with the acceptor molecule that involves their orbital overlap.\textsuperscript{125,126} Therefore, the donor and acceptor molecules need to be in close contact with each other. The reaction rate constant of Dexter energy transfer sharply decreases while the distance between donor and acceptor increase and the distance is generally smaller than 10 Å. The Dexter mechanism can be applied to produce the triplet state of some molecules of
interest and has found applications in novel light emitting materials. Figure 4.1 shows a schematic representation of FRET and Dexter energy transfer processes.

![Figure 4.1](image)

**Figure 4.1.** Schematic representation of (a) FRET and (b) Dexter energy transfer processes.

As in the case of proteins and other biological systems it is imperative to understand the energy transfer process in supramolecular assemblies. In the year 1995, Deshayes and coworkers reported the occurrence of triplet energy transfer between the hemicarcerand incarcerated acetophenone and cis-piperylene which is present freely in the solution that resulted in the photo-sensitized cis-trans isomerization to produce trans-piperylene. Moreover, they found that the energy transfer occurs at a slower rate when the guest is incarcerated which clearly states that though there is no close contact between
the donor and acceptor the triplet energy transfer occurs which in turn proves that the triplet energy transfer process can occur purely through space.\textsuperscript{126,127}

![Diagram of molecular structures]

**Figure 4.2.** Structures of hosts and guests.

![Spectra graphs]

**Figure 4.3.** (i) (a) Excitation and (b) emission spectra of OA ($\lambda_{ex} = 280$ nm). (ii) (a) Excitation and (b) emission spectra of MOA ($\lambda_{ex} = 280$ nm). ([OA] = [MOA] = 50 $\mu$M in 10 mM Na$_2$B$_4$O$_7$ buffer solution).

Similarly energy transfer between OA incarcerated guests and free molecules in solution were studied in detail in our group and the role of OA was considered to be just a partition to curtail the complete contact between donor and acceptor. Energy transfer
processes occur between guests incorporated inside conventional micelles, cyclodextrins, calixarenes, cucurbiturils reveal the passive nature of these reaction cavities, whereas larger cavitands, and inorganic assemblies with absorption extending to the UV-Vis region were proved to be active\textsuperscript{43,129,130} which prompted the importance of understanding the excited-state properties of the host itself. Excitation of OA and another host called modified octa acid (\textit{MOA} having eight –COOH groups at its bottom portal and the top –COOH groups are replaced by –H) at 280 nm resulted in weak fluorescence in the region 320 to 420 nm (\textbf{Figure 4.3}). Remarkable overlap between absorption and excitation spectra and mirror symmetric relationship between emission and absorption spectra suggested that the observed emission should be from the first excited singlet state of the hosts. Based on the above spectra, we believe that the \textit{S}_1 of OA and MOA has an approximate energy of 88 kcal mol\textsuperscript{-1}. We believed that the presence of carbonyl groups in OA and MOA would favor intersystem crossing and a triplet would be formed upon direct excitation of the host.\textsuperscript{131} Since no phosphorescence could be detected, we probed the possible triplet generation by carrying out classical triplet-sensitized photoreactions. In addition to OA and MOA, we also used iTATA, TATA and TATP to compare their energy transferring ability. \textbf{Figure 4.2} provides the structures of hosts and guests (\textit{4.1} and \textit{4.2}) that are investigated in the studies.
4.2. Complexation studies of OA, iTATA, TATA, TATP and MOA with 4.1 and 4.2.

Figure 4.4. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 4.1.

Figure 4.5. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O) spectra of (i) only OA $[OA] = 1$ mM; (ii) 0.5 mM 4.1 + 1 mM OA and (iii) 1 mM 4.1 + 1 mM OA. “∗” indicates the OA encapsulated guest proton peaks. "●" represents the residual solvent peak of water.
Figure 4.6. 2D DOSY NMR spectra (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O) of (i) OA ([OA] = 1 mM) and (ii) (4.1)$_2$@(OA)$_2$ ([OA] = 1 mM and [4.1] = 1 mM) and the determined diffusion constants are $1.88 \times 10^{-10}$ m$^2$/s and $1.22 \times 10^{-10}$ m$^2$/s, respectively. "●" represents the residual solvent peak of water.
Figure 4.7. $^1$H NMR (500 MHz, 10 mM NaOD/D$_2$O) spectra of (i) only iTATA [iTATA] = 1 mM; (ii) 1 mM 4.1 + 1 mM iTATA. “∗” indicates the iTATA encapsulated guest proton peaks. “●” represents the residual solvent peak of water.

Figure 4.8. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O) spectra of (i) only MOA [MOA] = 1 mM; (ii) 1 mM 4.1 + 1 mM MOA. “∗” indicates the MOA encapsulated guest proton peaks. “●” and “♦” indicate the residual solvent peak of water and DMSO-$d_6$. 
Figure 4.9. $^1$H NMR (500 MHz, 10 mM NaOD/D$_2$O) spectra of (i) only TATA [TATA] = 1 mM; (ii) 0.5 mM 4.1 + 1 mM TATA and (iii) 1 mM 4.1 + 1 mM TATA. "∗" indicates the TATA encapsulated guest proton peaks. “●” and “♦” indicate the residual solvent peak of water and DMSO-$d_6$. 
Figure 4.10. $^1$H NMR (500 MHz, 50 mM NaOD/D$_2$O) spectra of (i) only TATP [TATP] = 1 mM; (ii) 0.5 mM 4.1 + 1 mM TATP and (iii) 1 mM 4.1 + 1 mM TATP. “∗” indicates the TATP encapsulated guest proton peaks. “●” and “♦” indicate the residual solvent peak of water and DMSO-$d_6$. 
Figure 4.11. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O) spectra of (i) only OA [OA] = 1 mM; (ii) 0.5 mM 4.2 + 1 mM OA and (iii) 1 mM 4.2 + 1 mM OA. "●" represents the residual solvent peak of water.
Figure 4.12. $^1$H-NMR (400 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O) spectra of (i) $\text{4.2@(OA)}_2$ at 25 °C, (ii) $\text{4.2@(OA)}_2$ at 35 °C, (iii) $\text{4.2@(OA)}_2$ at 45 °C, (iv) $\text{4.2@(OA)}_2$ at 55 °C, (v) $\text{4.2@(OA)}_2$ at 65 °C, (vi) $\text{4.2@(OA)}_2$ at 75 °C, (vii) OA at 75 °C. [OA] = 1 mM and [$\text{4.2}$] = 0.5 mM. "●" represents the residual solvent peak of water.
Figure 4.13. $^1$H NMR (500 MHz, 10 mM NaOD/D$_2$O) spectra of (i) only iTATA [iTATA] = 1 mM; (ii) 0.5 mM 4.2 + 1 mM iTATA and (iii) 1 mM 4.2 + 1 mM iTATA. “●” indicates the residual solvent peak of water.
Figure 4.14. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O) spectra of (i) only MOA [MOA] = 1 mM; (ii) 0.5 mM 4.2 + 1 mM MOA and (iii) 1 mM 4.2 + 1 mM MOA. "●" represents the residual solvent peak of water.
Figure 4.15. $^1$H NMR (500 MHz, 10 mM NaOD/D$_2$O) spectra of (i) only TATA [TATA] = 1 mM; (ii) 0.5 mM 4.2 + 1 mM TATA and (iii) 1 mM 4.2 + 1 mM TATA. “●” and “♦” indicate the residual solvent peak of water and DMSO-$d_6$. 
Figure 4.16. $^1$H NMR (500 MHz, 50 mM NaOD/D$_2$O) spectra of (i) only TATP [TATP] = 1 mM; (ii) 0.5 mM 4.2 + 1 mM TATP and (iii) 1 mM 4.2 + 1 mM TATP. “●” and “♦” indicate the residual solvent peak of water and DMSO-$_d$.

From the $^1$H NMR titration spectra of 4.1 with OA, iTATA, TATA, TATP and MOA (Figure 4.5, 4.7, 4.8, 4.9 and 4.10) it is very clear that 4.1 forms a very good 2:2 complex with all the hosts which was concluded from the upfield shift in the $^1$H NMR signals of the protons attached to the saturated carbons of 4.1 and from DOSY experimental data. The diffusion constant estimated for 4.1@(OA)$_2$ by DOSY in Figure 4.6 was $1.22 \times 10^{-10}$ m$^2$/s, which is consistent with the reported values in the literature for OA capsular assemblies.$^{50,51}$ Excess addition of guest turned the solution turbid. Similar $^1$H NMR experiments with 4.2 and OA, iTATA, TATA, TATP and MOA (Figure 4.11,
4.13, 4.14, 4.15 and 4.16) established that 4.2 formed 2:1 host-guest capsular assemblies with these hosts. Based on the variable-temperature $^1$H NMR studies (Figure 4.12), we concluded that the guest 4.2 formed a weaker complex with OA. Unlike in the case of guest 4.1, upfield shifted signals due to the guest 4.2 could not be clearly identified upon its complexation with hosts. However, inclusion was suggested by the changes in the host’s aromatic signals.

4.3. Triplet sensitization of Guests by Host.

Figure 4.17. Absorption spectra of hosts (aqueous medium) and guests (hexane).
Scheme 4.1. Photochemistry of 4.1 and 4.2 in solution.

Figure 4.18. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O) spectra of (i) only OA [OA] = 1 mM; (ii) (4.1)$_2$@OA, (iii) (4.1)$_2$@OA (after 30 min irradiation) and (4.4)$_2$@OA. “*” indicates the OA encapsulated guest proton peaks. "●" represents the residual solvent peak of water.
Figure 4.19. $^1$H NMR (500 MHz, 10 mM NaOD/D$_2$O) spectra of (i) only iTATA \([\text{iTATA}] = 1 \text{ mM}\); (ii) \((4.1)_2@\text{(iTATA)}_2\), (iii) after 1 h irradiation of (ii), (iv) after 17 h irradiation of (ii), (v) after 24 h irradiation of (ii), (vi) after 36 h irradiation of (ii), (vii) after 54 h irradiation of (ii) and (viii) \((4.4)_2@\text{(iTATA)}_2\). “∗” indicates the iTATA encapsulated guest proton peaks. “●” represents the residual solvent peak of water.
Figure 4.20. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O) spectra of (i) only MOA [MOA] = 1 mM; (ii) (4.1)$_2$(MOA)$_2$, (iii) after 30 min irradiation of (ii), (iv) after 1 h irradiation of (ii), (v) after 3 h irradiation of (ii), (vi) after 7 h irradiation of (ii), (vii) after 12 h irradiation of (ii) and (viii) (4.4)$_2$(MOA)$_2$. “∗” indicates the MOA encapsulated guest proton peaks. "●" represents the residual solvent peak of water.
Figure 4.21. $^1$H NMR (500 MHz, 10 mM NaOD/D$_2$O) spectra of (i) only TATA [TATA] = 1 mM; (ii) (4.1)$_2$@TATA)$_2$, (iii) after 30 min irradiation of (ii), (iv) after 1 h irradiation of (ii) and (v) (4.4)$_2$@TATA)$_2$. “∗” indicates the OA encapsulated guest proton peaks. “●” represents the residual solvent peak of water.
Figure 4.22. $^1$H NMR (500 MHz, 50 mM NaOD/D$_2$O) spectra of (i) only TATP [TATP] = 1 mM; (ii) (4.1)$_2$(TATP)$_2$, (iii) after 12 h irradiation of (ii), (iv) after 24 h irradiation of (ii) and (v) after 36 h irradiation of (ii). “∗” indicates the OA encapsulated guest proton peaks. "●" represents the residual solvent peak of water.
Figure 4.23. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O) spectra of (i) only OA [OA] = 1 mM; (ii) 4.2@OA$_2$, (iii) 4.2@OA$_2$ (after 30 min irradiation) and 4.6@OA$_2$. “∗” indicates the OA encapsulated guest proton peaks. "●" represents the residual solvent peak of water.
Figure 4.24. $^1$H NMR (500 MHz, 10 mM NaOD/D$_2$O) spectra of (i) only iTATA [iTATA] = 1 mM; (ii) 4.2@iTATA), (iii) after 30 min irradiation of (ii), (iv) after 4 h irradiation of (ii), (v) after 16 h irradiation of (ii) and (vi) after 32 h irradiation of (ii). "●" represents the residual solvent peak of water.
Figure 4.25. \(^1\)H NMR (500 MHz, 10 mM Na\(_2\)B\(_4\)O\(_7\) buffer/D\(_2\)O) spectra of (i) only MOA [MOA] = 1 mM; (ii) 4.2@MOA\(_2\), (iii) after 30 min irradiation of (ii), (iv) after 1 h irradiation of (ii), (v) after 3 h irradiation of (ii) and (vi) after 8 h irradiation of (ii). "●" represents the residual solvent peak of water.
Figure 4.26. $^1$H NMR (500 MHz, 10 mM NaOD/D$_2$O) spectra of (i) only TATA [TATA] = 1 mM; (ii) 4.2@(TATA)$_2$, (iii) after 30 min irradiation of (ii) and (iv) after 1 h irradiation of (ii). "●" represents the residual solvent peak of water.

We examined the triplet energy transferring ability of OA, iTATA, TATA, TATP and MOA using guests 4.1 and 4.2 because these two guests produce distinctly different products from S$_1$ and T$_1$ and more conveniently, both molecules absorb at shorter wavelengths than the hosts (Figure 4.16). Photochemistry of 4.1 and 4.2 has been well investigated in solution and acetophenone sensitization of 4.1 and 4.2 yielded 4.4 and 4.6, respectively (Scheme 4.1).
Table 4.1. Reaction conversion for the photolysis of 4.1 in different media.

<table>
<thead>
<tr>
<th>Medium</th>
<th>Duration of irradiation</th>
<th>% Conversion to product (4.4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OA (borate buffer)</td>
<td>30 min</td>
<td>98 %</td>
</tr>
<tr>
<td>TATA (10 mM NaOD)</td>
<td>1 h</td>
<td>93 %</td>
</tr>
<tr>
<td>iTATA (10 mM NaOD)</td>
<td>54 h</td>
<td>93 %</td>
</tr>
<tr>
<td>MOA (borate buffer)</td>
<td>12 h</td>
<td>95 %</td>
</tr>
<tr>
<td>TATP (50 mM NaOD)</td>
<td>36 h</td>
<td>95 %</td>
</tr>
<tr>
<td>Acetophenone/hexane</td>
<td>30 min</td>
<td>15 %</td>
</tr>
<tr>
<td>Hexane</td>
<td>8 h</td>
<td>0 %</td>
</tr>
</tbody>
</table>

We examined the triplet energy transferring ability of OA, iTATA, TATA, TATP and MOA using guests 4.1 and 4.2 because these two guests produce distinctly different products from S₁ and T₁, and more conveniently, both molecules absorb at shorter wavelengths than the hosts (Figure 4.16). Photochemistry of 4.1 and 4.2 has been well investigated in solution and acetophenone sensitization of 4.1 and 4.2 yielded 4.4 and 4.6, respectively (Scheme 4.1).\textsuperscript{132-138} Irradiation (450 W medium pressure mercury lamp) of (4.1)₂@(OA)₂, (4.1)₂@(iTATA)₂, (4.1)₂@(TATA)₂, (4.1)₂@(TATP)₂ and (4.1)₂@(MOA)₂ resulted in the formation of (4.4)₂@(OA)₂, (4.4)₂@(iTATA)₂, (4.4)₂@(TATA)₂, (4.4)₂@(TATP)₂ and (4.4)₂@(MOA)₂, respectively (Figure 4.18 - 4.22). The clear 100 % formation of 4.4 from 4.1 within various capsules were confirmed by comparing the $^1$H
NMR spectrum recorded for the irradiated \((4.1)_2@\text{(host)}_2\) to \((4.4)_2@\text{(TATP)}_2\) in which 4.4 was independently synthesized. The reaction conversions were quantitatively analyzed by extracting the photoproducts from the irradiated samples using CHCl\(_3\) and injecting in GC and GC-MS.

**Table 4.2.** Comparison of 4.2 photolysis yields in different media.

<table>
<thead>
<tr>
<th>Medium</th>
<th>Duration of irradiation</th>
<th>4.6</th>
<th>4.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>OA (borate buffer)</td>
<td>30 min</td>
<td>98 %</td>
<td>0 %</td>
</tr>
<tr>
<td>TATA (10 mM NaOD)</td>
<td>30 min</td>
<td>99 %</td>
<td>0 %</td>
</tr>
<tr>
<td>iTATA (10 mM NaOD)</td>
<td>32 h</td>
<td>82 %</td>
<td>0 %</td>
</tr>
<tr>
<td>MOA (borate buffer)</td>
<td>8 h</td>
<td>67 %</td>
<td>0 %</td>
</tr>
<tr>
<td>Acetophenone/hexane</td>
<td>30 min</td>
<td>15 %</td>
<td>0 %</td>
</tr>
<tr>
<td>Hexane</td>
<td>8 h</td>
<td>3 %</td>
<td>37 %</td>
</tr>
</tbody>
</table>

Irradiation of 4.2@\text{(OA)}_2, 4.2@\text{(iTATA)}_2, 4.2@\text{(TATA)}_2 and 4.2@\text{(MOA)}_2 resulted in the formation of 4.6@\text{(OA)}_2, 4.6@\text{(iTATA)}_2, 4.6@\text{(TATA)}_2 and 4.6@\text{(MOA)}_2, respectively (Figure 4.23 – 4.26). The irradiated samples were separated between CHCl\(_3\) and injected in GC and GC-MS. The GC spectrum showed only the peak corresponding to 4.6 and no traces of product 4.5 was observed. The efficiency and products distributions for the photolysis of \((4.1)_2@\text{(host)}_2\) and 4.2@\text{(host)}_2 remained the same for both the degassed and aerated samples. The exclusive formation of only triplet
products (4.4 and 4.6) showed that the reaction must be possible only if the hosts reached the T₁ state via intersystem crossing from S₁ and transferred the energy to the guest. Moreover, the reaction seemed to undergo faster in OA and TATA but slower inside iTATA, TATP and MOA. The reason for the difference in efficiencies of the triplet sensitization between these hosts (Table 4.1 and 4.2) is most likely related to the difference in quantum yields of intersystem crossing from S₁ to T₁ and also the presence of a very good energy transferring benzoate anion (donor) at the top portal of OA and TATA. The dibenzoate anion present in MOA remains quite far from the guest (acceptor). Based upon the above observed triplet sensitized reactions we believe that the triplet energy of the hosts should be closer to that of acetophenone (73 kcal mol⁻¹),¹³⁹ which was used to sensitize the phototransformation of 4.1 in diethyl ether solution.¹³⁵,¹³⁶ The above results have unequivocally established that the deep cavity cavitands are photochemically “active”, and one must take this feature into consideration while utilizing them as reaction cavities.⁴³,¹²⁹

4.4 Experimental Section.

Guest molecules were prepared by following the literature procedure.¹⁴⁰-¹⁴²

Synthesis of benzonorbornadiene (4.1).
In 250 mL round bottom flask 1,2-dibromobenzene (5 g, 0.214 mole), freshly distilled cyclopentadiene (1.4 g, 0.214 mol) and toluene (30 mL) were added. The reaction mixture was cooled to 0 °C under N₂ atmosphere. To this n-butyl-Li (13 mL, 0.214 mol) was added drop wise for over 30 min. Then about 20 mL water was added slowly and the product was separated between hexane and water. The hexane layer was dried with anhydrous Na₂SO₄ and concentrated to obtain an orange colored viscous liquid. The crude product was passed through a silica gel column chromatography using hexane as the mobile phase in order to isolate the pure product. The structure of the product was confirmed from its ¹H NMR and GC-MS spectra. The yield of the product 4.1 obtained was 0.91 g.
Synthesis of dibenzobarrelene (4.2).

![Chemical structures](image)

Figure 4.28. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of the anthracene-dimethylacetylene dicarboxylate adduct. “●” indicates the residual solvent peak of CDCl$_3$.

In a 100 mL round bottom flask about 5 g of anthracene and 6 g of dimethylacetylene dicarboxylate were added. The mixture was heated to 170 $^\circ$C and maintained the same condition for 1 h under N$_2$ atmosphere. The temperature of the reaction was then raised to 180 $^\circ$C and maintained for 10 min. The reaction was stopped and cooled to room temperature. As the reaction mass was cooled the mass became very
thick. To this 50 mL methanol was added and sonicated to precipitate out the product. The suspension was the filtered and washed with methanol and dried under reduced pressure at room temperature for 30 min. The $^1$H NMR and mass spectrum of the product complies with the structure of the expected product. The obtained yield was 5.9 g with 95% purity (by GC).

![Chemical structures](image)

**Figure 4.29.** $^1$H NMR (500 MHz, DMSO-d$_6$) spectrum of the anthracene-acetylene dicarboxylic acid adduct. “●” indicates the residual solvent peak of DMSO-d$_6$.

In a 100 mL round bottom flask about 5 g of anthracene-dimethylacetylene dicarboxylate adduct and 25 mL of methanol were added. To this mixture 10 mL 2N NaOH solution was added. The mixture was heated to reflux and maintained the same condition for 1 h. The reaction was then stopped and cooled to room temperature and stored in the refrigerator for 12 h. The reaction mass was then taken out from the
refrigerator and filtered. The solid obtained was dissolved in 100 mL water and added 10 % HCl solution to precipitate out the product. The precipitate was then filtered and washed with water and then dried under reduced pressure at room temperature for 6 h. The yield obtained was 3.4 g.

Figure 4.30. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of the 4.2. “●” indicates the residual solvent peak of CDCl$_3$.

In a 50 mL round bottom flask about 1 g of anthracene-acetylene dicarboxylic acid adduct and 3 mL of quinoline were added. The mixture was heated to 170 °C and maintained the same condition for 12 h. The temperature of the reaction was raised to 180 °C and maintained it for 15 min. The reaction was then stopped and cooled to room temperature and added 25 mL CHCl$_3$. The mixture was filtered and washed with 50 mL CHCl$_3$. The CHCl$_3$ layer was given 50 mL 10 % NaOH wash, 50 mL 10 % HCl wash and 50 mL D.I. water wash. Then the CHCl$_3$ layer was dried with sodium sulfate and
concentrated under reduced pressure. The crude product was passed through a silica gel column using hexane and EtOAc as the mobile phase to isolate the pure product. The purity of the product was found to be > 99 % (by GC). The structure of the product was confirmed from its mass spectrum and $^1$H NMR spectrum.

General protocol for the binding studies of guests with hosts (NMR Characterization).

600µL of stock solution of hosts (1 mM OA and ROA in 10 mM Na$_2$B$_4$O$_7$, iTATA and TATA in 10 mM NaOD/D$_2$O, and TATP in 50 mM NaOD/D$_2$O) were added to NMR tubes separately. To these tubes, aliquots of guest solution were added such that 0.25 equivalents were added upon each addition (2.5 µL of a 60 mM solution in DMSO-$d_6$). The complex formation was achieved by shaking the NMR tube for 5 min. Spectra were recorded after each addition of the guest solution under aerated conditions on a Bruker 500 MHz NMR spectrometer at 25 °C. Complete complexation was observed after the addition of 1 equivalent of 4.1 to the host solutions and 0.5 equivalents in the case of 4.2. The addition of excess guest led to turbidity and NMR spectra demonstrated the formation of (2:2) (H:G) complex in the case of 4.1 and (2:1) (H:G) complex in the case of 4.2. To confirm the (2:2) (H:G) complex formation between 4.1 and OA, a 2D DOSY NMR spectrum was recorded using ‘stepbg1s’ pulse sequence, pulsed field gradients were incremented linearly from 1.06 (2 % of field gradient strength) to 50.35 G/cm (95 % of field strength) in 16 steps with each step containing 8 scans. The data was processed by $T_1/T_2$ relaxation module in the TOPSIN 2.1 software.
Photolysis of guests inside various capsules.

(4.1)_{2}@(OA)_{2} and 4.2@(OA)_{2} were prepared by following the same procedure as above. The solutions were irradiated with 450 W medium pressure mercury lamp. All the solutions were prepared in a pyrex NMR tube. The irradiated samples were analyzed by \(^1\)H NMR and also by GC after extracting into CDCl3.

Extraction and analysis of photoproduction from irradiated samples.

After photolysis, reactants and products were extracted from the aqueous solution using CHCl3, dried over anhydrous Na\(_2\)SO\(_4\), concentrated and analyzed on a HP-6890 gas chromatograph fitted with a SPB-5 capillary column. The products were also identified by GC-MS.
Chapter 5
Triplet Sensitized Geometric Isomerization of \textit{para}-Substituted Stilbenes Inside OA Capsule
5.1. Overview.

The importance of using triplet photosensitizers to carry out reactions from the triplet state of molecules that have only a small intrinsic triplet state yield have been well studied in the past. These triplet sensitizers can act as a catalyst in photochemical reactions because they can be efficiently excited to their triplet state which in turn transfers energy to the acceptor molecule to obtain the desired products. One of the most interesting photochemical reactions studied in the past is the *cis-trans* isomerization of olefins as it is very well associated with some of the very important biological process like light induced isomerization of cis-retinal to *trans*-retinal, a vital reaction involved in our vision process. Some of the major challenges involved in the *cis-trans* isomerization reactions involving direct irradiation are (i) obtaining 100 % conversion and (ii) avoiding side reactions like photocyclization, etc. Having a careful choice of triplet sensitizer can quantitatively enrich the ratio of the *cis*-product. Ramamurthy and Liu in the year 1973 had successfully achieved a 100 % conversion of *trans*-β-ionol to *cis*-β-ionol by using 2-acetylnapthalene as sensitizers.

![Scheme 5.1. Photoisomerization of stilbene.](image)

Photoisomerization of stilbene was a well investigated reaction in the literature. In our group we have been studying the *cis-trans* isomerization of stilbenes in confined media (Scheme 5.1). Our previous studies involving inclusion of
trans-stilbenes inside NaY zeolite cages in the presence of 2-acetonaphthone sensitizer to carry out photoisomerization weren’t very useful as the results remained the same as it was in solution.\textsuperscript{183} A great control on the photostationary state ratios of the para-substituted stilbenes were achieved when they were encapsulated inside OA capsule and carried out the triplet sensitized isomerization.\textsuperscript{55,67}

**Guest stilbenes**

\begin{align*}
\text{trans-4,4'}-\text{DiMestilbene} & \quad \text{trans-4-Me-stilbene} & \quad \text{trans-4-Et-stilbene} & \quad \text{trans-4-Pr-stilbene} \\
\text{cis-4,4'}-\text{DiMestilbene} & \quad \text{cis-4-Me-stilbene} & \quad \text{cis-4-Et-stilbene} & \quad \text{cis-4-Pr-stilbene}
\end{align*}

**Sensitizers**

\begin{align*}
\text{9FCOOH} & \quad \text{BPA salt} & \quad \text{4,4'}-\text{DMBdiCOOH}
\end{align*}

**Figure 5.1.** Structures of stilbene derivatives and sensitizers.

**Figure 5.2.** Pictorial representation of stilbene@\((\text{OA})_2\) triplet sensitization using OA encapsulated sensitizer.
In the previous studies the ortho/meta/para-substituted trans-stilbenes were excited to their triplet state using water insoluble triplet sensitizers that are solubilized by OA encapsulation (Figure 5.2). The formation of 2:1 (H:G) complex between the stilbene derivatives and OA were well established from their NMR studies. The separately prepared stilbene derivatives@(OA)$_2$ and sensitizer@(OA)$_2$ were mixed in equal amounts and irradiated $>380$ nm and the conversion was monitored by NMR and the final product ratio was analyzed by GC. Sensitization of trans-4,4'-DiMe-stilbene@(OA)$_2$ did not result in significant isomerization to the cis-4,4'-DiMe-stilbene@(OA)$_2$, whereas in benzene the ratio obtained was 20:80 (trans:cis). Sensitization of cis-4,4'-DiMe-stilbene@(OA)$_2$ resulted in quantitative conversion to the trans-isomer. This anomaly is due to the strong anchoring of the 4-methyl groups on both benzene rings of the guest that puts a heavy constrain on the isomerization process. Examination of the triplet sensitized isomerization of trans-4-Me-stilbene@(OA)$_2$ indicates that the trans:cis ratio were identical to the one observed in benzene (85 % cis-isomer). On the other hand triplet sensitized isomerization of trans-4-Et-stilbene@(OA)$_2$ and trans-4-Pr-stilbene@(OA)$_2$ yielded $>99$ % cis-isomers at the photostationary state. However, sensitization of cis-4-Et-stilbene@(OA)$_2$ and cis-4-Pr-stilbene@(OA)$_2$ did not yield their corresponding trans-isomers. These results threw some light on the importance of the length of the alkyl chain on the mono-substituted stilbenes in controlling the photostationary state ratio. The trans:cis ratio obtained for the ortho and meta-substituted stilbenes inside OA capsules and benzene were similar after triplet sensitization, suggesting the importance of the substitution at the para-position. The most important question raised was, does the energy transfer occurs through the walls of both the
capsules. Using 4,4’-dimethylbenzene@(OA)$_2$ as the triplet energy donor and acceptors of different kind (cationic, neutral and neutral@(OA)$_2$), it was proved that the energy transfer is diffusion controlled. This further raised a doubt that whether the capsule opens up during the triplet sensitization process. To clarify the process we employed three water soluble triplet sensitizers, 9FCOOH ($-E_T = 51$ kcal mol$^{-1}$) and 4,4’-DMBdiCOOH ($-E_T = 50$ kcal mol$^{-1}$) and BPA salt ($-E_T = 68$ kcal mol$^{-1}$) (Figure 5.1). Since stilbene@(OA)$_2$ capsule was negatively charged, the sensitizers were chosen such that one would stay closer to the capsule through dipolar attraction (BPA salt) and the other two (9FCOOH and 4,4’-DMBdiCOOH) would stay apart due to dipolar repulsion. This chapter will discuss the results obtained on the triplet sensitized isomerization of the stilbenes inside OA capsule using the above three water soluble sensitizers (Figure 5.3).

![Energy transfer](image)

**Figure 5.3.** Pictorial representation of stilbene@(OA)$_2$ triplet sensitization using water soluble sensitizers.
5.2. Results.

The 2:1 stilbene@(OA)$_2$ complexes were prepared by adding 5 µL of 60 mM solution of the guest stilbenes in DMSO-d$_6$ 1 mM solutions of OA in borate buffer. The $^1$H NMR spectra confirmed the inclusion of stilbene within OA capsule. To this solution 5 µL of 60 mM solution of the sensitizer in DMSO-d$_6$ was added. In order to confirm that the addition of sensitizers did not disturb the stability of stilbene@(OA)$_2$ complexes, we carried out few control experiments. Figure 5.6 and 5.7 show the $^1$H NMR titration spectra of OA with BPA salt and 4,4’-DMBdiCOOH, respectively, in which the presence of 4,4’-DMBdiCOOH did not really interfere with OA, whereas due to its positive nature the BPA salt was attracted towards OA, therefore the aromatic proton peaks of OA broadens which eventually got sharpened after forming complex with stilbenes (Figure 5.10(iii), 5.13(iii), 5.16(iii), 5.19(iii), 5.22(iii), 5.25(iii), 5.28(iii) and 5.31(iii)). The $^1$H NMR spectra of mixtures of 9FCOOH and OA solution showed a slight interaction between 9FCOOH and OA cavity (Figure 5.5) but the interaction seemed to have

**Figure 5.4.** Absorption spectra of cis- and trans-4-methylstilbenes and the three water soluble sensitizers.
disappeared in the presence of stilbenes (Figure 5.8(iii), 5.11(iii), 5.14(iii), 5.17(iii), 5.20(iii), 5.23(iii), 5.26(iii) and 5.29(iii)). Moreover, there wasn’t any change observed in the $^1$H NMR spectra when the sensitizer and stilbene@OA$_2$ mixtures were left for several days.

To carry out the triplet sensitized isomerization the mixture (stilbene@OA$_2$ and sensitizer) was first purged with N$_2$ for 15 min and irradiated with medium pressure mercury lamp (>330 nm) for 2 days. Progress of the isomerization was followed by recording $^1$H NMR spectra. After the reaction completion the products were extracted with CHCl$_3$ and analyzed by GC. In each case pss was reached starting from both trans and cis isomers and the percentage of the two isomers at pss as measured by $^1$H NMR and GC are provided in Table 5.1 and 5.2. Figure 5.8(iii), (iv) and (v) shows the triplet sensitized isomerization of trans-4-Et-stilbene@OA$_2$ in the presence of 9FCOOH to the cis-isomer within OA capsule while the cis-isomer did not isomerize to the trans-isomer. To confirm that the triplet sensitized reaction was the favored path, irradiation of trans-4-Et-stilbene@OA$_2$ in the absence of sensitizer was carried out as a control experiment. Its $^1$H NMR spectrum didn’t show a quantitative conversion to its cis-isomer which indicates that the conversion majorly occurs by the triplet sensitized. The same is true in the case of trans-4-Pr-stilbene@OA$_2$. On the other hand, cis- and trans-4-Me-stilbene behaved similarly in presence and absence of OA and yielded same trans:cis ratio at pss inside OA. trans-4,4’-DiMestilbene@OA$_2$ didn’t undergo isomerization where as cis-4,4’-DiMestilbene@OA$_2$ almost converted to its trans-isomer.
Figure 5.5. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O) titration spectra of OA with 9FCOOH. "●" represents the residual solvent peak of water.
Figure 5.6. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O) titration spectra of OA with 4,4'-DMBdiCOOH. "●" represents the residual solvent peak of water.
Figure 5.7. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O) titration spectra of OA with BPA salt. "●" represents the residual solvent peak of water.
Figure 5.8. Triplet sensitized isomerization of trans-4-Et-stilbene@(OA)$_2$ in the presence of 9FCOOH monitored by $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O). “*” and “∗” indicate the OA encapsulated trans-4-Et-stilbene and cis-4-Et-stilbene proton peaks. "●" represents the residual solvent peak of water.
Figure 5.9. Triplet sensitized isomerization of \textit{trans}-4-Et-stilbene@(OA)\textsubscript{2} in the presence of 4,4'-DMBdiCOOH monitored by \textit{\textsuperscript{1}}H NMR (500 MHz, 10 mM Na\textsubscript{2}B\textsubscript{4}O\textsubscript{7} buffer/D\textsubscript{2}O). “∗” and “∗” indicate the OA encapsulated \textit{trans}-4-Et-stilbene and \textit{cis}-4-Et-stilbene proton peaks. "●" represents the residual solvent peak of water.
Figure 5.10. Triplet sensitized isomerization of \textit{trans}-4-Et-stilbene@(OA)\textsubscript{2} in the presence of BPA salt monitored by $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O). "∗" and "∗" indicate the OA encapsulated \textit{trans}-4-Et-stilbene and \textit{cis}-4-Et-stilbene proton peaks. "." represents the residual solvent peak of water.
Figure 5.11. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O) spectra showing the resistance of cis-4-Et-stilbene@(OA)$_2$ towards isomerization in the presence of 9FCOOH. “∗” indicates the OA encapsulated cis-4-Et-stilbene proton peaks. "●" represents the residual solvent peak of water.
Figure 5.12. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O) spectra showing the resistance of cis-4-Et-stilbene@(OA)$_2$ towards isomerization in the presence of 4,4’-DMBdiCOOH. “*” indicates the OA encapsulated cis-4-Et-stilbene proton peaks. "●" represents the residual solvent peak of water.
Figure 5.13. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O) spectra showing the resistance of cis-4-Et-stilbene@(OA)$_2$ towards isomerization in the presence of BPA salt. “∗” indicates the OA encapsulated cis-4-Et-stilbene proton peaks. "●" represents the residual solvent peak of water.
Figure 5.14. Triplet sensitized isomerization of trans-4-Pr-stilbene@(OA)$_2$ in the presence of 9FCOOH monitored by $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O). “∗” and “∗∗” indicate the OA encapsulated trans-4-Pr-stilbene and cis-4-Pr-stilbene proton peaks. "●" represents the residual solvent peak of water.
Figure 5.15. Triplet sensitized isomerization of $trans$-4-Pr-stilbene@(OA)$_2$ in the presence of 4,4'-DMBdiCOOH monitored by $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O) “∗” and “∗” indicate the OA encapsulated $trans$-4-Pr-stilbene and $cis$-4-Pr-stilbene proton peaks. "●" represents the residual solvent peak of water.
Figure 5.16. Triplet sensitized isomerization of trans-4-Pr-stilbene@(OA)$_2$ in the presence of BPA salt monitored by $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O). “∗” and “∗∗” indicate the OA encapsulated trans-4-Pr-stilbene and cis-4-Pr-stilbene proton peaks. "●" represents the residual solvent peak of water.
Figure 5.17. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O) spectra showing the resistance of cis-4-Pr-stilbene@(OA)$_2$ towards isomerization in the presence of 9FCOOH. “∗” indicates the OA encapsulated cis-4-Pr-stilbene proton peaks. "●" represents the residual solvent peak of water.
Figure 5.18. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O) spectra showing the resistance of cis-4-Pr-stilbene@(OA)$_2$ towards isomerization in the presence of 4,4’-DMBdiCOOH. “*” indicates the OA encapsulated cis-4-Pr-stilbene proton peaks. "●" represents the residual solvent peak of water.
Figure 5.19. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O) spectra showing the resistance of cis-4-Pr-stilbene@(OA)$_2$ towards isomerization in the presence of BPA salt. “∗” indicates the OA encapsulated cis-4-Pr-stilbene proton peaks. "●" represents the residual solvent peak of water.
Figure 5.20. Triplet sensitized isomerization of \textit{trans}-4-Me-stilbene@\textit{(OA)}\textsubscript{2} in the presence of 9FCOOH monitored by \textit{\textsuperscript{1}H} NMR (500 MHz, 10 mM Na\textsubscript{2}B\textsubscript{4}O\textsubscript{7} buffer/D\textsubscript{2}O). “∗” and “∗∗” indicate the OA encapsulated trans-4-Me-stilbene and cis-4-Me-stilbene proton peaks. ”●” represents the residual solvent peak of water.
Figure 5.21. Triplet sensitized isomerization of \( \text{trans-4-Me-stilbene@}(\text{OA})_2 \) in the presence of 4,4’-DMBdiCOOH monitored by \(^1\text{H NMR (500 MHz, 10 mM Na}_2\text{B}_4\text{O}_7 \) buffer/D\(_2\text{O}) \). “\*” and “\*” indicate the OA encapsulated \( \text{trans-4-Me-stilbene} \) and \( \text{cis-4-Me-stilbene} \) proton peaks. "●" represents the residual solvent peak of water.
Figure 5.22. Triplet sensitized isomerization of \textit{trans}-4-Me-stilbene@(OA)$_2$ in the presence of BPA salt monitored by $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O). “•” and “*” indicate the OA encapsulated \textit{trans}-4-Me-stilbene and \textit{cis}-4-Me-stilbene proton peaks. "•" represents the residual solvent peak of water.
Figure 5.23. Triplet sensitized isomerization of \textit{cis}-4-Me-stilbene@(OA)$_2$ in the presence of 9FCOOH monitored by $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O). “∗” and “∗∗” indicate the OA encapsulated \textit{trans}-4-Me-stilbene and \textit{cis}-4-Me-stilbene proton peaks. "●" represents the residual solvent peak of water.
Figure 5.24. Triplet sensitized isomerization of cis-4-Me-stilbene@(OA)$_2$ in the presence of 4,4’-DMBdiCOOH monitored by $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O). “∗” and “∗∗” indicate the OA encapsulated trans-4-Me-stilbene and cis-4-Me-stilbene proton peaks. “●” represents the residual solvent peak of water.
Figure 5.25. Triplet sensitized isomerization of *cis*-4-Me-stilbene@((OA)$_2$) in the presence of BPA salt monitored by $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O). ‘*’ and ‘**’ indicate the OA encapsulated *trans*-4-Me-stilbene and *cis*-4-Me-stilbene proton peaks. ‘●’ represents the residual solvent peak of water.
Figure 5.26. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O) spectra showing the resistance of trans-4,4’-DiMestilbene@OA$_2$ towards isomerization in the presence of 9FCOOH. “∗” indicates the OA encapsulated trans-4,4’-DiMestilbene proton peaks. "●" represents the residual solvent peak of water.
Figure 5.27. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O) spectra showing the resistance of $trans$-$4,4'$-DiMestilbene@(OA)$_2$ towards isomerization in the presence of $4,4'$-DMBdiCOOH. “∗” indicates the OA encapsulated $trans$-$4,4'$-DiMestilbene proton peaks. "●" represents the residual solvent peak of water.
Figure 5.28. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O) spectra showing the resistance of trans-4,4'-DiMestilbene@(OA)$_2$ towards isomerization in the presence of BPA salt. "∗" indicates the OA encapsulated trans-4,4'-DiMestilbene proton peaks. "●" represents the residual solvent peak of water.
Figure 5.29. Triplet sensitized isomerization of *cis*-4,4'-DiMestilbene@(OA)$_2$ in the presence of 9FCOOH monitored by $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O). “∗” and “∗∗” indicate the OA encapsulated *trans*-4,4'-DiMestilbene and *cis*-4,4’-DiMestilbene proton peaks. "●" represents the residual solvent peak of water.
Figure 5.30. Triplet sensitized isomerization of \textit{cis}-4,4'-DiMestilbene@OA\textsubscript{2} in the presence of 4,4'-DMBdiCOOH monitored by \textsuperscript{1}H NMR (500 MHz, 10 mM Na\textsubscript{2}B\textsubscript{4}O\textsubscript{7} buffer/D\textsubscript{2}O). "\textdegree{}" and "\textdegree{}" indicate the OA encapsulated \textit{trans}-4,4'-DiMestilbene and \textit{cis}-4,4'-DiMestilbene proton peaks. "●" represents the residual solvent peak of water.
Figure 5.31. Triplet sensitized isomerization of cis-4,4′-DiMestilbene@(OA)$_2$ in the presence of BPA salt monitored by $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O). “*” and “∗” indicate the OA encapsulated trans-4,4′-DiMestilbene and cis-4,4′-DiMestilbene proton peaks. "●" represents the residual solvent peak of water.
Table 5.1. Percentage distribution of isomers at pss for triplet sensitized isomerization of various trans-stilbene@((OA)₂ (analyzed by GC).

<table>
<thead>
<tr>
<th>trans-4-Me-stilbene</th>
<th>sensitizer</th>
<th>% cis-product</th>
<th>% trans-product</th>
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<tbody>
<tr>
<td></td>
<td>9FCOOH</td>
<td>74</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>BPA salt</td>
<td>74</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>4,4’-DMBdiCOOH</td>
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<td>24</td>
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<tr>
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<td>10</td>
</tr>
<tr>
<td></td>
<td>BPA salt</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>4,4’-DMBdiCOOH</td>
<td>92</td>
<td>8</td>
</tr>
<tr>
<td>trans-4-Pr-stilbene</td>
<td>9FCOOH</td>
<td>87</td>
<td>13</td>
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<td>BPA salt</td>
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</tr>
<tr>
<td></td>
<td>4,4’-DMBdiCOOH</td>
<td>76</td>
<td>24</td>
</tr>
<tr>
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<td>-</td>
<td>100</td>
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<td>BPA salt</td>
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</tr>
<tr>
<td></td>
<td>4,4’-DMBdiCOOH</td>
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</tr>
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Table 5.2. Percentage distribution of isomers at pss for triplet sensitized isomerization of various cis-stilbene@(OA)$_2$ (analyzed by GC).

<table>
<thead>
<tr>
<th>Isomer</th>
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<th>% cis-product</th>
<th>% trans-product</th>
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<td>cis-4-Me-stilbene</td>
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<td>20</td>
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<tr>
<td></td>
<td>BPA salt</td>
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<td>35</td>
</tr>
<tr>
<td></td>
<td>4,4’-DMBdiCOOH</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
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<tr>
<td></td>
<td>4,4’-DMBdiCOOH</td>
<td>97</td>
<td>3</td>
</tr>
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<td>9FCOOH</td>
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<tr>
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<td></td>
<td>4,4’-DMBdiCOOH</td>
<td>17</td>
<td>83</td>
</tr>
</tbody>
</table>
5.3. Discussion.

Results presented above unequivocally established that triplet sensitization of stilbenes encapsulated within OA capsule could be achieved with the help of sensitizers present in aqueous solution. Since none of the sensitizers showed phosphorescence in aqueous solution at room temperature, the rate constants for energy transfer from sensitizers present in solution to stilbenes within OA capsule could not be measured. However, based on product studies we conclude that triplet-triplet energy transfer (TT-ET) across capsular wall has occurred. Similar TT-ET between Cram’s hemicarcerand encapsulated acetophenone and 1,3-pentadiene in solution is known. In Cram’s hemicarcerand system the reactant olefin is free in solution and the cage has no effect on the photochemical behavior of the diene. In the current study, the OA capsular assembly where the olefin is confined (and the sensitizer is free in solution) allows for capitalizing the influence of confinement on the triplet chemistry of an entrapped olefin.

In spite of the fact that we could not measure the rate constant for TT-ET for the current acceptor@OA₂-donor pairs, through a complimentary set of experiments by quenching the phosphorescence of 4,4′-dimethylbenzil@(OA)₂ using water soluble olefins, we previously reported the rate constants for TT-ET for cationic methyl stilbazolium salt (3.1 x 10⁹ M⁻¹ s⁻¹) to be an order of magnitude higher than for neutral olefins (stilbazole = 5.7 x 10⁸ M⁻¹ s⁻¹ and bispyridylethylene = 6.8 x 10⁸ M⁻¹ s⁻¹). The difference between cationic and neutral olefins was attributed to Coulombic attraction between cationic stilbazolium and anionic OA. It is important to note that the time constants for TT-ET are smaller by at least two orders of magnitude (ns range) compared to single electron transfer (ps range) across the molecular wall of OA capsule reported
This is attributable to the fact that the triplet excitation transfer is mediated by a two-electron exchange interaction between the localized orbitals of the donor and the acceptor as opposed to single-electron exchange interaction in the case of single electron-transfer. Clearly, the molecular walls of OA did not prevent TT-ET in sensitizer@OA-free reactant (previous study) and reactant@(OA)$_2$-free sensitizer (current study) systems. Although Dexter type triplet-triplet energy transfer (TT-ET) generally is believed to involve collision between the donor and the acceptor molecules, in fact the rate constant for transfer is dependent on $e^{-R}$. It is known that the TT-ET can occur even when the donor and acceptor molecules are separated by 15 Å. Examples of TT-ET in glassy matrix as well as in systems where the donor and acceptor are separated by covalent bonds are known. In the current study, of the three sensitizers the BPA salt is positively charged and is expected to be closer to the walls of the capsule. In this case rate constant is expected to be similar to 4,4’-dimethylbenzil@(OA)$_2$-stilbazole system. The other two sensitizers being negatively charged they are unlikely to get closer to the negatively charged OA capsule. The fact that sensitization still occurred is surprising. Most likely their longer triplet lifetime allowed for partial capsule opening favoring a better overlap between the donor and acceptor. The pss cis:trans ratios are similar to the sensitizer BPA salt suggests that the OA capsule controls the isomerization process.

The technique of sensitizing an entrapped molecule has allowed us to explore the usefulness of manipulating the isomerization behavior of triplet stilbenes within a capsule. Interestingly, sensitization of all the above stilbenes in benzene solution independent of the alkyl substituent gave a pss containing ~20% trans- and ~80% cis-isomers. However, within OA capsule 4-Me-stilbene upon triplet sensitization with all
three sensitizers gave a pss consisting of 26% *trans* and 74% *cis* closely similar to that in benzene. In this case OA capsule did not have much influence on the isomer composition at the pss. On the other hand, 4-Et-stilbene and 4-Pr-stilbene under similar conditions gave essentially the *cis*-isomer at the pss, different from that in benzene. The above pss isomer compositions in 4-Me-stilbene, 4-Et-stilbene and 4-Pr-stilbene appear to be related to the binding ability of the two isomers to OA capsule. Preference for *cis*-isomer within OA in the case of 4-Et-stilbene and 4-Pr-stilbene is consistent with the results of competition experiments presented in our earlier results where the *cis*-isomer completely displaced the trans isomer from the OA capsule. The model that we visualize for the above selective isomerization is as follows: While the triplet energy might be transferred to both *cis*- and *trans*- isomers with equal efficiency, the decay rate constants from the twisted olefin triplet within the capsule would be controlled by the binding properties of the two isomers to the capsule. The isomer that is held strongly would resist isomerization to the other isomer which has less binding affinity to the cavity. The fact that the *cis*-isomer of 4-Et-stilbene and 4-Pr-stilbene were able to displace the corresponding *trans*-isomer suggested that the twisted triplet preferred to decay to the *cis* rather than to the *trans*. 4-Me-stilbene whose *cis*- and *trans*-isomers displayed equal preference to OA, as expected, exhibited a similar behavior in solution and within capsule. The fact that the pss composition is independent of the sensitizer suggests that the cavity control plays a major role in the isomerization process.
5.4. Conclusion.

We have established the occurrence of triplet-triplet energy transfer between an encapsulated acceptor and a free donor. One could think of this phenomenon to be similar to energy transfer between a donor and acceptor separated by covalent linkers or solvent molecules. We have previously reported that through femto second (fs) singlet-singlet energy transfer studies the distance ($R_{DA}$) between an encapsulated donor (coumarins) and free acceptor (rhodamin-6G) separated by OA was determined to be $13\pm1$ Å. The distance between donor and acceptor in the current examples such as stilbenes@$(OA)_2$ and 9FCOOH is not likely to be more than the 10Å. In this distance range occurrence of TT-ET is not totally unexpected as long as one thinks of the capsular wall as a solvent molecule that separates the donor and acceptor. The other possibility could be the partial opening of capsule during the TT-ET process which is not studied in detail here.
5.5. Experimental Section.

Materials and Methods: 9-fluorenecarboxylic acid (9FCOOH) (Sigma-Aldrich) was used as received. Host OA, stilbene derivatives and sensitizers (BPA salt and 4,4-DMBdiCOOH) were synthesized by following literature procedure.

General protocol for sample preparation for NMR characterization and sensitization studies.

600 μL of stock solution of host (1 mM OA in 10 mM Na₂B₄O₇) was added to NMR tubes separately. To these tubes, 5 μL of a 60 mM solution of the stilbene derivatives in DMSO-d₆ were added. The complex formation was achieved by shaking the NMR tube for 5 min. The complex formation was confirmed by recording a ¹H NMR (Bruker 500 MHz NMR spectrometer at 25 °C). Each solution were added 5 μL of a 60 mM solution of the sensitizers and recorded a ¹H NMR. The solutions were purged with N₂ for 15 min and irradiated with medium pressure mercury lamp (>330 nm) for 2 days. Progress of the isomerization was followed by recording ¹H NMR spectra. When the solution reached photostationary state (pss) products were extracted with chloroform, dried over anhydrous Na₂SO₄, concentrated and analyzed by GC (HP-5890 series II gas chromatograph fitted with an HP-1 capillary column.)
Chapter 6

Study of Light Induced Controlled Release of Caged Cargo from Octa Acid Capsule

Photoremovable protecting groups (PPGs) are protecting groups that are covalently bonded to the intended cargo to be released, upon irradiation with light. These PPGs provide spatial and temporal control over the release of various chemical or biological agents like acids, bases, ions, peptides, neurotransmitters, cell signaling agents, etc. PPGs are also called photoreleasable, photocleavable or photoactivatable protecting groups. The photochemical deprotection reaction was first reported by Baltrop et al. in the year 1962, where they photolytically deprotected N-benzyloxy carbonyl glycine to release glycine (Scheme 6.1). Ever since their discovery, there has been an immense research activity in the development and application of PPGs by various groups. Engels and Schlaeger, and Kaplan and coworkers were the first to succeed in the application of PPGs in biological systems, where they used the photoremovable protecting groups to release cyclic adenosine monophosphate (cAMP) and adenosine triphosphate, respectively.

![Scheme 6.1. Photochemical deprotection of glycine.](image)

Some of the basic criteria put forth by earlier researchers to design good PPGs are as follows.

(i) In general PPGs should have strong absorption at wavelength >300 nm, and the photoreaction should be clean and occur with high quantum yield.
(ii) The departure of the substrate from the protecting group should be a primary photochemical process.

(iii) PPGs should be pure and stable in the media prior to and during the photolysis.

(iv) They should be soluble in the targeted media and show affinity to specific target components.

(v) The photochemical byproducts accompanying the release bioactive reagents should ideally be transparent at the irradiation wavelength to avoid competitive absorption of the excitation wavelengths. Moreover, they should be biocompatible.

Various chromophores have been exploited as PPGs in the last few decades and every PPGs have their own advantages and disadvantages. For example, nitrobenzyl and nitrophenethyl were one of the most commonly used PPGs and the photolysis of these compounds resulted in potentially toxic and strongly absorbing byproducts such as nitrosobenzaldehyde. There are various important PPGs reported in the literature. Among these PPGs, the $p$-substituted phenacyl esters seems to be a better system to encapsulate within OA capsule and study the light triggered capsular disassembly, provided the acid part of the ester is hydrophobic and has the appropriate size to be include in the OA cavity before photolysis.

6.2. Photochemistry of $p$-Methoxyphenacyl Esters Encapsulated Within Octa Acid.

In the year 1973, Sheehan and Umezawa established the $p$-methoxyphenacyl group as a photo removable protecting group to release various amino acids and peptides.\textsuperscript{221} The $p$-methoxyphenacyl group gets reduced to $p$-methoxyacetophenone by undergoing a $\beta$-cleavage at the C-O bond, and the resulting radical abstracts a proton
from the medium to give the product. Givens and coworkers later reported that the photolysis of \( p \)-methoxyphenacyl phosphate esters in methanol or tert-butanol proceeds via a spirodiketone intermediate by photo-Favorskii rearrangement mechanism to obtain \( p \)-methoxyphenylacetic acid as the major product. Since OA inner cavity is as hydrophobic as benzene, the most likely product from the photolysis of OA encapsulated \( p \)-methoxyphenacyl esters should be the \( p \)-methoxyacetophenone. A distinct feature of the OA capsuleplex is its dynamic character that assembles and disassembles in the time scale of few seconds. When pyrene is encapsulated, the capsuleplex disassembles in 2.7 s, and partially opens in the microsecond time scale,\(^{58}\) This dynamic nature of OA capsuleplexes are thus suited to store and release molecules of interest. With this notion, we had chosen three \( p \)-methoxyphenacyl esters (6.1-6.3) for our studies, shown in Scheme 6.2.

\[ \text{Scheme 6.2. Structures of OA (host) and } p\text{-methoxyphenacyl esters (6.1-6.3).} \]
6.2.1. \textsuperscript{1}H NMR Analysis of \textit{p}-Methoxyphenacyl Esters and Octa Acid Complexes.

The nature of the host-guest (H-G) complex between \textit{p}-methoxyphenacyl esters and octa acid were inferred from the \textsuperscript{1}H NMR titration spectra and PGSE experiments. All the three guests form 2:1 (H:G) complex with OA (\textbf{Figure 6.1, 6.2 and 6.3}).

\textbf{Figure 6.1.} \textsuperscript{1}H NMR titration (500 MHz, 10 mM Na\textsubscript{2}B\textsubscript{4}O\textsubscript{7} buffer/D\textsubscript{2}O) spectra of (i) 6.1 in DMSO-\textsubscript{d}\textsubscript{6}; (ii) only OA [OA] = 1 mM in 10 mM Na\textsubscript{2}B\textsubscript{4}O\textsubscript{7} buffer/D\textsubscript{2}O (pH = 8.7); (iii) 0.25 mM 6.1 + 1 mM OA in 10 mM Na\textsubscript{2}B\textsubscript{4}O\textsubscript{7} buffer/D\textsubscript{2}O and (iv) 0.5 mM 6.1 + 1 mM OA in 10 mM Na\textsubscript{2}B\textsubscript{4}O\textsubscript{7} buffer/D\textsubscript{2}O. “∗” Indicates the OA incarcerated guest 6.1 aliphatic proton peaks. “●” and “♦” indicate the residual solvent peak of water and DMSO-\textsubscript{d}\textsubscript{6}, respectively.
Figure 6.2. $^1$H NMR titration (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O) spectra of (i) 6.2 in DMSO-d$_6$; (ii) only OA [OA] = 1 mM in 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O (pH = 8.7); (iii) 0.25 mM 6.2 + 1 mM OA in 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O and (iv) 0.5 mM 6.2 + 1 mM OA in 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O. “∗” Indicates the OA incarcerated guest 6.2 aliphatic proton peaks. “●” and “♦” indicate the residual solvent peak of water and DMSO-d$_6$, respectively.
Figure 6.3. $^1$H NMR titration (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O) spectra of (i) 6.3 in DMSO-$d_6$; (ii) only OA [OA] = 1 mM in 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O (pH = 8.7); (iii) 0.25 mM 6.3 + 1 mM OA in 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O and (iv) 0.5 mM 6.3 + 1 mM OA in 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O. “∗” Indicates the OA incarcerated guest 6.3 aliphatic proton peaks. “●” and “♦” indicate the residual solvent peak of water and DMSO-$d_6$, respectively.
Table 6.1. Diffusion constants of various $p$-methoxyphenacyl ester complexes with OA measured from PGSE NMR experiment.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Diffusion constant x ($10^{-10}$ m$^2$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1@OA$_2$</td>
<td>1.31</td>
</tr>
<tr>
<td>6.2@OA$_2$</td>
<td>1.31</td>
</tr>
<tr>
<td>6.3@OA$_2$</td>
<td>1.48</td>
</tr>
<tr>
<td>OA</td>
<td>1.88</td>
</tr>
</tbody>
</table>

$^a$1 mM OA in 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O with host:guest (2:1) at 298 K.

The $^1$H NMR titration spectra of the guests 6.1-6.3 with OA shows the upfield shift of the guest’s aliphatic proton peaks which indicates the complex formation between OA and guest. The 2:1 complex pattern was confirmed from the unsymmetrical splitting of the OA aromatic peaks at 2:1 host-guest concentrations and formation of turbidity upon excess guest addition. Furthermore, the diffusion constant values measured for the complexes (Table 6.1) reflect the 2:1 capsular nature of the complex.
6.2.2. Photochemistry of 6.1-6.3@(OA)$_2$ Complexes.

**Figure 6.4.** Absorption spectra of guests 6.1 - 6.3 and $p$-methoxyacetophenone in hexane and OA in borate buffer.

**Figure 6.5.** $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O, pH = 8.7) spectra of (i) only OA [OA] = 1 mM; (ii) 6.1@OA$_2$ (before irradiation), [6.1] = 0.5 mM; (iii) after irradiation of (ii) ($\lambda \geq 280$ nm) and separately prepared 1-adamantanecarboxylic acid@OA, [OA] = 1 mM and [1-adamantanecarboxylic acid] = 0.5 mM. (“*” and “**” indicate the OA incarcerated guest proton peaks of 6.1 and 1-adamantanecarboxylic acid, respectively. “●” and “♦” represent the residual solvent peaks of water and DMSO-$d_6$, respectively).
Figure 6.6. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O, pH = 8.7) titration spectra of $p$-methoxyacetophenone with OA, [OA] = 1 mM and (ii) [p-methoxyacetophenone] = 0 to 1 mM. ("∗" indicates the OA incarcerated guest proton peaks of $p$-methoxyacetophenone. "●" and "♦" represent the residual solvent peaks of water and DMSO-$d_6$, respectively).

Figure 6.7. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O, pH = 8.7) spectra of (i) only OA, [OA] = 1 mM; (ii) 6.2@(OA)$_2$ (before irradiation), [6.2] = 0.5 mM; (iii) after irradiation of (ii) ($\lambda \geq 280$ nm); $o$-toluic acid + OA, [OA] = 1 mM and [$o$-toluic acid] = 0.5 mM and only $o$-toluic acid. ("∗" and "∗" indicate the OA incarcerated guest proton peaks of 6.2 and free $o$-toluic acid, respectively. "●" represents the residual solvent peaks of water.
Figure 6.8. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O, pH = 8.7) spectra of (i) only OA, [OA] = 1 mM; (ii) 6.3@OA$_2$ (before irradiation), [6.3] = 0.5 mM; (iii) after irradiation of (ii) ($\lambda \geq 280$ nm); 3,3-dimethyacrylic acid + OA, [OA] = 1 mM and [3,3-dimethyacrylic acid] = 0.5 mM and only 3,3-dimethyacrylic acid. (“#” and “∗” indicate the OA incarcerated guest proton peaks of 6.3 and free 3,3-dimethyacrylic acid, respectively. “●” represents the residual solvent peaks of water.

The 2:1 (H:G) complexes of 6.1-6.3 with OA were taken in Pyrex NMR tube and irradiated under 450 W medium pressure mercury vapor lamp. The reaction progress of all the three complex solutions was monitored by checking their $^1$H NMR spectra at different time intervals. The samples were irradiated until the starting guest molecules were completely reacted (30 min, 1 h and 8 h for 6.1, 6.2 and 6.3 respectively). In the case of 6.1@OA$_2$, comparison of $^1$H NMR spectrum of irradiated sample (Figure
6.5(iii)) and the NMR spectrum of samples that are separately prepared by adding OA and 1-adamantanecarboxylic acid (Figure 6.5(iv)) confirm that the released acid forms 1:1 cavitandplex. The second product \(p\)-methoxyacetophenone formed after photolysis wasn’t very clearly identified in the NMR either as a complex with OA or as a free species in solution but it does form complex with OA when independently added to OA (Figure 6.6). In this situation the products were extracted from the irradiated sample using CHCl\(_3\) and analyzed in GC and GC-MS, which clearly confirms it and also the ratio of products. Two other minor products formed are (i) radical recombined product and (ii) \(p\)-methoxyphenacyl appended OA (Figure 6.9). The mechanism of the formation of radical recombined product is fairly straightforward as the 1-adamantanecarboxylate radical formed would have lost a carbon dioxide molecule to obtain 1-admantyl radical that further reacts with the \(p\)-methoxyphenacyl radical to give the product. The formation of \(p\)-methoxyphenacyl appended OA can be most likely via the homolytic \(\beta\)-cleavage process followed by acyloxy radical abstracting the hydrogen (Hg) from the host OA and the cage partner \(p\)-methoxyphenacyl radical coupling to the radical site resulting from the hydrogen abstraction process. Since it has been reported that OA is a good hydrogen donor,\textsuperscript{77} we cannot rule out the possibility of hydrogen abstraction by triplet ketone followed by homolytic cleavage of the ester group to give the enol of the acetophenone. Further work is needed to completely understand the mechanism.

The ‘supramolecular photorelease’ technique was well observed in the cases of 6.2\textsubscript{2}@(OA)\(_2\) and 6.3\textsubscript{2}@(OA)\(_2\). Upon irradiation of these samples, the guest molecules did undergo \(\beta\)-cleavage to give \(p\)-methoxyacetophenone and their corresponding acid but
unlike the previous case the acids produced were released from the capsule to the aqueous environment. This phenomenon was well illustrated by comparing the NMR spectra of 6.2@(OA)₂ and 6.3@(OA)₂ after irradiation (Figure 6.7(iii) and Figure 6.8(iii), respectively) to the independently prepared samples of their corresponding acids with and without OA (Figure 6.7(iv), (v), and Figure 6.8(iv), (v), respectively). To identify the product nature and distribution, the irradiated samples were carefully separated between CHCl₃ to extract the products. The extracted solutions were injected in GC and GC-MS. The product distributions are shown in figure. The p-methoxyphenacyl appended OA product was identified by ESI-MS and LC-MS in collaboration with Dr. Jose P. Da Silva from Universidade do Algarve, Portugal. This product was readily seen under positive or negative polarity (Figure 6.10), which showed the first peak of the isotope series at m/z 1877.4 and 1875.4, respectively. The fragmentation behavior was similar to the one observed for OA, while the isotope pattern simulation indicates a singly charged ion with molecular formula C₁₀₅H₇₃O₃₄ under positive polarity. On the basis of the m/z values, fragmentation behavior, and isotope distributions, we assigned this product to a p-methoxyphenacyl-OA adduct. Although ESI-MS confirmed the formation of an adduct, the ¹H NMR spectra were not clean and did not permit identification of the exact structure of the adduct. Based on the abstractable hydrogen present in the interior of OA (Hg, Scheme 6.2), we tentatively assign the structure as shown in Figure 6.9.
Figure 6.9. Product distribution upon photolysis of 6.1 - 6.3@(OA)$_2$.

Figure 6.10. ESI-MS spectra of OA-adduct obtained after photo-transformation of 6.1@(OA)$_2$ (i) in the positive polarity — experimental; — simulation, molecular formula C$_{105}$H$_{73}$O$_{34}$+ (The inset shows the experimental mass spectra for OA adduct obtained after photo-transformation of 6.1-6.3@(OA)$_2$) and (ii) in the negative polarity — experimental; — simulation, molecular formula C$_{105}$H$_{71}$O$_{34}$-. (The inset shows the experimental mass spectra (negative polarity) for OA adduct obtained after photo-transformation of 6.1-6.3@(OA)$_2$).

The UV absorption spectra of guests 6.1-6.3, p-methoxyacetophenone and OA (Figure 6.5) suggested that under our irradiation conditions both OA and the guests
would be excited. In our earlier studies we have demonstrated that OA is an excellent triplet sensitizer with triplet energy close to 73 kcal mol\(^{-1}\).\(^{223}\) Hence, irrespective of which one absorbs light, we believe only the resulting triplet of the guest would be the species. On the basis of the known characteristics of \(p\)-methoxyacetophenone,\(^ {224,225}\) we expect that within the nonpolar capsule the lowest reactive triplet of \textbf{6.1-6.3} to have the \(\pi\pi^*\) configuration. There were several mechanisms proposed for the photorelease of acids from phenacyl derivatives in organic solvents in the literature which depend on polarity and hydrogen atom and electron-donating ability of the medium.\(^ {187,215,226,227}\) Based on our observations on the products obtained including the minor products isolated from the OA encapsulated \textbf{6.1-6.3} and the lack of formation of \(p\)-methoxyphenylacetic acid, we speculate that the reaction did not proceed via \(p\)-methoxy-assisted Favorskii rearrangement, instead it goes via a radical mechanism as shown in \textbf{Scheme 6.3}. Around 11-14 \% of \(p\)-methoxyphenylacetic acid was observed by Dr. \textbf{Nithyanandan} in our lab upon photolysis of other \(p\)-methoxyphenacyl esters of amino acid encapsulated within OA that are having bigger structures. This indicates that \textbf{6.1-6.3} are the perfect molecules that can be included within OA capsule very tightly, where as the other derivatives, due to their elongated structures they can’t form a tight complex.\(^ {78}\) This enables the guest molecules to be exposed to the aqueous exterior which allows them to proceed via \(p\)-methoxy-assisted Favorskii rearrangement path involving a polar intermediate.
6.3. Photochemistry of \( p \)-Hydroxyphenacyl Esters Encapsulated Within Octa Acid.

In our journey towards exploring the photochemical OA capsular disassembly process, we turned our attention quickly towards one of a previously well studied phototrigger of the phenacyl family, \( p \)-hydroxyphenacyl esters (pHP). Givens et al. first reported the use of pHP as a phototrigger\(^{228}\) to release ATP with an efficiency of 0.37 and claimed it to be a much better PPG when compared to the popularly known desyl group then. The efficacy of the later is very limited because of the poor solubility of its derivatives in aqueous medium and the complication involved in the separation of the diastereomers created by the chiral center present in the desyl group.\(^{229}\) Extensive studies had been done in the last fifteen years on the pHP triggers to understand the photorelease efficiency and mechanism, and also its applications in neurobiology and enzyme catalysis by Givens and coworkers.\(^{230,231}\) Some of the very interesting features about the pHP...
esters are their very clean conversion to \( p \)-hydroxyphenylacetic acid via the photo-Favorskii rearrangement concomitant to the release of acid with only one possible side product, high quantum yields and hydrophilicity of the pH ligand. Another important point to be noted about the pH esters is they exhibit distinct changes in their absorption properties at different pH conditions and also with respect to \( p \)-hydroxyphenylacetic acid. These intriguing properties of the pH esters led us to synthesize three pH derivatives (6.4 - 6.6) to study their photochemistry when encapsulated in OA and efficiently disassemble the capsule to release the acid without much complexity. This section also includes the results on the OA complexation and photochemical studies of pH esters (6.7 - 6.9) and pH ethers (6.10 and 6.11) provides to us by Dr. Givens, University of Kansas.

![Structures of p-hydroxyphenacyl esters (6.4 - 6.9) and ethers (6.10 and 6.11)](image)

**Scheme 6.4.** Structures of \( p \)-hydroxyphenacyl esters (6.4 - 6.9) and ethers (6.10 and 6.11).
6.3.1. $^1$H NMR Analysis of p-Hydroxyphenacyl Esters and Octa Acid Complexes.

The $^1$H NMR titration studies were carried out for all the seven pH-P derivatives. When 0.25 mM of 6.4 was added to a 1 mM OA solution, the aliphatic proton peaks of 6.4 were shifted to the upfield region indicating that 6.4 forms a complex with OA but the uncomplexed OA peak were also noticed when further 0.25 mM of 6.4 was added to the same solution to get the H-G ratio to 2:1 where the uncomplexed OA aromatic peaks disappeared. Addition of more 6.4 resulted in the appearance of uncomplexed guest aliphatic proton peaks in the downfield region indicating that 6.4 forms a 2:1 complex with OA (Figure 6.11). In the case of 6.5, incremental addition of 6.5 to OA solution resulted in the formation of 2:1 and 1:1 complex (Figure 6.12). Further addition of 6.5 turned the solution turbid. The $^1$H NMR titration of 6.6 and OA confirmed that 6.6 forms 2:1 complex with OA (Figure 6.13).
**Figure 6.11.** $^1$H NMR (500 MHz) titration spectra of (i) 6.7 in DMSO-$d_6$; (ii) only OA [OA] = 1 mM in 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O (pH = 8.7); (iii) 0.25 mM 6.7 + 1 mM OA in 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O; (iv) 0.5 mM 6.7 + 1 mM OA in 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O and (v) 0.75 mM 6.7 + 1 mM OA in 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O. “∗” Indicates the OA incarcerated guest 6.7 aliphatic proton peaks. “●” and “♦” indicate the residual solvent peak of water and DMSO-$_d_6$, respectively.
Figure 6.12. $^1$H NMR (500 MHz) titration spectra of (i) 6.5 in DMSO-$d_6$; (ii) only OA [OA] = 1 mM in 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O (pH = 8.7); (iii) 0.25 mM 6.5 + 1 mM OA in 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O; (iv) 0.5 mM 6.5 + 1 mM OA in 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O and (v) 0.75 mM 6.5 + 1 mM OA in 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O and (vi) 1 mM 6.5 + 1 mM OA in 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O. “∗” Indicates the OA incarcerated guest 6.5 aliphatic proton peak. “●” and “♦” indicate the residual solvent peak of water and DMSO-$d_6$, respectively.
Figure 6.13. $^1$H NMR (500 MHz) titration spectra of (i) only OA [OA] = 1 mM in 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O (pH = 8.7); (ii) 0.5 mM 6.6 + 1 mM OA in 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O; (iii) 0.75 mM 6.6 + 1 mM OA in 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O and (iv) 1 mM 6.6 + 1 mM OA in 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O. "∗" Indicates the OA incarcerated guest 6.6 aliphatic proton peaks. “●” indicates the residual solvent peak of water.
Figure 6.14. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O) titration spectra of 6.7 and OA. "●" and “♦” represent the residual solvent peak for D$_2$O and DMSO-$d_6$ respectively.

The $^1$H NMR spectra recorded after each addition of the 6.7 to 1 mM OA solution indicates that as the concentration of 6.7 increases the peaks corresponding to the OA aromatic protons ‘c’ and ‘d’ get upfield shifted and broadens, whereas the ‘g’ proton shifts to the downfield region and the aromatic proton peak of 6.7 moves upfield. Moreover, the chemical shifts of the aliphatic protons of the alkyl chain didn’t have significant change with respect to the varying concentration of the guest. These observations in Figure 6.14 suggest that probably the phenol part of the guest interacts with the top part of OA host.
Figure 6.15. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O) titration spectra of 6.8 and OA. "●" and "◇" represent the residual solvent peak for D$_2$O and DMSO-$d_6$ respectively.

The guest solution was prepared as such without any purification that had some hydrolyzed products. The $^1$H NMR spectra titration spectra of 6.8 and OA indicates that as the concentration of 6.8 increases the OA aromatic protons ‘d’ gets upfield shifted and ‘g’ gets downfield shifted. These results suggest that the phenol part of the guest could be interacting with the top portal of OA host, whereas the alkyl part holding the quaternary amine stays outside the OA host (Figure 6.15).
Figure 6.16. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O) titration spectra of 6.9 and OA. Symbol "∗" and "●" indicate the uncomplexed guest aliphatic proton peaks and the residual solvent peak for D$_2$O, respectively.

The $^1$H NMR titration spectra of 6.9 and OA clearly shows that the ethyl proton peaks of 6.9 remain unaltered in the presence of OA and only the OA proton peaks ‘c’, ‘d’ and ‘h’ get broadened that suggests that ethyl chains of 6.9 didn’t get included within OA whereas the phenol part interacts with OA (Figure 6.16).
Figure 6.17. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O) titration spectra of 6.10 and OA. Symbol "*$" and "●" indicate the OA incarcerated 6.10 aliphatic proton peaks and the residual solvent peak for D$_2$O, respectively.

The $^1$H NMR spectra recorded for every incremental addition of guest 6.10 to 1 mM OA solution till 0.5 mM display the upfield shifted MeO- proton peak due to the incarceration of 6.10 within OA cavity and also the changes in the aromatic region of OA. The methyl proton peak at -0.7 ppm disappeared upon adding another 0.25 mM 6.10 and further guest addition didn’t change the spectra except increasing the intensity of the aromatic proton peak of the uncomplexed guest at 7.7 pm. These observations indicates that 6.10 forms 2:1 complex with OA (Figure 6.17).
Figure 6.18. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O) titration spectra of 6.11 and OA. Symbol "●" and “♦” represent the residual solvent peak for D$_2$O and DMSO-$d_6$ respectively.

The incremental addition of guest 6.11 to a 1 mM OA solution resulted in the formation of a 2:1 complex. This was confirmed by the complete disappearance of the free OA peak when the H-G ratio was maintained at 2:1 and also there wasn’t any change in the chemical shifts of OA protons when excess guest was added (Figure 6.18), and infact the solution became turbid.
Figure 6.19. 2D-NOESY spectrum (500 MHz, mixing time: 300 ms) of 6.4@(OA)$_2$ ([OA] = 5mM, [6.7] = 2.5 mM) in 50 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O.
Figure 6.20. 2D-NOESY spectrum (500 MHz, mixing time: 300 ms) of 6.5@(OA)$_2$ ([OA] = 5mM, [6.7] = 2.5 mM) in 50 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O.
Figure 6.21. 2D-NOESY spectrum (500 MHz, mixing time: 300 ms) of $6.6@{(OA)}_{2}$ ([OA] = 5mM, [6.7] = 2.5 mM) in 50 mM Na$_{2}$B$_{4}$O$_{7}$ buffer/D$_{2}$O.
6.3.2. Stability of \( p \)-Hydroxyphenacyl Esters in the Presence and Absence of OA.

**Figure 6.22.** Monitoring the stability of 6.4 in 10 mM Na\(_2\)B\(_4\)O\(_7\) buffer/D\(_2\)O, pH = 8.7 in the absence of OA by \(^1\)H NMR (500 MHz) (i) 6.4 ([6.4] = 0.5 mM); (ii) spectra recorded after 24 h (indicating that the guest molecule is stable during the time period of photolysis), (iii) 48 h, and (iv) 96 h. ‘●’ and ‘♦’ indicate the residual solvent peak of water and DMSO-\( d_6 \), respectively.
Figure 6.23. Monitoring the stability of 6.4 in the presence of OA by $^1\text{H}$ NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O, pH = 8.7) (i) only OA [OA] = 1 mM; (ii) 6.4@(OA)$_2$ ([OA] = 1 mM, [6.4] = 0.5 mM); (iii) spectrum recorded after 24 h (indicating that the guest molecule is stable in borate buffer at pH 8.7 during the time period of photolysis); (iv) spectra recorded after 48 h and (v) and 96 h. “•” Indicates the OA incarcerated guest 6.4 aliphatic proton peak. “●” and “♦” indicate the residual solvent peaks of water and DMSO-$d_6$, respectively.
Figure 6.24. Monitoring the stability of 6.5 in 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O, pH = 8.7 in the absence of OA by $^1$H NMR (500 MHz) (i) 6.5 ([6.5] = 0.5 mM); (ii) spectra recorded after 24 h (indicating that the guest molecule is stable during the time period of photolysis), (iii) 48 h, and (iv) 96 h. “●” and “♦” indicate the residual solvent peak of water and DMSO-$d_6$, respectively.
Figure 6.25. Monitoring the stability of 6.5 in the presence of OA in 10 mM Na₂B₄O₇ buffer/D₂O, pH = 8.7 by ¹H NMR (500 MHz) (i) only OA [OA] = 1 mM; (ii) 6.5@(OA)₂ ([OA] = 1 mM, [6.5] = 0.5 mM); (iii) spectrum recorded after 24 h (indicating that the guest molecule is stable during the time period of photolysis); (iv) spectra recorded after 48 h and (v) after 96 h. “∗” Indicates the OA incarcerated guest 6.5 methyl proton peak. “●” indicates the residual solvent peak of water.
Figure 6.26. Monitoring the stability of 6.6 in 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O, pH = 8.7 in the absence of OA by $^1$H NMR (500 MHz), (i) 6.6 ([6.6] = 0.5 mM); (ii) spectra recorded after 24 h (indicating that the guest molecule is stable during the time period of photolysis), (iii) 48 h, and (iv) 96 h “●” and “♦” indicate the residual solvent peak of water and DMSO-$d_6$, respectively.
Figure 6.27. Monitoring the stability of 6.6 in the presence of OA in 10 mM Na₂B₄O₇ buffer/D₂O, pH = 8.7 by ¹H NMR (500 MHz) (i) only OA [OA] = 1 mM; (ii) 6.6@(OA)₂ ([OA] = 1 mM, [6.6] = 0.5 mM); (iii) spectrum recorded after 24 h (indicating that the guest molecule is stable during the time period of photolysis); (iv) spectra recorded after 48 h and (v) 96 h. "∗" Indicates the OA incarcerated guest 6.6 aliphatic proton peak. “●” indicates the residual solvent peak of water.

Comparison of the NMR spectra of guests 6.4 - 6.7 in the presence and absence of OA (Figure 6.22 - 6.27) after different time intervals indicate that the guest molecules are very much stable under basic condition within the time duration of photolysis.
Figure 6.28. Monitoring the stability of 6.7 in 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O, pH = 8.7 in the absence of OA by $^1$H NMR (500 MHz), (i) 6.7 ([6.7] = 0.5 mM); (ii) spectra recorded after 24 h; (iii) 2,4'-dihydroxyacetophenone ([2,4'-dihydroxyacetophenone] = 0.5 mM) and (iv) 4-hydroxyphenylacetic acid ([4-hydroxyphenylacetic acid] = 0.5 mM). “●” and “♦” indicate the residual solvent peak of water and DMSO-d$_6$, respectively.

Figure 6.29. Monitoring the stability of 6.7 in D$_2$O by $^1$H NMR (500 MHz), (i) 6.7 ([6.7] = 0.5 mM); (ii) spectrum recorded after 24 h and (iii) spectrum recorded after 96 h. “●” indicates the residual solvent peak of water.
Figure 6.30. Monitoring the stability of 6.7 in the presence of OA in 10 mM Na₂B₄O₇ buffer/D₂O, pH = 8.7 by ¹H NMR (500 MHz) (i) only OA [OA] = 1 mM; (ii) 6.7@OA₂ ([OA] = 1 mM, [6.7] = 0.5 mM); (iii) spectrum recorded after 24 h and (iv) 2,4’-dihydroxyacetophenone@OA₂ ([OA] = 1 mM, [2,4’-dihydroxyacetophenone] = 0.5 mM). “●” indicates the residual solvent peak of water.

Guest 6.7 did undergo hydrolysis in the presence and absence of OA (Figure 6.28 and 6.30, respectively) in basic medium but was stable under neutral condition (Figure 6.29). This is because the alkyl chain having the cationic tail cannot form a complex with OA whereas the phenolate part interacts with the OA inner cavity to form a 1:1 complex, this exposes the β-bond of the 6.7 to the basic medium where it undergoes hydrolysis easily.
Figure 6.31. Monitoring the stability of 6.8 in 10 mM Na₂B₄O₇ buffer/D₂O, pH = 8.7 in the absence of OA by ¹H NMR (500 MHz), (i) 6.8 ([6.8] = 0.5 mM) and (ii) spectra recorded after 24 h. “●” and “♦” indicate the residual solvent peak of water and DMSO-d₆, respectively.

Figure 6.32. Monitoring the stability of 6.8 in D₂O in the absence of OA by ¹H NMR (500 MHz), (i) 6.8 ([6.8] = 0.5 mM); (ii) spectra recorded after 24 h and (iii) spectra recorded after 96 h. “●” and “♦” indicate the residual solvent peak of water and DMSO-d₆, respectively.
Figure 6.33. Monitoring the stability of 6.8 in the presence of OA in 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O, pH = 8.7 by $^1$H NMR (500 MHz) (i) only OA [OA] = 1 mM; (ii) 6.8@(OA)$_2$ ([OA] = 1 mM, [6.8] = 0.5 mM) and (iii) spectrum recorded after 24 h. “●” indicates the residual solvent peak of water.

Guest 6.8 also was hydrolyzed in the presence and absence of OA (Figure 6.31 and 6.33, respectively) in basic medium but was stable under neutral condition (Figure 6.32). Similar to the previous guest due to the presence of the alkyl chain with a cationic tail 6.8 only forms 1:1 complex with OA which in turn exposes the β-bond of 6.8 to the basic medium for the hydrolysis reaction.
6.3.3. Photochemistry of $p$-Hydroxyphenacyl esters@(OA)$_2$ Complexes.

**Figure 6.34.** Absorption spectra of guests 6.4-6.6 in methanol ([6.4] = [6.5] = [6.6] = 50 µM).

**Figure 6.35.** Absorption spectra of 6.4 ([6.4] = 10 µM) (a) in 70% aqueous HClO$_4$ (pH < 2); (b) in water (pH = 7); (c) in 10 mM Na$_2$B$_4$O$_7$ buffer/H$_2$O (pH = 8.7); (d) 6.4@(OA)$_2$ in 10 mM Na$_2$B$_4$O$_7$ buffer/H$_2$O ([6.4] = 10 µM and [OA] = 20 µM (pH = 8.7)) and (e) transmission spectrum of Pyrex filter. Inset: absorption spectrum of OA ([OA] = 50 µM) in 10 mM Na$_2$B$_4$O$_7$ buffer/H$_2$O (pH = 8.7).
Figure 6.36. Absorption spectra (10 mM Na$_2$B$_4$O$_7$ buffer/H$_2$O, pH = 8.7) of (i) only 6.5 ([6.5] = 5 µM); (ii) 6.5@(OA)$_2$ ([6.5] = 2.5 µM) (iii) only 6.6 ([6.6] = 5 µM) and (iv) 6.6@(OA)$_2$ ([6.6] = 2.5 µM)
Figure 6.37. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O, pH = 8.7) spectra of (i) only OA [OA] = 1 mM; (ii) 6.4@(OA)$_2$ (before irradiation); (iii) after 20 min irradiation and (iv) after 40 min irradiation ($\lambda \geq 300$ nm). "■" represent the aliphatic (–CH$_2$–) peak corresponding to 4'-hydroxyphenylacetic acid. "∗" and "∗∗" indicate the OA incarcerated guest aliphatic proton peak of 6.4 and 1-adamantanecarboxylic acid respectively. "●" and "♦" indicate the residual solvent peak of water and DMSO-d$_6$, respectively.
Figure 6.38. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O, pH = 8.7) spectra of (i) only OA [OA] = 1 mM; (ii) 6.4@(OA)$_2$ (before irradiation); (iii) after irradiation of (ii) (λ ≥ 300 nm); (iv) a mixture of 4-hydroxyphenylacetic acid and OA ([4-hydroxyphenylacetic acid] = 0.5 mM and [OA] = 1 mM); (v) a mixture of 4-hydroxyphenylacetic acid, 1-adamantanecarboxylic acid and OA ([4-hydroxyphenylacetic acid] = 0.5 mM, [1-adamantanecarboxylic acid] = 0.5 mM and [OA] = 1 mM) and (vi) only 4-hydroxyphenylacetic acid ([4-hydroxyphenylacetic acid] = 0.5 mM). "■" represents the aliphatic (–CH$_2$–) peak corresponding to 4-hydroxyphenylacetic acid. (“∗” and “∗∗” indicate the OA incarcerated guest proton peaks of 6.4 and 1-adamantanecarboxylic acid, respectively. "●" and "♦" represent the residual solvent peaks of water and DMSO-d$_6$, respectively).
Figure 6.39. LC-Diode Array Detector (LC-DAD) traces at 275 nm of 6.4@(OA)_2 (25 µM) in a 10 mM Na_2B_4O_7 buffer solution (pH = 8.7), before (i) and after (ii) irradiation (30 minutes, xenon lamp, Pyrex filter). (iii) and (iv) are the LC-MS single ion traces obtained at m/z 179 ([1-adamantanecarboxylic acid -H]) and 151 ([2,4’-dihydroxyacetophenone-H] and [4-hydroxyphenylacetic acid-H]). The assignments were made by comparing the retention times, UV-Vis and mass spectral properties of the compounds formed by irradiation with those of authentic samples.
Figure 6.40. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O, pH = 8.7) spectra of (i) 6.4 ([6.4] = 0.5 mM); (ii) after 30 min irradiation of (i); (iii) after 1 h irradiation of (i) (450 W medium pressure mercury vapor lamp with Pyrex filter); (iv) only 4-hydroxyphenylacetic acid ([4-hydroxyphenylacetic acid] = 0.5 mM) and (v) only 2,4’-dihydroxyacetophenone ([2,4’-dihydroxyacetophenone] = 0.5 mM). “*” and “♦” indicate the –CH$_2$– proton peak of 4-hydroxyphenylacetic acid and aliphatic proton peaks of 1-adamantanecarboxylic acid, respectively. “*” indicates the –CH$_2$– proton peak of 2,4’-dihydroxyacetophenone. “●” and “♦” represent the residual solvent peaks of water and DMSO-$d_6$, respectively.
Figure 6.41. LC-MS traces at m/z 151 of 6.4 irradiated for 20 min (25 µM) in 25 % of an aqueous borate buffer solution (10mM) in acetonitrile (i), and in 25 % water in acetonitrile (ii).

Figure 6.42. Product distribution for the time-dependent photolysis of pHp ester 6.4 at λ > 300 nm (xenon lamp, Pyrex filter) as a 2:1 octa acid complex (6.4@(OA)₂, [6.4] = 25 µM) in aqueous borate buffer (10 mM; pH = 8.7) to 1-adamantanecarboxylic acid, p-hydroxyphenylacetic acid and 2,4'-dihydroxyacetophenone.
The UV-Vis spectra recorded for 6.4 at various (<2, 7, and 8.7) pH conditions (Figure 6.35) demonstrates that the pH chromophore is highly pH dependent and also the encapsulated esters exist in their conjugate base form (figure). Since the π,π* transitions of the conjugate bases absorb at 330 nm, a Pyrex filter was employed for the photolysis reaction in order to assure that the absorbing chromophores are exclusively the pH conjugate bases, and not OA. The 2:1 (H:G) complex solutions were irradiated under λ > 300 nm with a 450 W medium pressure lamp through a Pyrex filter. The progresses of the reactions were monitored by 1H NMR. The 1H NMR spectrum recorded for the irradiated solution of 6.4@(OA)2 have the chemical shift values at 0.5, -0.3, -0.45 and -1.1 ppm that are assigned to the 1:1 complex of the conjugate base of 1-adamantanecarboxylic acid in OA and a singlet at 3.3 ppm assigned to the cavitandplex of the chromophore’s rearrangement product, p-hydroxyphenyl acetate in OA (Figure 6.38). Product identifications were confirmed by liquid chromatography coupled to a diode array detector and to a mass spectrometer (LC-DAD-MS) or by GC-MS. Progress of the reaction was followed at 275 nm (DAD) and under single ion monitoring (SIM) in the negative polarity (MS). A minor photosolvolysis product, 2,4′-dihydroxyacetophenone was also detected (< 10%) by LC-MS (Figure 6.41) which is not clearly seen in the NMR spectrum.

Photolysis of 6.4 was also carried out without OA and result obtained was the same which shows that the photochemistry of 6.4 is independent of the presence or absence of OA.
Figure 6.43. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O, pH = 8.7) spectra of (i) only OA [OA] = 1 mM; (ii) 6.4@(OA)$_2$ (before irradiation); (iii) after 30 min irradiation of (ii); (iv) after 50 min irradiation of (ii); and (v) after 1 h 30 min irradiation of (ii) ($\lambda \geq$ 300 nm). ■ represents the aliphatic (–CH$_2$–) peak corresponding to 4-hydroxyphenylacetic acid. * and ** indicate the OA incarcerated guest 6.4 methyl proton peak and methyl proton peak of free 7, respectively. ● represents the residual solvent peak of water.
**Figure 6.44.** $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O, pH = 8.7) spectra of (i) only OA [OA] = 1 mM; (ii) 6.4@(OA)$_2$ (before irradiation); (iii) after irradiation of (ii) ($\lambda \geq 300$ nm); (iv) mixture of 5 and OA ([5] = 0.5 mM and [OA] = 1 mM); (v) mixture of 4-hydroxyphenylacetic acid, 7 and OA ([4-hydroxyphenylacetic acid] = 0.5 mM, [7] = 0.5 mM and [OA] = 1 mM) and (vi) only 7 ([7] = 0.5 mM). "■" represent the aliphatic (–CH$_2$–) peak corresponding to 4-hydroxyphenylacetic acid. “∗” and “∗∗” indicate the OA incarcerated guest 6.5 methyl proton peak and methyl proton peak of free 7, respectively. "●" represents the residual solvent peak of water.
Figure 6.45. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O, pH = 8.7) spectra of (i) 6.5 ([6.5] = 0.5 mM); (ii) after 30 min irradiation of (i); (iii) after 1 h irradiation of (i) (450 W medium pressure mercury vapor lamp with pyrex filter); (iv) only 5 ([5] = 0.5 mM) and (v) only 4 ([4] = 0.5 mM). "*" and "**" indicate the –CH$_2$– proton peak of 5 and –CH$_3$ proton peak of 7, respectively. "***" indicates the –CH$_2$– proton peak of 4. "●" and "◆" represent the residual solvent peaks of water and DMSO-d$_6$, respectively.
Figure 6.46. Reactant disappearance and product formation of 6.5@(OA)₂ (25 µM) in aqueous borate buffer (10 mM; pH = 8.7) upon irradiation (λ > 300 nm; xenon lamp; Pyrex glass filter). The lines are for ease of viewing only.
Figure 6.47. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O, pH = 8.7) spectra of (i) only OA [OA] = 1 mM; (ii) 6.6@OA$_2$ (before irradiation); (iii) after 50 min irradiation of (ii) ($\lambda \geq 300$ nm); (iv) after 1 h 30 min irradiation of (ii) and (v) after 3 h irradiation of (ii). "■" represent the aliphatic (–CH$_2$–) peak corresponding to 5. “∗” and “∗∗” indicate the OA incarcerated guest 6.6 methyl proton peak and free 8 proton peaks, respectively. "●" represents the residual solvent peak of water.
Figure 6.48. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O, pH = 8.7) spectra of (i) only OA [OA] = 1 mM; (ii) 6.6@(OA)$_2$ (before irradiation); (iii) after irradiation of (ii) ($\lambda \geq 300$ nm); (iv) mixture of 5 and OA ([5] = 0.5 mM and [OA] = 1 mM); (v) mixture of 5, 8 and OA ([5] = 0.5 mM, [8] = 0.5 mM and [OA] = 1 mM) and (vi) only 8 ([8] = 0.5 mM). "■" represent the aliphatic (–CH$_2$–) peak corresponding to 5. "∗" and "∗∗" indicate the OA incarcerated guest 6.6 methyl proton peak and free 8 proton peaks, respectively. "●" represents the residual solvent peak of water. [5] = [8] = [6.6] = 0.5 mM.
Figure 6.49. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O, pH = 8.7) spectra of (i) 6.6 ([6.6] = 0.5 mM); (ii) after 30 min irradiation of (i); (iii) after 1 h irradiation of (i) (450 W medium pressure mercury vapor lamp with pyrex filter); (iv) only 5 ([5] = 0.5 mM) and (v) only 2,4'-dihydroxyacetophenone ([2,4'-dihydroxyacetophenone] = 0.5 mM). "*" and "**" indicate the –CH$_2$– proton peak of 5 and aliphatic proton peaks of 8, respectively. "***" indicates the –CH$_2$– proton peak of 2,4'-dihydroxyacetophenone. "●" and "♦" represent the residual solvent peaks of water and DMSO-$d_6$, respectively.
**Figure 6.50.** Reactant loss and product formation of \( \text{6.6(OA)}_2 \) (25 µM) in aqueous borate buffer solution (10 mM; pH = 8.7) upon irradiation (\( \lambda > 300 \text{ nm; xenon lamp; Pyrex glass filter} \)). The lines are for easier observation.

**Table 6.2.** Comparisons of photolysis conversions and yields based on consumed pHP ester for 6.4, 6.5 and 6.6 with or without OA encapsulation in aqueous borate buffer at pH 8.7. Error limits are ± 10%.

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<th>Ester, with and without OA</th>
<th>Conversion</th>
<th>Released Acid&lt;sup&gt;a&lt;/sup&gt;</th>
<th>6.4, OA, aq&lt;sup&gt;b&lt;/sup&gt;</th>
<th>6.5, OA, aq&lt;sup&gt;c&lt;/sup&gt;</th>
<th>6.6, OA, aq&lt;sup&gt;b&lt;/sup&gt;</th>
<th>w/o OA, aq&lt;sup&gt;c&lt;/sup&gt;</th>
<th>w/o OA, aq&lt;sup&gt;c&lt;/sup&gt;</th>
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<sup>a</sup>1-adamantanecarboxylic acid, o-toluic acid and 3,3-dimethylacrylic acid from pHP esters 6.4, 6.5 and 6.6, respectively. <sup>b</sup> after a 30 min irradiation of the OA <sup>c</sup> after 50 min irradiation.
Irradiations of the OA encapsulated conjugate bases of the pHP esters 6.5 and 6.6 in aqueous borate buffer gave the expected carboxylic acid products o-toluic acid and 3,3-dimethylacrylic acid, respectively (Figure 6.44 and 6.48). The photo-Favorskii rearranged product 4-hydroxyphenylacetic acid and the minor photosolvolysis product 2,4'-dihydroxyacetophenone were also detected by LC. The interesting result obtained upon the photolysis of both 6.5@(OA)₂ and 6.6@(OA)₂ was that as the capsule broke the acid obtained was released to the aqueous medium. Furthermore, the efficiency of the reaction was much better and also there wasn’t any p-hydroxyphenacyl-OA appended product observed in contrast to the pMP esters, indicating the superiority of the pHP esters as phototrigger over its pMP counterpart. Table 6.2 displays the product distributions for the photolysis of 6.4 - 6.6 in the presence and absence of OA at two difference time intervals and 100 % conversion was observed after 50 min irradiation. The photorelease reactivities of the three esters appear to be essentially independent of both the nature of the leaving carboxylate moiety and the presence of OA as shown by the reaction profiles.

Scheme 6.5. Suggested mechanism for the photorelease of carboxylic acids from their pHP esters 6.4 – 6.6 within OA capsules.
Thus, the absence of radical attack on the OA by pHP ester photolysis as evidenced by the lack of OA adducts and the high yield of $p$-hydroxyphenyl acetic acid rearrangement product (>90%), suggests that the photorelease mechanism for encapsulated pHP esters differs from that of the pMP esters. In isotropic solutions, the $p$-hydroxyphenacyl esters proceed through the photo-Favorskii rearrangement from the pHP ester triplet forming a short-lived (0.5 ns) triplet biradical (Scheme 6.5). While we lack sufficient evidence to unequivocally assign a mechanistic pathway, the fact that release of acids from pHP esters 6.4 - 6.6 show no evidence of radical attack on OA and produce no decarboxylation products from the carboxylic acids released, two reactions that are observed for $p$-methoxyphenacyl cage reactions, it is reasonable to suggest that the encapsulated $p$-hydroxyphenacyl esters proceed exclusively via heterolytic cleavage to a short-lived biradical that proceeds through the photo-Favorskii mechanism.

\[ \text{Scheme 6.6. Suggested mechanism for the photolysis of pHP esters in methanol.} \]

The photochemistry of 6.4 - 6.6 in methanol was carried out in quartz tube. The major products obtained were methyl-$p$-hydroxyphenylacetate and their corresponding acids. The additional product obtained was $p$-hydroxyanisole, which is in agreement with the previous reported results. The mechanism for the formation of $p$-hydroxyanisole
involves the Favorskii intermediate which subsequently releases a CO molecule to obtain an alkene intermediate which further reacts with methanol (Scheme 6.6).

**Figure 6.51.** Product distribution upon photolysis of 6.4 - 6.6 in methanol (analyzed by GC and GC-MS.)
Figure 6.52. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O) titration spectra of 2,4'-dihydroxyacetophenone and OA; ([OA] = 1 mM and [2,4'-dihydroxyacetophenone] = 0 to 2 mM). "*" indicate the –CH$_2$– proton peak of 2,4'-dihydroxyacetophenone. "●" and "♦" represent the residual solvent peak for D$_2$O and DMSO-$d_6$ respectively.
Figure 6.53. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O) titration spectra of 4-hydroxyphenylacetic acid and OA ([OA] = 1 mM and [4-hydroxyphenylacetic acid] = 0 to 2 mM). “*” indicate the –CH$_2$– proton peak of 4-hydroxyphenylacetic acid. “•” and “♦” represent the residual solvent peak for D$_2$O and DMSO-d$_6$ respectively.
6.3.4 Photochemistry of \(p\)-Hydroxyphenacyl Ethers Encapsulated Within Octa Acid.

**Figure 6.54.** Absorption spectra of guests (in the presence and absence of OA) in buffer. \([6.10] = [6.11] = 50 \mu M\) and \([OA] = 100 \mu M\).

**Figure 6.55.** \(^1H\) NMR (500 MHz, 10 mM Na\(_2\)B\(_4\)O\(_7\) buffer/D\(_2\)O) titration spectra of 6.10 and OA (\([OA] = 1 mM\) and \([6.10] = 0\) to \(2 \text{ mM}\)).
Figure 6.56. 2D-NOESY spectrum (500 MHz, mixing time: 300 ms) of 6.10@OA₂ ([OA] = 5 mM, [6.10] = 2.5 mM) in sodium tetraborate (50 mM).
Figure 6.57. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O, pH = 8.7) spectra of 6.14@(OA)$_2$ irradiated at different time intervals. “∗” and “∗” indicate the OA incarcerated guest 6.10 methyl proton peak and 4-hydroxyphenylacetic acid proton peak, respectively. “●” represents the residual solvent peak of water.
**Figure 6.58.** $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O, pH = 8.7) spectra of 6.14@(OA)$_2$ complex (before and after irradiation). “$*$” and “$^*$” indicate the OA incarcerated guest 6.10 methyl proton peak and 4-hydroxyphenylacetic acid proton peak, respectively. "●" represents the residual solvent peak of water.

In the preliminary experiment we investigated the complexation of the guest with host. **Figure 6.58** shows the upfield shifted peak of MeO- at -0.8 ppm for 6.10 when the H:G ratio was 2:1 but the disappearance of the guest peak after increasing its concentration indicates that the excess guests added remain uncomplexed and exchanges with the complexed guest in NMR time scale which in turn suggests that 6.10 forms a 2:1 complex with OA. Irradiation of the 2:1 complex of OA and 6.10 under UV-light (in NMR tube, 450 W medium pressure mercury lamp with pyrex jacket) resulted in the formation of 4-hydroxyphenylacetic acid (major) and 2,4’-dihydroxyacetophenone.
(minor) along with anisole. Though the formation of 2,4’-dihydroxyacetophenone and anisole weren’t very clearly seen in the NMR, they were detected in LC-MS. Photolysis of 6.10 without OA resulted in multiple products that are very complicated to analyze.

![Figure 6.59](image)

**Figure 6.59.** $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O) titration spectra of 6.11 and OA ([OA] = 1 mM and [6.11] = 0 to 2 mM).
The complex formation between 6.11 and OA were confirmed from the change in the aromatic proton region of OA, when guest molecules were added to it (Figure 6.59). Since, the NMR spectra didn’t change when more than 0.5 equivalent guest was added to the OA solution, the complex nature is 2:1 between OA and 6.11. 6.11@(OA)₂ was irradiated under UV-light (in NMR tube, 450 W medium pressure mercury lamp with pyrex jacket) and the reaction progress was monitored by recording its ¹H NMR at different time intervals. A complete change in the peak pattern (mainly aromatic region) of OA indicated the completion of the reaction. The appearance of a peak at 3.3 ppm indicates the formation 4-hydroxyphenylacetic acid Figure 6.60. The formation of 2,4’-dihydroxyacetophenone and p-trifluoromethyl phenol were detected in LC-MS.
6.4. Photochemistry of \( p \)-Methyl and \( p \)-Chlorophenacyl Esters Encapsulated Within Octa Acid.

The \( p \)-methyl and \( p \)-chlorophenacyl esters (6.12 – 6.17) form 2:1 complex with octa acid (Figure 6.65(ii), 6.66(ii), 6.67(ii), 6.69(ii), 6.70(ii) and 6.71(ii)) and addition of excess guest solutions made the sample solution turbid. Though there is only very little literature reports on the photochemistry of \( p \)-methyl and \( p \)-chlorophenacyl compounds available that confirms that the nature of their photoproduct depends on the polarity of the medium. In high polar solvents these compounds undergo the photo-Favorskii rearrangement to give their corresponding phenylacetic acid product, whereas in the non-polar solvents they produce theirs corresponding acetophenone. Compounds 6.12-6.17 have a very weak absorption between 270 nm to 290 nm in methanol (Figure 6.61 and 6.62) and also 6.12@(OA)\(_2\) and 6.15@(OA)\(_2\) do not have a significant absorption above 300 nm (Figure 6.64). Irradiation of 6.12@(OA)\(_2\) and 6.15@(OA)\(_2\) in a pyrex NMR tube under 450 W medium pressure mercury lamp resulted in the formation of 1-adamantanecarboxylic acid@OA complex subsequently after the capsules break (Figure 6.65(iv) and 6.66(v)). In the case of 6.13@(OA)\(_2\) and 6.16@(OA)\(_2\) the \( o \)-toluic acid produced was released to the aqueous exterior (Figure 6.66 and 6.67, respectively). and so as in the case of 6.14@(OA)\(_2\) and 6.17@(OA)\(_2\) the released 3,3-dimethylacrylic acid stays outside OA cavitand (Figure 6.70 and 6.71, respectively). In all these reactions the major product obtained was \( p \)-methylacetophene and \( p \)-chloroacetophenone. No trace of \( p \)-substituted phenylacetic acid was observed when irradiated as OA complexes whereas when irradiated in methanol, about 10-15 % of the rearrangement product was observed. The presence of \( p \)-methylacetophene and \( p \)-chloroacetophenone were not very clearly
seen in the NMR, therefore the samples were extracted with CHCl₃ and analyzed by GC and GC-MS.


Figure 6.61. Absorption spectra of p-methylphenacyl esters 6.12 - 6.14.

Figure 6.62. Absorption spectra of p-chlorophenacyl esters 6.15 - 6.17.
Figure 6.63. Absorption spectra of 4-chloroacetophenone (red) and 4-methylacetophenone (green).

Figure 6.64. Absorption spectra of 6.12@(OA)_2 (red) and 6.15@(OA)_2 (green).
Figure 6.65. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O, pH = 8.7) spectra of 6.12@OA$_2$ complex (before and after irradiation). "∗" and "■" indicate the OA incarcerated guest 6.13 and 1-adamantanecarboxylic acid proton peaks, respectively. "●" represents the residual solvent peak of water.
Figure 6.66. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O, pH = 8.7) spectra of 6.13@(OA)$_2$ complex (before and after irradiation). “∗” and “■” indicate the OA incarcerated guest 6.13 methyl proton peak and free o-toluic acid proton peak, respectively. “●” represents the residual solvent peak of water.
Figure 6.67. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O, pH = 8.7) spectra of 6.14@(OA)$_2$ complex (before and after irradiation). “∗” and “■” indicate the OA incarcerated guest 6.14 methyl proton peaks and free 3,3-dimethylacrylic acid proton peaks, respectively. "●" represents the residual solvent peak of water.
Figure 6.68. $^1$H NMR titration spectra of 4-methylacetophenone@OA, "*" indicates the OA incarcerated guest proton peaks. "●" indicates the residual solvent peak of water.
Figure 6.69. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O, pH = 8.7) spectra of 6.15@(OA)$_2$ complex (before and after irradiation). “*” and “■” indicate the OA incarcerated guest 6.15 and 1-adamantanecarboxylic acid proton peaks, respectively. "●" represents the residual solvent peak of water.
**Figure 6.70.** $^1$H NMR (500 MHz, 10 mM $\text{Na}_2\text{B}_4\text{O}_7$ buffer/$\text{D}_2\text{O}$, $\text{pH} = 8.7$) spectra of $6.16@\text{(OA)}_2$ complex (before and after irradiation). “∗” and “■” indicate the OA incarcerated guest $6.16$ methyl proton peak and free $o$-toluic acid proton peak, respectively. ”○” represents the residual solvent peak of water.
Figure 6.71. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O, pH = 8.7) spectra of 6.17@(OA)$_2$ complex (before and after irradiation). “∗” and “□” indicate the OA incarcerated guest 6.17 methyl proton peaks and free 3,3-dimethylacrylic acid proton peaks, respectively. "●" represents the residual solvent peak of water.
**Figure 6.72.** $^1$H NMR titration spectra of 4-chloroacetophenone@OA, “•” indicates the OA incarcerated guest proton peaks. “*” indicates the residual solvent peak of water.

Thus, when comparing the results obtained from all the four derivatives of the phenacyl esters, the photochemistry of the encapsulated guests and the effective capsule opening process are most efficient with the $p$-hydroxyphenacyl derivatives due to the fact that they proceed via a different mechanism (heterolytic cleavage) to give the final product.
6.5. Complexation Studies of Guests 6.1 - 6.6 with MOA and OAm and Their Photochemistry.

Scheme 6.8. Structures of hosts MOA and OAm.

Figure 6.73. $^1$H NMR (500 MHz, 0.6 mL 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O) titration spectra of 6.4@MOA. [MOA] = 1 mM and [6.4] = 0 to 1 mM (“*” indicates the MOA bound guest proton peaks respectively). “●” and “♦” indicate the residual solvent peak of water and DMSO-$d_6$ respectively.
Figure 6.74. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O with 30 % DMSO-d$_6$) titration spectra of 6.4@MOA. [MOA] = 1 mM and [6.4] = 0 to 1 mM (“*” and “**” indicate the MOA bound and unbound guest proton peaks respectively). “●” and “♦” indicate the residual solvent peak of water and DMSO-d$_6$ respectively.
Figure 6.75. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O with 30 % DMSO-d$_6$) spectra of photolysis of 6.4@MOA$_2$. [MOA] = 1 mM and [6.4] = 0.5 mM. ("*" indicates the MOA bound guest 6.4 proton peaks.) ("**" and "***" indicate the MOA bound and unbound 1-adamantanecarboxylic acid proton peaks respectively). "□" represents the aliphatic (–CH$_2$–) peak corresponding to 4-hydroxyphenyl acetic acid “●” and “♦” indicate the residual solvent peak of water and DMSO-d$_6$ respectively.


Figure 6.76. Comparison of $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O with 30 % DMSO-$d_6$) spectra of photolysis of 6.4@MOA$_2$ and the corresponding photoproduct with MOA. [MOA] = 1 mM and [6.4] = [1-adamantanecarboxylic acid] = [4-hydroxyphenyl acetic acid] = 0.5 mM. ("*" indicates the OA bound guest 6.4 proton peaks.) ("**" and "***" indicate the OA bound and unbound guest 1-adamantanecarboxylic acid proton peaks respectively). "■" represents the aliphatic (–CH$_2$–) peak corresponding to 4-hydroxyphenyl acetic acid “●” and “♦” indicate the residual solvent peak of water and DMSO-$d_6$ respectively.

Host MOA has eight acid groups at the bottom that makes it solublize in buffer but its NMR spectrum shows multiple peaks which makes the assignment of the aromatic proton peaks difficult. When 6.4 was added to a 1 mM solution of MOA in borate buffer, the upfield shifted aromatic peaks of the 6.4 indicates that 6.4 forms complex with MOA.
but the presence of multiple peaks didn’t give a good idea of the type of complex formed (Figure 6.73). In this context, a 30% DMSO in borate buffer mixture was used to make the host solution followed by the addition of 6.4 to make the complex (Figure 6.74). Irradiation of 6.4@(MOA)$_2$ results in the formation of 1-adamantanecarboxylate@(MOA)$_2$ and 4-hydroxyphenyacetic acid (Figure 6.76).

**Figure 6.77.** $^1$H NMR (500 MHz, 0.6 mL 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O) titration spectra of 6.5@MOA. [MOA] = 1 mM and [6.5] = 0 to 1.5 mM. “●” and “♦” indicate the residual solvent peak of water and DMSO-$d_6$ respectively.
Figure 6.78. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O with 30 % DMSO-d$_6$) titration spectra of 6.5@MOA. [MOA] = 1 mM and [6.5] = 0 to 1 mM ("*" indicates the uncomplexed guest proton peak). “●” and “♦” indicate the residual solvent peak of water and DMSO-d$_6$ respectively.
Figure 6.79. $^1$H NMR (500 MHz, 0.6 mL 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O) titration spectra of 6.6@MOA. [MOA] = 1 mM and [6.6] = 0 to 1.5 mM. “●” and “♦” indicate the residual solvent peak of water and DMSO-$d_6$ respectively.
Figure 6.80. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O with 30 % DMSO-$d_6$) titration spectra of $6.6@$MOA. [MOA] = 1 mM and $[6.6] = 0$ to 1 mM (“*” indicates the uncomplexed guest proton peaks). “●” and “♦” indicate the residual solvent peak of water and DMSO-$d_6$ respectively.

Neither $6.5$ nor $6.6$ formed a clear complex with MOA in borate buffer (Figure 6.77 and 6.79, respectively) and also in 30 % DMSO in borate buffer (Figure 6.78 and 6.80, respectively). This could probably be due to the less hydrophobic nature of the guests $6.5$ and $6.6$ when compared to $6.4$. 

Figure 6.81. Absorption spectra of 4-methoxyphenacyl esters 6.1 (red), 6.2 (green) and 6.3 (blue) 10 mM in borate buffer solution having 20% DMSO. $[6.1] = [6.2] = [6.3] = 50 \mu M$.

Figure 6.82. Absorption spectra of MOA in 10 mM borate buffer solution having 20% DMSO. $[\text{MOA}] = 100 \mu M$. 
Figure 6.83. Absorption spectra of 6.1-6.3@MOA$_2$ in 10 mM borate buffer solution having 20 % DMSO. [MOA] = 100 µM and [6.1] = [6.2] = [6.3] = 50 µM.

Figure 6.84. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O having 20% DMSO-$d_6$) titration spectra of 6.1@MOA. [MOA] = 1 mM and [6.1] = 0 to 1.5 mM ("∗" indicates the MOA bound guest proton peaks of 6.1). "●" and "♦" indicate the residual solvent peak of water and DMSO-$d_6$ respectively.
Figure 6.85. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O having 20% DMSO-$d_6$) titration spectra of 6.2@MOA. [MOA] = 1 mM and [6.2] = 0 to 1.5 mM. “♦” indicates the residual solvent peak of DMSO-$d_6$. 
Figure 6.86. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O having 20% DMSO-$d_6$) titration spectra of 6.3@MOA. [MOA] = 1 mM and [6.3] = 0 to 1.5 mM ("*" indicates the MOA bound guest proton peaks of 6.3). ”●” and “♦” indicate the residual solvent peak of water and DMSO-$d_6$ respectively.
Figure 6.87. Photochemistry of $6.1@(MOA)_2$ monitored by $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O having 20% DMSO-$d_6$). [MOA] = 1 mM and [6.1] = 0.5 mM (‘∗’ and ‘∗∗∗’ indicate the MOA bound guest proton peaks of 6.1 and 1-adamantanecarboxylic acid respectively). ‘●’ and ‘♦’ indicate the residual solvent peak of water and DMSO-$d_6$ respectively.
Figure 6.88. Comparison of $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O having 20% DMSO-$d_6$) spectra of photolysis of 6.1@MOA$_2$ and the corresponding photoproduct with MOA. [MOA] = 1 mM and [6.1] = [1-adamantanecarboxylic acid] = [4-methoxyacetophenone] = 0.5 mM. (‘∗’ and ‘∗∗’ indicate the MOA bound guest proton peaks of 1-adamantanecarboxylic acid and 4-methoxyacetophenone respectively). ‘●’ and ‘♦’ indicate the residual solvent peak of water and DMSO-$d_6$ respectively.
Figure 6.89. Photochemistry of 6.3@(MOA)$_2$ monitored by $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O having 20% DMSO-$d_6$). [MOA] = 1 mM and [6.3] = 0.5 mM ("∗" indicates the MOA bound guest proton peaks of 6.3 and "∗" indicates the free methyl proton peaks of 3,3-dimethylacrylic acid). “●” and “♦” indicate the residual solvent peak of water and DMSO-$d_6$ respectively.

Among the $p$-methoxyphenacyl esters only 6.1 and 6.3 forms complex with MOA in 20% DMSO in borate buffer solution and the irradiation of 6.1@(MOA)$_2$ and 6.3@(MOA)$_2$ resulted in the formation of their corresponding acids (Figure 6.88 and 6.89, respectively) and $p$-methoxyacetophenone (analyzed by GC). 1-Adamantanecarboxylic acid released from 6.1 formed 1-
adamantanecarboxylate@/(MOA)_2 complex (Figure 6.88) whereas the 3,3-dimethylacrylic acid released from 6.3 remained freely in solution (Figure 6.89).

Figure 6.90. ¹H NMR (500 MHz, 0.6 mL DCl/D₂O) titration spectra of 6.1@OAm. [OAm] = 1 mM and [6.1] = 0 to 2 mM (“*” indicates the OAm bound guest proton peaks). “●” indicates the residual solvent peak of water.
Figure 6.91. $^1$H NMR (500 MHz, 0.6 mL DCl/D$_2$O) titration spectra of 6.2@OAm. [OAm] = 1 mM and [6.2] = 0 to 2 mM. "●" indicates the residual solvent peak of water.
Figure 6.92. $^1$H NMR (500 MHz, 0.6 mL DCl/D$_2$O) titration spectra of 6.3@OAm. [OAm] = 1 mM and [6.3 ] = 0 to 2 mM (“*” indicates the OAm bound guest proton peaks). “●” indicates the residual solvent peak of water.

The NMR titration spectra of 6.1 with OAm shows that excess amount of guest are needed to force the complex formation, therefore 6.1@(OAm)$_2$ may not be a right system to study the photochemistry of the encapsulated guest 6.1 because of the presence of both complexed and uncomplexed guest in the same solution (Figure 6.90). Guest 6.2 didn’t show a significant peak for the encapsulated methyl protons on the toluene part in the upfield region which in turn hard to confirm whether 6.2 is forming a complex with OAm or not (Figure 6.91). Incremental addition of 6.3 to OAm solution showed the upfield shifted proton peaks of the guest but their intensity remained very low indicating
that only a very low percentage of the guests added may be forming complex (Figure 6.92).

6.6. Experimental Section.

Materials and method.

2-Bromo-4’-hydroxyacetophenone, 2-bromo-4’-methylacetophenone, 2-bromo-4’-chloroacetophenone, 1-adamantanecarboxylic acid, o-toluic acid and 3, 3-dimethylacrylic acid (Sigma-Aldrich/Alfa Aesar) were used as received. The host, octa acid (OA), was synthesized by following the literature procedure.

\[ ^1 \text{H NMR studies with guests 6.1-6.3@OA.} \]

600 µL of a D$_2$O solution of host OA (1 mM OA in 10 mM Na$_2$B$_4$O$_7$) was taken in a NMR tube and to this 0.25 equivalent increment of guest (2.5 µL of a 60 mM solution in DMSO-$d_6$) was added. The 1H NMR experiments were carried out after shaking the NMR tube for 5 min after each addition. Capsular assembly formation was monitored by the appearance of upfield shifted aliphatic proton peaks of the guest and disappearance of the free host OA signals upon the addition of guest. Addition of excess amount of guests makes the solution turbid.

Gas Chromatography coupled to Mass Spectrometry (GC-MS).

The identification and quantification of the main reaction products was made by GC (Hewlett Packard 6890N) with MS detection (5973 series mass selective detector, E.I. 70 eV). The GC-MS was used with a Rtx-5MS capillary column with 30 m length,
0.25 mm I.D. and 0.5 Lm film thickness (Restek) with the following oven temperature program: 60 °C for 2 min, 5 °C min/min increase until 160 °C; 2 min at 160 °C followed by 10 °C min/min increase until 280 °C; 10 minutes at 280 °C. The flow was 1 mL/min, the injector was set to 280 °C, the injections were made in the splitless mode and the injection volume was 1 µL.

**Electrospray Ionization Mass Spectrometry (ESI-MS).**

ESI-MS spectra of the OA-adduct were obtained in aqueous solutions containing NH₃ (5 µL per mL) under positive and negative polarity. A Bruker Daltonics HCT ultra mass spectrometer, equipped with an ESI source (Agilent) was used. The ions were continuously generated by infusing the aqueous sample solution (4 µL/min) into the source with the help of a syringe pump (KdScientific, model 781100, USA). Typical experimental conditions were as follows: capillary voltage, 3.0 kV; capillary exit voltage, 300 V; skimmer voltage, 15 V; drying gas, 300 oC at 6 L/min; nebulizer gas pressure, 20 psi.

**Liquid Chromatography coupled to Mass Spectrometry (LC-MS).**

The analysis of the acids was made by LC-MS operating in the negative polarity. The LC-MS system is an Agilent Technologies 1200 Series LC coupled to a Bruker Daltonics HCT ultra (ion trap). A Hamilton PRP-1 reversed phase LC column (15.0 cm length, 2.1 mm internal diameter, 5 Lm), stabilized at 25 °C was used. The mobile phase was acetonitrile (A) water (B), both with 0.1 % of formic acid, and water with 0.1 % ammonia (C). The gradient started with 10 % of A and 90 % of B, during the first 2
minutes, followed by a linear increase of B to 100 % after 8 minutes. The system was allowed to stay at 100 % of B during four minutes and then a clean step of OA residues was made by flowing solvent C for four minutes. Finally the system was allowed to recover the initial composition of the mobile phase (5 % of A and 95 % o) in 1 min and then stabilize for additional 5 min before the next run.

Synthesis of 4’-hydroxyphenacyl ester derivative.

The method of Givens, et al. was followed with the following modifications. Carboxylic acid (212 mg, 1.0 equiv.) and 4’-hydroxyphenacyl bromide (215 mg, 0.85 equiv.) were added in a 50 mL round bottomed flask. To this, 4 mL THF was added and stirred for 5 min to completely dissolve the solid. To this, 16 mL benzene was added followed by the addition of 1, 8-diazabicyclo[5.4.0]undec-7-ene (0.18 mL, 1.0 equiv). The reaction mixture was stirred at room temperature for 15 h under N₂ atmosphere. The reaction was stopped and the solvent removed by distillation. About 25 mL EtOAc was added and the mixture was washed with water (3×100 mL), Na₂CO₃ solution (5 %, 3×100 mL), and then by brine (100 mL). The organic layer was dried over anhydrous Na₂SO₄, concentrated to a solid and purified by prep-TLC to obtain the ester as a white solid of 6.4, 6.5, or 6.6 (purity > 99% by GC, yield = 40 to 60 %).
Scheme 6.9. Synthesis of 4’-hydroxyphenacetyl ester derivatives.

Scheme 6.10. Synthesis of 4’-Methyl and 4’-chlorophenacetyl esters.

Carboxylic acid (212 mg, 1.0 equiv.) and 4’-hydroxyphenacetyl bromide (0.85 equiv.) were added in a 50 mL round bottomed flask. To this, 16 mL benzene was added followed by the addition of 1, 8-diazabicyclo[5.4.0]undec-7-ene (0.18 mL, 1.0 equiv). The reaction mixture was stirred at room temperature for 15 h under N₂ atmosphere. The reaction was stopped and the solvent removed by distillation. About 25 mL CHCl₃ was added and the mixture was washed with water (3 × 100 mL), Na₂CO₃ solution (5 %, 3 × 100 mL), and then by brine (100 mL). The organic layer was dried over anhydrous Na₂SO₄, concentrated to a solid and purified by prep-TLC to obtain the ester as pale
yellow solid of 6.12 - 6.17 (purity > 99% by GC, yield = 70 to 90 %). The mass of each compounds were determined by GC-MS and ESI-MS.

**NMR experiments.**

$^1$H NMR studies were carried out on a Bruker 400 and 500 MHz NMR spectrometer at 25 °C.

$^1$H NMR studies with guests@OA.

A 600 μL of 1 mM OA (10 mM Na$_2$B$_4$O$_7$, pH = 8.7) solution was placed in an NMR tube. To this was added incrementally 0.25 equivalents aliquots of the guest ester (2.5 μL of a 60 mM guest solution in DMSO-$_d_6$) was added. The $^1$H NMR experiments were carried out after shaking the contents of the NMR tube for 5 min after each addition. Complex formation was monitored by disappearance of the free host OA signals and the upfield shift of the aliphatic proton peaks of the guest. Addition of excess amounts of the guest either remains uncomplexed or makes the solution turbid.

**Sample preparation for the photochemical reactions.**

A 600 μL of 1 mM OA (10 mM Na$_2$B$_4$O$_7$, pH = 8.7) solution was placed in an NMR tube. To this was added 0.5 equivalent of guest (5 μL of a 60 mM solution in DMSO-$_d_6$). After shaking the NMR tube for 5 min, the $^1$H NMR was recorded to confirm the complex formation. The sample was irradiated with UV light and the progress of the reaction was monitored by NMR. Photochemical studies were carried out with different two UV-light sources, a 450 W medium pressure mercury vapor lamp and a TLC lamp.
Sample preparation for the photochemical reaction studies by LC-DAD-MS.

Irradiation of guests@OA₂ complexes were performed on aqueous solutions of Na₂B₄O₇ (10 mM, pH = 8.7) containing 25 μM of guest and 50 μM of host in air equilibrated conditions. All irradiations were performed using a high-pressure xenon lamp setup in conjunction with a water filter to prevent heating of the sample solutions. An additional Pyrex glass filter was inserted to remove UV light below 300 nm.

Sample analysis and quantification.

Compounds 6.4 - 6.6, 2,4’-dihydroxyacetophenone, 4-hydroxyphenylacetic acid and o-toluic acid were analyzed by LC-DAD at 275 nm. Product 1-adamantanecarboxylic acid was followed by LC-MS by monitoring its negative ion at m/z 179. The irradiated solutions were injected into the LC-DAD-MS system without further processing. Product 3,3-dimethyacrylic acid was extracted from the irradiated solutions before analysis. After irradiation, the pH of the aqueous solutions was adjusted to 2. Extraction was then performed with dichloromethane using a volume twice that of the irradiated solution. The extract was then analyzed by GC-MS in the single ion mode (SIM) by following the ion at m/z 100.

The peak assignments were made by comparing the retention times, and UV spectra (taken with the DAD), and ESI mass spectra with authentic samples. Quantitative analysis for each starting compound and photo-product was made using calibrations curves with authentic samples.
Equipment and analysis conditions.

The ESI mass spectra were obtained using Bruker Daltonics HCT ultra in the negative polarity. The ions were continuously generated by infusing the compounds in acetonitrile (50 µM) at 4 mLmin$^{-1}$ into the source with the help of a syringe pump (KdScientific, model 781100, USA). Typical experimental conditions were as follows: capillary voltage, 3.5 kV; capillary exit voltage (CE), 75 V; skimmer voltage, 40 V; drying gas, 300 °C at 6 Lmin$^{-1}$; nebulizer gas pressure, 20 psi.

The LC-DAD-MS analyses were performed using an Agilent Technologies 1200 Series LC, equipped with a diode array detector and coupled to a Bruker Daltonics HCT ultra. A Hamilton PRP-1 reversed phase LC column (15.0 cm length, 2.1 mm internal diameter, 5 µm), stabilized at 25 °C was used. The mobile phase comprises acetonitrile (A), water (B), both with 0.1 % of formic acid, and a mixture 1:1 (v/v) water/acetonitrile (C) containing 0.1 % of NH$_3$. The gradient started with 5 % of A and 95 % of B, increased linearly to 100 % of A after 10 minutes and keep this composition during four minutes. Then, 100% of C during 2 minutes was used to remove octa-acid. Finally the system was allowed to recover the initial composition of the mobile phase (5 % of A and 95 % B) in 1 min and then stabilized for additional 5 minutes before the next run.

GC-MS analyses were performed using an Agilent 6890N equipped with a 5973 series mass selective detector (E.I. 70 eV). An AT-WAXMS polar capillary column with 30 m length, 0.25 mm I.D., and 0.5 µm film thickness (GRACE) was used with the following oven temperature program: 90 °C for 1 min, 10 °C per min increase until a final temperature of 250 °C. The injector was set to 250 °C and the injection volume was 1 µL.
Figure 6.93. $^1$H NMR (500 MHz, DMSO-$d_6$) spectrum of 6.4. “●” and “♦” indicate the residual solvent peak of water and DMSO-$d_6$, respectively.

Figure 6.94. $^{13}$C NMR (100 MHz, DMSO-$d_6$) spectrum of 6.4. “●” indicates the residual solvent peak of DMSO-$d_6$. 
Figure 6.95. Electrospray (ESI) mass spectra of 6.4 at negative polarity. (i) Full scan; (ii) fragmentation of m/z 313.0. Assignment: m/z 313.0, [6.4-H]. The arrow indicates the fragment peak.
Figure 6.96. $^1$H NMR (500 MHz, DMSO-$d_6$) spectrum of 6.5. “●” and “♦” indicate the residual solvent peak of water and DMSO-$d_6$ respectively.

Figure 6.97. $^{13}$C NMR (100 MHz, DMSO-$d_6$) spectrum of 6.5. “●” indicates the residual solvent peak of DMSO-$d_6$. 
Figure 6.98. ESI mass spectra of 6.5 in the negative polarity. (i) Full scan; (ii) fragmentation of m/z 268.9. Assignment: m/z 268.9, [6.5-H]-. The arrow indicates the fragment peak.
**Figure 6.99.** $^1$H NMR (500 MHz, DMSO-$d_6$) spectrum of 6.6. “●” and “♦” indicate the residual solvent peak of water and DMSO-$d_6$, respectively.

**Figure 6.100.** $^{13}$C NMR (100 MHz, DMSO-$d_6$) spectrum of 6.6. “●” indicates the residual solvent peak of DMSO-$d_6$. 
**Figure 6.101.** ESI mass spectra of $6.6$ in the negative polarity. (i) Full scan; (ii) fragmentation of m/z 232.9. Assignment: m/z 232.9, [6.6-H]$^-$. The arrow indicates the fragment peak.
Figure 6.102. $^1$H NMR (500 MHz) spectra of 6.12 in DMSO-$d_6$. (‘●’ indicates the residual solvent peak of water and DMSO-$d_6$).

Figure 6.103. $^{13}$C NMR (125 MHz) spectra of 6.12 in DMSO-$d_6$. (‘●’ indicates the residual solvent peak of DMSO-$d_6$).
Figure 6.104. $^1$H NMR (500 MHz) spectra of 6.13 in DMSO-$d_6$. (“●” indicates the residual solvent peak of water and DMSO-$d_6$).

Figure 6.105. $^{13}$C NMR (125 MHz) spectra of 6.13 in DMSO-$d_6$. (“●” indicates the residual solvent peak of DMSO-$d_6$).
Figure 6.106. $^1$H NMR (500 MHz) spectra of 6.14 in DMSO-d$_6$. ("●" indicates the residual solvent peak of water and DMSO-d$_6$).

Figure 6.107. $^{13}$C NMR (125 MHz) spectra of 6.14 in DMSO-d$_6$. ("●" indicates the residual solvent peak of DMSO-d$_6$).
Figure 6.108. $^1$H NMR (500 MHz) spectra of 6.15 in DMSO-d$_6$. (●” indicates the residual solvent peak of water and DMSO-d$_6$).

Figure 6.109. $^{13}$C NMR (125 MHz) spectra of 6.15 in DMSO-d$_6$. (●” indicates the residual solvent peak of DMSO-d$_6$).
Figure 6.110. $^1$H NMR (500 MHz) spectra of 6.16 in DMSO-$d_6$. (”●” indicates the residual solvent peak of water and DMSO-$d_6$).

Figure 6.111. $^{13}$C NMR (125 MHz) spectra of 6.16 in DMSO-$d_6$. (”●” indicates the residual solvent peak of DMSO-$d_6$).
**Figure 6.112.** $^1$H NMR (500 MHz) spectra of 6.17 in DMSO-$d_6$. (‘●’ indicates the residual solvent peak of water and DMSO-$d_6$).

**Figure 6.113.** $^{13}$C NMR (125 MHz) spectra of 6.17 in DMSO-$d_6$. (‘●’ indicates the residual solvent peak of DMSO-$d_6$).
Chapter 7
Photophysics and Photochemistry of Organic Guests Inside iTATA and TATP Capsules that are Functionalized on Silica Gel
7.1. Overview.

Photochemistry of organic molecules supported on silica gel surface has been extensively studied by de Mayo and Turro and their coworkers\textsuperscript{235-237} Though silica gel is inert, the excited state chemistry of aromatic and carbonyl compounds adsorbed on it has been shown to be distinctively different from that in solution. Since silica gel has –OH groups on its surface, it would be easy to adsorb the cavitands having carboxylic acid and hydroxy groups at their surface with the help of H-bonding. Linking supramolecules covalently on silica surface to carry out functions in a more orderly manner than in solutions were achieved by various other groups in order to find their applications in regulating the controlled release of cargo/drug molecules under a range of external stimuli like light and pH.\textsuperscript{238-240} Although covalently linking the supramolecules to the silica surface ensures their presence on the surface, modifying the surface for functionalization could be a tedious process. Attempts to transfer the host-guest complexes from solution to the silica gel surface were successful with OA capsuleplexes in our lab. Following our previous work, we tried to adsorb iTATA and TATP capsuleplexes on silica gel surface. This chapter will discuss the stability of the iTATA and TATP capsuleplexes on silica gel surface along with the photophysics and photochemistry of guest molecules encapsulated inside the silica gel adsorbed iTATA and TATP capsules.
Figure 7.1. Structures of guest molecules investigated inside iTATA and TATP capsules.

The complexation nature of guests 7.1, 7.2, 7.3, 7.5, 7.6 and 7.7 with iTATA and TATP and their photophysics and photochemistry were well established in Chapter 2. The solution containing the capsules were transferred to silica gel surface and carried out the photochemical and photophysical studies.

7.2. Photophysics of Guest Molecules Encapsulated Inside iTATA Capsule Supported on Silica gel Surface.

Figure 7.2. Emission spectrum of iTATA adsorbed on silica gel surface, $\lambda_{ex} = 260$ nm.
Figure 7.3. Phosphorescence emission spectrum of $(7.1)_{2}@$(iTATA)$_2$ adsorbed on silica gel surface.

Figure 7.4. Phosphorescence decay spectrum of $(7.1)_{2}@$(iTATA)$_2$ adsorbed on silica gel surface. $\lambda_{ex} = 254$ nm.
Figure 7.5. Emission spectrum of (7.2)_{2}@({iTATA})_{2} adsorbed on silica gel surface.

Figure 7.6. Emission spectrum of only 7.2 adsorbed on silica gel surface.

Figure 7.7. Emission spectrum of (7.2)_{2}@({iTATA})_{2} adsorbed on silica gel surface under neutral conditions.
Figure 7.8. Emission spectrum of only 7.3 adsorbed on silica gel surface excited at different wavelengths.

Figure 7.9. Emission spectrum of 7.3@iTATA₂ adsorbed on silica gel surface under neutral conditions.
Figure 7.10. Phosphorescence decay spectrum of 7.3@iTATA$_2$ adsorbed on silica gel surface under neutral conditions. $\lambda_{ex} = 310$ nm.

Figure 7.11. Emission spectra of 7.4 in the presence and absence of iTATA adsorbed on silica gel surface under neutral conditions.

To initiate the studies in understanding the excited state behavior of guest molecules that are encapsulated inside iTATA capsule supported on silica gel, we first prepared a solution containing (7.1)$_2$@iTATA$_2$. The solution was then added silica gel,
shaken mechanically for 12 h and dried under reduced pressure. The phosphorescence emission presented in Figure 7.3 for (7.1)$_2$@iTATA$_2$ supported on silica gel looked very much similar to the one recorded in solution (chapter 2) and the lifetime of the excited camphorthione triplet state were determine to be 92 $\mu$s (Figure 7.4) which is better than what was measured in solution (69 $\mu$s). To continue with our studies in understanding the stability of capsules on silica gel, we transferred (7.2)$_2$@iTATA$_2$ on silica gel. The emission spectrum recorded (Figure 7.5) showed an increased intensity for the 7.2 monomer and decreased intensity for the excimer which indicated that during the experimental processes, the capsules were broken to a greater extent. Multiple attempts to keep the capsule intact on the silica surface were failed. To overcome this issue, we adsorbed 7.2 and iTATA under neutral conditions on the silica surface and mixed the two silica samples and mechanically shaken for 24 h. The emission spectrum recorded showed (Figure 7.6) no excimer band, that confirmed the absence of any (7.2)$_2$@iTATA$_2$. To the same sample, about 0.1 mL water was added and mechanically shaken for 10 days followed by drying under reduced pressure. A clear display of the excimer peak with high intensity along with the less intense monomer peak in the emission spectrum (Figure 7.7) proves that the host guest complex can be formed under neutral condition on silicagel surface in the presence of water.

We repeated the same process to construct (7.3)$_2$@iTATA$_2$ under neutral condition on the silica surface. The emission spectra recorded for silica gel adsorbed 7.3 at different excitation wavelengths showed a different peak pattern (Figure 7.8) which is very different from what was observed for (7.3)$_2$@iTATA$_2$ in solution. When neutral iTATA adsorbed on silica gel was added to this, followed my mechanical shaking for 2
days, there wasn’t any change observed in the emission band shape. To the above sample 0.1 mL water was added and mechanically shaken for 2 days. The sample was dried under reduced pressure and the emission spectrum recorded for the sample clearly showed the peak corresponding to the (7.3)\textsubscript{2}@iTATA\textsubscript{2} (Figure 7.9). The life time of (7.3)\textsubscript{2}@iTATA\textsubscript{2} adsorbed on silica gel having neutral iTATA was measured to be 1016 µs (Figure 7.10).

Pyrene (7.4) is one of a widely used polarity probes to study the polarity of various environment/active sites. Among its various vibronic bands in its fluorescence spectrum the most important one are the first (I\textsubscript{1}) and the third one (I\textsubscript{3}). The ratio (I\textsubscript{1}/I\textsubscript{3}) of the intensities of these peaks reflects the polarity of the medium under study. The ratio I\textsubscript{1}/I\textsubscript{3} is greater in polar medium, for example, I\textsubscript{1}/I\textsubscript{3} is 1.8 in borate buffer, whereas in benzene it is about 1. Since iTATA didn’t form a complex with 7.4 in NaOH/H\textsubscript{2}O, we wanted to check the possibility of their complex formation under neutral condition. The emission spectra of 7.4 recorded in the presence and absence of iTATA adsorbed on silica gel surface under neutral conditions showed a clear contrast in its I\textsubscript{1}/I\textsubscript{3} value and the I\textsubscript{1}/I\textsubscript{3} ratio for 7.4 in the presence of iTATA was determined to be 1.11 which is fairly closer to a system like benzene. Thus pyrene was forced to make complex with iTATA in its neutral form in the presence of water on silica gel surface.
7.3. Photochemistry of Guest Molecules Encapsulated Inside iTATA Capsule Supported on Silica gel Surface.

![Scheme 7.1. Reaction manifold for the photochemistry of 7.5.]

**Table 7.1.** Product distributions upon photolysis of 7.5@iTATA$_2$ adsorbed on silica gel surface.

<table>
<thead>
<tr>
<th>Medium</th>
<th>b</th>
<th>f</th>
<th>g-h</th>
</tr>
</thead>
<tbody>
<tr>
<td>iTATA (NaOH/H$_2$O)</td>
<td>55 %</td>
<td>31 %</td>
<td>14 %</td>
</tr>
<tr>
<td>iTATA (Silica gel)</td>
<td>11 %</td>
<td>77 %</td>
<td>12 %</td>
</tr>
</tbody>
</table>
**Scheme 7.2.** Reaction manifold for the photochemistry of 7.6.

**Table 7.2.** Product distributions upon photolysis of 7.6@iTATA$_2$ adsorbed on silica gel surface.

<table>
<thead>
<tr>
<th>Medium</th>
<th>A</th>
<th>B</th>
<th>E-H</th>
</tr>
</thead>
<tbody>
<tr>
<td>iTATA (NaOH/H$_2$O)</td>
<td>4%</td>
<td>12%</td>
<td>84%</td>
</tr>
<tr>
<td>iTATA (Silica gel)</td>
<td>14%</td>
<td>27%</td>
<td>59%</td>
</tr>
</tbody>
</table>
Scheme 7.3. Reaction manifold for the photochemistry of 7.7.

Table 7.3. Product distributions upon photolysis of 7.7@iTATA\(_2\) on silica gel surface.

<table>
<thead>
<tr>
<th>Medium</th>
<th>Norrish Type I product</th>
<th>Norrish Type II product</th>
</tr>
</thead>
<tbody>
<tr>
<td>iTATA (NaOH/H(_2)O)</td>
<td>100 %</td>
<td>0 %</td>
</tr>
<tr>
<td>iTATA (Silica gel)</td>
<td>100 %</td>
<td>0 %</td>
</tr>
</tbody>
</table>

Photolysis of 7.7@iTATA\(_2\), 7.7@iTATA\(_2\) and 7.7@iTATA\(_2\) resulted in the formation of only caged products (Table 7.1, 7.2 and 7.3) that indicates the stability of the capsules on silica gel surface.
7.4. Photophysics of guest molecules encapsulated inside TATP capsule supported on silica gel surface.

![Emission spectrum of TATP adsorbed on silica gel surface.](image1)

**Figure 7.12.** Emission spectrum of TATP adsorbed on silica gel surface.

![Emission spectrum of 7.3@(TATP)$_2$ adsorbed on silica gel surface under neutral conditions.](image2)

**Figure 7.13.** Emission spectrum of 7.3@(TATP)$_2$ adsorbed on silica gel surface under neutral conditions.
To study the complex formation ability of TATP on silica gel surface under neutral conditions we employed guest 7.3. Guest 7.3 forms a 2:1 complex with TATP which was well established in chapter 2. As in the case of the previous host, TATP was also adsorbed on silica surface under neutral conditions using THF. The mixture of dry samples of the host and guest on silica surface didn’t result in the complex formation even after shaking for several days. A clear complex formation between 7.3 and TATP was observed after the addition of 0.1 mL of water and shaking for 12 h followed by drying under reduced pressure from its emission spectrum in Figure 7.13. The lifetime of 7.3@(TATP)2 was determined to be 970 µs.

7.5. Experimental Section.

General protocol for emission studies.

Stock solution of iTATA (1 mM) was made in 10 mM NaOD/D2O (pH=11). Stock solutions of guest molecules (60 mM) were prepared in DMSO-d6. Appropriate
amount of the guest solutions were added to the host (0.6 mL) solutions to make the host@guest complexes. The solutions were transferred to a vial containing 100 mg of flash chromatographic grade silica gel (mesh size 63 to 200 µm). The vials were mechanically shaken at room temperature for about 12 h. The slurries were dried under reduced pressure at 65-75 °C. The dried samples were transferred to a quartz cuvette (1 mm path) and emission spectra were recorded by placing the cell at right angle in the cell holder using an Edinburgh FC900 spectrofluorometer equipped with a xenon lamp. Fluorescence/phosphorescence lifetime measurements were made using an Edinburgh single photon counter, fitted with a hydrogen arc lamp. Spectral plots were generated using Igor Pro software. For adsorption under neutral conditions iTATA (1 mM) solution was prepared in THF and the guest solutions were prepared according to the requirements (0.5 m/ 1mM) in THF. About 0.6 mL of both the solutions were transferred to a two different vials containing 50 mg of silica gel and mechanically shaken. The silica gel samples were dried and mixed together and added 0.1 - 0.2 mL water. Then it was mechanically shaken and dried under reduced pressure at 65-75 °C.

**General protocol for photolysis.**

The samples for photolysis were prepared as they were prepared for the emission studies. The samples were transferred to a quartz cuvette (1 mm path) and irradiated under 450 W mercury vapor lamp with a pyrex jacket. The photoproducts were extracted using CHCl₃ and the extracted solutions were injected in GC and GC-MS to analyze the identity and distribution ratio of the products.
Chapter 8

Exploring the Properties of Octa Acid Functionalized Gold Nanoparticles and Their Interaction with Organic Guests
8.1. Overview.

Gold nanoparticles (AuNPs) have gained enormous attention in the last couple of decades due to their unique properties such as surface Plasmon resonance (SPR), fluorescence enhancing and quenching effects, etc. Right from the beginning when Faraday in the year 1857 first observed the astonishing optical properties of AuNPs, the topic under study has flourished and found its applications in the area of biomedicine, optical devices, sensors and material sciences.\textsuperscript{241,242} Especially in biomedical applications the usage of AuNPs is preferred over quantum dots due to their high biocompatibility, noncytotoxicity, ease of synthesis, surface functionalization and high photostability.\textsuperscript{243-248} In addition, by tuning the shape, size and surface dependent properties of AuNPs one could greatly broaden their functionalities. As mentioned before the ease in synthesizing AuNPs functionalized with various organic molecules opened a gateway to explore the properties of various organic molecules when functionalized on AuNPs.

In general, the AuNPs were found to be very stable when the anchored ligands have thiol groups (-SH), this is due to the fact that the thiol groups of these compounds can bind covalently to the surface of AuNPs via a Au–S bond.\textsuperscript{249-257} However, AuNPs stabilized with various other functional groups like –COOH, -OH, etc, were also reported. Some of the most interesting studies done in the recent years involve the understanding of the influence of AuNPs on the optical properties of fluorescent dyes. When located in close proximity of the AuNPs, a dye exhibits strong changes in its electronic and optical properties, likely as a result of a mixing of the molecule and metal electronic levels as well as an interaction of the molecule with the SPR, which are modulated by the metal NP size.\textsuperscript{243} Most notably, anchoring of a dye on a AuNPs surface
results in a quenching of its fluorescence, while a fluorescence enhancement has been reported when the dye is located at distances higher than 10 nm from the metal surface. The usual way opted for bringing dye molecules closer to the AuNPs surface is by synthesizing the derivatives of the corresponding dye molecules having functional groups suitable for anchoring AuNPs. An indirect method employed to bring the dyes closer to AuNPs is by using supramolecular host functionalized AuNPs. Since, dye molecules can be brought to the proximity of AuNPs by incarcerating them inside the host which is sitting on the AuNPs, tedious steps involved in modifying the dye molecules can be avoided. Though some success was achieved in functionalizing thiolated cyclodextrins, calixarenes and resorcinarenes, their poor solubility and small cavity size limits their use.

In this context, we have previously used a thiol derivative of a deep cavity cavitand called tetra thiol tetra acid (TTTA) that can incarcerate bigger molecules whose photophysical properties were found to be very useful in understanding the nature of the environment. Following the successful results, we implemented the notion of functionalizing OA on AuNPs surface. This chapter will discuss the nature of the OA functionalized AuNPs (OA∩AuNPs) and its stability along with the emission quenching studies done with OA∩AuNPs and various organic guests.

8.2. Understanding the Stability of OA on AuNPs.

Figure 8.1: Structures of investigated guests.
Figure 8.2 shows the $^1$H NMR spectrum of OA∩AuNPs prepared by the reduction of HAuCl$_4$ using NaBH$_4$ and dialyzing further in water. It is seen from the spectrum that most of the OA proton peaks remained sharp which is in contradictory to what was observed so far in the literature for organic molecules that are covalently linked to AuNPs by Au-S bond. To understand whether the sharp peaks seen in the spectrum are from the OA that are functionalized on AuNPs or the ones that remained free in the solution, we carried out NMR studies with OA∩AuNPs and guest molecule 8.1 and 8.2 (Figure 8.1).

![Figure 8.2](image)

Figure 8.2. $^1$H NMR spectrum (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O) of OA∩AuNPs ([OA] = 1 mM). “●” and “♦” indicate the residual solvent peak of water and glycerol peaks respectively.
Figure 8.3. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O) titration spectra of 8.1 with OA∩AuNPs. [OA] = 1 mM and [8.1] = 0.5 mM ("*" indicates the OA bound 8.1 proton peaks). ● and ♦ indicate the residual solvent peak of water and glycerol peaks respectively.

Figure 8.4. DLS spectrum of OA∩AuNPs in 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O.
Figure 8.5. DLS spectrum of 8.1@OA∩AuNPs in 10 mM Na₂B₄O₇ buffer/D₂O.

Figure 8.6. ¹H NMR (500 MHz, 10 mM Na₂B₄O₇ buffer/D₂O) titration spectra of 8.2 with OA∩AuNPs. [OA] = 1 mM and [8.2] = 0.5 mM (”*” indicates the OA bound 8.2 proton peaks). “●” and “♦” indicate the residual solvent peak of water and glycerol peaks respectively.
Figure 8.7. DLS spectrum of OA∩AuNPs in 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O.

Figure 8.8. DLS spectrum of 8.2@OA∩AuNPs in 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O.

Figure 8.9. Absorption spectra of AuNPs with and without OA and 8.2@OA functionalization.
Figure 8.10. Monitoring the stability of AuNPs in the presence of OA using absorption spectra.

Figure 8.11. TEM images of (a) OA∩AuNPs, (b) AuNPs (post OA addition) and (c) AuNPs.
The $^1$H NMR titration studies of OA∩AuNPs with 8.1 and 8.2 indicate that the OA peaks getting much more sharper after guest addition to form 8.1@(OA)$_2$ and 8.2@(OA)$_2$, respectively (Figure 8.3 and Figure 8.6). The diffusion constants determined for OA∩AuNPs and 8.2@OA∩AuNPs were found to be 1.6 and 1.4 x 10$^{-10}$ m$^2$/s, respectively, which clearly showed that the sharp peaks of OA corresponds to the unbound OA. It was also previously reported in our work that the diffusion constant for 4,4’-dimethybenzil@OA∩AuNPs was 1.33 x 10$^{-10}$ m$^2$/s which is same as that of the free 4,4’-dimethybenzil@(OA)$_2$ complex. Hence, the OA peaks observed in the NMR spectrum belongs to the unbound OA but the OA∩AuNPs solution seemed very stable even after completely evaporating the solvent and redispersing the OA∩AuNPs in water. In the case of AuNPs prepared in the absence of OA, the particle became unstable and aggregated to obtain a dark black precipitate after evaporating the solvent. The dynamic light scattering (DSC) analysis shows the size of the OA∩AuNPs to be around 4 nm and not much increase was observed after adding guest (Figure 8.4, 8.5, 8.7 and 8.8), and also the absorption spectra recorded for these solutions after evaporating and redispersing in water shows the SPR band, a characteristic of AuNPs which was absent in the case of AuNPs prepared without OA, which supports the presence of stable OA∩AuNPs. This proves that OA is necessary to stabilize AuNPs. The question raised is whether the free OA are the unreacted OA left after the synthesis or is it in equilibrium with the AuNPs bound OA. To determine that, we carried out a control experiment that involved the synthesis of AuNPs by usual method. AuNPs obtained was added 1 mM OA solution and stirred for an hour. When the solvent was completely removed and the solid was redispersed in water, the absorption spectrum recorded (Figure 8.10b) for this solution
showed SPR band which confirmed the presence of stable AuNPs. Figure 8.11b shows the TEM image of AuNPs prepared with post OA addition. This shows that AuNPs can be stabilized in presence of OA even if OA is added after the nanoparticles are formed. Figure 8.10c shows the absorption spectrum of dried and redispersed AuNPs prepared in the absence of OA which doesn’t possess the SPR band, in addition to that, its TEM image displays a clear aggregation of AuNPs. These results indicate that the presence of OA is necessary to stabilize AuNPs and the sharp OA proton peaks observed for OA∩AuNPs corresponds to the free OA that could most probably be in equilibrium with the AuNPs bound OA.

8.3. Study of Guest Emission Quenching by OA∩AuNPs.

Figure 8.12. Structures of guests used for emission quenching studies.
Figure 8.13. Absorption spectra of $\text{(8.3)}_2@\text{(OA)}_2$ and $\text{(8.3)}_2@\text{OA} \cap \text{AuNPs}$.

Figure 8.14. Absorption spectra of $\text{8.4}@\text{(OA)}_2$ and $\text{8.4}@\text{(OA)}_2 \cap \text{AuNPs}$.

Figure 8.15. Absorption spectra of $\text{8.5}@\text{(OA)}_2$ and $\text{8.5}@\text{(OA)}_2 \cap \text{AuNPs}$.
Figure 8.16. Absorption spectra of $8.6@({\text{OA}})_{2}$ and $8.6@({\text{OA}})_{2} \cap \text{AuNPs}$.

Figure 8.17. Emission spectra of $(8.3)_{2}@({\text{OA}})_{2}$ and $(8.3)_{2}@({\text{OA}})_{2} \cap \text{AuNPs}$.

Figure 8.18. Emission spectra of $8.4@({\text{OA}})_{2}$ and $8.4@({\text{OA}})_{2} \cap \text{AuNPs}$.
Figure 8.19. Emission spectra of $8.5@\text{(OA)}_2$ and $8.5@\text{(OA)}_2 \cap \text{AuNPs}$.

Figure 8.20. Emission spectra of $8.6@\text{(OA)}_2$ and $8.6@\text{(OA)}_2 \cap \text{AuNPs}$.

Figure 8.13, 8.14, 8.15 and 8.16 display the absorption spectra of $(8.3)_2@\text{(OA)}_2$, $8.4@\text{(OA)}_2$, $8.5@\text{(OA)}_2$ and $8.6@\text{(OA)}_2$ that are free in solution and functionalized on AuNPs. The SPR band between 500 – 600 nm present in all the above spectra confirms the presence of AuNPs. Figure 8.17 shows the emission spectra of 8.3 having its both monomer and excimer peak which is characteristic of a 2:2 complex between 8.3 and OA. In the presence of AuNPs the emission intensity of 8.3 had decreased drastically. Similarly, the emission intensity of $8.4@\text{(OA)}_2$, $8.5@\text{(OA)}_2$ and $8.6@\text{(OA)}_2$ were also decreased to a greater extent when functionalized on AuNPs surface. These results
indicate that when the guest molecules are brought closer to the AuNPs surface their emission was quenched and the emission quenching could be due to energy or electron transfer. However, another possible pathway which we can’t rule out is the absorption of light emitted from the guest by AuNPs itself. Further studies to understand the right mechanism of emission quenching are underway in our lab.

8.4. Experimental Section.

**Synthesis of OA∩AuNPs.**

In a 50 mL round bottomed flask 0.6 mL of 1mM OA was added followed by the addition of 0.2 mL HAuCl₄ solution (from the stock solution of 11 mg HAuCl₄ /1 mL H₂O). About 3.2 mL H₂O was added. To this solution 0.8 mg NaBH₄ in 1 mL water was added immediately. The reaction mixture was stirred at room temperature for 1 h. The solution was distilled to remove the solvent completely under reduced pressure (residue). The solid obtained was redispersed in buffer solution.

**General protocol for NMR, absorption and emission studies.**

The OA∩AuNPs was prepared as mentioned above and dialyzed for 12 h in D.I.water. The solution was then distilled to remove solvent completely. The solid OA∩AuNPs obtained was redispersed in 0.6 mL 10 mM Na₂B₄O₇ buffer/D₂O solution and record an NMR spectrum. Titration studies were done by adding 2.5 µL aliquots of the guest solution to the host solution and mixing it by shaking the tube for 2 min. The solutions were diluted to obtain the guest concentration to 50 µM for absorption and emission studies.
Chapter 9

Photochemistry of Triplet Nitrene Precursors Inside Octa Acid capsule.
9.1. Overview.

Nitrenes are reactive intermediates that have a monovalent nitrogen atom. Nitrenes can exist in their singlet form where the non-bonding electrons on the monovalent nitrogen are paired or in triplet form with unpaired electrons. Singlet nitrenes are highly reactive that insert into surrounding chemical bonds and have therefore been used in various applications, such as photoaffinity labelling crosslinking of polymers, and modification of surfaces. Triplet nitrenes are generally less reactive, and because of their high-spin characteristics, they are used to construct organic magnets but generation of triplet nitrenes aren’t straight forward because of the high reactivity of their precursor. Since direct irradiation of azide precursors produce singlet nitrene that intersystem cross to triplet nitrene but the generation of triplet nitrene has to compete with other reactions of the singlet nitrene. Selective formation of triplet alkyl nitrenes from alkylazides was achieved using triplet sensitizers. Gudmundsdottir et al. reported that the irradiation of simple α-azidopropiophenones, which had a built-in triplet sensitizer, resulted in selective formation of triplet alkyl nitrene intermediates. However, Intramolecular triplet sensitization of alkyl azides does not always lead to the formation of alkyl nitrenes. For example, photolysis of α-azidoacetophenone derivatives resulted in both triplet energy transfer to form triplet alkyl nitrenes and α-cleavage to form benzoyl radicals. Photolysis of β-azidoacetophenone derivatives selectively yields triplet alkyl nitrene, which preferentially react with another nitrene molecule to form azo dimers. The lifetime of the triplet nitrene intermediate formed from the photolysis of β-azidoacetophenone was reported to be 27
ms using flash photolysis. Due to their high stability they don’t abstract H-atom from the solvent or other reactants like their singlet counterpart.

Generation of singlet nitrenes inside OA capsule and its reactivity towards the host was studied previously in our group. In this chapter, we used OA to encapsulate a series of azido aryl ketones (triplet nitrene precursors) (9.1 – 9.4) having 4-methoxyacetophenone as the in-built triplet sensitizer to produce triplet nitrenes by photolysis inside the cavity. The azido aryl ketones and their solution chemistry data were provided by from University of Cincinnati. The structures of investigated guests are displayed in Figure 9.1. All the azido ketones undergo reaction via different mechanism to produce different set of products in solution. Our goal is to investigate whether these molecules undergo the same reaction to give products inside OA as they do in solution or is there any change in their excited state properties due to confinement. We have previously reported that how OA and its analogous hosts had influenced the outcome of the photolysis of various guests. We believe that OA confinement can alter the photoproducts from the photolysis of the azido ketones also.

Figure 9.1. Structures of investigated azido aryl ketones.
9.2. Complexation Studies of Guests 9.1 – 9.4 with OA.

Guests 9.1 – 9.4 which are not very well soluble in buffer solution were solubilized in water by OA encapsulation. In order to identify the nature of the complex formation between OA and the azido ketone, first we carried out a $^1$H NMR titration studies with 9.1 and OA. Figure 9.2(ii) to (vi) shows that the intensity of the OA encapsulated 9.1 increases slowly in the upfield region until the ratio of the guest:host was maintained 1:2. When the concentration of 9.1 was increased further the peaks corresponding to the encapsulated 9.1 broadened and disappeared completely (Figure 9.2(vii) to (viii)). This is because when the host:guest (H:G) ratio was maintained 2:1, the capsule formed between 9.1 and OA remained stable. Moreover, sharp splitting of the OA aromatic peaks indicated the unsymmetrical nature of the capsule which is characteristic of a 2:1 (H:G) complex having an unsymmetrical guest inside the cavity. As the concentration of 9.1 increased, OA begin to form a very weak or unstable 1:1 complex with the guest that diffuses in and out of the OA cavity in the NMR time scale which resulted in the disappearance of the encapsulated 9.1 peaks.

Similarly 9.2 formed a strong 2:1 (H:G) complex with OA when the ratio of OA and 9.2 was maintained 2:1 (Figure 9.3(v)). Excess addition of 9.2 resulted in the broadening of the OA encapsulated guest peaks indicating the weak nature of their 1:1 complex (Figure 9.3(vi)). Following the above experiments, $^1$H NMR titration studies were done for both 9.3 and 9.4 with OA (Figure 9.4 and 9.5). Both 9.3 and 9.4 form a stable 2:1 (H:G) complex with OA which is evident from their $^1$H NMR spectra in Figure 9.4(vii) and 9.5(v), respectively. Excess addition of guest resulted in turbidity. The DOSY experiments for 9.1@OA)$_2$, 9.2@OA)$_2$ and 9.4@OA)$_2$ were performed by
Dr. Gupta and the diffusion constant values were determined to be 1.28, 1.26 and 1.23 x \(10^{-10}\) m\(^2\) s\(^{-1}\), respectively, confirming their stable 2:1 (H:G) complex nature.

**Figure 9.2.** \(^1\)H NMR (500 MHz, 10 mM Na\(_2\)B\(_4\)O\(_7\) buffer/D\(_2\)O) titration spectra of 9.1 with OA. OA [OA] = 1 mM and [9.1] = 0.1 to 0.7 mM. “*” indicates the OA encapsulated 9.1 aliphatic proton peaks. "●" represents the residual solvent peak of water.
Figure 9.3. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O) titration spectra of 9.2 with OA. OA [OA] = 1 mM and [9.2] = 0.2 to 0.7 mM. “*” indicates the OA encapsulated 9.2 aliphatic proton peaks. "●" represents the residual solvent peak of water.
Figure 9.4. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O) titration spectra of 9.3 with OA. OA [OA] = 1 mM and [9.3] = 0.1 to 0.5 mM. “*” indicates the OA encapsulated 9.3 aliphatic proton peaks. "●" represents the residual solvent peak of water.
Figure 9.5. $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O) titration spectra of 9.4 with OA. OA [OA] = 1 mM and [9.4] = 0.1 to 0.7 mM. "*" indicates the OA encapsulated 9.4 aliphatic proton peaks. "○" represents the residual solvent peak of water.


Photolysis of 9.1 was well reported in solution and solid state.$^{281}$ Scheme 9.1 displays the photoproducts obtained from 9.1 under different conditions. The p-methoxyacetophenone part of 9.1 acts as the intramolecular sensitizer. Since 9.1 has its azide group at its β-position, i.e. the benzoyl part of the molecule is separated from the azide group by two carbon atoms, the possibility of 9.1 to undergo α-cleavage is ruled out. Due to the presence of MeO- group at the para-position in the benzene ring, the π-$\pi^*$
configuration is the lowest triplet excited state of the ketone moiety. It has been known that triplet ketones with $\pi-\pi^*$ configuration do not undergo intramolecular H-atom abstraction efficiently,\textsuperscript{284} hence the triplet nitrene produced from 9.1 is not photoreactive, it decays by producing only 9.1a subsequently from an azo dimer rather than reacting with the solvent or precursors. The azo dimer is formed from two nitrene intermediates that have a co-existing tautomer, which cyclizes after losing a water molecule to give 9.1a (Scheme 9.2).

![Scheme 9.1](image)

**Scheme 9.1.** Products obtained from the photolysis of 9.1 in (i) solution and (ii) crystals.

Photolysis of 9.1 in solid state resulted in the formation of 9.1b, which is a cis-product (Scheme 9.1(ii)). The dimerization of two nitrene intermediates formed upon irradiation of 9.1 in crystals obtained 9.1b and it was assumed that alkyl nitrenes are also long-lived in crystals and the restricted mobility of the nitrenes in the crystal lattice forces them to form 9.1b.
With the knowledge that we had on the photochemistry of 9.1 in solutions and crystals, we carried out the photochemistry of 9.1@(OA)$_2$. 9.1@(OA)$_2$ was irradiated in a pyrex tube using Rayonet reactor and the reaction progress was monitored from its $^1$H NMR spectra (Figure 9.6). From both samples of 30 % and 100 % conversion of the starting material to product were extracted with CHCl$_3$. The extracted CHCl$_3$ layers were injected in GC and GC-MS to analyze the product nature. The only product observed was 9.1c in both the cases indicating that there are no secondary products formed after 9.1c. Since only one guest molecule sitting inside the OA capsule, the nitrene intermediate formed upon photolysis could not able to find another nitrene to react and form a dimer. With no choice left the nitrene intermediate had to decay by itself and it did via forming an imine biradical which subsequently formed $p$-methoxyacetophenone (9.1c) after losing a HCN molecule. This mechanism by which 9.1c is formed from 9.1 was previously reported in argon matrix. Thus, as expected, confinement of 9.1 inside OA capsule had a great influence in the mechanism by which the nitrene intermediate decayed to obtain an entirely different product from that in solution.
**Figure 9.6.** Photolysis of **9.1@**[OA]$_2$ monitored by $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O) spectra. OA [OA] = 1 mM and [**9.1**] = 0.5 mM. “∗” indicates the OA encapsulated **9.1** aliphatic proton peaks. “●” represents the residual solvent peak of water.

**Scheme 9.3** displays the number of products that are obtained upon photolysis of **9.2** under various solvent conditions. **9.2b** is the major product obtained upon photolysis of **9.2** in argon saturated toluene, whereas **9.2c** was obtained as the major product when **9.2** was irradiated under O$_2$ saturated toluene. It has been proposed that upon irradiation, **9.2** reaches its lowest triplet state (T$_{1K}$) (**Scheme 9.4**) that presumably has a n,π* configuration, abstracts a γ-H-atom to form biradical. This biradical further expulses a N$_2$ molecule to form an iminyl radical which cyclizes and releases a water molecule to form **9.2b**. A small fraction of the diradical undergoes cleavage at the α-carbon to yield 1-
phenylethenol that tautomerizes to give \(9.1c\). A second mechanism that has been suggested involves an energy transfer from the second excited state of the triplet ketone (\(T_{2K} (\pi,\pi^*)\)) of \(9.2\) to its azido group to form the triplet excited state of the azido chromophore (\(T_{1A}\)) of \(9.2\) which further expels a \(N_2\) molecule followed by dehydration to obtain \(9.2a\).

Scheme 9.3. Products obtained from the photolysis of \(9.2\) in various solvents.

Scheme 9.4. Proposed reaction mechanism for the photolysis of \(9.2\) in toluene.
Scheme 9.5 illustrates the mechanism that has been proposed for the photolysis of 9.2 in O₂ saturated toluene which involves the reaction of O₂ with the biradical to form an imine biradical. The imine biradical is assumed to decay by abstracting H-atoms from the solvent, followed by auto oxidation to form an imine that further hydrolyze to give 9.2c.

Scheme 9.5. Proposed reaction mechanism for the photolysis of 9.2 in O₂ saturated toluene.

Figure 9.7. Photolysis of 9.2@(OA)₂ monitored by ¹H NMR (500 MHz, 10 mM Na₂B₄O₇ buffer/D₂O) spectra. OA [OA] = 1 mM and [9.2] = 0.5 mM. “*” indicates the OA encapsulated 9.2 aliphatic proton peaks. "●" represents the residual solvent peak of water.
9.2@(OA)₂ was irradiated under UV-light and the reaction progress was monitored by \(^1\)H NMR (Figure 9.7) and the photo products were extracted using CHCl₃. The extracted CHCl₃ layers were injected in GC and GC-MS to analyze the product nature. Table 9.1 gives the ratio of products obtained from the photolysis of 9.2 in various environment. It shows that 9.2b is the major product obtained inside OA capsule. The formation of the cyclic product 9.2b indicates that the generated biradical could able to abstract the γ-H-atom within the OA cavity without much intervention from the aqueous medium present outside the cavity which eventually closes the ring to form 9.2b, although a 5 % formation of 9.2a shows a slight interaction of water molecule resulted in the H-abstraction to give 9.2a. Formation of only about 5 % of 9.2c could be due to the interaction of residual O₂ in the buffer solution with the biradical (Scheme 9.5). Thus, the increase in 9.2b product percentage inside OA capsule suggests the important role of confinement in controlling the reaction of the intermediate produced. In addition, the free space inside the capsule and the orientation of the abstractable Hs may also play a major role in deciding the product distribution.
Table 9.1. Distribution ratios of products obtained upon photolysis of 9.2 in various media.

<table>
<thead>
<tr>
<th>Medium</th>
<th>9.2a</th>
<th>9.2b</th>
<th>9.1c</th>
<th>9.2c</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.2 in Toluene (Ar)</td>
<td>19</td>
<td>67</td>
<td>7</td>
<td>0</td>
</tr>
<tr>
<td>9.2 in Toluene (O₂)</td>
<td>0</td>
<td>34</td>
<td>3</td>
<td>55</td>
</tr>
<tr>
<td>9.2@OA₂</td>
<td>5</td>
<td>90</td>
<td>0</td>
<td>5</td>
</tr>
</tbody>
</table>

Following the above experiments, we studied the photolysis of 9.3 inside OA capsule and the reaction progress was monitored by ¹H NMR (Figure 9.8). 9.3 has only one extra methylene group in the alkyl chain that connects the azido group and acetophenone chromophore when compared to 9.2. Scheme 9.6 shows the products that are obtained upon photolysis of 9.3 in both deaerated and oxygen saturated CH₃CN.

Scheme 9.6. Products obtained from the photolysis of 9.3 in deaerated and oxygen saturated CH₃CN.
Figure 9.8. Photolysis of 9.3@(OA)$_2$ monitored by $^1$H NMR (500 MHz, 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O) spectra. OA [OA] = 1 mM and [9.3] = 0.5 mM. “*” indicates the OA encapsulated 9.3 aliphatic proton peaks. "●" represents the residual solvent peak of water.

The major product produced upon photolysis of 9.3 in argon saturated CH$_3$CN is 9.3a along with 9.3b and 9.3c but under aerated conditions the major product observed was 9.3c and 9.3d (Table 9.2). Irradiation of 9.3 inside OA capsule produces 9.3a and 9.3b as the major products without any trace of 9.3c and 9.3d. The absence of 9.3d can be attributed to the restricted interaction of the intermediate produced from 9.3 with other reactants due to OA confinement.
Table 9.2. Distribution ratios of products obtained upon photolysis of 9.3 in various media.

<table>
<thead>
<tr>
<th>Medium</th>
<th>9.3a</th>
<th>9.3b</th>
<th>9.3c</th>
<th>9.3d</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.3 in CH$_3$CN (Ar)</td>
<td>56</td>
<td>20</td>
<td>24</td>
<td>0</td>
</tr>
<tr>
<td>9.3 in CH$_3$CN (O$_2$)</td>
<td>0</td>
<td>0</td>
<td>34</td>
<td>66</td>
</tr>
<tr>
<td>9.3@(OA)$_2$</td>
<td>56</td>
<td>44</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

The last triplet nitrene precursor that we studied is 9.4. Irradiation of 9.4 in toluene in the presence and absence of oxygen obtains two sets of products. Under argon saturated conditions 9.4 produces 9.4a, 9.4b and 9.4c (Scheme 9.7), and the percentage of 9.4b seems to be higher (Table 9.3). Photolysis of 9.4 in oxygen saturated toluene obtains 9.4c as the major product along with 9.4b and 9.4d in substantial amounts (Scheme 9.7). It has been previously reported that the formation of triplet nitrenes can be detected by carrying out the reaction in the presence of oxygen that traps the nitrene intermediate to form nitro compounds. Photoysis of 9.4@(OA)$_2$ yielded 9.4c as the major product with trace amount of 9.4a and 9.4b (Table 9.3). The absence of 9.4d can be attributed to the fact that, since the reaction happens inside the OA capsule, the possibility of the triplet nitrene produced to react with the oxygen molecule dissolved in the external buffer solution has been curtailed by the confinement.
Scheme 9.7. Products obtained from the photolysis of 9.4 in deaerated and oxygen saturated toluene.

Table 9.3. Distribution ratios of products obtained upon photolysis of 9.4 in various media.

<table>
<thead>
<tr>
<th>Medium</th>
<th>9.4a</th>
<th>9.4b</th>
<th>9.4c</th>
<th>9.4d</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.4 in Toluene (Ar)</td>
<td>16</td>
<td>55</td>
<td>29</td>
<td>0</td>
</tr>
<tr>
<td>9.4 in Toluene (O₂)</td>
<td>0</td>
<td>23</td>
<td>60</td>
<td>17</td>
</tr>
<tr>
<td>9.4 @(OA)_2</td>
<td>3</td>
<td>3</td>
<td>94</td>
<td>0</td>
</tr>
</tbody>
</table>

9.4. Conclusion.

The results presented in this chapter clearly establish the importance of confinement in controlling the nature of the photoproducts obtained from triplet nitrenes generated from their precursors having a inbuilt triplet sensitizer. The NMR spectra recorded after extracting the photoproducts from the irradiated samples indicate that the triplet nitrenes generated inside the OA capsule are not hostile to the host. The absence of dimer formation and other products that would have formed by interacting with solvents
or oxygen suggests that, restricting the reactive species within a confined space governs the outcome of the whole reaction. Thus the above results corroborate the feasibility of controlling reaction mechanisms that involve a triplet nitrene towards a particular path by supramolecular incarceration of the starting compound.

9.5. Experimental Section.

General protocol for determining the host-guest complex nature using $^1$H NMR.

600µL of stock solution of host (1 mM OA in 10 mM Na$_2$B$_4$O$_{7}$) was added to an NMR tube. To this, aliquots (1 µL, 0.1 mM) of a 60 mM solution of the azido triplet nitrene precursor in DMSO-$d_6$ was added until the ratio of the host:guest (H:G) was achieved 1:0.7. The NMR tube was sonicated for a minute after each addition of the guest solution. $^1$H NMR (Bruker 500 MHz NMR spectrometer at 25 °C) spectrum was recorded after each addition of the guest aliquots to the host solution.

General protocol for the photolysis of azido guests@(OA)$_2$.

A 2:1 (H:G) solution was prepared in a Pyrex NMR tube. The solution was purged with N$_2$ for 15 min and irradiated in a Rayonet reactor. The progress of the reaction of was followed by recording $^1$H NMR spectra at different time intervals. The reaction was stopped when about 30-40 % of the starting material was converted to products in order to avoid any secondary photoreactions. The photoproducts were extracted with CHCl$_3$, dried over anhydrous Na$_2$SO$_4$, concentrated and analyzed by GC (HP-5890 series II gas chromatograph fitted with an HP-1 capillary column to obtain the product distribution. The sample was also injected in GC-MS to confirm product identity products.
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