Controlling Photoreactions in Crystals and through Confinement in Water Soluble Supramolecules

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CONTROLLING PHOTOREACTIONS IN CRYSTALS AND THROUGH CONFINEMENT IN WATER SOLUBLE SUPRAMOLECULES

By

Barnali Mondal

A DISSERTATION

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CONTROLLING PHOTOREACTIONS IN CRYSTALS AND THROUGH
CONFINEMENT IN WATER SOLUBLE SUPRAMOLECULES

Barnali Mondal

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The research presented in this thesis reports various uses of supramolecules in steering photochemical and photophysical properties of small organic guest molecules. Crystals possess long range periodic arrangement of highly ordered building units and are considered as supramolecular systems. The first part of the thesis reports the use of crystals as a confined media (solid state) in directing photochemical reactions. In particular, olefins (trans 4-stilbazoles) have been directed to undergo selective [2+2] cycloaddition in solid state. Selective photoproduct in crystals is controlled by various weak interactions in crystal lattice, which bring (pack) the reactive C=C bonds within 4.2 Å. Photoreaction is achieved by irradiating solid samples with UV light (>320 nm); products are analyzed by $^1$H NMR and crystal structure analysis. Although, trans 4-stilbazole molecules are photo inert, they have been directed to yield selective photoproduct (anti head-tail dimer) by forming 4-stilbazole. HCl. Crystal structure analysis of seven trans 4-stilbazole. HCl derivatives undoubtedly confirm that H$_2$O molecules and Cl$^-$ plays an important role in packing the trans 4-stilbazole. HCl derivatives within reactive distance (Chapter 2). Our curiosity to understand the role of H$_2$O molecules in the packing, drove us to study the photoreaction of anhydrous trans 4-stilbazole. HCl salts. The anhydrous stilbazole.HCl salts were either found to be photo
inert or slow reacting compared to the H₂O containing crystals and crystal structure analysis of the anhydrous crystals provided evidence of observed photoinertness or slow reaction.

To investigate cis –trans isomerization in crystals we studied the photoreaction of cis 4-stilbazole. HCl in solid state (Chapter 3). cis –trans isomerization in crystals requiring ample molecular motion was achieved by irradiating solid samples of cis 4-stilbazole. HCl salts. ¹H NMR studies of irradiated samples provide evidence of cis to trans isomerization and upon prolonged irradiation produce anti head-tail dimer.

The second part of this thesis reports use of water-soluble supramolecular host molecules in solution (H₂O). Our interest in exploring interaction between an excited organic molecule and gold atoms required us to synthesize water-soluble gold nanoparticles stabilized by water soluble hosts molecules (Chapter 4). Water soluble hosts known as octa acids (OA, ROA), each containing eight acid groups were effective in stabilizing water soluble gold-nanoparticles (~10 nm sized). Gold nanoparticles were characterized using UV-Vis, DLS, TEM, TGA, IR, and ¹H NMR analysis. Guest inclusion within cavitand-functionalized nanoparticles resulted in quenching of excited singlet and triplet state due to the influence of gold via energy and electron transfer process.

Although water soluble host molecules are already known to control and direct reactivity of small guest molecules, when encapsulated within the host cavity, its potential to act as electron donor/acceptor is not well explored (Chapter 5). We investigated the water-soluble host molecules OA and ROA and established their usefulness as an electron donor to positively charged electron acceptors (external guests)
and also established their potential as a triplet sensitizer. **Chapter 6** establishes that water-soluble gold-glutathione clusters (< 1nm size) can act as a good electron donor. Unlike gold nanoparticles, small sized gold clusters are emissive and low toxicity, ultra small size, and good biocompatibility, makes them ideal as imaging probes. Glutathione protected Au-clusters (~1 nm) are water soluble, has a strong emission around 600 nm and is established to be a good electron donor in the research discussed in **Chapter 6**.
I dedicate my dissertation work to my family. A special feeling of gratitude to my grandfather (Haripada Mondal) for being my inspiration, loving parents Chabbi and Purnendu Mondal for their encouragement, my sister Bipasha, for always being on my side and husband Chiradip, for his constant support.
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**Chapter 3**

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**Chapter 4**

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Chapter 1. Introduction

1.1 Background of supramolecular chemistry

Over the past century, growth of synthetic organic chemistry has resulted in a robust control over making and breaking covalent bonds.\(^1\,^2\) Synthesis of complex molecules could be often a challenging task where every functional group needs to be placed in a specific position and conformation. So, organic synthesis is referred to as “an exact science and a fine art”.\(^3\) The birth of organic syntheses occurred in the 1800’s, when researchers were focused in exploring chemical reactions, mechanism, and their applications to build new molecules. In the 1900’s with enormous scientific and technological evolution, research on organic syntheses was focused on more complex strategy known as “target oriented synthesis”.\(^4\) Development of retrosynthetic analysis (deconstructing a target molecule into simpler precursor) by E. J. Corey had a immense impact in opening up new synthetic strategies in organic syntheses.\(^5\) Brilliant contributions from great chemist like Woodward,\(^6\,^11\) Stork,\(^12\,^14\) Barton,\(^15\,^16\) Johnson,\(^17\,^18\) Robinson,\(^19\) Diels, Alder\(^20\) etc. resulted in impressive development and insights in organic syntheses. With the innovations in technology in analytical chemistry, targeted organic synthesis is considered to be accountable for the significant and most exciting breakthroughs in chemistry, biology, and medicine.

Although chemists had mastered the syntheses of complex molecules, they were still striving to understand the behavior of small molecules in biological environment. In biological environment, molecules work in a cooperative fashion to form complex entities (e.g., DNA, proteins, enzymes) with properties and functions outside the competence of the individual components. Biological structures are typically made from
loose aggregates that are held together by weak, noncovalent interactions. These weak interactions, hold the individual components together and are responsible for most of the processes occurring in biological systems.\textsuperscript{21} Researchers have applied the importance of non-covalent interactions in preorganizing smaller structural units into complex, well-defined entities (i.e., supramolecules) with unique structures, properties, and functions. The use of noncovalent interactions to design synthetic supermolecules created a new chemical discipline. Jean-Marie-Lehn named this branch of chemistry as “supramolecular chemistry” and defined it as “chemistry beyond molecules”.\textsuperscript{22}

In supramolecular chemistry, the emphasis has been shifted from the study of individual molecules to molecular assemblies. The structure and properties of a supramolecule is often distinct from the properties of the chemical species or units of which it is composed. The importance of this branch of chemistry was recognized by the 1987 Nobel Prize for Chemistry to Donald J. Cram,\textsuperscript{23,24} Jean-Marie Lehn, and Charles J. Pedersen,\textsuperscript{25} for their pioneering work on crown ethers, cryptand and carcerandes. Since then, with the growth of supramolecular chemistry, researchers have been able to gain control over the behavior and reactivity of small molecules. Generally these supramolecules are referred as ‘host’ molecule, with a cavity where small molecules, ‘guest’ could be accommodated. The literature has examples of a variety of synthetic supramolecules, where some are formed by self-assembly of small molecules (held by weak non-covalent interaction), e.g. micelles, liquid crystals, Fujita’s host etc. and some are synthesized by covalent attachments of one or more units, e.g. crown ethers, cyclodextrin, cucurbituril, octa acid, dendrimers etc.
**Figure 1.1** Structure of some supramolecular host systems

1.2 Non-covalent interactions

Weak interactions such as cation –π, π- π, H-bond, van der Waals interactions etc. are extremely important to construct self assembled supramolecules and in binding small molecules within the supramolecular cavity. These interactions also play a pivotal role in controlling the chemical behavior of the encapsulated small molecules. Although, these interactions are much feebler than covalent interactions, but multiple weak interactions are crucial in forming self-assembly and host-guest binding. Various weak interactions and there importance are discussed in brief.

(i) Electrostatic interaction includes ion-ion, and ion-dipole interactions. Ion-ion interactions are strongest with energies in the range of 100-350 kJ/mol and ion-dipole interactions have energies in the range of 50-200 kJ/mol. While ion-ion interaction is direction independent, ion-dipole interaction requires a particular
orientation to interact strongly (ion and dipole should be face-to-face). Cation – π interaction is also a form of ion-dipole interaction. Cations binding to crown-ethers, cationic guests binding within electron rich cucurbiturils are some examples of electrostatic interactions in supramolecular chemistry. Mg ions associated with RNA and DNA molecules in vivo are examples of electrostatic interaction in nature.

(ii) Van der Waals interactions are attractive or repulsive interactions between neutral molecules. The individual interaction energy is small (0.5-5 kJ/mol), and includes dipole-dipole, dipole-induced dipole, and induced dipole-induced dipole interactions. Although these interactions are weak, they are crucial for formation of cell walls, vesicles, membranes, micelles, and also important for holding self-assembled supramolecules.

(iii) π- π interactions are the attractive interactions between two aromatic rings. Alignment of positive electrostatic potential of one ring with negative electrostatic potential on another ring forms stacking of π clouds. The stacking could be displaced (off-set), edge-to face (T-shaped), or sandwich type. (Figure 1.2). π- π interactions play an important role in folding and stability of proteins, base pair stacking of DNA, template-directed synthesis etc.

(iv) Hydrogen–bonding is one of the most important non-covalent interactions, and is crucial for forming double stranded-DNA, secondary and tertiary structures of protein, nucleic acids. H bonding also plays an important role in supramolecular chemistry. Strength of H-bonds can vary from 1-40 kJ/mol.
Figure 1.2 Various non-covalent weak interactions.

1.3 Water soluble hosts

With the advancements in the various synthetic macromolecules and understanding of non-covalent interactions, researchers were interested in synthetic macromolecules (host), which could bind to guest in water, to mimic the biological system. Most of the macromolecules synthesized so far were soluble in organic solvents (crown ether, cryptand, resorcinarene etc.). To develop model systems comparable to nature, water-soluble hosts systems were important. With the progress in supramolecular chemistry, researchers have synthesized water-soluble host molecule, e.g. cyclodextrins, calixerenes, cucurbiturils, Pd-nanocage, dendrimers, and octa acid. Cyclodextrin (CD) are a family of hosts made up of glucopyranose units, usually having six (α), seven (β), or eight units (γ). The shape of the cyclodextrins are like a truncated cone with the wider rim lined with secondary alcohol groups, and narrow rim lined up with primary alcohol. This makes the upper rim of CD
hydrophilic, while the lower rim is hydrophobic in nature (Figures 1.3). CDs have a variety of commercial applications, including drug delivery system, food, cosmetic, deodorizer, and catalysis. CDs have also been successfully used in selective photoreactions.\textsuperscript{30}

![Figure 1.3 Structure and cavity diameter of $\alpha$, $\beta$, and $\gamma$ cyclodextrin.\textsuperscript{31}}

Cucurbit[n]urils (CB[n]) are a family of supramolecules made up of glycouril units. (Figure 1.4) These pumpkin-shaped host molecules derive its name from the Latin word, \textit{cucurbitaceae} (family name of pumpkin plant).

![Figure 1.4 Structure and cavity diameter\textsuperscript{35} of cucurbit[5]uril, cucurbit[6]uril, and cucurbit[7]uril.]

The carbonyl-lined portals of CBs make it suitable for binding cationic guests, while the hydrophobic interior also binds to hydrophobic guest molecules. CBs have been extensively used in molecular recognition, sensors, catalyzing selective photodimerization.\textsuperscript{32-34} Synthesis of water-soluble host molecule named octa-acid (OA) was reported by Gibb and co-workers in 2004.\textsuperscript{36} The host molecule owes its name from the eight acid group present in its structure. There are four acid groups in the top rim and four acid groups in the bottom rim, which makes it soluble in basic pH ~9. This host molecule stays as a monomer in borate buffer solution at low concentration (~1mM), but has a tendency of aggregation at higher concentration.\textsuperscript{37} OA (Figure 1.5) is able to encapsulate a variety of guest molecules and can form host-guest complexation in three different stoichiometry 1:1, 2:1, or 2:2 (host: guest ratio), depending on the size and nature of guest molecule.\textsuperscript{37} Guest binding, unique photochemical and photo physical properties of guest molecules within octa acid has been extensively studied in the last decade.\textsuperscript{38,39} The research presented in this thesis shows that OA could be useful to stabilize water soluble gold nanoparticles and also as an active cavitand, to undergo electron and energy transfer reaction upon excitation.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{octa_acid.png}
\caption{Structure of octa acid (OA), with cartoon representation showing dimensions.}
\end{figure}
1.4 Crystal as supramolecule and reactive crystals

A crystal is in a sense macroscopic matter where millions of molecules are held together by non-covalent interactions, in a very periodic arrangement. Also, the process of crystallization is a remarkable display of self-assembly, involving exact molecular recognition at an incredible level of precision. Long-range periodicity is a result of directionally specific short-range interactions, which make crystals ordered supramolecular systems.

Crystal engineering was developed with the need to understand intermolecular interactions and recognition phenomena in crystal packing. Building crystals by design is the central goal of crystal engineering. The molecules are the building block of a crystal structure (supramolecule), which are held by weak non-covalent interactions. Ionic interactions (e.g., dipole-dipole) and hydrogen bonds are the two strongest interactions in crystal engineering. Targeted synthesis in organic synthesis, deals with covalent connectivity of atoms, whereas in crystal engineering it deals with weak interaction connectivity, which makes the network to build the crystal. The reactivity of molecules in crystal is solely dependent on the crystal packing. Compare to targeted synthesis in solution, ordered packing in crystals, provides a clean pathway for reaction with high percentage of conversion and ease of purification. Photochemical reactions are the most common reactions carried out in solid state because of simple reaction condition (i.e., UV source), little to no by-products, and in many cases crystallinity of the material is maintained during reaction, while UV light penetrates through the crystal ensuring homogeneity. In this context, cycloaddition reactions e.g., [2+2], [4+4] photo dimerization, [2+2] photo polymerization are common reactions studied in solid state
(Figure 1.6).

![Diagram of photochemical reactions](image)

**Figure 1.6** Photochemical reactions in solid-state a) photo-polymerization, b) [2+2] photo dimerization, and c) [4+4] photo dimerization.

Following the original work by Liebermann in 1871, photoreactions in crystal have been extensively explored with several elegant approaches. In 1970’s Schmidt and co-workers established the symbiotic relationship between molecular packing and photoreactivity of crystals. According to the postulate, two C=C bonds could undergo [2+2] cycloaddition, only if they are parallel and within 4.2 Å distance (Figure 1.7).

![Schmidt’s postulate](image)

**Figure 1.7** Schmidt’s postulate for solid-state photo dimerization.
Schmidt pioneering work also identified, that chloro and fluoro groups, are able to steering groups to close pack olefins within 4.2 Å for photo dimerization (Figure 1.2). This required structural modification of the olefin of interest. Researchers came up with a convenient approach of using independent molecules to steer olefins through non-covalent interactions.

![Figure 1.8 Schematic diagram of photoreaction by templation.](image)

Templation or molecular recognition is the process of using molecules to recognize and bind molecules of interest in a well-defined pattern via non-covalent interactions (Figure 1.8). Toda and co-workers had successfully used various diols to orient olefins through weak intermolecular hydrogen bonds and achieved photo dimerization of chalcone, dibenzylideneactone, pyridones, coumarin, thiocoumarin and cyclohexenone in the crystals. Ito, Scheffer and co-workers had used a similar approach, to make a diamine salt of cinnamic acid towards photo dimerization. This templating strategy has gained much attention with extensive works of groups like MacGillivray and Vittal to study photo dimerization in crystals. In this thesis, we present our results to photodimerize stilbazole derivatives in crystals, in combination with X-ray crystallography, NMR spectroscopy and computational studies.
Chapter 2. Templating photodimerization of trans-stilbazoles in crystals

2.1 Controlling photoreactions in crystals

Although targeted syntheses are mostly exploited in solution, reaction in crystals (solid state) has emerged as a green alternative. The highly ordered structure of crystals provides a fascinating pathway for covalent syntheses. The molecules within the crystalline boundary could be aligned to favor a reaction path resulting in a stereo-selective product. Thus reaction in crystals has potential to improve reaction yield and simplify purification methods. Also molecules can pack in crystal to adopt geometries that might not be possible in solution and consequently provide products that are otherwise challenging to synthesis. In the 1970’s, the pioneering works by Schmidt and co-workers investigating photo dimerization of cinnamic acids established the relationship between molecular packing and photo reactivity of crystals. Since then, several techniques have been exploited to pack molecules in a reactive alignment in crystals. The most popular approach is co-crystallization. This approach requires two-component mixed crystals in which one acts as a template. Weak interactions like H-bonding, vander Waal, π–π, etc., play an important role in packing molecules in crystals. In studying [2+2] cyloaddition reactions, bispyridyl ethylene (two H-bond site) and stilbazole (one H-bond site) derivatives are molecules of interest both in solution and solid state. In recent studies, supramolecular hosts such as curcurbituril, calixarene, and cycloextrin are able to prompt selective dimerization in bispyridyl ethylenes and stilbazole molecules in solution. In solid state, thiourea has been successfully used as a template to result in a selective photodimerized product with bispyridyl ethylenes (containing two hydrogen-bonding center) and stilbazoles (containing one hydrogen-
bonding center). In this chapter, we report the results of our efforts to steer selective photo-dimerization of stilbazoles\textsuperscript{67} (containing single hydrogen-bonding center). We explored the photoreactions of the HCl salt of sixteen substituted \textit{trans}-stilbazoles in solid state. Out of the sixteen substituted \textit{t} stilbazoles investigated, only three (compounds 2.14-2.16) salts did not react by this method. The non-reactive ones helped us to set the limitation of this approach.

![Scheme 2.1](image)

**Scheme 2.1.** Selective photo dimerization of \textit{t} stilazole to anti head-tail dimer

The simple strategy used in this work has been known in the literature since 1961 following the contributions of Williams’ group\textsuperscript{68–70}. It was reported that although 2-stilbazole is inert in solid state, its HCl salt photodimerized when irradiated. We were interested to understand and establish whether the strategy could orient other stilbazole derivatives by correlating the packing of HCl salt crystals (determined through X-ray crystal structure analysis) with their photoreactivity. The strategy used in this study is simple (Scheme 2.1) and provides solvent free ‘green’ approach with considerable potential for further exploration.
Figure 2.1. Structure of trans 4-stilbazoles investigated.

Scheme 2.2 Compound shown in green is obtained while the other possible products (shown in red) are not obtained from irradiation of protonated and hydrated crystals of 2.1-2.13. In the product structures H = head, T = tail.
2.2. Results and discussions

This study consisted of the following aspects: crystallization and crystal structure analysis of the stilbazole. HCl salt, irradiation, and characterization of photoproducts. Irradiation of trans-stilbazoles in solution gives trans-cis isomerization as the major product, \(^{71}\) while their inertness in solid state was evident from the \(^1\)H NMR, after irradiation of several hours. X-ray crystal packing of crystalline trans-4-stilbazoles 2.1\(^{72}\), 2.2 and 2.12 obtained, explains their non-reactivity. The packing arrangement indicates that the C-C bonds of adjacent molecules in them are neither parallel nor within the required 4.2 Å (Schmidt’s postulate), shown in Figure 2.7 a-c. The crystal packing of seven of the thirteen reactive trans stilbazole. HCl salts obtained in this work reveals the reactivity triggering capability of protonation. Results indicated that only three (2.14–2.16) of the trans stilbazoles HCl salt either did not react in the crystalline state or gave a mixture of dimers in low yield, and the remaining thirteen salts resulted in a single (anti-head-tail) dimer in high % conversion (Scheme 2.2). The HCl salts of the stilbazoles were prepared by grinding ~10 mg of trans 4-stilbazole with two equivalents of HCl (37%). After irradiation for hours, the sample was dissolved in water, extracted with CHCl\(_3\) following neutralization with NaOH, and characterized by \(^1\)H NMR spectra. We speculated that long irradiation hours might be result of non-uniform exposure of crystals sandwiched between Pyrex plates, so we irradiated the HCl salt as a suspension in hexane (as the salt was insoluble in hexane). Irradiation as a suspension resulted in smaller irradiation hours and conversion to a single dimer in 95–100% yield with thirteen (2.1–2.13, Figure 2.1) of the sixteen stilbazoles investigated. \(^1\)H NMR analysis of the photoproducts clearly shows there was no other photochemical pathway competing with dimerization of HCl.
salts of 2.1–2.13 in the solid state. Packing of the reactive HCl salts of 2.1, 2.2, 2.3, 2.4, 2.5, 2.8, 2.9 (obtained during this study) and 2.13 (known from literature\textsuperscript{73}) clearly shows that they contain water molecules in their lattice (Figure. 2.2–2.5), while the two unreactive \textit{t} stilbazole salts do not contain water molecules (Figure. 2.6).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2}
\caption{Packing arrangement of (a) \textit{t} 4-stilbazole. HCl (2.1\(\cdot\)HCl\(\cdot\)3H\textsubscript{2}O) (b) \textit{t} 2-napthyl 4-stilbazole.\textit{HCl} (2.13\(\cdot\)HCl\(\cdot\)3H\textsubscript{2}O)\textsuperscript{73} Oxygen of H\textsubscript{2}O represented as red sphere and Cl\textsuperscript{−} as green sphere.}
\end{figure}
This suggests the possible role of water for their reactivity. Close examination of packing arrangements of the photo reactive $\tau$ stilbazole-HCl salts with water molecules in their lattice leads to the following conclusions:

(a) Adjacent pairs of stilbazole molecules are within 4.2 Å and parallel to one another.

(b) The two olefins are arranged in a head to tail centro-symmetric fashion with respect to one another (i.e., $\alpha$- packing as per Schmidt’s cinnamic acid nomenclature$^{74}$).

(c) The pairs of molecules upon excitation could smoothly transform to anti-head–tail dimer.

(d) Although the elegant ladder-like stacking of stilbazole molecules in the lattice seems similar between the diagrams, the side rails holding the rungs of the ladder differ significantly between the eight reactive molecules. Last observation is quite different from the thiourea template we reported earlier$^{66}$ where the rungs and side rails looked closely similar for the ten different stilbazoles.

(e) As illustrated (Figure 2.8), there are six different arrangements for the side rails made up of water molecules and chloride ions for the eight protonated stilbazoles.

(f) In all cases, the ladder-like packing of the reactive protonated stilbazoles are held by the rungs made up of water molecules or chloride ions. A combination of water and chloride ion holds the stilbazoile–H$^+$ through either N–H⋯O or N–H⋯Cl$^-$ interactions. Five packing arrangements are held by N–H⋯O bonding (Figure 2.2-2.3)$^{75,76}$ and three by N–H⋯Cl$^-$ (Figure 2.4).
(g) The hydrogen bonding between the three, pyridinium N–H, H₂O and Cl⁻ ions are interdependent for the stability and arrangement of the lattice.

The expected anti-head-tail dimers from these olefins are evident from the packing arrangements (Figure 2.3-2.4) and was also confirmed with the X-ray crystal structures of the dimers, isolated after irradiation of the HCl salts of 2.3, 2.4 and 2.5 (Figure 2.6). Comparison of ¹H NMR spectra of cyclobutane signals from dimer obtained from irradiation of salts of 2.1, 2.2, and 2.6-2.13 and with those from 2.3, 2.4 and 2.5 (Figure 2.20) is suggest anti-head-tail configuration in all of them. As expected -CH₂CH₃ and -OCH₃ substituents (2.7 and 2.8), despite the large size favored dimerization.

All mono halogen substituents (generally considered to be inductively electron withdrawing) also favored close packing in head-tail fashion, suggesting that with respect to the pyridinium group, the halogen-substituted phenyl is electron rich. Surprisingly, even electron withdrawing NO₂ and CF₃ substitution did not prevent the two molecules of stilbazolium salts from packing within 4 Å. To test the limitation of this protonation strategy three molecules (2.14, 2.15 and 2.16), substituted with highly electron withdrawing groups, were examined.
Figure 2.3 Packing arrangement of (a) 4-Bromo-stilbazole.HCl (2.4·HCl·3H₂O) (b) 4-Iodo-stilbazole.HCl (2.5·HCl·2H₂O) (c) 4-CF₃-stilbazole.HCl (2.9·HCl·3H₂O). Oxygen of H₂O represented as red sphere and Cl⁻ as green sphere.
Figure 2.4 Packing arrangement of (a) *t*-4-Fluoro-stilbazole.HCl (2.2.HCl·3H₂O) (b) *t*-4-Chloro-stilbazole.HCl (2.3.HCl·3H₂O) (c) *t*-4-MeO-stilbazole.HCl (2.8·HCl·3/8H₂O) Oxygen of H₂O and –OCH₃ represented as red sphere and Cl⁻ as green sphere.
Figure 2.5 Packing arrangement of non-reactive derivatives (a) t 3,5 diChloro-stilbazole.HCl (2.14.HCl) (b) t 2,3,4,5,6,7 penta Fluoro-stilbazole.HCl (2.16.HCl). Cl\(^{-}\) is represented as green sphere.

Figure 2.6 Crystal structure of dimer obtained from irradiating HCl salts of (a) 4-Cl stilbazole (2.3) (b) 4-Br stilbazole (2.4) (c) 4-I stilbazole (2.5)
The presence of dichloro or pentafluoro substituents is expected to deactivate the phenyl group in these examples from charge transfer interaction with another electron-deficient π-cloud (pyridinium). Stilbazoles 2.14 and 2.15 upon irradiation as a crystal gave *syn*-**head-head** dimers quantitatively, while 2.16 gave *anti*-**head-tail** dimer as observed from the crystal structure and 1H NMR studies (*Figure 2.7 and 2.23-2.25*).
Upon protonation and irradiation as salts, all three molecules were photoinert. Of the sixteen stilbazolium salts used in this study, only these three did not dimerize. The packing arrangement for HCl salts of 2.14 and 2.16 (Figure 2.5) is distinctly different from that of the reactive ones. The distance between C=C bonds is ~5 Å (much larger than the topochemical criterion of 4.2 Å) and the bonds are displaced with respect to one another. Interaction between Cl$^-$ atoms is also evident in the packing.
**Figure 2.9** $^1$H NMR in CDCl$_3$ of cyclobutane protons in dimer products obtained from HCl salts of stilbazole derivatives.

Although unsuccessful at obtaining good quality crystals for 2.15·HCl, we believe that based on its photochemical behavior that the packing in this case would not favor dimerization. Thus, HCl salt of stilbazoles 2.14, 2.15 and 2.16 with highly electron-deficient phenyl groups set the limit for protonation strategy.

To conclude this section we report that protonation of the pyridyl ring of stilbazole is efficient enough in bringing two unreactive C=C closer in the crystalline state to result in dimerization. The molecular packing reveals that the two olefins are held by hydrogen bonding tapes on both sides of the stilbazole. HCl salts with the aid of H$_2$O and counter ion Cl$^-$. 
2.2.1 $^1$H NMR analysis of photoproducts of hydrous $\tau$ Stilbaze. HCl

After irradiation the photoproducts were neutralized with aqueous solution of NaOH, extracted with chloroform and analyzed by $^1$H NMR. Similarly, samples irradiated in hexane suspension, were also neutralized and analyzed by $^1$H NMR. For comparison $^1$H NMR of neutral stilbazoles were also recorded. $^1$H NMR of all the stilbazoles (2.1-2.16) investigated are presented below.

**Figure 2.10** (a) $^1$H NMR in CDCl$_3$ of 4-stilbaze (2.1) (b) after irradiation of 4-stilbaze for 20 h in solid state, (c) neutral extract of 4-Stilbaze. HCl, irradiated for 37 h in solid state, (d) neutral extract of 4-Stilbaze. HCl irradiated for 10 h as suspension in hexane. Aromatic proton *ortho* to N in pyridyl ring is denoted by ‘★’ for *trans* and ‘■’ for *anti* H-T dimer.
Figure 2.11 (a) $^1$H NMR in CDCl$_3$ of 4F-stilbazole (2.2) (b) after irradiation of 4F-stilbazole for 52 h in solid state, (c) neutral extract of 4F-stilbazole. HCl, irradiated for 62 h in solid state, (d) neutral extract of 4F-stilbazole. HCl irradiated for 12 h as suspension in hexane. Aromatic proton ortho to N in pyridyl ring is denoted by ‘★’ for trans and ‘■’ for anti H-T dimer.
Figure 2.12 (a) $^1$H NMR in CDCl$_3$ of 4Cl-stilbazole (2.3) (b) after irradiation of 4Cl-stilbazole for 52 h in solid state, (c) neutral extract of 4Cl-stilbazole. HCl, irradiated for 44 h in solid state, (d) neutral extract of 4Cl-stilbazole. HCl irradiated for 6 h as suspension in hexane. Aromatic proton ortho to N in pyridyl ring is denoted by ‘★’ for *trans* and ‘■’ for *anti* H-T dimer.
Figure 2.13 (a) $^1$H NMR in CDCl$_3$ of 4Br-stilbazole, (2.4) (b) after irradiation of 4Br-stilbazole for 10 h in solid state, (c) neutral extract of 4Br-stilbazole. HCl, irradiated for 5 h in solid state, (d) neutral extract of 4Br-Stilbazole. HCl irradiated for 3 h as suspension in hexane. Aromatic proton ortho to N in pyridyl ring is denoted by ‘★’ for trans and ‘■’ for anti H-T dimer.
Figure 2.14 (a) $^1$H NMR in CDCl$_3$ of 4I-stilbazole, (2.5) (b) after irradiation of 4I-stilbazole for 91 h in solid state, (c) neutral extract of 4I-stilbazole. HCl, irradiated for 91 h in solid state, (d) neutral extract of 4I-stilbazole. HCl irradiated for 31 h as suspension in hexane. Aromatic proton ortho to N in pyridyl ring is denoted by ‘★’ for trans and ‘■’ for anti H-T dimer.
Figure 2.15 (a) $^1$H NMR in CDCl$_3$ of 4-methyl-stilbazole, (2.6) (b) after irradiation of 4-methyl-stilbazole for 98 h in solid state, (c) neutral extract of 4-methyl-stilbazole. HCl, irradiated for 37 h in solid state, (d) neutral extract of 4-methyl-stilbazole. HCl irradiated for 23 h as suspension in hexane. Aromatic proton ortho to N in pyridyl ring is denoted by ‘★’ for trans and ‘■’ for anti H-T dimer.
Figure 2.16 (a) $^1\text{H}$ NMR in CDCl$_3$ of 3-methyl-stilbazole, (2.11) (b) after irradiation of 3-methyl-stilbazole for 37 h in solid state, (c) neutral extract of 3-methyl-stilbazole. HCl, irradiated for 19 h in solid state, (d) neutral extract of 3-methyl-stilbazole. HCl irradiated for 19 h as suspension in hexane. Aromatic proton ortho to N in pyridyl ring is denoted by ‘★’ for trans and ‘■’ for anti H-T dimer.
Figure 2.17 (a) $^1$H NMR in CDCl$_3$ of 4-ethyl-stilbazole, (2.7) (b) after irradiation of 4-ethyl-stilbazole for 120 h in solid state, (c) neutral extract of 4-ethyl-stilbazole. HCl, irradiated for 130 h in solid state, (d) neutral extract of 4-ethyl-stilbazole. HCl irradiated for 112 h as suspension in hexane. Aromatic proton ortho to N in pyridyl ring is denoted by ‘★’ for $trans$ and ‘■’ for $anti$ H-T dimer.
Figure 2.18 (a) $^1$H NMR in CDCl$_3$ of 4-methoxy-stilbazole, (2.8) (b) after irradiation of 4-methoxy-stilbazole for 52 h in solid state, (c) neutral extract of 4-methoxy-stilbazole. HCl, irradiated for 60 h in solid state, (d) neutral extract of 4-methoxy-stilbazole. HCl irradiated for 46 h as suspension in hexane. Aromatic proton ortho to N in pyridyl ring is denoted by ‘★’ for trans and ‘■’ for anti H-T dimer.
Figure 2.19 (a) $^1$H NMR in CDCl$_3$ of 3, 4-dimethoxy-stilbazole, (2.12) (b) after irradiation of 3, 4- dimethoxy-stilbazole for 72 h in solid state, (c) neutral extract of 3, 4- dimethoxy-stilbazole. HCl, irradiated for 168 h in solid state, (d) neutral extract of 3, 4- dimethoxy-stilbazole. HCl irradiated for 72 h as suspension in hexane. Aromatic proton ortho to N in pyridyl ring is denoted by ‘★’ for trans and ‘■’ for anti H-T dimer.
Figure 2.20 (a) $^1$H NMR in CDCl$_3$ of 4-CF$_3$-stilbazole, (2.9) (b) after irradiation of 4-CF$_3$-stilbazole for 52 h in solid state, (c) neutral extract of 4-CF$_3$-stilbazole. HCl, irradiated for 37 h in solid state, (d) neutral extract of 4-CF$_3$-stilbazole. HCl irradiated for 42 h as suspension in hexane. Aromatic proton ortho to N in pyridyl ring is denoted by ‘★’ for trans and ‘!’ for anti H-T dimer.
Figure 2.21 (a) $^1$H NMR in CDCl$_3$ of 4-NO$_2$-stilbazole (2.10) (b) after irradiation of 4-NO$_2$-stilbazole for 69 h in solid state, (c) neutral extract of 4-NO$_2$-stilbazole. HCl, irradiated for 65 h in solid state, (d) neutral extract of 4-NO$_2$-stilbazole. HCl irradiated for 150 h as suspension in hexane. Aromatic proton ortho to N in pyridyl ring is denoted by ‘★’ for trans and ‘■’ for anti H-T dimer.
Figure 2.22 (a) $^1$H NMR in CDCl$_3$ of 2-naphthyl-stilbazole,(2.13) (b) after irradiation of 2-naphthyl- stilbazole for 40 h in solid state, (c) neutral extract of 2-naphthyl-stilbazole. HCl, irradiated for 140 h in solid state, (d) neutral extract of 2-naphthyl-stilbazole. HCl irradiated for 22 h as suspension in hexane. Aromatic proton ortho to N in pyridyl ring is denoted by ‘★’ for trans and ‘■’ for anti H-T dimer.
Figure 2.23 (a) $^1$H NMR in CDCl$_3$ of 3,5-dichloro-stilbazole (2.14) (b) after irradiation of 3,5- dichloro-stilbazole for 96 h in solid state, (c) neutral extract of 3,5-dichloro-stilbazole. HCl, irradiated for 150 h in solid state, (d) neutral extract of 3,5-dichloro-stilbazole. HCl irradiated for 150 h as suspension in hexane. Aromatic proton ortho to N in pyridyl ring is denoted by ‘★’ for trans and ‘■’ for anti H-T dimer.
Figure 2.24 (a) $^1$H NMR in CDCl$_3$ of 2,4-dichloro-stilbazole, (2.15) (b) after irradiation of 2,4- dichloro-stilbazole for 96 h in solid state, (c) neutral extract of 2,4-dichloro-stilbazole. HCl, irradiated for 183 h in solid state, (d) neutral extract of 2,4-dichloro-stilbazole. HCl irradiated for 158 h as suspension in hexane. Aromatic proton ortho to N in pyridyl ring is denoted by ‘★’ for trans and ‘■’ for anti H-T dimer.
Figure 2.25 (a) $^1$H NMR in CDCl$_3$ of 2,3,4,5,6 pentafluoro-stilbazole, (2.16) (b) after irradiation of 2,3,4,5,6 pentafluoro-stilbazole for 84 h in solid state, (c) neutral extract of 2,3,4,5,6 pentafluoro- stilbazole. HCl, irradiated for 129 h in solid state, (d) neutral extract of 2,3,4,5,6 pentafluoro- stilbazole. HCl irradiated for 84 h as suspension in hexane. Aromatic proton ortho to N in pyridyl ring is denoted by ‘★’ for trans and ‘■’ for anti H-T dimer.
2.3 Photo reactions of anhydrous \( \text{t Stilbazole. HCl} \)

To crystal structures of reactive stilbazole·HCl salts shows the water plays an important role in bringing the C=C to close proximity necessary for cycloaddition. To understand the role of H\(_2\)O in the packing we crystallized the stilbazole·HCl salts under dry conditions and examined for reactivity by irradiation (for the same time periods by which time the hydrated crystals dimerized). The anhydrous stilbazole. HCl salts were either found to be photo inert or slow reacting compared to the H\(_2\)O containing crystals (hydrated salts). The progresses of the reaction of the anhydrous and hydrous crystals were monitored by irradiating the two samples under same condition and for same duration of time. crystals of 4-iodo- stilbazole, an example indicates that while the hydrous sample has dimerized to about 49%, (with 5 h of irradiation) the dry sample has not reacted.\(^8^0\) Reaction observed with other anhydrous crystals was slower compared to hydrous crystals. For comparative (dry and wet samples) studies the solids were irradiated for a shorter time to prevent the dry samples from absorbing moisture from the humid laboratory. Presence of H\(_2\)O in hydrous and absence of H\(_2\)O in anhydrous crystalline powder were confirmed by estimating the water content by TGA (Table 1). The water content as measured by thermogravimetry and estimated from crystal unit cell are close and in the range of 10–20%. The difference in water content in some cases between TGA measurements and that estimated from X-ray crystal structures is possibly due to the nature of samples used for these two studies; powder for TGA and single crystals for X-ray data collection. To shed more light on the lack of reactivity of anhydrous crystals attempts were made to obtain single crystals of anhydrous HCl salts. However, only three anhydrous samples (2.3–2.5) gave single crystals suitable for X-ray
analysis. The packing arrangements as obtained from X-ray structure shows two of these crystals (Figure 2.26) contained methanol from the crystallization solvent instead of water in the lattice and two of the them had no solvent in their lattice (Figure 2.27 a and b). The crystal packing of anhydrous crystals accounts for their inertness as in all the cases the C=C distance is >4.7 Å apart and the olefinic π-bonds are slipped with respect to each other. Experiments with anhydrous salts make it is clear that water molecules play a critical role in templating the protonated stilbazoles toward photo dimerization in crystals.

**Figure 2.26** Anhydrous structures (a) 3·HCl·MeOH (b) 4·HCl·MeOH. Oxygen of methanol represented as red sphere and Cl− as green sphere.
Figure 2.27 Anhydrous structures (a) 5·HCl (b) 6·HCl·Cl− is represented as green sphere. Data for (b) taken from ref. 81.
**Figure 2.28** TGA of t 4-chloro stilbazole. HCl.2H₂O showing 11% mass loss (red line) and anhydrous t 4-chloro stilbazole. HCl showing no mass loss (green line).

<table>
<thead>
<tr>
<th>Sample</th>
<th>% H₂O loss from TGA experiment</th>
<th>% H₂O present in crystal structure</th>
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<td>2.1.HCl.3H₂O</td>
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<td>19</td>
</tr>
<tr>
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<td>19</td>
</tr>
<tr>
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<td>12</td>
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<tr>
<td>2.4.HCl.2H₂O</td>
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<td>10</td>
</tr>
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<td>9</td>
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<tr>
<td>2.13.HCl.3H₂O</td>
<td>13.1</td>
<td>17*</td>
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**Table 2.1.** Water content measured by TGA compared to water content in crystal structure. *Data taken from ref. 73
It is apparent from Figure 2.26 and 2.27 that without water, Cl\(^{-}\) alone cannot build a rail to hold the rungs of the ladder. The above studies have established that templation of the protonated \(t\)-stilbazoles could be brought about with a composite of H\(_2\)O and Cl\(^{-}\) ion. Both are essential for the photo dimerization of protonated \(t\)-stilbazoles in the solid state.

2.3.1 Computational analysis

Literature study proposes cation–\(\pi\) interaction to be important in packing of protonated \(trans\)-stilbazole molecules in a photodimerizable arrangement.\(^{73,81-83}\) In our study crystal structure of anhydrous \(t\) stilbazole. HCl salts provides evidence for their non reactivity and suggests that cation–\(\pi\) interaction is less important than hydrogen bonding of N–H with H\(_2\)O and Cl\(^{-}\) ion. More importantly, we reasoned that in protonated stilbazoles the positive charge would be localized on the N–H \(\sigma\)-bond rather than on the \(\pi\)-cloud of the pyridyl ring. If this is true we believed that the two reactive olefins would be perpendicular to each other and would not be in the correct geometry for dimerization.

![Figure 2.29](image)

**Figure 2.29** Charge distribution in the case of protonated \(trans\)-stilbazole as calculated by at the B3LYP/6-311+G(d,p) level
Figure 2.30 Structures and energies of pairs of protonated trans-stilbazole molecules in the gas phase optimized at the second-order Møller–Plesset (MP2) level of theory using the 6-31G(d) basis set.

To understand the geometry by computation we collaborated with Dr. Prabhakar group. The location of the positive charge in the protonated stilbazole was examined by optimizing the structure at the B3LYP/6-311+G (d,p) level and the charges on all atoms were calculated. The charges on the optimized structure (Figure 2.29) shows that the carbon atoms carry the negative charge and all the hydrogen atoms are positively polarized. As intuitively predicted the hydrogen atom bound to the nitrogen atom (N–H) carries the largest positive charge (+0.43) and the negative charge (−0.47) resides on the nitrogen atom. This clearly suggests that the protonated stilbazole is positively polarized along the N–H σ bond. To probe how this positively polarized N–H bond would interact with another protonated stilbazole we optimized four structures (Figure 2.30 a–d) at the
second-order Møller–Plesset (MP2) level of theory using the 6-31G(d) basis set.\textsuperscript{84-86} In Figure 2.30 two structures (a and d) correspond to the N–H bond being oriented towards the $\pi$ cloud of the two rings (cation–$\pi$ interaction), pyridyl and phenyl and the other two structures correspond to the two olefin molecules being one on top of each other in a parallel fashion in head to tail (b) and head to head (c) fashion. Because the pyridyl part is electron deficient and the phenyl part is relatively electron rich the structure (b) could be more stable due to charge transfer interaction and the arrangement (d) would be least stable due to charge repulsion. Of the four structures shown only the head–tail arrangement (Figure 2.30 b) would give the observed dimer. According to MP2 calculations, of the four arrangements the most stable one in the gas phase is the structure shown in Figure 2.30 a, in which the two olefins are nearly perpendicular to each other. The next most stable one is the head–tail arrangement shown in Figure 2.30 b, in this case the stability (although lower than cation–$\pi$ interaction) results from charge-transfer interaction between the electron deficient pyridyl and electron rich phenyl rings. The fact that this arrangement is preferred in crystals, according to crystal structure analysis (Figure 2.2–2.4), suggests that hydrogen bonds between stilbazole–H$^+$ and water molecules or chloride ions provide enough energy to overcome the cation–$\pi$ interaction. Thus based on MP2 calculations we conclude that the packing in protonated stilbazoles are stabilized by hydrogen bonds and charge transfer interaction\textsuperscript{67} rather than by cation–$\pi$ interaction. Quantum chemical calculations could be a valuable tool in solid-state photochemistry to understand molecular packing in crystals. Photochemistry and crystallography and quantum chemistry can be combined as a valuable technique in answering challenging problems in solid-state photochemistry.
Photo dimerization continues to play a key role in the development of the field of organic solid-state photochemistry. Although history of solid-state photoreactions dates back in the 1800s, the unpredictability of these reactions, retain considerable research interest, as it is yet to become a predictable science. In this work we have identified a mixture of H$_2$O and Cl$^-$ ion can serve as a template to orient protonated stilbazoles toward photo dimerization in the solid state. The weak interactions identified here is specific to the olefins investigated here. However, two common molecules, H$_2$O and Cl$^-$ ion together are able to template a number of protonated stilbazoles is interesting and requires investigation for further understanding of principles of crystal engineering.

By combining X-ray crystallography and photochemistry we have established that H$_2$O and Cl$^-$ ion ion has the potential to be a general template (13 of the 16 protonated stilbazoles reacted). The templation is facilitated by weak interaction between PyN$^+$–H and water or PyN$^+$– H and Cl$^-$. In spite of the reported success, it is not obvious which of the two interactions is going to be dominant in a given case and it is also not clear whether this approach would apply to other olefins as well. During the last decade several templates have been identified, each one with its own advantages and disadvantages, but they all suggest that further work is needed. The field of organic solid-state photochemistry combined with crystal engineering has plenty of opportunities for those interested in combining crystallography and photochemistry. More importantly, the combination of quantum chemical calculations with crystallography and photochemistry should help in the understanding of weak interactions in solids, and predicting reactivity of molecules in the crystalline state.
2.3.2 Comparison of photoreaction of anhydrous and hydrous t Stilbazole. HCl by \(^1\)H NMR (300 MHz)

After irradiation of hydrous and anhydrous stilbazole HCl salts, photoproducts were neutralized with aqueous solution of NaOH, extracted with chloroform and analyzed by \(^1\)H NMR. For comparison, hydrous and anhydrous stilbazole. HCl salts were irradiated for identical hours (~5 h). \(^1\)H NMR of all the stilbazoles (2.1-2.5, 2.8, 2.12, 2.13) investigated are presented below.

Figure 2.31 (a) \(^1\)H NMR in CDCl\(_3\) of t 4- stilbazole,  (b) neutral extract of anhydrous t 4- stilbazole. HCl, irradiated for 5 h in solid state (38% dimer) (c) neutral extract of hydrous t 4-stilbazole. HCl, irradiated for 5 h in solid state (87% dimer). Aromatic proton ortho to N in pyridyl ring is denoted by ‘★’ for trans, and ‘■’ for anti H-T dimer.
Figure 2.32 (a) $^1$H NMR in CDCl$_3$ of t 4 F- stilbazole, (b) neutral extract of anhydrous t 4 F- stilbazole. HCl, irradiated for 5 h in solid state (10% dimer) (c) neutral extract of hydrous t 4 F-stilbazole. HCl, irradiated for 5 h in solid state (94 % dimer). Aromatic proton ortho to N in pyridyl ring is denoted by ‘★’ for trans and ‘■’ for anti H-T dimer.
Figure 2.33 (a) $^1$H NMR in CDCl$_3$ of $t$4 chloro-stilbazole, (b) neutral extract of anhydrous $t$4 chloro-stilbazole. HCl, irradiated for 5 h in solid state (28 % dimer) (c) neutral extract of hydrous $t$4 chloro-stilbazole. HCl, irradiated for 5 h in solid state (90% dimer). Aromatic proton ortho to N in pyridyl ring is denoted by ‘★’ for trans and ‘ ■ ’ for anti H-T dimer.
Figure 2.34 (a) $^1$H NMR in CDCl$_3$ of t 4 bromo-stilbazole, (b) neutral extract of **anhydrous** t 4 bromo-stilbazole. HCl, irradiated for 5 h in solid state (10 %) (c) neutral extract of **hydrous** t 4 Bromo-stilbazole. HCl, irradiated for 5 h in solid state (97 % dimer). Aromatic proton ortho to N in pyridyl ring is denoted by ‘★’ for trans and ‘■’ for **anti** H-T dimer.
Figure 2.35 (a) $^1$H NMR in CDCl$_3$ of $t$ 4 Iodo-stilbazole, (b) neutral extract of anhydrous $t$ 4 Iodo-stilbazole. HCl, irradiated for 5 h in solid state (no reaction) (c) neutral extract of hydrous $t$ 4 Iodo-stilbazole. HCl, irradiated for 5 h in solid state (49% dimer). Aromatic proton ortho to N in pyridyl ring is denoted by ‘★’ for trans and ‘◼’ for anti H-T dimer.
Figure 2.36 (a) $^1$H NMR in CDCl$_3$ of t 4 Methoxy-stilbazole, (b) neutral extract of anhydrous t 4 Methoxy-stilbazole. HCl, irradiated for 5 h in solid state (35% dimer) (c) neutral extract of hydrous t 4 Methoxy-stilbazole. HCl, irradiated for 5 h in solid state (60 % dimer). Aromatic proton ortho to N in pyridyl ring is denoted by ‘★’ for trans and ‘■’ for anti H-T dimer.
Figure 2.37 (a) $^1$H NMR in CDCl$_3$ of t 2 Napthyl-stilbazole, (b) neutral extract of anhydrous t 2 Napthyl-stilbazole. HCl, irradiated for 5 h in solid state (no reaction) (c) neutral extract of hydrous t 2 Napthyl-stilbazole. HCl, irradiated for 5 h in solid state (18% dimer). Aromatic proton ortho to N in pyridyl ring is denoted by ‘★’ for trans and ‘■’ for anti H-T dimer.
**Figure 2.38** (a) $^1$H NMR in CDCl$_3$ of $t$ 3,4 di Methoxy-stilbazeole, (b) neutral extract of **anhydrous** $t$ 3,4 di Methoxy-stilbazeole. HCl, irradiated for 5 h in solid state (no reaction) (c) neutral extract of **hydrous** $t$ 3,4 di Methoxy-stilbazeole. HCl, irradiated for 5 h in solid state (8% dimer). Aromatic proton *ortho* to N in pyridyl ring is denoted by ‘★’ for *trans* and ‘■’ for *anti* H-T dimer.
2.4 Experimental section

Synthesis of trans-stilbazole derivatives

All stilbazole derivatives were synthesized following literature procedures.\textsuperscript{77,78} In brief, mixture of 4-picoline and the corresponding benzaldehyde (1:1), KOBu\textsuperscript{t} (1.2 eq) and DMF was heated at 80 \degree C for 8 h. The DMF was removed and the crude product was dissolved in dichloromethane and washed with 1N NaOH solution. The organic phase is separated and dried on Na\textsubscript{2}SO\textsubscript{4} and concentrated. The crude product was purified column chromatography using ethylacetate/hexane mixture (1:1). 4-Iodo stilbazole was synthesized via Wittig reaction\textsuperscript{79}. Stilbazole. HCl salts were prepared by adding 2 equivalents of conc. HCl to stilbazoles in a mortar and ground well with a pestle to give a pasty mass.

This pasty mass was air dried overnight to give stilbazole. HCl salts. Addition of conc. HCl to most of stilbazoles showed color change indicative of formation of HCl.
salts. This visual color change is also confirmed by the red shifted absorbance in diffuse reflectance spectra (Figure 2.11). These salts were dried at ~110 °C under reduced pressure, for 7-9 h to afford anhydrous stilbazole HCl salts.

**Irradiation technique**

Irradiations were performed using a 450 W medium pressure mercury arc lamp placed in a water-cooled Pyrex immersion well. Light emitted from a Hanovia lamp was filtered through Pyrex (transmission λ ≥ 290 nm). About 8-10 mg of powdered stilbazole HCl salts were spread uniformly between two Pyrex glass plates sealed with parafilm and irradiated. The plates were turned around every 6 hours. The same experiments were also done in hexane, where stilbazole HCl salts were suspended in hexane in a Pyrex tube and irradiated with stirring. In most cases, irradiation in hexane suspension was faster than in Pyrex plates. After irradiation the crude product was dissolved in H₂O and neutralized with 1N NaOH. For experiments in hexane suspension, hexane was removed at reduced pressure, and the crude product was dissolved in H₂O and neutralized with 1N NaOH. This neutral solution was extracted with CHCl₃ four times and the combined organic layer was dried over anhydrous Na₂SO₄. Evaporation of the solvent gave a product that was characterized by ¹H NMR in CDCl₃. For comparison crystalline powder of stilbazole derivatives (without making HCl salt) were also irradiated and characterized by ¹H NMR in CDCl₃.
2.5 Crystallographic analysis

Yellow single crystals of 2.2.HCl.3H₂O (t 4F-Stilbazole. HCl 3H₂O), 2.3.HCl.2H₂O (t 4Cl-Stilbazole. HCl.2H₂O), 2.4.HCl.2H₂O (t 4Br-Stilbazole. HCl.2H₂O), 2.5.HCl.2H₂O (t 4I-Stilbazole. HCl.2H₂O), 2.8.HCl.8/3 H₂O (t 4MeO-Stilbazole. HCl.8/3 H₂O) and 2.16.HCl (t 2,3,4,5,6 penta F-Stilbazole. HCl) suitable for X-ray diffraction analyses were obtained by evaporation of solvent from an ethanol/toluene solvent mixture at 25 °C. Colorless single crystals of 2.2 (t 4F-Stilbazole) and 2.12 (t 3,4 diMeO-Stilbazole) suitable for X-ray diffraction analyses were obtained by evaporation of solvent from chloroform/toluene solvent mixture at 25 °C. Yellow single crystals of dimer of 2.3 (t 4Cl-Stilbazole), dimer of 2.4 (t 4Br-Stilbazole), dimer of 2.5 (t 4I-Stilbazole) and 2.16 (t 2,3,4,5,6 penta F-Stilbazole) suitable for X-ray diffraction analyses was obtained by evaporation from chloroform solvent at 25 °C. Colorless single crystals of 2.9.HCl.3H₂O (t 4CF₃-Stilbazole. HCl.3H₂O) suitable for X-ray diffraction analyses were obtained by evaporation of solvent from an acetonitrile/toluene solvent mixture at 25 °C. Pale yellow single crystals of 2.14.HCl (t 3,5 diCl-Stilbazole. HCl) suitable for X-ray diffraction analyses were obtained by evaporation of solvent from a methanol/toluene/chloroform solvent mixture at 25 °C. Yellow single crystals of anhydrous 2.3.HCl and 2.4.HCl, suitable for X-ray diffraction analyses were obtained by evaporation of solvent from an anhydrous methanol solution at 25 °C in a glove box. Yellow single crystals of anhydrous 2.5.HCl suitable for X-ray diffraction analyses were obtained by evaporation of solvent from an anhydrous ethanol solution at 25 °C in a glove box. Crystal data, data collection parameters, and results of the analyses are listed in Table 2.2-2.6.
Each data crystal was glued onto the end of a thin glass fiber. X-ray intensity data were measured by using a Bruker SMART APEX2 CCD-based diffractometer using Mo Kα radiation ($\lambda = 0.71073 \text{ Å}$). The raw data frames were integrated with the SAINT+ program by using a narrow-frame integration algorithm. Corrections for Lorentz and polarization effects were also applied with SAINT+. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied using the program SADABS. All structures were solved by a combination of direct methods and difference Fourier syntheses, and refined by full-matrix least-squares on $F^2$, by using the SHELXTL software package. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in geometrically idealized positions and included as standard riding atoms during the least-squares refinements. Crystal data, data collection parameters, and results of the analyses are listed in Tables 2.2-2.7.

Although the crystal structure of 2.1.HCl is reported in literature containing two H$_2$O molecules, our efforts to crystallize resulted in three H$_2$O molecules in the lattice. 2.1.HCl.3H$_2$O (t Stilbazole. HCl.3H$_2$O) crystallized in the triclinic crystal system. The space group $P\overline{1}$ was assumed and confirmed by the successful refinement and solution of the structure. The alkene group of the stilbazole molecule is disordered two orientations, which were refined in a 70:30 ratio. There are three water molecules that cocrystallized with the complex. Reasonable peak positions for the H atoms on the water molecules were located in the difference map and then refined with geometric restraints.

2.2 (t 4F-Stilbazole) crystallized in the orthorhombic crystal system. The systematic absences in the intensity data were consistent with the unique space group.
During the final stages of the structural analysis, the nitrogen atom N1 was found disordered at both ends of the molecule. This can be viewed as the whole molecule being disordered over two orientations such that the two molecules lie on top of each other. Appropriately, the N1 site and the C1 site were refined as a mixed N/C site in the ratio 50:50. The atomic coordinates and thermal parameters at these two mixed sites were constrained (SHELX: EXYZ and EADP instructions) to remain equal during the refinement cycles.

2.3.HCl.2H2O (t 4Cl-Stilbazole. HCl.2H2O) crystallized in the triclinic crystal system. The space group $P \bar{1}$ was assumed and confirmed by the successful refinement and solution of the structure. There are two water molecules that cocrystallized with the complex. Reasonable peak positions for the H atoms on the water molecules were located in the difference map and then refined with geometric restraints.

Dimer of 2.3 (t 4 Chloro-Stilbazole-Dimer) crystallized in the monoclinic crystal system. The systematic absences in the intensity data were consistent with the unique space group $P2_1/n$

2.4.HCl. 2H2O (t 4Br-Stilbazole. HCl.2H2O) crystallized in the triclinic crystal system. The space group $P \bar{1}$ was assumed and confirmed by the successful refinement and solution of the structure. There are two water molecules that cocrystallized with the complex. Reasonable peak positions for the H atoms on the water molecules were located in the difference map and then refined with geometric restraints.

Dimer of 2.4 (t 4Br-Stilbazole dimer) crystallized in the monoclinic crystal system. The systematic absences in the intensity data were consistent with the unique space group $P2_1/n$
2.5. HCl. 2H₂O (t 4I-Stilbazole. HCl. 2H₂O) crystallized in the triclinic crystal system. The space group $P \overline{1}$ was assumed and confirmed by the successful refinement and solution of the structure. There are two water molecules that cocrystallized with the complex. Reasonable peak positions for the H atoms on the water molecules were located in the difference map and then refined.

Dimer of 2.5 (t 4I-Stilbazole dimer) crystallized in the monoclinic crystal system. The systematic absences in the intensity data were consistent with the unique space group $P2_1/n$.

2.8. HCl.8/3 H₂O (t 4MeO-Stilbazole. HCl. 8/3 H₂O) crystallized in the triclinic crystal system. The space group $P \overline{1}$ was assumed and confirmed by the successful refinement and solution of the structure. The asymmetric crystal unit contains three molecules of the 4 methoxy-Stilbazole salts. In two of the 4methoxy-Stilbazole cationic molecules, the alkene group is disordered over two orientations, which were refined in the ratio 80:20. There are eight water molecules that cocrystallized with the complex. Reasonable peak positions for the H atoms on the water molecules were located in the difference map and then refined with geometric restraints. There is also an additional peak in the difference map, which was assigned as Cl, resulting from excess HCl present under the crystallization conditions.

Compound 2.12 (t 3,4 diMeO-Stilbazole) crystallized in the monoclinic crystal system. The systematic absences in the intensity data were consistent with the unique space group $P2_1/c$.

Compound 2.9. HCl. 3H₂O (t 4CF₃-Stilbazole. HCl. 3H₂O) crystallized in the triclinic crystal system. The space group $P \overline{1}$ was assumed and confirmed by the
successful refinement and solution of the structure. The CF$_3$ group is disordered over two orientations and was refined in the ratio 70:30. There are three water molecules that cocrystallized with the complex. Reasonable peak positions for the H atoms on the water molecules were located in the difference map and then refined with geometric restraints.

Compound **2.14.HCl** ($t\ 3,5\ diCl$-Stilbazole. HCl) crystallized in the triclinic crystal system. The space group $P\ \bar{I}$ was assumed and confirmed by the successful refinement and solution of the structure. The alkene group of the cationic $t\ 3,5\ diCl$-Stilbazole molecule is disordered in two orientations, which were refined in a 68:32 ratio.

Compound **2.16** ($t\ 2,3,4,5,6\ penta\ F$-Stilbazole) crystallized in the triclinic crystal system. The space group $P\ \bar{I}$ was assumed and confirmed by the successful refinement and solution of the structure.

Compound **2.16.HCl** ($t\ 2,3,4,5,6\ penta\ F$-Stilbazole. HCl) crystallized in the triclinic crystal system. The space group $P\ \bar{I}$ was assumed and confirmed by the successful refinement and solution of the structure. The alkene group of the cationic $t\ 2,3,4,5,6\ penta\ F$-Stilbazole molecule is disordered in two orientations, which were refined in a 70:30 ratio.

Compound **2.2.HCl.3H$_2$O** ($t\ 4F$-Stilbazole. HCl 3H$_2$O) crystallized in the monoclinic crystal system. The systematic absences in the intensity data were consistent with the unique space group $P2_1/c$. The alkene group of the cationic $t\ 4F$-Stilbazole. HCl 3H$_2$O molecule is disordered in two orientations, which were refined in a 60:40 ratio. There are three water molecules that co-crystallized with the complex. Reasonable peak positions for the H atoms on the water molecules were located in the difference map and
then refined with geometric restraints. The R-values during the final stage of the refinement are high due to poor crystal quality. Repeated attempts to grow high quality crystals were unsuccessful. The structure reported is the ‘best’ we were able to obtain.

Compounds **2.3.HCl.MeOH** (*t* 4Cl-Stilbazole. HCl.MeOH) and **2.4.HCl. MeOH** (*t* 4Br-Stilbazole. HCl.MeOH) crystallized in the monoclinic crystal system. The systematic absences in the intensity data were consistent with either of the space groups *P*2₁ or *P*2₁/m. The latter was chosen and confirmed by the successful refinement and solution of the structure. With *Z* = 2, both molecules have crystallographic mirror symmetry. The alkene group of the cationic stilbazole molecule in both complexes is disordered over two orientations, which were refined in a 50:50 ratio. One molecule of methanol cocrystallized with the complex and was included in the analysis. Compound **2.5.HCl** (*t* 4I-Stilbazole. HCl) crystallized in the triclinic crystal system. The space group *P* ̅̅̅₂ was assumed and confirmed by the successful refinement and solution of the structure. The asymmetric crystal unit contains two molecules.
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*R = Σ_{hkl} | F_{obs} | F_{calc} | Σ_{hkl} F_{obs} ; R_w = [Σ_{hkl} w(F_{obs} | F_{calc})^2]^{1/2} / Σ_{hkl} wF_{obs}^2 ; w = 1/σ^2(F_{obs}) ; GOF = [Σ_{hkl} w(F_{obs} | F_{calc})^2]^{1/2} / (n_{data} − n_{var})^{1/2}.

**Table 2.2** Crystallographic Data for Compounds 2.1.HCl, 2.2, 2.3.HCl
<table>
<thead>
<tr>
<th>Description</th>
<th>4-Chloro Stilbazole Dimer</th>
<th>4-Bromo Stilbazole HCl</th>
<th>4-Bromo Stilbazole Dimer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C$<em>{26}$H$</em>{20}$N$_2$Cl$_2$</td>
<td>C$<em>{13}$H$</em>{11}$NBr$\cdot$Cl$\cdot$H$_2$O</td>
<td>C$<em>{26}$H$</em>{20}$N$_2$Br$_2$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>431.34</td>
<td>332.62</td>
<td>520.26</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Triclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Lattice parameters</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>9.6675(6)</td>
<td>8.0476(5)</td>
<td>9.8477(5)</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>13.8938(8)</td>
<td>9.7384(6)</td>
<td>9.4161(5)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>16.3247(9)</td>
<td>9.9178(6)</td>
<td>24.1091(12)</td>
</tr>
<tr>
<td>$\alpha$ (deg)</td>
<td>90</td>
<td>99.575(1)</td>
<td>90</td>
</tr>
<tr>
<td>$\beta$ (deg)</td>
<td>94.2639(8)</td>
<td>98.575(1)</td>
<td>90.2071(9)</td>
</tr>
<tr>
<td>$\gamma$ (deg)</td>
<td>90</td>
<td>108.029(1)</td>
<td>90</td>
</tr>
<tr>
<td>$V$ (Å$^3$)</td>
<td>2186.6(2)</td>
<td>711.93(8)</td>
<td>2235.5(2)</td>
</tr>
<tr>
<td>Space group</td>
<td>$P_2_1/n$ (#14)</td>
<td>$P\bar{1}$ (# 2)</td>
<td>$P_2_1/n$ (#14)</td>
</tr>
<tr>
<td>$Z$ value</td>
<td>4</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>$\rho_{\text{calc}}$ (g / cm$^3$)</td>
<td>1.310</td>
<td>1.552</td>
<td>1.546</td>
</tr>
<tr>
<td>$\mu$ (Mo K$\alpha$) (mm$^{-1}$)</td>
<td>0.312</td>
<td>3.068</td>
<td>3.641</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>296</td>
<td>296</td>
<td>296</td>
</tr>
<tr>
<td>$2\Theta_{\text{max}}$ (°)</td>
<td>58.00</td>
<td>50.10</td>
<td>56.00</td>
</tr>
<tr>
<td>No. Obs. (I &gt; 2σ(I))</td>
<td>4201</td>
<td>2309</td>
<td>3737</td>
</tr>
<tr>
<td>No. Parameters</td>
<td>271</td>
<td>167</td>
<td>271</td>
</tr>
<tr>
<td>Goodness of fit</td>
<td>1.024</td>
<td>1.082</td>
<td>1.028</td>
</tr>
<tr>
<td>Max. shift in cycle</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>Residuals*:R1; wR2</td>
<td>0.0463; 0.1127</td>
<td>0.0406; 0.1100</td>
<td>0.0432; 0.1070</td>
</tr>
<tr>
<td>Absorption Correction, Max/min</td>
<td>Multi-scan</td>
<td>Multi-scan</td>
<td>Multi-scan</td>
</tr>
<tr>
<td>Largest peak in Final Diff. Map</td>
<td>0.9815/0.8646</td>
<td>0.7465/0.5846</td>
<td>0.7461/0.4780</td>
</tr>
<tr>
<td>($e^{-}$ / Å$^3$)</td>
<td>0.496</td>
<td>1.807</td>
<td>1.013</td>
</tr>
</tbody>
</table>

$*R = \Sigma_{hkl}( | F_{\text{obs}} | - | F_{\text{calc}} | )/\Sigma_{hkl} | F_{\text{obs}} | ; R_w = [\Sigma_{hkl}w( | F_{\text{obs}} | - | F_{\text{calc}} | )^2/\Sigma_{hkl}wF_{\text{obs}}^2]^{1/2}, w = 1/\sigma^2(F_{\text{obs}}); \text{GOF} = [\Sigma_{hkl}w( | F_{\text{obs}} | - | F_{\text{calc}} | )^2/(n_{\text{data}} - n_{\text{vari}})]^{1/2}.$

**Table 2.3** Crystallographic Data for Compounds 2.4.HCl salt and dimers from 2.3 and 2.4.
<table>
<thead>
<tr>
<th></th>
<th>4-Iodo Stilbazole. HCl</th>
<th>4-Iodo Stilbazole Dimer</th>
<th>4MeO Stilbazole. HCl</th>
<th>C₂₆H₂₀N₂I₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₁₃H₁₁NI•Cl 2H₂O</td>
<td>C₂₆H₂₀N₂I₂</td>
<td>C₄₂H₃₂N₃O₅•4Cl 8H₂O</td>
<td></td>
</tr>
<tr>
<td>Formula weight</td>
<td>379.61</td>
<td>614.24</td>
<td>922.71</td>
<td></td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
<td>Monoclinic</td>
<td>Triclinic</td>
<td></td>
</tr>
<tr>
<td>Lattice parameters</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a (Å)</td>
<td>8.0309(3)</td>
<td>9.5861(4)</td>
<td>9.4503(4)</td>
<td></td>
</tr>
<tr>
<td>b (Å)</td>
<td>9.9249(4)</td>
<td>9.7404(4)</td>
<td>12.2691(5)</td>
<td></td>
</tr>
<tr>
<td>c (Å)</td>
<td>10.0973(4)</td>
<td>24.7898(10)</td>
<td>21.7240(9)</td>
<td></td>
</tr>
<tr>
<td>α (deg)</td>
<td>97.9228(5)</td>
<td>90</td>
<td>78.4586(6)</td>
<td></td>
</tr>
<tr>
<td>β (deg)</td>
<td>99.4160(5)</td>
<td>90.1197(7)</td>
<td>86.8176(6)</td>
<td></td>
</tr>
<tr>
<td>γ (deg)</td>
<td>108.9995(5)</td>
<td>90</td>
<td>84.1447(6)</td>
<td></td>
</tr>
<tr>
<td>V (Å³)</td>
<td>734.79(5)</td>
<td>2314.68</td>
<td>2453.43(18)</td>
<td></td>
</tr>
<tr>
<td>Space group</td>
<td>P ̅ ( # 2)</td>
<td>P 2_1/n ( # 14)</td>
<td>P ̅ ( # 2)</td>
<td></td>
</tr>
<tr>
<td>Z value</td>
<td>2</td>
<td>4</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>ρcalc (g / cm³)</td>
<td>1.716</td>
<td>1.763</td>
<td>1.249</td>
<td></td>
</tr>
<tr>
<td>μ (Mo Kα) (mm⁻¹)</td>
<td>2.355</td>
<td>2.732</td>
<td>0.297</td>
<td></td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>296</td>
<td>296(2)</td>
<td>296(2)</td>
<td></td>
</tr>
<tr>
<td>2Θmax (°)</td>
<td>58.00</td>
<td>60.00</td>
<td>50.00</td>
<td></td>
</tr>
<tr>
<td>No. Obs. ( I &gt; 2σ(I))</td>
<td>3707</td>
<td>4849</td>
<td>6738</td>
<td></td>
</tr>
<tr>
<td>No. Parameters</td>
<td>179</td>
<td>271</td>
<td>645</td>
<td></td>
</tr>
<tr>
<td>Goodness of fit</td>
<td>1.122</td>
<td>1.015</td>
<td>1.035</td>
<td></td>
</tr>
<tr>
<td>Max. shift in cycle</td>
<td>0.001</td>
<td>0.002</td>
<td>0.007</td>
<td></td>
</tr>
<tr>
<td>Residuals*:R1; wR2</td>
<td>0.0277; 0.0758</td>
<td>0.0386; 0.0975</td>
<td>0.0451; 0.1201</td>
<td></td>
</tr>
<tr>
<td>Absorption Correction,</td>
<td>Multi-scan</td>
<td>Multi-scan</td>
<td>Multi-scan</td>
<td></td>
</tr>
<tr>
<td>Max/min</td>
<td>0.8340/0.4105</td>
<td>0.8532/0.4078</td>
<td>0.7461/0.6876</td>
<td></td>
</tr>
<tr>
<td>Largest peak in Final</td>
<td>1.542</td>
<td>1.682</td>
<td>0.273</td>
<td></td>
</tr>
<tr>
<td>Diff. Map (e⁻ / Å³)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*R = Σ_hkl([F_{obs} - |F_{calc}|] / Σ_hkl |F_{obs}|)^2 + 0.04 (|F_{calc}|)^2 / Σ_hkl |F_{calc}|)^2 / Σ_hkl |F_{calc}||F_{obs}|; w = 1/σ²(F_{obs}); GOF = Σ_hkl[wF_{obs} - F_{calc}]² / Σ_hkl[w]².

Table 2.4 Crystallographic Data for Compounds 2.5.HCl, dimer from 2.5, and 2.8.HCl
<table>
<thead>
<tr>
<th>Crystallographic data for compounds 2.12, 2.9.HCl and 2.14.HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
</tr>
<tr>
<td><strong>Lattice parameters</strong></td>
</tr>
<tr>
<td><strong>a (Å)</strong></td>
</tr>
<tr>
<td><strong>b (Å)</strong></td>
</tr>
<tr>
<td><strong>c (Å)</strong></td>
</tr>
<tr>
<td><strong>α (deg)</strong></td>
</tr>
<tr>
<td><strong>β (deg)</strong></td>
</tr>
<tr>
<td><strong>γ (deg)</strong></td>
</tr>
<tr>
<td><strong>V (Å³)</strong></td>
</tr>
<tr>
<td><strong>Space group</strong></td>
</tr>
<tr>
<td><strong>Z value</strong></td>
</tr>
<tr>
<td><strong>ρ_{calc} (g / cm³)</strong></td>
</tr>
<tr>
<td><strong>μ (Mo Kα) (mm⁻¹)</strong></td>
</tr>
<tr>
<td><strong>Temperature (K)</strong></td>
</tr>
<tr>
<td><strong>2Θ_{max} (°)</strong></td>
</tr>
<tr>
<td><strong>No. Obs. (I &gt; 2σ(I))</strong></td>
</tr>
<tr>
<td><strong>No. Parameters</strong></td>
</tr>
<tr>
<td><strong>Goodness of fit</strong></td>
</tr>
<tr>
<td><strong>Max. shift in cycle</strong></td>
</tr>
<tr>
<td><em><em>Residuals</em>:R1; wR2</em>*</td>
</tr>
<tr>
<td><strong>Absorption Correction</strong></td>
</tr>
<tr>
<td><strong>Max/min in Largest peak in Final Diff. Map (e⁻ / Å³)</strong></td>
</tr>
</tbody>
</table>

*R = Σ_{hkl} (|F_{obs}|-|F_{calc}|)/Σ_{hkl} |F_{obs}|; \(R_w^2 = \left[\frac{Σ_{hkl}w(|F_{obs}|-|F_{calc}|)^2}{Σ_{hkl}wF_{obs}^2}\right]^{1/2}\), \(w = 1/\sigma^2(F_{obs})\); GOF = \(\left[\frac{Σ_{hkl}w(|F_{obs}|-|F_{calc}|)^2}{(n_{data} - n_{vari})}\right]^{1/2}\).

**Table 2.5** Crystallographic data for compounds 2.12, 2.9.HCl and 2.14.HCl
<table>
<thead>
<tr>
<th>Empirical formula</th>
<th>Pentafluoro Stilbazole HCl</th>
<th>Pentafluoro Stilbazole Monomer</th>
<th>4-Fluoro. Stilbazole. HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula weight</td>
<td>307.65</td>
<td>271.19</td>
<td>281.73</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
<td>Triclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Lattice parameters</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a (Å)</td>
<td>8.3749(5)</td>
<td>5.8613(4)</td>
<td>7.0809(4)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>8.3985(5)</td>
<td>9.2231(6)</td>
<td>9.6992(6)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>10.2024(7)</td>
<td>10.9709(7)</td>
<td>22.3919(14)</td>
</tr>
<tr>
<td>α (deg)</td>
<td>66.6060(8)</td>
<td>71.3900(9)</td>
<td>90</td>
</tr>
<tr>
<td>β (deg)</td>
<td>71.9947(9)</td>
<td>85.3708(9)</td>
<td>98.4170(10)</td>
</tr>
<tr>
<td>γ (deg)</td>
<td>84.0524(9)</td>
<td>80.5834(9)</td>
<td>90</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>626.21(7)</td>
<td>554.24(6)</td>
<td>1521.29(16)</td>
</tr>
<tr>
<td>Space group</td>
<td>P ̅T (# 2)</td>
<td>P ̅T (# 2)</td>
<td>P2₁/c (# 14)</td>
</tr>
<tr>
<td>Z value</td>
<td>2</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>ρ&lt;sub&gt;calc&lt;/sub&gt; (g / cm³)</td>
<td>1.632</td>
<td>1.625</td>
<td>1.2230</td>
</tr>
<tr>
<td>μ (Mo Kα) (mm⁻¹)</td>
<td>0.354</td>
<td>0.155</td>
<td>0.260</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>296(2)</td>
<td>296(2)</td>
<td>296(2)</td>
</tr>
<tr>
<td>2Θ&lt;sub&gt;max&lt;/sub&gt; (°)</td>
<td>52.00</td>
<td>58.00</td>
<td>50.00</td>
</tr>
<tr>
<td>No. Obs. (I &gt; 2σ(I))</td>
<td>2145</td>
<td>2170</td>
<td>2115</td>
</tr>
<tr>
<td>No. Parameters</td>
<td>200</td>
<td>173</td>
<td>212</td>
</tr>
<tr>
<td>Goodness of fit</td>
<td>1.070</td>
<td>1.079</td>
<td>1.717</td>
</tr>
<tr>
<td>Max. shift in cycle</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Residuals*: R&lt;sub&gt;1&lt;/sub&gt;; wR&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.0565; 0.1532</td>
<td>0.0477; 0.1394</td>
<td>0.1094</td>
</tr>
<tr>
<td>Absorption Correction, Max/min</td>
<td>Multi-scan</td>
<td>Multi-scan</td>
<td>Multi-scan</td>
</tr>
<tr>
<td>Largest peak in Final Diff. Map (e⁻/Å³)</td>
<td>0.438</td>
<td>0.259</td>
<td>1.267</td>
</tr>
</tbody>
</table>

*R = Σₘₙₜₖ{[F<sub>obs</sub> - F<sub>calc</sub>]²/ΣₘₙₜₖF<sub>obs</sub>²}^{1/2}; w = 1/σ²(F<sub>obs</sub>); GOF = [Σₘₙₜₖw(F<sub>obs</sub> - F<sub>calc</sub>)²/ΣₘₙₜₖwF<sub>obs</sub>²]^{1/2};

Table 2.6 Crystallographic data for compounds 2.16.HCl, 2.16 and 2.2.HCl
<table>
<thead>
<tr>
<th>Compound</th>
<th>Empirical formula</th>
<th>Formula weight</th>
<th>Crystal system</th>
<th>Lattice parameters</th>
<th>Z value</th>
<th>( \rho_{\text{calc}} ) (g/cm(^3))</th>
<th>( \mu ) (Mo K( \alpha )) (mm(^{-1}))</th>
<th>Temperature (K)</th>
<th>( 2\Theta_{\text{max}} ) (°)</th>
<th>No. Obs. (I &gt; 2( \sigma(I) ))</th>
<th>No. Parameters</th>
<th>Goodness of fit</th>
<th>Max. shift in cycle</th>
<th>Residuals*:R1; wR2</th>
<th>Absorption Correction, Max/min</th>
<th>Largest peak in Final Diff. Map (e(^-)/Å(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3.HCl</td>
<td>( \text{C}<em>{13}\text{H}</em>{11}\text{NCl} \cdot \text{Cl} \cdot \text{MeOH} )</td>
<td>284.17</td>
<td>Monoclinic</td>
<td>( a = 4.7953(5) \text{ Å} )</td>
<td>2</td>
<td>1.323</td>
<td>0.443</td>
<td>296</td>
<td>50.00</td>
<td>1090</td>
<td>109</td>
<td>1.054</td>
<td>0.000</td>
<td>0.0379; 0.0988</td>
<td>Multi-scan</td>
<td>0.9825/0.8291</td>
</tr>
<tr>
<td>2.4.HCl</td>
<td>( \text{C}<em>{13}\text{H}</em>{11}\text{NBr} \cdot \text{Cl} \cdot \text{MeOH} )</td>
<td>328.63</td>
<td>Monoclinic</td>
<td>( b = 8.5668(8) \text{ Å} )</td>
<td>2</td>
<td>1.499</td>
<td>2.994</td>
<td>296</td>
<td>53.98</td>
<td>1270</td>
<td>109</td>
<td>1.025</td>
<td>0.002</td>
<td>0.0370; 0.0841</td>
<td>Multi-scan</td>
<td>0.7457/0.5597</td>
</tr>
<tr>
<td>2.5.HCl</td>
<td>( \text{C}<em>{13}\text{H}</em>{11}\text{NI} \cdot \text{Cl} \cdot \text{MeOH} )</td>
<td>343.58</td>
<td>Triclinic</td>
<td>( c = 17.3529(18) \text{ Å} )</td>
<td>4</td>
<td>1.808</td>
<td>2.720</td>
<td>296</td>
<td>56.00</td>
<td>5290</td>
<td>289</td>
<td>1.035</td>
<td>0.002</td>
<td>0.0272; 0.0654</td>
<td>Multi-scan</td>
<td>0.8538/0.4764</td>
</tr>
</tbody>
</table>

* \( R = \frac{\sum_{hkl}[|F_{\text{obs}}| - |F_{\text{calc}}|]}{\sum_{hkl}|F_{\text{obs}}|} ; R_w = \frac{\sum_{hkl}w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2}{\sum_{hkl}wF_{\text{obs}}^2}^{1/2} \), \( w = 1/\sigma^2(F_{\text{obs}}) \); GOF = \( \frac{\sum_{hkl}w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2/(n_{\text{data}} - n_{\text{vari}})}{1/2} \).

**Table 2.7** Crystallographic data for anhydrous compounds 2.3.HCl, 2.4.HCl and 2.5.HCl
Chapter 3. Photoreactions of cis-stilbazole. HCl salts in crystal

3.1 cis-trans isomerization in crystal

Although cis –trans isomerization in olefins is common in solution chemistry, it is a rare event in solid-state photochemistry, as it requires molecular motion in crystals. In the 1960’s the concept of “reaction cavity” was introduced by Cohen and Schmidt, to describe photo dimerization reactions in crystals.\(^90\),\(^91\) This concept explains that reaction requiring large distortion motion is not allowed in crystalline state. However, later literature provides ample evidence of molecules undergoing large motions in the crystalline state upon excitation.\(^92\)–\(^95\) Ogawa et al. reported the presence of orientational disorder in stilbenes and azobenzenes\(^96\),\(^97\) while Garcia–Garibay et al. reported large crankshaft-type motion in crystals of the highly congested bis(triaryl)methyl peroxide. Photo dimerization reaction of a diamine double salt of substituted cinnamic acids with trans-1,2-diaminocyclohexane in the solid state requiring large pedal-like motion of the a C=C prior to dimerization is also known.\(^99\) These literatures undoubtedly supports that certain amounts of molecular motions are tolerated within a crystal. In 1964, Schmidt et al. reported that several crystalline cis-cinnamic acids produce corresponding trans isomers\(^100\) upon irradiation. The authors proposed that the isomerization occurred through a mechanism involving a metastable cyclobutane (dimer) intermediate between an excited molecule and its closest neighbor (Scheme 3.1). According to Schmidt, the isomerization was “lattice-controlled” to yield trans-acid which, after a recrystallization step is either trapped in a light-stable structure or reacts to give the dimer(s) characteristic of its crystal structure. Bryan et al. contradicted this mechanism with their report\(^101\) on photoreaction of 2-ethoxy-cis-cinnamic acid.
Their study clearly supports, that there are no close approaches between the neighboring C=C in the crystal, which indicates probable absence of “lattice control” in cis-trans isomerization (closest C=C distance > 5Å). Later literature reports also suggested that the mechanism of isomerization involving a metastable cyclobutane intermediate (lattice control) might not be general approach.

Irradiation of trans-stilbazole.HCl salts (discussed in Chapter 2), resulted in [2+2] cycloaddition, without any observed isomerization. Isomerization in olefins is known to take place from singlet-excited state (Sₙ) either via a simple configurational isomerization about a single bond known as one-bond-flip (OBF), or via a more complex higher energy motion that achieves double bond isomerization in restrictive environments, named as the Hula-Twist (HT). In both the mechanism, there is molecular motion involved, requiring considerable space around the excited molecules. The planar trans-olefins tend to pack tight compared to slightly twisted cis-olefins. This compact packing reduces the possibility of trans to cis isomerization in crystals, while the cis-olefins are
known to undergo cis-trans isomerization. In this chapter, we discuss our results of investigating geometric isomerization of cis-stilbazole. HCl salts in crystals. Irradiation of five cis-stilbazole·HCl salts to light resulted in conversion to the trans isomer and upon prolonged irradiation gave dimer. Surprisingly the dimer obtained was anti head-tail (H-T) dimer, which could only be obtained by [2+2] cycloaddition of two neighboring trans molecules.

![Figure 3.1 Structure of cis-stilbazoles investigated](image)

3.2 Results and discussions

The cis-stilbazoles (Figure 3.1) were obtained by irradiation of the trans compound in chloroform, and purification by preparative-TLC. Although most of the cis stilbazoles are liquid, their HCl salts were solid and were used to investigate photochemistry in crystals. The cis-stilbazole. HCl salts obtained by adding HCl (37%) was air dried and then dried under reduced pressure to get rid of any moisture, prior to photoreaction. Out of the five cis-stilbazole. HCl investigated, we obtained the crystal structure of four (Figure 3.2-3.3). The packing arrangement of cis-stilbazole. HCl is facilitated by N-H …Cl⁻ and π….π interaction, and none of the crystals had solvent in
their lattice. Interestingly the protonated pyridyl rings are arranged parallel and possibly π…π interaction favors stacking of the two rings. Unlike the trans-stilbazole. HCl salts, the distance between adjacent C=C are far apart (> 6 Å). Such loose packing of these crystals as compared to their trans analogue is likely to favor geometric isomerization upon excitation. The crystal structures shows that all the cis salts are twisted from planarity along the –C=C bond. –C=C bond angle for all the cis salts is ~129° and the parallel C=C bonds are not within the required distance (<4.2 Å) for [2+2] cycloaddition.

To understand the available space around the excited olefin, we did cavity plot using Platon for the cis crystals obtained. Cavity plot clearly shows there is space on both side of the C=C bond, for molecular motion of the excited molecule (Figure 3.4-3.5). cis 4F-Stilbazole. HCl has cavities of three sizes with volume 5.73, 5.58, and 4.19 Å³. cis 4Cl-Stilbazole. HCl has cavities of two sizes with volume 5.27, and 4.71 Å³. cis 4Br-Stilbazole. HCl has cavities with volume 4.99 Å³ and cis 4I-Stilbazole. HCl has cavities with volume 5.13 Å³. The red circles (Figure 3.4-3.5) shows the available space on both sides of C=C.

1H NMR studies (Figure 3.6-3.10) show that all the cis.stilbazole. HCl salt upon irradiation, first produces corresponding trans compound and during the initial few hours of irradiation have no dimer formed. Although, the percentage of trans and dimer formation for each of the cis.HCl salts vary, but they all have the same trend of forming trans at the very beginning and then the dimer is formed.

Upon prolonged irradiation of cis-Stilbazole. HCl salts, the dimer obtained is the same dimer (anti head-tail) obtained form the irradiation of trans stilbazole. HCl salts.
The dimer formed after irradiation of cis 4-Br stilbazole. HCl and cis 4-Cl stilbazole. HCl was isolated by pre-TLC, and comparison of $^1$H NMR confirms that the dimer is anti head-tail (Figure 3.11-3.12). It is apparent that anti H-T dimer cannot be formed upon [2+2] cycloaddition of cis stilbazoles. Thus the only possible mechanism for the observation is cis to trans isomerization and then dimer formation.

Figure 3.2 Packing arrangement of (a) cis -4F stilbazole.HCl (3.1·HCl) (b) cis -4Cl stilbazole.HCl (3.2·HCl). Cl$^-$ is represented as green sphere.
Figure 3.3 Packing arrangement of (a) cis-4Br stilbazole.HCl (3.3·HCl) (b) cis-4I stilbazole.HCl (3.4·HCl). Cl\(^-\) is represented as green sphere.
Figure 3.4 Cavity plot of (a) cis-4F stilbazole. HCl (3.1·HCl) (b) cis-4Cl stilbazole. HCl (3.2·HCl) using Platon.
3.2.1 $^1$H NMR analysis of photoproducts of cis-stilbazole. HCl

After irradiation the photoproducts were neutralized with aqueous solution of NaOH, extracted with chloroform and analyzed by $^1$H NMR. Similarly, samples irradiated in hexane suspension, were also neutralized and analyzed by $^1$H NMR. For comparison $^1$H NMR of neutral stilbazoles were also recorded. $^1$H NMR of all the stilbazoles (2.1-2.16) investigated are presented below.
Figure 3.6 $^1$H NMR (400 MHz) in CDCl$_3$. (a) $^1$H NMR in CDCl$_3$ of cis 4- F stilbazole, (b) neutral extract of cis 4-F stilbazole. HCl, irradiated for 1h, (c) neutral extract of cis 4- F stilbazole. HCl, irradiated for 2h (d) neutral extract of cis 4- F stilbazole. HCl, irradiated for 4 h (e) neutral extract of cis 4- F stilbazole. HCl, irradiated for 6 h (f) neutral extract of cis 4- F stilbazole. HCl, irradiated for 10 h. Aromatic proton ortho to N in pyridyl ring is denoted by ■ for trans, * for cis and □ for anti H-T dimer.
Table 3.1 Top: Percent conversion upon irradiation of anhydrous *cis* 4-F stilbazol. HCl for various time (calculated by integration of $^1$H NMR peaks). Bottom: Graphical presentation of % conversion vs time of irradiation.
Figure 3.7 $^1$H NMR (400 MHz) in CDCl$_3$. (a) $^1$H NMR in CDCl$_3$ of cis 4-Cl stilbazole, (b) neutral extract of cis 4-Cl stilbazole. HCl, irradiated for 1h, (c) neutral extract of cis 4-Cl stilbazole. HCl, irradiated for 2h (d) neutral extract of cis 4-Cl stilbazole. HCl, irradiated for 4h (e) neutral extract of cis 4-Cl stilbazole. HCl, irradiated for 7h (f) neutral extract of cis 4-Cl stilbazole. HCl, irradiated for 12h. Aromatic proton ortho to N in pyridyl ring is denoted by ■ for trans, * for cis and ■ for anti H-T dimer.
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Table 3.2 Top: Percent conversion upon irradiation of anhydrous cis 4-Cl stilbazole. HCl for various time (calculated by integration of $^1$H NMR peaks). Bottom: Graphical presentation of % conversion vs time of irradiation.
Figure 3.8 $^1$H NMR (400 MHz) in CDCl$_3$. (a) $^1$H NMR in CDCl$_3$ of cis 4-Br stilbazole, (b) neutral extract of cis 4-Br stilbazole. HCl, irradiated for 1 h, (c) neutral extract of cis 4-Br stilbazole. HCl, irradiated for 4 h (d) neutral extract of cis 4-Br stilbazole. HCl, irradiated for 6 h (e) neutral extract of cis 4-Br stilbazole. HCl, irradiated for 20 h (f) neutral extract of cis 4-Br stilbazole. HCl, irradiated for 26 h. Aromatic proton ortho to N in pyridyl ring is denoted by ■ for trans, * for cis and ■ for anti H-T dimer.
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Table 3.3 Percent conversion upon irradiation of anhydrous cis 4-Br stilbazole. HCl for various time (calculated by integration of $^1$H NMR peaks). Bottom: Graphical presentation of % conversion vs time of irradiation.
Figure 3.9 $^1$H NMR (400 MHz) in CDCl$_3$ (a) $^1$H NMR in CDCl$_3$ of cis 4- I stilbazole, (b) neutral extract of cis 4-I stilbazole. HCl, irradiated for 1h, (c) neutral extract of cis 4-I stilbazole. HCl, irradiated for 2.5 h (d) neutral extract of cis 4- I stilbazole. HCl, irradiated for 6 h (e) neutral extract of cis 4- I stilbazole. HCl, irradiated for 10 h (f) neutral extract of cis 4- I stilbazole. HCl, irradiated for 15 h. Aromatic proton ortho to N in pyridyl ring is denoted by ■ for trans, * for cis and ■ for anti H-T dimer.
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Table 3.4 Top: Percent conversion upon irradiation of anhydrous cis 4-I stilbazole. HCl for various time (calculated by integration of $^1$H NMR peaks). Bottom: Graphical presentation of % conversion vs time of irradiation.
Figure 3.10 $^1$H NMR (400 MHz) in CDCl$_3$ (a) $^1$H NMR in CDCl$_3$ of cis 3,4-diOMe stilbazole, (b) neutral extract of cis 3,4-diOMe stilbazole. HCl, irradiated for 1h, (c) neutral extract of cis 3,4-diOMe stilbazole. HCl, irradiated for 4 h (d) neutral extract of cis 3,4-diOMe stilbazole. HCl, irradiated for 6 h (e) neutral extract of cis 3,4-diOMe stilbazole. HCl, irradiated for 20 h (f) neutral extract of cis 3,4-diOMe stilbazole. HCl, irradiated for 26 h. Aromatic proton ortho to N in pyridyl ring is denoted by ■ for trans, * for cis and ■ for anti H-T dimer.
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Table 3.5 Percent conversion upon irradiation of anhydrous cis 3,4-diOMe stilbazole. HCl for various time (calculated by integration of $^1$H NMR peaks). Bottom: Graphical presentation of % conversion vs time of irradiation.

Figure 3.11 (a) $^1$H NMR (400 MHz) in CDCl$_3$ of anti H-T dimer obtained from neutralization and separation of product mixture from irradiated cis 4- Br stilbazole. HCl.
Figure 3.12 $^1$H NMR (400 MHz) in CDCl$_3$ of anti H-T dimer obtained from neutralization and separation of product mixture from irradiated cis 4-Cl stilbazole. HCl.

3.3 Experimental section

Synthesis of cis-stilbazole derivatives

The cis-stilbazoles were prepared by irradiation of the trans compounds in a CHCl$_3$ solution in Pyrex test tubes ($\lambda \geq 290$ nm), to afford a mixture of cis & trans. Preparative TLC was used to separated the mixture, to afford liquid cis compound. After separation, the purity of cis compound was checked by $^1$H NMR and also by UV-Vis (Figure 3.11). On addition of 3 equivalents HCl (37%), the cis stilbazole salt is formed which was air dried overnight to give powder of the cis stilbazole. HCl salt. These salts were vacuum dried for 12 h to make it completely dry, prior to irradiation.

Irradiation technique

Irradiations were performed using a 450 W medium pressure mercury arc lamp placed in a water-cooled Pyrex immersion jacket. About 8-10 mg of powdered stilbazole. HCl salts were spread uniformly between two Pyrex glass plates sealed with parafilm and irradiated. The plates were turned around every 1 h. After irradiation the crude product was dissolved in H$_2$O and neutralized with 1N NaOH. This neutral solution was extracted
with CHCl$_3$ four times and the combined organic layer was dried over anhydrous Na$_2$SO$_4$. After evaporation of the solvent, product was characterized using $^1$H NMR in CDCl$_3$.

**Figure 3.13** Absorption spectra in methanol solution of (a) $cis$ 4-Br stilbazole (red line) and $trans$ 4-Br stilbazole (black line) (b) $cis$ 4-Cl stilbazole (red line) and $trans$ 4-Cl stilbazole (black line).

### 3.4 Crystallographic analysis

Light yellow single crystals of 3.1.HCl ($cis$ 4F-Stilbazol.HCl) suitable for X-ray diffraction analyses, were obtained by evaporation of solution in chloroform/ethyl acetate solvent mixture at 25 °C, crystallized in the monoclinic crystal system. The systematic absences in the intensity data were consistent with the unique space groups $P2_1/c$.

Light yellow single crystals of 3.2.HCl ($cis$ 4Cl-stilbazol.HCl) suitable for X-ray diffraction analyses, were obtained by evaporation of solution in chloroform/ethyl acetate solvent mixture at 25 °C, crystallized in the monoclinic crystal system. The systematic absences in the intensity data were consistent with the unique space group $P2_1/c$. With $Z = 8$, there are two formula equivalents of the $cis$ 4Cl-stilbazol.HCl present in the asymmetric crystal unit.
Light yellow single crystals of (3.3.HCl) cis 4Br-stilbazol.HCl suitable for X-ray diffraction analyses, were obtained by evaporation of solution in chloroform/ethyl acetate solvent mixture at 25 °C, crystallized in the monoclinic crystal system. The systematic absences in the intensity data were consistent with either of the space groups $P2_1/m$ or $P2_1$. The structure could only be solved in the latter space group. With $Z = 4$, there are two formula equivalents of the cis 4Br-stilbazol.HCl present in the asymmetric crystal unit.

Light yellow single crystals of cis 4I-stilbazol.HCl suitable for X-ray diffraction analyses, were obtained by evaporation of solution in chloroform/ethyl acetate solvent mixture at 25 °C, crystallized in the monoclinic crystal system. The systematic absences in the intensity data were consistent with the unique space groups $P2_1/c$.

Each data crystal was glued onto the end of a thin glass fiber. X-ray intensity data were measured by using a Bruker SMART APEX2 CCD-based diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å). The raw data frames were integrated with the SAINT+ program by using a narrow-frame integration algorithm. Corrections for Lorentz and polarization effects were also applied with SAINT+. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied using the program SADABS. All structures were solved by a combination of direct methods and difference Fourier syntheses, and refined by full-matrix least squares on $F^2$, by using the SHELXTL software package. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in geometrically idealized positions and included as standard riding atoms during the least-squares refinements.
Crystal data, data collection parameters, and results of the analyses are listed in Table 3.6-3.7.

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Table 3.6 Crystallographic Data for Compounds 3.1.HCl and 3.2.HCl
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</tbody>
</table>

*R = Σhk$ι$($|F_{\text{obs}}| - |F_{\text{calc}}|$)/Σhk$ι$|F_{\text{obs}}|$; $R_w = [Σhk$ι$w( |F_{\text{obs}}| - |F_{\text{calc}}|)^2]/Σhk$ι$wF_{\text{obs}}^2]^{1/2}$, $w = 1/\sigma^2(F_{\text{obs}})$; GOF = [Σhk$ι$w( |F_{\text{obs}}| - |F_{\text{calc}}|)^2/(n_{\text{data}} - n_{\text{vari}})]^{1/2}$.

**Table 3.7** Crystallographic data for compounds 3.3.HCl and 3.4.HCl
Chapter 4. Nanoparticles stabilized with carboxylic acid groups of organic cavitands

4.1 Overview

Unusual chemical and physical properties of gold nanoparticles, compared with those of metal atoms or bulk metal due to the quantum size effect and their large superficial area, make them attractive for applications such as optics, electronics, catalysis, and biomedicine.\textsuperscript{111-113} Our interest in exploring interaction between an organic molecule and gold atoms with one of them being in its excited state required bringing the two closer. We believed that this could be easily achieved in water where the hydrophobic organic molecule would seek out a hydrophilic environment. This interested us to synthesize water-soluble gold nanoparticles decorated with organic ligands. With the background in supramolecular chemistry, we visualized that if one can functionalize gold nanoparticles with organic cavitand hosts it would be possible to place organic molecules closer to the gold atoms. Based on the well-known fact that gold atoms strongly bind to thiol group (\textendash\textendash\textendash SH), in the past gold nanoparticles have been functionalized with thiolated cavitands such as cyclodextrins, calixarenes and resorcinarenes.\textsuperscript{114-120} However, to our knowledge no molecule of photochemical or photo physical interest has been included in such systems and investigated. Along this line, our group recently reported functionalization of gold nanoparticles with a thiolated deep cavity cavitand tetrathiol tetra acid (TTTA) and demonstrated that the adjacent gold atoms altered the excited state properties of organic molecules included in TTTA.\textsuperscript{121} One shortcoming of this system was that the guests could be included within TTTA\textendash AuNP (\textendash represents the host TTTA is located on top of AuNP) only through heterocapsule formation requiring a second host molecule. It was observed that homocapsular assembly led to aggregation.
With the interest to functionalize surfaces using water-soluble cavitands, our group has recently established that cavitands with acid or amine functionality could be adsorbed on surfaces of silica, clay, titanium oxide and zirconium phosphate.\textsuperscript{122-124} The excited state chemistry of organic guests included within surface adsorbed cavitand was significantly different from that in solution. Considering the easier synthesis of acid functionalized cavitand \textsuperscript{36,124} (OA and ROA) (Figure 4.1) compared to thiol functionalized cavitand (TTTA), we were interested in exploring the use of water-soluble functionalized gold nanoparticles to probe the interaction between excited organic molecules and gold atoms. Although following the report of Schiffrin and Brust,\textsuperscript{113} most studies utilized thiol group to stabilize gold nanoparticles, our motivation of using acid group instead of thiol could be used to stabilize gold nanoparticles came from the classic report of Turkevich\textsuperscript{125-128} that utilized citric acid both as the reducing and stabilizing
agent. This early observation prompted us to explore octa acid (OA) and resorcinol capped octa acid (ROA), as stabilizing agents. These cavitands with COOH groups were ideal to test whether RCOOH (R=cavitand) could be used to make stable nanoparticles.  

4.2 Results and discussions

4.2.1 Gold nanoparticle (AuNP) synthesis and characterization

AuNP functionalized with cavitands OA and ROA were prepared in water by drop wise addition of 4 equivalents of NaBH₄ solution, to a vigorously stirred aqueous basic (NaOH) solution containing 10:1 equivalents of HAuCl₄ and cavitand. The solution turned red, indicating the formation of AuNP. At this stage water was evaporated at reduced pressure and elevated temperature (~40° C) to obtain dark red solid particles. To make sure that these solid particles are not aggregates, they were redispersed in water. Upon stirring with fresh water AuNP functionalized with cavitand OA and ROA regained their color and were stable for several weeks. The synthesized nanoparticles were dialyzed through a cellulose membrane (Spectra/Por 1, MWCO: 6–8000) to remove the unbound cavitands before using the cavitand∩AuNP for NMR and guest inclusion studies.

The nanoparticles functionalized with cavitands OA and ROA were characterized by UV-Vis absorption, TEM, thermogravimetric analysis (TGA), IR, ¹H NMR, and dynamic light scattering (DLS). The plasmon bands characteristic of AuNP in the region 520 – 550 nm were recorded for OA and ROA functionalized AuNP (Figure 4.2). The UV-visible absorption spectra of the same samples immediately after preparation and
after removal of water and redispersion in water clearly show that AuNP functionalized with OA and ROA are stable. Similarly, UV-visible absorption spectra of ‘bare’ nanoparticles (AuNP prepared by reduction with NaBH$_4$ in the absence of stabilizing agent) immediately after preparation and after removal of water and redispersion (Figure 4.2c) shows its instability.

![Absorption spectra](image)

**Figure 4.2** Absorption spectra of (a) OA∩AuNP immediately after preparation (red line), OA∩AuNP after distillation of H$_2$O and redispersing in H$_2$O (blue line); (b) ROA∩AuNP immediately after preparation (red line), ROA∩AuNP after distillation of H$_2$O and redispersing in H$_2$O (blue line); (c) bare AuNP immediately after preparation (red line), bare AuNP after distillation of H$_2$O and redispersing in H$_2$O (blue line).

TEM images of the above-prepared samples evaporated on copper grid coated with carbon, confirmed the formation of AuNP. TEM photographs of OA∩AuNP (Figure 4.3) and ROA∩AuNP (Figure 4.4) suggested lack of aggregation and the
nanoparticles to be spherical and narrowly distributed. While the TEM image of bare AuNP (Figure 4.5) shows aggregation.

![TEM photographs of OA∩AuNP (8.4 ± 1.6 nm)](image)

Figure 4.3 TEM photographs of OA∩AuNP (8.4 ± 1.6 nm) (a) & (c) with (b) histogram of particle size distribution.

Consistent with the TEM photographs, the hydrodynamic diameters of cavitand functionalized AuNP dispersed in water estimated by DLS were uniform and slightly larger than the ones measured by TEM indicating a coating of organic layer around AuNP (discussed in experimental section).
Theromogravimetric analysis (TGA) data confirmed the presence of both organic and metallic components in the nanoparticles prepared in the presence of cavitands OA and ROA. As expected, heating of only OA resulted in 100% combustion of the sample.
around 500° C. Nearly at the same temperature OA∩AuNP resulted in loss of 38.5% weight (Figure 4.6). This suggested that AuNP prepared in presence of OA contained both organic and metallic components. Similar observation was made with ROA∩AuNP sample, which showed 39% weight loss (Figure 4.7). $^1$H NMR spectra of the cavitand alone and cavitand∩AuNP discussed in the experimental section also supports the stabilization of AuNP by cavitand.

**Figure 4.6** TGA traces showing weight loss with respect to temperature 100% for OA cavitand (black) and 38.5% for OA∩AuNP (red).
Figure 4.7 TGA traces showing weight loss with respect to temperature 100% for ROA cavitand (black) and 39% for ROA∩AuNP (red).

4.3 Inclusion of guests within water-soluble cavitand functionalized AuNP

All complexation studies with OA∩AuNP, ROA∩AuNP were carried out in aqueous solution. We choose two guest molecules, fluorescent coumarin-1 (C-1) and phosphorescent 4,4’-dimethybenzil (DMB) (Figure 4.1). These guests helped us to probe the interaction between excited guests and gold atoms. Adding guest with prepared cavitand∩AuNP achieved guest inclusion within the cavitands decorated on AuNP. This is represented as guest@[cavitand∩AuNP]. Support for the existence of guest@[OA∩AuNP] came from UV-visible absorption spectra presented in (Figure 4.7-4.8). Samples with DMB and C-1 within OA∩AuNP and ROA∩AuNP showed the expected plasmon band with a maximum at ~520 nm as well as absorption due to the guests.
Figure 4.7 Absorption spectra of (a) OA∩AuNP (red line); DMB@[OA∩AuNP] (blue line); DMB@OA₂ in H₂O (green line) (b) ROA∩AuNP (red line); DMB@[ROA∩AuNP] (blue line) in DMSO (20%) /H₂O (80%) mixture; DMB@ROA₂ in DMSO (20%) /H₂O (80%) mixture (green line) [OA]= [ROA]=4×10⁻⁵ M, [DMB]=2×10⁻⁵ M (host: guest = 2:1), in nanoparticle, nanoparticle DMB complex and OA, ROA complex.

Figure 4.8 Absorption spectra of (a) OA∩AuNP (red line); (b) C-1@[OA∩AuNP] (blue line); C-1@OA₂ in H₂O (green line) (b) ROA∩AuNP (red line); C-1@[ROA∩AuNP] (blue line); C-1@ROA₂ in DMSO (20%) /H₂O (80%) mixture (green line) [OA]= [ROA]=4×10⁻⁵ M, [C-1]=2×10⁻⁵ M (host: guest = 2:1), in nanoparticle, nanoparticle C-1 complex and OA, ROA complex.
The overlap between the bands due to cavitand∩AuNP and guest@[cavitand∩AuNP] seen in the figures suggested that the structure, shape and size of cavitand∩AuNP were not affected by the inclusion of guests. Further confirmation for guest inclusion came from TGA data (Figure 4.9) for DMB@[OA∩AuNP]. The TGA data reveal a distinct increase in organic content between OA∩AuNP and DMB@[OA∩AuNP]. This increase we believe represented guest DMB that was included within OA∩AuNP.

**Figure 4.9** TGA traces showing weight loss with respect to temperature: green, 100% loss for OA; red, 38.5% for OA∩AuNP, and blue, 41% for DMB@[OA∩AuNP].

The $^1$H NMR spectra of guests included in OA∩AuNP and ROA∩AuNP and DLS measurements for representative samples (discussed in experimental section), also support guest inclusion. TEM photographs for DMB@[OA∩AuNP] and
DMB@[ROA∩AuNP] samples (Figure 4.10) further confirmed that OA∩AuNP were not disrupted by the inclusion of DMB within OA. Most importantly, in the case of OA and ROA TEM, DLS and UV-Vis data did not suggest any aggregation of Au nanoparticles. From the results presented above it is clear that guest could be included within cavitands appended with COOH groups that stabilize AuNP. Based on the data on hand we can’t be certain of the orientation of the capsular assembly on AuNP surface.

**Figure 4.10** TEM photographs with histograms of particle size distributions of (a) DMB@[OA∩AuNP] (7.5 ± 2.5 nm), and (b) DMB@[ROA∩AuNP] (6 ± 2 nm).
There could be two possibilities, (i) benzoic acid groups at the broader rim of the cavitand binds to the AuNP (ii) propionic acid at the bottom of the cavitand binds to the AuNP (Figure 4.12). Experiments were done in collaboration with cavitands iTATA (top –OH and bottom –COOH) and TATA (top –COOH, bottom –OH) to understand the orientation of the capsular assembly (Figure 4.11).

![Hosts iTATA and TATA](image)

**Figure 4.11** Hosts used to understand orientation of capsular assembly on AuNP.

![Cartoon representations](image)

**Figure 4.12** Cartoon representations of visualized orientations of host–guest capsules on gold nanoparticles.
It was found that, TATA stabilized the AuNP while iTATA was incapable of AuNP stabilization. This suggests that the benzoic acid group at the broader rim plays a more important role in stabilizing AuNP, than the propionic acid at the bottom.

4.3.1 Photophysics of guests included in cavitand functionalized AuNP

Excited state behavior of organic molecules in confined environments such as water-soluble micelles, dendrimers, cavitands (cyclodextrins, cucurbiturils, and calixarenes and octa acid capsules) and solid surfaces such as silica, clay and zeolites and crystals\textsuperscript{133, 134} have been well studied. Most confining media with the exception of zeolites were inert and did not directly influence the excited state properties except providing a confining environment. With this background were interested in examining the excited state chemistry of organic molecules within cavitands, positioned on gold nanoparticles. We visualized that cavitand adsorbed on AuNP surface would provide confinement and this assembly would provide an opportunity to examine the influence of AuNP on excited state chemistry of organic guest molecules. Enhancement as well as quenching of fluorescence of guests adsorbed on AuNP has been reported due to gold atoms influencing the radiative as well as non-radiative rate constants of the excited chromophores\textsuperscript{135-140}. While photoreactions on AuNP surface, such as cis-trans isomerization of stilbenes\textsuperscript{141-143} and Norrish Type II reactions of phenyl alkyl ketones\textsuperscript{144} are known to occur via triplet state, influence of AuNP on the triplet state of organic molecules has not been clearly established, except a recent report no phosphorescence quenching by AuNP from our group\textsuperscript{121}. To examine the quenching of excited singlet and triplet of organic molecules we recorded the fluorescence C-1 and phosphorescence of DMB (Figure 4.1) included with OA and ROA located on AuNP. The fluorescence
spectra of C-1 included in cavitand OA and ROA and in OA∩AuNP and ROA∩AuNP in water at room temperature were measured (Figure 4.13). It is obvious that C-1 included within OA∩AuNP and ROA∩AuNP is only weakly emissive. Given that C-1 is a good electron donor the quenching could be due to electron transfer from S₁ of C-1 to AuNP. DMB phosphoresce in solution when oxygen is thoroughly excluded. Upon encapsulation within a capsule it phosphoresce even in presence of oxygen. DMB included in cavitand OA and ROA is strongly phosphorescent at room temperature in water but when included in OA∩AuNP and ROA∩AuNP the phosphorescence was quenched (Figure 4.14). This observation bears analogy to the effect of smaller stabilize metal nanoparticles.¹⁴⁵⁻¹⁴⁷ These observations has opened a new approach to prevent probe-aggregation. This finding extend the type of functional groups that could be used AuNP (dia: 1-50 nm) has on fluorescence from various organic molecules. The AuNPs that we have used have the core diameter between 5 and 10 nm. The observed results are consistent with the conclusion that a non-radiative pathway quenches the triplet of DMB. Fluorescence quenching is believed to occur by both energy and electron transfer process.

Figure 4.13 Fluorescence spectra of (a) C-1@OA₂ (red line), C-1@[OA∩AuNP] (blue line); (b) C-1@ROA₂(red line), (b) C-1@[ROA∩AuNP] (blue line); (λex = 350 nm; solvent, water). [OA] = [ROA] = 4 × 10⁻⁵ M, [C-1] = 2 × 10⁻⁵ M (host/guest = 2:1).
Being able to include guests within a cavitand linked to AuNP, eliminates the previous adopted method of synthetically modifying a probe with anchor groups to hold on to AuNP.\textsuperscript{135-140} Also, the use of probes encapsulated in a host molecule would avoid probe-aggregation. This finding expands the type of functional groups that could be used to stabilize AuNP.\textsuperscript{145-147} This observation opens a new approach to bring a photoactive organic chromophore and metal nanoparticles closer without any covalent bonds.

![Phosphorescence spectra](image)

**Figure 4.14** Phosphorescence spectra of (a) DMB@OA\textsubscript{2} (red line), DMB@[OA∩AuNP] (blue line); (b) DMB@ROA\textsubscript{2} (red line), (b) DMB@[ROA∩AuNP] (blue line); (\(\lambda_{ex} = 318\) nm; solvent, water. [OA] = [ROA] = 4 × 10\textsuperscript{−5} M, [DMB] = 2 × 10\textsuperscript{−5} M, (host/guest = 2:1).

**4.4 Experimental section**

**Synthesis of cavitands OA and ROA functionalized AuNP**

Cavitand modified AuNP were synthesized by NaBH\textsubscript{4} reduction of HAuCl\textsubscript{4} in the presence of cavitand. In the synthesis of AuNP with OA and ROA, 600 \(\mu\)L (1 mM) cavitand in 8 mM NaOH was added to 10 mL D.I. water with 200 \(\mu\)L (32 mM) aqueous
solution of HAuCl₄. This solution was stirred for 5 min and 2 mL of 21 mM of freshly prepared aqueous NaBH₄ solution was added drop wise and stirred for 30 min at RT. The reaction mixture turned wine red with addition of NaBH₄ solution and cavitand modified AuNP were obtained. The cavitand stabilized AuNP was purified by dialysis. The AuNP solution was loaded into 4 in. segments of cellulose dialysis membrane (Spectra/Por 1, MWCO: 6-8,000), placed in 1 L beakers of water, recharging with fresh water every 5 h over the course of 24 h. After dialysis the rose red AuNP solutions were collected from the dialysis tubes, and the solvent was removed under reduced pressure at ~ 40 °C, dried for 1h under the same condition and then characterized. AuNP with OA and ROA was dispersed in water after removal of solvent.

Control experiment was carried out following the same method without the addition of cavitand (bare AuNP), which resulted in formation of wine red solution but did not disperse in water after removal of solvent.

For comparison study, citrate capped gold nanoparticles were synthesized. In synthesis, 4 ml of trisodium citrate (0.1 M) was added to a 50 mL aqueous solution of HAuCl₄ (1 mM) under boiling conditions. The solution initially turned to grey color then gradually changed to red within a few minutes with continued boiling. Citrate capped AuNP particles did not disperse in water after removal of solvent and surface plasmon resonance (SPR) disappeared similar to bare AuNP (Figure 4.15).
Characterization

![Absorption spectra](image)

**Figure 4.15** Top: Absorption spectra of (a) OA∩AuNP immediately after preparation (red line), OA∩AuNP after distillation of H₂O and redispersing in H₂O (blue line); (b) ROA∩AuNP immediately after preparation (red line), ROA∩AuNP after distillation of H₂O and redispersing in H₂O (blue line); (c) citrate∩AuNP immediately after preparation, (red line), citrate∩AuNP after distillation of H₂O and redispersing in H₂O (blue line); (d) bare AuNP immediately after preparation (red line), bare AuNP after distillation of H₂O and redispersing in H₂O (blue line). Bottom: Photographs of (L-R) OA, ROA, citrate and bare AuNP after distillation of H₂O and redispersing in H₂O.

**Transmission electron microscopy (TEM)**

The morphology of AuNP samples was observed with FEI TECNAI G2 F30 TWIN transmission electron microscope, with an accelerating voltage of 200 kV. A drop of aqueous sample from each of OA∩AuNP, ROA∩AuNP, bare AuNP, DMB@[OA∩AuNP], and DMB@[ROA∩AuNP] was deposited directly onto a copper grid covered with a thin carbon film and the solvent was allowed to evaporate at room temperature. The average size of core of gold nanoparticles measured by TEM for OA∩AuNP, ROA∩AuNP, DMB@[OA∩AuNP], and DMB@[ROA∩AuNP] were
8.4±1.6 nm, 6.5±3.5 nm, 7.5±2.5, and 6 ± 2 nm respectively and aggregation of bare AuNP was observed by TEM.

**Dynamic light scattering (DLS)**

The hydrodynamic diameter of the OA∩AuNP, ROA∩AuNP (before and after distillation), bare AuNP, and for complexes DMB@[OA∩AuNP], C-1@[OA∩AuNP] was measured by dynamic light scattering technique using a Zetasizer Nano ZS DLS system equipped with a red (633 nm) laser an Avalanche photodiode detector (APD) (quantum efficiency >50% at 633 nm) (Malvern Instrument Ltd., England). Ten measurements were conducted with a fixed 10 runs and each runs lasts 3 s to obtain the average size. DLS measurement was done for samples before and after distillation.

![Size Distribution by Volume](image)

**Figure 4.16** Percentage volume versus hydrodynamic diameter profiles monitored by dynamic light scattering experiments for OA∩AuNP recorded in H₂O. The average size of the particle is 14 ± 0.6nm (10 scans).
Figure 4.17 Percentage volume versus hydrodynamic diameter profiles extracted from dynamic light scattering experiments for OA∩AuNP recorded after distillation of H₂O and redispersing in H₂O. The average size of the particle is 13.3±1.5 nm (10 scans).

Figure 4.18 Percentage volume versus hydrodynamic diameter profiles monitored by dynamic light scattering experiments for ROA∩AuNP recorded in H₂O. The average size of the particle is 9.5 ± 0.2 nm (10 scans).
Figure 4.19 Percentage volume versus hydrodynamic diameter profiles monitored by dynamic light scattering experiments for ROA∩AuNP recorded after distillation of H$_2$O and redispersing in H$_2$O. The average size of the particle is 9.3 ± 1.2 nm (8 scans).

Figure 4.20 Percentage volume versus hydrodynamic diameter profiles monitored by dynamic light scattering experiments for bare AuNP in H$_2$O.
Figure 4.21 Percentage volume versus hydrodynamic diameter profiles monitored by dynamic light scattering experiments for DMB@[OA∩AuNP] recorded in H₂O. The average size of the particle is 15.2±1.5 nm (10 scans).

Figure 4.22 Percentage volume versus hydrodynamic diameter profiles monitored by dynamic light scattering experiments for C-1@[OA∩AuNP] recorded in H₂O. The average size of the particle is 16±1.4 nm (10 scans).
Fourier transformed infrared (FTIR) spectroscopy

Figure 4.23 Transmission FT-IR spectra of Bare AuNP (black), OA∩AuNP (red) and sodium salt of OA (blue).
Figure 4.24 Transmission FT-IR spectra of ROA∩AuNP (red) and sodium salt of ROA (blue).

Thermogravimetric analysis of OA∩AuNP:

Thermal Gravimetric analysis of neat cavitands and AuNP were carried out using NETZSCH TG 209 F3 equipment. Dry, purified samples placed in an alumina crucible under airflow, with a flow rate of 30 ml/min. The data was recorded from 25 to 900 °C at a heating rate of 20 °C min$^{-1}$. The weight loss is for OA∩AuNP, ROA∩AuNP, and DMB@[OA∩AuNP] is from the organic component of the nanoparticles.

$^1$H NMR analysis of OA∩AuNP

$^1$H NMR spectra (Figure 4.25-4.27) of the cavitand alone and cavitand∩AuNP was obtained. Slightly broad $^1$H NMR signals of cavitand∩AuNP while sharp signals of various protons of the cavitand in D$_2$O is suggestive of the cavitand functionalized AuNP
The line broadening in the $^1$H NMR spectra is consistent with literature reports$^{132}$ for various organic coated AuNP. In addition, the diffusion constants measured by DOSY for OA and OA∩AuNP were 1.7 $\times$ 10^{-10} m² s⁻¹ and 1.03 $\times$ 10^{-10} m² s⁻¹ (Figure 4.28-4.29) respectively confirmed the differences in sizes of free OA and AuNP adsorbed OA. $^1$H NMR spectra suggested that these guests formed the expected 2:1 (host: guest) capsular assemblies. For example in the case of DMB, the presence of a single signal for both the methyl groups suggested the formation of a symmetrical capsuleplex rather than an unsymmetrical cavitandplex. Had this been a 1:1 cavitandplex the two methyl groups would be in distinctly different magnetic environments (one within and the other outside the cavity) and the two methyl groups would have different chemical shifts.

The $^1$H NMR spectra of guests C-1 and DMB included in OA∩AuNP, ROA∩AuNP provide evidence of guest inclusion from the expected upfield shift of the guest signals, especially that of methyl and methylene protons$^{37}$ (Figure 4.25-4.27). DLS measurements for representative samples (Figure 4.21-4.22) supported the above inference. The hydrodynamic radii for OA∩AuNP and DMB@[OA∩AuNP] were 14±0.6 nm and 15.2±1.5 nm. It is not clear whether the slight increase in hydrodynamic radius is the result of guest inclusion.

Comparison of the IR spectra of sodium salt of OA and ROA with that of OA∩AuNP, ROA∩AuNP suggests, AuNPs are coated with the above cavitands (Figure 4.23-4.24). Based on TEM, UV-Vis absorption, IR, $^1$H NMR, dynamic light scattering (DLS) and thermogravimetric analysis (TGA) results we conclude that stable AuNP could be stabilized with organic cavitands carrying COOH group.
Figure 4.25 $^1$H NMR (500 MHz) spectra of (a) C-1@[OA∩AuNP] in D$_2$O (b) C-1@OA$_2$ in tetraborate buffer D$_2$O (c) OA∩AuNP in D$_2$O (d) OA in tetraborate buffer D$_2$O. Here ‘▲’ is residual H$_2$O in D$_2$O, ‘■’ is residual DMSO, ‘***’ is bound guest signal.
Figure 4.26 $^1$H NMR (500 MHz) spectra of (a) DMB@[OA∩AuNP] in D$_2$O (b) DMB@[OA$_2$] in tetraborate buffer D$_2$O (c) OA∩AuNP in D$_2$O (d) OA in tetraborate buffer D$_2$O. Here ‘▲’ is residual H$_2$O in D$_2$O, ‘▲’ is glycerol from dialysis membrane, ‘*’ is bound guest signal.
Figure 4.27 $^1$H NMR (500 MHz) spectra of (a) C-1@ROA∩AuNP in 80% D$_2$O +20% DMSO (b) C-1@ ROA$_2$ in 80% tertaborate buffer D$_2$O +20% DMSO (c) ROA∩AuNP in D$_2$O (d) ROA in tetraborate buffer D$_2$O. Here ‘**’ is bound guest signal, ‘■’ is residual DMSO and ‘▲’ is residual H$_2$O in D$_2$O.
Figure 4.28 2D DOSY (500 MHz, in 10 mM buffered D$_2$O) spectra of (a) OA, diffusion constant $1.7 \times 10^{-10}$ m$^2$/s (b) DMB@OA$_2$, diffusion constant $1.33 \times 10^{-10}$ m$^2$/s.
Figure 4.29 2D DOSY (500 MHz, in 10 mM buffered D$_2$O) spectra of (a) OA, diffusion constant $1.7 \times 10^{-10}$ m$^2$/s (b) DMB@OA$_2$, diffusion constant $1.33 \times 10^{-10}$ m$^2$/s.
Chapter 5: Deep cavity cavitand as electron transfer agent.

5.1 Overview

Water soluble supramolecular assemblies have become a powerful tool to control and direct chemical reactivity, stabilize reactive intermediates and result in unusual physical or chemical phenomenon that can only be achieved by complexation.\textsuperscript{133,134,148} In this context hosts such as micelles, cyclodextrins, calixarenes, cucurbiturils, larger cavitands and inorganic assemblies have been extensively explored in aqueous solution.\textsuperscript{147-152} Of these, larger cavitands and inorganic assemblies constructed with aromatic rings have been demonstrated to show a great promise.\textsuperscript{151,155} However, in contrast to conventional micelles, cyclodextrins, calixarenes, cucurbiturils that could be considered to possess ‘inert’ reaction cavities, larger cavitands and inorganic assemblies could be considered to have ‘active’ reaction cavities because of their absorption extending to 350 nm.\textsuperscript{156-158} This requires one to understand the excited state properties of the host itself. During the last decade, deep cavity cavitand commonly known as octa acid (\textbf{Figure 5.1}) has been well established as a valuable reaction vessel to manipulate photoreactions.\textsuperscript{36, 155,159,160} Confinement of guest within the octa acid cavity influence selectivity, excited state behavior of guest molecules, and dictate the product formation.\textsuperscript{161-163,165,166}

To further explore its value as a photochemical reaction vessel we felt it to be important to understand the energy and electron donor/acceptor properties of cavitands. We choose two cavitands, OA and ROA each containing eight acid group.\textsuperscript{36,124} In this chapter we discuss the results that establish that two related deep cavity cavitands, both commonly known as octa acid (OA and ROA in \textbf{Figure 5.1}) are not inert and in fact can serve as an
electron donors in the ground state to excited acceptors and as a triplet energy donors in the excited state. 164

5.2 Results and discussions

The absorption spectra of hosts OA and ROA reflects absorption up to 320 nm. This is in contrast with the absorption properties of cyclodextrins and cucurbutrils, which absorb below 220 nm. Excitation of OA and ROA at 280 nm results in weak fluorescence in the region 320 to 420 nm (Figure 5.2). Remarkable overlap between absorption and excitation spectra and mirror symmetric relationship between emission and absorption spectra suggested the observed emission to be from first excited singlet state of the hosts. Based on the above spectra we believe that the S1 has an approximate energy of 88 Kcal mol\(^{-1}\). To examine the electron donating ability of OA and ROA we chose three positively charged electron acceptors N-methylacridinium iodide (5.1), dimethyldiazaphenathrenium iodide (5.2), and dimethyldiazapyrenium iodide (5.3) (Figure 5.1) 167-169

The choice was dictated by the fact that these systems (a) are expected to be approach closer to the exterior of the anionically charged cavitand through Columbic attraction, (b) absorb above 350 nm where OA and ROA don’t absorb (Figure 5.3), (c) show intense fluorescence in aqueous solution and (d) have low reduction potentials (< − 0.5 eV, SCE). It was established previously, that pyridinium iodide and dimethyl viologen chloride remain closer to the exterior of OA capsule.170
Figure 5.1 Structure of hosts and acceptors used in the study.

Figure 5.2 (a) Excitation (red line) and emission spectra (blue line) of OA ($\lambda_{ex} = 280$ nm) (b) Excitation (red line) and emission spectra (blue line) of ROA ($\lambda_{ex} = 280$ nm). ([OA] = [ROA] = $5 \times 10^{-5}$ M in 10 mM Na$_2$B$_4$O$_7$ buffer solution.)
In this study we noted that when methyl acridinium iodide was added to the octa acid solution there were no changes in the $^1$H NMR spectrum of the former indicating that it is not included within the cavitand (Figure 5.4). The fluorescence of all three acceptors was quenched upon gradual addition of OA (Figure 5.5). Similar quenching was noticed upon addition of ROA to the acceptors (Figure 5.7). Although fluorescence was quenched there were no changes in the $S_1$ lifetime of the above three acceptors. Stern-Volmer plots with various concentrations of OA and ROA using steady state fluorescence intensity ($I_0/I$) and $S_1$ lifetimes ($\tau_0/\tau$) of N-methylacridinium iodide (5.1) were obtained (Figure 5.6). Stern-Volmer plot suggested that the quenching is static and the rate constant must be in subnano second regime. If the quenching had been dynamic, the Stern-Volmer plots based on steady state fluorescence intensity and lifetime measurements should have fully overlapped, but this was not the case.
Figure 5.4 $^1$H-NMR (500 MHz), 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O) spectra of (a) OA (b) 5.1@OA (c) ROA and (d) 5.1@ROA (e) 5.1 [OA] = [ROA] = [5.1] = 1mM. ‘▲’ represents the residual proton resonance from D$_2$O and ‘■’ represents the unbound proton peaks of 5.1.
Figure 5.5 Fluorescence quenching titration (i) 5.1 with OA, [5.1] = 6×10⁻⁶ M (λ_ex = 380 nm) and [OA] = 0 to 7.4×10⁻⁵ M, (b) 5.2 with OA, [5.2] = 6×10⁻⁶ M (λ_ex = 360 nm) and [OA], 0 to 2.75×10⁻⁶ M, (c) 5.3 with OA, [5.3] = 4×10⁻⁵ M (λ_ex = 390 nm) and [OA] = 0 to 5.66×10⁻⁵ M.

Based on the fact that the S₁ energy of OA and ROA being higher than that of 5.1, 5.2, and 5.3 fluorescence quenching due to singlet-singlet energy transfer is ruled out. Given the low reduction potentials of the three acceptors, the quenching due to electron transfer from ground state OA to the excited 5.1, 5.2 and 5.3 is most likely. For the electron transfer from OA to S₁ of N-methylacridinium iodide (5.1) to be exothermic the oxidation potential of OA should be lower than 2.31 eV, i.e., the difference in S₁ energy and reduction potential of N-methylacridinium iodide (S₁ energy 2.73 eV and reduction potential in acetonitrile −0.42 eV).

Although we could not measure the oxidation potential of OA in borate buffer, we suspect it to be in the same range as that of electron rich benzene units that form the basic structure of OA (~1.5 eV).¹⁷¹ We suspected the 3,5-dimethoxybenzoate anion present on the top row of OA (Figure 5.1) to be the electron donor. To test this possibility we recorded the fluorescence of N-methylacridinium iodide (5.1) in presence of varying
amounts of 3,5-dimethoxybenzoic acid (DMBA) in borate buffer (Figure 5.8). As expected the emission of N-methylacridinium iodide (5.1) was quenched.

![Figure 5.6](image)

**Figure 5.6** Stern-Volmer plot for the quenching study of (a) 5.1 with OA (b) 5.1 and ROA ‘■’ and ‘□’ represent steady state and time resolved study respectively ($\lambda_{em} = 490$).

![Figure 5.7](image)

**Figure 5.7** Fluorescence quenching titration of (a) 5.1 with ROA, $[5.1] = 6 \times 10^{-6}$ M ($\lambda_{ex} = 380$ nm) and $[\text{ROA}] = 0$ to $1.2 \times 10^{-5}$ M, (b) 5.3 with ROA, $[5.3] = 4 \times 10^{-5}$ M ($\lambda_{ex} = 390$ nm) and $[\text{ROA}] = 0$ to $2.9 \times 10^{-5}$ M in 10 mM Na$_2$B$_4$O$_7$ buffer.
Figure 5.8 Fluorescence quenching titration of 5.1 with 3, 5-dimethoxy benzoic acid (DMBA), \([5.1] = 6 \times 10^{-6} \text{ M}\) and \([\text{DMBA}] = 0 \text{ to } 7.4 \times 10^{-3} \text{ M}\) in 10 mM Na₂B₄O₇ buffer (\(\lambda_{ex}=380 \text{ nm}\)).

The above observations are consistent with the suggestion that cation radicals of OA and ROA could be generated by irradiating electron acceptors such as N-methylacridinium iodide, dimethyldiazaphenathrenium iodide and dimethyldiazapyrenium iodide with wavelengths >350 nm where the hosts don’t absorb. This provides an opportunity to generate radical cations of host-encapsulated guest molecules by relay electron transfer process (guest to host OA radical cation) and explore the chemistry organic cation radicals enclosed in a confined space.

We believed that the presence of carbonyl groups in the host would favor intersystem crossing and triplet would be formed upon direct excitation of the host.\(^{172}\) Since no phosphorescence could be detected, as outlined below we probed the triplet generation by classical triplet sensitized photoreactions.
In collaboration with Pradeep, we tested the possibility of the host itself acting as a triplet sensitizer for a guest molecule. The photochemistry of two aromatic molecules benzonorbornadiene (5.4) and dibenzobarrelene (5.7) that give distinctly different products from \( S_1 \) and \( T_1 \) (Figure 5.9) were examined. Conveniently both molecules absorb at shorter wavelengths than the host (Figure 5.10). Photochemistry of 5.4 and 5.7 has been well investigated in solution. Triplet sensitization using acetophenone for 5.4 and acetone for 5.7 has been established to yield 5.5 and 5.8 respectively. The host-guest complexes of the guest 5.4 and 5.7 with host OA and ROA were prepared and monitored by \(^1\)H NMR titration experiments and diffusion constants measurements (DOESY). NMR experiment established that the guest 5.4 formed 2:2 (host-guest) complexes with the hosts OA and ROA, while guest 5.7 formed 2:1 host-guest capsular complex with both the hosts.

![Figure 5.9 Photochemistry of 5.4 and 5.7 in solution](image)
Figure 5.10 Absorption spectra of (a) OA, [OA]=5×10^{-5} M (blue line); and ROA, [ROA]=5×10^{-5} M (red line) in 10 mM Na_{2}B_{4}O_{7} buffer solution. (b) Absorption spectra of 5.4, [5.4] = 5×10^{-5} M (blue line); and 5.7, [5.7] = 5×10^{-5} M in hexane.

Figure 5.11 ^{1}H-NMR (500 MHz) spectra of (i) OA ([OA] = 1 mM) in 10 mM Na_{2}B_{4}O_{7} buffer/D_{2}O, (ii) 5.4 in CDCl_{3}, (iii) (5.4)_{2}@OA_{2} in 10 mM Na_{2}B_{4}O_{7} buffer/D_{2}O, (iv) (5.4)_{2}@OA_{2} (after 30 mts irradiation) and (v) (synthesized 5.5)_{2}@OA_{2}. ‘•’ represents the bound guest proton peaks. ‘*’ and ‘◊’ represent the residual proton resonance from D_{2}O and DMSO-\textit{d}_{6} respectively.
Irradiation (450 W medium pressure mercury lamp) of **5.4$_2$@OA$_2$** (two molecules of **5.4** included within two molecules of OA) dissolved in borate D$_2$O buffer solution in Pyrex NMR tube resulted in quantitative conversion of **5.4** to **5.5**. $^1$H NMR spectrum of the complex of the independently synthesized **5.5** and OA gave identical NMR spectrum as the 30 mins irradiated sample (**Figure 5.11**). This indicates that irradiation of **5.4$_2$@ OA$_2$** where the light was absorbed mainly by the host resulted in the quantitative conversion of **5.4$_2$@ OA$_2$** to **5.5$_2$@ OA$_2$** without disassembly of the capsular complex. Comparison of the product extracted with chloroform with independently synthesized **5.5** confirmed the formation of the triplet product **5.5**. Similar results were obtained with irradiation of **5.4$_2$@ROA$_2$**. However in case of ROA the reaction was slow requiring longer irradiation time (~12 h). The triplet product obtained, is only possible if the hosts OA and ROA reached the T$_1$ state via intersystem crossing from S$_1$ and transferred the energy to the guest. Investigation with probe **5.7**, under similar conditions resulted in expected triplet product **5.8** in quantitative yield. We believe that the benzoic acid part of the cavitand acted as the triplet sensitizer in both hosts. The reason for the poor efficiency of triplet sensitization by host ROA is most likely has to do with the longer distance between the guest molecule (acceptor) residing within the host and the energy transferring dibenzoic acid donor site. In OA it is present as a part of the cavity while in ROA it is present as an apendant at the bottom (**Figure 5.1**). Based on triplet-sensitized reaction observed here we believe that the triplet energy of the hosts should be close to that of acetophenone (73 kcal mol$^{-1}$),$^{179}$ which was used to sensitize the phototransformation of **5.4** in diethyl ether solution. The above results have unequivocally established that the deep cavity cavitands OA and ROA possess ‘active’
reaction cavities and one must take this feature into consideration while utilizing them as reaction cavities.

5.3 Experimental section

Materials and methods

OA was synthesized according to literature procedure\textsuperscript{36} and ROA was synthesized as reported in previous publication.\textsuperscript{124} Acceptors N-methylacridinium iodide (5.1), dimethylidiazaphenanthrenium iodide (5.2) and dimethylidiazapyrenium iodide (5.3) were synthesized and characterized following the literature procedures\textsuperscript{180-182} respectively. Benzonorbornadiene (5.4) and dibenzobarrelene (5.7) was synthesized following literature procedures\textsuperscript{183-185} respectively. Di-methoxy benzoic acid (DMBA) was purchased from Sigma-Aldrich. All $^1$H NMR spectra were recorded on a Bruker 500 MHz NMR spectrometer.

Procedure for fluorescence study

Fluorescence emission spectra were recorded on a FS920CDT Edinburg steady-state fluorimeter and the lifetime measurements on FL900CDT fluorescence lifetime spectrometer. Required solution of cationic guests were prepared in 10 mM borate buffer and used for steady state fluorescence study and lifetime measurements. Calculated amounts of quencher solution (5.1, 5.2, 5.3 or DMBA) were added and mixed thoroughly and fluorescence spectra were recorded.
General protocol for the adding acceptors and guests to host solution and characterization

600 µL of a D₂O stock solution of hosts OA and ROA (1 mM in 10 mM Na₂B₄O₇) were added to two NMR tubes separately. To the host solution 10 µL of 60 mM solution (in DMSO-d₆) of acceptor 5.1 was added, sonicated and ¹H NMR was recorded. Similarly, slowly aliquots of guest solution were added to 600 µL of 1mM host solution such that 0.25 equivalents were added upon each addition (2.5 µL of a 60 mM solution in DMSO-d₆). 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 5.4 to the OA/ROA solution and 0.5 equivalents in the case of 5.7.
Chapter 6. Gold glutathione cluster as an electron donor

6.1 Nanoclusters

Metal nanoparticles like gold, silver, platinum are characterized by their distinct surface plasmon band in the visible region.$^{186-188}$ Although metal nanoparticles are non-emissive, nanoclusters are known to have emission.$^{189-192}$ The nanoclusters are usually smaller than nanoparticles (< 1 nm) and their absorption and emission depends on the size of the cluster and also on the stabilizing ligand.$^{193,194}$ A number of methods to synthesize gold and silver nanocluster has been recently reported in literature.$^{189, 190, 194-201}$ Thiolate-protected water soluble gold nanoclusters have gained lot of interest in the last few years.$^{202,203}$ The recent interest in this ultra small nanoclusters are due to their potential importance in applied research utilizing their molecular like properties and emission.$^{204-208}$ The most important feature of Au–thiolate clusters is their luminescence properties. The emissive property of these Au-thiolate clusters, their low toxicity, ultra small size, and good biocompatibility, makes them ideal as bio imaging probes.$^{209-211}$

Thiolate stabilized Au-clusters are commonly synthesized by reducing Au(I)-thiolate complexes using reducing agent (NaBH$_4$).$^{211-215}$ The clusters prepared by reduction using strong reducing agents, show emission in the blue to near-IR region with low quantum yield. Recent research has established that slow decomposition of large Au-nanocrystals$^{213}$ or Au-thiolate complex$^{217}$ can also be used to synthesize Au-clusters. A much more facile one-pot synthesis of Au-thiolate has been reported recently by Xie$^{218}$ and co-workers. We synthesized L-glutathione-protected gold clusters using the method reported by Xie et al. and nanoclusters having a few-gold-atom core capped with Au(I)-
thiolate complex shell were formed as the solution aged for 24 h. These core shell structure Au-cluster has a strong emission ~ 600 nm and we investigated the usefulness of Au-glutathione cluster (Au NCs) as a donor. The absorption shows a tail up to 490 nm with a shoulder at 400 nm and an emission maximum at 612 nm. It is reported\textsuperscript{219} that these clusters consists of a mixture of different sized cluster consisting 29-43 Au atoms capped with glutathione molecules. These emissive properties of these clusters segregate them form larger nanoparticles that have characteristic plasmonic properties. The large Stroke shift observed in the emission, is suggestive that the excited-state being a ligand-metal charge-transfer type.\textsuperscript{220,221} Literature reports,\textsuperscript{218,222} Au in these clusters have mixed oxidation state.

\[
\text{Glutathione} + \text{HAuCl}_4 \\
\begin{array}{c}
27 \text{mg} \\
24 \text{mg}
\end{array} \xrightarrow{\text{Stir 45 min, RT}} \text{Au NCs cluster (yellow solution)} \\
\begin{array}{c}
(i) +30 \text{ ml } \text{H}_2\text{O} \\
(ii) 70 \degree\text{C, 24 h}
\end{array}
\]

\[
L\text{-Glutathione} = \begin{array}{c}
\text{HOOC} \\
\text{N} \\
\text{N} \\
\text{COOH}
\end{array}
\]

\textbf{Scheme 6.1} Synthesis of Au-glutathione nanocluster (Au NC)
6.2 Quenching studies with various acceptors

With our interest to examine if these clusters could act as a good donor, we studied fluorescence quenching experiments with various acceptors. The list of acceptors studied and their literature value of redox potential\textsuperscript{171, 223} is listed in Scheme 6.2. Quenching of emission of cluster was monitored by fluorescence measurement as well as lifetime measurements. Cluster emission was quenched by methyl viologen (6.2) and its derivative (6.1). Stern-Volmer plot, of quenching studies with methyl viologen (6.2), shows that the I/I\textsubscript{0} and \(\tau/\tau_{0}\) do not overlap, indicative of static quenching (Figure 6.2-6.3). This result interested us to study the quenching of cluster using 6.2@CB[7] (Figure 6.4a). As expected when 6.2 is complexed with CB[7] it was not efficient to quench the cluster emission. In a separate experiment, once 6.2 quenched the emission of Au NCs, we added excess CB[7] to revive the quenched emission (Figure 6.4b). CB[7] is
expected to complex 6.2 and the emission intensity should be recovered. Failure to recover the emission is consistent with the static quenching observed from Stern Volmer plot.

Scheme 6.2 Structures of molecules used as acceptors and donors. Redox potential reported vs. SCE in CH$_3$CN. ‘*’ redox potential vs. SCE in DMF.$^{220}$
Figure 6.2 Quenching of emission of Au NCs by 6.1 in H₂O (a) Emission spectra (b) Lifetime measurements (c) Stern-Volmer plot for emission and lifetime. \( \lambda_{ex} = 400 \text{ nm} \), \( \lambda_{em} = 600 \text{ nm} \), [Au NCs] = \( 10^{-4} \text{ M} \) [6.1] = 0 to 3.44×10⁻³ M.
**Figure 6.3** Quenching of emission of Au NCs by **6.2** in H₂O (a) Emission spectra (b) Lifetime measurements (c) Stern-Volmer plot for emission and lifetime. \( \lambda_{ex} = 400 \) nm, \( \lambda_{em} = 600 \) nm, \([\text{Au NCs}] = 10^{-4} \text{ M}\) \([6.2] = 0 \) to \(3.09 \times 10^{-3} \text{ M} \).
Molecular oxygen was also found to quench the emission of cluster (Figure 3 and 4). Quenching of emission with O$_2$ (6.6) was studied in three different solvent H$_2$O, DMSO and MeOH. Depending on the solubility of O$_2$ in these solvents the extent of quenching was effected. MeOH having the highest solubility of O$_2$ quenched the cluster emission more than H$_2$O and DMSO when 100% O$_2$ was purged (Figure 6.5-6.7). To investigate the reason behind O$_2$ quenching of cluster emission we tried to look at $^1$O$_2$ emission. But no $^1$O$_2$ emission around 1268 nm was observed (Figure 6.8). Our efforts to detect superoxide (O$_2^-$) using ESIPT based probe was also unsuccessful. With these results in hand we also tried to quench the Au NCs emission with acceptors 2, 4 dinitro phenol (6.3), 1,2,4,5, tetracyano benzene (6.4), 2,2’ bipyridinium N, N’ dimethyl (6.5), 4 nitro benzaldehyde (6.7), and nitro benzene (6.8).

**Figure 6.5** Quenching of emission of AuNCs by 6.6 in H$_2$O (a) Emission spectra (b) Lifetime measurements (c) Stern-Volmer plot for emission and lifetime. $\lambda_{ex}$=400 nm, $\lambda_{em}$= 600 nm, [Au NCs]$= 10^{-4}$ M.
Figure 6.6 Quenching of emission of AuNCs by 6.6 in MeOH (a) Emission spectra (b) Lifetime measurements. Quenching studies in DMSO (c) Emission spectra (d) Lifetime measurements in DMSO ($\lambda_{ex}=400$ nm). In the spectra 0% $O_2$ purged i.e. N$_2$ purged (red line), 21% $O_2$ purged (green line) and 100% $O_2$ purged (blue line). $\lambda_{ex}=400$ nm, $\lambda_{em}=600$ nm, [Au NCs] = $10^{-4}$ M.

Figure 6.7 Stern-Volmer plot for fluorescence quenching of AuNCs by $O_2$ 6.6 in various solvents, $\lambda_{ex}=400$ nm. In H$_2$O [O$_2$] = 0-1.27 mM, in DMSO [O$_2$] = 0-2.22 mM, in MeOH [O$_2$] = 0-10.3 mM.
Figure 6.8 Emission of 100% oxygen purged Au NCs in (a) D$_2$O and (b) DMSO-d$_6$.

![Graph showing emission spectra](image)

Figure 6.9 Stern-Volmer plot for fluorescence quenching experiment with various acceptors.

Quenching studies with a variety of acceptors, indicate that Au-glutathione can act as a good donor. Stern-Volmer plot for quenching experiment with various acceptors (Figure 6.9), reflect that the extent of quenching is dependent on their redox potential. We also investigated if the clusters could act as an acceptor and used donor molecules 1,4 dimethoxy benzene and 1,3,5, trimethoxy benzene (6.9 and 6.10). Quenching experiments done with 6.9 and 6.10 shows that Au NCs are not efficient acceptor (Figure 6.10-6.11).
Figure 6.10 Quenching of emission of Au NCs by 6.9 in H$_2$O (a) Emission spectra (b) Lifetime measurements. $\lambda_{ex}$=400 nm, $\lambda_{em}$=600 nm, [Au NCs]= $10^{-4}$ M [6.9] = 0 to 1.57×$10^{-3}$ M.

Figure 6.11 Quenching of emission of Au NCs by 6.10 in H$_2$O (a) Emission spectra (b) Lifetime measurements. $\lambda_{ex}$=400 nm, $\lambda_{em}$=600 nm, [Au NCs]= $10^{-4}$ M [6.2] = 0 to 1.96×$10^{-3}$ M.

6.3 Experimental section

Synthesis

0.24 g of gold (III) chloride trihydrate and 0.276 g of L-glutathione were mixed in 30 mL ultrapure water (DI water) at room temperature. The mixture was kept stirring until a colorless solution was obtained and subsequently heated to 70 °C for 24 hr.
Samples were taken out at various time interval to monitor the growth of absorbance and emission, (Figure 6.12) until no further changes were observed after 24 hr.

![Figure 6.12](image)

**Figure 6.12** (a) Absorbance and (b) emission monitored at various time interval during synthesis.

**Characterization of synthesized Au CNs:**

The synthesis of the Au-cluster was monitored by UV-Vis and Emission spectra (Figure 6.12). With the progress of the cluster synthesis, there is a appearance of absorption band at 400 nm and an emission at 612 nm. There was no further change observed after 24 hr. The cluster solution was refrigerated for later use. $^1$H NMR of glutathione in D$_2$O shows well-resolved peaks, while the cluster shows broad peaks in D$_2$O (Figure 6.13). The dynamic light scattering shows size ~1 nm, which was also observed by TEM image (Figure 6.14 -6.15). Cluster sample purified by dialysis using membrane with 30 kDa cutoff, was dried and used for TGA, which shows 63 % weight loss in the temperature range of 25- 900 °C (Figure 6.16).
Figure 6.13 $^1$H NMR (500 MHz) in D$_2$O. Top: Glutathione and bottom: Au-Glutathione cluster.
Results

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<td>0.000</td>
</tr>
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</table>

Result quality: Refer to quality report

Figure 6.14 Percentage volume versus hydrodynamic diameter profiles extracted from dynamic light scattering experiments for cluster recorded in H$_2$O. The average size of the particle is 1 ± 0.6 nm (10 scans).

Figure 6.15 TEM image of Au CNs
**Figure 6.16** TGA traces showing weight loss with respect to temperature for cluster (green line) and glutathione (red). Cluster shows ~63% weight loss while glutathione shows 100% weight loss.

**Fluorescence and lifetime experiments**

Quenching experiments were carried out with 1.5 ml of $5 \times 10^{-4}$ M solution of Au NCs in H$_2$O with various acceptors. The quencher solution was prepared in H$_2$O for 6.1, 6.2 and 6.5. While solution of rest of the quenchers 6.3, 6.4, 6.7, 6.8, 6.9, and 6.10 were prepared in DMSO. O$_2$ was purged form cylinder with known % of O$_2$ for 45 mins, before recording emission.
Figure 6.17 Quenching of emission of Au NCs by 6.3 in H$_2$O (a) Emission spectra (b) Lifetime measurements (c) Stern-Volmer plot for emission and lifetime. $\lambda_{ex}$=400 nm, $\lambda_{em}$= 600 nm, [Au NCs]= $10^{-4}$ M, and [6.3] = 0 to 0.96×$10^{-3}$ M.
Figure 6.18 Quenching of emission of Au NCs by 6.4 in H2O (a) Emission spectra (b) Lifetime measurements (c) Stern-Volmer plot for emission and lifetime. \(\lambda_{ex}=400\) nm, \(\lambda_{em}=600\) nm, [Au NCs] = 10^{-4} M, and [6.4] = 0 to 1.37×10^{-3} M.
Figure 6.19 Quenching of emission of Au NCs by 6.5 in H₂O (a) Emission spectra (b) Lifetime measurements (c) Stern-Volmer plot for emission and lifetime. λₜₚ=400 nm, λₜₑ= 600 nm, [Au NCs]= 10⁻⁴ M, and [6.5] = 0 to 1.8×10⁻³ M.
Figure 6.20 Quenching of emission of Au NCs by 6.7 in H$_2$O (a) Emission spectra (b) Lifetime measurements (c) Stern-Volmer plot for emission and lifetime. $\lambda_{ex}$=400 nm, $\lambda_{em}$= 600 nm, [Au NCs]= $10^{-4}$ M, and [6.7] = 0 to $4.03 \times 10^{-3}$ M.
Figure 6.21 Quenching of emission of Au NCs by 6.8 in H₂O (a) Emission spectra (b) Lifetime measurements (c) Stern-Volmer plot for emission and lifetime. $\lambda_{\text{ex}}=400$ nm, $\lambda_{\text{em}}=600$ nm, [Au NCs] = $10^{-4}$ M, and [6.8] = 0 to $3.27 \times 10^{-3}$ M.

Figure 6.22 Absorption spectra in H₂O of (a) 6.1 (b) 6.3, (c) 6.4, (d) 6.5, (e) 6.7 and (f) 6.8.
Figure 6.23 Absorption spectra in H₂O of (a) 6.9 and (b) 6.10

Figure 6.24 Absorption of Au CNs in various solvents.
Figure 6.25 $^1$H NMR in D$_2$O (400 MHz) of (a) 6.2 (b) 6.2@CB[7] and (c) CB[7], ‘*’ show the complexed peaks of 6.2 in CB[7].
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