Chapter-I

Introduction

The award of the 1987 Nobel prize to Cram, Pederson, and Lehn brought the field of supramolecular chemistry to the forefront of chemistry. The use of weak labile interactions to control the formation of multicomponent assemblies has resulted in the rational synthesis of species which could scarcely be imagined a few decades ago.\(^1\) As chemists have taken control of self-assembly, functional supramolecular assemblies have started to emerge in areas as diverse as catalysis, artificial photosynthesis, and molecular scale electronics. The field of self-assembly is going through an evolution, but it has greater synthetic challenges because of the weakness of the interactions involved. The ability to make molecules through covalent bond-based synthesis with useful functions is quite advanced, but our ability to make supramolecular assemblies with useful functions is a challenging area not only because of the greater synthetic challenges but also because the function of a multicomponent assembly may not be closely related to the properties of the individual components. A long term goal of supramolecular chemistry is to accomplish the synthesis of functional supramolecular assemblies with the structural and functional complexity of biological systems by the use of molecular synthons and noncovalent interactions.

The 1980s and 1990s witnessed a rapid development of self-assembly based on complexes with labile metal ions. Metallosupramolecular chemistry lends itself well to the rational design because the metal-ligand bonds involved are relatively strong and have directional preferences, which gives synthetic chemists a sporting chance of being able to control the outcome of a self-assembly process. Double helicates were amongst the first examples and were followed by entities such as molecular grids, ladders, cyclic helicates, and interlocked species. The development in this field has been well reviewed.\(^1,2\) The most impressive examples of self-assembly based on metal complexes have been polyhedral coordination cages\(^3\) in which metal ions and bridging ligands combine to form three-dimensional capsules with hollow central cavities. The resulting high symmetry structures, often based on Platonic or
Archimedean solids,⁴ are mathematically appealing and also reminiscent of biological polyhedral assemblies such as viruses. In addition, their central cavities provide them with useful functions involving recognition and binding of small molecules.

Function arising from a supramolecular assembly is not simply a bulk property of a single component, but is something that arises from a specific combination of different components. The ordering of components within this assembly is crucial and the function may not be related in any simple way to the properties of the individual components. The photosynthetic reaction centre is an ideal illustration: the properties such as absorption of light, electron transfer, and energy transfer of the individual components contribute to the overall function (vectorial charge separation). The problem of interfacing the components correctly may be more challenging than the problem of fabricating them.

1.1 Photochemistry of Polypyridyl Ligands

The rich photochemistry of polypyridine ligands undoubtedly stems from the classical role played by pyridine in coordination chemistry, where it forms complexes with almost all metals often stabilized by π-back bonding. For over a century, 2,2′-bipyridine (1) has been used as the classical bidentate chelating heterocyclic ligand.⁵ It is well known that six-membered heterocycles such as pyridine are π-deficient and, therefore, good π-acceptors,⁵ whereas five-membered aromatic rings such as pyrazole are π-excessive and hence π-donors. Varying the heterocycles can effect dramatic changes on the physicochemical properties of metal complexes. However, other more subtle differences exist between heterocyclic ring systems that can impart significant effect upon the properties of their metal complexes. Polypyridyl complexes of low-spin $d^6$ metal ions such as Ru(II), Os(II), Re(I), Rh(III), and Ir(III) feature a favorable electrochemical, photophysical, and photochemical properties.⁷ The luminescent and redox properties of ruthenium(II) and osmium(II) complexes of 2,2′-bipyridine (bpy) and related bi- and tridentate ligands such as 1,10-phenanthroline (phen) (2), and 2,2′:6′,2″-terpyridine (3), respectively, have been extensively studied due to their significant MLCT absorption in the visible region,⁸ their ability to undergo MLCT excitations,⁷ᵇ,⁸ᵇ,⁹ the relative longevity¹⁰ and photoreactivity¹¹ of the MLCT excited states, the relative inertness of the metal
centers in a variety of oxidation states, and the rapidity of redox reactions involving the excited states. These complexes have been employed as building blocks for the design of supramolecular assemblies\textsuperscript{12} and metallodendrimers,\textsuperscript{13} in the design of molecular electronics\textsuperscript{14} and molecular machines and motors,\textsuperscript{15} for the fabrication of dye-sensitized solar cells,\textsuperscript{16} in artificial photosynthesis,\textsuperscript{17} in light-to-chemical energy conversion schemes,\textsuperscript{18} as light harvesting antennas,\textsuperscript{13d,e,19} in nonlinear optics,\textsuperscript{20} as DNA probes,\textsuperscript{21} and as building blocks for macromolecular assemblies that are of interest in biochemistry and chemical diagnosis.\textsuperscript{22} Ruthenium(II) polypyridyl complexes represent a keystone in the development of photochemistry with their strong MLCT absorption and long-lived, emitting \( ^3 \)MLCT excited states.\textsuperscript{23}

![Chemical structures](image)

Polypyridyl ruthenium(II) complexes exhibit desirable light absorption in the visible spectral region and there is a well developed synthetic chemistry for the preparation of an extensive range of complexes.\textsuperscript{7a,24} Complications arise from low lying, metal centered \( dd \) excited states which are populated by thermally activated barrier crossing following the MLCT excitation. Their population leads to shortened lifetimes and net ligand-loss photochemistry.\textsuperscript{25} The ruthenium(II) complexes are typically visible absorbers, but at higher energy than the corresponding Os(II) complexes. On the basis of photochemical, photophysical, and electrochemical properties, ruthenium(II) and osmium(II) complexes of 2,2′-bipyridine and related bidentate bpy-type ligands are probably the best photosensitizers among the metal complexes.\textsuperscript{7a,c,26} Especially in the case of ruthenium(II), several hundreds of bpy-type complexes have been reported, thereby making available a wide choice of photosensitizer components for the design of photoluminescent molecular devices (PMDs).

2,2′-Bipyridine gives rise to stereoisomerism at six-coordinate centers due to their bidentate nature. A \([\text{M(bpy)}_3]^{n+}\) complex exists in two enantiomeric forms. The bpy ligand bearing a single substituent exists in two geometrical forms with \textit{facial} and \textit{meridional} arrangements; each isomer can exist as one of the two enantiomers. Thus,
supramolecular structures based on the [M(bpy)$_3$]$^{n+}$ building block are formed with no control of isomer formation. In contrast to the behavior with bpy, tpy forms an achiral [M(tpy)$_2$]$^{n+}$ complex. The introduction of a single substituent in the 4′-position of each tpy ligand presents no additional problems that there is a single form of the resulting complex. Furthermore, the geometry of [M(tpy)$_2$]$^{n+}$ complexes offers the possibility to design triads in which the two additional components lie on opposite directions with respect to the photosensitizer. Because of its geometry, tpy is also a good candidate to play the role of a ligand in the binding sites of macrocyclic rings. In fact, a three-dimensional template synthesis of two interlocked tpy-containing macrocycles around a ruthenium(II) ion (4) has been devised to prepare the first catenate containing an octahedral binding site.

1.2 Photochemistry and Electrochemistry of Bis(terpyridine)ruthenium(II) Complexes

The prototype [Ru(tpy)$_2$]$^{2+}$ complex exhibits very intense electronic absorption bands in the UV region assignable to ligand-centered $\pi \rightarrow \pi^*$ transitions. The relatively intense and broad absorption band in the visible region, which is responsible for the deep red color, is due to a spin-allowed $d \rightarrow \pi$ MLCT transition. In rigid matrix at 77 K, [Ru(tpy)$_2$]$^{2+}$ exhibits a strong and long lived luminescence characteristic of a $^3$MLCT level. On increasing the temperature, the luminescence intensity and lifetime decreases. At room temperature, [Ru(tpy)$_2$]$^{2+}$ is practically not luminescent and its
excited state lifetime is estimated to be 1.5 ns by flash photolysis,\textsuperscript{9c,30a,b} but later found to be 250 ps from excited state absorption studies.\textsuperscript{31}

The weak emission of [Ru(tpy)\textsubscript{2}]\textsuperscript{2+} at room temperature compared with the strong emission of most ruthenium(II) bpy-type complexes is due to the quenching of the \( ^3 \)MLCT emission by the neighbouring \( ^3 \)MC states.\textsuperscript{7a} Photophysical properties can be fine-tuned by the introduction of aromatic groups at the 4\textquoteleft-position of terpyridine. 4\textquoteleft-Tolyl-2,2\prime;6\prime;2\prime\prime-terpyridine (ttpy) (5) was one of the first examples of such an approach by connecting aromatic rings to the terpyridine moiety. The photochemistry of such systems has been reviewed by Sauvage et al.\textsuperscript{12a} The [Ru(tpy)\textsubscript{2}]\textsuperscript{2+}-type complexes are electrochemically active. They exhibit a reversible Ru(II/III) oxidation process and a variable number of reversible or quasireversible reductive ligand-centered processes. The presence of strongly electron releasing substituents allows stabilization of the Ru(III) state and a shift of the oxidative process to less positive potentials. In the same way, electron releasing substituents shift the reductive processes to more negative potentials.

The absorption spectra of [Ru(tpy)\textsubscript{2}]\textsuperscript{2+} and [Os(tpy)\textsubscript{2}]\textsuperscript{2+} are characterized by the well known LC bands in the UV region and MLCT bands in the visible region.\textsuperscript{32} Comparison of the spectroscopic properties of [Ru(tpy)\textsubscript{2}]\textsuperscript{2+} and [Ru(tppy)\textsubscript{2}]\textsuperscript{2+} indicates a small red shift and a substantially larger molar absorption coefficient for the latter compound, thus confirming that light absorption actually leads to electron promotion to a ligand system that, to a certain degree, includes the tolyl fragment. Similar conclusions were reached by studying the influence of geometrical restraints and of electron-withdrawing and electron-repelling groups attached to the remote positions of ttpy on the intensity of the electronic absorption bands.\textsuperscript{33}

1.3 Manipulating the Properties of MLCT Excited States

In ruthenium(II) polypyridyl complexes, ligand substitution can be used to vary the spectral properties systematically.\textsuperscript{8c,9d,24d,e,34} Lowering the \( \pi^* \)-level of an acceptor ligand by incorporating an electron withdrawing substituent can red shift the lowest energy MLCT absorption. However, the resulting decrease in the ground-to-excited
state energy gap leads to a concomitant shortening of the excited state lifetime. This effect is described quantitatively by the energy gap law.\textsuperscript{35} It predicts that, in the absence of competing nonradiative events, the nonradiative lifetime should vary exponentially with the energy gap for a common acceptor ligand.\textsuperscript{35a,36} The first criterion is to systematically manipulate ligand properties in ruthenium(II) based chromophores in order to maximize the $\pi \rightarrow \pi^*$ and MLCT absorptivity throughout the UV-visible spectral region. This is an important requirement for an efficient light-to-chemical conversion system and has been emphasized by the work of Bignozzi,\textsuperscript{37} Grätzel,\textsuperscript{38a-d} and others\textsuperscript{38e-g} in their attempts to prepare practical solar energy devices using ruthenium(II) dye-derivatized nanocrystalline TiO$_2$ substrates. The second criterion is to overcome the limitation on excited state lifetimes imposed by the energy gap law. It follows that black chromophores will have small energy gaps and consequently will have short lifetimes. This would decrease their applicability in studies of excited state dynamics, in assays based on emission anisotropy, or as sensitizers. The third criterion is to minimize complications from $dd$ state deactivation and ligand loss population of these states which shortens lifetimes and can lead to photodecomposition.\textsuperscript{25a,b,f,g}

Strategies have been developed to red shift absorbance in tris(heteroleptic) ruthenium(II) complexes by lowering the $\pi^*$-energy level of a ligand by using electron withdrawing substituents or by stabilizing the hole at Ru(III) in the MLCT excited state by using electron-rich ligands or a combination of the two.\textsuperscript{24d,34a} Following MLCT excitation of heteroleptic complexes, the excited electron ultimately resides on the ligand having the lowest energy $\pi^*$-orbital and nonradiative lifetimes can be controlled by controlling its structure.\textsuperscript{39} The key to the energy gap law is the role that the energy gap plays in dictating the extent of the vibrational overlap of the ground and excited states. This vibrational overlap is coupled to the nonradiative transition.

\textbf{1.4 Modelling Photosynthetic Light Harvesting Supramolecular Assemblies}

The photosynthetic reaction centre remains a paradigm in this field because it represents a perfect example of how valuable function can arise from combination of the properties of individual components in a spatially well defined array. In addition, the looming energy shortage has put the whole issue of light harvesting and solar
energy at the top of the research agenda.\textsuperscript{40} At the core of photosynthesis is the light harvesting centre, a cyclic array of chlorophyll chromophores. Interaction among the molecular components in this array gives the assembly the unique light absorption characteristics and the ability to transfer the excited state energy to the reaction center which is crucial to the function. Self-organization of the components of the reaction center is one of the key features for its efficiency. Supramolecular chemistry has shown that noncovalent interactions such as solvophobic forces, electrostatic interactions with permanent or induced dipoles, dispersive and charge-transfer interactions, and hydrogen bonds can be used to induce self-organization of molecular components. Supramolecular assemblies based on noncovalent interactions which undergo light-induced electron transfer have been discussed extensively.\textsuperscript{12g}

Natural as well as artificial photosynthetic systems possess efficient light harvesting units for the conversion of solar energy as their primordial characteristics.\textsuperscript{7a,12f,41} The basic reaction to be realized is light induced charge separation leading to the cleavage of water. In artificial photosynthesis this is achieved by sensitizer $S$ or donor $D$ absorbing in the visible region of the solar spectrum and by acceptor $A$ functioning as short time reservoir of chemical energy and redox-active component that can be used for energy storage.\textsuperscript{12g} The main task of modern research in the field of artificial photosynthesis is to better understand nature’s processes by employing model compounds. Dürr and Bossmann\textsuperscript{41b-f} have demonstrated the significance of ruthenium polypyridine complexes as biomimetic models for the photosynthetic reaction center. The extension of simple ruthenium polypyridine complexes to supramolecular polyads acting as good sensitizers actually depends on the following properties: absorption in the solar emission maximum, excited states with long lifetimes, suitable redox potentials, stability, and fast inter- or intramolecular electron transfer.

Ruthenium complexes having polyether bipyridines as building blocks exhibit excellent photostability.\textsuperscript{17,42} Fine-tuning of the molecular properties of these complexes allows the design of structures which are well suited for electron transfer. Two-shell biomimetic model systems display more efficient electron transfer than one-shell systems.\textsuperscript{43} Covalently linked assemblies are more efficient for electron
Assemblies using covalent interactions of ruthenium polypyridines forming pseudorotaxanes such as triads and tetrads are among the most efficient systems to produce a charge-separated state. The lifetimes of the charge-separated states are high for the covalently linked assemblies when compared to the noncovalently linked ones. Thus, biomimetic systems based on ruthenium polypyridines leads to highly efficient electron-transfer systems.

1.5 Ligand Design in Multimetallic Architectures

The controlled assembly of discrete metallosupramolecular architectures usually relies on the use of combinations of linear and angular components that logically selfassemble into predictable structures by means of directional information encoded within the metal and ligand precursors. Generally, control over the selfassembly process is achieved by using structurally rigid species. However, this approach is limited to a relatively few molecular architectures that are highly symmetrical. Access to other topologies is best achieved by incorporating some flexibility into the ligand in the form of conformationally free subunits such as short alkyl chains. The vast majority of ligands used for the formation of metallosupramolecular species utilize polypyridyl ligands. The fundamental principles involved in nature have also guided chemists in the design and construction of luminescent sensors and probes which mimic natural light harvesting antennas or light concentrators. The exceptional coordinative properties, chemical stability, and synthetic versatility of the oligopyridino ligands renders them as key molecular building blocks through which construction of multicomponent wires, insulators, and sensors are feasible.
1.5.1 Flexible Ligand Design

The most common approach to the rational design of two- and three-dimensional metallosupramolecular species has been to use appropriate combinations of rigid angular and linear components. However, many topologies are not accessible through such an approach. Incorporation of flexible linker units into the bridging ligands provides access to other architectures. An obvious disadvantage of the inclusion of flexible subunits is that the ligand itself can adopt different conformations as a consequence of rotations about single bonds. This can lead to a loss of control in the design and assembly of the resulting metal containing aggregates. The loss of control associated with the use of flexible ligands can be partly compensated by a number of subtle approaches. One way is to make use of preorganization which involves controlling the conformations of the free ligand by orienting substituents with respect to a given reference plane. An example is ligand 6 where six pyridylpyrazole units are attached via methylene groups to a central benzene ring. This approach can be extended to larger systems such as ligand 7 which has eight 2-pyridyl substituents attached by flexible two atom spacers to a central biphenylene core. The crystal structure of the free ligand, which could potentially adopt many conformations, shows that it has eight arms locked into a specific conformation in which the donor groups alternate on opposite faces of the central core. Thus, the use of flexible ligands can provide access to interesting molecular architectures without complete loss of control in the selfassembly process.

1.5.2 Multiple Interactions

The primary interaction in metallosupramolecular selfassembly processes is between a metal atom and a heteroatom donor. The strength of this interaction depends on the specific metal involved and varies between relatively weak bonds (for $d^{10}$ metals such as silver(I)) to much stronger bonds [for platinum(II) or ruthenium(II)]. Other weak interactions usually play important roles in providing thermodynamic stability to such assemblies. Individually these may be weak, but the combined thermodynamic return from multiple interactions can be very significant. Nature employs this approach to hold together the strands of DNA, protein assemblies, and the majority of cellular machinery. Most of the structures involve stabilizing
secondary interactions such as $\pi$-$\pi$ interactions\(^{49}\) (including multiple aryl embraces\(^{50}\)), weak hydrogen bonds,\(^{51}\) or other weak noncovalent interactions with noncoordinated anions, solvate, or guest molecules. These weak interactions play important roles in defining the structures of metallosupramolecular architectures. A challenge for the future is to logically incorporate these weak interactions into ligand design for use in heterosupramolecular chemistry. New ligands are being reported for use as components in the construction of novel molecular architectures of increasing complexity.\(^{15}\) Metallosupramolecular compounds will find truly useful applications as functional resources in material science and nanotechnology.\(^{52}\)

### 1.6 Photoluminescent Molecular Devices

A progressive advancement in scientific knowledge concerns the design of materials for use in molecular scale electronic devices.\(^{53}\) Photoluminescent molecular devices (PMDs) are present in nature where they perform functions essential to life such as photosynthesis and vision. The conversion of light energy into chemical energy in natural photosynthetic processes is based on two types of PMDs:\(^{54}\) (1) antenna devices which are made of hundreds of pigments able to collect solar light and to convey the resulting electronic excitation energy to specific sites (reaction centers) and (2) reaction centers where the excitation energy is used to perform a charge separation process which converts electronic energy into redox chemical energy. Valuable photochemical functions such as light energy conversion can only be obtained upon a complex elaboration of the absorbed light energy input in the dimensions of space, energy, and time by means of a suitably organized supramolecular system. A first obstacle in the construction of artificial PMDs for light energy conversion is the assembly of appropriate molecular components into a suitably organized supramolecular array. In natural systems, supramolecular organization is the “evolutionary” result of a spontaneous self organization process strictly controlled by intermolecular forces. In principle, chemists are able to design and construct chemically stable and geometrically well controlled supramolecular structures by linking molecular building blocks via covalent bonds.\(^{12e-h,j,19b-d,41i,55}\) Most of the artificial PMDs investigated for antenna or charge separation purposes are, in fact, based on covalently linked molecular components.\(^{12f,55a}\)
To perform a particular function a PMD needs to be constructed of suitable molecular components, each having a specific role. In principle, it has been distinguished into three fundamental types of components:  

(a) active components, which are directly involved in light absorption and/or electron/hole migration,  
(b) perturbing components, which can be used to modify the properties of active components, and  
(c) connecting components, which can be used to link together the active components. The connecting components, besides having a structural function such as controlling the distance between the active components and the degree of rigidity of the supramolecular structure, may also have the important role of connecting the active components in an electronic sense.

1.7 Design of Photochemical Supramolecular Assemblies

From a photochemical and electrochemical viewpoint the distinction between a large molecule and a supramolecular species can be based on the degree of interaction between the electronic subsystems of the component units. When the interaction energy between subunits is small compared to other relevant energy parameters, the system can be considered a supramolecular species. In principle, the properties of the molecular components of a supramolecular species can be obtained from the study of the isolated components or of suitable model molecules. Many transition metal complexes of polypyridine ligands exhibit interesting redox and photochemical properties and strenuous efforts have been made to incorporate such complexes into highly organized multicomponent molecular arrays. The best route to assemble molecular building blocks according to a desired pattern is the use of a covalent bond. The building blocks to be assembled must exhibit suitable photochemical, photophysical, and electrochemical properties. Key components are the photosensitizers, i.e., species capable of absorbing light and transferring energy, electron, or hole to another component. Polypyridyl complexes of low-spin $d^6$ metal ions such as Ru(II), Os(II), and Re(I) have been used extensively as photosensitizers for studies of photoinduced electron- and energy transfer in molecular assemblies.
1.7.1 Two Component Systems—Electron Donors and Acceptors

Two component systems (dyads) can be obtained by connecting the photosensitizer (P) either to an electron acceptor (A) or to an electron donor (D) having suitable redox properties. In such two component systems the back electron transfer is usually too fast to allow any practical use of the charge separation process. Systems containing three- or more components are expected to be more efficient because fast secondary electron transfer steps can compete with the back electron transfer reactions resulting in a charge separation over larger distances. The donor and acceptor components should not absorb light of the wavelength used to excite the photosensitizer. They should exhibit appropriate redox potentials, a reversible redox behavior, and the oxidation of the donor and the reduction of the acceptor should be accompanied by intense absorption changes in the appropriate spectral regions in order to detect the occurrence of electron transfer by flash spectroscopy. Since most of the molecules absorb in the UV region, the growth or disappearance of intense and narrow bands in the visible region is quite useful. Time resolved microwave conductivity measurements can also be used to detect the formation of a charge separated state. 57

1.7.2 Two Component Systems—Energy Acceptors

The components to be used as acceptors in energy transfer processes in two component systems must also meet several requirements. They should possess excited levels at suitably low energy and should not undergo excited state reactions. The most straightforward proof that energy transfer has occurred is the sensitized emission of the acceptor. Therefore, luminescent coordination compounds are commonly used as energy acceptors. Several supramolecular systems based on Re(I), Ru(II), Os(II), and Cr(III) complexes have been investigated.12,58 Re(I) and Ru(II), which exhibit high energy luminescent levels, usually play the role of photosensitizers and Os(II) and Cr(III) complexes, whose luminescent levels lie at much lower energy, usually play the role of energy acceptors. Complexes of the same metal and different ligands can also be coupled for energy transfer purposes.
1.7.3 Spacers

Bipyridine and its tridentate analogue 2,2′:6′,2″-terpyridine (3) have been incorporated into many bridging ligands. Other bridging ligands containing 2-, 3-, or 4-substituted pyridines such as 1,10-phenanthroline (phen) (2), phenanthrenequinone (phi) (8), dipyrido[3,2-α:2′,3′-c]phenazine (dppz) (9), 5,6-chrysene quinone diimine (chrysi) (10), benzo[a]phenazin-5,6-quinone diimine (phzi) (11), dipyrido[3,2-d:2′,3′-f]quinoxaline (dpq) (12), benzo[i]dipyrido[3,2-a:2′,3′-c]phenazine (dpn) (13), and eilatin (14), dipyrido[2,3-α:2′,3′-h]phenazine (dpop) (15), 2,3-bis(2-pyridyl)pyrazine (2,3-dpp) (16), 2,5-bis(2-pyridyl)pyrazine (2,5-dpp) (17), 3,6-bis(2-pyridyl)tetrazine (BPTZ) (18), 2,3-bis(2′-pyridyl)benzo[g]quinoxaline (dpbq) (19), 2,2′,3,3′-tetra-2-pyridyl-6,6′-biquinoxaline (dpq-dpq) (20), 4′,7′-phenanthrolino-5′,6′:5,6-pyrazine (ppz) (21), 1,4,5,8,9,12-hexaazatriphenylene (HAT) (22), 2,6-bis(2′-pyridyl)benzimidazole (dpimbH₂) (23), deprotonated 2,2′-bibenzimidazole (BiBzIm⁻) (24), deprotonated 3,5-bis(pyrazin-2-yl)-1,2,4-triazole (bpzt⁻), (25) and 2,3,5,6-tetrakis(2′-pyridyl)pyrazine (tp) (26) have been reported.
The spacers play a 2-fold role: (a) control of the supramolecular structure (in particular the intercomponent distances and angles) and (b) control of the electronic communication between components in case of through bond energy- or electron transfer. Obviously, rigid spacers such as those based on aromatic rings,\textsuperscript{61} bicyclo aliphatic species,\textsuperscript{62} and bridges containing ethynyl groups\textsuperscript{63} are more preferred than flexible spacers for structural reasons. From the electronic viewpoint aromatic spacers allow a better communication than aliphatic ones.

1.8 Photoinduced Energy- and Electron Transfer in Supramolecular Systems

In multicomponent systems photoinduced charge separation and/or energy migration can only be achieved when the various molecular building blocks are assembled according to well designed geometric patterns. With improved temporal resolution and application of sophisticated spectroscopic tools it becomes possible to delve deeply into the mechanism of information transfer, thereby stimulating the rational design of advanced molecular systems. Perhaps the most active area of current research relating to molecular electronics concerns the identification of appropriate means by which redox- or photoactive units can be inserted into well
defined and stable arrays so that they are maintained in mutual electronic communication (photoactive molecular scale wires), in electronic insulation (molecular scale insulators), or in close spatial proximity under external stimulation.\textsuperscript{53} The major task of development of molecular arrays is the insertion of an intelligent bridge that can both direct electron flow and function as a switch to reverse that flow. Unidirectional triplet energy transfer by way of a small cascade of individual steps can be achieved by incorporating in the bridge polycyclic hydrocarbons such as anthracene, naphthalene, and pyrene. The harvesting of solar energy by antennas and its migration to the reaction centers are pivotal processes.\textsuperscript{64}

1.8.1 Intramolecular Energy Transfer and Laser Spectroscopy

Excitation of compounds with a short duration laser pulse results in rapid establishment of the lowest energy excited triplet state. This metastable species may luminesce in solution and the triplet lifetime is conveniently measured by temporally resolving the luminescence decay. This technique works very well provided that the triplet lifetime is not too short ($\tau > 100$ ps) and that the luminescence can be properly resolved from the background light. In other cases, the triplet state can be detected by transient absorption spectroscopy, where, a second photon, delivered by a delayed laser pulse or from a continuous light source, is absorbed by molecules in the triplet state giving rise to a triplet-triplet absorption transition. This absorption spectrum can be recorded in the same way as the ground state absorption spectra are measured, while kinetic measurements can be made at fixed wavelengths. This technique is also appropriate for recording the absorption spectra of other reaction intermediates and for determining their lifetime under particular conditions. Such measurements can be made on time scales as short as 100 fs and other detection modes such as resonance Raman, infrared, circular dichroism, or EPR can be used. In this manner, it becomes possible to follow the course of a photochemical reaction to determine the kinetic parameters for important intermediates and to identify major reaction pathways.

The rate constant ($k_{\text{obs}}$) for light induced electron transfer or triplet energy transfer can be determined by measuring the triplet lifetime ($\tau_t$) of the appropriate multicomponent compound and comparing it with that of the reference compound ($\tau_0$) in deoxygenated solution:
\[ k_{\text{obs}} = (1/\tau_t) - (1/\tau_0) \]  

In this method it is assumed that the difference in triplet lifetimes between the two compounds arises solely from the quenching process (i.e., electron or energy transfer).

1.8.2 Mechanisms of Intramolecular Energy Transfer

Two basic mechanisms involved in intramolecular energy transfer process (Scheme 1) are the Förster mechanism\(^6\) which takes place via a dipole-dipole interaction and the Dexter mechanism\(^6\)\(^6\) which takes place via a double electron exchange (Figure 1).

\[ k_{\text{obs}} = k_D = k_0 \exp[-\beta R_{MM}] \]  

Scheme 1. The intramolecular energy transfer process.

In the first mechanism, the excited state \( D^* \) behaves as an oscillating dipole creating an electric field. When \( A \) is driven in the collisional space of \( D^* \) it will enter in resonance resulting in simultaneous formation of \( A^* \) and \( D \) (Figure 1a). No exchange of electrons occurs. The rate of triplet energy transfer \( (k_F) \) is proportional to \( E^2 \) (\( E \) is the energy of the oscillating dipole) and is weakly dependant on the distance \( R_{MM} \) between the donor \( D^* \) and the acceptor \( A \). However, \( k_F \) strongly depends on the spectral overlap integral between the emission of the donor and the absorption of the acceptor. The Förster mechanism is effective mostly with highly colored compounds and when singlet excited states are involved.\(^6\)\(^5\) In the Dexter mechanism the rate of energy transfer \( (k_D) \) strongly depends on the distance between the donor and the acceptor subunits\(^6\)\(^6\) and a double exchange of electrons is involved in this process (Figure 1b). If quenching involves through bond electron and/or hole transfer, the derived rate constant can be related to the distance \( (R_{MM}) \) separating the two reactants:
In this expression, $k_0$ refers to the rate constant when the reactants are within orbital contact (i.e., $R_{MM} = 0$) and $\beta$ is an attenuation factor (expressed in units of Å$^{-1}$) that describes the electronic “resistivity” of the intervening medium. Detailed discussions on the mechanism of energy transfer or electron transfer have been reported.$^{67}$

Figure 1. Schematic representation of energy transfer with a Förster-type or Dexter-type mechanism and the equation used to calculate the rates: $k_F = \text{Förster rate constant}$, $\Phi_L = \text{quantum yield}$, $\tau_L = \text{lifetime of the triplet excited state of L}_1\text{Ru or L}_2\text{Ru}$, $K = \text{reorientation factor of the optical transition dipoles}$, $J_F = \text{spectral overlap integral}$, $n = \text{solvent refractive index}$, $R_{MM} = \text{metal-metal separation distance}$, $V = \text{electronic coupling matrix}$, $\lambda = \text{reorganization energy for energy transfer}$, $\Delta E = \text{difference between the excited state energies of the donor and acceptor}$.

1.9 Terpyridine-Based Metallodendrimers

High nuclearity metallodendrimers are of interest as photoconversion and light harvesting devices.$^{7a,c,12a,f,68}$ Constable et al.$^{59}$ have developed convergent methodologies for homo- and heterometallic dendritic systems. They adopted the ligand-reactivity approach$^{70}$ to the convergent synthesis of metallodendrimers and demonstrated the facile formation of nonaruthenium dendrimers.$^{71}$ Star-like macromolecules containing terpyridine metal complexes in the outer-sphere have been reported by diverse groups.$^{55h,72}$ Constable et al.$^{71,72f}$ have reported the formation of a star-like macromolecule 27 with 18 ruthenium(II) centers by the reaction of hexakis(bromomethyl)benzene and six dendrons, each containing three ruthenium complexes. Osawa et al.$^{73}$ have reported a series of rigid dendritic nanosized
architectures with 6-, 12-, and 18-peripheral [Ru(tpy)2]2+ moieties. The synthesis of these dendrimers were carried out in high yield applying Sonogashira cross-coupling reactions of functionalized heteroleptic ruthenium(II) complexes.73a The ruthenium(II) metalloendrimer 28 has a diameter of 9 nm with an overall 38 positive charges.

An interesting chiral architecture was achieved by Jiang et al.74 by the successful preparation of a chiral terpyridine-dendrimer molecule consisting of four terpyridine-ruthenium(II) complexes (29-31). Terpyridine groups were attached to the binaphthyl units, subsequently reacted with RuCl3, and further complexed to the terpyridinyl functionalized pentaerythritol which acts as the dendrimer core. Newkome et al.75 have reported a m-bis(terpyridyl) phenyl derivative which on complexation with ruthenium(II) leads to the formation of the hexameric cycle 32. Furthermore
Newkome and his co-workers \textsuperscript{76} have reported shape-persistent, truxene-based, nanosized bisterpyridine ruthenium(II) polynuclear complex \textsuperscript{33}, using thiophene-functionalized bisterpyridine ruthenium(II) and truxene moieties as the nodes.

Newkome and his co-workers \textsuperscript{77} have reported a class of shape persistent metalldendrimer \textsuperscript{34}, developed through self-assembly strategy, in which ruthenium(II) bis(terpyridine) connectivity is utilized as branching moieties or nodes. Newkome and his co-workers \textsuperscript{78} also have reported a series of metalldendrimers \textsuperscript{35-37} utilizing perylene as a functional core and ruthenium(II)bis(terpyridine) as the termini. These nanoscale dendritic architectures possess large molecular weights and broad absorption spectrum as well as molar absorption coefficients directly related to the number of photoactive scaffolds.
1.10 Calixarenes and Calixresorcarenes

The calixarenes are a popular and versatile class of macrocycle formed from the base catalysed condensation of a \( p \)-substituted phenol with formaldehyde. Since they contain bridged aromatic rings, they are formally members of the cyclophane family. The descriptive name ‘calixarene’ was coined by C. David Gutsche because of the resemblance of the bowl shaped conformation of the calixarenes to a Greek vase called *calix crater*. The number of phenolic residues is denoted by a number in square brackets. Thus, the most common cyclic tetramer with \( p-t \)-butyl substituents is termed \( p-t \)-butylcalix[4]arene. Calixarenes are attractive building blocks for a variety of supramolecular architectures\(^7\)\(^9\) owing to their ability to bind neutral and cationic molecules inside their electron rich cavity and simultaneously to form multiple hydrogen bonds with the hydroxy groups.\(^8\) Appealing possibilities are offered by the hydrophilic and functional outer surface capable of both complexing small guest molecules and binding to hydrogen bonding surfaces. In particular, functionalization of the lower rim of calixarenes with suitable binding groups has produced a series of cation receptors.\(^7\)^\(^9\)\(^g\)^\(^8\)^\(^1\)

Calixresorcarenes hold a special place in the history of encapsulation\(^8\)\(^2\) and their simple synthesis, developed by Högberg,\(^8\)\(^3\) accounts for their active pursuit in laboratories worldwide.\(^8\)\(^4\) Calixresorcarenes serve as an interesting multipurpose scaffold\(^8\)\(^5\) for numerous applications ranging from the assembly of capsules such as the resorcarene hexamers,\(^8\)\(^4\) coordination cages,\(^8\)\(^6\) and molecular loops\(^8\)\(^7\) to applications such as sensors\(^8\)\(^8\) and as phase transfer catalysts.\(^8\)\(^9\) Calixresorcarenes are prepared by the condensation of resorcinol with aldehydes. In this case, acid catalyzed conditions are used and the preparation does not work with formaldehyde because of the polymerization reactions occurring from the 2-position. A wide range of other aldehydes are highly effective, however, and commonly acetaldehyde (giving methyl ‘feet’ to the resorcarene bowl) or 2-phenylethanal (resulting in enhanced solubility of the product in organic solvents) are used.

stabilize the bowl by intramolecular hydrogen bonding. Both calixarenes and calixresorcarenes bearing small substituent groups are relatively conformationally mobile, adopting partial cone, 1,2-alternate and 1,3-alternate conformations. Indeed, calixresorcarenes are significantly more conformationally mobile compared with calix[4]arenes and in both cases, it is generally the cone conformation which exhibits significant binding of organic guest molecules.

Intracavity inclusion of a wide range of aromatic guest molecules has been observed for numerous calix[n]arenes. In every case, the complexes are generally stabilised by CH$_3$···π interactions of about 3 Å from the upper-rim alkyl substituents of the host to the guest aryl ring. A wide range of solid state inclusion complexes are formed by both calix[4]arenes and calix[4]resorcarenes with aromatic and aliphatic guests, generally stabilized by weak interactions of the C–H···π type. In aqueous solution, water-soluble calixarenes have the potential to bind much more strongly to organic guests than in lipophilic media because of the hydrophobic effect. Sulfonated calix[4]resorcarenes have also been prepared and their ability to bind a range of sugars and cyclohexanols in aqueous solution has been examined.

While the native calixarenes and resorcarenes do not generally possess significant solution affinity for organic molecules, their binding ability may be enhanced markedly by elaboration of the cavity. Synthesis of deeper cavities has the dual effect of increasing the degree of guest shielding from solvent and often results in rigidification of the host, increasing its degree of preorganisation and preventing the cavity from collapsing in on itself. Calixarenes may also be transformed into effective solution hosts by elaborating the upper rim. The readily available nature of the calixarene framework has resulted in the synthesis of a number of hosts that use the calixarene as a spacer and rigid three-dimensional anchor or molecular platform upon which to build other binding groups.

1.11 Historical Development of Calixarenes

Work as early as 1872 on the reaction between phenol and formaldehyde had resulted in the formation of various polymeric tar or cement like materials. In 1902, Leo Bakeland, carried out the reaction of phenol and formaldehyde in the presence of very carefully controlled amounts of base and produced a much more homogeneous
and appealing material, which he called Bakelite, thought to consist of highly cross linked polymer of phenol moieties joined by –CH₂– and –CH₂OCH₂– bridges both ortho- and para- to the phenolic hydroxyl groups. He filed a patent for his process in 1907, thus beginning the age of modern synthetic plastics. The use of Bakelite plastics underwent an exponential growth with moulded Bakelite objects entering every aspect of modern life by petrochemical derived materials.⁹²

1.11.1 The Zinke Products

In 1942, as part of a study of the Bakelite process, Alois Zinke (University of Graz, Austria) decided to simplify the reaction by examining the condensation of p-substituted phenols, particularly, p-tert-butylphenol with formaldehyde. Zinke was able to isolate a crystalline product of empirical formula C₁₁H₁₄O and, because the substituted phenol can only react at the ortho position, he postulated a cyclic tetrameric structure 38. Further evidence for the tetrameric structure came from a rational, step by step synthesis of the p-methyl derivative in 1956 by Hayes and Hunter.⁹³ Their final cyclization step (Scheme 2) was effected under high dilution conditions to give the product 39.


In 1955, the British Chemist, Cornforth,⁹⁴ interested in the cyclic structures as possible tuberculostatic substances, repeated the Zinke syntheses and isolated two products of similar but distinct melting points, from both the t-butylphenol and 1,1,3,3-tetramethylbutylphenol reactions. A combination of preliminary X-ray crystallographic evidence and molecular weight determinations led Cornforth to agree
with Zinke and assign tetrameric structures to all four of his materials. He suggested that the observation of two compounds of each type was due to restricted rotation about the bonds joining the phenolic nuclei to the methene bridges resulting in the formation of diastereoisomers. These diastereoisomers are known as the cone, partial cone, 1,2-alternate, and the 1,3-alternate conformers (Figure 2). The cone conformer is by far the most common because it is stabilized by a cyclic network of intramolecular hydrogen bonds between the hydroxyl groups at the lower rim of the molecule. Cornforth originally suggested that restricted rotation about the aryl-methene bonds should result in these materials being noninterconvertable. In fact, interconversion is slow on the NMR timescale at room temperature (about 150 s\(^{-1}\)) but readily observed at 60 °C.

![Figure 2. Conformational isomers of calix[4]arene.](image)

In 1972 David Gutsche revived the chemistry of these cyclic oligophenol products in the hope of producing a range of cavity-containing substances suitable for the construction of enzyme mimics, particularly using the basket-like cone conformation. Gutsche has examined more closely the various reports of calixarene synthesis. Careful recrystallisation of the crude condensation produced a sharp melting material with an osmometric molecular weight of 1330 Da, consistent with a cyclic octamer. The mass spectrum of the trimethylsilyl derivative also suggested an octameric structure. The mystery was finally solved by an X-ray crystal structure that showed the high melting materials of Cornforth are indeed cyclic octamers, the calix[8]arenes.
Indeed, it is now known that the base catalyzed reaction of \( p \)-alkylphenols with formaldehyde rarely gives pure cyclic tetramers although many of Zinke’s products were indeed such. Mixtures of products of cyclic tetramers, hexamers, and octamers are common. Odd numbered calixarenes are less common although both calix[5]- and calix[7]arenes are now well known. Careful chromatographic work has lead to the isolation of species all the way up to calix[16]arenes.

1.1.1.2 The Niederl Products

Resorcinol was among the reactants that Baeyer used in his investigations with phenols and aldehydes and he discovered that it reacts with aldehydes such as acetaldehyde and benzaldehyde under acidic conditions to produce crystalline, high-melting 1:1 condensation products. The reaction was reinvestigated a decade later by Michael\(^{95}\) who succeeded in isolating a pair of crystalline materials for which he postulated cyclic dimeric structures. Similar experiments were carried out in 1894 by Möhlau and Koch\(^ {96}\) and again in 1904 by Liebermann and Lindebaum,\(^ {97}\) and thereafter it remained unattended until 1940 when Niederl and Vogel\(^{98}\) reinterpreted their chemistry. These workers isolated solid, high melting condensation products from the reaction of resorcinol and aldehydes and concluded that the products are best represented as cyclic tetramers (Scheme 3). In contrast to the Zinke tetroles in which four OH groups are intraannular (also designated as “endo-annular”), the eight OH groups in the Niederl octols are extraannular (also designated as “exo-annular”). The past decade has seen an explosion in calixarene chemistry. The calixarene framework with its fascinating hydrophobic cavity has been used as the basis for a vast range of host materials for cations, anions, and neutral molecules, and as an enzyme mimic.

\[
\begin{align*}
\text{HO-} & \overset{+}{\text{RCHO}} \overset{\Phi}{\underset{H}{\text{H}}} \rightarrow \\
\end{align*}
\]

**Scheme 3.** Acid catalyzed resorcinol-aldehyde condensation.
1.12 Mechanism of Calixarene Formation

1.12.1 Mechanism of base-induced reaction

The mechanism of the base-induced oligomerization of phenols and formaldehyde has been the subject of study for many years, dating back to the early twentieth century. The process is initiated by the formation of a phenoxide which, acting as a carbon nucleophile, effects a nucleophilic addition to the highly reactive carbonyl group of formaldehyde (Scheme 4). Under mild conditions the reaction can be terminated at this point and hydroxymethyl phenols can be isolated and characterized. Under more strenuous conditions, the reaction proceeds further to give diarylmethyl compounds, presumably via a pathway that involves o-quinonemethide intermediates, which react with the phenoxide in a Michael-like process (Scheme 5). The suggestion that o-quinonemethides are intermediates in the formation of these oligomers was made as long ago as 1910 and was subsequently resurrected by Hultzsch, Euler, and others. Although a contrary view has been expressed because of the very high temperatures that are required to transform methoxymethylphenols to quinonemethides, it is known that reactions such as the oxy-Cope rearrangement proceed with far greater facility with the anions than with the corresponding neutral compounds. It seems reasonable, therefore, to invoke the existence of quinonemethides under the conditions of the phenol-formaldehyde oligomerization reactions.

Another reaction of hydroxymethylphenols that can occur instead of the formation of the diarylmethanes is the dehydration to dibenzyl ethers (Scheme 6). Thus, the mixtures from which calixarenes arise contain diphenylmethane-type and dibenzyl ether-type compounds in various degrees of oligomerization. The fact that KOH and RbOH give better yields than LiOH, NaOH, and CsOH suggest that a template effect is operative, a phenomenon well documented for crown ether syntheses. The formation of the even numbered calix[4]-, [6]-, and [8]arenes may be the result of their stronger intramolecular hydrogen bonding as compared with that in the odd numbered calix[5]- and [7]arenes. The outcome of the base-induced condensation of formaldehyde with p-substituted phenols is remarkably sensitive to the p-substituent and appears to be particularly critical in the formation of the cyclic...
tetratermer. p-Cresol and p-phenylphenol react with formaldehyde to form a little, cyclic tetratermer but significant amounts of larger calixarenes. It is conjectured that the ease with which the cyclic tetratermer forms is related to the degree to which the p-substituents cover the cavity in the preferred cone conformation.

Scheme 4. Nucleophilic addition of phenoxide to formaldehyde.

Scheme 5. Pathway involving o-quinonemethide intermediates.

Scheme 6. Dehydration of hydroxymethylphenol to dibenzyl ether.

1.12.2 Mechanism of the acid-catalyzed reaction

The acid-catalyzed condensation of resorcinol with aldehydes is most logically interpreted in terms of cationic intermediates and electrophilic aromatic substitution reactions as portrayed in Scheme 7. A kinetic and molecular modeling study\textsuperscript{106} of the acid-catalyzed reaction of resorcinol and acetaldehyde concludes that (a) ring closure to the calix[4]resorcarene is at least as fast as chain propagation, (b) the macrocyclic products are the thermodynamic sink of the reactions and, (c) linear oligomers longer than four aryl units depolymerize fast in comparison with the ring opening, thus promoting the formation of the cyclic tetratermer.
1.13 Metal Complexes as Luminescence Sensors for Cations

An understanding of the photophysical processes in metal complexes along with advances in preparative methods has led to the design of anion and cation sensors that are capable of discriminating one analyte over another based on the luminescence properties of inorganic chromophores. In its most rudimentary form, a discriminating sensor requires a molecular recognition component capable of binding one particular species among a mixture and a responsive fragment capable of producing a distinct signal change immediately after the binding act. Inspired by natural complexation phenomena in biological processes, chemists have successfully designed and synthesized a number of intricate abiotic molecules such as crown ethers, cryptands, spherands, cyclophanes, and calixarenes that are able to specifically sequester ions and molecules. Generally, crown ethers and related compounds themselves cannot generate distinctive changes in physical properties upon complexation that would serve as a basis for signal transduction and sensing. A variety of host molecules containing responsive functions based on MLCT excited states have been reported. These chromophores are predominantly derived from \( d^6 \) metals and polypyridine ligands (40–43). In addition, studies on organic-based sensors provide an intellectual backdrop for sensor design.
The complex 44 is a pH-sensing system that combines the tris(bipyridyl)-ruthenium(II) moiety as a luminophore with free phenolic units of a calix[4]arene acting as acid-base sites. Complex 45 is a vinyl-linked benzocrown ether bipyridyl ruthenium(II) complex designed with conjugated linkages between the 2,2'-bipyridine moiety and the macrocyclic binding sites. The covalent attachment of calixarenes by suitable bridges to luminophores opens the way to new molecules capable of sensing metal ions. Electronic absorption and fluorescence emission spectroscopic measurements have demonstrated spectrochemical recognition of alkali and alkaline earth metal cations by the functionalized crown ethers. Among the luminescent molecules used for sensing or labeling purposes the [Ru(bpy)_3]^{2+} unit is one of the most extensively used. The MLCT excited states of the polypyridyl complexes of $d^6$ metal ions have been extensively used as the probe of the binding interaction owing to their thermal and photochemical stability, solubility in water, and preparative flexibility. By varying the polypyridine or an ancillary ligand in the coordination sphere the absorption and emission energies can be tuned over a range.
(ca. 8000 cm\(^{-1}\)) in the visible spectrum and the excited state lifetimes can vary from tens of nanoseconds to microseconds\(^{115}\).

\[\text{Diagram Image}\]

### 1.14 Luminescent Lanthanide Complexes

A particularly interesting class of luminescent metal ions is the lanthanide family because of their long-lived and line-like emission bands which cover a spectral range from the near ultraviolet to the visible and the near infrared region\(^{116}\). Direct excitation of lanthanide ions is difficult because of the forbidden nature of their electronic transitions\(^{116}\). To overcome this difficulty, the luminescent lanthanide ions are usually coordinated to ligands containing organic chromophores whose excitation, followed by energy transfer, causes the sensitized luminescence of the metal ion (antenna effect). Indeed, a light conversion process, via an absorption/energy transfer/emission (A/ET/E) sequence of photochemical events, is realized in photoactive lanthanide macrocyclic systems\(^{117}\). These supramolecular complexes are considered to function as molecular scale light conversion devices transforming UV-light absorbed by the surrounding chelators into visible lanthanide emission via intramolecular energy transfer. Most of the investigations in the field of luminescent lanthanide complexes have been devoted to Eu(III) and Tb(III) compounds\(^{117}\) which emit in the visible spectral region (red light from Eu(III) and green from Tb(III)) and are used as sensors\(^{117}\) and as luminescent labels in fluoroimmunoassays\(^{118}\) and in time-resolved microscopy\(^{119}\). However, much interest is also devoted to lanthanide ions emitting in the near infrared region\(^{120}\) for both fundamental reasons and possible applications in long range optical data transport.
Beer et al.\textsuperscript{121} have reported a series of luminescent ruthenium bipyridyl complexes \textbf{46-48} covalently linked to the lower rim of acid-amide modified calix[4]arene moieties designed to sense luminescent lanthanide ions. Supramolecular systems composed of a metal recognition site and a luminophore constructed by fusing the principles of crown or cavitands with that of inorganic excited state chemistry are robust and can be used in aqueous solution. Crucial to this union is the role of the chemical linker between the analyte binding site and the luminophore. Studies on the immobilization of such sensor arrays on surfaces are highly desirable since they could lead to stable, reversible, fiber optic based devices using designed transition metal systems.\textsuperscript{122}

Harrimann et al.\textsuperscript{123} have reported the triad \textbf{49} with a central [Ru(tpy)\textsubscript{2}]\textsuperscript{2+} complex as spacer for a zinc(II)-gold(III)bis(porphyrin). The central [Ru(tpy)\textsubscript{2}]\textsuperscript{2+} complex also acts as an electroactive component in the two step electron transfer process. Thus, selective excitation of the zinc porphyrin subunit results in rapid electron
transfer to the adjacent ruthenium(II) chelate and subsequently to the gold(III) porphyrin. The mixed ligand complexes are very effective photosensitizers in systems involving fast photoinduced electron transfer.

![Image](image1)

Tosta et al.\textsuperscript{124} have reported terpyridine functionalized cyclam 50 and the complex [Ru(50)](mtpy)\textsuperscript{2+}. The macrocyclic framework allows binding of an appropriate guest that might trigger a change in the luminescence of the ruthenium(II) centre, thus allowing access to new potential chemosensors based on the fluorophore-spacer-receptor concept. Balzani et al.\textsuperscript{125} have reported Eu(III), Tb(III), and Gd(III) complexes of the branched triazacyclononane ligand 51 containing three 2,2′-bipyridine coordinating units.

Gunnlaugsson et al.\textsuperscript{126} have designed robust multifunctional Ln(III) complexes from cyclen. The synthesis and photophysical properties of 1,10-phenanthroline based Eu(III) complex 52, the first example of a fully reversible pH controlled “off-on-off” signaling system, that employs lanthanide luminescence has been reported.\textsuperscript{127} Terpyridine as an antenna was used to design 53 whose emission was switched on at pH 7.4. The addition of Fe(II) gave rise to the formation of a new band in the absorption spectra at 570 nm corresponding to the MLCT band of the newly formed
Fe(II) complex. Furthermore, the Eu(III) emission was switched off signifying the formation of the new supramolecular species in solution.

Josceanu et al.\textsuperscript{128} have reported the tetranuclear complex 54 appended on cyclam. It exhibits fluorescence characteristic of the [Ru(bpy)\textsubscript{3}]\textsuperscript{2+} chromophore at 600 nm which is greatly reduced upon protonation or inclusion of either Ni(II) or Cu(II) into the cyclam macrocycle. Pope et al.\textsuperscript{129} have reported the MLCT sensitization of NIR emitting lanthanides in trimetallic arrays of the composition M\textsubscript{2}Ln (55-63) [M = Ru(II), Re(I), or Os(II); Ln = Nd(III), Er(III), or Yb(III)]. All these trimetallic species exhibit NIR emission from the lanthanide(III) cation.

Ziessel and Lehn\textsuperscript{130} have reported the Tb(III) and Eu(III) complexes of the 2,2′-bipyridine-based macrocycles 64 and 65. Encinas et al.\textsuperscript{131} have reported the intercomponent energy transfer between ruthenium and rhenium in 66. In the absence of metal ions such as Ba(II) in the macrocyclic cavity, energy transfer from Ru(II) to Re(I) occurs and intense Re(I)-based emission was observed. However, upon the incorporation of Ba(II) into the macrocyclic cavity emission from the ruthenium(II) center is switched on resulting in dual luminescence of both Re-based and Ru-based
chromophores at ca. 530 and 610 nm, respectively. Loiseau et al.\textsuperscript{132} have reported the polytopic ligand 67 containing three different coordination domains (phenanthroline, terpyridine, and diazacrown ether subunits) and mononuclear Zn(II) and di- and tetranuclear ruthenium(II) complexes. The absorption and luminescent properties of the ruthenium compounds are dominated by the MLCT transitions and behave as independent components in the multicomponent array.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{images/64_65_66_67}
\end{figure}

\textbf{1.15 Ruthenium(II) Polypyridine Complexes Conjugated Metalloproteins}

Reactions involving the transfer of a single electron are very common in many biological processes. Respiration and photosynthesis require several one electron transfer reactions. Cytochrome \( c \), which functions as an electron transfer shuttle, is probably the most intensely studied metalloprotein involved in these reactions. One of its primary roles is to shuttle electrons from the cytochrome \( bc_1 \) complex to cytochrome \( c \) oxidase, where the electrons are used to reduce molecular oxygen to water. The reduction is accompanied by the formation of a proton gradient across the membrane in which cytochrome \( c \) oxidase is embedded. The proton gradient is used in the conversion of adenosine diphosphate (ADP) to adenosine triphosphate (ATP). ATP is used by the cell as an energy source for numerous other reactions. Several researchers have utilized cytochrome \( c \) with the iron replaced by zinc or other metals.\textsuperscript{133} These metal substituted analogues have long lived excited states that can transfer electrons.
Pioneering studies by Gray and his co-workers\cite{gray1992} and Isied and his co-workers\cite{isied1993} demonstrated that [Ru(NH$_3$)$_5$]$^{2+}$ could be covalently linked to the nitrogen atom of histidine residues on the surface of cytochrome $c$. In subsequent studies with cytochrome $c$ and many other proteins, the rate constants for electron transfer between the metal center of the protein and the ruthenium complex were reported.\cite{gray1993} Several studies focused on the question of how electrons were transferred over long distances through a protein and theoretical developments describing electron transfer in such an environment have been reported.\cite{isied1995} Later developments demonstrated the utility of ruthenium complexes containing bipyridine ligands in the study of electron transfer in proteins. Photoexcitation of a ruthenium bipyridine complex bonded to a metalloprotein produces a long lived excited state that can act as a strong oxidant or reductant. In many cases, rapid electron transfer to the iron center of the protein follows photoexcitation. Ruthenium labelled proteins have been used extensively to study intramolecular electron transfer (Ru to Fe) as well as intermolecular electron transfer between two metalloproteins.

1.1.5 Covalently Linked Ruthenium Complexes to Cytochromes

A number of different chemical means have been developed for the covalent conjugation of ruthenium complexes to metalloproteins particularly on cytochrome $c$ and cytochrome $b_5$. Initial success in this area relied heavily on the fact that ruthenium(II) shows a strong tendency to bind to nitrogen containing heterocyclic bases. The amino acid histidine contains an imidazole ring and ruthenium complexes such as [Ru(bpy)$_2$(H$_2$O)$_2$]$^{2+}$ selectively binds to the nitrogen donor in the imidazole ring.\cite{gray1994} The resulting complex [Ru(bpy)$_2$(H$_2$O)(His-cytochrome $c$)] has a very short excited-state lifetime. However, further reaction with excess imidazole yields the complex [Ru(bpy)$_2$(imidazole)(His-cytochrome $c$)] which has an excited state lifetime of 80 ns\cite{gray1995} and has been used extensively in the study of electron transfer reactions.\cite{isied1996} This reaction is specific for histidine residues found on the surface of the protein. Progress in this area has been aided greatly by genetic engineering. Through this technology, histidine residues can be selectively placed at specific locations on the surface of the protein. Gray and his co-workers\cite{gray1996} have used this strategy to
explore electron transfer between the metal center of various proteins and the covalently bound ruthenium complex.

Beratan and his co-workers, Marcus and his co-workers, and Kuki have focused on the theoretical aspects of the electronic coupling and developed models describing how the electron travels through or is coupled through the protein. One of the most popular models is that of Beratan and his co-workers based on the idea of dominant coupling pathways, derived by searching combinations of covalent bonds, hydrogen bonds, and through space jumps that maximize the coupling between the redox centers. The use of ruthenium polypyridyl complexes to photoinitiate electron transfer represents a powerful means of obtaining kinetic measurements of intraprotein and interprotein electron transfer reactions. It has been successfully applied to the reactions of cytochrome c with cytochrome c oxidase, cytochrome c peroxidase, cytochrome b₅, cytochrome c₁, and plastocyanin.

1.16 Identification of the Research Problem

The high efficiency of natural photosynthesis is an outcome of the proper organization of a multitude of chromophores in space that exhibit distinct absorption, emission, and redox properties. Such biofunctional systems have inspired chemists to explore artificial structures containing multiple chromophores that provide sequential energy transfer, but the realization of high efficiency and directionality remains a challenging task. 2,2′:6′,2′′-Terpyridine (tpy) and its structural analogs have gained much interest in recent years as functional templates in the fields of supramolecular and coordination chemistry as well as materials science. The high binding affinity of terpyridine ligands toward transition and rare earth metal ions and the interesting redox and photophysical properties of their complexes have given rise to diverse metallosupramolecular architectures which find a multitude of potential applications covering light-to-electricity conversion, light-emitting electrochemical cells (LECs), electroluminescent systems, and nonlinear optical devices.

Polypyridine complexes of the d⁶ metal ions such as Ru(II), Ir(III), Os(II), and Re(I) exhibit exceptional spectroscopic properties featuring intense absorption in the visible region and photostability. The relatively long lived excited states of these complexes, which are of MLCT in character, established comprehensive photophysical
and photochemical studies\textsuperscript{12b,16c,151} and have been extensively used to construct polynuclear species by modular synthetic approach.\textsuperscript{12i,152} From a geometrical viewpoint, 2,2′:6′,2″-terpyridine is a superior ligand compared to the bidentate 2,2′-bipyridine-type ligands. However, [Ru(tpy)_2]\textsuperscript{2+} is non-luminescent at room temperature and its luminescence lifetimes may be finetuned by manipulating the excited state properties which are ligand dependent.\textsuperscript{23c} The most popular approach has focused on manipulating the energy difference between the \(3^\text{MLCT}\) and \(3^\text{MC}\) states of the complex inorder to minimize the non-radiative decay through the \(3^\text{MC}\) state to the ground state. Destabilization of the \(3^\text{MC}\) state and/or stabilization of the \(3^\text{MLCT}\) state leads to a greater energy gap between the two states. Alternatively, an additional chromophore may be introduced which produces a bichromophoric effect\textsuperscript{153} leading to a substantial increase in the room temperature luminescence lifetimes.

Calixarenes and calixresorcarenes are attractive building blocks for a variety of supramolecular architectures\textsuperscript{79a-c} owing to their ability to bind neutral and cationic molecules inside their electron rich cavity. The reactive –OH functionalities of calixarenes and calixresorcarenes can be functionalized with polypyridyl ligands, thus producing a range of supramolecular assemblies. Furthermore, both of them are good candidates on account of their chromophoric nature which might be useful in manipulating the properties of the MLCT excited states of terpyridine-based ruthenium(II) complexes. The diverse application potential of terpyridine-based complexes calls for highly structured assembly of polynuclear Ru\textsuperscript{II}(tpy)-type complexes. In particular, the terpyridine motifs featuring \(\pi\)-conjugated substituents attached in the 4′-position are of increasing interest. Thus, appending 4′-(p-tolyl)-2,2′:6′,2″-terpyridine (ttpy) onto the calixarene and calixresorcarene moieties via covalent linkage would give rise to polynuclear ruthenium(II) complexes. Therefore, the present investigation, \textit{Synthesis, luminescence, and electrochemical studies of polynuclear ruthenium(II) complexes of tolyterpyridine appended calixarenes and calixresorcarenes} is undertaken.