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SUPRAMOLECULAR PHOTOCHEMISTRY

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Contents

1. Introduction	10444
2. Supramolecular Species	10445
3. Photochemical and Photophysical Processes	10448
4. Cage-type Systems	10454
4.1 Cage-type metal complexes	10454
4.1.1 Cobalt complexes	10455
4.1.2 Ruthenium complexes	10458
4.1.3 Lanthanide complexes	10461
4.2 Photo-cleavable and photo-flexible cages	10464
4.3 Photochemistry of incarcerated molecules	10466
5. Host-Guest Systems	10467
5.1 Polyammonium macrocyclic receptors with $\text{Co}(\text{CN})_6^{3-}$	10468
5.2 Aromatic crown ethers with $\text{Pt}(\text{bpy})(\text{NH}_3)_2^{2+}$	10471
5.3 Lasalocid A anion with $\text{Cr}(\text{bpy})_3^{3+}$	10477
6. Rotaxanes, Catenanes, and Related Species	10479
6.1 Catenands and metal catenates	10480
6.2 Rotaxanes and catenanes featuring charge-transfer interaction	10483
7. Covalently-linked Molecular Components	10488
7.1 Photoinduced electron and energy transfer in two-component model systems	10489
7.1.1 Electron transfer	10490
7.1.2 Energy transfer	10492
7.2 Multicomponent systems for photoinduced charge separation	10493
7.3 Polynuclear metal complexes for light harvesting	10496
7.3.1 Trinuclear metal complexes of tripod-type bipyridine ligands	10496
7.3.2 Polynuclear complexes of the bis(2-pyridyl)pyrazine bridging ligands	10498
8. Conclusion	10502

1. Introduction

Photochemistry is a natural phenomenon as old as the world and a modern branch of science, at the interface between light and matter and at the crossroads of chemistry, physics, and biology. Photochemistry is of paramount importance to life (photosynthesis, vision, phototaxis, etc.) as well as to technology (image reproduction, photocatalysis, photodegradation, etc.). In the last two decades photochemistry has reached a remarkable level of experimental and theoretical efficacy. The photochemical and photophysical processes of thousands of organic molecules, coordination compounds, and organometallic complexes have been elucidated, and suitable theoretical treatments are now available to rationalize the structural, energetic, and dynamic properties of the most important excited states of several families of molecules. Up until now most of the fundamental photochemical investigations have dealt with molecular species (*molecular photochemistry*).

In the same way as combination of atoms leads to molecules, combination of molecular components leads to *supramolecular species*. Current literature clearly shows that chemical research is rapidly moving from molecular to supramolecular species. There are at least four reasons for this trend: 1) the high degree of knowledge reached on molecular species; 2) the extraordinary progress made by synthetic methods; 3) the continuous search for new materials (e.g., for a "small-upward" approach to nanostructures); 4) the need to fill the gap which separates chemistry from biology.

One of the most interesting aspects of the chemistry of supramolecular species is their interaction with light and the great variety of processes that may ensue. This is the realm of *supramolecular photochemistry*.¹ In the last few years

supramolecular photochemistry has grown very rapidly along several directions. Photochemistry and supramolecular chemistry are, by their own nature, interdisciplinary areas, and this is even more true for supramolecular photochemistry.

In this review emphasis will be given to supramolecular systems made of a *small number of discrete molecular components* held together by some type of chemical bond. Specifically, we will deal with the four types of supramolecular species schematized in Fig. 1. Systems like polymers, semiconductors, micelles, films, liquid crystals, and derivatized electrodes, which can in some way be considered supramolecular systems, will not be discussed. Most of the examples illustrated have been studied in the author laboratory, but relevant examples from other laboratories will also be considered.

2. Supramolecular species

Any definition of supramolecular species is necessarily arbitrary and the word may have different meanings depending on the area to which it is applied.¹⁻⁶ Conceptually, the feature that distinguishes a "supramolecular species" from a "large molecule" is the possibility to split the system into individual molecular subunits (*components*) that are capable, as such or with minor modifications, of separate existence.¹ According to this concept, systems where the components are individual molecules interlocked (e.g., catenanes, Fig. 1) or held together by intermolecular forces (e.g., host-guest systems, Fig. 1) can straightforwardly be defined supramolecular species. The situation is less clear, however, for systems where the "components" are kept together by coordinative or covalent bonds. Macrocyclic complexes (Fig. 1) where metal ions and ligands maintain most of their intrinsic properties, and systems made of covalently-linked but clearly identifiable subunits (Fig. 1) can also

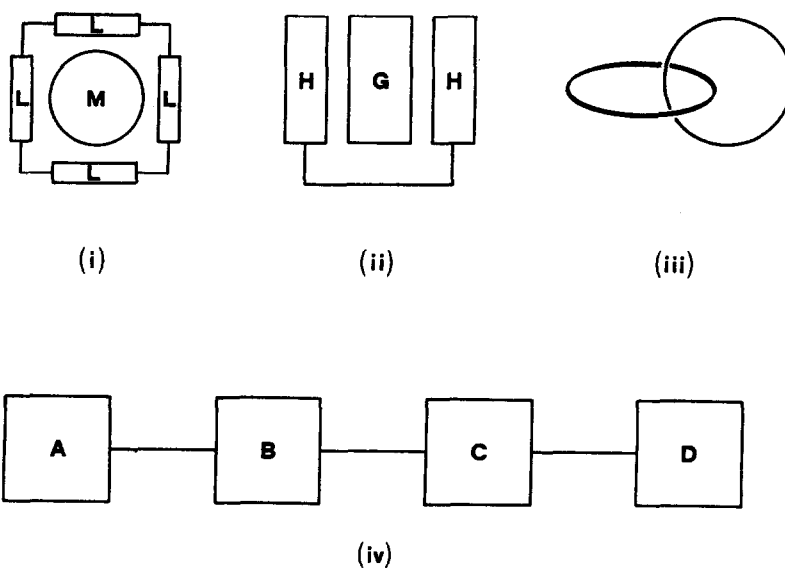


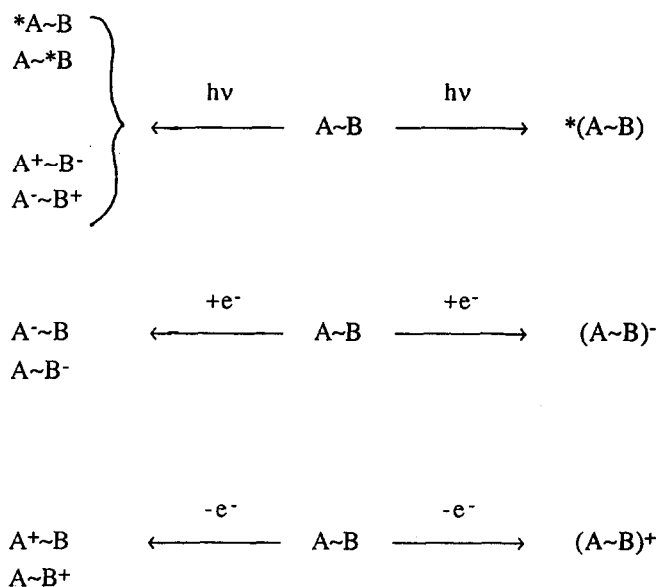
Fig. 1. Schematic representation of four types of supramolecular species: (i) cage-type systems; (ii) host-guest systems; (iii) catenanes; (iv) covalently-linked molecular components.

be considered supramolecular species. By contrast, species like fullerenes are better defined as large molecules.

In practice, the distinction between large molecules and 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 defined a supramolecular species. As shown in Scheme 1, light excitation of a supramolecular species $A \sim B$ (where \sim indicates any type of "bond" that keeps together the A and B subunits) leads to excited states that are substantially localized on A or B, or causes an electron transfer from A to B (or viceversa). When the excited states are substantially delocalized on both A and B, the species is better considered as a large molecule. Similarly, oxidation and reduction of a supramolecular species can substantially be described as oxidation and reduction of specific components, whereas oxidation

Scheme 1

supramolecular species
compound
large molecule



and reduction of a large molecule leads to species where the hole or the electron are substantially delocalized on the entire system (Scheme 1).

In principle, the properties of the molecular components of a supramolecular structure can be obtained from the study of the isolated components or of suitable model molecules. In several cases, however, the identification of real molecules that constitute suitable models for molecular components of a supramolecular species is not a trivial problem. Strictly speaking, in a covalent A-L-B species in which A and B are active components and L is a connector, A and B would be radicals or coordinatively unsaturated species that can never exist as such. In some cases, e.g. when the connector is bound to the components via carbon-carbon bonds, this is not a problem since molecular species such as AH and BH or

AR and BR (R=alkyl group) will be indeed almost identical in properties to A and B in the supramolecular species. In other cases, however, the connector may interact more deeply with the electronic subsystem of the active components. In such a case, compounds that include the connector, such as A-L and B-L, should be used to approach the properties of A and B in the supramolecular species.

3. Photochemical and photophysical processes

The first act of any photochemical and photophysical process is the absorption of a photon by a molecule (eq. 1). The excited state that is formed in this way is a high energy, unstable species which must undergo some type of deactivation.⁷ As shown in Fig. 2,



excited state deactivation can occur via (i) disappearance of the original molecule and formation of products (photochemical reaction), (ii) emission of light (radiative deactivation, also called luminescence), (iii) degradation of excess energy into heat (radiationless deactivation), and (iv) some type of interaction with other species present in the solution (quenching processes).

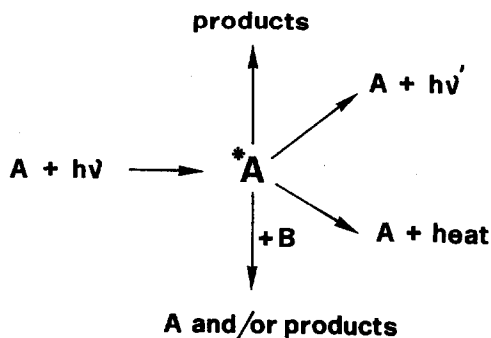


Fig. 2. Light excitation of a molecule and deactivation of the electronically excited state.

As is well known from electronic spectroscopy,⁷ the probability of light absorption (and thus the intensity of the corresponding absorption band) is related to the characteristics of the states involved and particularly to their spin quantum number. Transitions from the ground state to excited states having the same spin value are allowed and give rise to intense bands, whereas transitions to excited states of different spin value are forbidden and can hardly be observed in the absorption spectra. In most molecules the ground state is a singlet and the lowest excited state is a triplet that cannot be directly populated by light absorption but can be obtained from the deactivation of upper excited states. For this reason, at least three states (e.g., ground state singlet and excited singlet and triplet) are involved in a photochemical process, as is shown in the Jablonski diagram of Fig. 3, where deactivation by chemical reaction is not represented for the sake of simplicity. Emission of light (luminescence) is called fluorescence or

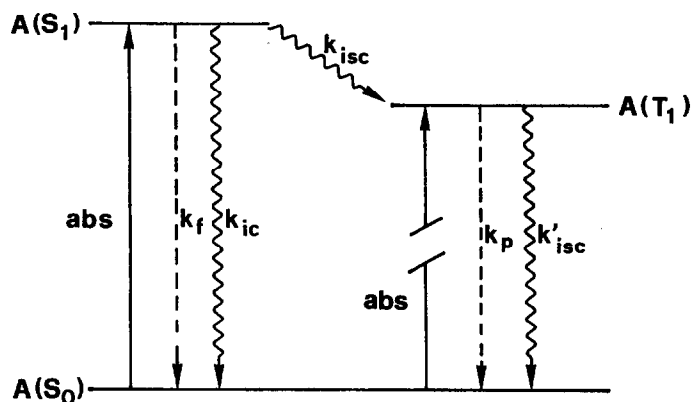


Fig. 3. Schematic energy level diagram for a typical molecular species. S_0 , S_1 , and T_1 are the ground state singlet, excited state singlet, and excited state triplet, respectively; k_f , k_{ic} , k_{isc} , k_p , and k'_{isc} are the unimolecular rate constants for fluorescence, internal conversion, $S_1 \rightarrow T_1$ intersystem crossing, phosphorescence, and $T_1 \rightarrow S_0$ intersystem crossing, respectively.

phosphorescence depending on whether the excited state has the same or different spin compared to the ground state. In the same way, radiationless deactivation is called internal conversion when it occurs between states of the same spin and intersystem crossing when it occurs between states of different spin. Fluorescence and internal conversion are spin-allowed steps, whereas phosphorescence and intersystem crossing are spin-forbidden steps.

Each intramolecular decay step is characterized by its own rate constant (Fig. 3) and each excited state is characterized by its lifetime, given by

$$\tau = 1/\sum_i k_i \quad (2)$$

where k_i is the first order rate constant for a generic unimolecular process that causes the disappearance of the excited state.⁷ For each process one can define the quantum yield, Φ , which is the ratio between the number of moles of species (photons or molecules) produced and the number of moles of photons that have been absorbed. For example, making reference to Fig. 3, the quantum yield of emission from the lowest spin-forbidden excited state (phosphorescence quantum yield Φ_p) can be expressed by the following equation

$$\Phi_p = \eta_{isc} k_p \tau_{T_1} \quad (3)$$

where η_{isc} is the efficiency of population of the emitting excited state from the state populated by light absorption

$$\eta_{isc} = k_{isc} / (k_{isc} + k_f + k_{ic}) \quad (4)$$

and τ_{T_1} is the lifetime of the emitting excited state

$$\tau_{T_1} = 1/(k_p + k'_{isc}). \quad (5)$$

When the intramolecular deactivation steps are not too fast, i.e. when the lifetime of the excited state (eq. 2) is sufficiently long, the excited molecule may have a chance to encounter a molecule of another solute, B (Fig. 2). In such a case, some specific interaction may occur (Fig. 4) and the process taking place is called a bimolecular process.⁷⁻¹⁰ Simple kinetic arguments show that only those excited states that live longer than $\sim 10^{-9}$ s may have a good chance to be involved in encounters with other solute molecules. The excited states that satisfy this condition are the lowest spin-allowed and spin-forbidden excited states for organic molecules, and the lowest spin-forbidden excited state for coordination compounds.¹⁰

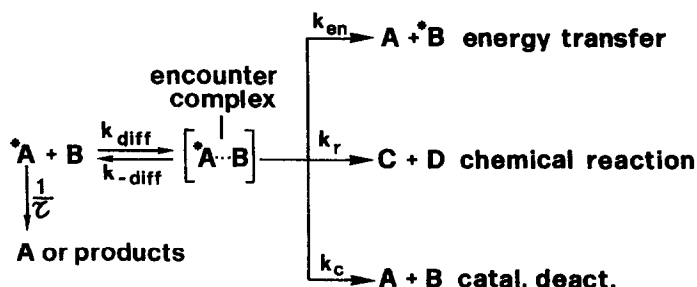
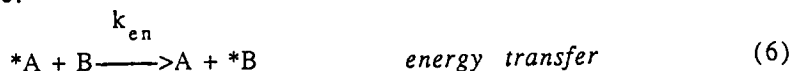


Fig. 4. Schematic representation of bimolecular processes that may take place following an encounter between an excited state and another chemical species.⁸

The most important bimolecular processes are energy transfer⁷⁻¹¹ and electron transfer;^{7-10,12-14} the latter process may involve either the oxidation or the reduction of the excited state:



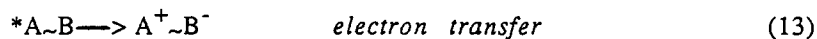
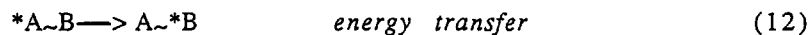
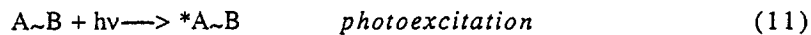
The thermodynamic ability of an excited state to intervene in energy transfer processes is related to its zero-zero spectroscopy energy, E^{0-0} . For the electron transfer processes, the relevant thermodynamic parameters are the oxidation (eq. 7) and reduction (eq. 8) potentials of the $*A/A^+$ and $*A/A^-$ couples. It should be emphasized that, because of its higher energy content, *an excited state is both a stronger reductant and a stronger oxidant than the corresponding ground state*. To a first approximation, the redox potentials for the excited state couples may be calculated from the potentials of the ground state couples and the one-electron potential corresponding to the zero-zero excitation energy:

$$E(A^+/*A) = E(A^+/A) - E^{0-0} \quad (9)$$

$$E(*A/A^-) = E(A/A^-) + E^{0-0} \quad (10)$$

Kinetic parameters (i.e., intrinsic barrier and electronic transmission coefficient) can also play an important role in energy and electron transfer processes.^{11,12} Figure 5 shows schematically some molecular quantities that characterize an excited state from the point of view of energy and electron transfer processes.

Photoinduced energy transfer and electron transfer processes can take place, of course, also between molecular components of supramolecular species,¹ e.g:



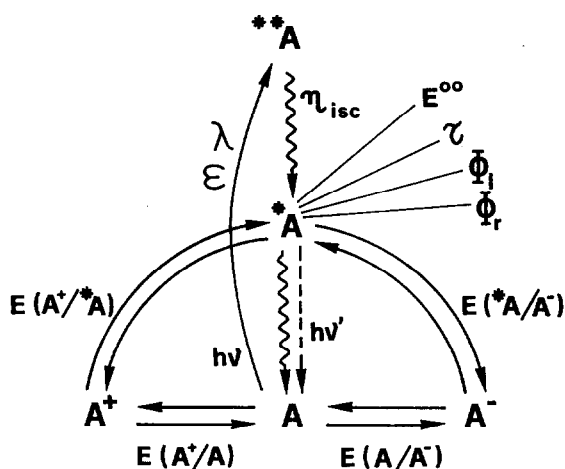


Fig. 5. Schematic diagram indicating the molecular quantities relevant to the discussion of photoinduced energy and electron transfer processes.

In supramolecular species constituted by several molecular components, successive energy or electron transfer steps may lead to energy migration or charge separation over long distances (Section 7-2).

Another interesting event that can take place upon light excitation of a supramolecular species is the so called *optical electron transfer* process, which leads to the direct formation of an intercomponent charge-transfer state (Fig. 6):



Both photoinduced electron transfer (eq. 11 plus eq. 13) and optical electron transfer (eq. 14) may be followed by a thermal back electron transfer process:



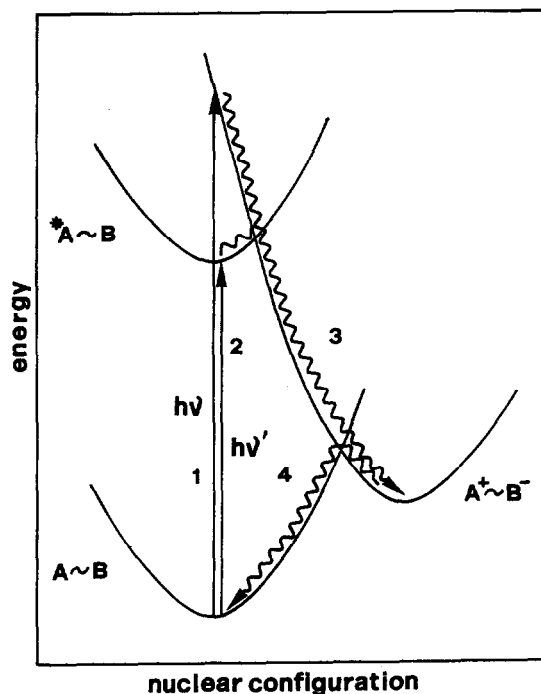


Fig. 6. Optical (1), photoinduced (2+3), and thermal back (4) electron transfer processes in supramolecular species.

The relationships between optical, photoinduced, and back electron transfer processes in a supramolecular species are schematized in Fig. 6. Several examples of energy and electron transfer processes in supramolecular species have been discussed in a number of books and review articles.^{1,5,6,15-20}

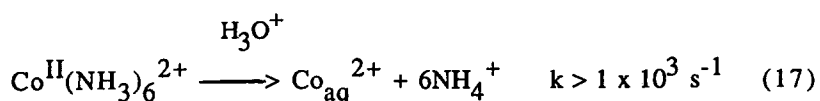
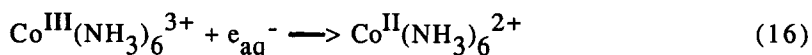
4. Cage-type systems

4.1 Cage-type metal complexes

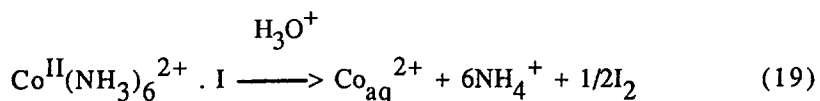
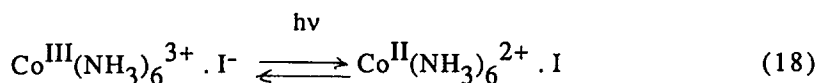
Systems made of a metal ion enclosed into a macrocyclic ligand or encapsulated by a cage-type ligand may often be considered as supramolecular species.^{1,2,4} In this review we will only recall

three paradigmatic examples of metal complexes where the presence of cage-type ligands modifies the photochemical and photophysical properties.

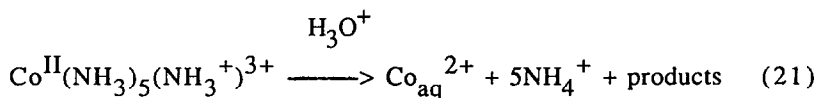
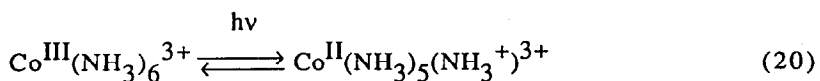
4-1-1 Cobalt complexes. It is well-known that the Co(III) complexes are kinetically inert while the Co(II) complexes are very labile because of the presence of electrons in the $\sigma^*_M(e_g)$ antibonding orbitals.²¹ As a consequence, reduction of the central metal ion of $\text{Co}(\text{NH}_3)_6^{3+}$ in aqueous solution causes the decomposition of the complex. Such a reduction may be carried out by the following methods: (i) pulse radiolysis,²²



(ii) ion pair charge-transfer (IPCT) photoexcitation ($\Phi = 0.2$),²³



or (iii) intramolecular ligand-to-metal charge-transfer (LMCT) photoexcitation ($\Phi = 0.16$)²³



Simple chelation does not substantially change the situation because Co(en)_3^{3+} (en = ethylenediamine) after pulse radiolysis reduction loses its ligands with $k > 25 \text{ s}^{-1}$,²² and upon LMCT excitation undergoes redox decomposition with $\Phi=0.13$.²³

In 1977 Sargeson and coworkers²⁴ performed a capping reaction of Co(en)_3^{3+} along its C_3 axis with NH_3 and CH_2O (Fig. 7). The encapsulated metal ion so obtained, (1,3,6,8,10,13,16,19-octaazabicyclo-[6,6,6]-icosane)-cobalt(III) ion, was called cobalt(III) sepulchrate, Co(sep)^{3+} . Since then, a great number of similar cage-type complexes of a variety of metal ions have been synthesized and studied by Sargeson's group.²⁵⁻²⁸

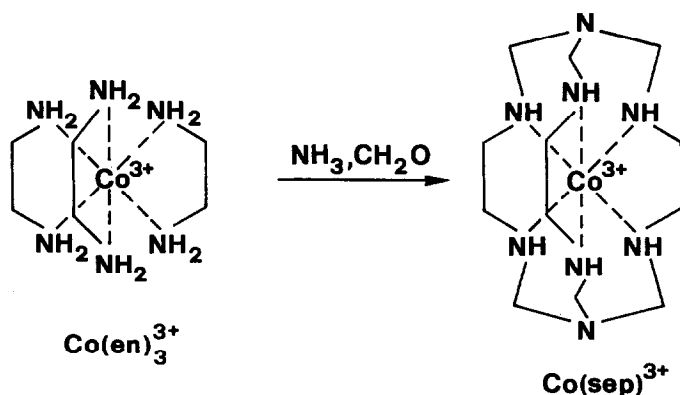
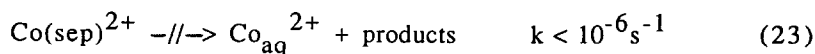
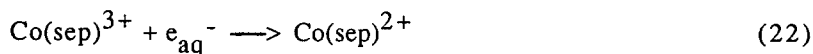
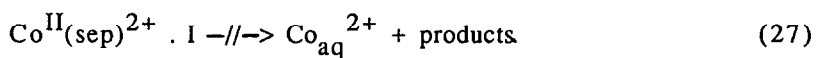
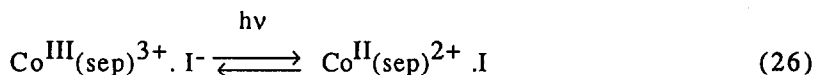
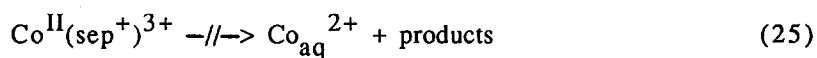
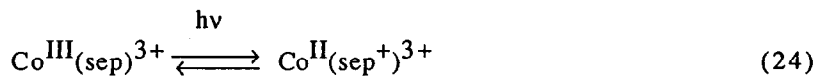


Fig. 7. Synthesis of the Co(III) sepulchrate

Co(sep)^{3+} and the analogous cage-type complexes exhibit several quite interesting properties. From the photochemical point of view, the most important consequence of encapsulation is the kinetic inertness of the reduced species. Upon one-electron reduction of Co(sep)^{3+} in pulse radiolysis experiments, in fact, formation of $\text{Co}_{\text{aq}}^{2+}$ cannot be observed (except in strong acid solution):²⁹



Such a kinetic inertness prevents photodecomposition ($\Phi < 10^{-6}$) on intramolecular LMCT excitation and also on IPCT excitation:³⁰



In spite of their completely different photochemical behavior, $\text{Co}(\text{NH}_3)_6^{3+}$ (or $\text{Co}(\text{en})_3^{3+}$) and $\text{Co}(\text{sep})^{3+}$ have quite similar absorption spectra. These differences and similarities between caged and uncaged hexamine complexes can be explained on the basis of the potential energy curves shown in Fig. 8.³¹

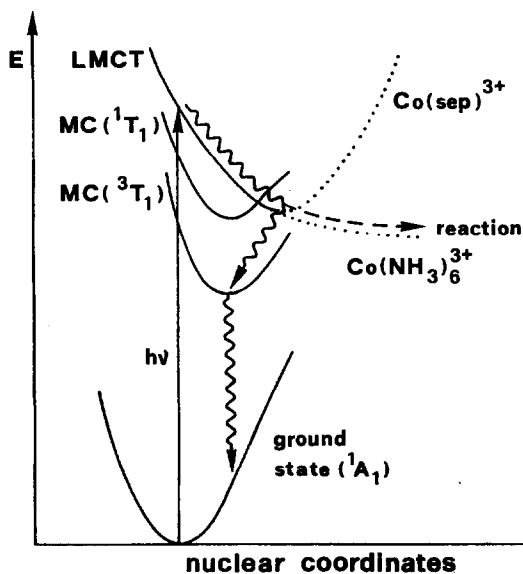


Fig. 8. Schematic potential energy curves for $\text{Co}(\text{NH}_3)_6^{3+}$ and $\text{Co}(\text{sep})^{3+}$.³¹

Encapsulation does not substantially modify the composition and symmetry of the first coordination sphere which is constituted by the ligand atoms surrounding the metal ion. Thus, the potential energy curves for the caged and uncaged complexes in the spectroscopic region are nearly the same, which accounts for the strong similarity in the absorption spectra. The photodecomposition reaction of $\text{Co}(\text{NH}_3)_6^{3+}$ on LMCT (or IPCT) excitation is due to dissociation along the LMCT (or IPCT) potential energy curve in competition with radiationless decay to the ground state (Fig. 8). Encapsulation, however, introduces nuclear constraints to large amplitude nuclear motions and particularly to the dissociation of the coordinated units, which are kept in almost fixed positions by the pattern of covalent bonds. Therefore, for the sepulchrate complex the dissociative branch of the MLCT (or IPCT) potential energy curve is replaced by an upward steep curve (Fig. 8), so that ligand detachment can no longer compete with radiationless decay to the ground state.³¹

Because of the inertness of their one-electron reduction products, $\text{Co}(\text{sep})^{3+}$ and other Co(III) cage complexes can be used as relays for photogeneration of hydrogen from water³²⁻³⁷ and as electron transfer photosensitizers for photooxidation of anions and simultaneous evolution of hydrogen.^{30,38,39}

4.1.2 Ruthenium complexes. In the last ten years Ru(II)-polypyridine complexes have attracted the attention of several research groups because of a unique combination of ground and excited state properties.^{9,10,14,40} The prototype of these complexes, the well known $\text{Ru}(\text{bpy})_3^{2+}$ species, is extensively used as (i) a photoluminescent compound, (ii) an excited state reactant in energy and electron transfer processes, (iii) an excited state product in chemiluminescent and electrochemiluminescent reactions, and (iv) a mediator in the interconversion of light and chemical energy.

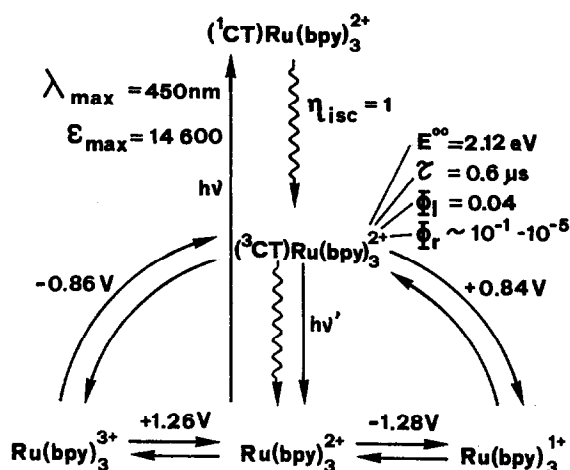


Fig. 9. Ground and excited state properties of Ru(bpy)₃²⁺.⁴¹

Some relevant data concerning this complex are summarized in the scheme of Fig. 9. Comparison with the requirements needed for ideal photosensitizers^{41,42} and luminophores⁴³ shows that the main drawbacks of Ru(bpy)₃²⁺ are (a) the relatively fast radiationless decay of the ³CT excited state to the ground state (with, as a consequence, a relatively short excited state lifetime and a small luminescence efficiency), and (b) the occurrence of a ligand photosubstitution reaction whose efficiency is strongly dependent on the experimental conditions (from $\sim 10^{-5}$ in water at room temperature to $\sim 10^{-1}$ in CH₂Cl₂ solutions containing Cl⁻ ions). It is generally agreed^{10,40} that the ligand photosubstitution reaction proceeds *via* a thermally activated radiationless transition from the luminescent ³CT level to a distorted ³MC level, with subsequent competition between radiationless decay to the ground state and cleavage of a Ru-N bond with formation of an intermediate containing a monodentate bpy ligand.^{44,45} Such an intermediate can undergo either loss of bpy, or chelate ring closure with reformation of Ru(bpy)₃²⁺.

Ligand photodissociation can be prevented if the bpy ligands are linked together to make a cage around the ruthenium ion. A suitable cage-type ligand can also confer more rigidity to the molecular structure, thereby slowing down the radiationless decay processes with consequent increase of both emission intensity and lifetime. It may also happen, however, that the cage-type ligand does not allow the metal to attain an appropriate coordination geometry and/or suitable Ru-N bond distances. In such a case, the 3MC level would drop below the 3CT level and most of the valuable properties of the complex would disappear. Molecular models show that this must be the case for the bpy.bpy.bpy cryptand **1**. As we will see later, such a ligand is appropriate for the larger, not symmetry-demanding Eu^{3+} ion, but it is clearly too rigid to create the octahedral coordination required by Ru^{2+} . This is apparently confirmed by the lack of luminescence at room temperature from a complex claimed to be the $[\text{Ru} \subset \mathbf{1}]^{2+}$ cryptate.⁴⁶ The cage-type ligand⁴⁷ shown in Fig. 10a is clearly more suitable for Ru^{2+}

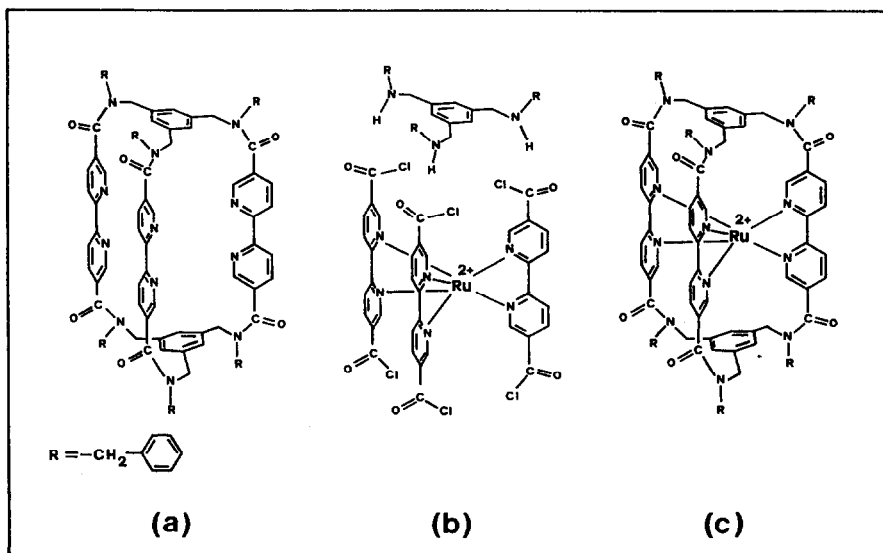


Fig.10. (a) Cage-type ligand suitable for Ru^{2+} coordination;⁴⁷ (b) synthesis and (c) representation of the cage complex.⁴⁸

coordination because its larger spacers make the cage flexible and allow the bpy ligands to create an almost ideal octahedral coordination environment. The Ru(II) complex of this ligand has been prepared⁴⁸ *via* a template reaction starting from a derivative of Ru(bpy)₃²⁺ (Fig. 10b). Such a Ru(II) cage-type complex (Fig. 10c) exhibits absorption and emission spectra very similar to those of the parent Ru(bpy)₃²⁺ complex, a longer excited state lifetime at room temperature (1.7 vs 0.8 μs) and, as expected, an extremely greater (about 10⁴ times) stability towards ligand photosubstitution.⁴⁹ This assures a quite high turnover number when the Ru-cage bpy complex is used as a photosensitizer.

4.1.3 Lanthanide complexes. Molecular and supramolecular species capable of exhibiting a strong luminescence are quite interesting not only from a fundamental point of view, but also because of their potential use for a variety of applications. Some lanthanide ions, particularly Eu³⁺ and Tb³⁺, possess strongly luminescent and long-lived excited states. For example (Fig. 11), the lowest excited state of Eu_{aq}³⁺, ⁵D₀, lives 3.2 ms and emits with an efficiency of 0.8 in D₂O solution.⁵⁰ Unfortunately, these ions are very poor light absorbers. The strongest absorption band of Eu_{aq}³⁺

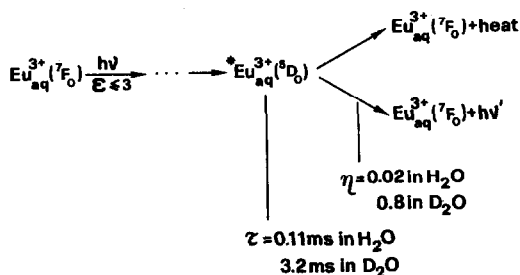


Fig.11. Excitation and deactivation of Eu_{aq}³⁺.⁵⁰

in the near UV and visible region occurs at 393 nm with molar absorption coefficient lower than $3 \text{ M}^{-1}\text{cm}^{-1}$. To make use of the excellent emitting properties of these ions one has thus to find ways to populate their excited states, *i.e.* to overcome the lack of absorption bands.

Complexation of the lanthanide ion with suitable ligands is, of course, a possibility, but lanthanide ions do not exhibit strong coordinating ability. By using cage-type ligands, three important goals can be reached: (i) the complexes can be fairly stable because of the cage effect; (ii) light absorption can be assured by the chromophoric groups on the ligands, and electronic energy can then be transferred to the luminescent metal ion (antenna effect); (iii) the cage-type ligand can shield the lanthanide ion from interaction with water (solvent) molecules, thereby decreasing the rate of radiationless decay of the luminescent excited state, which mainly takes place *via* coupling with the high energy O-H vibrations.⁵¹ Following these guidelines, Lehn and co-workers⁵² have synthesized the Eu^{3+} complex of the bpy.bpy.bpy ligand 1, which indeed displays excellent luminescent properties. The energy level diagram for this complex is shown in Fig. 12.⁵³ Excitation in the spin-allowed ^1LC bands is followed by intersystem-crossing to the lowest spin-forbidden ^3LC level that lies at higher energy than the luminescent $^5\text{D}_0$ *f-f* level of Eu^{3+} . The efficiency of energy transfer from the ^3LC level of the bpy ligand to the $^5\text{D}_0$ metal level is sufficiently high ($\eta = 0.1$), so that such a complex is an efficient molecular device for the conversion of UV light absorbed by the ligands into visible luminescence emitted by the metal ion. Even in very dilute aqueous solution ($\sim 10^{-5} \text{ M}$) this complex is able to convert about 1% of the incident UV photons into emitted visible photons⁵⁴, a quite interesting result for several applications, in particular for labelling biological materials.

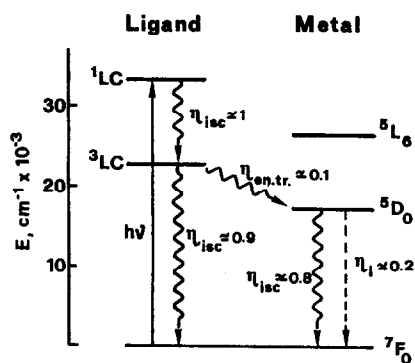
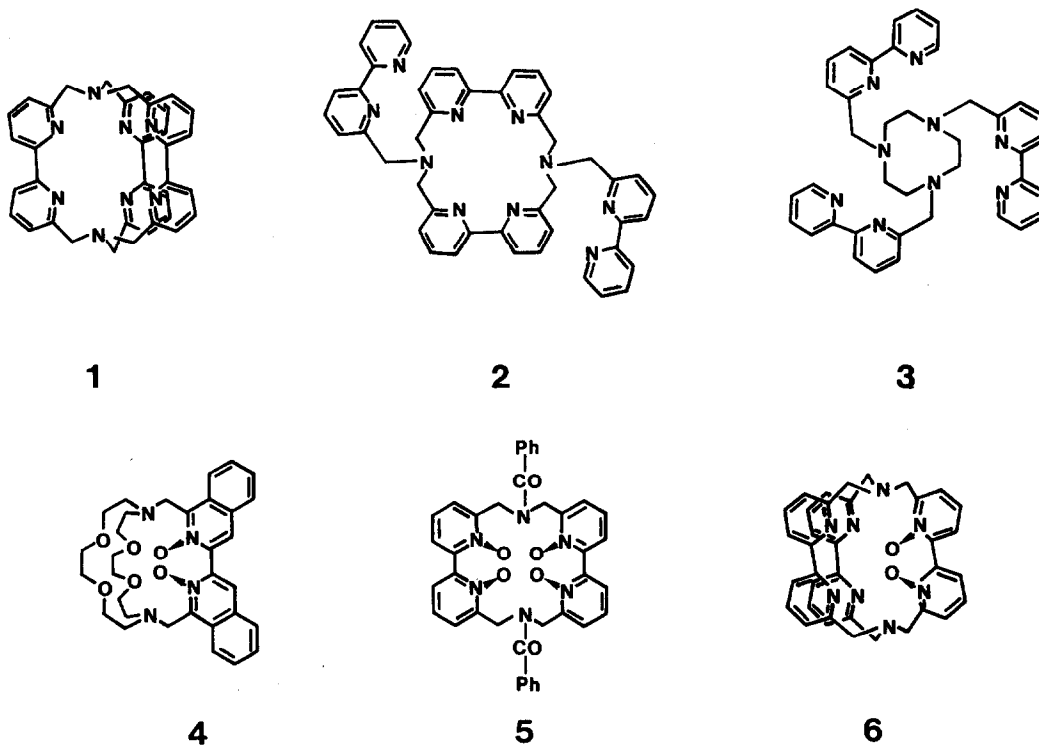


Fig.12. Energy level diagram for $[\text{EuL}1]^{3+}$.⁵³

Considerable effort is currently devoted to further improve the luminescence properties of Eu^{3+} and Tb^{3+} complexes by using other caging ligands.⁵⁵ In doing that, two additional requirements have to be taken into consideration: (a) the presence of the ligand should not imply the occurrence of ligand-centered or charge-transfer levels at lower, or slightly higher, energy than that of the luminescence metal-centered level; otherwise, new channels for fast radiationless decay of the luminescence level would be available and the luminescence efficiency would be compromised; (b) energy transfer from the ligand-centered excited states populated by light absorption to the metal centered levels should be efficient; this implies some degree of interaction (and, therefore, a close contact) between the metal and the coordinated atoms of the ligands.

Excellent luminescent properties are exhibited by the Eu^{3+} complexes of 2,⁵⁶ and by the Tb^{3+} complexes of 2⁵⁶ and 3.⁵⁷ Promising results have also been obtained by using cryptate ligands like 4,⁵⁸ 5,⁵⁹ and 6⁶⁰ which incorporate N-oxide groups.



4-2 Photo-cleavable and photo-flexible cages

For several types of applications, it would be necessary to have cages that can be opened and/or closed by light excitation. Two different approaches to this problem have recently been reported.

It is well known that the 2.1.1, 2.2.1, and 2.2.2 polyoxadiazamacrobicyclic cryptands, prepared long ago by Lehn and coworkers,⁶¹ exhibit a high selectivity towards alkali metal ion complexation due to the different cavity size. Photocleavage of one of the cryptand strand would cause a substantial affinity decrease, with a consequent release of the metal cation into the solution. To obtain this result, Lehn, *et al.*⁶² have recently introduced the photocleavable 2-nitrobenzyl ether bond into one of the bridges of the cryptand (Fig. 13). In principle, these compounds could be used to create light-controlled jumps or pulses of cation concentrations,

that would be quite useful for physiological investigations. Photo-cleavable chelating ligands for alkaline-earth cations have also been described.⁶³

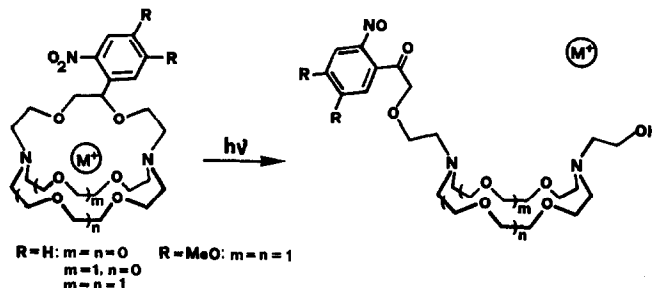
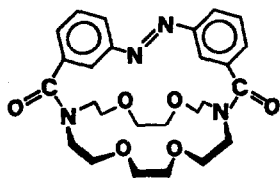
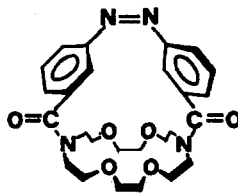


Fig.13. Photocleavable cryptands.⁶²

Control of the cavity size without disruption of the cage can be obtained by taking advantage of the structural changes caused by a reversible photoisomerization reaction. For example, the *trans*-azobenzene capped crown ether **7** binds preferentially small metal cations such as Li^+ and Na^+ . On excitation with UV light, the well known *trans* \rightarrow *cis* photoisomerization of the azobenzene unit takes place, yielding **8**, whose larger cavity preferably binds large metal cations like K^+ and Rb^+ .⁶⁴ When the azobenzene bridge is replaced by the 2,2'-azopyridine bridge, in the *trans* conformation the pyridine nitrogens are directed towards the crown plane and can coordinate metal ions enclosed in the crown ether ring, whereas this is not possible in this *cis* conformation of the bridge. As a consequence, the ability to extract heavy metal ions (Cu^{2+} , Ni^{2+} , Co^{2+} , and Hg^{2+}) from aqueous solution to an organic phase can be photocontrolled.⁶⁵ A photoresponsive cylindrical crown ether containing two isomerizable azo-benzene units has also been described.⁶⁶ In azobenzene-capped cyclodextrin, the bridging ability towards various substrates and the catalytic activity towards the rate of hydrolysis of *p*-nitrophenylacetate can be photocontrolled.⁶⁷



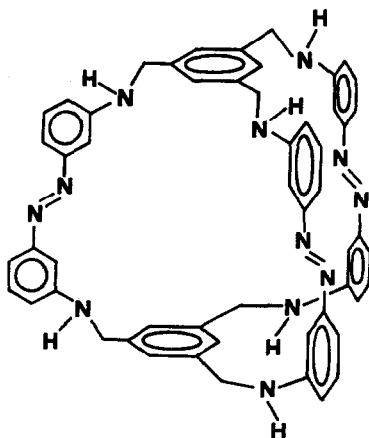
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8

Vögtle and co-workers⁶⁸ have synthesized the very interesting macrocyclic species 9 which contains three azobenzene units. Upon light excitation, each unit can undergo a *trans*→*cis* isomerization with a consequent change in the size of the cage cavity. All possible configurational isomers (E,E,E; E,E,Z; E,Z,Z; Z,Z,Z) have been isolated.

For a review on structural changes in photoflexible systems, see chapter 7 of ref. 1.



9

4.3. Photochemistry of incarcerated molecules

Two main families of spherical-type molecules with internal voids are currently attracting much attention: carcerands⁶⁹ and fullerenes.⁷⁰

In carcerands the internal cavity is large enough to host other molecules, providing them "inner phases" which exhibit peculiar characteristics and which are maintained regardless of the bulk phase. The possibility then arises to perform photochemical reactions within these new phases of matter where the guest molecule is prevented to interact with other species. Many highly reactive species like radicals or unstable isomers can likely be prepared and studied in appropriate inner phases.

The first, very exciting example of this new branch of photochemistry is the "taming" of cyclobutadiene performed by Cram and co-workers.^{69e} They studied the photoisomerization/photofragmentation of α -pyrone within a carcerand-type species and found that of the two photoproducts cyclobutadiene remains imprisoned into the cage while CO_2 escapes. The cyclobutadiene is thermally stable in the inner phase at room temperature, and exists as a singlet. On further irradiation, cyclobutadiene breaks down to acetylene, as it does when is prepared in argon matrix at 8 K. Interesting questions arises as to how the exciting light (200-250 nm) required for the formation of cyclobutadiene and its reaction to give acetylene is effective. Absorption by the dimethoxybenzene-type units and photosensitization is a possibility.

The luminescent properties of a large-cavity compound which contains three Cu^+ ions have been recently studied.⁷¹

5. Host-Guest Systems

Life is based on molecular recognition, transformation, and translocation processes carried out by extremely complicated chemical systems (enzymes, genes, antibodies, etc.). The fundamental discovery of crown ethers by Pedersen⁷² in 1967 opened the way to the study of molecular recognition,

transformation, and translocation processes with simple, synthetically accessible molecular species. In the last 25 years a "concave-oriented" chemistry⁷³ has thus begun to complement the almost exclusively "convex-oriented" chemistry previously developed, and a great variety of concave molecular species (*hosts*) have been prepared for selective complexation of convex molecular species (*guests*). This section illustrates examples of light-induced processes that occur in host-guest systems, defined as supramolecular species made of synthetic components where structure-specific interactions (particularly, complementarity between concave and convex shapes) play a key role in determining the photochemical and photophysical properties. Supramolecular systems based on intermolecular forces but not characterized by structure-specific interactions will not be discussed. Reviews on the photochemical and photophysical properties of ion-pairs,⁷⁴⁻⁷⁷ electron donor-acceptor complexes,^{78,79} chromoionophores and fluoroionophores,⁸⁰⁻⁸⁴ cyclodextrin inclusion compounds,⁸⁴⁻⁸⁷ and adducts of DNA,^{84,88} can be found elsewhere. Cage-type compounds are discussed in Section 4.

The approach taken in the investigations described in this section is the following: (i) molecular species capable to give host-guest adducts are chosen; (ii) the photochemical and photophysical properties of the two separated species are studied; (iii) the photochemical and photophysical properties of the adduct are investigated and then compared to those exhibited by the separated components.

5.1 Polyammonium macrocyclic receptors with $\text{Co}(\text{CN})_6^{3-}$

Because of their high electric charge and their capacity to form hydrogen bonds, cyanide complexes are very suitable species for adduct formation. $\text{Co}(\text{CN})_6^{3-}$ gives rise to very stable 1:1 adducts

with the protonated forms of the polyazamacrocyclic receptors shown in Fig. 14.⁸⁹ The resulting absorption spectrum is essentially the same as that of free $\text{Co}(\text{CN})_6^{3-}$,⁹⁰ as expected for adducts between partners that cannot give rise to low-energy charge-transfer transitions. The relatively high values of the association constants (10^3 - 10^6 M^{-1}) reflect an ionic-type interaction, probably with a large contribution from hydrogen bonds between the peripheral nitrogen atoms of the complex anion and hydrogen atoms of the polyammonium cation.

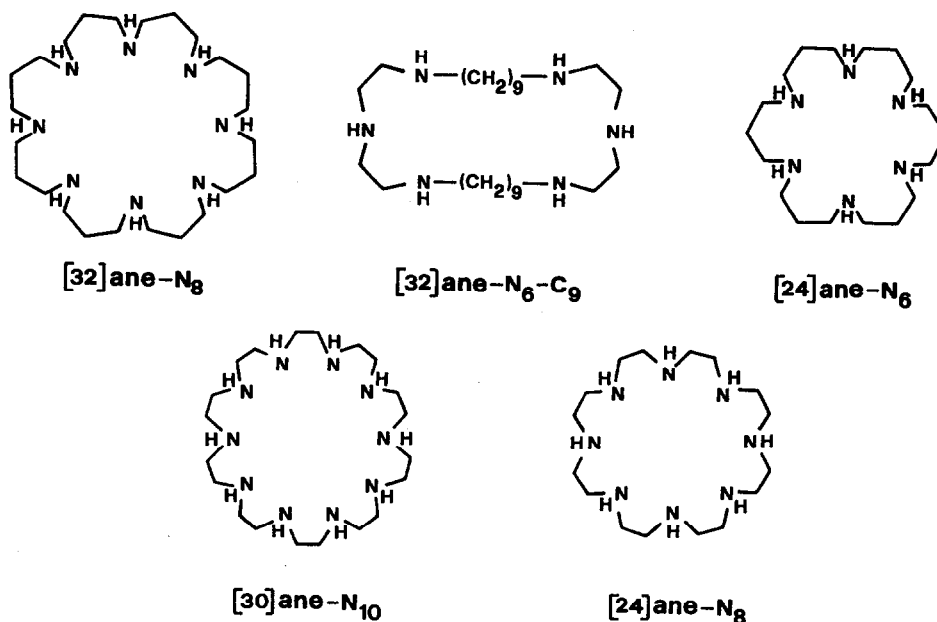
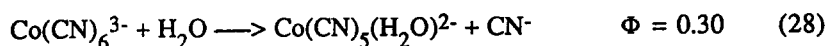


Fig.14. Structures of some polyazamacrocyclics.

$\text{Co}(\text{CN})_6^{3-}$ undergoes a very clean photoaquation reaction (eq. 28) that can be easily followed from spectral changes in the



near UV region, where two isosbestic points are maintained throughout the photoreaction.²³ The quantum yield of the photoreaction is high ($\Phi_0=0.30$) and independent of excitation

wavelength, acidity of the solution (pH 1.2-5.0), and solvent. The primary photochemical process is thought to be a CN⁻ photodissociation. A simple dissociative initial step without significant concerted rearrangement of the five coordinate fragment is predicted theoretically.⁹¹

When aqueous solutions containing the adducts are photoexcited, the same photoaquation reaction exhibited by $\text{Co}(\text{CN})_6^{3-}$ alone, i.e. CN⁻ release, is observed. However, the quantum yield of the photoreaction is noticeably lower than that found for free $\text{Co}(\text{CN})_6^{3-}$ (Table 1).⁹² Since adduct formation does not introduce new energy levels at low energy, it seems fair to assume that the reactive excited state of the adducts is the same as that of free $\text{Co}(\text{CN})_6^{3-}$. One striking observation (Table 1) is that adduct formation reduces the quantum yield Φ to values essentially equal to a multiple of $(1/6)\Phi_0$, which suggests that in the adducts only a discrete number of CN⁻ groups are permitted to undergo photodissociation.

Table 1. Quantum yields for the photoaquation of $\text{Co}(\text{CN})_6^{3-}$ alone (Φ_0) and its adducts with polyazamacrocycles (Φ)^a.

	pH	Φ_0	Φ	Φ_0/Φ
$\text{Co}(\text{CN})_6^{3-}$	1.0	0.33		
	1.2-5.0	0.30		
$([24]\text{ane-N}_6\text{H}_6)^{6+} \cdot \text{Co}(\text{CN})_6^{3-}$	2.5		0.15	2
$([24]\text{ane-N}_8\text{H}_7)^{7+} \cdot \text{Co}(\text{CN})_6^{3-}$	2.5		0.15	2
$([24]\text{ane-N}_8\text{H}_8)^{8+} \cdot \text{Co}(\text{CN})_6^{3-}$	1.0		0.16	2
$([30]\text{ane-N}_{10}\text{H}_{10})^{10+} \cdot \text{Co}(\text{CN})_6^{3-}$	2.3		0.14	2
$([32]\text{ane-N}_6\text{H}_6\text{-C}_9)^{6+} \cdot \text{Co}(\text{CN})_6^{3-}$	1.2		0.11	3
$([32]\text{ane-N}_8\text{H}_8)^{8+} \cdot \text{Co}(\text{CN})_6^{3-}$	2.5		0.10	3

^aAqueous solution, room temperature; from ref. 92.

In agreement with the indications of space-filling models, the results obtained can be rationalized in the following way. In adducts with the large 32-atom ring receptors, the octahedral cobalt complex can be enclosed within the macrocycle so that four CN^- ligands are involved in hydrogen bonding (Fig. 15a), leaving only 2 of the 6 CN^- ligands free to escape. For the smaller macrocycles, encirclement of $\text{Co}(\text{CN})_6^{3-}$ by the ring is not possible, and the most likely structure is that shown in Fig. 15b, with 3 labile CN^- ligands.⁹²

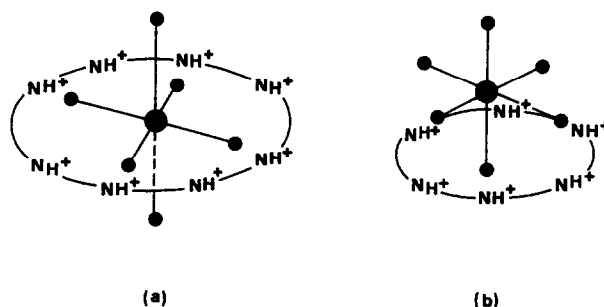


Fig.15. Proposed supramolecular structures of the adducts formed in solution between $\text{Co}(\text{CN})_6^{3-}$ and polyammonium macrocyclic receptors of different size.⁹²

Besides offering a generic protection against photodissociation, adduct formation might also find interesting applications in the case of mixed-ligand complexes by orienting photosubstitution reactions toward specific products. In favorable cases, photochemistry appears also to be a valuable probe for the structure of the adducts.

5-2 Aromatic crown ethers with $\text{Pt}(\text{bpy})(\text{NH}_3)_2^{2+}$

$\text{Pt}(\text{bpy})(\text{NH}_3)_2^{2+}$ is a square-planar complex which exhibits most of the properties needed to give stable adducts, namely electric charge, residual interaction ability on the metal ion, and residual

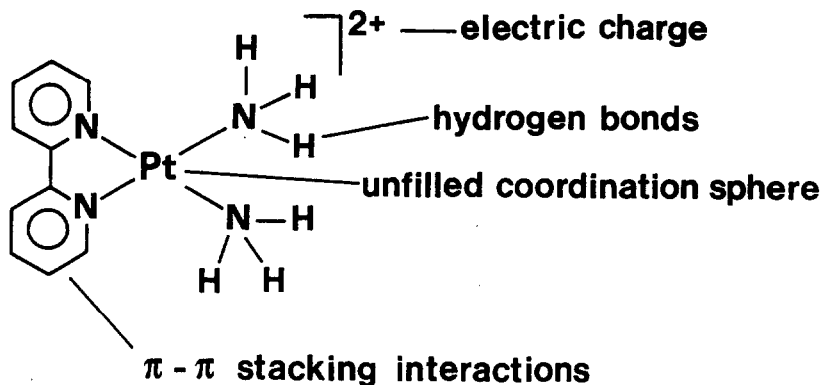


Fig.16. $\text{Pt}(\text{bpy})(\text{NH}_3)_2^{2+}$, an excellent potential guest.⁹³

interaction ability on both bpy and NH_3 ligands (Fig. 16). Furthermore, this complex undergoes a clean photochemical reaction and exhibits luminescence at low and high temperature in a variety of solvents.⁹³ Because of these properties, $\text{Pt}(\text{bpy})(\text{NH}_3)_2^{2+}$ is suitable for the design of adducts of photochemical and photophysical interest.⁹⁴

$[\text{Pt}(\text{bpy})(\text{NH}_3)_2](\text{PF}_6)_2$ is insoluble in CH_2Cl_2 , but it can be dissolved by addition of 18C6 (Fig. 17) to give a 1:1 adduct. The absorption and emission spectra of the adduct in CH_2Cl_2 (Fig. 18) are practically identical to those of free $\text{Pt}(\text{bpy})(\text{NH}_3)_2^{2+}$ in acetonitrile, showing that there is a negligible electronic interaction between $\text{Pt}(\text{bpy})(\text{NH}_3)_2^{2+}$ and 18C6, which are kept together by hydrogen bonds. The intense absorption with maxima at 319 and 307 nm are due to spin-allowed $\pi\pi^*$ transitions on the bpy ligand. The structured luminescence band shows its maximum at 486 nm ($\tau = 25 \mu\text{s}$) at 77 K and at 488 nm ($\tau = 100 \text{ ns}$) at room temperature (Fig. 19). These data indicate that the luminescent excited state is a metal-perturbed triplet ligand-centered level. When aromatic

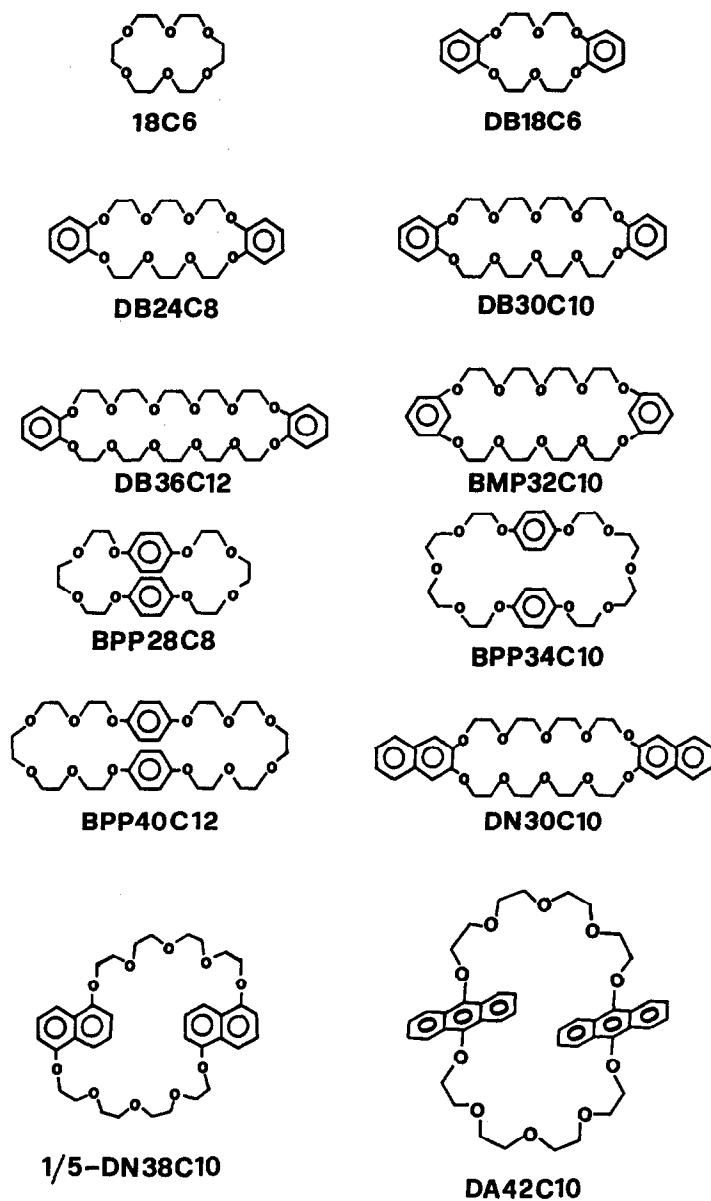


Fig.17. Crown ethers used as hosts for $\text{Pt}(\text{bpy})(\text{NH}_3)_2^{2+}$.

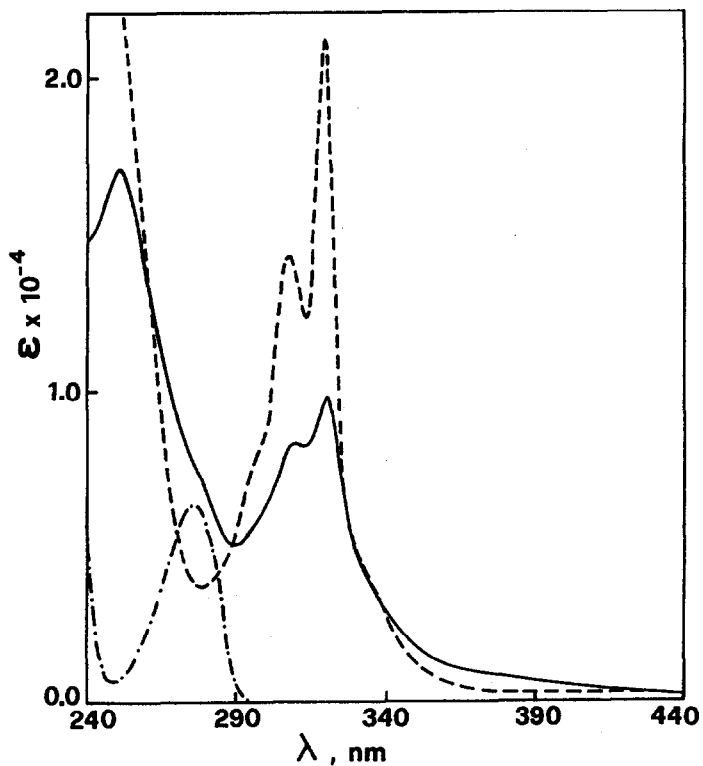


Fig.18. Absorption spectra of DB30C10 (---), and of the adducts of $\text{Pt}(\text{bpy})(\text{NH}_3)_2^{2+}$ with 18C6 (---) and DB30C10 (—).⁹³

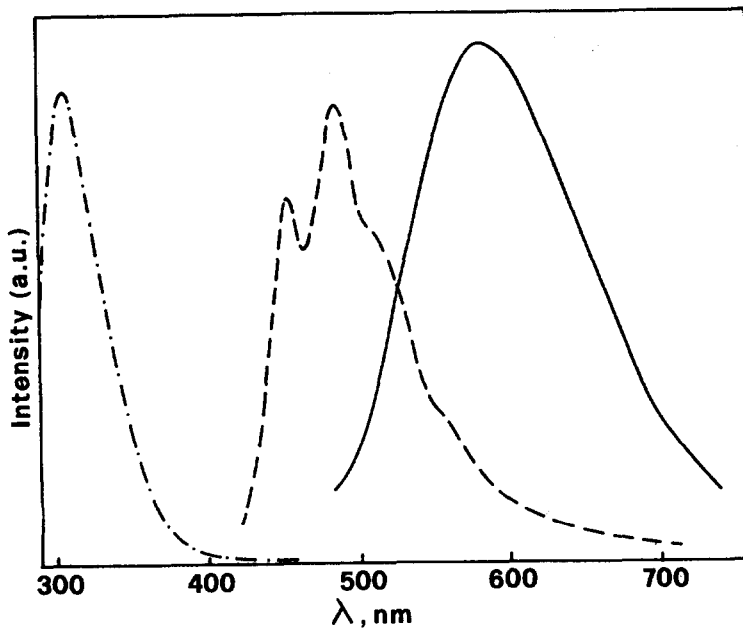


Fig.19. Luminescence spectra of DB30C10 (---), and of the adducts of $\text{Pt}(\text{bpy})(\text{NH}_3)_2^{2+}$ with 18C6 (---) and DB30C10 (—).⁹³

macrocyclic polyethers (Fig. 17) are used in the place of 18C6, 1:1 adducts are again formed. For the adduct with DB30C10, single crystal X-ray diffraction studies showed that the receptor assumes a U-shaped configuration around the metal complex.^{95,96} This suggests that, besides hydrogen bonding, a $\pi\pi^*$ interaction between the aromatic units of the macrocyclic polyether (donor) and the bpy ligand of the metal complex (acceptor) can take place.

The spectroscopic, photophysical, and photochemical behavior of $\text{Pt}(\text{bpy})(\text{NH}_3)_2^{2+}$ adducts with the aromatic crown ethers shown in Fig. 17 have been investigated in detail.^{93,94,97,98} As shown in Figs. 18 and 19 for the case of DB30C10, adducts formation causes strong changes in the absorption spectra and the quenching of the luminescence of the two components. In several cases a new, broad, and short-lived luminescence band appears in the red region of the spectrum (see, e.g., Fig. 19). Furthermore, the $\text{Pt}(\text{bpy})(\text{NH}_3)_2^{2+}$ guest is protected against photoreactivity. Particularly interesting is the case of the adduct with DA42C10 (Fig. 17).⁹⁷ When the free anthracenophane host is photoexcited in CH_2Cl_2 solution, a photocyclization reaction takes place (Fig. 20). In its adduct with $\text{Pt}(\text{bpy})(\text{NH}_3)_2^{2+}$, however, no photoreaction is observed. This

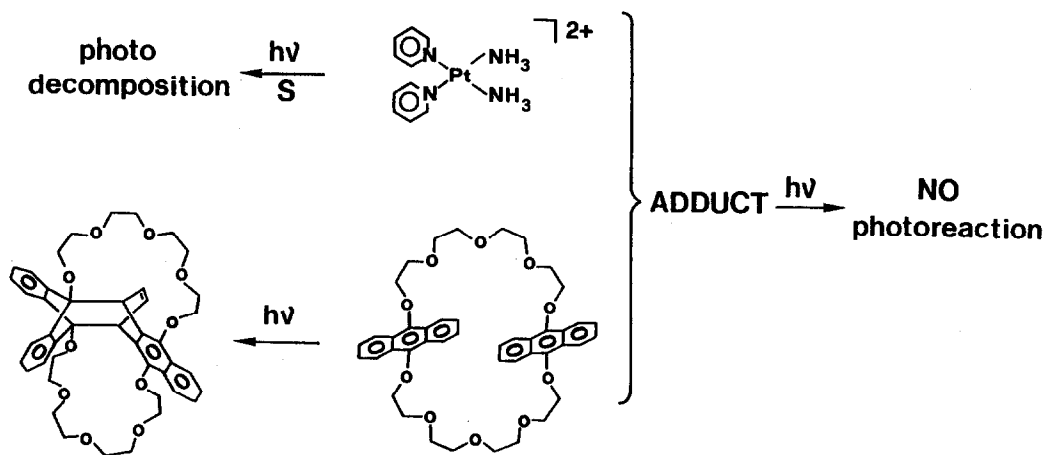


Fig.20. Photochemical behaviour of $\text{Pt}(\text{bpy})(\text{NH}_3)_2^{2+}$, DA42C10, and their adduct.

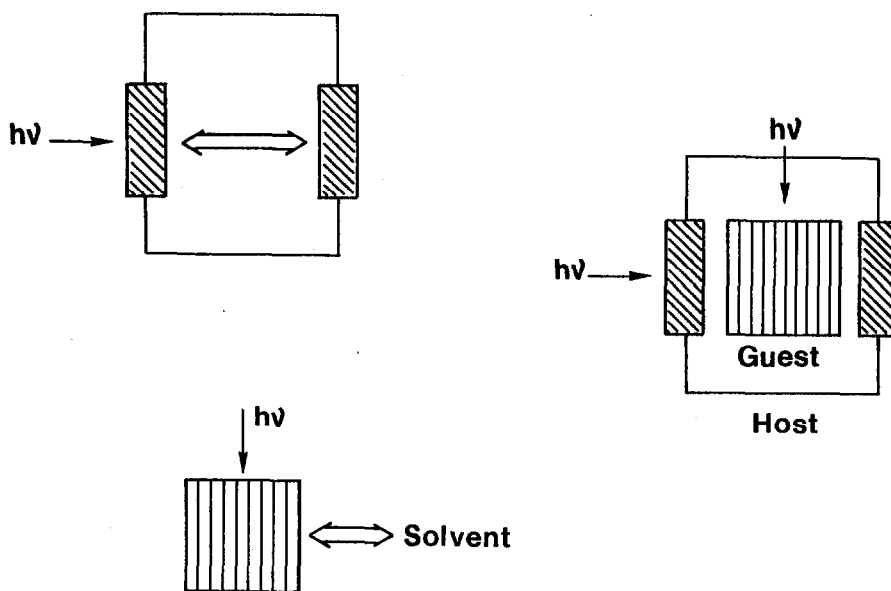


Fig.21. Schematic explanation of the different photochemical behavior of $\text{Pt}(\text{bpy})(\text{NH}_3)_2^{2+}$, DA42C10, and their adduct (see text).

suggests that, as schematized in Fig. 21, the Pt complex is inserted between the two aromatic moieties of the anthracenophane host in a structure which protects the guest from photoreaction with the solvent and prevents the photocyclization of the host. In terms of an energy level diagram, the quenching of the luminescence and/or reactivity of the host and guest on adduct formation can be accounted for by the presence of a charge-transfer state below the luminescent and/or reactive excited states of the two components.

In conclusion, the assembly of two components into an appropriate supramolecular structure can protect the components towards photoreactions and can profoundly change their spectroscopic and photophysical properties.

5.3 Lasalocid A anion with $\text{Cr}(\text{bpy})_3^{3+}$

The absorption, luminescence, and photochemical properties of $\text{Cr}(\text{bpy})_3^{3+}$ (bpy=2,2'-bipyridine, Fig. 22) have been extensively investigated.⁹⁹ This complex is only slightly soluble in CH_2Cl_2 as a perchlorate or hexafluorophosphate salt. Its absorption spectrum is dominated by an intense ligand centered (LC) band ($\lambda_{\text{max}}=307$ nm, $\epsilon=25000$ $\text{M}^{-1}\text{cm}^{-1}$ in CH_2Cl_2 solution). The $\text{Cr}(\text{bpy})_3^{3+}$ luminescence ($\lambda_{\text{max}}=728$ nm, $\tau=70$ μs for the PF_6^- salt)¹⁰⁰ originates from the ${}^2\text{E}$ metal centered (MC) excited state. Detailed studies have shown that the energy of the luminescence band is nearly independent of the nature of the solvent and ionic strength, while the luminescence lifetime is strongly affected by the medium.⁹⁹ No photodecomposition can be observed in CH_2Cl_2 solution.

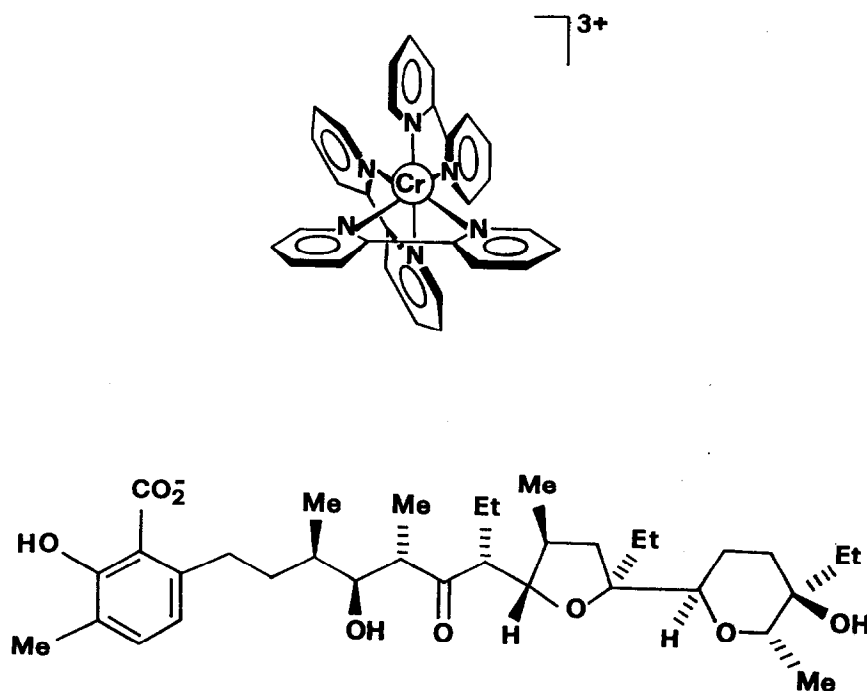


Fig.22. $\text{Cr}(\text{bpy})_3^{3+}$ and the lasalocid A anion LAS^- .

The lasalocid A anion (LAS^- , Fig. 22) exists as a monomer in nonpolar solvents. This molecule contains an aromatic ring which displays a $\pi\pi^*$ absorption band at 307 nm ($\epsilon=4550 \text{ M}^{-1}\text{cm}^{-1}$) and a strong fluorescence band ($\lambda_{\text{max}}=418 \text{ nm}$; $\tau=6 \text{ ns}$) in CH_2Cl_2 solution. The fluorescence intensity is much weaker for the protonated LASH species.

Since $\text{Cr}(\text{bpy})_3^{3+}$ and LAS^- absorb in the same spectral region, in the absence of electronic interaction addition of LAS^- to a $\text{Cr}(\text{bpy})_3^{3+}$ solution should cause an increase in absorbance. By contrast, at the beginning the absorbance decreases and only for $[\text{LAS}^-]/[\text{Cr}(\text{bpy})_3^{3+}]$ ratios higher than one it increases as expected for the contribution of the added LAS^- .¹⁰⁰ This behavior clearly indicates that $\text{Cr}(\text{bpy})_3^{3+}$ and LAS^- give rise to a 1:1 adduct where electronic interaction causes a strong perturbation in the LC band of the metal complex. Confirmation of 1:1 adduct formation comes from luminescence measurements. The fluorescence intensity of LAS^- at 418 nm is strongly quenched until the amount of LAS^- added is close to the amount of $\text{Cr}(\text{bpy})_3^{3+}$ present in the solution. Since the excited state lifetime of LAS^- is very short (6 ns) and the $\text{Cr}(\text{bpy})_3^{3+}$ concentration is very low ($2 \times 10^{-5} \text{ M}$), quenching of the LAS^- luminescence can only take place by a static mechanism. Further addition of LAS^- causes a strong increase in the LAS^- fluorescence intensity up to values close to those expected for LAS^- in the absence of the Cr complex. An association constant of $\sim 10^6 \text{ M}^{-1}$ was obtained from both absorption and emission measurements. The addition of LAS^- also causes a noticeable increase in the intensity of the $\text{Cr}(\text{bpy})_3^{3+}$ luminescence at 728 nm; for $[\text{LAS}^-]/[\text{Cr}(\text{bpy})_3^{3+}]$ values higher than unity, a plateau is reached with an intensity about 6 times higher than that observed in the absence of LAS^- . A parallel increase was also observed in the luminescence lifetime.

Looking at CPK molecular models one can see that the carboxylate group of LAS^- can approach the Cr^{3+} ion in an intraligand pocket of the metal complex (presumably by replacing a PF_6^- anion). This leads the phenyl ring of LAS^- close and parallel to a bpy ligand, with the tail of LAS^- wrapped around the complex. The expected results of this association are (i) an electronic interaction between the phenyl moiety of LAS^- and a bpy ligand, (ii) some screening of the Cr^{3+} ion from interaction with solvent or other anions (e.g., PF_6^-), and (iii) increasing rigidity of the coordination sphere of the metal ion. The electronic interaction can account for the observed variation in the absorption intensity and the static quenching of the LAS^- fluorescence, while the effects described under points (ii) and (iii) can account for the increase in the lifetime (and, as a consequence, in the luminescence intensity) of the ${}^2\text{E}$ metal centered level of $\text{Cr}(\text{bpy})_3^{3+}$.¹⁰⁰

6. Rotaxanes, catenanes, and related species

Rotaxanes (Fig. 23a) are formed by a ring which is threaded by a linear fragment with bulky groups on either end. *Catenanes* (Fig. 23b) are species composed of interlocked rings. Catenanes,

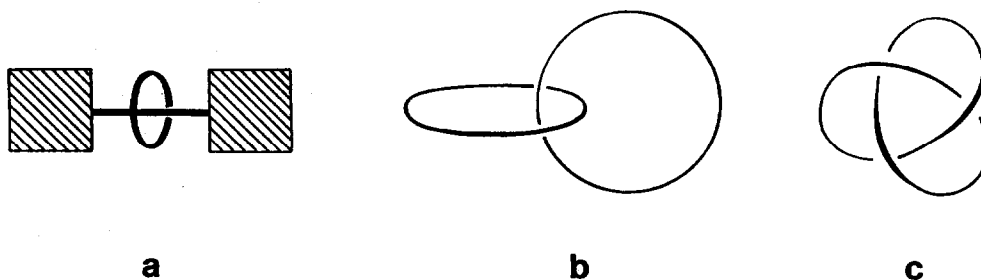


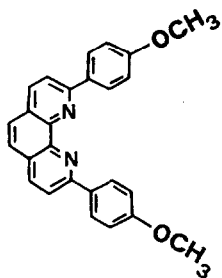
Fig.23. Schematic representation of rotaxanes, catenanes, and knots.

rotaxanes and related species (like *knots*, Fig. 23c) are supramolecular architectures¹⁰¹ very attractive from an aesthetical viewpoint. The design of such sophisticated systems has since long received much attention, but only recent achievements in synthetic and analytical methods have made possible their synthesis with fairly high yields. Nowadays several catenanes, rotaxanes, knots, helicates, etc. have been prepared, but a few photochemical and photophysical investigations have been performed so far on such species.

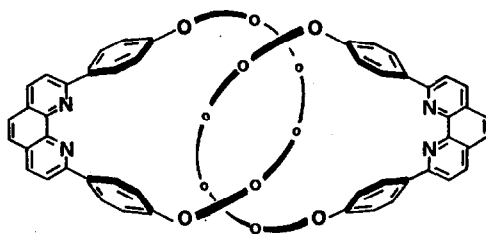
6.1 Catenands and metal catenates

A clever route to obtain interlocked species is the template synthesis around a metal complex. Taking advantage of the tetrahedral-type coordination geometry imposed by the Cu^+ metal ion and its affinity for the 2,9-dianysil-1,10-phenanthroline (*dap*) unit **10**, Sauvage and coworkers¹⁰² have prepared the metal *catenates* $\text{Cu}(2\text{-cat})^+$ **12** and $\text{Cu}_2(3\text{-cat})^{2+}$ **14**. Demetalation of these catenates leads to the corresponding free ligands (*catenands*) **11** and **13**, where the coordinating subunits are disentangled. In the cases of $\text{Cu}_2(3\text{-cat})^{2+}$ **14**, partial demetalation yields the $\text{Cu}(3\text{-cat})^+$ species **16**, which contains a catenate and a catenand moieties. Starting from the free catenands a number of catenates of other metal ions have also been prepared.¹⁰²

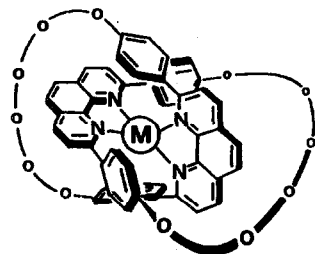
The luminescence properties of several catenands and catenates have been investigated (Table 2).^{103,104} The catenand moieties, as expected, behave essentially as the *dap* chromophoric unit **10**. Upon addition of trifluoroacetic acid to the CH_2Cl_2 solution, however, the properties of the catenands differ from those of *dap*,¹⁰⁵ showing that catenand protonation does not concern independent *dap* units, but involves coordination of two *dap* units around a proton in a catenate-type structure.¹⁰⁴ The $\text{Li}(2\text{-cat})^+$ and $\text{Zn}(2\text{-cat})^{2+}$ species exhibit ligand-centered (LC) fluorescence and



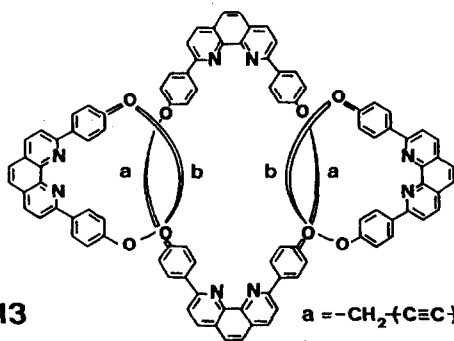
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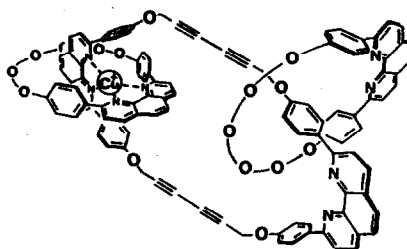
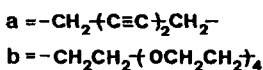
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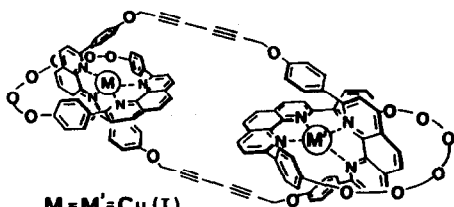
12



13



16

14 $M = M' = \text{Cu(I)}$ 15 $M = \text{Cu(I)}$ $M' = \text{Co(II)}$

phosphorescence, considerably more perturbed in the case of the divalent ion. The Co(2-cat)^{2+} and Ni(2-cat)^{2+} complexes are not luminescent, as expected because of a fast radiationless decay which occurs via low energy metal-centered levels. The Cu(2-cat)^+ and $\text{Cu}_2(\text{3-cat})^{2+}$ complexes exhibit an emission band in the red spectral region, that can be assigned to the lowest-energy triplet metal-to-ligand charge transfer excited state. The Cu(3-cat)^+ species 16, as expected, displays two luminescence bands, which originate from the catenand and catenate moieties, respectively. The luminescence of the catenand moiety, however, is strongly

quenched by the adjacent Cu-catenate unit.¹⁰³ For Ag(2-cat)⁺ no emission can be observed at room temperature, whereas in rigid matrix at 77 K a very intense band is observed at 498 nm ($\tau=0.012$ s) that can be assigned to the lowest ³LC level.¹⁰⁴ The mixed metal CuCo(3-cat)³⁺ species 15 does not exhibit luminescence. This indicates that the Co-containing moiety quenches the luminescence of the Cu-containing one. In conclusion, 11, 13, and their derivatives display a varied and interesting photophysical behavior. In particular, their luminescence can be tuned over the whole visible region (Table 2).

Table 2. Luminescence properties of 2-cat, 3-cat, and their metal complexes.^a

	λ_{\max} (nm) ^b	τ (ns) ^c	Φ ^d
dap	396	2.2	0.29
2-cat	400	2.0	0.42
H(2-cat) ⁺	555	11.0	0.022
Li(2-cat) ⁺	400	2.5	0.35
Cu(2-cat) ⁺	730	175	0.0011
Ag(2-cat) ⁺	e	e	-
Co(2-cat) ²⁺	-	-	-
Ni(2-cat) ²⁺	-	-	-
Zn(2-cat) ²⁺	463	2.0	0.082
3-cat	400	2.4	0.33
Cu(3-cat) ⁺	400;725	2.4;181	0.054;0.0011
Cu ₂ (3-cat) ²⁺	730	177	0.0007
CuCo(3-cat) ³⁺	-	-	-

^aCH₂Cl₂ solution, room temperature; from refs. 103 and 104

^bMaximum of the luminescence band

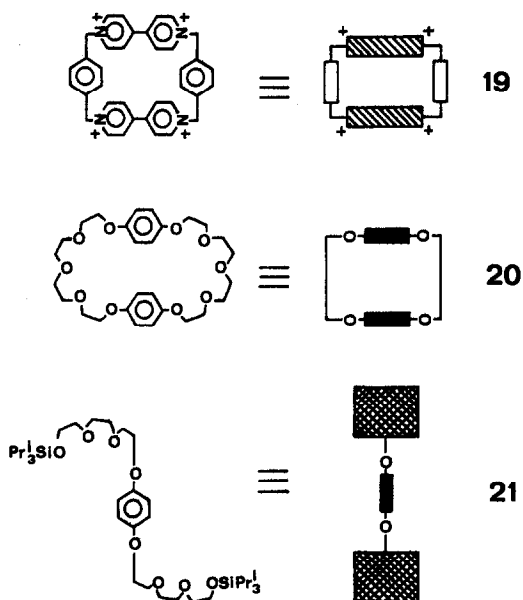
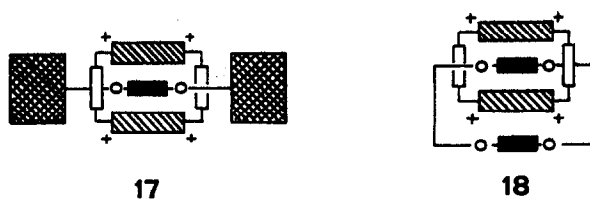
^cLifetime of the luminescent excited state

^dLuminescence quantum yield

^eNo luminescence at room temperature; at 77 K: $\lambda_{\max} = 498$ nm, $\tau = 0.012$ s.

6.2 Rotaxanes and catenanes featuring charge-transfer interaction

Electron donor-acceptor interaction provides the basis for the highly efficient template-directed synthesis of rotaxane **17** and catenane **18** performed by Stoddart and coworkers.¹⁰⁶⁻¹⁰⁸ The groups involved in the electron donor-acceptor interaction are the electron-rich hydroquinol units and the electron-deficient bipyridinium (paraquat, PQ^{2+}) units. In the rotaxane **17** the tetracationic macrocycle **19** is threaded by a hydroquinol unit that is then stopped with bulky Si-derivatives (**21**). In the catenane **18** the tetracationic macrocycle **19** is interlocked with the macrocycle **20** which contains two hydroquinol units.



The electrochemical and spectroscopic properties of **17** and **18** have been investigated.¹⁰⁸ Figs. 24 and 25 compare the results obtained on oxidation and reduction of **17**, **18**, and their components. Oxidation of **17** takes place at a more positive potential compared to the oxidation of 1,4-dimethoxybenzene (*DMB*) as expected because in **17** the hydroquinol unit is involved in electron donation to the paraquat units of the tetracationic macrocycle **19**. For the macrocycle **20** two distinct oxidation waves are observed, which indicates that there is some electronic interaction between the two hydroquinol units. Both such waves are displaced towards more positive potentials in **18**, and their splitting is much larger than in **20**. This is indeed an expected behavior because (i) the interaction with the electron-acceptor paraquat units makes the hydroquinol units more difficult to oxidize, and (ii) the two hydroquinol units are not equivalent. The "alongside" hydroquinol unit, which interacts with only one paraquat unit, is the first to be oxidized, and the "inside" hydroquinol unit, which interacts with two paraquat unit, is oxidized only at a much higher potential.

Similar correlations can be observed in the electrochemical reduction of **17**, **18**, and their components (Fig. 25). The electrochemistry of paraquat is characterized by two consecutive monoelectron reduction processes. For the bis-paraquat cyclophane **19**, the two paraquat units are reduced simultaneously at less negative potential than paraquat since reduction decreases the electrostatic repulsion between the two charged units. Second simultaneous reduction of both units follows at more negative potential. Reduction of the bis-paraquat macrocyclic ring of rotaxane **17** is similar to that of the bis-paraquat cyclophane **19**,

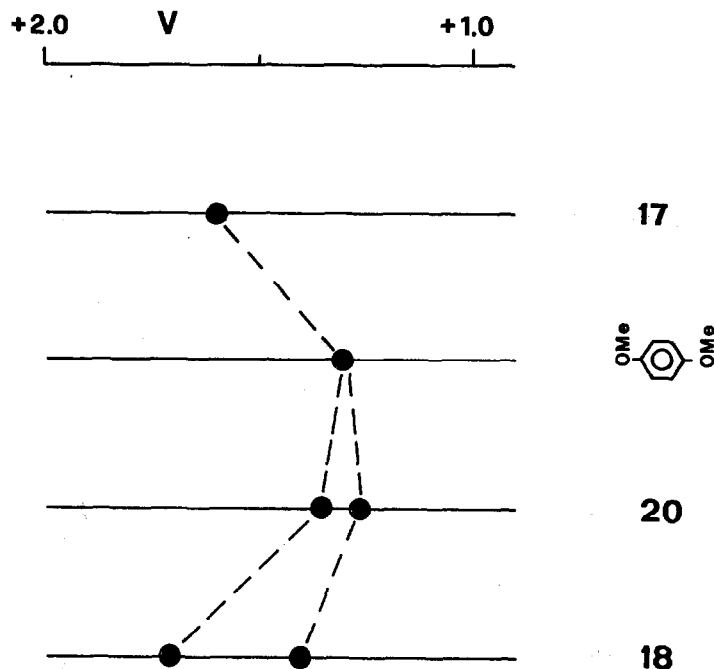


Fig.24. Oxidation of rotaxane 17, catenane 18, and their components.¹⁰⁸

except that the reduction occurs at more negative potentials because of the interaction of the paraquat units with the hydroquinol unit. Interestingly, in a rotaxane model species, which does not have the bulky triisopropylsilyloxy stoppers, the bead unthreads spontaneously after first reduction. In the catenane 18 the "alongside" paraquat unit is less involved in donor-acceptor interaction with the hydroquinol compared to the "inside" paraquat unit. Such a positional difference between the two otherwise identical units creates an electrochemical gradient (Fig. 25). The second reduction, however, occurs at the same potential for both paraquat units indicating that the charge-transfer interaction is very weak after the first reduction of the paraquat units.

Clear evidence for electron donor-acceptor interaction in 17 and 18 is also obtained from absorption and emission spectroscopy.¹⁰⁸ The absorption spectra of 17 and 18 are

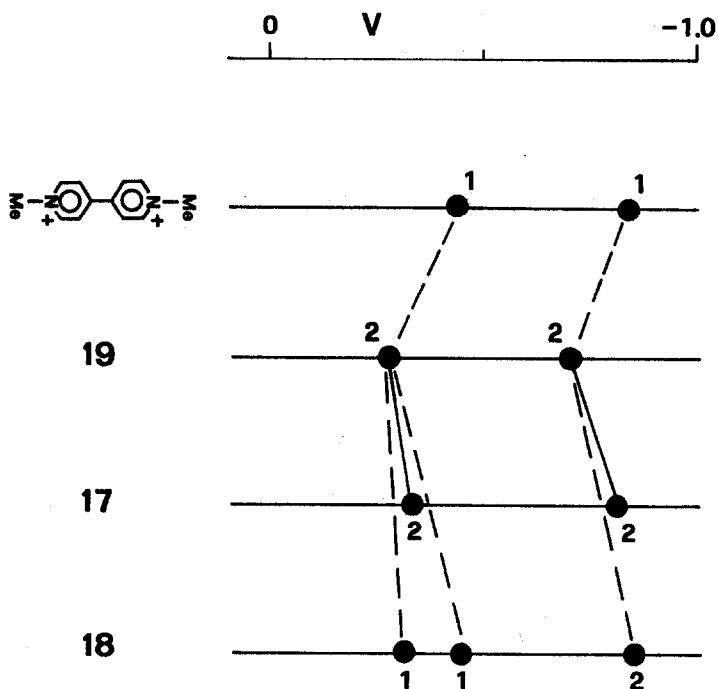
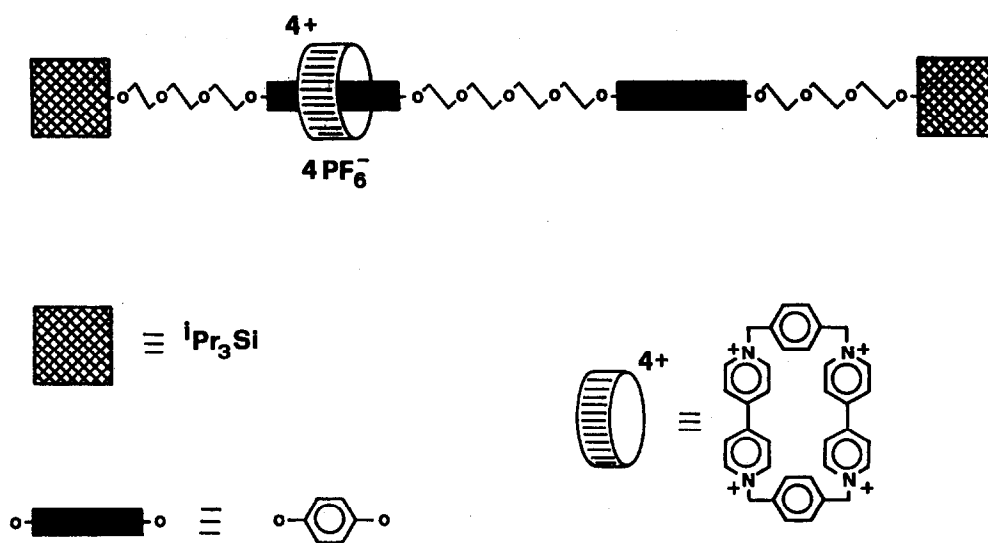


Fig.25. Reduction of rotaxane 17, catenane 18, and their components.¹⁰⁸

noticeably different from the sum of the spectra of the respective components. In particular a broad, weak band is present in the visible region for both 17 and 18 that can be assigned to a charge transfer transition from the π -electron-rich hydroquinol units to the π -electron-deficient paraquat residues. The maxima of these bands coincide ($\lambda=478$ nm), as expected because of the identical nature of the interacting units in the two cases. Furthermore the molar absorption coefficient (at $\lambda=478$ nm) of 18 is practically twice that of 17, suggesting that in 18 both the hydroquinol-type units of 20 interact with a paraquat residue. This conclusion is consistent with the luminescence results which show that the fluorescence of the hydroquinol units is almost completely quenched in both 17 and 18.

Investigations are presently extended to more complex rotaxane and catenane structures. The supramolecular system

Fig.26. A molecular "shuttle".¹⁰⁹

shown in Fig. 26 consists of a polyether chain containing two hydroquinol units and a bis(paraquat) bead.¹⁰⁹ Dynamic NMR experiments have demonstrated that the bead *shuttles* back and forth between the two hydroquinol "stations" of the supramolecular species at a rate which can be controlled by varying the temperature. The two most favorable positions of the bead along the thread are those in which the bead surrounds one of the two hydroquinol groups due to the favorable charge transfer interactions between the π -electron acceptor paraquat residues in the bead and the π -electron donor hydroquinol stations in the thread. The free energy barrier to the shuttling process is 13.2 kcal mol⁻¹, which means that at room temperature the shuttle frequency is much smaller than the rate of decay of the photoexcited hydroquinol units ($\tau = 1$ ns). As a consequence, only 50% of the luminescence of the hydroquinol residues is quenched.¹¹⁰

The shuttle shown in Fig. 26 is a first step towards the construction of molecular machines.^{108,109} If the position of the bead could be controlled by an external signal, such a shuttle might

be used as a molecular memory in a molecular computer. In order to reach such a result, one should first make a shuttle where the bead prefers to stay in one of the two stations. This can be done by using two different electron donors: the bead will preferentially reside on the better electron donor, X. Then, the more stable station (X) should be destabilized in order to displace the bead to station Y. In principle, this can be done by electrochemical or (more difficult) photochemical oxidation of X. Electric or light signals could then be used to play with this molecular abacus.

7. Covalently-linked molecular components

Photosynthesis, the natural process where sunlight is converted into chemical energy (food, firewood, fossil fuels) that maintains life on the earth, is based on photoinduced energy and electron transfer processes. In green plants, light is absorbed by ordered arrays of pigments, and the resulting excitation energy is channeled to specific sites (reaction centers) where a charge separation reaction takes place. The reducing and oxidizing species so obtained give rise to secondary chemical reactions which lead to the final products. An important aim of current chemical research is the design of supramolecular species to be used for building up artificial photosynthetic systems.

As mentioned in Section 2, supramolecular species can also be obtained by linking molecular components via covalent bonds (Fig. 1). In this way it is possible to synthesize linear or bi- and tri-dimensional arrays of molecular components where photoinduced electron and energy transfer processes can take place in a controlled manner.

7.1 Photoinduced electron and energy transfer in two-component model systems.

In the last few years many experimental and theoretical investigations have explored the mechanism of photoinduced electron and energy transfer processes, with particular emphasis on the problem of electronic interaction between two components linked by rigid connectors. A detailed discussion of the theoretical aspects of electron and energy transfer processes can be found in several books and reviews (Section 3).

Photoinduced electron and energy transfer processes in supramolecular species made of two covalently-linked molecular

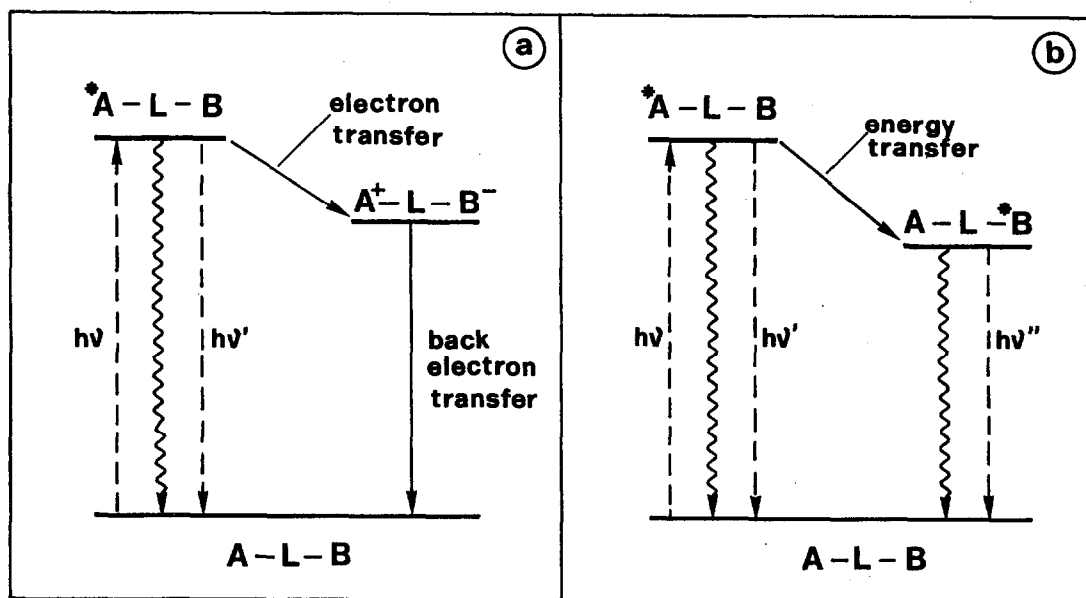


Fig.27. Schematic representation of photoinduced electron (a) and energy (b) transfer processes in a supramolecular system made of two components (A and B) linked by a connector (L).

components can be schematized as in Fig. 27. In general, photoinduced electron transfer is followed by a fast back electron transfer process, and energy transfer is followed by the radiative

and radiationless deactivation of the excited state of the acceptor. From an experimental viewpoint, both electron and energy transfer cause the quenching of the luminescence of the absorbing species (A). Formation of the transient $A^+ \cdot L \cdot B^-$ species can be demonstrated by recording its absorption spectrum in flash spectroscopy experiments. The presence of the $A \cdot L \cdot B^*$ species can be demonstrated by flash spectroscopy as well as by luminescence experiments. Kinetic information (i.e., the lifetime of the $A \cdot L \cdot B^*$, $A^+ \cdot L \cdot B^-$, and $A \cdot L \cdot B^*$ species) can also be obtained by the above mentioned experimental techniques.

In this section we will illustrate only a few examples of photo-induced electron and energy transfer processes in supramolecular systems based on covalently-linked molecular species. A few other examples will be discussed in the next section. For detailed reviews of these processes, see chapters 5 and 6 of ref. 1.

7.1.1 Electron transfer. Verhoeven, Paddon-Row, Hush and coworkers¹¹¹⁻¹¹⁴ have carried out systematic investigations on the photoinduced electron transfer processes that take place in systems like those shown in Fig. 28. The components of these systems are an electron donor dimethoxynaphthalene chromophoric unit (A in the schematic representation of Fig. 27a), an electron acceptor dicyanovinyl group (B), and norbornylogous spacers of various length as connectors (L). The spacers are saturated and rigid, and the attachments are such that no orientational freedom of the A and B components is possible. The systems investigated span a range of centre-to-centre A-B distances of ~ 7 -15 Å and of 4 to 12 interposed C-C bonds. The kinetics of the electron transfer step (Fig. 27a) has been studied in various organic solvents by comparing the fluorescence of the $A \cdot L \cdot B^*$ species with that of a suitable methoxynaphthalene-spacer A-L model. For a linear arrangement of the connector L the rate constants decrease exponentially with

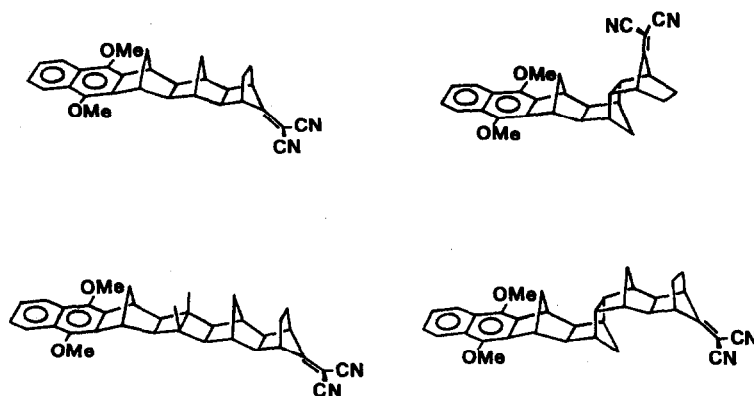


Fig.28. Dimethoxynaphthalene-dicyanovinyl two-component systems with rigid bridges.^{113,114}

increasing length of the connector, being, for example, 3.3×10^{11} , 1.2×10^{10} , and $1.3 \times 10^9 \text{ s}^{-1}$ for 6-, 10-, and 12-bond separation. A detailed analysis of these constants is complicated by the fact that, for a charge separation reaction, two of the parameters that determine the activation free energy, namely the free energy change and the outer sphere reorganizational energy, depend on both solvent and distance. On the same series of compounds the dipole moment of the $A^+ \cdot L \cdot B^-$ charge-separated states have been measured by using time-resolved microwave conductivity.¹¹² The very high values obtained for the dipole moments (26-77 D) are in substantial agreement with the expected values. The decay of the conductivity signal has been used to monitor the disappearance of the charge-separated state and to obtain rate constants for the charge-recombination (back electron transfer, Fig. 27a) reaction. Such charge-recombination rates lie in the Marcus inverted region¹² and therefore are much slower than the activationless charge-separation reactions. Comparison between the rate constants of systems differing in the stereochemistry of the connectors (Fig. 28) shows that electron transfer through bent bridges is slower

with respect to the stretched ones. These results show that electron transfer takes place via a through-bond coupling and are consistent with theoretical predictions that an all-*trans* arrangement of σ bonds is the optimum one for through bond interactions.^{115,116}

In several cases, charge transfer absorption (optical electron transfer, Section 3, Fig. 6) and emission have also been observed.^{117,118} Such processes, that have not been represented in Fig. 27a for the sake of simplicity, are important because the molar absorption coefficient of the charge transfer absorption band and the radiative rate constant of the emission (obtained by quantum yield and lifetimes data) can be used to calculate the donor-acceptor electronic coupling.

7.1.2 Energy transfer. It has been recognized for some time that electron transfer and (exchange) energy transfer have certain features in common.¹¹⁹ This is even more apparent in supramolecular species where both processes may be viewed as radiationless transitions between two electronic states.¹ Recent work on two-component supramolecular species has further developed this concept.

Closs, Miller, and coworkers^{17,120-122} have synthesized a series of A-L-B species where A is benzophenone, B is naphthalene, and L are steroid-type connectors. Following pulsed laser excitation of the benzophenone chromophore, the lowest triplet state of benzophenone is populated and energy transfer to naphthalene, with formation of its lowest triplet, takes place, according to the scheme of Fig. 27b. As usual for triplet-triplet processes, this energy transfer occurs by an exchange mechanism. The rate of the energy transfer processes fall-off is exponential, with a coefficient which is about twice that obtained for electron transfer in analogous systems.^{17,123} Such a relationship can be explained on the basis of the fact that exchange energy transfer can be viewed as a double electron transfer.

Singlet-singlet energy transfer has been studied by Verhoeven and co-workers^{124,125} on A-L-B systems identical to those previously discussed for electron transfer (Fig. 28), except for a carbonyl group replacing the dicyanovinyl fragment. In these systems the fluorescence of the dimethoxynaphthalene component is quenched to a different extent depending on the number of C-C bonds in the bridge. The coefficient of the exponential fall-off is again about twice the value obtained for electron transfer across the same connectors.¹²⁶⁻¹²⁸ As far as the mechanism is concerned, the exponential dependence of the rate constant on distance indicates again an exchange mechanism.¹²⁴

7.2. Multicomponent systems for photoinduced charge separation.

In an A-L-B system, i.e. in a system made of two active components (dyad), the photoinduced charge separation is usually too short-lived to be useful for energy conversion purposes. A strategy to obtain an efficient and long-lived charge separation is to increase the number of molecular components. Several triads^{15,16,18,20,129-131} and a few tetrads^{18,20,129-131} and pentads^{131,132} have thus been synthesized and their photochemical behavior has been investigated. These species mimic the function of the photosynthetic reaction centre and their development is of paramount importance on the way towards the design of artificial photosynthetic systems.

For illustration purposes, we will briefly discuss the triad developed by Wasielewski, *et al.*¹³³ which is made of a porphyrin (electron transfer photosensitizer, Pel) a quinone (electron acceptor, Rel) and an aromatic amine (electron donor, Rel') linked together by rigid connectors. As illustrated in Fig. 29, the photoinduced charge separation process involves the following sequence of events (rate constants for butyronitrile solutions): (1)

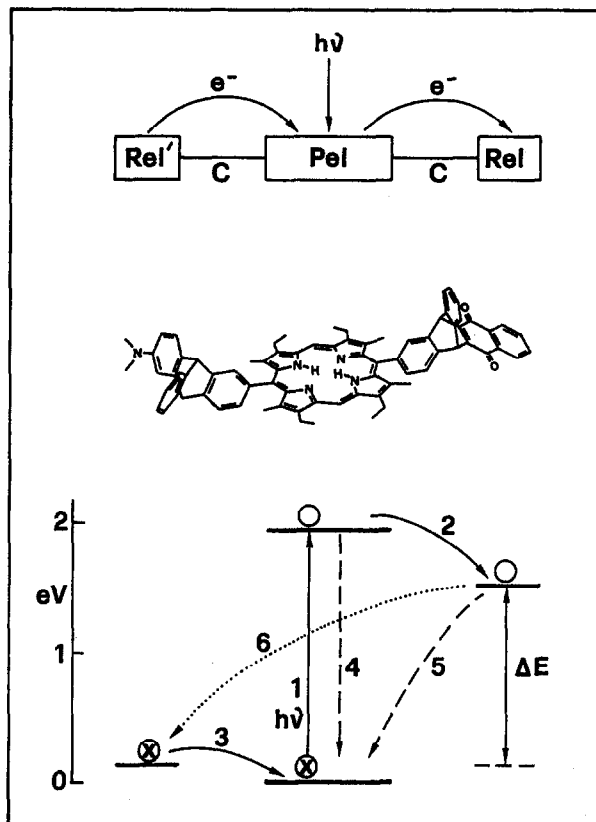


Fig.29. Block diagram, molecular structure, and one-electron energy level diagram for a triad.¹³³ The porphyrin plays the role of photosensitizer (Pel); the quinone and the aromatic amine play the role of electron acceptor and electron donor, respectively.

light absorption; (2) electron transfer from the excited porphyrin to the quinone ($1.1 \times 10^{11} \text{ s}^{-1}$); (3) electron transfer from the amine to the oxidized porphyrin ($1.4 \times 10^{10} \text{ s}^{-1}$). It should be pointed out that the design of a multicomponent system capable of performing an efficient charge separation is not at all simple since several thermodynamic and kinetic requirements have to be satisfied. In the illustrated example (Fig. 29), the electron transfer reaction 2 must prevail over the excited state decay 4, the electron transfer reaction 3 must prevail over the back electron transfer 5, the charge recombination reaction 6 must be as slow as possible, and

the converted energy must be as large as possible. In the triad of Fig. 29, the charge separation reaction occurs with 71% efficiency and stores 1.39 eV for 2.5 μ s (which is the reciprocal of the rate constant of the charge recombination reaction 6). This result can be compared with the performance of the reaction center of photosynthetic bacteria where ~ 0.6 eV are produced with 100% efficiency and stored for ~ 0.1 s.

Ru(II) and Os(II) polypyridine-type complexes are also good candidates to play the role of electron transfer photosensitizers in multicomponent systems.^{10,19} However, with the basic $M(\text{bpy})_3$ (bpy=2,2'-bipyridine) arrangement, the building up of supramolecular structures leads to systems where the components linked to the photosensitizer are relatively close to each other (*cis*-type configuration). The geometry of $M(\text{trpy})_2$ complexes (trpy=2,2':6',2''-terpyridine), on the contrary, offers the possibility to design supramolecular species where the electron donor and electron acceptor components lie on opposite directions with respect to the photosensitizer (*trans*-type configuration, Fig. 30). In

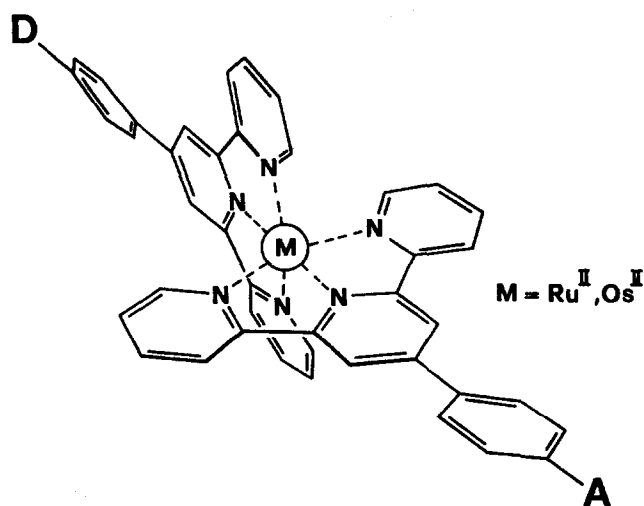


Fig.30. A triad based on the $\text{Ru}(\text{trpy})_2^{2+}$ photosensitizer. A and D are an electron acceptor (MV^{2+}) and an electron donor (di-*p*-anisylamine).¹³⁵

addition, $M(\text{trpy})_2$ complexes bearing substituents at the 4'-position do not lead to isomeric mixtures contrary to their equivalent substituted $M(\text{bpy})_3$ systems.¹³⁴ Detailed investigations on the dyads and triads illustrated in Fig. 30 have been recently performed.^{135,136}

7.3 Polynuclear metal complexes for light harvesting

The possibility of governing the direction of electronic energy transfer in supramolecular arrays may open the way to the design of photochemical molecular devices that can perform a variety of useful functions.¹³⁷ Therefore much activity is presently devoted to the synthesis of multicomponent systems that exhibit extensive light absorption and where the resulting electronic excitation can be channeled towards a specific site (antenna effect). Transition metal complexes appear to be particularly useful building blocks for systems of this type.

In the last few years a synthetic strategy has been developed to obtain polynuclear metal complexes of desired nuclearity and chemical structure. Such a strategy is based on the use of *complexes* in the place of both the metal (M) and the ligands (L) in the synthetic reaction



The place of M can be taken by mono- or oligonuclear complexes that contain easily replaceable ligands, and the place of L can be taken by mono- or oligonuclear complexes that contain free chelating sites ("complexes as metals" and "complexes as ligands" strategy).

7.3.1 Trinuclear metal complexes of tripod-type bipyridine ligands.

Using the tripod-type bipyridine ligands shown in Fig. 31, it is possible to obtain homo- and heteronuclear trimetallic complexes as shown in Fig. 32. In such complexes each metal-based unit exhibits

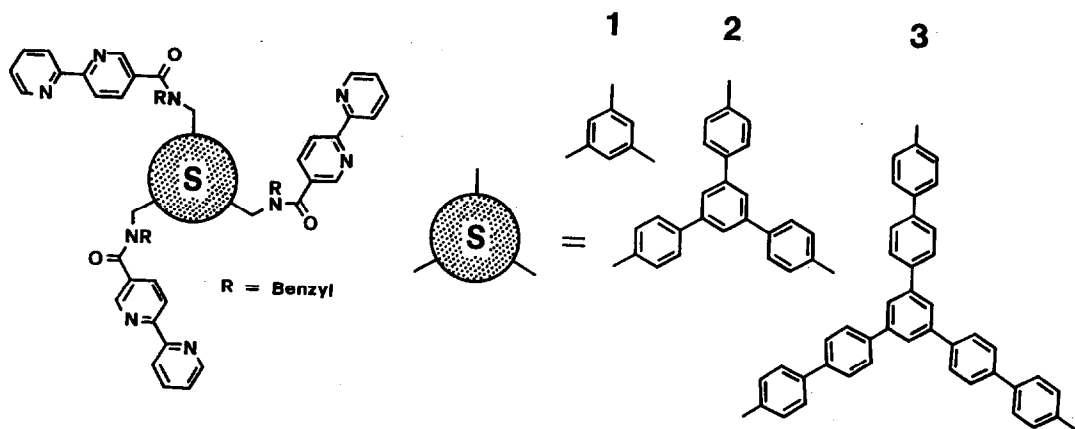


Fig.31. Tripod-type tris-bipyridine ligands.¹³⁸

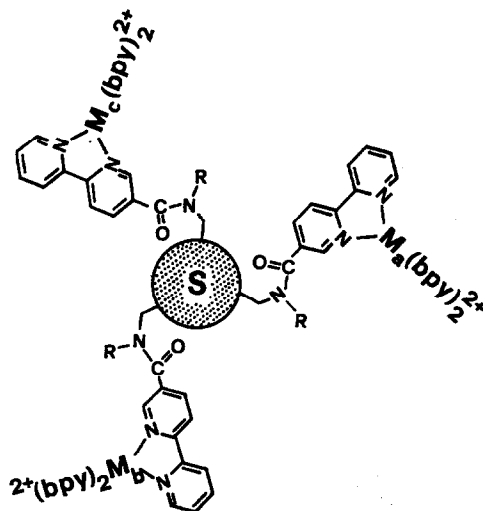


Fig.32. Trimetallic complexes of the tripod-type ligands shown in Fig. 31; M_a , M_b , and M_c may be Ru and/or Os. ¹³⁸

its own absorption spectrum and electrochemical properties, regardless of the number and type of metal-based units that are present in the supramolecular structure.¹³⁸ Luminescence investigations, however, show that in the mixed-metal complexes electronic energy transfer takes place from Ru-based to Os-based components, as expected because of the relative position of their lowest excited energy levels. The efficiency of energy transfer decreases as the size of the spacer which links the three arms of the

tripod ligand increases. Detailed investigations have shown that in the compounds with larger spacers there are conformers where energy transfer does not take place and conformers where energy transfer is very fast.

7.3.2 Polynuclear complexes of the bis(2-pyridyl)pyrazine bridging ligands. The "complexes as metals" and "complexes as ligands" synthetic strategy has revealed particularly successful for the synthesis of polynuclear complexes containing Ru(II) and/or Os(II) as metal ions, 2,3- and/or 2,5-bis(2-pyridyl)pyrazine (abbreviated as 2,3- and 2,5-dpp) bridging ligands (BL), and 2,2'-bipyridine (bpy) and/or 2,2'-biquinoline (biq) as terminal ligands (L) (Fig. 33). Species with nuclearity between 2 and 13, containing different metals, bridging ligands, and terminal ligands have been obtained.¹³⁹⁻¹⁴⁸ The syntheses of the decanuclear and tridecanuclear compounds are illustrated in Figs. 34¹⁴³ and 35.¹⁴⁵ A schematic view of the structural formulas of a decanuclear compound is given in Fig. 36.¹⁴³

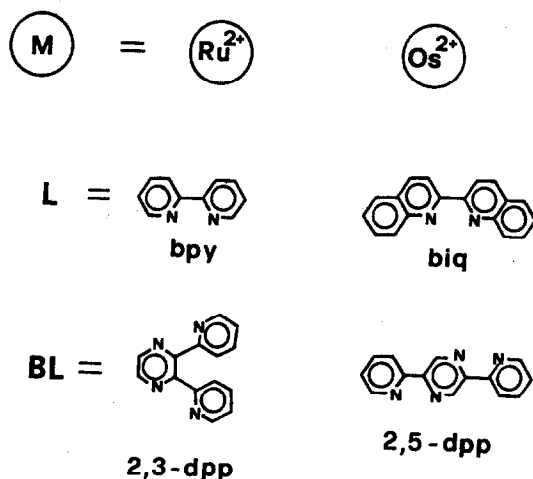
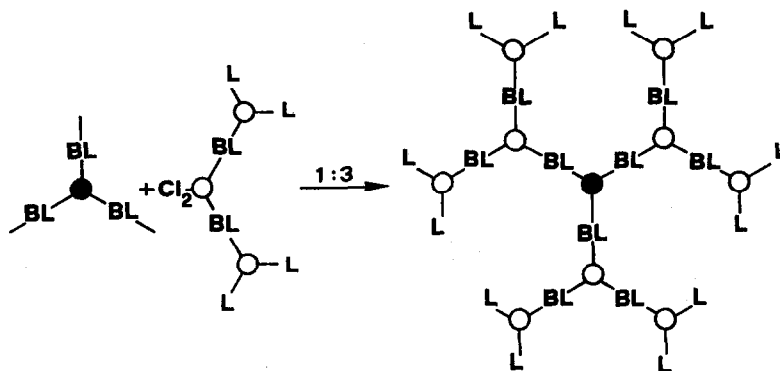
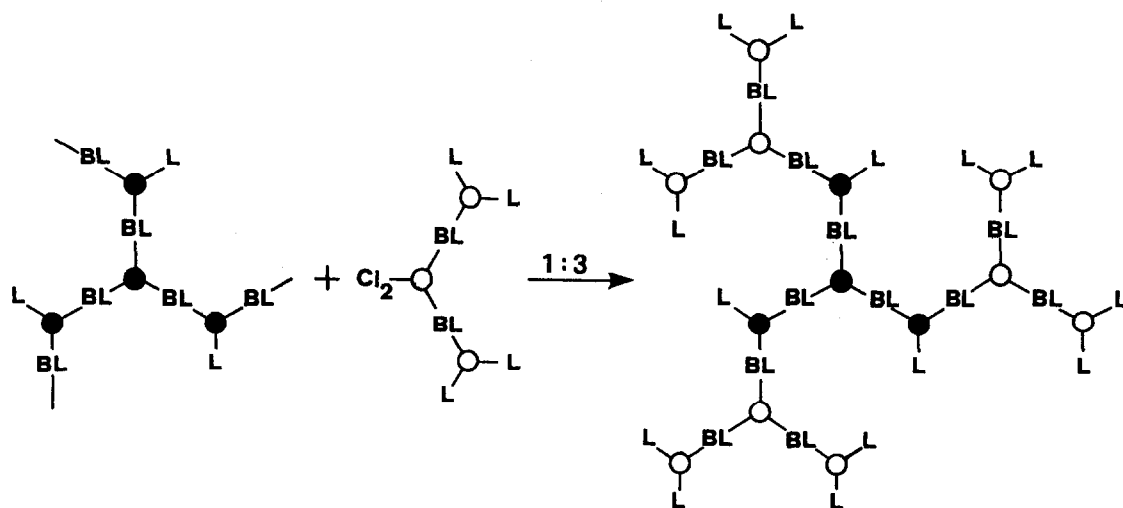


Fig.33. Components of the polynuclear complexes.

Fig.34. Synthesis of a decanuclear compound.¹⁴³Fig.35. Synthesis of a tridecanuclear compound.¹⁴⁵

These polynuclear complexes exhibit several interesting properties including: (i) very intense absorption bands in the uv and visible region ($\epsilon = 133000 \text{ M}^{-1} \text{ cm}^{-1}$ at 544 nm for the tridecanuclear $\text{Ru}\{(\mu\text{-}2,3\text{-dpp})\text{Ru}(\text{bpy})(\mu\text{-}2,3\text{-dpp})\text{Ru}[(\mu\text{-}2,3\text{-dpp})\text{Ru}(\text{bpy})_2]_2\}_3(\text{PF}_6)_{26}$ compound); (ii) luminescence both in rigid matrix at 77 K and in fluid solution at room temperature; (iii) a very rich electrochemical behaviour (each metal center can be oxidized and each ligand can be reduced). As far as energy collection is concerned, the interest of these compounds lies on the fact that the

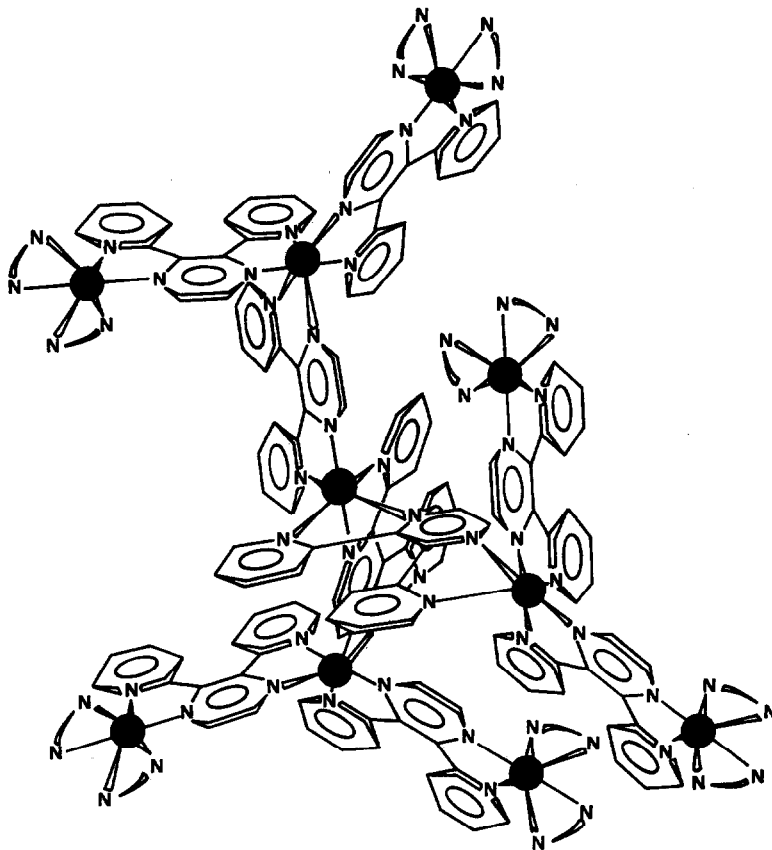


Fig.36. Schematic view of a decanuclear compound.¹⁴³

site containing the lowest energy excited state can be synthetically controlled. Each building block, in fact, is characterized by its own energy levels (determined mainly by the nature of the metal and of the ligands, and slightly by the surrounding units), and the position of the various metal-based units in the supramolecular array can be predetermined by a suitable choice of the building blocks used in the synthetic reaction. Exoergonic energy transfer between metal-based units which share the same bridging ligand takes place with 100% efficiency.

In the case of the tetranuclear compounds, for example, it has been possible to design species where the direction of energy transfer can be predetermined according to the four patterns shown in Fig. 37.^{140c} In the case of the decanuclear compounds, six

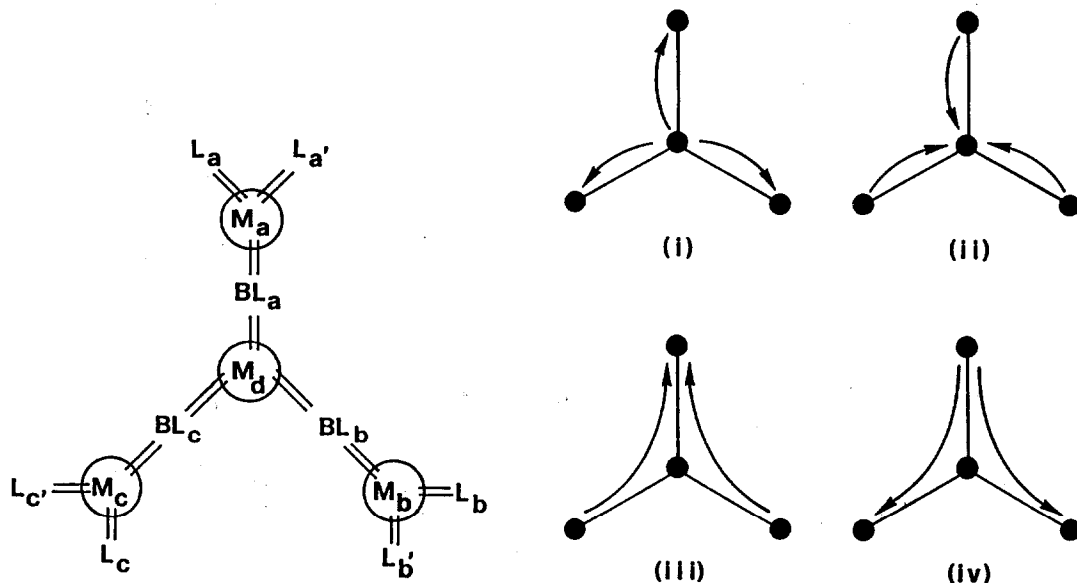


Fig.37. Made-to-order control of the direction of electronic energy transfer in tetranuclear compounds:

- (i) $M=Ru^{2+}$; $BL=2,3\text{-dpp}$; $L=bpy$.
- (ii) $M_a=M_b=M_c=Ru^{2+}$; $M_d=Os^{2+}$; $BL=2,3\text{-dpp}$; $L=bpy$.
- (iii) $M=Ru^{2+}$; $BL_a=2,5\text{-dpp}$; $BL_b=BL_c=2,3\text{-dpp}$; $L=bpy$.
- (iv) $M=Ru^{2+}$; $BL=2,3\text{-dpp}$; $L_a=L_a'=biq$; $L_b=L_b'=L_c=L_c'=bpy$.

different complexes have been synthesized which exhibit the energy migration patterns shown in Fig. 38.¹⁴³

Because of the presence of an ordered array of chromophoric groups, redox centres, and potentially luminescent centres, these polynuclear complexes are of outstanding interest not only from the point of view of energy transfer and its applications, but also for investigations in the fields of photo-, chemi-, and electrochemiluminescence, electrochemistry, spectroelectrochemistry, intervalence transfer, photosensitization, and multielectron transfer catalysis.

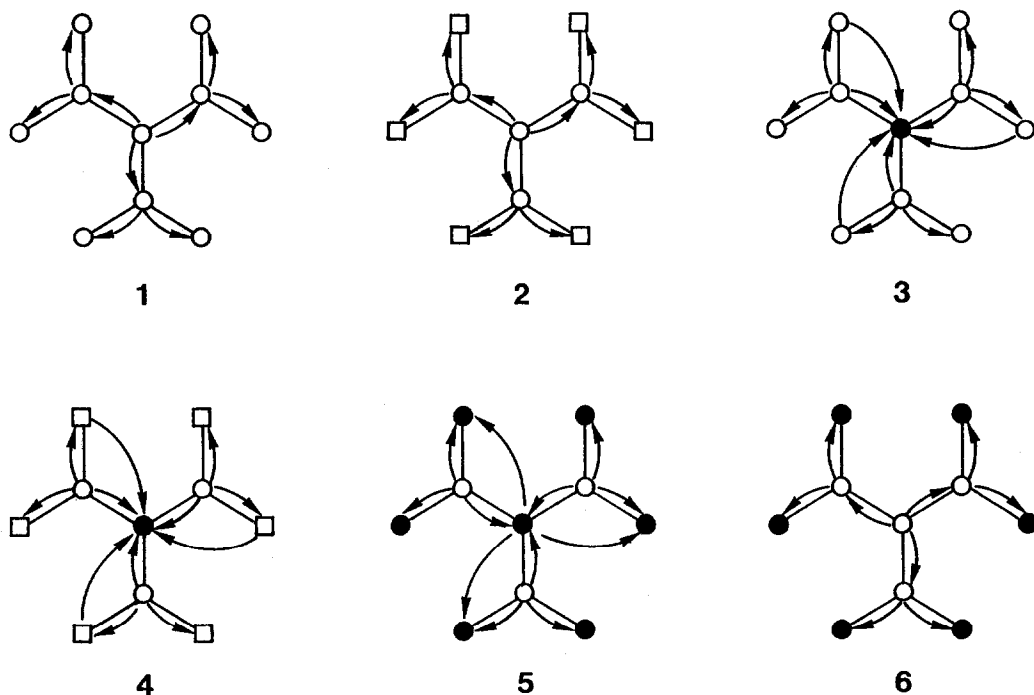


Fig.38. Schematic representation of the energy transfer processes in the decanuclear compounds. The arrows indicate the exoergonic energy transfer steps. Empty and full circles indicate Ru^{2+} and Os^{2+} , respectively. In the peripheral positions, circles and squares indicate $\text{M}(\text{bpy})_2$ and $\text{M}(\text{biq})_2$ components, respectively. The bridging ligands are 2,3-dpp in all cases.^{143b}

8. Conclusion

A photon is at the same time a quantum of energy and a bit of information. The interaction of light with "matter" can therefore be used for energy or information purposes. The results that can be obtained depend on the degree of organization of the receiving "matter".

The simplest form of organization is that of a small number of atoms in a molecule. The interaction of photons with molecules can cause *simple acts*, such as a change in the molecular structure

(isomerization), which can be exploited, in principle, for both energy and information purposes. For example, solar energy can be converted in (and stored as) chemical energy by transforming norbornadiene in its higher energy quadricyclene isomer,¹⁴⁹ and laser beams can write (and also erase) bits of information on spiropyran photochromic molecules.¹⁵⁰

A higher level of organization is the assembly of a discrete number of molecular components to yield supramolecular species. Supramolecular organization can be attained by intermolecular forces of various types (coulombic interactions, hydrogen bonds, etc.) or by linking together molecular components by covalent bonds. By these routes it is possible to put together prefabricated molecular components that carry the desired light-related properties: absorption spectrum, excited state lifetime, luminescence spectrum, excited state redox properties, etc. That is, it is possible to design structurally organized and functionally integrated systems² (photochemical molecular devices)^{137a} capable of elaborating the energy and information input of photons to perform *complex functions* (light harvesting,^{140,143} conversion of light into electrical energy,¹⁵¹ collection of information in a molecular shift register,¹⁵² etc.).

Interrogation of a supramolecular species by photon can yield important, and sometimes unique, pieces of information on its geometrical structure and on the degree of reciprocal perturbation of the various components. This, in turn, may help to extend and refine current theories of chemical reactivity and spectroscopy with a positive feedback on the design of more valuable supramolecular systems.

Research in the area of supramolecular photochemistry has been made possible by the high degree of knowledge reached in the field of molecular photochemistry and supramolecular chemistry. We are, however, at a very early stage of development of

supramolecular photochemistry. In fact, the supramolecular structures that have been the object of photochemical investigations are very few compared with those already available (this is particularly true for host-guest systems). It should also be pointed out that high quality chemical syntheses and high quality photochemical investigations can hardly be carried out by the same research group. Therefore, strict collaboration of synthetic chemists and photochemists is required for the development of supramolecular photochemistry.

As soon as the research activity in the field of supramolecular photochemistry is sufficiently consolidated, it will be possible to explore the photochemical behavior of macroscopic assemblies of supramolecular species in a way less occasional and less empirical than that used so far. This will help in elucidating the light-induced processes which occur in nature and will also facilitate interfacing photochemical molecular devices with the macroscopic world.

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