

## Photochemistry of supramolecular species

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**Abstract** - As molecules are made up by atoms, supermolecules are made up by suitably arranged molecular components. Investigations on the great variety of supermolecules that are now available because of the progress made by synthetic methods offer the dual opportunity to broaden our knowledge of the fundamental principles of photochemistry and to discover new functions and applications of photoinduced processes. Photochemical studies on some selected supramolecular species, including covalently linked components, ion pairs, host-guest systems, and cage-type complexes, are briefly reviewed.

### INTRODUCTION

Photochemistry is a modern branch of science, at the interface between light and matter and at the crossroads of chemistry, physics, and biology. The state of the art in this field can be briefly summarized as follows. On one hand, 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. On the other hand, the natural photochemical processes which occur in living organisms are revealing more and more their intrinsic complexities and are not yet completely understood. It seems now important to realize that in between molecular photochemistry and photobiology there is an immense and yet scarcely explored territory: that of supramolecular photochemistry (refs. 1,2), where the knowledge accumulated from molecular photochemistry can be profitably used to elucidate the photochemical behavior of systems more complex than single molecules. Research in this field will be most useful for a better understanding of photobiological processes and also appears to be a necessary step towards the design of artificial systems capable of performing useful light-induced functions.

### SUPERMOLECULES

Any general definition of *supermolecule* is necessarily arbitrary and the word may have different meanings depending on the area to which it is applied (refs. 1-5). Conceptually, the feature that distinguishes a "supermolecule" from a "large molecule" is the possibility to split the supermolecule into individual molecular subunits, *components*, that are capable, as such or with minor modifications, of separate existence. The subunits are characterized by a set of intrinsic properties which can in principle be derived from the study of the isolated components or of suitable model compounds. Many intrinsic properties of each component are expected to be maintained in the supramolecular structure, with relatively minor changes that can be ascribed to mutual perturbations. However, the properties of a supermolecule will not generally be a simple superposition of those of the component units. In fact, it is possible that

processes involving two or more components take place in a supermolecule, such as (i) intercomponent transfer processes (e.g., electron or energy transfer) or (ii) cooperative effects (e.g., complexation of other species by two or more components).

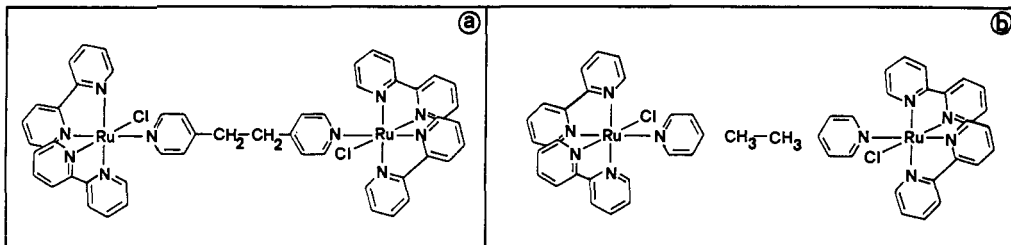


Fig. 1 A "supermolecule" (a) and its molecular components (b)

The above definition of supermolecule is clear-cut when the components are individual molecules held together by intermolecular forces (e.g., the host-guest systems discussed later on). Such a definition can also be extended to systems containing covalently linked components which satisfy specific conditions. For example, for the system depicted in Fig. 1a (ref. 6), the classification as supermolecule is straightforward, since molecular subunits with well-defined intrinsic properties can be easily identified (Fig. 1b). At the other extreme, the system shown in Fig. 2 (ref. 7) is clearly a large molecule that upon fragmentation would completely lose its chemical identity. There are systems, however, for which a clear-cut decision is difficult. For example, in the case of the so-called Creutz-Taube ion (ref. 8) (Fig. 3) individual molecular fragments or models thereof could still be identified, but their properties as free molecules would be remarkably different from those found in the whole system. Formally, such system could still be viewed as a supermolecule in which, however, the mutual perturbation of the fragments is so strong as to make this approach relatively useless.

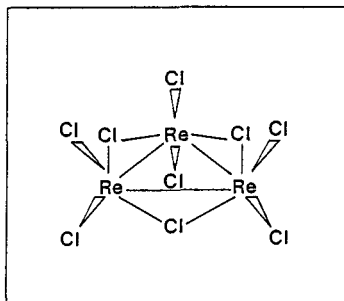


Fig. 2 A "large molecule"

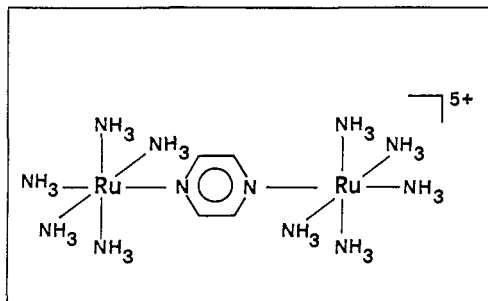


Fig. 3 A borderline case

From the above examples, it is clear that the heart of the "supermolecule" vs. "large molecule" problem lies in the degree of interaction between the electronic subsystems of the component units. Provided that this interaction is small with respect to other relevant energy parameters, any multicomponent system approaches the ideal concept of a supermolecule.

Looking at the current chemical literature, one is impressed by the great number of species that can be defined as supermolecules: host-guest species, electron donor-acceptor complexes, ion pairs, adducts, inclusion compounds, supercomplexes, polynuclear metal complexes, covalently linked molecular components (diads, triads, tetrads, pentads), cage-type compounds, second-sphere coordination compounds,

helicates, catenanes, rotaxanes, and a variety of other systems made up by molecular components in the same way as molecules are made up by atoms (ref. 9). It is also easy to forecast that the field of supramolecular chemistry will grow very rapidly in the future because of the extraordinary progress made by synthetic methods. It follows that there is already (and there will be even more in the future) the possibility to perform photochemical and photophysical investigations on a great variety of quite interesting systems, with ample opportunity to broaden our knowledge of the fundamental aspects of the interaction between light and matter, and to discover new functions and applications of photoinduced processes.

In the following sections we will briefly review examples of photochemical processes in supramolecular species, focussing on systems made by a small number of discrete molecular components held together by covalent bonds or intermolecular forces.

### COVALENTLY LINKED SYSTEMS: ELECTRONIC ENERGY TRANSFER

Light absorption by a component of a supermolecule generates "localized" electronic energy. For several purposes an important function is represented by the possibility to transmit this electronic energy to another component of the supermolecule over a more or less long distance, where the energy will be used for chemical reactions or reconverted into light (luminescence). This function only obtains upon elaboration of the light energy input in the dimensions of energy, space, and time in a appropriate sequence of molecular components. A supramolecular structure capable of performing light induced functions can be called photochemical molecular device, PMD (ref. 10).

In PMDs performing this function, the interface towards light must be an energy transfer photosensitizer (Pen), i.e. a molecular species capable of absorbing light and donating electronic energy. The requirements needed for a good Pen have been discussed elsewhere (ref. 10,11). For remote transfer of the light energy input, the device must contain energy relay components (Ren), i.e. species capable of accepting and donating electronic energy, and it must be assembled so as to have an energy cascade along a chain of components. Some interesting applications of PMDs based on energy transfer (Fig. 4) concern (a) spectral sensitization, (b) antenna effect, (c) remote photosensitization (long-range energy transfer), and (d) light energy up-conversion. We will briefly illustrate the case of the antenna effect. This effect consists in an enhanced light-sensitivity obtained by an increase in the overall cross-section for light absorption. To reach this result, energy should be conveyed from several Pens to a common component that represents the interface toward use. In the scheme shown in Fig. 4b such a component is a luminophore (L), but components playing other roles (e.g., Pels, vide infra, as in the natural photosynthetic process) could also be used. Many PMDs performing the antenna effect based on coordination compounds have been reported (ref.12). An illustrative case is given by the tetrametallic  $\text{Os}[(\mu\text{-}2,3\text{-dpp})\text{Ru}(\text{bpy})_2]_3^{8+}$  polychromophoric system (Fig. 5), where the photon energy collected by the peripheral Ru-containing chromophores is conveyed to the central Os-containing luminescent core (ref.13). Fig. 5 also reports a schematic energy level diagram for this system. For the sake of simplicity, only one singlet and triplet CT level is shown for each metal-containing unit. Although a coulombic singlet-singlet energy transfer cannot be excluded, an exchange triplet-triplet mechanism is more likely because intersystem crossing is known to be very fast in these systems. The energy transfer process is 100% efficient and fast enough to prevent the radiative and radiationless decay of the lowest  $^3\text{CT}$  excited state within each Ren unit. Interestingly, when the central  $\text{Os}^{2+}$  ion is replaced by  $\text{Ru}^{2+}$ , the

energy levels of the central unit become higher than the corresponding levels of the peripheral units, so that energy transfer takes place in the reverse direction (i.e., from the center to the periphery) (refs. 13,14). Complexes of higher nuclearicity are also conceivable. A heptanuclear Ru(II) complex of the 2,3-dpp bridge ligand has recently been synthesized (ref. 15).

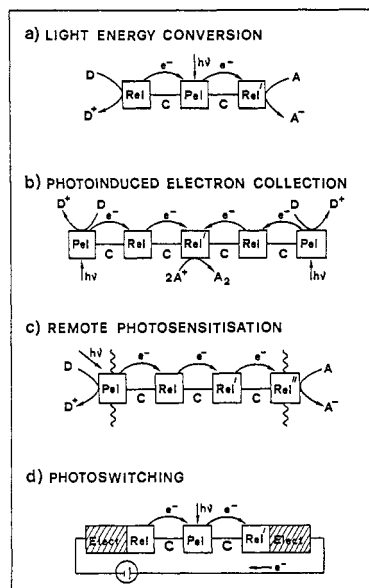


Fig. 4 Block diagrams of PMDs based on energy transfer

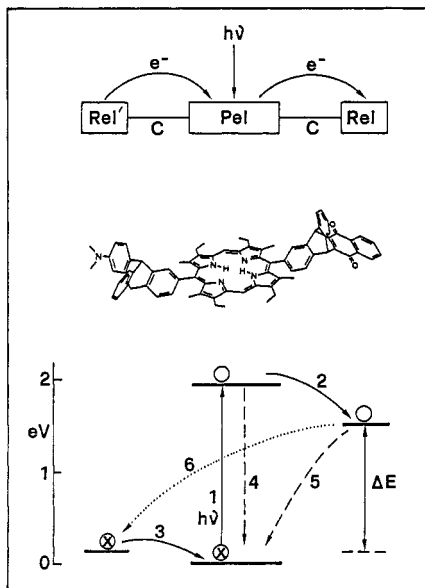


Fig. 5 Antenna effect in a tetranuclear Osmium-Ruthenium complex (ref. 13)

The  $\text{Os}[\mu\text{-}2,3\text{-dppRu}(\text{bpy})_2]_3^{8+}$  device mimics some of the features of natural photosynthetic antennae, with the hetero-metal (Os) playing the role of the special pair as an energy trap.

### COVALENTLY LINKED SYSTEMS: PHOTOINDUCED ELECTRON TRANSFER

The electronically excited states of a molecule are usually good oxidants and/or reductants. One can take advantage of this property to photoinduce charge separation or vectorial transport of electric charge. This occurs when a light-absorbing electron transfer photosensitizer (PeI) transfers an electron to a relay (Rel) or to a chain of relays. Some interesting applications of PMDs based on photoinduced electron transfer (Fig. 6) concern (a) light energy conversion, (b) photoinduced electron collection, (c) remote photosensitization, and (d) photoswitching. We will briefly illustrate the case of light energy conversion.

Particularly enlightening examples are the so-called molecular triads designed to obtain photoinduced charge separation in a way that mimics the process occurring in natural photosynthesis (ref. 16). Such PMDs are of the type shown in Fig 6a. A classic example is that studied by Wasielewski *et al.* (ref. 17), shown in Fig. 7. In such a triad the electron transfer photosensitizer is a porphyrin and the two other components are aniline (electron donor) and a quinone (electron acceptor). Light excitation of the photosensitizer is followed by a very fast (less than 10 ps) electron transfer to the quinone. The back electron transfer process from the reduced quinone to the oxidized porphyrin is slower ( $k = 5.6 \times 10^9 \text{ s}^{-1}$ ) than electron transfer from aniline to the oxidized porphyrin ( $k = 1.4 \times 10^{10} \text{ s}^{-1}$ ), so that one obtains a

charge-separated state over a center-to-center aniline-quinone distance of 25 Å. The back electron transfer over such a large separation is relatively slow (microsecond time scale). More complex (tetrads) devices for photoinduced charge separation have also been investigated (ref.18).

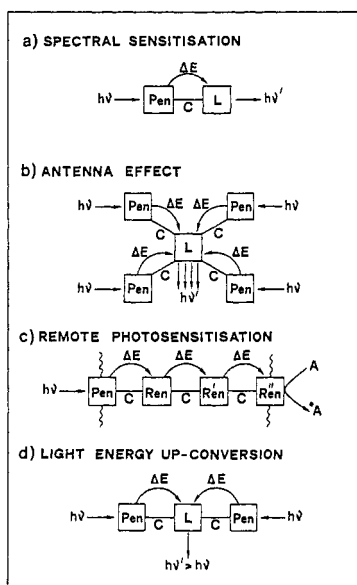


Fig. 6 Block diagram of PMDs based on electron transfer

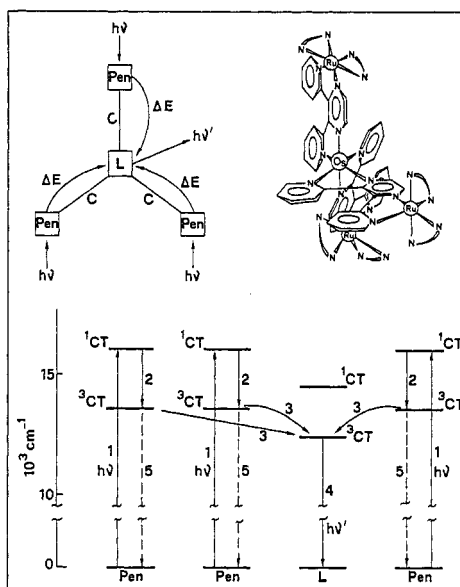


Fig. 7 Photoinduced charge separation in a triad system (ref. 17)

### CONFORMATIONAL CHANGES IN PHOTOFLEXIBLE SUPRAMOLECULAR SYSTEMS

Light excitation can induce conformational changes in several classes of molecules. When a photoisomerizable species (Pi) is a component of a supramolecular species, the light-induced conformational change of that component can be exploited for a variety of potential utilizations, such as switch on/off of (a) electrical signals, (b) receptor ability, (c) access to cavities, (d) cooperative effects (ref. 10,19).

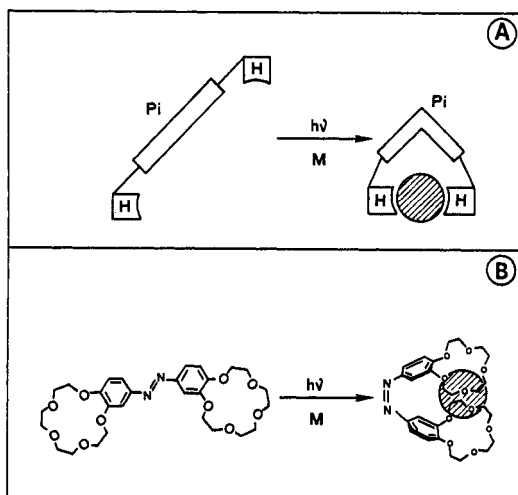


Fig. 8 Schematic representation of light-induced switching of receptor ability (ref. 19)

Fig. 8a shows schematically the operational way of a PMD for switching on/off the receptor ability. On light excitation a photoisomerizable component Pi undergoes a conformational change which brings two potential ligands (holders, H) at suitable distance to enclose a metal ion. Such a conformational change can be obtained by cis-trans photo-isomerization, and appropriate holder components are crown ethers. Fig. 8b shows a classic example of photoresponsive crown ether designed by Shinkai and coworkers (ref. 19). In the trans conformation of the azobenzene

chromophore the supermolecule has a weak coordinating ability for large metal ions. Light excitation causes the trans $\rightarrow$ cis isomerization of the azobenzene component yielding a supramolecular conformation suitable to enclose a metal ion between the two crown ethers, with a large increase in the coordination ability. Suitable photoinduced conformational changes can also modify the electronic conduction in a sequence of components and can therefore switch on/off electrical signals. In an attempt to find systems capable of performing this function, the attention of several research groups is presently focussed on molecules with twisted intramolecular charge transfer states (the so called TICT compounds) (refs. 20-22).

## ION PAIRS

Many ion-pair systems, involving inorganic (ref. 23) or organic (ref. 24) components, exhibit quite interesting photochemical and photophysical properties. For space reasons, only some ion pairs of lanthanide cryptates will be mentioned here.

The  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  ions can be encapsulated into the 2.2.1 cryptand to yield stable and luminescent cage-type complexes (ref. 25). Molecular models show that in the structure of the cryptate there are three "holes" through which, in aqueous solution, three water molecules can be coordinated to the metal ion. When  $\text{F}^-$  ions are added to an aqueous solution of the cryptate, 1:1 and 1:2 (cryptate: $\text{F}^-$ ) adducts are formed where one or two  $\text{F}^-$  ions replace water molecules in the holes of the cryptate structure (refs. 26,27). This causes (i) an increase in the luminescence intensity and lifetime because the main radiationless decay path is that involving the coupling with the high frequency O-H oscillators, (ii) a change in the pattern of the luminescence spectrum because of the change in the symmetry of the coordination sphere, and (iii), in the case of the  $\text{Eu}^{3+}$  complex, a shift towards higher energies of the ligand(cryptate)-to-metal charge transfer bands (ref. 27).

Ion pairs are also formed between the  $[\text{Ln}\subset 2.2.1]^{3+}$  cryptates and  $[\text{M}(\text{CN})_6]^{z-}$  complexes (ref. 28). In the case of  $\text{Ln} = \text{Eu}^{3+}$  and  $\text{M} = \text{Fe}^{2+}$ ,  $\text{Ru}^{2+}$ , or  $\text{Os}^{2+}$ , a broad absorption band appears in the visible region. The displacement of the absorption maximum towards the UV region as the cyanide complex becomes more difficult to oxidize suggests that the new band is due to a CT transition within the  $[\text{Eu}\subset 2.2.1]^{3+} \cdot [\text{M}(\text{CN})_6]^{4-}$  ion-pair adduct (ref. 29). For such systems, the  $[\text{Eu}\subset 2.2.1]^{3+}$  luminescence is completely quenched. For  $\text{Ln} = \text{Tb}^{3+}$  and  $\text{M} = \text{Cr}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Co}^{3+}$ ,  $\text{Os}^{2+}$ , and  $\text{Ru}^{2+}$ , and for  $\text{Ln} = \text{Eu}^{3+}$  and  $\text{M} = \text{Cr}^{3+}$  and  $\text{Co}^{3+}$ , no new low energy band can be observed, in agreement with the very high reduction potential of  $\text{Tb}^{3+}$  and the high oxidation potential of  $\text{Cr}(\text{CN})_6^{3-}$  and  $\text{Co}(\text{CN})_6^{3-}$ . In all cases, except for  $[\text{Tb}\subset 2.2.1]^{3+} \cdot [\text{Os}(\text{CN})_6]^{4-}$ ,  $[\text{Tb}\subset 2.2.1]^{3+} \cdot [\text{Ru}(\text{CN})_6]^{4-}$ , and  $[\text{Eu}\subset 2.2.1]^{3+} \cdot [\text{Co}(\text{CN})_6]^{3-}$ , luminescence quenching by an energy transfer mechanism can be expected on energy grounds, but this process is too slow to occur during the lifetime of the adduct and it can only take place under dynamic conditions.

Extension of these systematic investigations to the quenching of the luminescence of the  $\text{Ln}(\text{H}_2\text{O})_n^{3+}$  and  $[\text{Ln}\subset 2.2.1\text{-F}_2]^+$  species has suggested that ion association occurs according to three distinct structures (ref. 28). For the aquo  $\text{Ln}^{3+}$  ions, some water molecules of the coordination sphere can be replaced by a cyanide complex anion to yield an intimate ion pair. For the  $[\text{Ln}\subset 2.2.1]^{3+}$  complexes, a water molecule coordinated to the metal through the cryptand holes may be replaced by a  $\text{CN}^-$  ligand of the cyanide complex, thereby giving rise to a CN-bridged ion pair. Finally, for the  $[\text{Ln}\subset 2.2.1\text{-F}_2]^+$  species, neither intimate nor CN-bridged ion pairs are plausible in

view of the smaller positive charge and of the presence of  $F^-$  ions in the cryptand holes, so quenching can only occur via outer-sphere ion pairs.

## HOST-GUEST SYSTEMS

Organization in biological systems is quite often the result of molecular association phenomena based on noncovalent intermolecular forces (electrostatic interactions, hydrogen bonding, donor-acceptor interactions, etc.). Enzymes, genes, antibodies, ionophores, and other biological systems, possess receptor sites that can selectively bind suitable substrates, giving rise to highly specific molecular recognition, transformation, and translocation processes which form the chemical basis of life.

Natural receptors (and, sometimes, substrates) are extremely complicated molecules, but molecular recognition, transformation, and translocation processes can be performed, in principle, by smaller molecules that are synthetically accessible. This concept, introduced in 1967 by the fundamental discovery of the synthetic crown ethers (ref. 30), has strongly stimulated the imagination and ingenuity of chemists.

Investigations on the interactions between hosts and guests of known chemical composition and structure are indeed quite interesting and useful since they can help in elucidating the factors that control receptor-substrate interactions in biological systems, and can also lead to the creation of novel species and to the invention of novel chemical processes (ref. 31). Specific hosts for several metal cations, organic cations, organic and inorganic anions, and some classes of organic molecules and coordination compounds are already available but only a few photochemical investigations have been performed on host-guest systems. In the following, we review some results obtained for systems involving  $Pt(bpy)(NH_3)_2^{2+}$  as a guest. This complex is particularly suitable to be involved in host-guest type interactions because of its electric charge, ability to give hydrogen bonds, presence of an aromatic group, and presence of a covalently unsaturated metal. Furthermore, it exhibits luminescence (at low and high temperature) and photoreactivity that can be perturbed upon association with other species (ref. 32).  $[Pt(bpy)(NH_3)_2](PF_6)_2$  is insoluble in  $CH_2Cl_2$ , but it can be dissolved by addition of the aliphatic crown ether 18C6 to give a 1:1 adduct (ref. 33). The absorption and emission spectra of the adduct in  $CH_2Cl_2$  are practically identical to those of free  $Pt(bpy)(NH_3)_2^{2+}$  in acetonitrile, showing that there is a negligible electronic interaction between  $Pt(bpy)(NH_3)_2^{2+}$  and 18C6, which are associated by hydrogen bonds. When aromatic macrocyclic polyethers (for example, DB30C10) are used in the place of 18C6, 1:1 adducts are again formed. For the  $Pt(bpy)(NH_3)_2^{2+}$ .DB30C10 adduct, single crystal X-ray diffraction studies have shown (ref. 33) that the receptor takes a U-shaped configuration around the metal complex (Fig. 9). This suggests that beside hydrogen bonding, some interaction between the bpy ligand of the metal complex and the aromatic units of the macrocyclic polyether also takes place.

We have investigated in detail (refs. 34,35) the spectroscopic, photophysical, and photochemical behavior of the  $Pt(bpy)(NH_3)_2^{2+}$  adducts with several dibenzo and dinaphtho crown ethers.

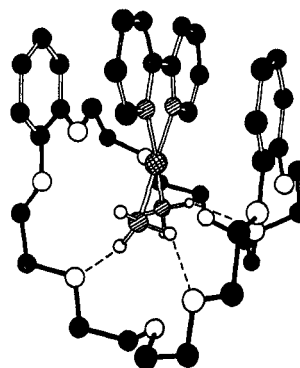


Fig. 9 X-ray structure of the  $Pt(bpy)(NH_3)_2^{2+}$ .DB30C10 adduct (ref. 33)

The results obtained can be summarized as follows. Adduct formation causes: (i) a decrease of the crown ether absorption band below 320 nm, (ii) a strong decrease of the bpy-centered absorption bands of  $\text{Pt}(\text{bpy})(\text{NH}_3)_2^{2+}$  in the 260-330 nm region, (iii) the appearance of a weak and broad absorption band in the 340-450 nm region, (iv) the complete or partial quenching of the crown ether fluorescence and of the ligand-centered phosphorescence of  $\text{Pt}(\text{bpy})(\text{NH}_3)_2^{2+}$ , (v) the appearance of a new, broad, and short-lived luminescence band in the 550-630 nm region, (vi) the quenching of the photoreaction of  $\text{Pt}(\text{bpy})(\text{NH}_3)_2^{2+}$  in  $\text{CH}_2\text{Cl}_2$ , and (vii) a perturbation in the electrochemical reduction potential of  $\text{Pt}(\text{bpy})(\text{NH}_3)_2^{2+}$ . These results clearly imply an electronic interaction, in the ground and excited state, between the bpy ligand of the Pt complex and the aromatic rings of the crown. The intensity of such electronic interaction depends on the size of the crown ring and on the nature and substitution positions of the aromatic rings present in the crown. These investigations have recently been extended to an anthraceno-crown ether (ref. 36). In its host-guest adduct with  $\text{Pt}(\text{bpy})(\text{NH}_3)_2^{2+}$ , the two components protect each other toward photoreaction in  $\text{CH}_2\text{Cl}_2$  solution. In rigid matrix at 77 K a broad luminescence band is present with  $\lambda_{\text{max}} = 565 \text{ nm}$  and  $\tau = 30 \mu\text{s}$ , attributed to an intercomponent CT transition.

The results obtained with the host-guest adducts of aromatic crown-ethers and  $\text{Pt}(\text{bpy})(\text{NH}_3)_2^{2+}$  show that the assembly of a coordination compound into an appropriate supramolecular structure can protect the compound towards the photoreaction and can profoundly change its spectroscopic, photophysical, and electrochemical properties.

### CAGE-TYPE COMPLEXES

For a variety of fundamental studies as well of practical applications there is a need for molecules that, when excited, are able to give luminescence (luminophores) and/or to transfer energy or electrons (photosensitizers) without undergoing photodecomposition. From a spectroscopic and photophysical point of view, several coordination compounds would be quite suitable to play these roles (refs. 11,37). In most cases, however, such compounds do not exhibit a sufficient chemical or photochemical stability.

A way to remedy this drawback is to link the ligands together so as to make a cage around the metal ion. As discussed elsewhere (ref. 38), this effect may be considered a supramolecular perturbation effect that does not change the composition and symmetry of the first coordination sphere of the metal ion (and thus, the spectroscopic properties), but prevents processes requiring extensive nuclear motion such as ligand dissociation or excited state radiationless decay via strongly distorted structures. The photochemical and photophysical properties of several cage-type complexes have been recently reviewed (ref. 11). For space reasons, we will only mention here an investigation concerning Ru complexes.

In the last 15 years Ru(II)-polypyridine complexes have attracted great attention because they exhibit a unique combination of ground and excited states properties (ref. 39). The prototype of these complexes is the famous  $\text{Ru}(\text{bpy})_3^{2+}$  that is extensively used as photoluminescent compound and sensitizer in the interconversion of light and chemical energy. Comparison between the properties of this complex and the requirements needed for luminophores and sensitizers shows that the main drawbacks of  $\text{Ru}(\text{bpy})_3^{2+}$  are (i) the relatively fast radiationless decay of the luminescent triplet charge transfer excited state via activated crossing to a triplet metal-centered level



(with, as a consequence, a relatively short excited state lifetime and a small luminescence efficiency), and (ii) the occurrence of a ligand photosubstitution reaction. If the bpy ligands are linked together to make a cage around the ruthenium ion, ligand photodissociation can be prevented. A suitable cage ligand can also confer more rigidity to the molecule, slowing down radiationless decay processes and thereby making stronger the luminescence emission and longer the excited state lifetime. It could also happen, however, that the cage ligand does not allow the metal to attain an appropriate octahedral coordination geometry and/or suitable Ru-N bond distances; in such a case, the triplet metal centered level would go down in energy and the excited state deactivation would be facilitated. Molecular models show that the cage-type ligand of Fig. 10 is quite appropriate because its larger spacers allow the bpy moieties to bend, making an almost ideal octahedral coordination environment.

In practice, the best way to obtain the  $\text{Ru}^{2+}$  complex shown in Fig. 10 resulted to be a template reaction starting from a derivative of  $\text{Ru}(\text{bpy})_3^{2+}$  (ref. 40). Photochemical and photophysical studies (ref. 41) have shown that this caged  $\text{Ru}(\text{II})$  complex exhibits absorption and emission spectra very similar to those of the parent  $\text{Ru}(\text{bpy})_3^{2+}$ , a longer excited state lifetime and, as expected, a much greater (about  $10^4$  times) stability towards ligand photosubstitution. The last property should assure a quite high turnover number when this complex is used as a photosensitizer.

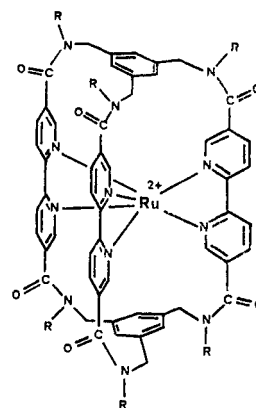


Fig. 10 Cage-type  $\text{Ru}(\text{II})$ -bpy complex (ref. 40)

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