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FROM A MOLECULAR TO A SUPRAMOLECULAR PHOTOCHEMISTRY

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Abstract

Following a current trend of chemical research, photochemical investigations are moving from molecular to supramolecular species. Some of the results obtained by the authors with supramolecular species containing metal complexes are briefly reviewed, with particular emphasis on (i) cage-type complexes, (ii) host-guest systems, (iii) metal catenates, and (iv) oligonuclear metal complexes.

1. INTRODUCTION

In 1957-58 four laboratories published their first photochemical paper [1-4]: the photochemistry of coordination compounds was born. After a few years, an autocatalytic growth of this branch of chemistry took place [5] and by the early seventies the published results had been so abundant that books were needed to rationalize the field [6,7]. Nowadays, hundreds of scientists are involved in the study of the photochemical and photophysical properties of coordination compounds, a research field extremely interesting from a fundamental viewpoint and more and more related to a wealth of applications.

Up to now most of the photochemical investigations in the field of coordination chemistry have dealt with simple molecular species. Current

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literature, however, clearly shows that chemical research is rapidly moving from molecular to supramolecular species. Following this general trend, a new branch of photochemistry, *supramolecular photochemistry* [8], is growing very rapidly. Several supramolecular species involve coordination compounds, and their photochemical and photophysical properties are strongly influenced by the metal-containing components.

In this paper we review some of the most recent results obtained in our group, with special emphasis on (i) cage-type complexes, (ii) host-guest systems, (iii) metal catenates, and (iv) oligonuclear metal complexes (Fig. 1).

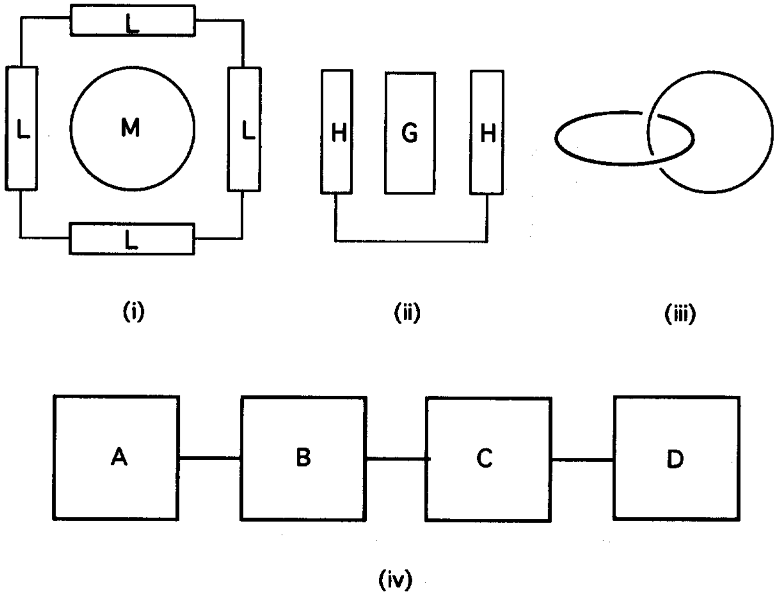


Fig. 1 - Schematic representation of some types of supramolecular species.

2. CAGE-TYPE 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 luminescent lanthanide ions show very small absorption coefficients in the visible and U.V. spectral region. In coordination chemistry, this drawback may be overcome, in principle, using complexes in which light absorption takes place in ligand-centered or charge-transfer bands. Lanthanide ions, however, do not exhibit strong coordination ability because of their electronic configuration. For this reason, conventional ligands are not able to give rise to inert complexes, especially in aqueous solution where solvent molecules efficiently compete for coordination sites. Recent developments in the field of supramolecular chemistry have permitted to rationalize the synthesis of ligands suitable for lanthanide complexation. A paradigmatic example of complexes of lanthanide ions are the cryptates [9]. In fact, the cryptand ligands possess spheroidal cavities and binding sites which are "hard" in nature, like oxygens and nitrogens. Potential applications of complexes with this type of ligands make use of their high stability and ligand capability of shielding the encapsulated ion from interaction with the surroundings.

In complexes of lanthanide ions with encapsulating ligands, an intense luminescence of the ion may be obtained by the "antenna effect", which is defined as a light conversion process via an absorption-energy transfer-emission sequence involving distinct absorbing (ligand) and emitting (metal ion) components [9-11]. In such a process, the quantities that contribute to the luminescence intensity are (i) the molar absorption coefficient of the ligand, (ii) the efficiency of the ligand-to-metal energy transfer, and (iii) the efficiency of the metal luminescence.

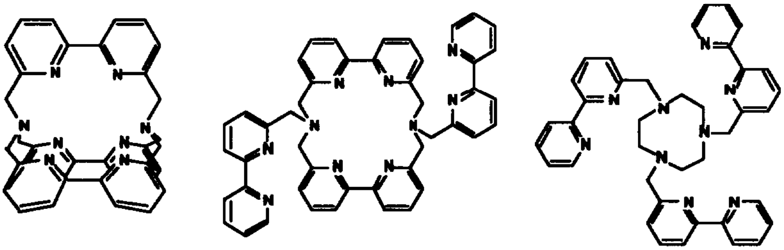


Fig. 2 - Schematic representation of cage-type ligands, used for Eu^{3+} and Tb^{3+} coordination.

In collaboration with J.-M. Lehn and co-workers, we have carried out a systematic investigations on the luminescence properties of encapsulation complexes of Eu^{3+} and Tb^{3+} ions, i.e. complexes where the ligand presents a three dimensional conformation and forms a cage around the metal ion. Some of the ligands used are shown in Fig. 2. The results of this research have been recently reviewed [12]. Among the complexes examined, the most intense luminescence is shown by the Eu^{3+} cryptate incorporating the 2,2'-bipyridine and 3,3'-biisoquinoline subunits [13] and the Tb^{3+} complex with the ligand containing the triazacyclononane cycle and three pendant 2,2'-bipyridine units [14].

A caged-version (Fig. 3) of the $Ru(bpy)_3^{2+}$ complex has also been prepared. As expected, it exhibits luminescence properties very similar to those of the parent $Ru(bpy)_3^{2+}$ complex, but a much greater (about 10^4 times) stability towards ligand photodissociation thereby remedying the most dangerous drawback of that well known photosensitizer [15].

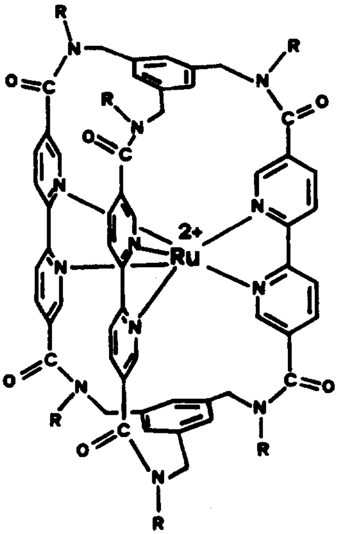


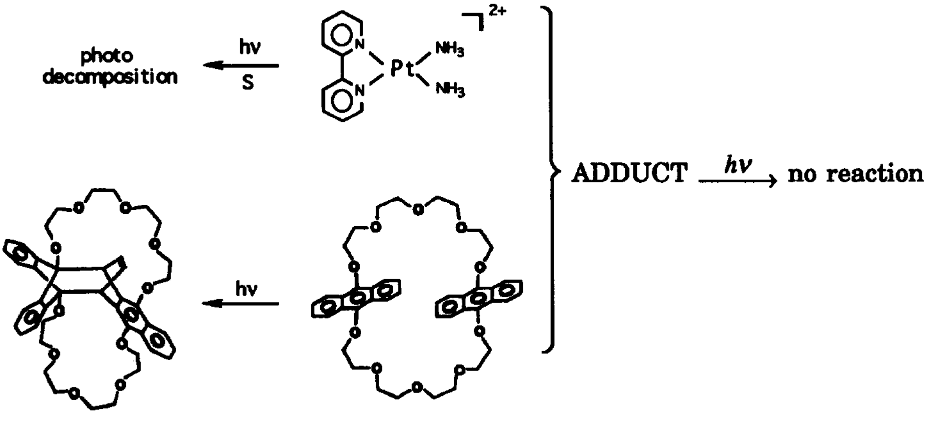
Fig. 3 - Cage-type Ru(II) complex.

3. HOST-GUEST SYSTEMS

The approach taken in our investigations of host-guest systems is the following [16]: (i) molecular species capable of giving host-guest interactions are chosen; (ii) the photochemical and photophysical properties of the separate species are studied; (iii) the photochemical and photophysical properties of the adduct are investigated and then compared with those exhibited by the separate components.

Among the several systems examined [17], we will only recall here that concerning the adduct of $Pt(bpy)(NH_3)_2^{2+}$ with the anthracenophane host DA42C10 (Scheme 1) [18]. When separated, the two components of the adduct exhibit characteristic absorption and luminescence spectra and photochemical reactions. In the adduct, the absorption spectra of the two components are strongly perturbed and their luminescence bands disappear and are replaced by a new, broad and red shifted emission. Furthermore, the photochemical reactions given by the two separate components are no longer observed (Scheme 1). All these results can be accounted for by the presence of a charge-transfer interaction between host and guest in the adduct. Mutual protection towards photoreactivity is of particular interest since it can be useful for a variety of applications.

Scheme 1

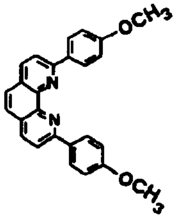


Other adducts which are very interesting from the photochemical point of view are those formed by $Co(CN)_6^{3-}$ with polyammonium macrocycles and polyethyleneimines [19]. In the latter case, information about the structure of the polymer was obtained from the ligand photodissociation reaction of the adduct.

4. METAL CATENATES

Catenates (Fig. 1 iii) are species composed by interlocked rings. 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 **1**, Sauvage and coworkers [20] have prepared the metal *catenates* Cu(2-cat)$^+$ **3** and Cu$_2$(3-cat)$^{2+}$ **6**. Demetalation of these catenates leads to the corresponding free ligands (*catenands*) **2** and **4**, where the coordinating subunits are disentangled. In the cases of Cu$_2$(3-cat)$^{2+}$ **6**, partial demetalation yields the Cu(3-cat)$^+$ species **5**, 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 [20].

The luminescence properties of several catenands and catenates have been investigated [21,22]. The catenand moieties, as expected, behave essentially as the *dap* chromophoric unit **1**. Upon addition of trifluoroacetic acid to the CH_2Cl_2 solution, however, the properties of the catenands differ from those of



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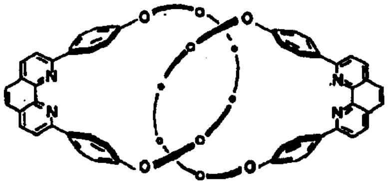

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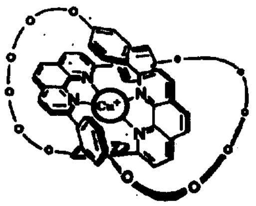

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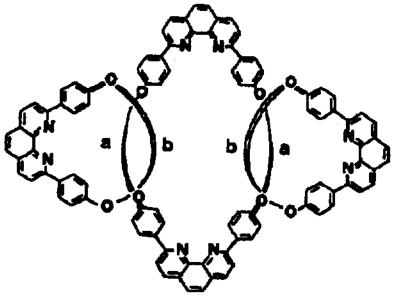

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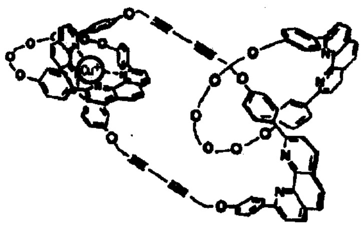

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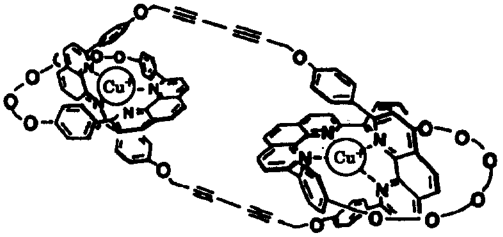

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dap [23] showing that catenand protonation does not concern independent *dap* units, but involves coordination of two *dap* units around a proton in a catenate-type structure [22]. The Li(2-cat)$^+$ and Zn(2-cat)$^{2+}$ species exhibit ligand-centered (LC) fluorescence and 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 Cu$_2$(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 **5**, 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 [21]. 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 (τ=0.012 s) that can be assigned to the lowest ^{3}LC level [22]. The mixed metal CuCo(3-cat)$^{3+}$ species does not exhibit any luminescence. This indicates that the Co-containing moiety quenches the luminescence of the Cu-containing one. In conclusion, **2**, **4**, and their derivatives display a varied and interesting photophysical behavior. In particular, their luminescence can be tuned over the whole visible region.

The photochemical and photophysical properties of several other catenates and rotaxanes not involving coordination compounds have been studied in collaboration with the group of J.F. Stoddart [24].

5. OLIGONUCLEAR METAL COMPLEXES

Covalently-linked multicomponent systems (Fig. 1 iv) can be obtaiend linking together metal-containing building blocks by appropriate bridging ligands. In collaboration with the groups of A. von Zelewsky and F. Vögtle we have investigated mono-, di-, and tri-metallic complexes obtained by tripod-type ligands (see, e.g., Fig. 4) [25]. Very interesting systems are those in which (a) $M_a = M_b = Ru(bpy)_2^{2+}$ and $M_c = Os(bpy)_2^{2+}$, and (b) $M_a = M_b = Ru(bpy)_2^{2+}$ and $M_c = Ru(bpy)_2^{3+}$. In case (a), the luminescent $Ru(bpy)_2^{2+}$ units are quenched via energy transfer by the $Os(bpy)_2^{2+}$ units, whereas in case (b) the quencher is the unit containing Ru(III) and the quenching mechanism is most likely electron transfer. The efficiency of the quenching processes depends on the size of the spacer which separates the three bpy arms of the tripod ligand.

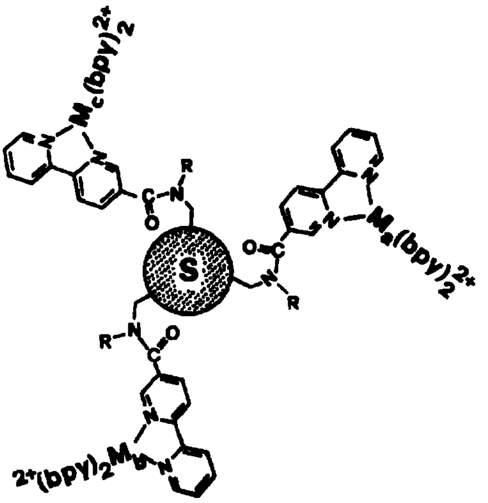


Fig. 4 - Schematic representation of trimetallic complexes of tripod-type ligands. S is benzene or triphenylbenzene.

Two- and three-component systems based on the $Ru(terpy)_2^{2+}$ photosensitizer have also been investigated for photoinduced charge-separation processes [26].

In collaboration with G. Denti, S. Serroni and S. Campagna, we are engaged in a systematic study of the photophysical properties of oligometallic

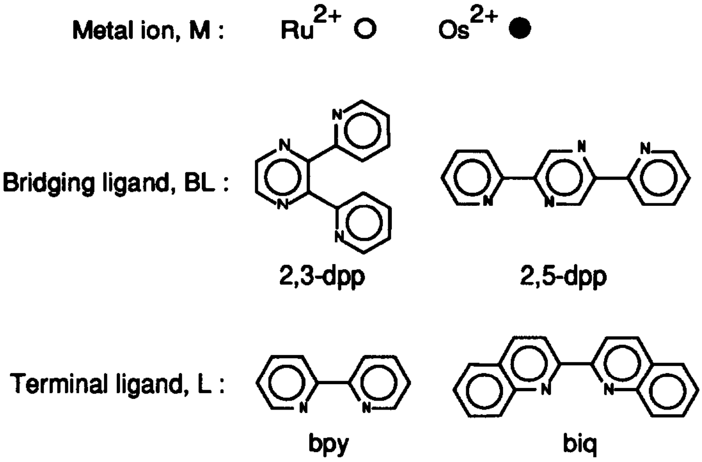
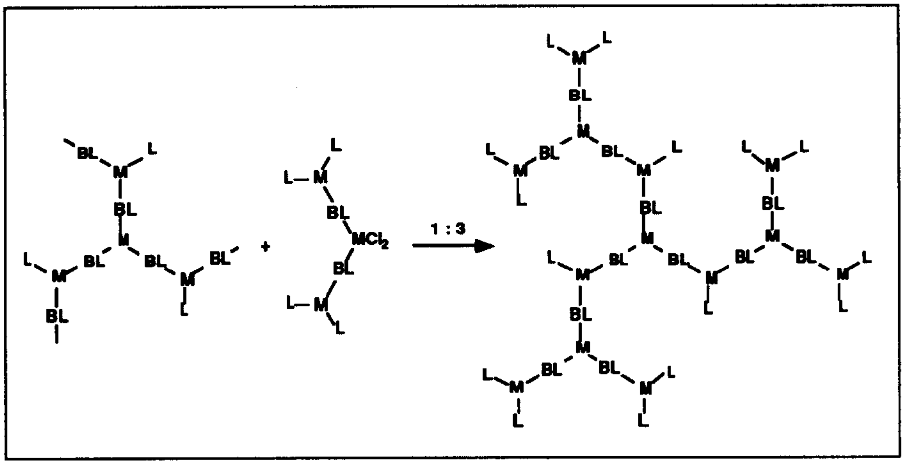


Fig. 5 - Components of the oligometallic complexes.

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. 5). Species with nuclearity up to 22, containing different metals, bridging ligands, and terminal ligands have been obtained [27-32]. The synthesis of the tridecanuclear compound is illustrated in Scheme 2. A schematic view of the structural formula of a decanuclear compound is given in Fig. 6.

These polynuclear complexes exhibit several interesting properties including: (i) very intense absorption bands in the U.V. and visible region ($\varepsilon = 133000\ M^{-1}\ cm^{-1}$ at 544 nm for the tridecanuclear $Ru\{(\mu\text{-}2,3\text{-}dpp)Ru(bpy)(\mu\text{-}2,3\text{-}dpp)Ru[(\mu\text{-}2,3\text{-}dpp)Ru\text{-}(bpy)_2]_2\}_3(PF_6)_{26}$ compound [30]); (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). Much of the interest of these compounds lies in the fact that the site containing the lowest-energy excited state can be synthetically controlled. Each building block, in fact, is characte-

Scheme 2



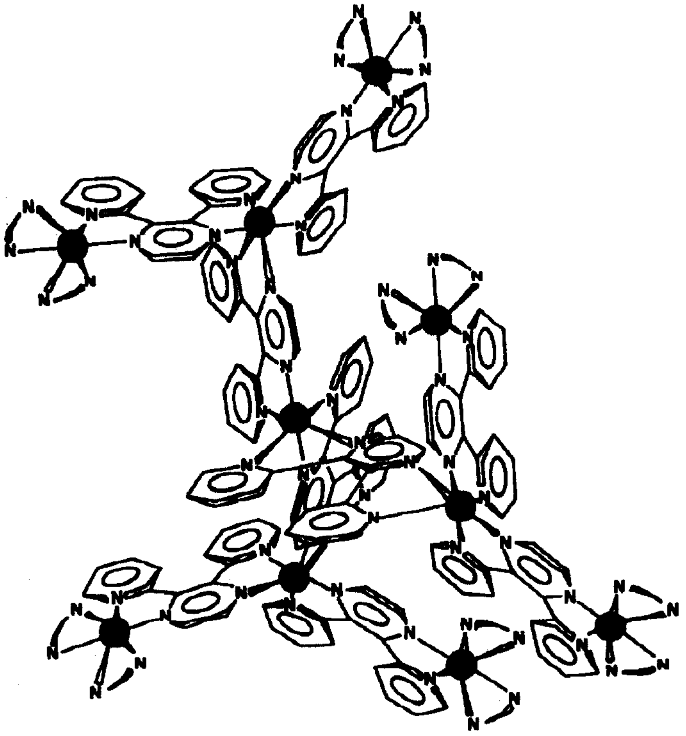
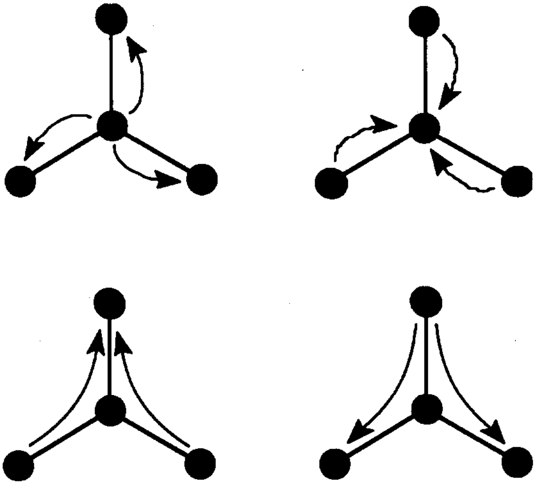


Fig. 6 - Schematic representation of decanuclear compound. N-N stands for bpy.

-rized 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 [27], 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 Scheme 3. In the case of the decanuclear compounds, six different complexes have been synthesized which exhibit a variety of energy migration patterns [29].

Scheme 3



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, photosensitization, and multielectron transfer catalysis.

6. 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.

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, as we have seen above, 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 systems [33] (photochemical molecular devices [34]) capable of elaborating the energy and information input of photons to perform *complex functions* such as light harvesting and charge separation.

We have also seen that interrogation of a supramolecular species by a 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.

7. ACKNOWLEDGMENT.

We are very glad to dedicate this paper to Prof. V. Carassiti who introduced us into the wonderful world of photochemistry and inspired much of our early work.

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