Pure & Appl. Chem., Vol. 62, No. 6, pp. 1099–1102, 1990.
Printed in Great Britain.

Supramolecular photochemistry

Vincenzo Balzani

"G. Ciamician" Department of Chemistry of the University and
F.R.A.E.- C.N.R. Institute, Bologna, Italy.

Abstract. The photochemistry of supramolecular species is an emerging and rapidly growing research field. A review is presented of recent results concerning the photochemical behavior and/or the luminescence of (i) second-sphere coordination compounds of $Co(CN)_6^{3-}$ and $Pt(bpy)(NH_3)_2^{2+}$, (ii) cage-type complexes of Co^{3+}, Eu^{3+}, and Ru^{2+}, and (iii) polynuclear Ru^{2+} complexes of polypyridine bridging ligands.

INTRODUCTION

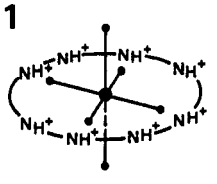
In the field of photochemistry, which is at the crossroads of chemistry, physics and biology and at the interface between matter and light, the quantitative growth of the last 20 years has been accompanied by profound qualitative changes. The interest of the research workers has progressively moved from photoreactions taking place inside molecules (intramolecular photochemistry) to processes taking place between long-lived excited states and suitable reaction partners (intermolecular electron and energy transfer processes). In the last few years a trend to study artificial assemblies of two or more molecular components (supramolecular photochemistry) has also emerged with the dual aim of making progress toward the understanding of photobiological processes and the design of artificial systems capable of performing useful functions (ref. 1). In the area of coordination chemistry, one can distinguish three types of supramolecular systems: (i) second-sphere coordination compounds, i.e. complexes associated to other species by electrostatic interactions, hydrogen bonds, or other intramolecular forces; (ii) cage-type coordination compounds, i.e. complexes in which a metal ion is encapsulated in a single, polydentate ligand; (iii) molecular building blocks linked via bridging units by means of covalent or coordinated bonds. In this paper, we will illustrate and discuss the photochemical and photophysical behavior of selected examples of these three types of supramolecular systems.

SECOND-SPHERE COORDINATION COMPOUNDS

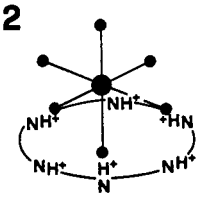
Hexacyanocobaltate(III) anion with polyammonium macrocyclic receptors

$Co(CN)_6^{3-}$ gives rise to 1:1 adducts with the fully protonated forms of the macrocyclic receptors [32]ane-N_8 and [24]ane-N_6. The quantum yield of ligand photodissociation is reduced by a factor of 3 for the $(H_8[32]ane\text{-}N_8)[Co(CN)_6]^{5+}$ adduct and by a factor of 2 for the $(H_6[24]ane\text{-}N_6)[Co(CN)_6]^{3+}$ adduct (ref. 2). Such a discrete quenching effect is taken as an indication that the adducts possess well-defined supramolecular structures. The protonated forms of the larger 32-atom ring is thought to encircle the complex giving rise to hydrogen bonds with four equatorial CN^- ligands (1). In this way, four out of six CN^- ligands are prevented to photodissociate, accounting for the reduction in the quantum yield by a factor of 3. For the protonated form of the smaller 24-atom ring, encircling of $Co(CN)_6^{3-}$ is not possible and only the three cyanide ligands of an octahedral face can be hydrogen bonded to the macrocyclic receptor (2). This accounts for the reduction in the quantum yield by a factor of 2

1



2



3

since in such a supramolecular structure only three CN^- ligands are allowed to dissociate. Recent results (ref. 3) obtained for the $Co(CN)_6^{3-}$ adducts with $H_8[24]ane\text{-}N_8^{8+}$, $H_7[24]ane\text{-}N_8^{7+}$, and $H_{10}[30]ane\text{-}N_{10}^{10+}$ are in agreement with the formation of the two types of structures described above, depending in a critical way on the size of the macrocyclic ring.

2,2-bipyridine-diamineplatinum(II) with dibenzocrownethers

$Pt(bpy)(NH_3)_2^{2+}$ gives rise to host-guest adducts with aromatic crown ethers like dibenzo-30-crown-10, DB30C10. We have recently investigated (ref. 4) the photochemical and photophysical behaviour of the DB30C10 host, the $Pt(bpy)(NH_3)_2^{2+}$ guest, and the $[Pt(bpy)(NH_3)_2\text{-}DB30C10]^{2+}$ adduct (3) in CH_2Cl_2. The results obtained can be summarized as follows: (i) in the adduct, the absorption band of the aromatic crown ether and the ligand (bpy) centered band of $Pt(bpy)(NH_3)_2^{2+}$ decrease in intensity, while a new broad band appears at lower energies; (ii) the fluorescence emission of the aromatic crown ether and the phosphorescence (ligand centered) emission of $Pt(bpy)(NH_3)_2^{2+}$ disappear on adduct formation, while a new, broad, short-lived emission appears at lower energies; (iii) the photoreactivity of the metal complex is prevented in the adduct. Extension of these studies to a family of aromatic crown ether hosts (ref. 5) has shown that the electronic interaction between the bpy ligand of the metal complex and the aromatic rings of the crown ether depends on the size of the crown rings and the nature of the aromatic rings.

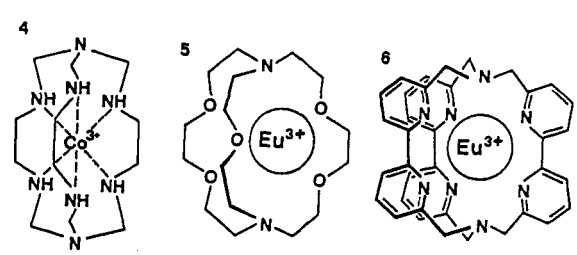
CAGE-TYPE COMPLEXES

Cage-type cobalt(III) complexes

Simple host-guest systems are coordination compounds in which a metal ion is encapsulated in a cage-type ligand. One of the first prepared cage-type coordination compounds is the Co(III) sepulchrate ion, $Co(sep)^{3+}$ (4) (ref. 6), which may be considered as the caged version of $Co(NH_3)_6^{3+}$. The spectroscopic properties of the two complexes are quite similar because the composition and symmetry of the first coordination sphere are the same. The photochemical and redox properties, however, are completely different. Upon one-electron reduction or photoexcitation in the ligand-to-metal charge-transfer bands the hexamine complex undergoes fast release of the amine ligands, as expected because of the d^7 electronic configuration of the reduced or excited complex, leading to complete decomposition of the molecular structure. By contrast, reduction or photoexcitation of $Co(sep)^{3+}$ does not cause any disruption of the structure of the complex because no simple ligand can be ejected and the metal cannot escape from the cage (refs. 7,8). Because of its stability towards redox decomposition, $Co(sep)^{3+}$ can be used as an electron relay and photosensitizer (in ion-pair systems), while $Co(NH_3)_6^{3+}$ is useless in this regard.

Cage-type complexes of luminescent lanthanide ions

Some lanthanide ions, particularly Eu^{3+} and Tb^{3+}, possess strongly luminescent and long-lived excited states. For example, the lowest excited state of Eu_{aq}^{3+}, $^5D_0$, lives 3.2 ms and emits with an efficiency of 0.8 in D_2O solutions. Unfortunately, these ions are very poor light absorbers and to make use of their excellent emitting properties one has to remedy for the difficulty to populate their excited states. Complexation of the lanthanide ion with suitable ligands is a possibility, but to obtain stable complexes lanthanide ions must be enclosed into cage-type ligands like the 2.2.1 cryptand (5) or the bpy.bpy.bpy cryptand (6). The $[Eu \subset 2.2.1]^{3+}$ complex exhibits ligand-to-metal charge transfer bands with $\varepsilon \sim 100\ M^{-1}\ cm^{-1}$ in the U.V. region. Its greatly improved absorption capacity compared to the aquo ion, however, is counterbalanced by the small efficiency of conversion (0.6%) of the originally populated charge transfer states to the luminescent f-f level (ref. 9). Much better results are obtained (refs. 10-12) when Eu^{3+} is encapsulated in the bpy.bpy.bpy cryptand (6) which exhibits very strong

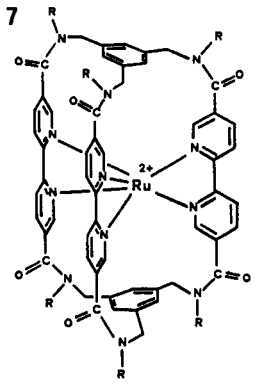


absorption bands ($\varepsilon \sim 25000\ M^{-1}cm^{-1}$) in the near U.V. Excitation in these spin-allowed ligand centered bands is followed by energy transfer to the $^5D_0$ level of Eu^{3+} with a reasonably high efficiency (10%), with the result that such a complex is an efficient molecular device for the conversion of U.V. light absorbed by the ligands into visible luminescence emitted by the metal ion (antenna effect). $[Tb\subset bpy.bpy.bpy]^{3+}$ (ref. 11) and other Eu^{3+} and Tb^{3+} cryptates of the same family have also been investigated in our laboratories.

Cage-type ruthenium(II) polypyridine 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 states properties (ref. 13). The prototype of these complexes is the famous $Ru(bpy)_3^{2+}$ 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 $Ru(bpy)_3^{2+}$ are (i) 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 (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 may 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. Molecular models show that the cryptand of **6** is suitable for the larger, not symmetry-demanding Eu^{3+} ion, but it is clearly unsuitable to create the octahedral coordination required by Ru^{2+}. The cage-type ligand of **7** is much more suitable in this regard because its larger spacers allow the bpy ligands to bend, making an almost ideal octahedral coordination environment. In practice, the best way to obtain the Ru^{2+} complex **7** resulted to be a template reaction starting from a derivative of $Ru(bpy)_3^{2+}$ (ref. 14). Recent studies (ref. 15) have shown that this caged Ru(II) complex exhibits absorption and emission spectra very similar to those of the parent $Ru(bpy)_3^{2+}$, a longer excited state lifetime and, as expected, an extremely 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 sensitizer.

7



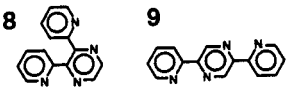
BUILDING BLOCKS LINKED BY BRIDGING LIGANDS

Mononuclear complexes may be highly luminescent species and powerful redox reactants for light-induced and light-generating electron transfer processes (ref. 13). For a variety of practical applications, however, multicenter luminescent and redox systems are expected to be more useful. The synthesis and characterization of polynuclear coordination compounds having the desired photophysicsl and photochemical properties is currently an important research field and dozens of papers have recently appeared on this subject. We only mention here some of the studies carried out recently in our laboratories.

Dinuclear ruthenium(II) complexes

The dinuclear complexes $(\mu\text{-}2,3\text{-dpp})[Ru(CO)_2Cl_2]_2$ and $(\mu\text{-}2,5\text{-dpp})[Ru(CO)_2Cl_2]_2$ (for dpp, see **8** and **9**) show a quite interesting behaviour (ref. 16). The unusual combination of polypyridine, carbonyl, and chloride ligands leads to the presence of closely lying ligand centered, charge transfer, and metal centered excited states. The interplay of these three types of levels on changing temperature results in the presence of a strong ligand centered luminescence at low temperature and a strong photosensitivity at room

8 **9**



temperature. The properties related to the aromatic bridging ligands (e.g. the reduction potentials) are affected by coordination to the metal centers, but the two $Ru(CO)_2Cl_2$ moieties practically do not communicate in the bimetallic complexes because of the strong withdrawing effect of the CO ligands.

Homo- and hetero-tetrametallic complexes

The tetrametallic complexes $M[(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2]_3^{8+}$ (M = Ru or Os) have been prepared and their electrochemical and luminescent properties have been studied (ref. 17; for M = Ru, see also ref. 18). For both complexes, reduction first takes place on the dpp ligands, while oxidation first occurs in the central metal for M = Os and in the peripherical metals for M = Ru. Both complexes feature the so-called "antenna effect" (ref. 19), but in opposite directions: for M = Os luminescence takes place from the central chromophore, which receives the energy collected by the peripherical chromophores (concentration effect), whereas the reverse occurs for M = Ru (diffusion effect).

Acknowledgements

I would like to thank my colleagues and co-workers, whose names appear in the references quoted, and Mr. G. Gubellini for the drawings.

REFERENCES

1. V. Balzani, Ed. Supramolecular Photochemistry, Reidel, Dordrecht (1987).
2. M.F. Manfrin , L. Moggi, V. Castelvetro, V. Balzani, M.W. Hosseini, and J.M. Lehn, J. Am. Chem. Soc. 107, 6888 (1985).
3. F. Pina, L. Moggi, M.F. Manfrin, V. Balzani, M.W. Hosseini, and J.M. Lehn, Gazz. Chim. Ital. 119, 65 (1989).
4. R. Ballardini, M.T. Gandolfi, V. Balzani, F.H. Kohnke, and F.J. Stoddart, Angew. Chem. Int. Ed. Engl. 27, 692 (1988).
5. R. Ballardini, M.T. Gandolfi, L. Prodi, M. Ciano, V. Balzani, F. Kohnke, H.S. Zavareh, N. Spencer, and J.F. Stoddart, J. Am. Chem. Soc., in press.
6. I.I. Creaser, R.J. Gene, J.M. Harrowfield, A.J. Herlt, A.M. Sargeson, M.R. Snow, J. Spingborg, J. Am. Chem. Soc., 104, 6016 (1982).
7. F. Pina, M. Ciano, L. Moggi, and V. Balzani, Inorg. Chem., 24, 844 (1985).
8. F. Pina, Q.G. Mulazzani, M. Venturi, M. Ciano, and V. Balzani, Inorg. Chem. 24, 848 (1985).
9. N. Sabbatini, S. Perathoner, G. Lattanzi, S. Dellonte, and V. Balzani, J. Phys. Chem., 91, 6136 (1987), and references therein.
10. B. Alpha, J.M. Lehn, and G. Mathis, Angew. Chem. Int. Ed. Engl., 26, 266 (1987).
11. N. Sabbatini, L. Perathoner, V. Balzani, B. Alpha, and J.M. Lehn, in Supramolecular Photochemistry, V. Balzani ed., p. 187, Reidel, Dordrecht (1987).
12. R. Ballardini, et al., manuscript in preparation.
13. A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, and A. von Zelewsky, Coord. Chem. Rev., 84, 85 (1988).
14. P. Belser, L. De Cola, and A. von Zelewsky, J. Chem.Soc.Chem. Commun. 1057 (1988).
15. L. De Cola, F. Barigelletti, V. Balzani, P. Belser, A. von Zelewsky, F. Ebmeyer, F. Voegtle, and S. Grammenudi, J. Am. Chem. Soc., 110, 7210 (1988); ibidem, in press.
16. S. Campagna, G. Denti, G. De Rosa, G. Sabatino, M. Ciano, and V. Balzani, Inorg. Chem., in press.
17. S. Campagna, G. Denti, L. Sabatino, S. Serroni, M. Ciano, and V. Balzani, submitted for publication.
18. W.R. Murphy, K.J. Brewer, G. Gettliffe, and J.D. Petersen, Inorg. Chem. 28, 81 (1989).
19. V. Balzani, L. Moggi, and F. Scandola, in "Supramolecular Photochemistry, V. Balzani ed., p.1, Reidel, Dordrecht, 1987.