Supramolecular Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

Electronic energy transfer in supramolecular species. "Self-poisoning" and "self-educating" systems

Luisa De Cola[a]; Vincenzo Balzani[a]; Peter Belser[b]; Roland Dux[b]; Marcel Baak[b]
[a] Dipartimento di Chimica ,G. Ciamician', Università di Bologna, Bologna, Italy [b] Institut für Anorganische und Analytische Chemie der Universität, Freiburg, Switzerland

To cite this Article De Cola, Luisa , Balzani, Vincenzo , Belser, Peter , Dux, Roland and Baak, Marcel(1995) 'Electronic energy transfer in supramolecular species. "Self-poisoning" and "self-educating" systems', Supramolecular Chemistry, 5: 4, 297 — 299

To link to this Article: DOI: 10.1080/10610279508233957

URL: http://dx.doi.org/10.1080/10610279508233957

SUPRAMOLECULAR CHEMISTRY, Vol. 5, pp. 297–299
Reprints available directly from the publisher
Photocopying permitted by license only

Electronic energy transfer in supramolecular species. "Self-poisoning" and "self-educating" systems

LUISA DE COLA[1], VINCENZO BALZANI[1], PETER BELSER[2], ROLAND DUX[2] and MARCEL BAAK[2]

[1]*Dipartimento di Chimica "G. Ciamician", Università di Bologna, 40126 Bologna (Italy) and* [2]*Institut für Anorganische und Analytische Chemie der Universität, 1700 Freiburg (Switzerland)*

(Received February 13, 1995)

We examine the possibility to design supramolecular systems where the photoinduced energy flow can be either interrupted or initiated by a *self-photosensitized* reaction. Systems of the first type are called "self-poisoning", whereas those of the second type are called "self-educating". An example of a "self-poisoning" system, are made of Ru(bpy)$_3^{2+}$- and Os(bpy)$_3^{2+}$-type units (bpy is 2,2′-bipyridine) linked to the 9,10-positions of an anthracene ring is discussed.

INTRODUCTION

Exploitation of photons for information purposes by supramolecular systems[1] can be performed by two different routes (Figure 1).[2] The first one ("photon-writing") involves the occurrence of a photoreaction that causes ("writes") some changes in the properties of the supramolecular system, reflected in a monitorable signal. The second route ("photon-reading") is based on some kind of interaction, between a component of a supramolecular system and an external species, which affects the photon response of the system. This response (any excited state manifestation, most commonly luminescence) can be used "to read" the interaction.

In this paper we will briefly discuss some devices, based on intercomponent energy transfer in supramolecular systems, where light "writes" and "reads" at the same time. More specifically, we will examine the possibility to design systems where a photoinduced energy flow can be either interrupted or initiated by a *self-photosensitized* reaction. Systems of the first type will be called "self-poisoning", whereas those of the second type will be called "self-educating". Very interesting photoswitchable supramolecular species in some way related to those discussed in this paper have recently been reported by Walz, *et al.*[3] and Lehn and co-workers.[4]

"Self-poisoning" systems

Let us consider a supramolecular system made of two molecular components D and A linked by a central component P^a which has its lowest excited state at a suitable energy to act as an intermediate in the energy transfer process from *D to A (Figure 2a). In this system, the energy transfer process is expected to be very efficient, and its occurrence can be monitored by the quenching of the luminescence of the donor excited state *D and the sensitization of the luminescence by the excited acceptor *A. For some reason it may happen that in such a system light excitation of D causes a photochemical reaction that converts P^a into another species P^b. Therefore in the energy-level diagram $*P^a$ has to be replaced by $*P^b$. If $*P^b$ lies at higher energy than *D (Figure 2a), it no longer plays the role of an intermediate

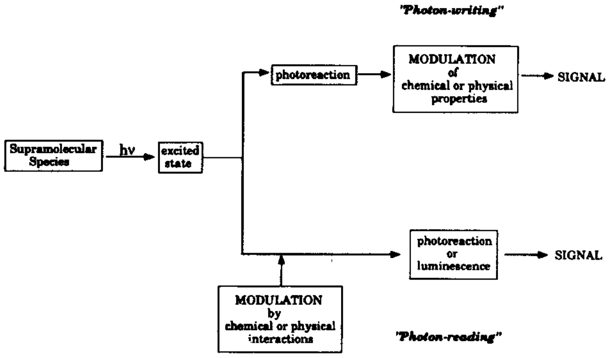


Figure 1 Schematic representation of the two routes by which the interaction of light with a supramolecular system can be exploited for information purposes.

---

*To whom correspondence should be addressed.

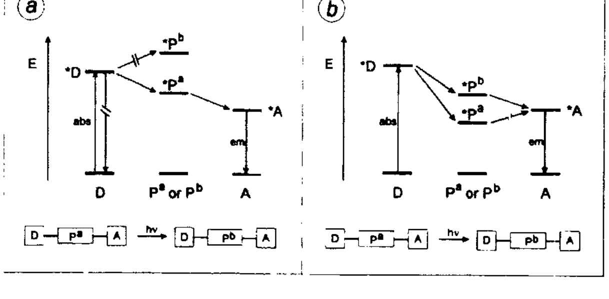


Figure 2 Energy transfer in three-component supramolecular systems. Stars indicate electronically excited states. Light absorption by D (abs) and sensitized emission from *A (em) are indicated by vertical arrows. Part *a* refers to a *self-poisoning* system and part *b* to a *self-educating* system. For more details, see text.

in the energy transfer process, and *D and A are therefore electronically "isolated" by the bridging component P^b. As a consequence, the rate of the energy-transfer process will be strongly reduced. From the experimental viewpoint, in such a system the flux of energy from *D to A decreases as irradiation proceeds, which implies a progressive recovering in the luminescence of *D and a corresponding decrease of the sensitized luminescence of *A. Since this device loses its ability to transfer energy while operating, we can say that it undergoes "self-poisoning".

We have designed and synthesized a system that performs according to the above description. Such a system, shown in Figure 3 (top) and schematically indicated by **Ru-An-Os**, is made of $Ru(bpy)_3^{2+}$- and $Os(bpy)_3^{2+}$-type units (**Ru** and **Os**, respectively; bpy is 2,2′-bipyridine), linked to the 9,10-positions of an anthracene (**An**) ring. A detailed description of the photophysical properties of this and related systems will be given elsewhere.[5] Here we only wish to point out its "self-poisoning" character.

The relevant energy levels of the **Ru-An-Os** system are shown in Figure 3. Excitation to the Ru-based ^{1}CT excited state (460-nm light) leads to efficient conversion to the Ru-based ^{3}CT level which undergoes energy transfer to the T_1 anthracene level, as demonstrated by the quenching of the Ru-based phosphorescence (λ_{max} = 640 nm) in the parent $Ru(bpy)_3^{2+}$- anthracene (**Ru-An**) dyad. In the **Ru-An-Os** triad, energy flows from the T_1 anthracene triplet to the Os-based ^{3}CT level, whose phosphorescence (λ_{max} = 770 nm) is sensitized with 100% efficiency. The rate constant of the energy transfer process, measured from the quenching of the phosphorescence of the Ru-based moiety, is 4.7×10^8 s^{-1}. For the Os-based emission, a risetime close to the decay rate of the Ru-based phosphorescence is observed.

Continuous irradiation with visible light of *deaerated* acetonitrile solutions of **Ru-An-Os** does not cause any change in the absorption and luminescence spectra. The energy absorbed by the Ru-based unit flows, via the An-based intermediate component, to the Os-based one, where it is dissipated by radiative and radiationless transitions. In *air-equilibrated* solutions, however, continuous irradiation causes "self-poisoning". The intensity of the Ru-based phosphorescence band at 640 nm increases, and the intensity of the sensitized Os-based phosphorescence at 770 nm decreases. A progressive disappearance of the structured anthracene absorption spectrum in the 350–400 nm region is also observed. When such changes level off, the lifetime of the recovered Ru-based emission is about 90 ns, showing that in the photomodified species the Ru-based luminescence is quenched with rate constant 0.6×10^7 s^{-1}, a value about 80 times smaller than that found for the original **Ru-An-Os** species (vide supra). NMR measurements on the irradiated solutions indicate that the central component of our supramolecular system has been converted in an anthracene endoperoxide species or in other derivatives where the anthracene aromaticity is no longer present.

The results obtained in aerated solution show that the **Ru-An-(^{3}CT)Os** excited state transfers energy to the dissolved oxygen molecules with formation of singlet oxygen which reacts with the anthracene ring[6] to form an endoperoxide derivative **Ru-An0$_2$-Os**. This compound can then rearrange[7] to give other species (indicated by **Ru-X-Os**) where the central ring of anthracene has lost its aromatic character. **An** and **An0$_2$** (or **X**) are like P^a and P^b in figure 2a, respectively. In the **An0$_2$** or **X**

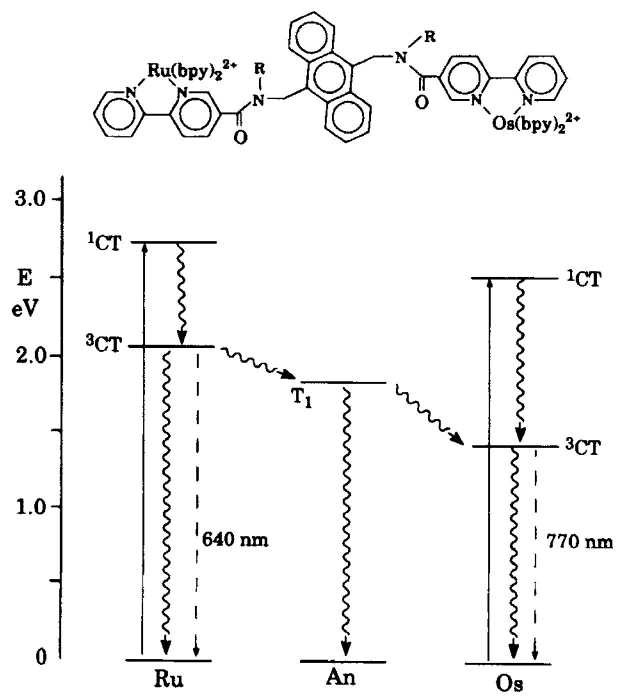
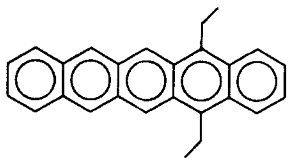


Figure 3 Schematic representation of the investigated three-component supramolecular system and of the relevant electronic energy levels of the Ru-based (Ru), anthracene-based (An), and Os-based (Os) molecular components. In the chemical formula, bpy stands for 2,2′-bipyridine and R stands for CH_2-C_6H_5.

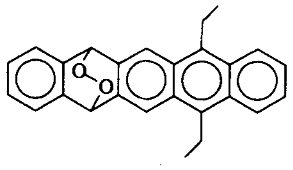
species, in fact, the T_1 level (Figure 3), characteristic of the **An** aromatic structure, is no longer present and the lowest excited state lies at much higher energy than that of the Ru-based ^{3}CT donor level.

In conclusion, the **Ru-An-Os** system is a molecular device for vectorial energy transfer which undergoes "self-poisoning" when it operates in the presence of oxygen. Such a drastic change of performance could in principle be exploited to reveal the presence of oxygen.

An interesting point for further developments is the following. The reaction of singlet oxygen with aromatic compounds in several cases can be reversed thermally and/or photochemically.[8] This is not the case for simple 9,10-anthracene derivatives like the central component used in our system, but other anthracene derivatives are known to exhibit a high degree of reversibility.[7] A supramolecular system of the type described above containing an anthracene derivative which undergoes reversible photooxygenation would perform as a reversible switch for electronic energy transfer.



pentacene



7,12-pentacene endoperoxide

Figure 4 Pentacene and pentacene endoperoxide as hypothetical central components of the supramolecular system.

"Self-educating" systems

The working principle of the energy-transfer "self-poisoning" system described above suggests the design of an energy-transfer "self-educating" system, i.e. a system where the efficiency of energy transfer *increases* on operating. Energy-transfer self-education is likely to play an important role in the antenna devices of natural photosynthesis, where the number of energy traps decreases with increasing irradiation time.[9] In principle, an artificial "self-educating" system can be designed by using the same donor and acceptor units of the "self-poisoning" device described above, with a more extended aromatic structure (e.g., pentacene, Figure 4) as a central component. The relevant energy level diagram would be of the type shown in Figure 2b with D, P^a, and A representing the Ru-based, pentacene-based, and Os-based components, respectively. In fact the pentacene T_1 level ($^*P^a$) lies below[10] the ^{3}CT Ru-based (*D) and Os-based (*A) levels. Under such conditions, irradiation of the Ru-based unit would lead to the formation of the T_1 excited state of the pentacene-based intermediate component which, however, would not be able to transfer energy to the Os-based component. In other words, energy transfer from the Ru-based to the Os-based component is switched off. In aereated solutions, however, the T_1 excited state of the pentacene-based component would react with dioxygen to produce an endoperoxide derivative. By means of suitable substituents on the pentacene structure one could favor the formation of a 7,12-pentacene endoperoxide, which would contain an anthracene aromatic moiety (Figure 4). Therefore the T_1 excited state of the central component of the photoreacted supramolecular system ($^*P^b$ in Figure 2b) would be placed at the right energy position to efficiently mediate energy transfer from the $Ru(bpy)_3{}^{2+}$ donor to the $Os(bpy)_3{}^{2+}$ acceptor. As a consequence of such a "self-educating" process, progressive quenching of the Ru-based and sensitization of the Os-based luminescence would be observed.

ACKNOWLEDGMENTS

This work was supported by CNR and MURST (Italy) and Swiss National Science Foundation.

REFERENCES

1 Balzani, V.; Scandola, F. *Supramolecular Photochemistry* Horwood, Chichester **1991**.

2 Balzani, V.; Scandola, F. in *Comprehensive Supramolecular Chemistry*, Reinhoudt, D.N. (Ed), Pergamon Press, Oxford, vol. 10 in press.

3 Walz, J.; Ulrich, K.; Port, H.; Wolf, H.C.; Wonner, J.; Effenberger, F. *Chem. Phys. Lett.* **1993**, *213*, 321.

4 Gilat, S.L.; Kawai, S.H.; Lehn, J.M. *J. Chem. Soc., Chem. Commun.* **1993**, 1439.

5 Belser, P.; Dux, R.; Baak, M.; De Cola, L.; Balzani, V. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 595.

6 Gilbert, A.; Baggott, J. *Essentials of Molecular Photochemistry*, Blackwell, London **1991**.

7 Schmidt, R.; Bauer, H-D. *J. Photochem.* **1986**, *34*, 1.

8 Bauer, H-D.; Schmidt, R. in *Photochromisms: Molecules and Systems* Dürr, H. and Bouas-Laurent, H. (Eds.), Elsevier, Amsterdam, **1990** Chap. 15.

9 Rebane, K.K. *J. Phys. Chem.* **1992**, *96*, 9583.

10 Murov, S.L.; Carmichael, I.; Hug, G.L. *Handbook of Photochemistry* Dekker, M. Inc., New York, **1993**.