

## Abstract of the PhD Thesis entitled “Supramolecular Photoactive Systems”

Chemists deal with matter and its transformations. They create molecules rearranging atoms –but handling molecules– into an infinite variety of combinations, at least until they have imagination. Some of them hold molecules together trying to gain control on increasing matter complexity.

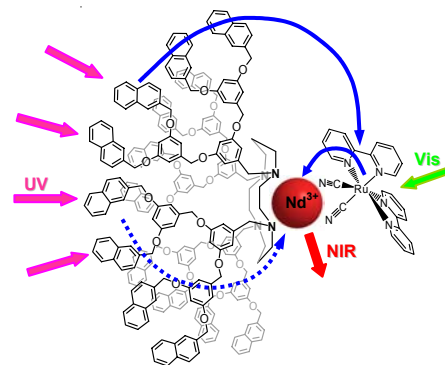
Complexity does not result by mere addition of molecular components, but implies their mutual interactions. Novel features appear at each level of complexity, peculiar of the whole system rather than of the sum of its components. Such features characterize each level of complexity and cannot exist, even conceptually, at the levels below. It's however on the basis of the chemical components at lower levels, their mutual interactions and integrating them in order to connect a level to the others that increasing complexity can be described and explained. Supermolecules are organized entities resulting from the self-assembly of two or more chemical species held together by intermolecular forces.<sup>1</sup> Supermolecules thus represent a further step towards complexity compared to molecules as the latter do to atoms.

Nuclei and electrons are charged particles and their motions in atoms and molecules generate oscillating electric and magnetic fields. Light consists of oscillating electric and magnetic fields. Whether the frequencies of such oscillations in light and chemical species match, matter can absorb energy from light. Light absorption is indeed widely used to investigate matter. In this regard, photochemistry describes chemico-physical processes occurring in molecules that undergo electronic transitions upon absorption of near ultraviolet and visible light.

As a result, supramolecular photochemistry deals with entities constituted by self-assembled photoactive components that may undergo mutual perturbation upon light absorption. Novel photophysical and photochemical properties peculiar of the supramolecular systems thus arise and such properties do not result from the simple superposition of those of the component units. Photoinduced processes involving two or more self-assembled components, such as energy, electron or proton transfer, substrate binding, photochemical reactions, catalysis, etc. take place in a supermolecule rather than between its constituting isolated units.

Self-assembly of molecular components by weak, non covalent interactions is a widespread concept to Nature's forms and functions<sup>2</sup> and is attracting increasing interest in artificial systems conceived to control mechanical movements, process information, and harvest sunlight.<sup>3</sup> In this regard, the present PhD thesis has been dedicated to the study of some supramolecular photoactive systems that act as antennas capable of collecting incident light and exploiting it to transfer electronic energy or electrons from one molecular component to another. The molecular components of the supramolecular systems investigated in this thesis are dendrimers, molecular tweezers, macrocycles and metal complexes that have been synthesised elsewhere (Bonn, Los Angeles, Essen, Zurich, Strasbourg, Moscow).

A noteworthy example is represented by the self-assembly of a three-component light-harvesting antenna comprising a dendrimer, a ruthenium complex and a neodymium ion (see figure). New features arise from their self-assembly. The dendrimer has a very high molar absorption coefficient in the near UV spectral region due to 12 dimethoxybenzene and 16 naphthyl chromophoric units constituting its framework; it is luminescent and presents a single coordinating site located in the core, which can strongly bind trivalent lanthanide ions, but it is unable to sensitize their luminescence. The  $[\text{Ru}(\text{bpy})_2(\text{CN})_2]$  complex shows absorption and emission properties highly sensitive to the presence of cations and can coordinate  $\text{Nd}^{3+}$  ions by the cyanide ligands and sensitize its emission. Mixing such three species in 1:1:1 molar ratio an unusual  $\text{Nd}^{3+}$  complex, exploiting the dendrimer and the  $\text{Ru}^{2+}$  complex as ligands, self-assembles in solution. The resulting supramolecular system behaves as a molecular-level antenna that harvests ultraviolet and visible light and exhibits luminescence in the near infrared region. The sensitization of the  $\text{Nd}^{3+}$  ion luminescence has been achieved upon excitation of the naphthyl chromophores of the dendrimer through the  $\text{Ru}^{2+}$  complex that behaves as a luminescent mediator (full blue lines in figure), while in the absence of the  $\text{Ru}^{2+}$  complex component the dendrimer is unable to transfer the excitation energy to the  $\text{Nd}^{3+}$  ion, even though it is directly coordinated to it (dotted blue line in figure).<sup>4</sup>



[1] J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, 1995.

[2] F. Cramer, *Chaos and order*, Wiley-VCH: Weinheim, 1993.

[3] V. Balzani, M. Venturi, A. Credi, *Molecular Devices and Machines- Concepts and Perspectives for the Nanoworld*, 2<sup>nd</sup> Edition, Wiley-VCH: Weinheim, 2008.

[4] C. Giansante, P. Ceroni, V. Balzani, F. Vogtle, *Angew. Chem. Int. Ed.* 2008, 47, 5422-5425.