

## **Supramolecular boxes, made of metallacycles of metallo-porphyrins axially connected by chromophores such as porphyrins, PDI's and corroles.**

We have developed the facile and efficient preparation of supramolecular multi-porphyrin assemblies with a sandwichlike geometry. They are made by two metallacycles of zinc-porphyrins,  $[t,c,c\text{-RuCl}_2(\text{CO})_2(\text{Zn-4}'c\text{-DPyP})]_2$  connected through two linear linkers L, axially bound to the zinc ions inside the porphyrins, and can be formulated as  $\{[t,c,c\text{-RuCl}_2(\text{CO})_2(\text{Zn-4}'c\text{-DPyP})]_2\}_2\{\mu\text{-L}\}_2$ . Typically, also the L linkers are photoactive molecules. In particular, in collaboration with group of Prof. F. Würthner (Würzburg, Germany), we have prepared and structurally characterized supramolecular sandwiches in which L = perylene-bisimide dyes (PDI). The modular nature of these systems makes their construction particularly flexible and amenable of future developments. In fact, both the nature of the axial ligands L and that of the porphyrin metallacycle **1** can be varied. We have exploited this great potential for preparing a new series of assemblies, in which the cavity is more defined, and therefore potentially capable of including appropriate guest molecules. For this purpose we have used axial ligands L with three pyridyl appended groups. Two of such ligands are able to assemble three molecular metallacycles of zinc-porphyrins **1**, leading to the formation of box-shaped assemblies, that can be formulated as  $\{[t,c,c\text{-RuCl}_2(\text{CO})_2(\text{Zn-4}'c\text{-DPyP})]_2\}_3\{\mu\text{-L}\}_2$ .

All the assemblies obtained have been completely characterized both in solution and in the solid state. The use of the synchrotron radiation at X-ray diffraction beamline of ELETTRA, Trieste (Italy) has been crucial to obtain the solid state structure of the above assemblies. Four other projects have been developed. They are partly completed and partly undergoing: introduction of linear linkers L possessing spin-cross over properties in order to obtain supramolecular assemblies for magnetic memories applications, in collaborations with the group of Dr. S. Bonnet, University of Leiden, The Netherlands and with Prof. A. Cornia, University of Modena, Italy; employment of another metallacycle consisting of two zinc 3'*cis*dipyridylporphyrins (Zn-3'*cis*DPyP) in place of two zinc 4'*cis*dipyridylporphyrins, and the same ruthenium fragments. This novel metallacycle,  $[t,c,c\text{-RuCl}_2(\text{CO})_2(\text{Zn-3}'c\text{-DPyP})]_2$ , has the same stoichiometry described for **1**, but has a step-like, rather than planar, geometry, both in solution and in the solid state. The connection of two step-like metallacycles, through linear and/or multi-topic linkers L is expected to yield unprecedented discrete multi-chromophores assemblies in which the linkers L are distinctly closer to one another, and therefore might have entirely new photophysical properties compared to those investigated previously; investigating the nature of the metal fragments connecting the two Zn-porphyrins. We are now trying to obtain similar porphyrin metallacycles with charged metal fragments, as to increase the solubility of the final assemblies in polar solvents. The best results have been achieved by replacement of the Ru(II) neutral fragments with Pd(II) positively charged fragments. A new series of metallacycles containing two zinc 3'*cis*dipyridylporphyrins of formula  $[\text{Pd}(\text{NN})(\text{Zn-3}'c\text{-DPyP})]_2[\text{X}]_4$  (NN = 2,2'bpy and X = CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> or PF<sub>6</sub><sup>-</sup>), have been obtained, which shows a very good solubility in more polar solvents like acetonitrile. These novel adducts contains two porphyrin in a face to face disposition, they therefore provide an hydrophobic pocket for inclusion of flat aromatic guests. Host-guest inclusion experiments are currently undergoing; constructing triad systems for stepwise electron transfer process based on metallo-porphyrin and fullerenes connected via coordination to a Re(I)(CO)<sub>3</sub> fragment.

## **Stability, photophysical and electrochemical characterization – response to light inputs.**

A detailed stability and photophysical characterization, via steady-state and time-resolved laser techniques, of all the assemblies have been carried out in collaboration with the of Prof. F. Scandola (University of Ferrara, Italy). Due to the rigidity of the modules, the inertness of the ruthenium fragments, and the simultaneous formation of minimum four pyridine-zinc ion bonds, these multi-chromophore assemblies are remarkably stable, even in dilute (>10<sup>-5</sup> M) solution. Distinct and useful photophysical processes occur depending on the nature L linkers; upon light irradiation of the peripheral zinc-porphyrins either electron transfer or energy transfer processes towards the inner part of the assemblies take place, making these structures viable for further applications.

## **Interactions and response to guest molecules (photoactive species, catalytic substrates, and others) – determination of binding constants, characterization of photoinduced processes, catalysis.**

We are now investigating on the possible non-covalent inclusion of guests within the cavity defined by the axial linkers,

and in particular we are addressing a series of host-guest inclusion complexes. In collaboration with the group of Prof. M. Prato (University of Trieste, Italy), a series of differently functionalized fullerenes are being tested as guest molecules. UV/VIS, emission and NMR studies are in progress in this sense.

A small project for the construction of photoactive systems for the generation of hydrogen has been started. Different metallo-porphyrins have been axially connected to a cobaloxime complex via coordination of a peripheral pyridine to the cobalt(II) center. The redox potentials of the different units are in principle in the right order as to promote a two-step electron transfer process, after generation with visible light of the metallo-porphyrin excited state. Gas chromatography in order to monitor the development of hydrogen upon irradiation of the metallo-porphyrin with visible light, in the presence of a suitable sacrificial electron donor, is in progress.

## **Water-soluble ruthenium-porphyrin adducts for medical applications.**

In collaboration with the group of Dr. T. Gianferrara (Pharmaceutical Department, Trieste, Italy) we have prepared and characterized, both in solution and in the solid state, a new classes of porphyrin-ruthenium conjugates with potential

bio-medical applications. Ruthenium was chosen because several ruthenium-based compounds have shown promising anticancer activity. Most of the ruthenium-porphyrin conjugates described in this work are soluble - at least moderately - in aqueous solution and are thus suitable for biological investigations, in particular for cytotoxicity and photocytotoxicity tests.

### General achievements

A big part of the results obtained have been published or submitted for publications in peer-reviewed journals and presented to several international congresses as Invited Lecture, Oral Communications and Poster (plus several contributions as co-author); the researcher has directly supervised PhD students and master degree students, and has been enrolled in the teaching scheme of the Master Degree program in Chemistry (subject – Supramolecular Chemistry); the researcher has spent one month as invited researcher in another European Research Institution; the researcher has been granted a two years grant from her own institution; the researcher has been appointed a permanent position:

M. T. Indelli,\* C. Chiorboli, F. Scandola, **E. Iengo**,\* P. Osswald, F. Würthner\* “Photoinduced Processes in Self-Assembled Porphyrin/Perylene Bisimide Metallosupramolecular Boxes” *J. Phys. Chem. B* **2010**, *45*, 14495-14504.

#### Invited paper, special issue dedicated to Mike Wasielewski.

**E. Iengo**,\* T. Gatti, E. Zangrando, F. Scandola, M. T. Indelli, E. Alessio\* “Concerted motions in supramolecular systems: Metal-mediated assemblies of porphyrins that behave like nanometric step-machines” *Chem. Commun.* **2011**, *47*, 1616-1618.

T. Gianferrara, I. Bratsos, **E. Iengo**, B. Milani, A. Oštrić, C. Spagnol, E. Zangrando, E. Alessio “Synthetic strategies towards ruthenium-porphyrin conjugates for anticancer activity” *Dalton Trans.* **2009**, 10742–10756.

**E. Iengo**,\* G. D. Pantoş, J. K. M. Sanders, M. Orlandi, C. Chiorboli, S. Fracasso, F. Scandola\* “A fully self-assembled non-symmetric triad for photoinduced charge separation” *Chem. Sci.* **2011**, *2*, **676-685**.

#### **E. Iengo**

Invited lecture at the IX Congresso Nazionale di Chimica Supramolecolare, Parma, September 6-9 2009.

**E. Iengo**, T. Gatti, E. Zangrando, E. Alessio

Poster at the 5th International Symposium on Macrocyclic and Supramolecular Chemistry, Nara, Japan, June 6-10, 2010.

**E. Iengo**, E. Zangrando, E. Alessio, M. T. Indelli, F. Scandola, F. Würthner

Oral Communication at the XXIIIrd IUPAC Symposium on Photochemistry, Ferrara, Italy, July 11-16, 2010.

**E. Iengo**, E. Zangrando, E. Alessio, M. T. Indelli, F. Scandola, F. Würthner

Oral Communication at the ECC-1 (First EhChemS Inorganic Chemistry Conference) Manchester, UK, April 11-14, 2011.

**E. Iengo**, M. Natali, M. Orlandi, C. Chiorboli, F. Scandola

Oral Communication at the 1st International Conference on BioInspired Materials for Solar Energy Utilization, Crete, Greece, September 12-17, 2011.

The researcher has spent one month as invited researcher as a Short Term Scientific Mission (STSM) to the laboratories of Prof. P. Ballester, ICIQ, Tarragona, Spain, within the COST Project D31/0003/04 “Metal-mediated nanoscopic assemblies of chromophores for molecular electronics, light energy conversion, and molecular recognition”..

A PhD student, and a Master degree student have been working on the project under the direct supervision of the researcher; a third year PhD student from the Department of Chemistry, University of Copenhagen, Denmark, has spent 6 months under the supervision of the researcher in a joint project within a collaboration with Dr. M. Pittelkow on novel supramolecular adducts containing corroles and porphyrins. A new PhD student has started a three year project under the direct supervision of the researcher and in collaboration with the group of Prof. M. Prato on the continuation of the results developed so far. A master degree student from the Department of Chemistry, University of Amsterdam, The Netherlands, will do three months of her final experimental project with the researcher within a collaboration with the group of Prof. J. Reek, on supramolecular catalysis. A PhD student from the Department of Chemistry, University of Trieste, Italy has done her three year project partly supervised by the researcher within a collaboration with the group of Prof. P. Tecilla, University of Trieste, Italy, on the construction of metallacycles of porphyrins as artificial nanopores for ion transport across the membrane.

In May 2011, the researcher has been granted from her the University of Trieste a two years grant on a project titled: “Modular synthesis of multi-chromophore systems for molecular recognition and photocatalysis”.

In June 2011, the researcher has been appointed a permanent position as Assistant Professor of Inorganic Chemistry at the Faculty of Sciences, University of Trieste, Italy.

The resources have been used following the Indicative breakdown of costs reported in the project, and the Work Plan has been mostly fulfilled.