DESIGN AND SYNTHESES OF PORPHYRIN AGGREGATES

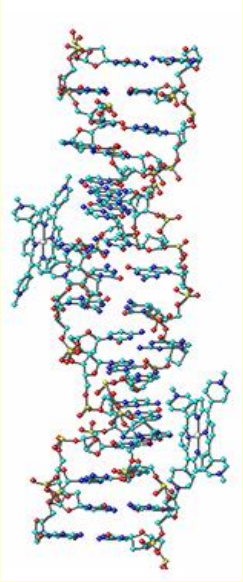
Roberto Purrello (Full Professor)

rpurrello@unict.it

Santo Di Bella (Associate Professor)

Ivan Pietro Oliveri (Ph.D-Student)

D'Urso Alessandro (Post-Doc)



Interaction of a cationic metalloporphyrin with Z-DNA

The research interests of the group focus on the achievement, in aqueous environment, of synthetic non-covalent methods able to approach the precision (in terms of sequence and stoichiometry of the components) and reproducibility of the classical covalent syntheses carried out in non-aqueous media. An additional goal of our research (perhaps even more challenging that the previous one) is to attain the control of supramolecular chirality.

Keywords: Porphyrins, inorganic chemistry, self-assembly, chirality, fluorescence

Induction, memory and (self-)propagation of supramolecular chirality

The aim of this research topic is to study the induction, transfer and propagation of chirality from chiral templates to achiral porphyrins. These studies are relevant for technological applications spanning from non-linear optical devices to membranes for racemate resolution. This approach led to the synthesis of porphyrin hetero-aggregates able to retain the memory of the induced chirality to cycle between states in which the memory is switched ON ad OFF. (Reference 1-3)

Template-aided non-covalent syntheses of supramolecular systems

Multi-porphyrin systems have been extensively investigated for their numerous applications as supramolecular devices. We have recently considered the templated synthesis of assemblies of the tetracationic porphyrins with octa-anionic calixarenes or bis-calixarenes. Interaction of porphyrins with opposite templates allows for the formation of stable species and the modulation of the complex stoichiometry. This type of synthesis presents the same "accuracy" of the covalent approach and a 100% yield, but it is not as time-consuming as the latter method (Reference 4-5)

Interactions of porphyrins with B- and Z-DNA: chiroptical probes and logic gates

The main goal is to find chiroptical probes able to discriminate between the right-handed B- and left-handed Z-forms of DNA. Our interest on Z-DNA – a rare form that differently from the "regular" B is a left-handed helix- has a twofold reason. On one hand there is a growing number of data pointing to a possible biological role of this "rare" form of DNA. Yet, its detection by means of typical spectroscopic approach is difficult because the only noticeable difference between the B- and Z-DNA is the different circular dichroism (CD). We have used cationic, non chiral porphyrins as chiroptical probes. Indeed,

interactions of these molecule with B or Z-DNA lead to opposite induced signals (ICD) reporting the two different handedness. On the other hand, interaction of anionic metallo-porphyrinwith B- and Z-DNA has been modulated with pH leading to a nice, smart logic device in solution. (Reference 6-7).

Schiff-base Zn(II) complexes as supramolecular fluorescent probes

Tetracoordinated Zn(II) complexes are Lewis acidic species capable to saturate their coordination sphere by coordinating donor Lewis bases, or in their absence, are stabilized through intermolecular axial coordination. We have demonstrated that some amphiphilic Zn(II) Schiff base complexes form dimer aggregates in dilute solutions of dichloromethane. The switching to the monomer can be driven by addition of a coordinating species and involves substantial optical variations and a dramatic enhancement of the fluorescence emission. Thus, we have developed a sensitive fluorescent probe for N-donor species, with high selectivity and nanomolar sensitivity for pyridine-based and cinchona alkaloids. (Reference 8-9)

Collaborations and Research Grants

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Selected Publications

1) D'Urso, Alessandro; Randazzo, Rosalba; Lo Faro, Letizia; Purrello, Roberto. **Angewandte Chemie, International Edition (2010), 49, 108-112**

2) Randazzo, Rosalba; Mammana, Angela; D'Urso, Alessandro; Lauceri, Rosaria; Purrello, Roberto. **Angewandte Chemie, International Edition (2008), 47, 9879-9882**

3) Mammana, Angela; D'Urso, Alessandro; Lauceri, Rosaria; Purrello, Roberto. **Journal of the American Chemical Society (2007), 129, 8062-8063.**

4) D'Urso, Alessandro; Cristaldi, Domenico Andrea; Fragala, Maria Elena; Gattuso, Giuseppe; Pappalardo, Andrea; Villari, Valentina; Micali, Norberto; Pappalardo, Sebastiano; Parisi, Melchiorre F.; Purrello, Roberto.. **Chemistry--A European Journal (2010), 16, 10439-10446**.

5) Gulino, Fabio G.; Lauceri, Rosaria; Frish, Limor; Evan-Salem, Tamar; Cohen, Yoram; De Zorzi, Rita; Geremia, Silvano; Di Costanzo, Luigi; Randaccio, Lucio; Sciotto, Domenico; Purrello, Roberto. **Chemistry--A European Journal (2006), 12, 2722-2729**

6) D'Urso, Alessandro; Mammana, Angela; Balaz, Milan; Holmes, Andrea E.; Berova, Nina; Lauceri, Rosaria; Purrello, Roberto. **Journal of the American Chemical Society (2009), 131, 2046-20472.**

7) Balaz, Milan; De Napoli, Massimo; Holmes, Andrea E.; Mammana, Angela; Nakanishi, Koji; Berova, Nina; Purrello, Roberto. **Angewandte Chemie, International Edition (2005), 44, 4006-4009.**

8) Consiglio, Giuseppe; Failla, Salvatore; Finocchiaro, Paolo; Oliveri, Ivan Pietro; Purrello, Roberto; Di Bella, Santo.. **Inorganic Chemistry, (2010), 49, 5134-5142.**

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