

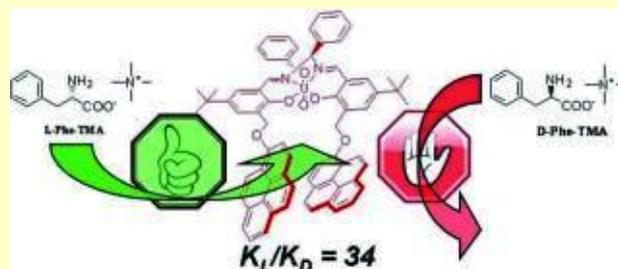
DESIGN AND SYNTHESIS OF CHIRAL MACROCYCLES FOR MOLECULAR RECOGNITION, BIOMIMETIC CATALYSIS, CHEMOSENSORS AND ORGANIC PHOTOVOLTAIC DEVICES.

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Molecular recognition of amino acid derivatives.

The aim of the research is to tailor and to synthesize chiral molecules which might be useful:

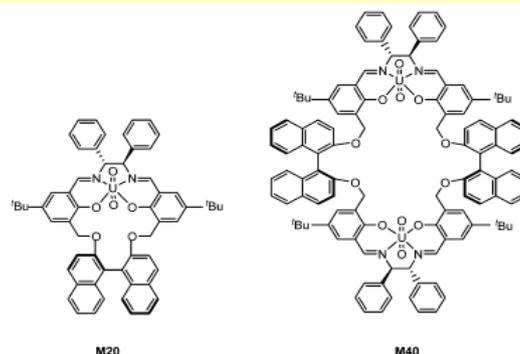
- to obtain pure aminoacids, that represent important building blocks in the pharmaceutical industry
- to work as sensors of metal ions in order to reveal their presence in biological fluids or in the environment
- as catalysts (their metal complexes) in oxygen transfer reactions
- as light harvesters or semiconducting p-conjugated organic materials in organic solar cells.

Keywords: Chiral molecular recognition, Selective oxygen transfer processes, Design and synthesis of chemosensors, Organic photovoltaic systems.

1. Chiral molecular recognition: design and synthesis of receptors

Enantiomeric recognition is an essential property of various natural systems, which is reliant on the capacity of a chiral molecular receptor to preferentially form a diastereomeric complex with one of the enantiomers of chiral molecules by exploiting noncovalent weak forces including hydrogen bonding and hydrophobic and electrostatic interactions. The development of synthetic receptors for this appealing aim is an important research area, as it can provide precious information for a better understanding of the interactions between molecules in nature.

Recently, our research group has synthesized a mononuclear (M20) and a dinuclear (M40) uranyl chiral macrocyclic complexes, incorporating both a salen unit containing two phenyl rings linked to a chiral diimine bridge and the (R)-BINOL unit, that behave as an efficient ditopic receptors for achiral and chiral quaternary ammonium salts. Binding affinities in chloroform solution have been measured for 1:1



complexes of many quaternary salts encompassing tetramethylammonium (TMA), tetraethylammonium (TEA), tetrabutylammonium (TBA), and acetylcholine (ACh), as well as trimethylanilinium (TriMAN), benzyltrimethylammonium (BnTriMA), (R-methylbenzyl)trimethylammonium and pyrrolidinium cations.

The anion of the salt is bound by the hard Lewis acidic uranyl site, with an increasing binding efficiency on increasing the anion hardness ($I < Br < Cl$), whereas CH- π or π - π attractions by binaphthyl moiety, or the salicylaldehyde unit, or the phenyl rings of diimine bridge ensure the recognition of the cation partner.

With this aim, we designed and synthesized a new heteroditopic chiral uranyl-salen complex incorporating two pyrenyl groups the recognition of ammonium salts, tetrabutylammonium (TBA) and tetramethylammonium (TMA) amino acids. UV/Vis measurements indicate the formation of 1:1 host-guest complexes with high association constants and an excellent enantiomeric discrimination between the two enantiomers of phenylalanine-TMA. T-ROESY NMR experiments confirm cation- π and CH- π interactions between the TBA and TMA cations and the two pyrenyl arms, leading to the strong stability of the complexes.

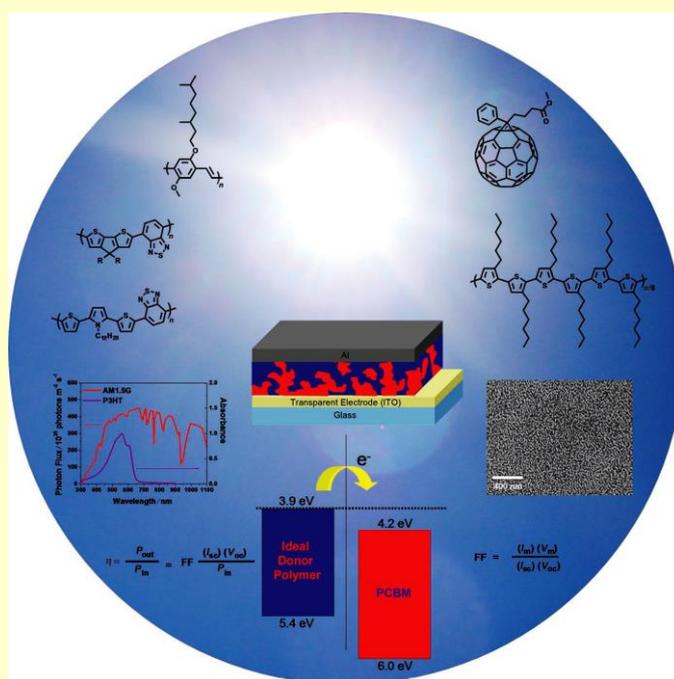


Figure 1. Organic solar cells

2. Organic Photovoltaic Systems

Since the early discovery of the photovoltaic effect by Becquerel, silicon-based solar cells represent the most efficient photovoltaic devices that help to transform solar light into electrical energy. More recently, a wide range of novel inorganic semiconducting materials, including GaAs and CdTe, have been tested as photo- and electroactive building blocks. The development of organic photovoltaic materials as potent alternatives to inorganics has, however, drawn much less attention.

Shortly after the first practical applications were found for conjugated polymers, the basic structural and electronic properties of well-structured, monodisperse p-conjugated oligomers were surveyed to mimic and to understand the features of the related, but more complex and polydisperse, polymer

analogs. In recent years, the study of monodisperse p-conjugated oligomers has advanced into its own, strong field. This advance is, for the most part, driven by the discovery of a remarkable optoelectronic phenomenon. At the forefront of current initiatives are the developments of new synthetic strategies that permit the synthesis of p-conjugated oligomeric materials with precise length and constitution. The advent of fullerenes and their production in multigram quantities at the beginning of the nineties launched a major effort to explore their outstanding electron acceptor features. In this light, blends of semiconducting p-conjugated organic polymers, including p-phenylenevinylenes (PPVs), polythiophenes (PTs), and C60, afford new types of plastic solar cells with comparatively moderate (i.e., relative to silicon-based solar cells), but nevertheless promising, energy transformation efficiencies. As far as the activity aspects of these composite materials are concerned, it is crucial to realize that electron transfer events between the electron donating polymers and the electron accepting fullerenes evolve with ultrafast dynamics and high quantum efficiencies. In this context, our research project is to achieve organic photovoltaic devices employing “small” organic molecules and oligomers.

3. Selective oxygen transfer processes

Scientific attention toward the design of catalytic systems for the selective oxygen transfer is due to their relevance in the asymmetric synthesis of oxygenated molecules and to the role they can play to elucidate oxygen transfer mechanisms in biological systems. Catalytic peroxide activators and their uses are becoming extensively patented in many parts of the world. Hydrogen peroxide is a convenient oxygen donor to employ in key transformations and its use is also benign to the environment, since its reduction product is water. Popular approach to perform oxygen transfer reactions with hydrogen peroxide is based on the catalytic activation of hydrogen peroxide by transition metal ions. In order to prepare enantioselective catalysts, chiral organic ligands, able to yield metal complexes with the chosen metal ion, are designed and synthesized. Such catalysts must be able to produce from the oxygen donor precursor an active intermediate which is significantly more reactive, yet more selective than the parent precursor. Under this respect an activation strategy is based on the mimesis of cytochrome P-450 enzymes. This class of catalysts (biomimetic catalysts) employ Mn as metal and several chiral organic ligands ad hoc synthesized. Our research group has been working for many years in developing this kind of biomimetic catalysts, in its applications and in the study of oxygen transfer mechanisms which might be of potential interest for analogous biological reactions.

Collaborations and Research Grants

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