State of the Art

There has been great interest in the synthesis of porphyrin systems because the peripheral substituent on the macrocyclic core can modulate the physical properties at will. In our laboratory we synthesized this highly luminescent Porphyrins with fluorenyl groups:

We have shown that this system affords a much higher fluorescence quantum yield (24 %) than the corresponding tetraphenyl derivative (TPP), a remarkable enhancement for this type of structure. This high quantum yield clearly demonstrates that strong electronic communication exists between the fluorenyl-arms attached to the meso positions and the central core of the porphyrin. Consequently, they present wide potential applications in different fields: such as for instance light-harvesting, Organic Light Emitting Diodes (OLEDs) or switches. Pt(II) and Pd(II) complexes of Porphyrins with fluorenyl groups directly at the meso-positions have been synthesized and characterized by our group, and the fluorescence properties studied, following selective excitation, these complexes emit red-light. In comparison to the reference tetraphenylporphyrin TPP complexes, the luminescence properties are reported. For the first time an OLED was prepared for PtTFP, as seen below:
Light-harvesting on this Porphyrins with fluorenyl groups systems can be optimized by attaching four energy donor dendrons to the porphyrin skeleton, to obtain an antenna system comprising a central porphyrin unit linked to four peripheral photon-harvesting hydrocarbon moieties.

As a consequence Synthesis of new luminescent supramolecular assemblies from fluorenyl porphyrins and polypyridyl isocyanurate-based spacers were tried, followed by the Synthesis of new luminescent molecular assemblies from fluorenyl porphyrins with diphenylacetylene bridges like dimers or trimers:

Goal of the project

In this project, first porphyrins will be synthesis and then by using these building blocks, organometallic assemblies will be elaborated. These porphyrin macrocycles possessing
fluorene substituants and phenyl-ethynyl arms will be obtained by classical organic synthesis. Then, these organic building blocks will be used for organometallic assemblies. Such assemblies "rich in carbon" should present very interesting optical properties. Indeed, we will develop redox-switchable organometallic multiphoton absorbers based on porphyrin-type molecular architectures. This work constitutes a strategic opening on innovative international collaborations, since part of its optical properties will be examined in collaboration with the Australian group of Prof. M. Humphrey, belonging to the prestigious Australian National University (ANU) in Canberra and the photophysical measurement done by Dr J.A. Gareth Williams from Durham University-UK.

In more details, we will develop new organometallic multi-photon absorbers (MPA) based on porphyrin-type molecular architectures A or B (Scheme 1). The modular nature of these compounds should be ideally suited to a component-by-component screening, allowing the rapid identification of the most promising architectures of this kind amongst a given pool of spacers, porphyrins or organometallic endgroups. For the moment architectures A has been studied and shows some very promising optical results.\textsuperscript{14-16} More specifically, in this proposal, we intend to examine dendrimeric porphyrin-type molecular architectures B:

(i) the most appropriate design of each arm to achieve the optimal switching of the multi-photon absorption cross-section

(ii) the most favorable way to connect each arm to the central core to optimize the multi-photon absorption of the molecular assembly in the various redox states, in order to optimize the switching effect

(iii) briefly investigate the role played by the metal center in the porphyrin ring on the multi-photon absorption properties
Multi-photon absorption (MPA) underpins a broad range of unique applications in the field of optics, from strictly military uses, such as the protection of materials or personnel, to the more universal concerns, such as the imaging of living organisms or the facile nanofabrication of submicrometer-sized objects, and encompassing specific uses in the field of information-processing such as light beam re-shaping, frequency up-conversion or ultradense information storage.\textsuperscript{17,18} Not surprisingly, chemistry research dealing with this very important phenomenon has, over the past decade, focussed largely on the development of new molecules with enhanced two-photon absorption (TPA) cross-sections together with one or more additional desirable properties (thermal stability, synthetic flexibility, etc). The search for such molecules was often undertaken as the initial step towards new (smart) materials tailored for one of the applications cited above.\textsuperscript{14-16}

### Original aspects of the project

Organic molecules have thus far attracted significantly more interest than inorganic or organometallic complexes as new MPA materials.\textsuperscript{17,18} Recently, very large multi-photon absorption cross-sections for polynuclear organometallic assemblies from systematic studies of their third-order NLO properties have been reported. It simultaneous incorporation of distinct redox-active centers in such molecules can lead to facile redox switchability between several redox states each exhibiting a different TPA cross-section. Thus, while reinforcing the multi-photon absorption properties of such molecules, inclusion of electron-rich metal
acetylide centers in carbon-rich networks also leads to the additional possibility of achieving a redox-control or modulation of this remarkable property at the molecular level, paving the way for the genesis of electrically-switchable TPA materials. The critical requirement now is to identify highly-active redox-switchable organometallic molecular architectures.

Organic macrocycles such as phthalocyanines and porphyrins have recently attracted significant attention as multi-photon absorbers.\textsuperscript{19} Because of their low-lying excited states, many of these macrocycles are efficient two-photons absorbers.\textsuperscript{20} We have shown that fluorenyl-porphyrin affords a much higher fluorescence quantum yield (24 \%) than the corresponding tetraphenyl derivative (TPP), a remarkable enhancement for this type of structure.\textsuperscript{1} This high quantum yield clearly demonstrates that strong electronic communication exists between the fluorenyl-arms attached to the meso positions and the central core of the porphyrin.\textsuperscript{1,2}

The TPA properties of molecular structures based on 2,7-fluorene units have been thoroughly explored by international experts in organic molecule-based two-photon absorption.\textsuperscript{21} Of particular importance, this group has recently shown that very active two-photon absorbers can be obtained based on poly(ethynylfluorenyl) arrays, particularly when these groups are substituted in the 2 and 7 positions by organic donor groups such as amines.\textsuperscript{22} A further improvement in the TPA activity of these compounds can be obtained when the active components are organized in octopolar-type geometries around a central unit.

**Synthetic targets and studies**

It is now of significant interest to assess whether efficient multi-photon absorbers are obtained when the porphyrin arms (fluorenyl in \textbf{1} and phenyl in \textbf{2}) are functionalized with redox-active organometallic groups, for example "Cl(dppe)\textsubscript{2}Ru-C≡C-" and "(dppe)CpFe-C≡C-" (Scheme 2) in the zinc porphyrin \textbf{1}.
The interaction between the various arms and the central core will initially be studied by fluorescence techniques on the more common tetraphenyl derivatives $2_i$, but will also be assessed by Z-scan. The R groups may be protons or alkyl chains, the latter being installed if solubility problems are encountered. Any strong electronic coupling existing between the metal centres may be evidenced by electrochemistry of the redox-active fragments, or by spectro-electrochemistry if specific spectral signatures of the electron-exchange event (IVCT band) can be found. 

Note that with the ruthenium-containing example, the organometallic units can also serve as an organometallic clip, which may be used to further extend the organic framework appended to each meso position. It is of significant interest to compare extended, but purely organic, structures such as $4$-$\text{Ar}$ with organometallic structures such as $3$-$\text{Ar}$ (Scheme 3, Ar = fluorenyl or fluorenyl dendrons for example). Such a comparison affords crucial information about the capacity of the "(dppe)$_2$Ru" connector to transmit the electronic coupling; indeed, several researchers have proposed that two $\pi$-manifolds linked by such units might behave as extended $\pi$-manifolds. If this also proves true for multi-photon absorption properties, such a finding would provide a simple mean to simply obtain porphyrins bearing large $\pi$ unsaturated arrays containing conjugated fluorenyl units on the meso positions.
The outcomes of these experimental studies will permit design and construction of an **optimized dendrimeric porphyrin-based structure** exhibiting several stable redox states, one of which will possess an optimal multi-photon absorption cross-section.

**Investigation of the influence of the central metal of an optimized porphyrin-based redox-switchable organometallic multi-photon absorber**

The nature of the metal center in the porphyrin ring will also be screened. Indeed, when redox active, this metal can lead to the genesis of additional redox states during the oxidation/reduction sequence (Scheme 4). Such an approach will initially be examined using various fluorescent model porphyrins with different metal centers, and will subsequently be extended to the most active organometallic porphyrins.
Scheme 4: Expected redox sequence for a metallated porphyrin with a redox-active metal centre

References


