
RESEARCH PROJECT

Dendrimeric Porphyrin-based Assemblies for Optics

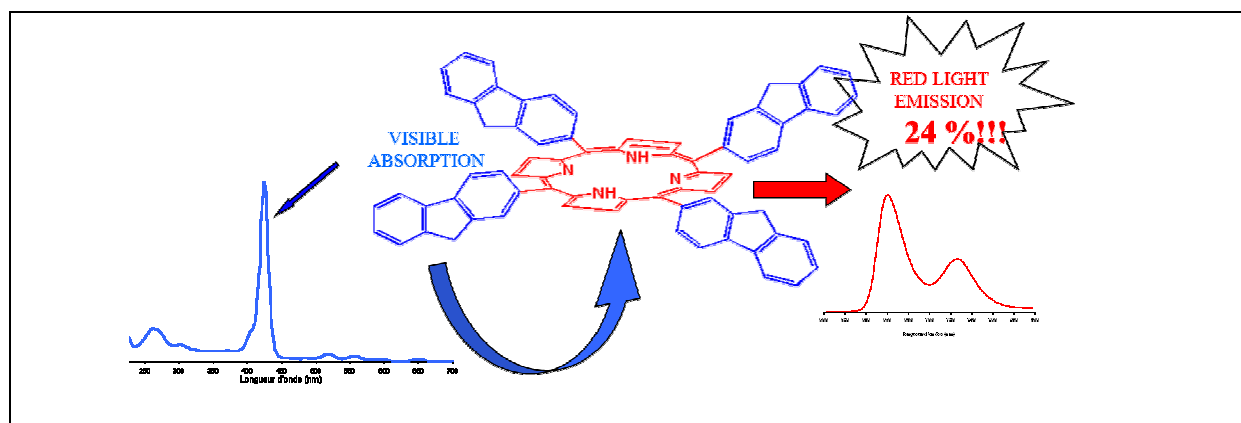
Supervisor: Dr C. O. PAUL-ROTH

The PhD student will be a member of The “Institute of Chemical Sciences of Rennes (UMR 6226)” one of the more prestigious Chemistry Laboratory in France. In consequence, all the facilities that will be needed (NMR, UV-Vis, IRTF, Fluorimeter etc...) for this research project, are available.

During the thesis, the student will learn organic and organometallic synthesis, coordination chemistry and he will use different technics such as luminescence measurements and different NMR spectroscopy technics.

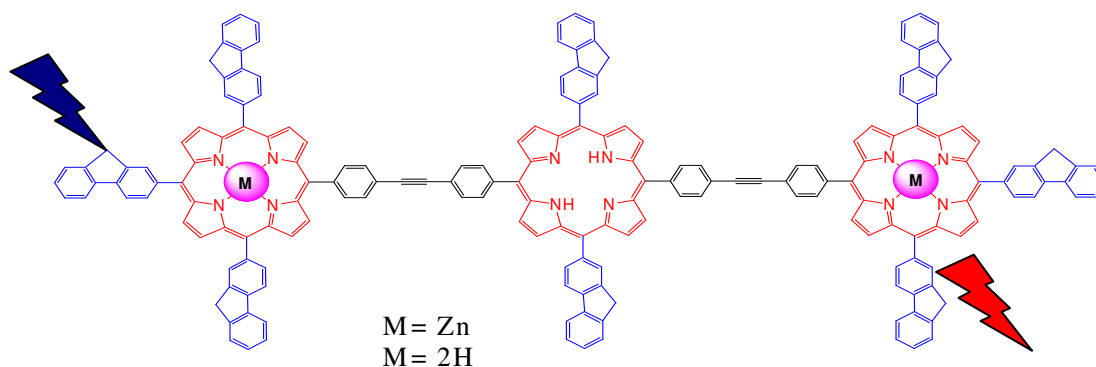
State of the Art

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 Porphyrins¹ with fluorenyl groups:



We have shown that this system affords a much higher fluorescence quantum yield : **24 %** than the corresponding tetraphenyl derivative (**TPP: 11%**), a remarkable enhancement for this type of structure.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.^{1,2} Consequently, they present wide potential applications in different fields: such as for instance light-harvesting, **Organic Light Emitting Diodes (OLEDs)**^{3,4} 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**,¹ as seen below:

Light-harvesting on this Porphyrins with fluorenyl groups systems can be optimized⁵⁻⁸ 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.⁹⁻¹¹ As a consequence Synthesis of new luminescent supramolecular assemblies from fluorenyl porphyrins and polypyridyl isocyanurate-based spacers were tried⁷, followed by the Synthesis of new luminescent molecular assemblies from fluorenyl porphyrins with diphenylacetylene bridges like dimers¹² or trimers¹³ :



In the molecular world, **Dendrimers** form a wonderful family of molecules with a tree like structure with properties that can be adapted and controlled such as the size, the shape of the molecule and the position of the functional groups.

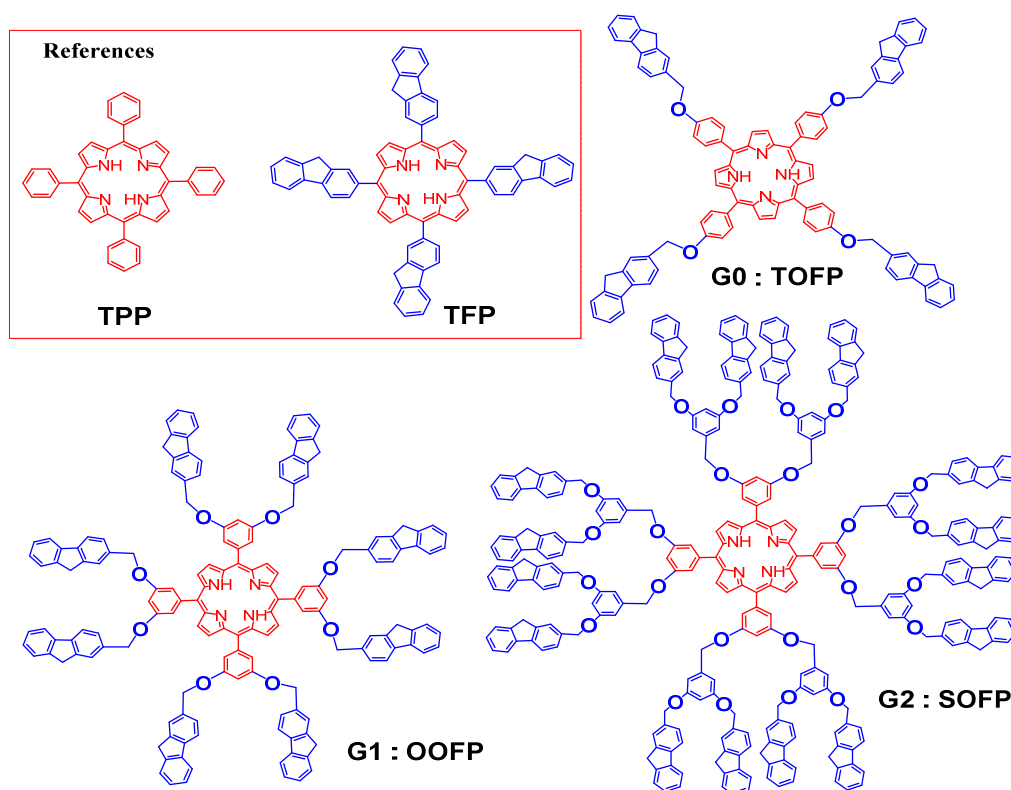


Figure 1: Consecutive generations of *non- conjugated* porphyrin dendrimers (G0, G1 and G2) and references TPP and TFP.

Trying to enhance the luminescence quantum yields, we synthesized a series of substituted *meso*-substituted **TPP**-based porphyrin dendrimers incorporating, as shown in Figure 1, increasing number of fluorenyl units, featuring *non-conjugated* ether linkers.^[14]

In 2016, to improve these systems, our team released a second group of porphyrin dendrimers fully *conjugated* with alkynyl linkers, such as for the second TPP series (**TPP1** to **TPP6** as described in Figure 2), and their photophysical properties were explored.^[15] We could show that the various fluorene-containing dendrons act as light-harvesting antenna, before transferring energy to the central porphyrin core which radiatively decays to the ground state by emission of strong red fluorescence.

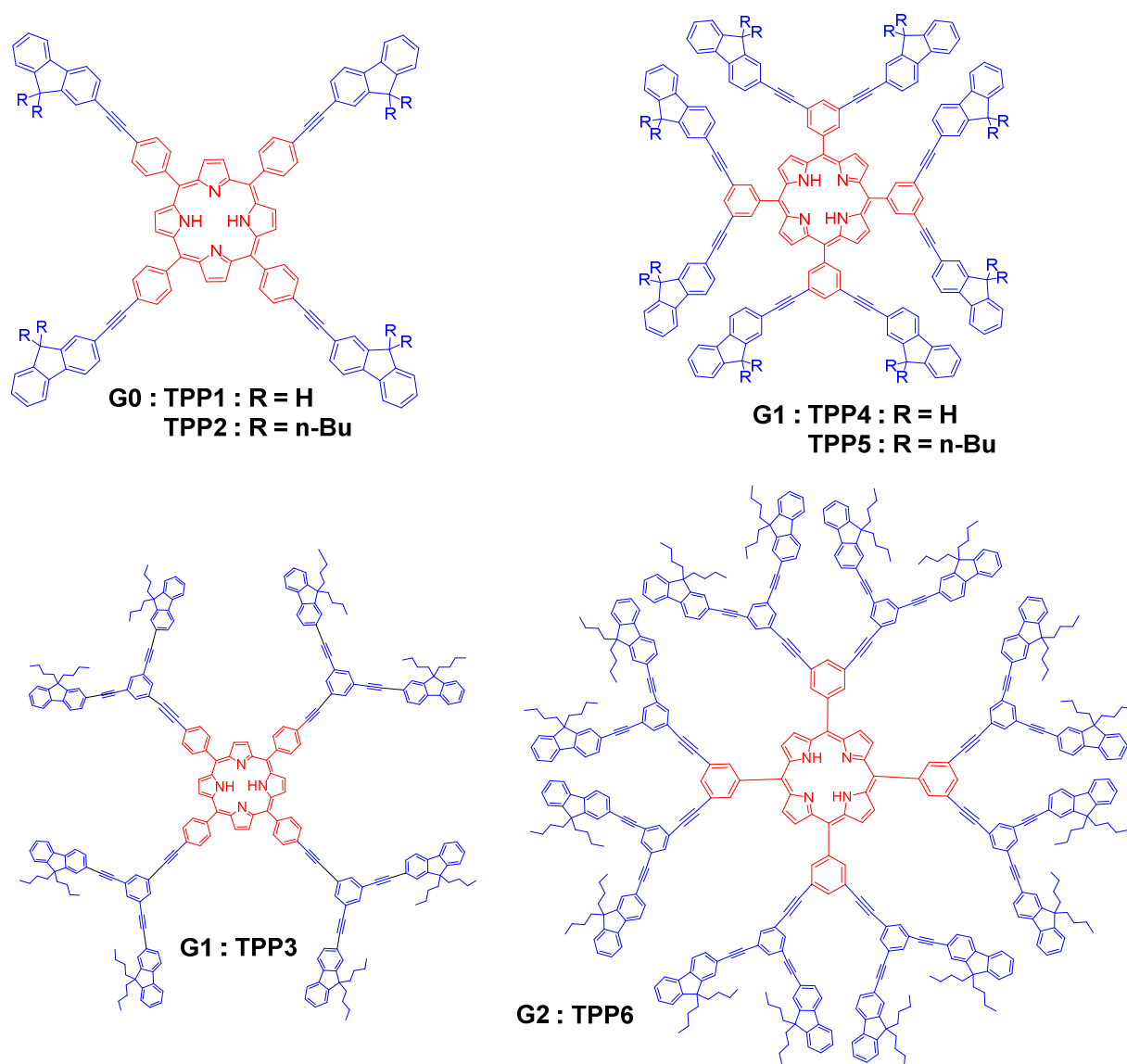


Figure 2. Consecutive generations of *conjugated* porphyrin dendrimers (G0, G1 and G2).

Goal of the project

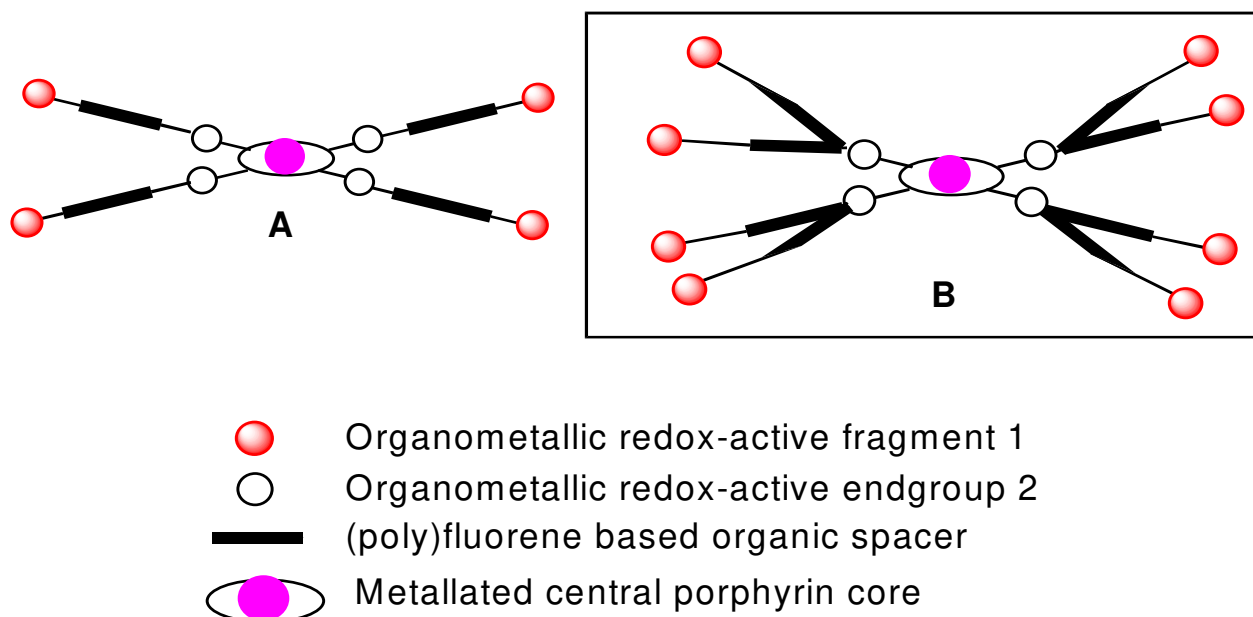
In this project, first **new porphyrin dendrimers** will be synthesis and the optical properties studied, then by using these building blocks, **organometallic assemblies** will be elaborated. These porphyrin macrocycles possessing fluorene substituents and phenyl-ethynyl arms will be obtained by classical organic synthesis.¹⁶⁻¹⁸

Then, these organic building blocks will be used for organometallic assemblies. Such assemblies "rich in carbon" should present very interesting optical properties. For the PhD student in charge of this project, it 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**.

The student in charge of this project will particularly focus his attention on developing **new organometallic assemblies** 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.¹⁶⁻¹⁸

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



Scheme 1

These new porphyrin dendrimers and the optical results will hopefully demonstrate that these porphyrin based complexes constitute a promising family of organometallic assemblies for the futur. So Investigation of the influence of the central metal and of the dendrons of porphyrin-based organometallic assemblies is very promising.

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