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Molecular Dendrimeric Porphyrin-based Assemblies for Optics

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The CSC 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 various photophysical 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 first, this highly luminescent Porphyrin (**TFP**)¹ with four fluorenyl Antennae:

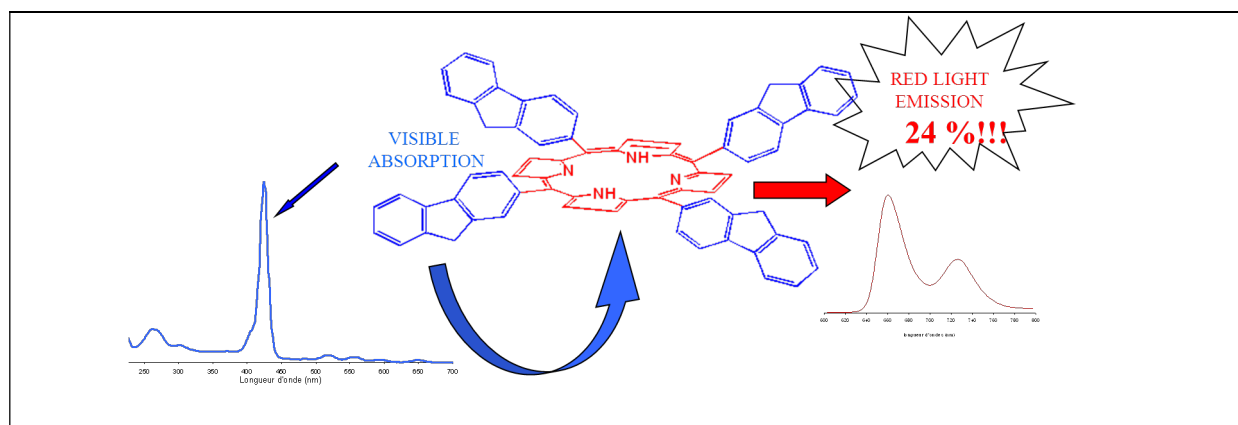


Figure 1: Absorption and Emission of tetrafluorenylporphyrin (**TFP**)¹

The high red luminescence of **TFP** (fluorescence yield $\phi_F = 24\%$), more than twice as large as that of the reference tetraphenylporphyrin (for **TPP** : $\phi_F = 11\%$), clearly demonstrates that strong electronic communication exists between the fluorenyl-arms 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) or switches. So Pt(II) and Pd(II) complexes of Porphyrins with fluorenyl groups directly at the *meso*-positions have been synthesized and characterized by our group, for the first time an OLED was prepared for **PtTFP**.^{3,4} Light-harvesting on these Porphyrins-fluorenyl systems can be optimized⁵⁻⁸ by attaching large energy donor dendrons to the porphyrin skeleton. Different series of antenna systems comprising a central porphyrin unit linked to four peripheral photon-harvesting hydrocarbon moieties have been reported successfully.⁹⁻¹¹ Followed the synthesis of new luminescent molecular assemblies based on fluorenyl-porphyrins with diphenylacetylene bridges like **dimers**¹² or **trimers**¹³ :

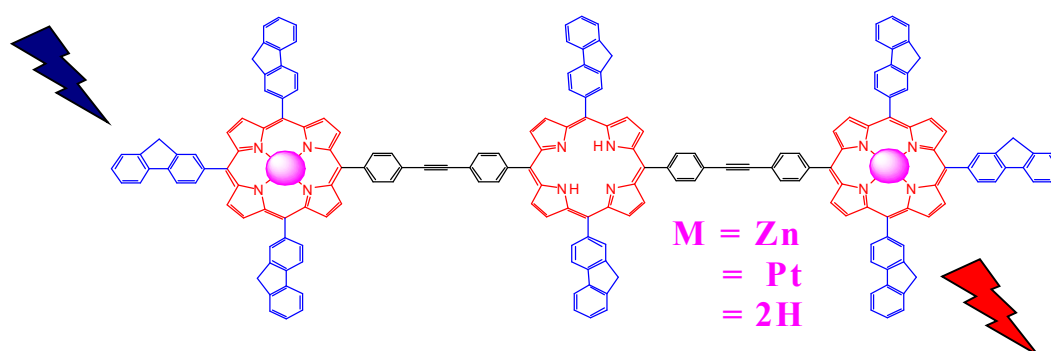


Figure 2: Absorption and Emission of **Trimer of Porphyrins**

In the continuation of this project, in trying to enhance the luminescence quantum yields, we synthesized a series of substituted *meso*-substituted porphyrin **Dendrimers**, first based on tetraphenylporphyrin (**TPP**) incorporating an increasing number of **fluorenyl units**, featuring *non-conjugated* ether linkers.¹⁴ In 2016, to improve these systems, Dandan YAO, a CSC PhD student, in our team released a second group of **porphyrin dendrimers** fully *conjugated* with alkynyl linkers, such as for the second TPP series and their photophysical properties, meaning Linear (LO) and Non Linear Optical (NLO) properties were explored.¹⁵

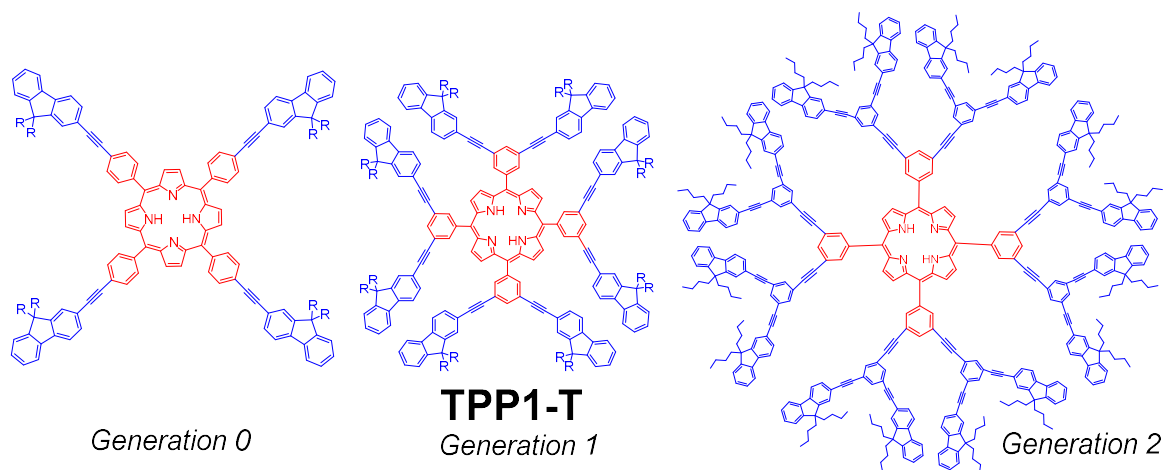


Figure 3: Porphyrin Dendrimers based on **TPP**, with triple bonds **T**

Through recent research, so we first exploited this capacity to enhance the luminescence by using dendritic systems (see Figure 3) based on **TPP**: like *generation 1* and *2* dendrimers with *triple bonds T* (**TPP1-T**) or *double bonds D* as connectors (see Figure 4: **TPP1-D**).¹⁶

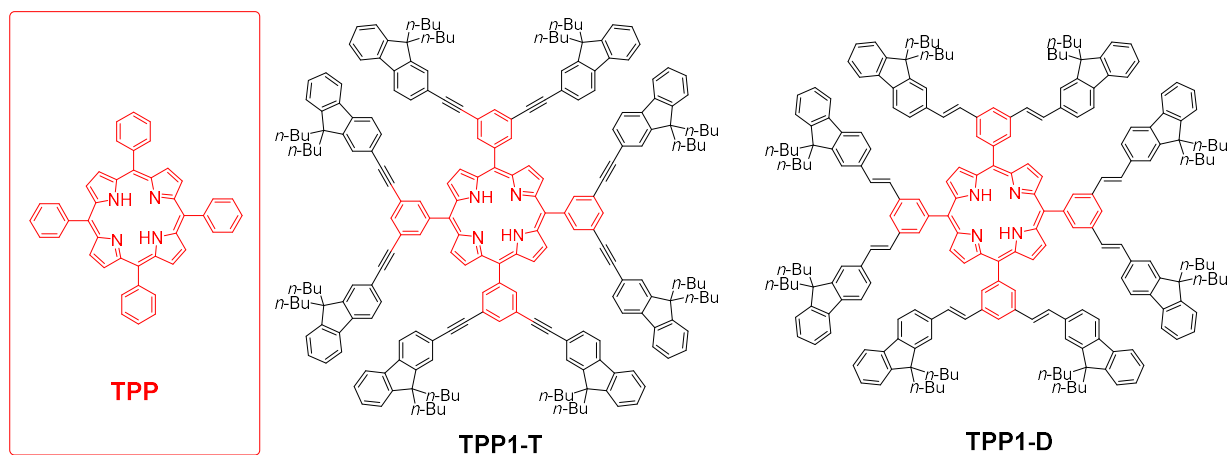


Figure 4: Porphyrin Dendrimers based on **TPP**, with triple bonds **T** and double bonds **D**

In the triple bond series **T**, we can also compare the *dendrimer* **TPP1-T** (Fig. 4) with the *linear* compound **TFP-T** (Fig. 5) because these two compounds have exactly the same number of fluorenyl units, meaning eight.

We observe strong enhancement in the optical properties, probably also due to the replacement of **TPP** core by very efficient **TFP** core as observed by comparing equivalent *generation 1* dendrimers **TPP1-T** to **TFP1-T**. But, apparently the increase in generation (G1 to G2) does not improve optical property.

We can notice that as for **TPP** series, the double bond connector **D** for **TFP1-D** has the best performance reaching a particularly high result.

Based on these previous observations and experiences, our future strategy to enhance the optical properties is then to focus on increasing the number of fluorenyl antennae in a *linear structure* rather than a *dendrimeric one*, and by using promising *double bond D connection* to extend the π -system.¹⁷

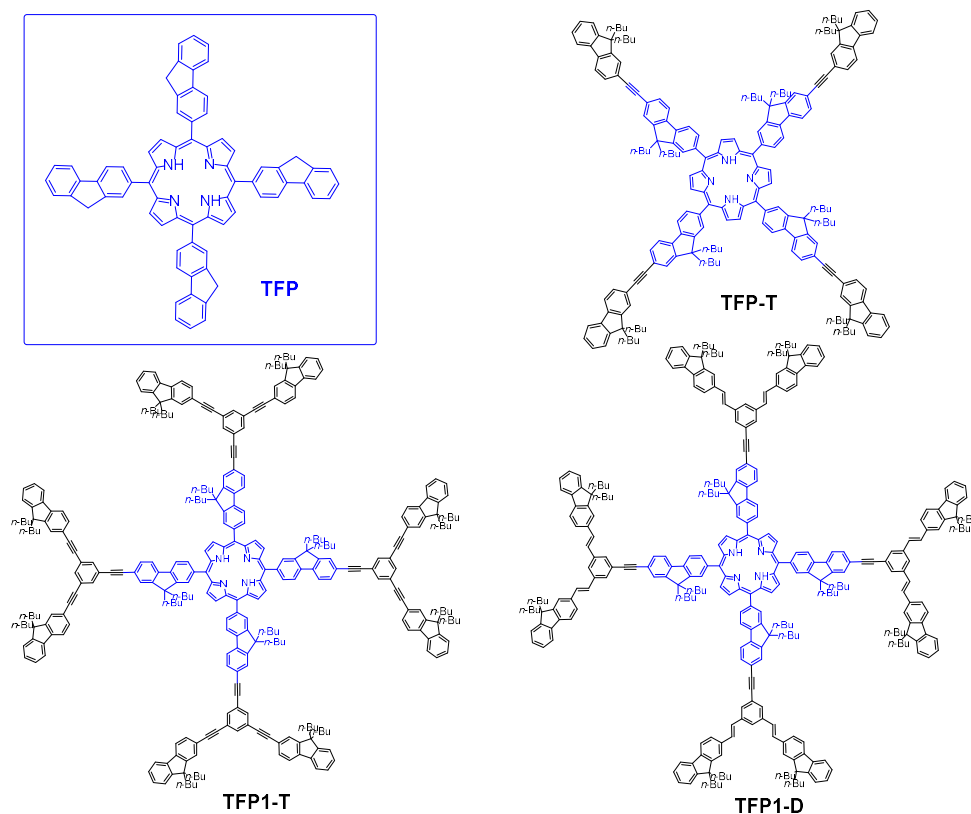


Figure 5: Porphyrin Dendrimers based on **TFP**, with triple bonds **T** and double bonds **D**

Taking into account these observations and Linear (LO) and Non-Linear Optical (NLO) properties, we decided very recently, to synthesize a new series of free-base porphyrins and corresponding metal complexes containing double bonded connected fluorenyl arms with increasing lengths, up to three double bonds, meaning four fluorenyl units per arm.¹⁸

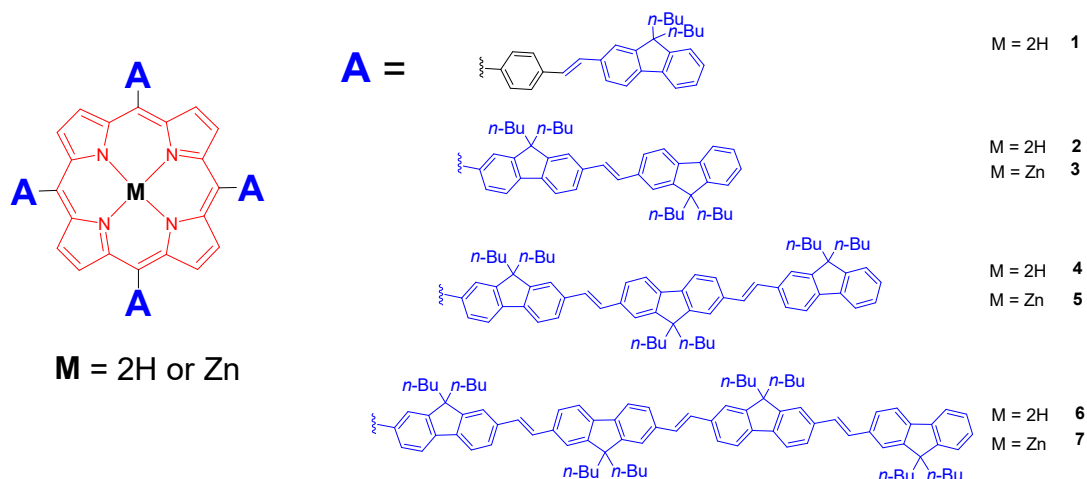


Figure 6. Star porphyrins and corresponding zinc complexes

TASK 1: The results obtained from our latest series of porphyrins, featuring fluorenyl arms connected by double bonds, show great promise and warrant further investigation. In this

project, we will focus on synthesizing enhanced systems by incorporating donor (D) or acceptor (A) endgroups on the fluorenyl arms, and examine their effects on photophysical properties.

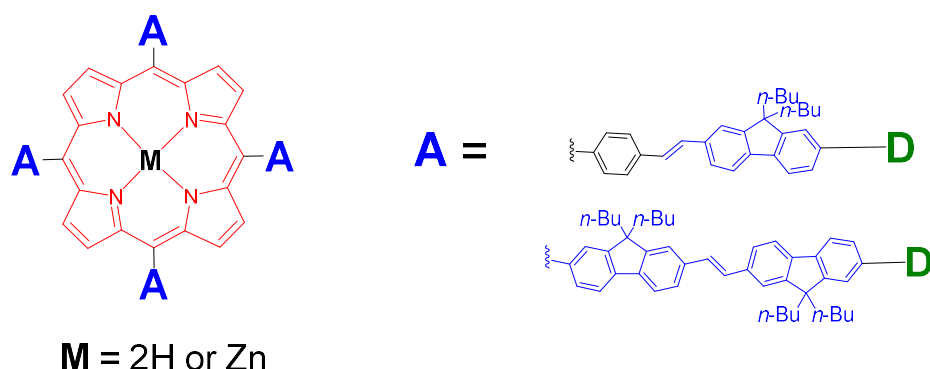


Figure 7. Star porphyrins decorated with donating **D** endgroups

Going from tripods to tetrapods:

Earlier **Organic and Organometallic dendrimers based on a tripod** (see Fig. 8) have been synthesized for NLO applications, in this project, we will now consider porphyrin tetrapods to obtain new efficient and stable assemblies:

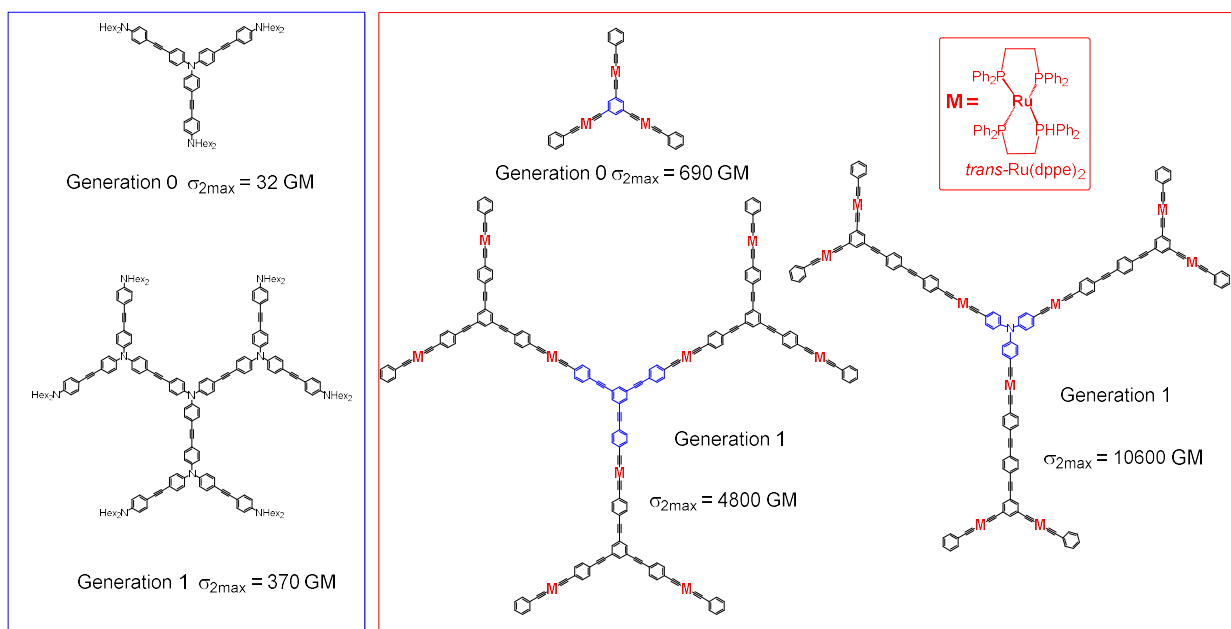


Figure 8. Tripods decorated with metal acetylide endgroups

TASK 2: In this project, first **new porphyrin dendrimers** will be synthesis on the model below, and the optical properties studied, then by using these building blocks, **organometallic assemblies** will be elaborated.

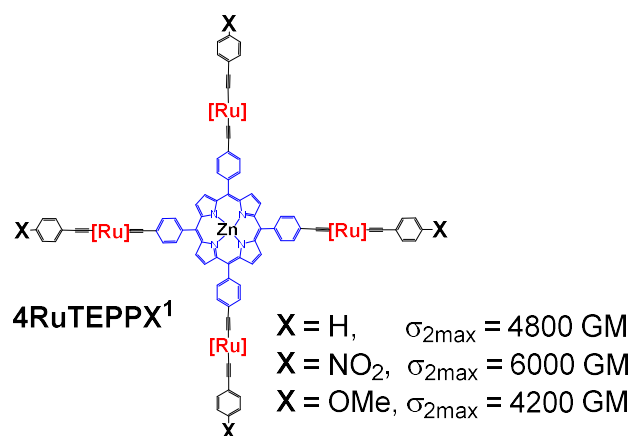


Figure 9. Tetrapod Porphyrins decorated with metal acetylide endgroups and NLO results

These porphyrin macrocycles possessing fluorene substituents and phenyl-ethynyl arms will be obtained by classical organic synthesis.¹⁹⁻²¹ Then, these organic building blocks will be used for organometallic assemblies, very interesting NLO results have been obtained for a **Organometallic dendrimers**.²² Such assemblies "rich in carbon" presenting very interesting optical properties to elaborate new materials of interest. For the future CSC 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**. The student will particularly focus his attention on developing **new organometallic assemblies** based on porphyrin-type molecular architectures. 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. 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 future. 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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