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# New luminescent fluorenyl-armed linear porphyrin trimers with diphenylacetylene bridges

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ABSTRACT

First a series of porphyrins bearing various fluorenyl donor groups is presented; an intermediate porphyrin bearing three fluorenyl arms (zinc complex **12**) and compound **13**, bearing only two fluorenyl groups. Then starting from these building blocks, synthesis of new porphyrin trimers **7** and **8**, with in totally eight peripheral fluorenyl arms is performed by using a palladium catalyst. Photophysical properties; absorption and luminescence, of new trimers **7** and **8** are presented. We can then compare these properties to those of reference porphyrin monomer **TFP** (**2**), as well as to those of porphyrin dendrimers bearing various numbers of fluorenyl arms (**3** and **4**) and finally to those of the corresponding dimers **5** and **6**, which are the precursor models of this work.



## 1. Introduction

Modular synthetic approaches called great attention for the preparation of multicomponent systems. The synthesis of photosynthetic or related model systems requires strategies for joining large number of components into functional arrays. Assemblies of porphyrins have shown interesting properties for the fabrication of electronic and optical devices, as well as for the conversion of solar energy [1]. In nature, the photosynthetic light-harvesting systems (I and II) consist of well-organized porphyrin antennas in sophisticated three-dimensional structures [2]. Thus, the ability to design and construct molecular architectures in which the energy flow can be controlled constitutes a great (and timely) challenge. One approach is to use porphyrins as building blocks and to assemble them by different coupling methods.

Different ways to connect porphyrins have been studied earlier; one of the first examples, in 1976, was the synthesis of diporphyrins and triporphyrins bridged by an ester bond for energy and electron transfer in biological processes [3]. Later in 1983, porphyrins connected by ether bond were used for light collecting [4]. Few years later, many other examples were shown; Therien et al. published a porphyrin dimers and trimers linked at *meso* position by two triple bonds as models for light collecting antenna [5]. Assemblies in which the porphyrins are directly connected by a single bond, usually between the *meso* positions, have been prepared by Smith's group [6]. Later, the synthesis of dimers and trimers linked by ethynyl bond at positions like *meso-meso*, or *meso-beta* were proposed [7–11].

In 2004, we have reported the synthesis of a porphyrin monomer possessing four fluorenyl arms (**TFP**, compound **2**) [12–16]. Surprisingly, **TFP** exhibited a remarkably high quantum yield (24%), compared to the reference tetraphenylporphyrin (**TPP**, compound **1**) demonstrating the capacity of the fluorenyl units to enhance quantum yields (Fig. 1). Then, to exploite this efficiency, a series of porphyrin dendrimers bearing fluorenyl dendrons was prepared, namely: **3** and **4** [17,18]. As an applications, we next tested corresponding platinum(II) complexes in the fabrication of red Organic Light Emitting Diodes (OLEDs) [19–21]. Also, supramolecular assemblies possessing 12 or 24 fluorenyl arms, using these efficient building blocks, have been prepared by our group [22]. Very recently, the synthesis of smaller systems possessing 6 fluorenyl arms like dimers **5** and **6** were synthesized successfully by our group [21]. Encouraged by these results, we will synthesize trimers of porphyrins substituted by eight fluorenyls units in the *meso* position.

Linear porphyrin trimers will be formed by coupling a porphyrin with two iodo groups and two porphyrins with one terminal alkyne

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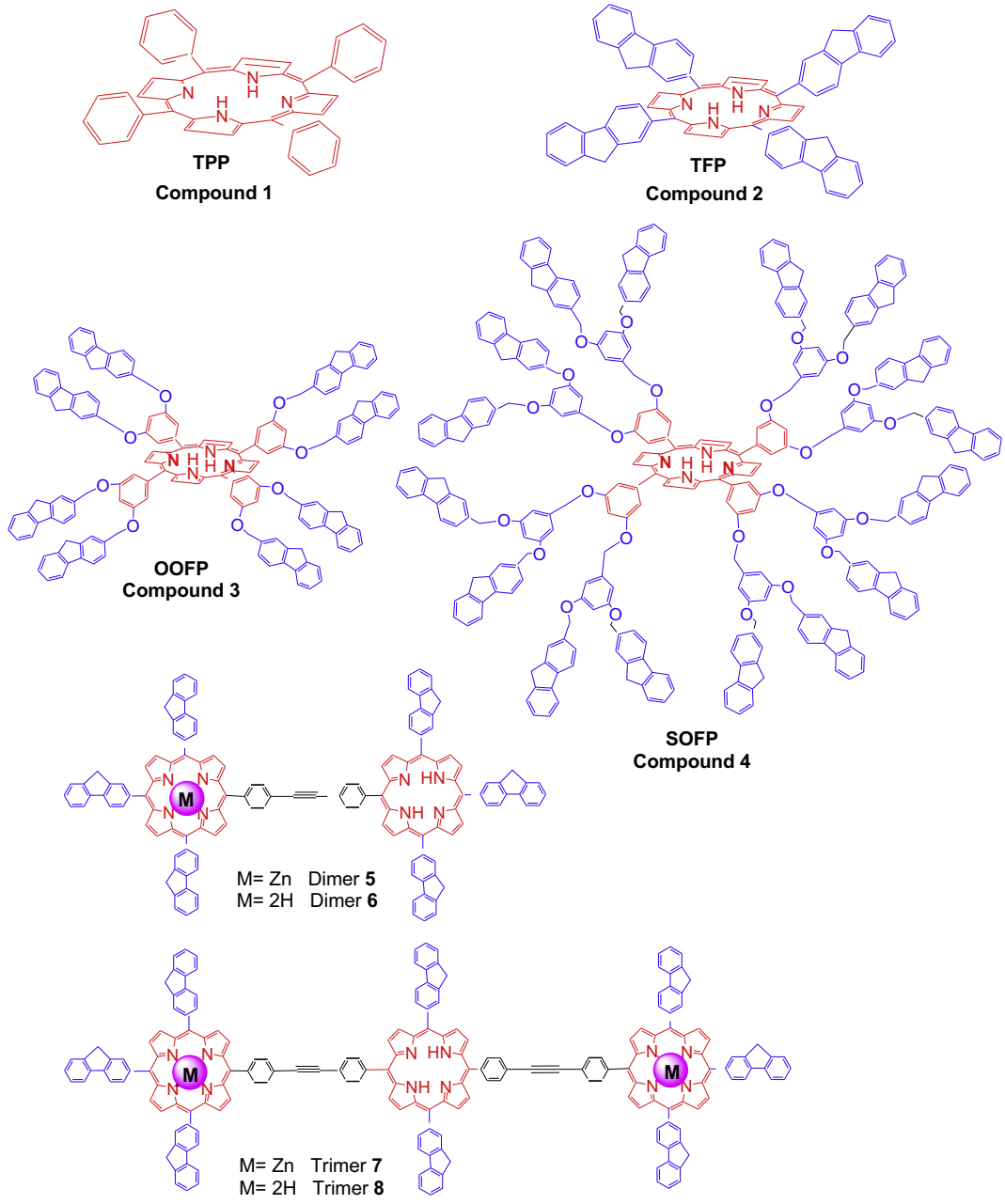


**Fig. 1.** Monomers **1** – **4** and dimers **5**, **6** and target trimers **7**, **8**.

function, catalyzed by a palladium complex. To this aim, zinc porphyrin with three peripheral fluorenyl groups and one anchoring point (**12**), as well as new building block with two peripheral fluorenyl groups and two anchoring points are described (**13**).

Preliminary photophysical results for new trimers **7** and **8**, are reported. These results are first compared to previous data for precursor **TFP**, [23] secondly to the porphyrin dendrimers **3** and **4**, [17,18,22] and finally to the corresponding dimers **5** and **6** [21].

## 2. Experimental

### 2.1. General remarks

All reactions were performed under argon and were magnetically stirred. Solvents were distilled from appropriate drying agent prior to use, DCM and $CHCl_3$ from $CaH_2$ and THF was distilled using sodium/benzophenone system. The other solvents