



## Synthesis of new luminescent supramolecular assemblies from fluorenyl porphyrins and polypyridyl isocyanurate-based spacers

Samuel Drouet<sup>a</sup>, Areej Merhi<sup>b</sup>, Gilles Argouarch<sup>a</sup>, Frédéric Paul<sup>a</sup>, Olivier Mongin<sup>c</sup>, Mireille Blanchard-Desce<sup>c</sup>, Christine O. Paul-Roth<sup>a,b,\*</sup>

<sup>a</sup>Sciences Chimiques de Rennes, SCR-UMR CNRS 6226, Université de Rennes 1, 35042 Rennes Cedex, Université Européenne de Bretagne, France

<sup>b</sup>Institut National des Sciences Appliquées, INSA-SCR, 35043 Rennes Cedex, Université Européenne de Bretagne, France

<sup>c</sup>Chimie et Photonique Moléculaires UMR CNRS 6510, Université de Rennes 1, 35042 Rennes Cedex, Université Européenne de Bretagne, France

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### ABSTRACT

Two new dendrimeric supramolecular assemblies bearing twelve and twenty-four fluorenyl peripheral donor groups surrounding an organic core have been prepared and studied. These assemblies are composed of three zinc porphyrins possessing each four (**ZnTFP**) and eight fluorenyl chromophores (**ZnOOPF**) linked together by a central tris-pyridyl organic ligand. Due to efficient energy transfer between the fluorenyl arms, which act as antennas, and the Zn centres, which act as emitters; these assemblies behave as red emitters after selective UV or visible irradiation. The kinetic stability of these supramolecular assemblies and its impact on their photophysical properties are discussed.

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### 1. Introduction

Porphyrin systems present wide potential applications in different fields, such as, for instance, light-harvesting, Organic Light Emitting Diodes (OLEDs) or switches. For efficient solar energy harvesting, several chromophores are needed in order to collect light from the entire solar spectrum.<sup>1</sup> In this connection, the photosynthetic light-harvesting systems (I and II) consist of well organized porphyrin antennas in sophisticated three-dimensional structures.<sup>2</sup> As in nature, construction of multichromophoric systems is important to ensure maximum use of solar energy. Thus, the ability to design and construct (super- or supra-) molecular architectures in which the energy flow can be controlled constitutes a great (and timely) challenge.

We have previously reported the synthesis of porphyrins possessing several fluorenyl arms and focused on their photophysical properties,<sup>3–5</sup> along with their possible use in OLEDs.<sup>6</sup> Notably, a high fluorescence quantum yield (24%) was evidenced for **1**, demonstrating the good capacity of the fluorenyl units to enhance quantum yields by increasing the radiative deactivation process. By

the fact that **1** exhibits good red chromaticity and enhanced emission efficiency, it is now interesting to incorporate the corresponding zinc complex **3** and the related zinc porphyrin **4** in oligomeric assemblies and to study their luminescence.

Arrays containing different kinds of dyes can be engineered in several ways: either by using covalent bonds or by self-assembly. On the one hand, star-shaped trimer structures in which the porphyrin building blocks are connected covalently by a purely organic spacer have been largely studied. In 1999, Osuka synthesized a model of benzene connected in the 1,3 and 5 positions to three zinc porphyrins.<sup>7</sup> Other triangular spacers have been employed with the same 1,3,5 topology.<sup>8</sup> Subsequently, a series of arrays containing three, four and six tetraphenylporphyrin (**TPP**) units were synthesized.<sup>9</sup> For covalently bonded star-shaped pentamers, the use of (phenylethynyl)benzene spacers connected at the *meso* position of a central porphyrin unit has also been made by Lindsey and co-workers.<sup>10</sup> Recently, Sanders reported a large scale synthesis of tripodal porphyrin arrays: in these assemblies, the three zinc porphyrins are covalently linked by an alkyne bridge to a tripodal unit.<sup>11</sup> On the other hand, supramolecular approaches offer an alternative way to assemble the nano-objects in a desired manner, like in the photosynthetic light-harvesting complexes. An interesting approach for mimicking these complicated systems is to design small-sized chromophores, which can self-organize into light-harvesting architectures. Supramolecular synthetic methods<sup>12</sup> have

\* Corresponding author. Tel.: +33 (0)2 23 23 63 72; fax: +33 (0)2 23 23 56 37; e-mail addresses: [christine.paul@univ-rennes1.fr](mailto:christine.paul@univ-rennes1.fr), [christine.paul@insa-rennes.fr](mailto:christine.paul@insa-rennes.fr) (C.O. Paul-Roth).

developed rapidly and porphyrins proved particularly useful for the design of robust architectures because of their rigid framework.<sup>13</sup> One-, two-, and three-dimensional materials are now routinely accessible by synthetic strategies based on hierarchical organization of porphyrins. Thus, porphyrins are very useful not only as active molecular components for light-harvesting antenna systems, but also as rigid building blocks for the construction of variety of functional devices.<sup>14</sup>

In the present contribution, the synthesis of the desired porphyrin trimer is based on the pyridine-to-metal coordination. Thus, porphyrins are connected by dative bonds to a new kind of organic bridge having three pyridine sites pointing at 120° from each other.<sup>15</sup> This bridge consists of an original tripodal ligand (**7**), which was synthesized in a straightforward way from a readily available tris-alkynyl isocyanurate precursor, independently developed by some of us.<sup>15</sup> Such a ligand is expected to exhibit a better transparency in the near UV and visible range, and therefore to impart a higher photostability to the supramolecular assembly than related 1,3,5-phenylene based derivatives. Two different porphyrins were used to test this approach: (i) the known monomeric zinc porphyrin **3** bearing four fluorenyl units rigidly held on the *meso* positions and (ii) a new zinc porphyrin mentioned above (**4**), bearing eight pendant fluorenyl units more flexibly connected to the same positions via methylene linkers. Following the synthesis of these new building blocks, we will describe the self-assembly and characterization of the desired porphyrin oligomers **5** and **6**, respectively. Finally, the photophysical studies of the building blocks and related supermolecular systems will be reported and discussed.

## 2. Results and discussion

### 2.1. Synthesis

**Zinc porphyrins 3 and 4.** The *meso*-tetrafluorenylporphyrin free base **1** was prepared as previously reported,<sup>16</sup> while the synthesis of the dendrimeric free base **2**<sup>17</sup> is based on the condensation reaction reported by Fréchet. The metallation of these porphyrin monomers by zinc acetate proceeds in dichloromethane at reflux,<sup>18</sup> to give the corresponding zinc porphyrins **3**<sup>5</sup> and **4**, in 87% and 81% yield, respectively (Scheme 1). The new complex **4** was fully characterized by means of NMR spectroscopy, microanalysis and high resolution mass spectrometry.

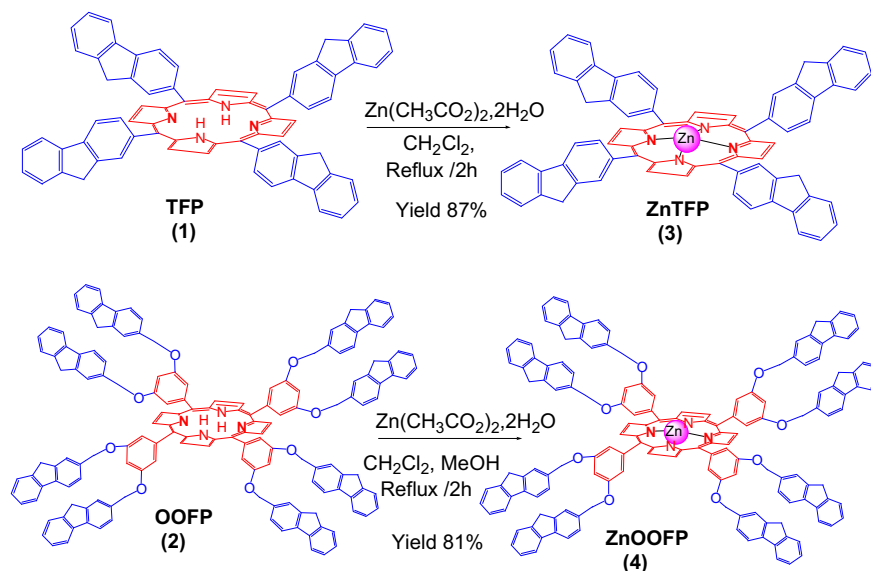
**New tris-pyridyl spacer 7.** This new isocyanurate-based ligand was obtained in one step from the corresponding triyne **8**,<sup>15</sup> and 4-bromopyridine (**9**) following a Sonogashira coupling protocol in DMF (Scheme 2). After purification, **7** is obtained as a beige solid in 51% yield. This new ligand was also fully characterized by usual means. Its high symmetry allows monitoring the progress of the catalytical coupling reaction, in a straightforward way, by <sup>1</sup>H NMR.

**Supramolecular assemblies 5 and 6.** To a solution of 3 equiv of **3** or **4** in CH<sub>2</sub>Cl<sub>2</sub>, 1 equiv of tris-pyridyl ligand **7** is added (Scheme 3). After 1 h, the desired porphyrin trimers **5** or **6** can be isolated, as deep violet powders. These new products were characterized by usual solution spectroscopies (NMR, UV–vis and IR) and microanalysis, but proved too fragile to be characterized by mass spectrometry, since only the constitutive fragments were detected by LSI-MS.

Ligation of pyridyl rings to zinc porphyrins is intrinsically weak (association constant, ca.  $1 \times 10^3 \text{ M}^{-1}$ ) and relatively labile; thus, in solution, coordination oligomers are generally in equilibrium with the monomers.<sup>19</sup> For these supramolecular systems, stability in (dilute) solution is therefore a key question. The stability of the supramolecular assemblies **5** and **6** in CH<sub>2</sub>Cl<sub>2</sub> solution was thus checked by a combination of <sup>1</sup>H NMR, UV–vis absorption and spectrofluorimetric measurements.

The <sup>1</sup>H NMR signals obtained in deuterated chloroform for zinc complexes **3** and **4** are fine and well resolved. A clear difference in shift is observed for the bridging tripodal ligand **7** when free and in the corresponding assemblies **5** and **6** (Figs. 1 and 2). The latter is induced by axial coordination of **7** to zinc porphyrin units. In both cases, H–H polarization transfer studies (COSY) allowed to assign the various signals detected, the integration of the signals revealed that adducts **5** and **6** have the correct stoichiometry.

For example, the <sup>1</sup>H NMR spectrum of **5** reveals the two <sup>1</sup>H resonances of the pyridine units, H<sub>A</sub> and H<sub>B</sub>, significantly upfield of their positions in **7**, as expected for protons located within the shielding cone of a porphyrin (Fig. 2).<sup>19,20</sup> This effect decreases gradually as the proton distance from the shielding macrocycles increases, with  $\Delta\delta = -3.0$  and  $\Delta\delta = -0.8$  for H<sub>A</sub> and H<sub>B</sub>, respectively. These signals are also broader and less resolved, in line with the highly fluxional nature of the ligand at ambient temperature. In addition, we can notice that all the twelve peripheral protons on the porphyrin *meso*-fluorene arms are equivalent. Similar statements hold for the larger assembly **6**, except that H<sub>A</sub> is not observed at 25 °C, in reason of its strong fluxionality.



Scheme 1. Synthesis of zinc complexes **3** and **4**.

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