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Graphical Abstract

New luminescent fluorenyl-armed linear porphyrin trimers with diphenylacetylene bridges

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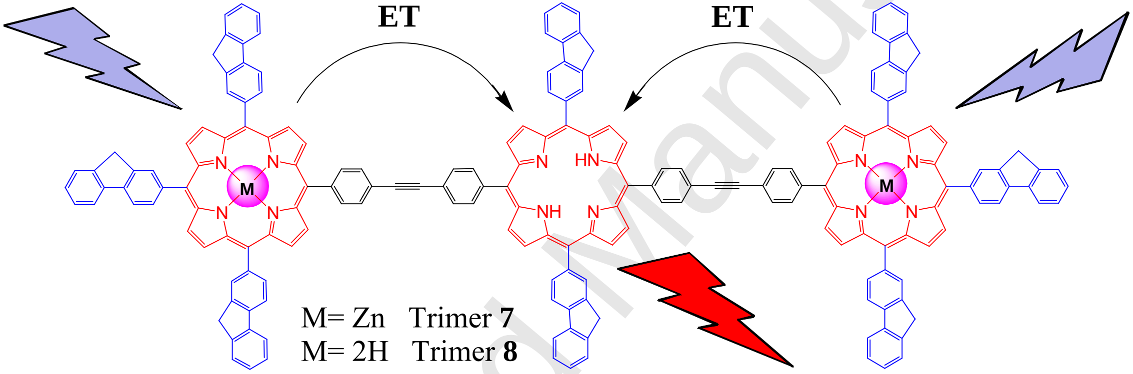

New luminescent fluorenyl-armed linear porphyrin trimers with diphenylacetylene bridges

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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.

Keywords : Porphyrins; Fluorene; trimer; diphenylacetylene; Luminescence

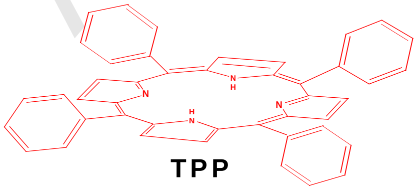
1. Introduction

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.

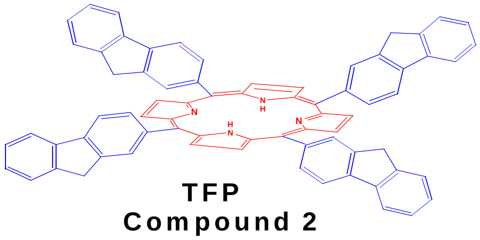
Different ways to connect porphyrins have been studied earlier; one of the first examples, in 1976, was the synthesis of diporphyrins and triporphyrins bridged by an ester bond for energy and electron transfer in biological processes.[3] Later in 1983, porphyrins connected by ether bond were used for 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 synthesised 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 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**).



TPP
Compound 1



TFP
Compound 2

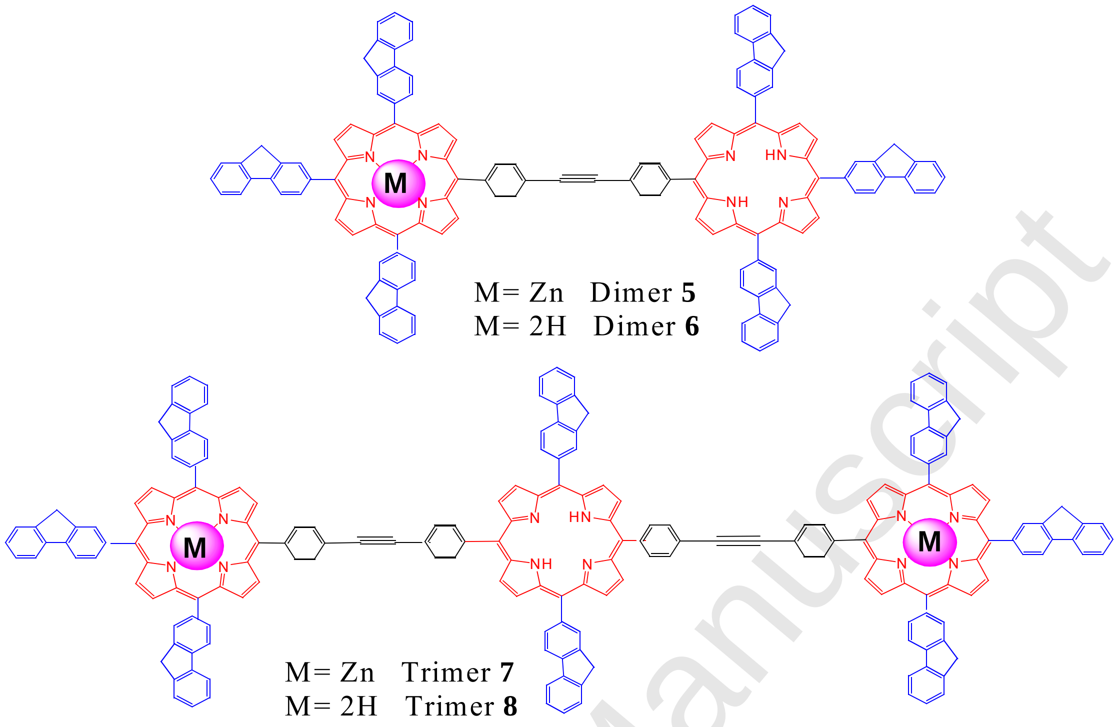


Figure 1: Monomers **1, 2** and dimers **5, 6** and target trimers **7, 8**

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 used were of HPLC grade. Commercially available reagents were used without further purification unless otherwise stated. Pyrrole and 2-fluorenecarboxaldehyde were purchased from Aldrich and were used as received. References **TFP** = tetrafluorenylporphyrin, **TPP** = tetraphenylporphyrin. ^{1}H NMR and ^{13}C NMR in $CDCl_3$ were recorded using Bruker 200 DPX, 300 DPX and 500 DPX spectrometers. The chemical shifts are referenced to internal TMS. The assignments were performed by 2D NMR experiments: COSY (Correlation

Spectroscopy), HMBC (Heteronuclear Multiple Bond Correlation) and HMQC (Heteronuclear Multiple Quantum Coherence). UV spectra were recorded on UVIKON XL from Biotek instruments. PL emission was recorded on a Photon Technology International (PTI) apparatus coupled on an 814 Photomultiplier Detection System, Lamp Power Supply 220B and MD-5020. *Steady-state fluorescence* measurements were performed at room temperature (R. T.) with dilute solutions (ca. 10^{-6}M) using an Edinburgh Instruments (FLS 920) spectrometer working in photon-counting mode, equipped with a calibrated quantum counter for excitation correction. Fluorescence quantum yields were measured using standard methods; **TPP** in DCM ($\Phi = 0.12$ at $\lambda_{ex} = 417$ nm) was used as a reference. The reported fluorescence quantum yields are within ± 10%.

2.2. Synthesis of the Monomers

*2.2.1. Synthesis of 5,10,15-tris(9H-fluoren-2-yl)-20-(4-ethynylphenyl)porphyrinato Zn(II) (**12**).*

First, the synthesis of 4-((trimethylsilyl)ethynyl)benzaldehyde **9** was done following given reference.[24] Then, 2-Fluorenecarboxaldehyde (3.00 g, 15.4 mmol), 4-trimethylsilylbenzaldehyde (1.03 g, 5.1 mmol) and pyrrole (1.4 mL, 20.5 mmol) were added to distilled chloroform (1.5 L). The expected compound **10** was obtained as a purple solid to yield 756 mg (15%).[21] For the Synthesis of 5,10,15-tris(9H-fluoren-2-yl)-20-(4-ethynylphenyl)porphyrin (**11**): a solution of porphyrin **10** (200 mg, 0.21 mmol) in distilled DCM (36 mL) and distilled methanol (12 mL) was prepared in a schlenk tube under argon. Potassium carbonate (145 mg, 1.05 mmol) was added and the reaction mixture was stirred during 47 h at R.T. The deprotected porphyrin **11** was obtained as a purple powder to yield 187 mg (98%).[21] For the Synthesis of 5,10,15-tris(9H-fluoren-2-yl)-20-(4-ethynylphenyl)-porphyrinato Zn(II) (**12**) : A solution of porphyrin **11** (185 mg, 0.2 mmol) in distilled DCM (127 mL) and distilled methanol (63 mL) was prepared in a schlenk under argon. Then, $Zn(CH_3CO_2)_2.2H_2O$ (220 mg, 1.0 mmol) was added and the reaction mixture was stirred during 24h at room temperature. The metallated porphyrin **12** was obtained as a purple solid to yield 188 mg (97%), for complete work up see previous reference of our groups.[21]

*2.2.2. Synthesis and characterization of new 5, 15-(9H-fluoren-2-yl)- 10,20-(4-iodophenyl)porphyrin (**13**).*

A solution of p-iodobenzaldehyde (2.12 g, 9.2 mmol), 2-fluorenecarboxaldehyde (1.80 g, 9.2 mmol) and pyrrole (1.27 mL, 18.4 mmol) in distilled chloroform (1.5 L) was placed in a two necked flask under an argon atmosphere. The chloroform solution was degassed by argon bubbling for 20 minutes, the flask was protected from light and boron trifluoride diethyl etherate; $BF_3.OEt_2$ (560 µL) was added with a syringe. The solution was stirred for 2 hours at room temperature, then, three equiv of the oxidant, p-chloranil (3.78 g, 15.4 mmol) are added and the reaction mixture was refluxed for 1 h (light protection was removed). After neutralization of the acid catalyst by triethylamine, the solvent was removed, and the resulting black solid was purified by two column chromatographies (column 1: CH_2Cl_2/pentane 1:1; column 2: CH_2Cl_2/pentane 1:4) affording 407 mg (9%) of the desired porphyrin **13** as a purple solid. New intermediate porphyrin **13** was characterized; the hydrogen atom-labeling scheme for this synthon is shown in **Figure 2**. ^1H NMR (400 MHz, $CDCl_3$, δ in ppm) : 8.95 (d, 4H, $^3J_{HH}$ = 5.0 Hz, $H_{\beta\text{-pyrrolic}}$); 8.85 (d, 4H, $^3J_{HH}$ = 5.0 Hz, $H_{\beta\text{-pyrrolic}}$); 8.40 (s, 2H, $H_{fluorenyl}$, H_1); 8.26 (d, 2H, $^3J_{HH}$ = 8.0 Hz, $H_{fluorenyl}$, H_4); 8.17 (d, 2H, $^3J_{HH}$ = 8.0 Hz, $H_{fluorenyl,}$ H_3); 8.12 (d, 4H, $^3J_{HH}$ = 8.0 Hz, H_{phenyl}, H_A); 8.06 (d, 2H, $^3J_{HH}$ = 7.6 Hz, $H_{fluorenyl,}$ H_5); 7.98 (d, 4H, $^3J_{HH}$ = 8.0 Hz, H_{phenyl}, H_B); 7.70 (d, 2H, $^3J_{HH}$ = 7.6 Hz, $H_{fluorenyl,}$ H_8); 7.55 (t, 2H, $^3J_{HH}$ = 7.6 Hz, $H_{fluorenyl,}$ H_6); 7.46 (t, 2H, $^3J_{HH}$ = 7.6 Hz, $H_{fluorenyl,}$ H_7); 4.20 (s, 4H, $CH_{2\text{-fluorenyl}}$); -2.60 (s, 2H, NH). UV-vis (λ max, CH_2Cl_2, nm) : 288, 424; Q bands : 513, 550, 590, 645. MALDI TOF-MS calcd for $C_{58}H_{36}I_2N_4$: 1043.10294 $[MH]^+$, found 1043.15030 $[MH]^+$. Analysis: calcd for $C_{58}H_{36}I_2N_4{\cdot}3CHCl_3$: C, 52.30 ; H, 2.81 ; N, 4.00 ; found C, 51.75 ; H, 2.87 ; N, 2.73.

*2.3. Synthesis of Trimers **7** and **8***

*2.3.1. Synthesis and characterization of new trimer **7**.*

To a solution of 2 equiv of **12,** 5,10,15-tris(9H-fluoren-2-yl)-20-(4-ethynylphenyl)porphyrinato Zn(II) (80 mg, 0.08 mmol) and 1 equiv of **13**, 5,15-(9H-fluoren-2-yl)-10,20-(4-iodophenyl)porphyrin (36 mg, 0.04 mmol), 0.3 equiv of $Pd_2(dba)_3.CHCl_3$ (11 mg, 0.01 mmol) are added. Then, 2.4 equiv of $AsPh_3$ (25 mg, 0.083 mmol) in 20 mL of freshly distillate THF and 6 mL of triethylamine were added. This solution was stirred for 5 days at 35 °C under argon. Then, the reaction mixture was cooled at room temperature, filtered rapidly over silica gel with DCM and evaporated to dryness. The residue was purified by column chromatography on silica gel using a mixture heptane/DCM 40/60 as an eluent affording the desired product **7**, as a dark red powder with a yield of 10%. The reaction was followed by MALDI-TOF MS as well as by NMR. The hydrogen and carbon atom-labeling scheme for the porphyrin trimer **7** as well as for precursors **12** and **13** are shown in **Figure 2** and **3**. This new compound **7** is very soluble in most organic solvents and can be purified by precipitation (THF, heptane). Compound 7 is well-behaved in silica gel chromatography and was fully characterized by usual solution spectroscopies (NMR and mass spectrometry) and microanalysis. ^1H NMR (400 MHz, $CDCl_3$, δ in ppm) : 9.03 (m, 16H, $H_{\beta\text{-pyrrolic}}$); 8.97 (m, 8H, $H_{\beta\text{-pyrrolic}}$); 8.40 (s, 8H, $H_{\text{fluorenyl}}$, H_1); 8.32 (m, 8H, H_{phenyl}); 8.26 (m, 8H, $H_{\text{fluorenyl}}$, H_4); 8.17 (m, 8H, $H_{\text{fluorenyl,}}$ H_3); 8.06 (m, 16H, $8H_{\text{fluorenyl:}}$ H_5 and $8H_{\text{phenyl}}$); 7.69 (m, 8H, $H_{\text{fluorenyl,}}$ H_8); 7.53 (large t, 8H, $H_{\text{fluorenyl,}}$ H_6); 7.43 (large t, 8H, $H_{\text{fluorenyl,}}$ H_7); 4.21 (m, 16H, $8CH_{2\text{-fluorenyl}}$). ^{13}C NMR ($CDCl_3$): 150.6-150.4 (m, C_q, $C_{1\text{-}4\text{-}6\text{-}9\text{-}11\text{-}14\text{-}16\text{-}19}$); 143.8 ($C_q$, $C_{9''}$); 141.6 (m,C_q, $C_{4''}$, $C_{8''}$, $C_{5''}$); 133.4 (C_q, $C_{2'}$, $C_{4'}$); 132.1 (m, CH, $C_{2\text{-}3\text{-}7\text{-}8\text{-}12\text{-}13\text{-}17\text{-}18}$); 131.3 ($C_{1'}$); 127.0 ($C_{6'}$ and $C_{7'}$);125.2 ($C_{8'}$); 120.6-120.3 (m, C_q, $C_{5\text{-}10\text{-}15\text{-}20}$); 120.2 ($C_{5'}$); 117.8 ($C_{3'}$); 114.6, 37.1 ($C_{9'}$). Rf on silica plate using DCM/heptane (60 : 40) : 0.32. UV-vis (λ max, (ε, 10^{-3} $M^{-1}.cm^{-1}$), CH_2Cl_2, nm) : 265 (160), 429 (1 035), 521 (22), 555 (54), 596 (24), 649 (4). FT-IR (n, KBr, cm^{-1}): 2363 (C≡C). Analysis: calcd for $C_{192}H_{114}N_{12}Zn_2\cdot 6CHCl_3$: C, 69.21; H, 3.52; N, 4.89; found C, 68.72; H, 4.06 ; N, 4.31. MALDI TOF-MS calcd for $C_{192}H_{114}N_{12}Zn_2$: 2715.78723 $[MH]^+$; found : 2715.66750 $[MH]^+$.

*2.3.2. Synthesis and characterization of the free trimer **8**.*

Compound **8** was obtained from the bis-zinc complex **7** by acidic treatments as following: to a solution of 1 equiv of trimer **7** (10 mg, 0.005 mmol), in 5 mL of freshly distilled DCM under argon, was added trifluoroacetic acid in large excess (TFA, 0.05 mL, 75 mg, 0.66 mmol), immediately, the dark red DCM solution turned green. The reaction mixture was stirred for 30 min at room temperature and was controlled by UV-Visible spectrometry to be sure that zinc was entirely eliminated from the porphyrin macrocycle, to obtain the totally free and protonated porphyrin trimer. Finally, TEA was added to neutralize this dark green solution, to obtain the free, but non protonated porphyrin trimer **8**. The red solution was stirred for 30 min at room temperature. Then, the residue was filtered on silica gel using DCM as eluent to afford neutral **8**, as a pure product: a dark red powder with 95% yield. ^1H-NMR (300 MHz, $CDCl_3$, δ in ppm): 9.06 (m, 16H, $H_{\beta\text{-pyrrolic}}$); 9.05 (m, 8H, $H_{\beta\text{-pyrrolic}}$); 8.43 (m, 8H, $H_{\text{fluorenyl}}$, H_1); 8.28 (m, 16H, $H_{\text{fluorenyl}}$: H_4 and $8H_{\text{phenyl}}$); 8.18 (m, 8H, $H_{\text{fluorenyl,}}$ H_3); 8.07 (m, 16H, $8H_{\text{fluorenyl:}}$ H_5 and 8 H_{phenyl}); 7.71 (m, 8H, $H_{\text{fluorenyl,}}$ H_8); 7.54 (large t, 8H, $H_{\text{fluorenyl,}}$ H_6); 7.44 (large t, 8H, $H_{\text{fluorenyl,}}$ H_7); 4.22 (m, 16H, $8CH_{2\text{-fluorenyl}}$) ; -2.70 (s, 6H, NH). UV-vis (λ max, (ε, 10^{-3} $M^{-1}.cm^{-1}$), CH_2Cl_2, nm) : 263 (299), 427 (1 023), 520 (47), 557 (44), 594 (22), 649 (16). FT-IR (n, KBr, cm^{-1}): 2363 (C≡C). HRMS (ESI) calcd for $C_{192}H_{118}N_{12}$: 2591.9675 $[MH]^+$; found : 2591.9590 $[MH]^+$. MALDI TOF-MS calcd for $C_{192}H_{118}N_{12}$: 1296.4874 $[M+2H]^{2+}$; found : 1296.4870 $[M+2H]^{2+}$.

3. Results and discussion

3.1. Synthetic strategy

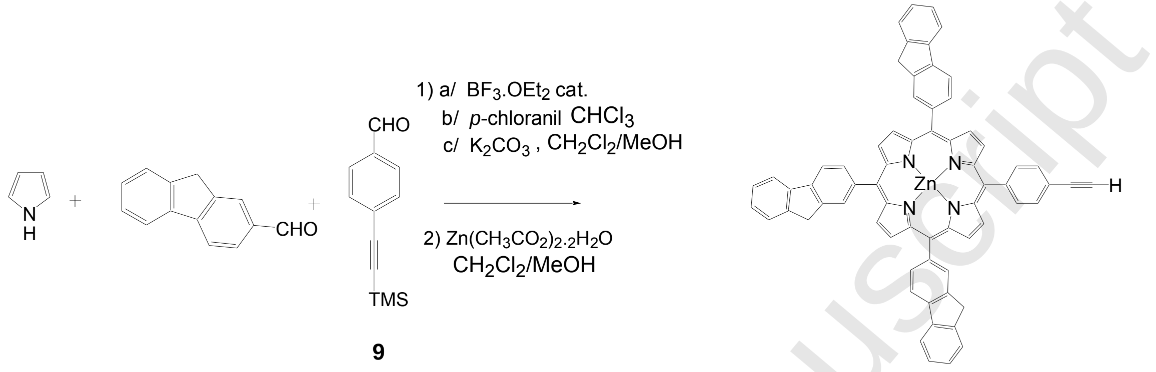
The aim of this work consists in the synthesis of porphyrin trimers composed of two types of porphyrins: one substituted at three positions by *meso* fluorenyl units and an acetylenic group on purpose to future link by a tolane (phenyl-C≡C-phenyl) bridge, another, in the middle, with two fluorenyl units in the *meso* positions with two activable iodo groups to link in trans with two same bridges. The synthetic strategy is based on the coupling of two metallized A_3B porphyrins, and another A_2B_2 free base. The trisporphyrin assembly is made by Sonogashira coupling, under conditions optimized by Lindsey.[8, 9]

First, we will describe the synthesis of the intermediate porphyrins **12** and **13,** possessing different anchoring points. In a second time, intermediate **12** and **13** are connected to obtain the trimer zinc complex porphyrins **7** and finally by dematallation : free trimer **8**.

It should be noted that in the conditions used, the non-substituted methylene of the fluorenyl arm is stable but alkyl chains have often been introduced on the position-9 of the fluorenyl units to increase the solubility.[25] For this project, due to the encouraging results obtained for synthesis of the monomers and dimers, this was voluntary avoided.

*3.1.1. Preparation of the intermediate zinc porphyrin complex **12***

First, the synthesis *of 4-((trimethylsilyl)ethynyl)benzaldehyde* **9**, is done in one step by Sonogashira coupling reported in 1981.[24] The aldehyde **9** is obtained as a white powder with a yield of 92%. Then, the protected A_3B free-base porphyrin **10**, was prepared from two aldehydes: the fluorenylcarbaldehyde (commercial) and previously prepared 4-((trimethylsilyl)ethynyl)benzaldehyde **9**. The synthesis of porphyrin **10** is made by the method of Lindsey: it consists in mixed condensation between two different aldehydes and pyrrole (Scheme 1) as described by us in 2013.[21] Porphyrin **10** is isolated as a purple solid with a yield of 15%. The porphyrin **10** is then basified to give the free-base porphyrin **11**, with the deprotected acetylenic function (Scheme 1). Deprotected porphyrin **11** was obtained as a dark red-violet powder with a yield of 98%. The free base porphyrin **11** is then metallated in the presence of 5 equiv of zinc acetate, $Zn(CH_3CO_2)_2.2H_2O$, to give the zinc porphyrin complex **12** (Scheme 1). The zinc complex **12** is obtained as a dark red powder with a yield 97%.[21]

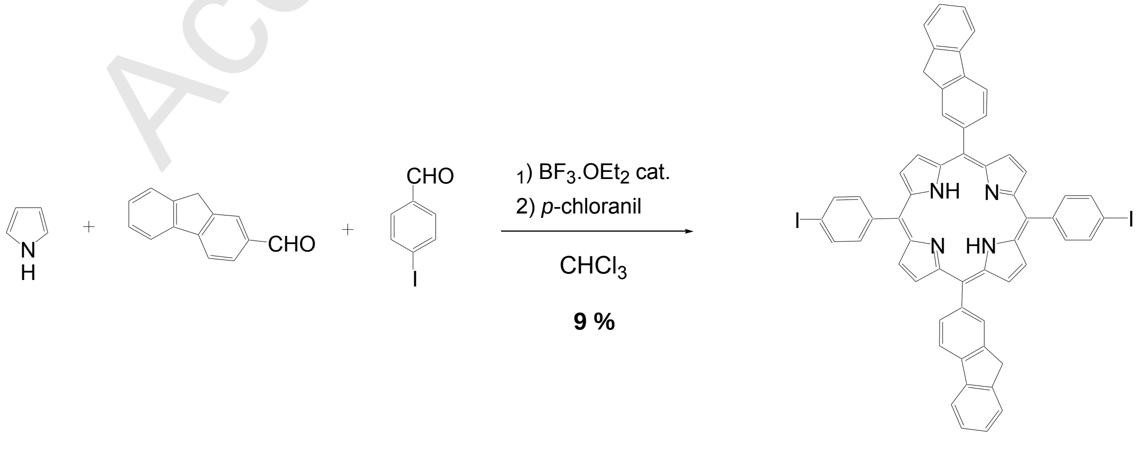


12

Scheme 1: Synthesis of zinc porphyrin complex **12**

3.1.2. Synthesis and characterization of new porphyrin-free base ***13****, possessing two fluorenyl arms.*

The second type A_2B_2 porphyrin, is prepared in one step, according to the method of Lindsey and consists in mixed condensation between two aldehydes and pyrrole (Scheme 2), the reaction is by the Lewis acid: $BF_3.OEt_2$. Porphyrin **13** is isolated as a violet powder, from other reaction products (polymers as well as mono fluorenyl, tri fluorenyl, etc.) by several successive chromatographies on silica gel, with a yield of 9%. New intermediate diodoporphyrin **13** was characterized; the hydrogen and carbon atom-labeling scheme are shown in **Figure 2**.



13

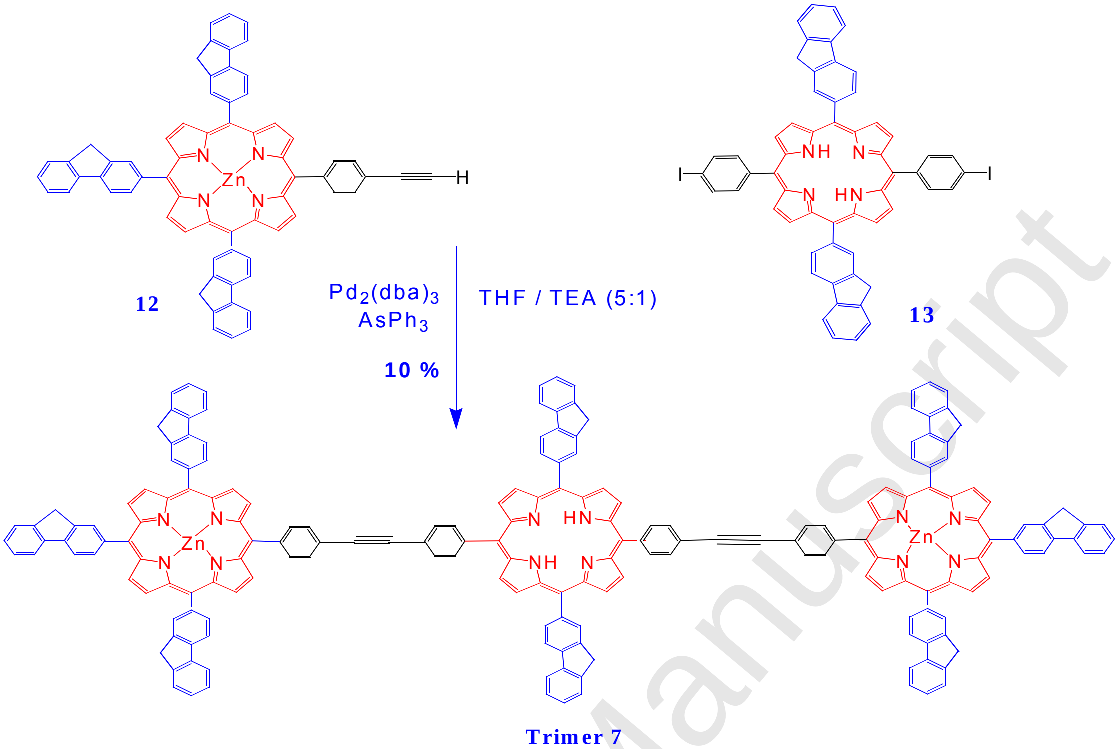
Scheme 2: Synthesis of new porphyrin-intermediate **13**

*3.1.3. Synthesis and characterization of the new trimer possessing eight fluorenyl arms **7**.*

We have to link by rigid bridges, three porphyrins with in the middle; one free-base **13** and at the ends; two others zinc metallated **12**. These linkers, are phenyl-phenyl triple bonds. This new trimer possesses in full eight fluorenyl groups directly attached in *meso* position; this should exalt the luminescence.

First, the reaction is performed by adding zinc porphyrin complex **12** and free base diodo-porphyrin **13** in a mixture of (THF/triethylamine) in the presence of a Pd(0) catalyst and a large excess of triphenylarsine ($As(Ph)_3$) as a ligand (Scheme 3). These conditions optimized by Lindsey[9, 26] are preferred to standard conditions for Sonogashira coupling involving copper iodide, in order to avoid any risk of porphyrin copper formation. This solution was stirred for 5 days at 35 °C under argon, then; the reaction mixture was cooled at room temperature, filtered rapidly over silica gel with DCM and purified by column chromatography affording the desired product **7**, as a dark red powder with a yield of 10%.

The connection of all three units was confirmed by matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) as well as by NMR. The hydrogen and carbon atom-labeling scheme for the trimer **7** as well as for precursors **12** and **13** are shown in **Figure 2** and **3**. This new compound **7** is very soluble in most organic solvents and can be purified by precipitation (THF, heptane). Compound **7** is well-behaved in silica gel chromatography and was characterized by usual spectroscopies in solution (NMR and UV-Vis) and microanalysis.



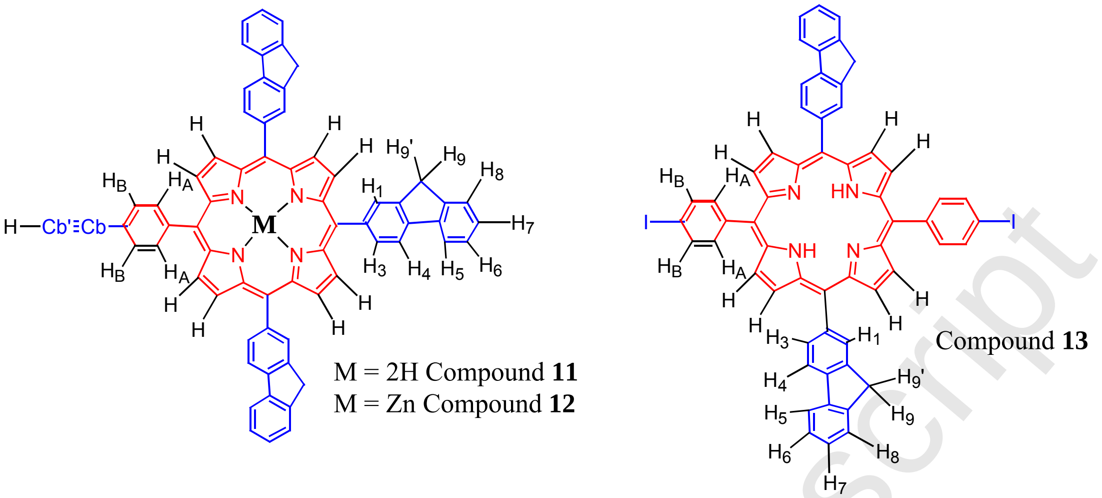
Scheme 3: Synthesis of trimer **7**

*3.1.4. Synthesis and characterization of the free trimer **8** possessing eight fluorenyl arms.*

This new trimer **8** was obtained from the previous bis-zinc complex **7** by acidic treatments with a Bronsted acid, like trifluoro-acetic acid (TFA), the dark red DCM solution turns immediately green. The reaction mixture was stirred and controlled by UV-Vis spectrometry, to be sure the entire zinc complex is eliminated and to obtain the totally free and protonated porphyrin trimer. Finally, a base; TEA was added to neutralize acid and to get a red solution, to obtain the free, not protonated porphyrin trimer **8**. Then, the residue was purified by column chromatography on silica gel using DCM to obtain neutral **8**. This free trimer **8** was characterized by NMR, UV-Vis, and by mass spectrometry (MALDI-TOF MS) as well as by HRMS.

3.2. NMR studies

The ^{1}**H-NMR** signals obtained in deuterated chloroform for porphyrins **11**, **12**, **13** and finally **7** and **8**, were carried out at room temperature.



M = 2H Compound **11**
M = Zn Compound **12**

Compound **13**

Figure 2: Hydrogen and carbon atom-labeling for porphyrins **11**, **12** and for diiodo porphyrin-intermediate **13.**

*3.2.1. Characterization of zinc complex **12**.*

For this zinc complex and for the corresponding free macrocycle **11**, there is only a clear difference for the protons carried by the nitrogen atoms in the heart of the porphyrin; around -3 ppm, these protons are not observed for the zinc complex **12**. The other proton signals are quite similar.

*3.2.2. Characterization of compound **13**.*

At high field, around -3 ppm, we observe the protons carried by the nitrogen atoms in the core of the porphyrin. At 4.2 ppm, are the CH_2 protons of the two fluorenyl groups. In the region between 7.5 and 8.5 ppm resonate the aromatic protons (fluorenyl and phenyl) of the porphyrin *meso* substituents: we can notice that all the seven protons on the two fluorenyl arms are equivalent, and in expected position: 8.40 (s, 2H); 8.26 (d, 2H); 8.17 (d, 2H); 8.06 (m, 2H); 7.70 (d, 2H); 7.55 (t, 2H) and 7.46 (t, 2H). At low field; around 9 ppm, there are two signals, an AB system; two doublets, for four protons each; they are all assigned to the protons pyrrole-β.

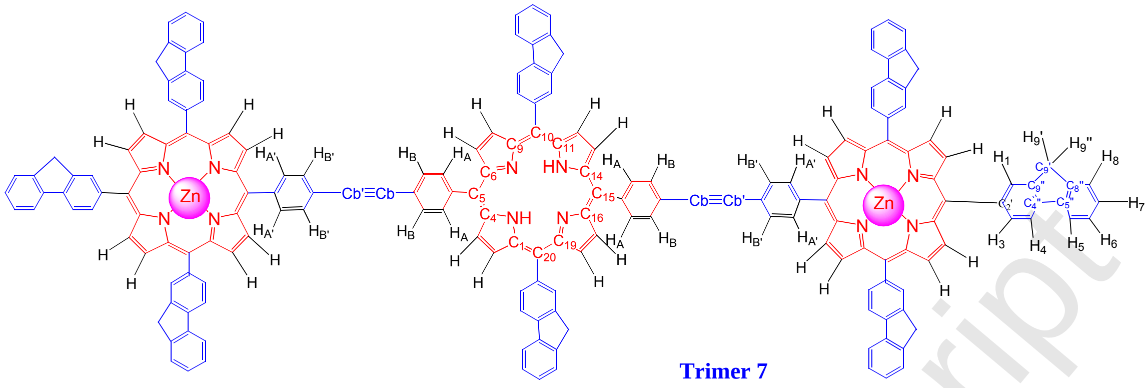


Figure 3: Hydrogen and carbon atom-labeling for new Trimer **7**

*3.2.3. Characterization of bis zinc trimer **7**.*

Around -3 ppm, the two protons carried by the nitrogen atoms of the porphyrin-free base in the center of the trimer are not observed. At 4.2 ppm, there is a large singlet for the sixteen protons of the CH_2 protons of fluorenyl groups. In the region between 7.4 and 8.4 ppm resonate the aromatic protons (fluorenyl and phenyl) of the porphyrin *meso* substituents: we can notice that all the seven protons on the eight fluorenyl arms are equivalent, and in expected position: 8.40 (s, 8H); 8.26 (m, 18H); 8.17 (m, 8H); 8.06 (m, 8H); 7.69 (m, 8H); 7.53 (t, 8H); 7.43 (t, 8H). Around 9 ppm, there are three signals, a singulet integrating for eight protons and a doublet for eight protons and another doublet for eight protons as well, assigned to the protons pyrrole-β, due to the symmetry of this molecule **7**. One can note the disappearance of the singlet corresponding to the acetylenic proton at 3.33 ppm of the starting zinc porphyrin complex **12** (**Figure 4**).

*3.2.4. Characterization of free trimer **8**.*

Between this free base and the corresponding bis-zinc complex **7**, there is only a clear difference for the protons carried by the nitrogen atoms in the core of the porphyrin; around -3 ppm, these protons are not observed for the zinc complex **7**. The other proton signals are quite similar (**Figure 4**).

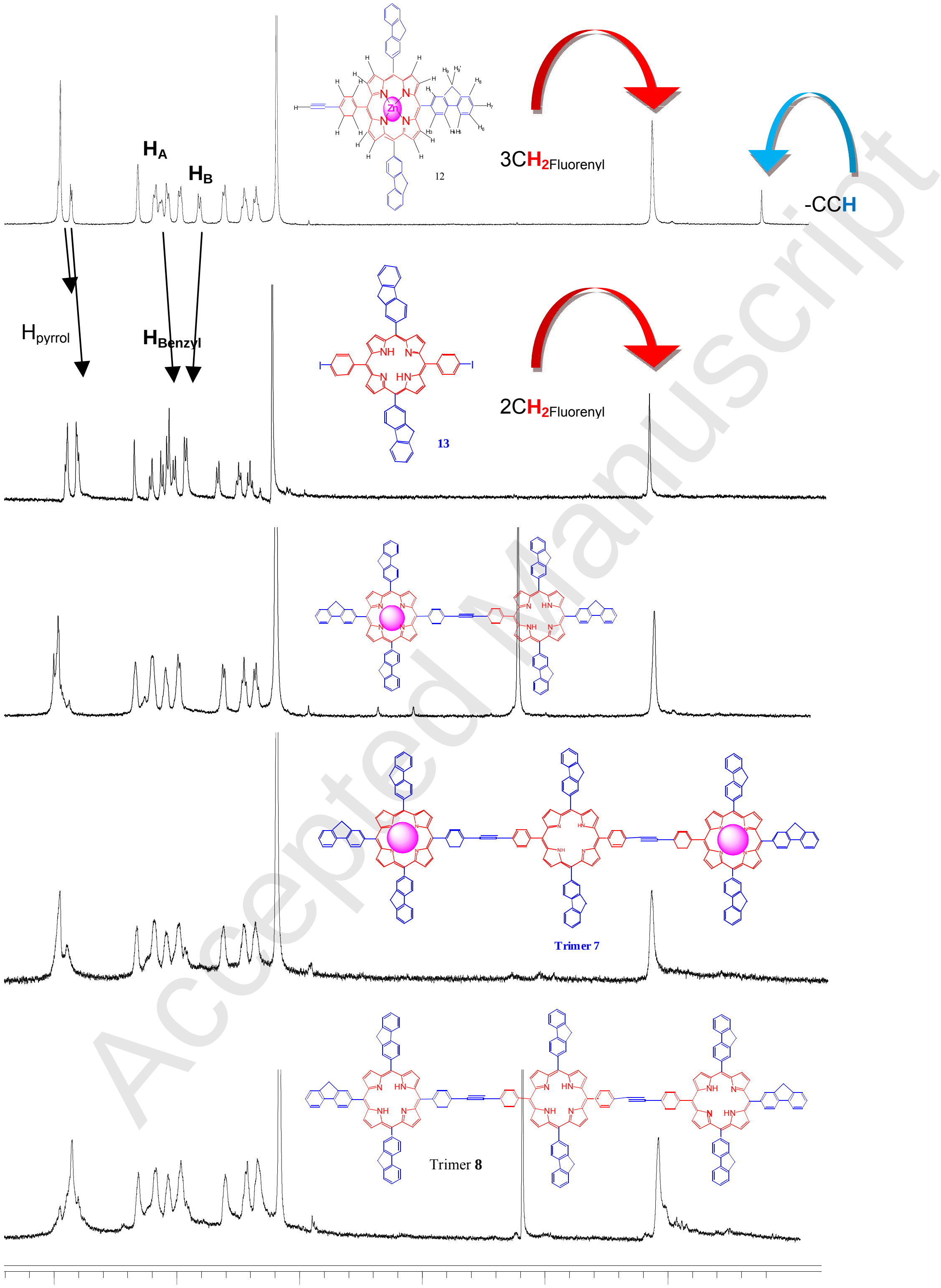


Figure 4: ^{1}H-NMR studies (in $CDCl_3$) of Dimer **5** (with a CH_2Cl_2 peak), trimers **7** and **8**, in comparison to zinc porphyrin complex **12** (on the top) and for diiodo porphyrin-intermediate **13** showing the shift as indicated by the arrows.

3.3. Photophysical properties

3.3.1 Absorption spectra.

The recording of the UV-visible absorption spectra of the porphyrins **11**, **12**, **13**, dimers **5** and **6,** and finally trimers **7** and **8** was carried out at room temperature in dichloromethane. For these compounds, measurements at different concentrations were performed; a more concentrated solution is used to display the Q bands and a less concentrated for the Soret band of porphyrin (Figure 5a). We will first consider the two parent molecules: free porphyrin **13** and zinc complex **12** and then the new trimer **7**.

The UV-visible spectra of free porphyrin **13** exhibit an intense Soret band with a maximum absorption around 422 nm and four Q bands characteristic of a porphyrin free base which are located at 513 nm, 550 nm, 590 nm and 645 nm. In addition, there is a broad band at 288 nm corresponding to the absorption of the two fluorenyl arms (Figure 5a). The Soret band is slightly red shifted compared to 417 nm for **TPP** (**1**), but not as much as for **TFP** (**2**) (426 nm). This tendency in red shifting is observed as well for the Q bands (Table 1). The π-π* absorption in the UV range is clearly apparent, due to the presence of fluorenyl arms: for reference compound **2**, the four fluorenyls absorb with a maximum absorption peak at 272 nm, while for compound **11** possessing only three arms the absorption is weaker with a maximum at 275 nm, and for compound **13** with only two fluorenyl arms the absorption is weaker at 288 nm.

Zn(II) porphyrin complexes exhibit characteristic change in the electronic spectra compared to the free-base porphyrins. The absorption spectra of Zn(II) porphyrins display a single Q band absorption which is a combination of the Q_X and Q_Y bands due to the D_{4h} symmetry of metal porphyrins, instead of the D_{2h} symmetry of free base porphyrins, with two discernible sub-bands (Q(0,1) and Q(0,0)).[27-29] Thus, the zinc complex **12** exhibit an intense Soret band at 426 nm, together with two weak Q-bands in the visible range: located at 554 nm and 595 nm (Table 1). An additional broad band is also observed in UV range which corresponds to π-π* absorption of the three fluorenyl chromophores. As mentioned before, the UV absorption, at 273 nm, is weaker for the zinc complex **12** than for reference **TFP** (**2**), due to the smaller number (three *vs.* four) of fluorenyl groups (Figure 5a).

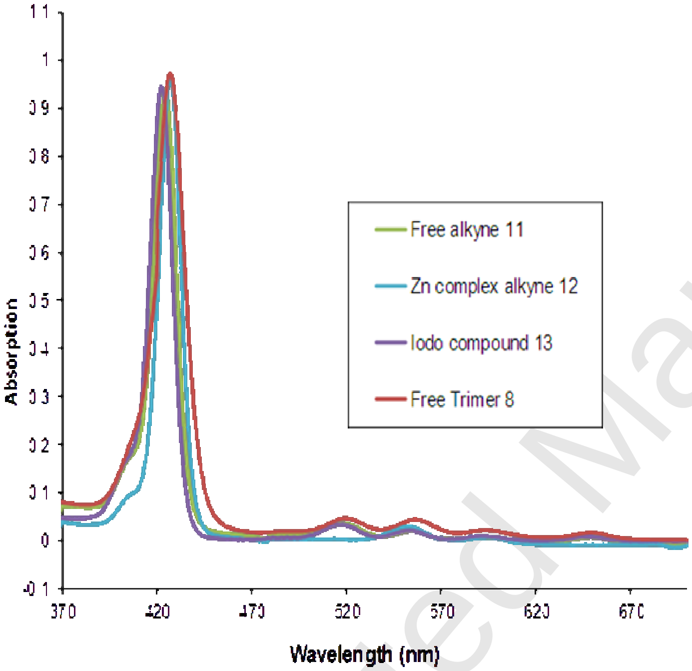
The absorption spectrum of porphyrin trimer **7** shows the presence of a Soret band at 429 nm and four sub-bands which are located at 521 nm (Qy(0, 1), very weak), 555 nm (Qy(0, 0), strong), 596 nm (Qx(0, 1), strong) and 649 nm (Qx(0, 0), weak), corresponding to the superposition of visible absorption of a free base porphyrin and two terminal zinc complexes. This indicates that, in the ground state, no major interaction occurs between the porphyrin subunits of the trimer, which can be related to the presence of phenyl-ethynyl-phenyl linkers. In addition, there is a broad band at 265 nm corresponding to the absorption of the eight fluorenyls arms (Table 1).

3.3.2. Absorption spectra of titration

The formation of free trimer **8** by adding TFA to bis zinc complex **7** was followed by UV-Visible spectrophotometry (Figure 5b). Dissolution of trimer **7** in neutral DCM solution results in a UV-Vis spectrum with a maximum absorbance at 429 nm, the evolution of visible spectra by protonation (adding regular small quantities of TFA) is shown in Fig. 5b. During this titration, the Soret band, initially at 429 nm, for trimer **7**, is red shifted to 461 nm, due to protonation and consequently loss of encapsulated zinc.

During the evolution of these spectra for protonation steps, we observe an isobestic point at 440 nm; illustrating the formation of a totally protonated distinct species. For this **hexacation** porphyrin trimer, we observe the presence of a band at 461 nm and a broad band which is located at 684 nm corresponding to the superposition of Vis absorption of similar protonated porphyrins.[30] No evolution of the spectrum is observed when more acid is added. Then, this **hexacation** was neutralized by adding a base (NEt_3). The evolution of visible spectra by basifying is shown in Fig. 5b. Deprotonation occurred upon titration with NEt_3, transforming the **hexacation** into the free base, so absorbance at 462 nm disappeared and an isobestic point at 440 nm, is again observed. We can notice that the original spectrum of trimer **7**, is not restored because of the irreversible loss of encapsulated zinc but no partial degradation is observed. A new compound is obtained corresponding to the neutral species named free trimer **8**. In Figure 5a, the UV-Vis absorption of monomers **11**, **12** and **13** are compared to the absorption of free trimer **8**. The profiles of parent monomers **11**, **12** (except Q bands) and **13** are quite similar.

The absorption spectrum of free base porphyrin trimer **8** shows the presence of a Soret band at 427 nm: this band is slightly blue shifted compared to 429 nm for trimer **7**, due to the loss of zinc. This tendency in blue shifting is not observed for the Q bands; they are slightly red shifted compared to trimer **7**, and the relative intensities are different. They are located at 520 nm (Qy(0, 1); strong), 557 nm (Qy(0, 0); strong), 594 nm (Qx(0, 1); strong) and 649 nm (Qx(0, 0); weak), corresponding typically to Visible absorption of a free porphyrin. Again, this confirms that, in the ground state, no major interaction occurs between the porphyrin subunits of the trimer. In addition, as expected, there is a broad UV absorption band at 263 nm corresponding to the absorption of the eight fluorenyl arms. We can notice in Figure 5c, that in this conjugated system possessing 8 fluorenyl arms and three porphyrin macrocycles; meaning a ratio (antenna/porphyrin unit) = 2.7, the antenna absorption is however stronger for trimer **8** than for **TFP** possessing 4 arms per porphyrin core, so a ratio (antenna/porphyrin unit) = 4.



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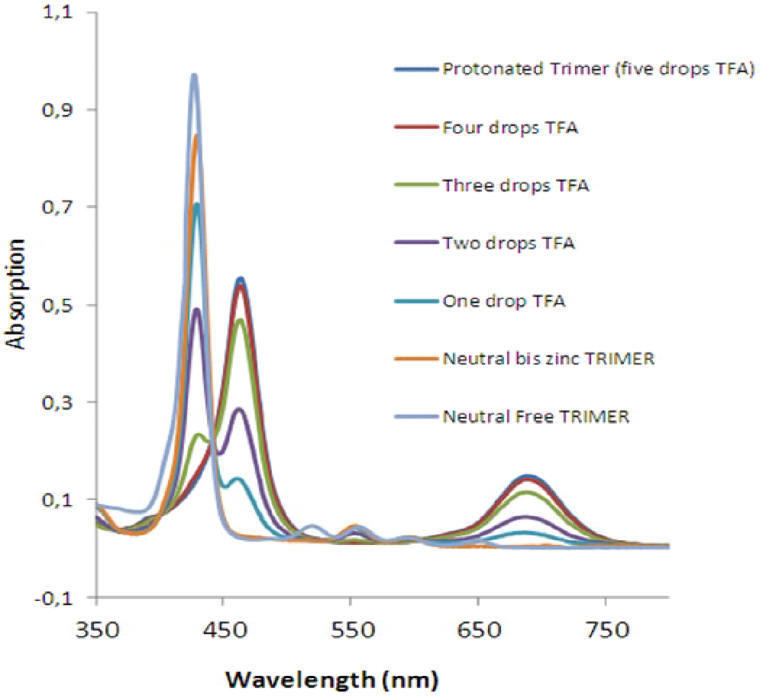

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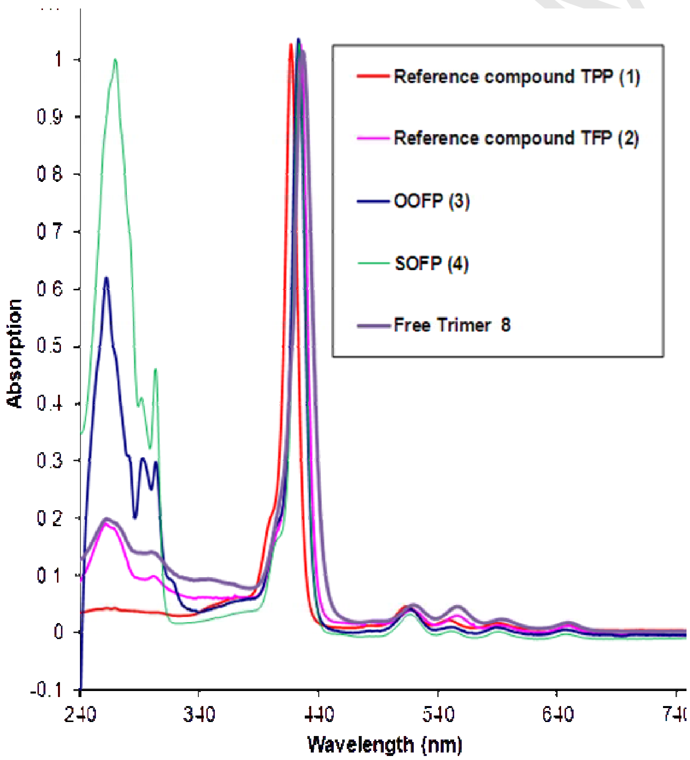

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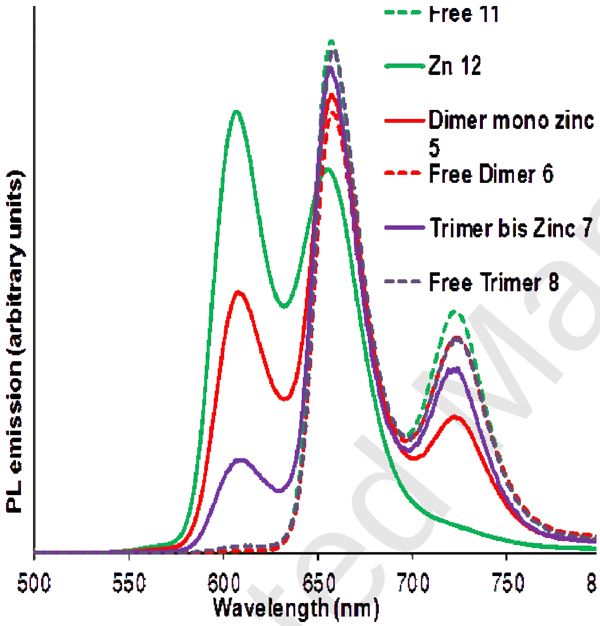
Figure 5: **a/** Absorption spectra of precursors **11**, **12**, **13** and new trimer **8** in DCM at room temperature.
b/ Formation of free trimer **8** by protonation of bis zinc complex **7**.

c/ Absorption spectra of **TPP** (red), **TFP** (pink), **OOFP** (dark blue), **SOFP** (green) and new trimer **8** (violet) in DCM at room temperature. All the spectra are normalized to the Soret band of the spectrum of the reference **TPP** at 417 nm (concentration ~2.0 10^{-6} M).

3.3.3. Emission spectroscopy

Generally, the emission spectra of porphyrin zinc complexes consist of three sub-bands assigned to a vibronic progression from a Q state: the band near 720 nm is very weak whereas the strongest emission band is typically around 600 nm and the second peak is at ~ 650 nm, due to the metal coordination.[15]



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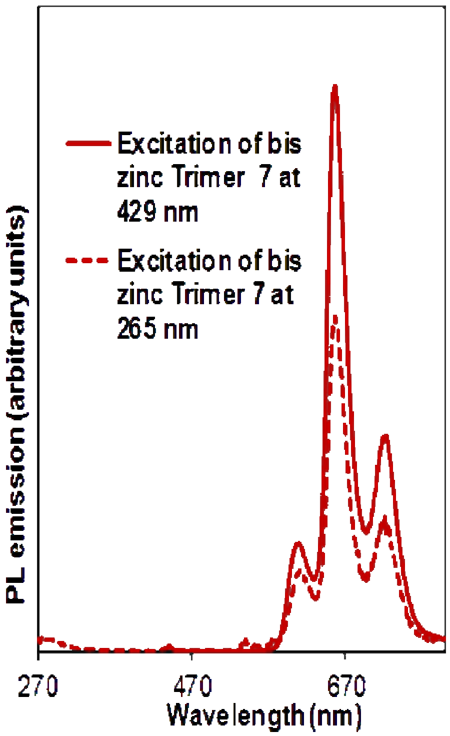

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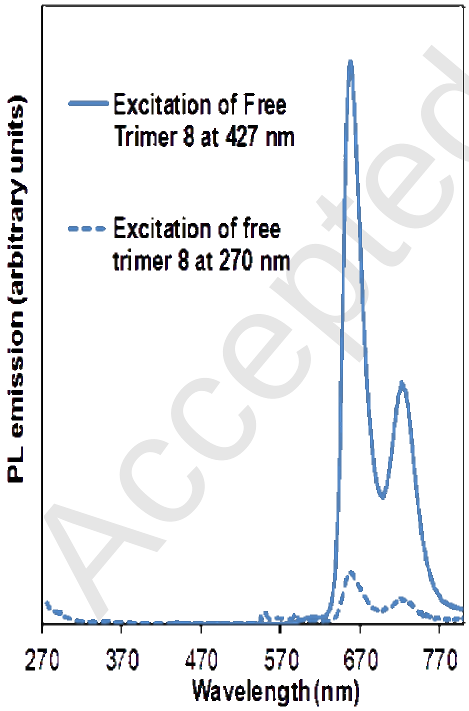

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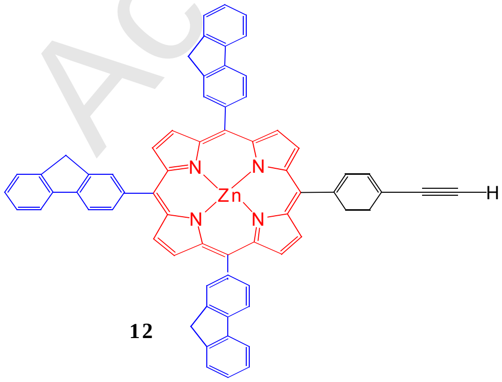
Figure 6: **a**/ Emission spectra of monomers **11** and **12,** dimers **5** and **6**, compared to trimers **7** and **8** in DCM at room temperature. All the spectra are normalized to the spectrum of dimer **7** at 657 nm (concentration ~2.0 10^{-6} M).

b/ Fluorescence emission spectrum of **7** in DCM at room temperature upon excitation at 265 nm (red dashed lines) compared to that upon direct excitation of the porphyrins at 429 nm (red plain).

c/ Fluorescence emission spectrum of **8** in DCM at room temperature upon excitation at 270 nm (red dashed lines) compared to that upon direct excitation of the porphyrins at 427 nm (red plain).

The fluorescence spectra at 25 °C of the zinc(II) complex **12**, after excitation in the Soret band at 426 nm, reveals a strong red fluorescence with a peak maximum at 607 nm and a second peak, at 655 nm (Fig. 6a). We can notice that the band near 720 nm does not appear for this complex.

For comparison, the emission spectrum of free compound **11** is also reported. After excitation in the Soret band, at 425 nm, strong red emission at 657 nm and a weaker peak at 700 nm are observed (Fig. 6a). That means that by emission spectroscopy, we should be able to clearly distinguish between free base and zinc complex parts of the dimer and trimer molecules. Concerning dimer **5**, actually after excitation in the Soret band, a weak emission at 600 nm, a strong red emission at 657 nm and a weaker peak at 720 nm are observed. Similarly for trimer **7**, after excitation in the Soret band, a weak emission at 609 nm, a strong red emission at 657 nm and a weaker peak at 722 nm are observed (Fig. 6a). It should be noticed that the contribution of the zinc complex to the emission of trimer **7** is lower than for dimer **5**, despite trimer **7** contains two zinc porphyrins instead of a single one for dimer **5**. This clearly indicates that in contrast with dimer **5**, energy transfer occurs in trimer **7** from the zinc complex(es) to the central free base porphyrin. In Figure 7, comparison is made between the emission spectra of dimer **5** (top) and trimer **7** (bottom) with the corresponding solution of the porphyrin moieties (i. e. the zinc complex **12** and the free base porphyrin **14**[16, 31]) in a 1 : 1 and 2 : 1 ratios, respectively. The emission spectrum of dimer **5** closely resembles to that of the 1 : 1 mixture, indicating that almost no energy transfer occurs, whereas for dimer **7**, the intramolecular energy transfer efficiency can be estimated to about 70%.



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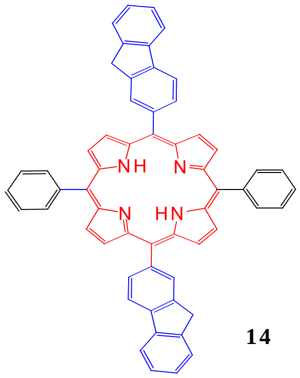

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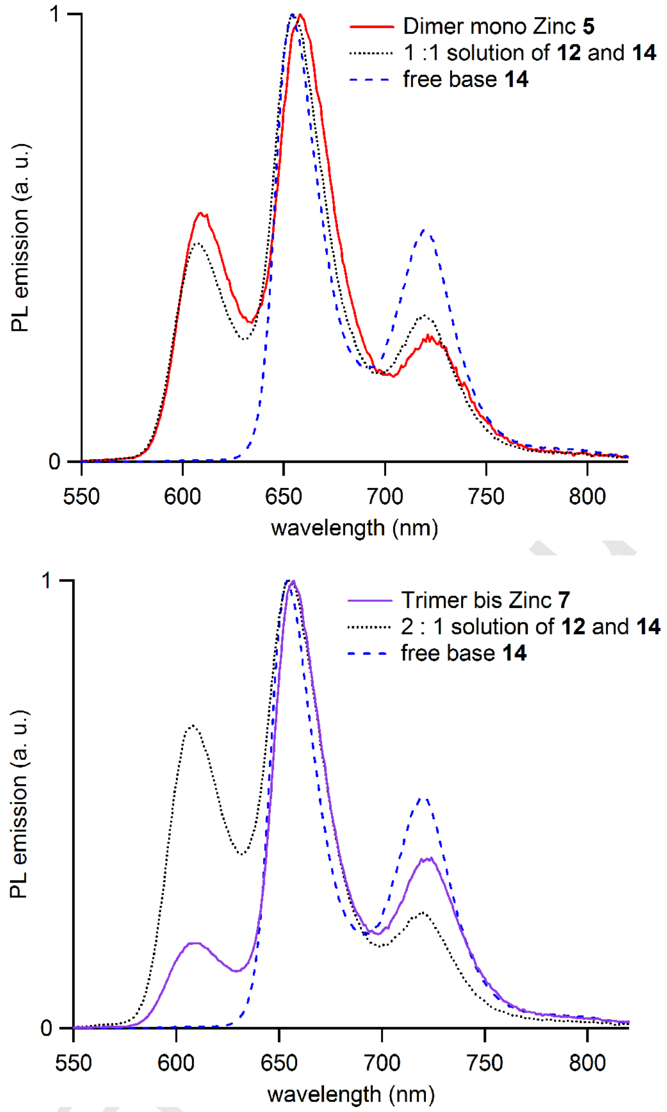

Figure 7: Top: measured emission spectra of dimer **5**, of a solution of the porphyrin moieties **12** and **14** in a 1 : 1 ratio and of the free base acceptor **14** in DCM at room temperature. Bottom: measured emission spectra of trimer **7**, of a solution of the porphyrin moieties **12** and **14** in a 2 : 1 ratio and of the free base acceptor **14** in DCM at room temperature (λ_{exc} = 429 nm).

Finally, for demetallated dimer **6**, and trimer **8** possessing respectively two and three similar free base moieties, we observe, as expected, two peaks: at 657, 720 nm and 658, 724 nm (Figure 6a).

3.3.4. *Fluorescence quantum yields*

The fluorescence quantum yields of these compounds were determined by comparing with a calibration standard of compound **1** (**TPP**) in degassed toluene solution presenting a fluorescence quantum yield of 0.12,[32] preferentially to a benzene solution with a fluorescence quantum yield of 0.13.[33]

Values of quantum yield obtained in degassed toluene, of free ligands **1**, **2**, **3** and **4** are reported in **Table 1**. Compounds **3** and **4** present luminescence quantum yields (13 and 14% respectively) similar to that of the reference **1** (12%). We have shown earlier that increasing the number of dendrons does not have any significant influence on the quantum yield. As a result, a system in which a 5,10,15,20-tetraphenylporphyrin is linked, *via* ether bridges, to eight or sixteen fluorenyl donor moieties in position 3 and 5, presents the same luminescence efficiency as the parent **TPP** compound.[17, 34] For these reasons, recently dimers[21] were considered and currently trimers with direct connection of fluorenyl on *meso* position are presented.

For free trimer **8**, a conjugated system possessing 8 fluorenyl arms and three free porphyrin macrocycles, an interesting luminescence quantum yield (13%) is obtained in non-degassed DCM, which is similar to that of non-conjugated dendrimers; with 8 or 16 fluorenyl arms (compounds **3** and **4** respectively) and to that of the reference **TPP** compound (**1**), but not as high as the parent compound **TFP** (**2**). However, the brightness (defined by the product $\varepsilon.\Phi_f$) of trimer **8** is higher than that to **TFP** (**2**), taking into account the very large absorptivities of **8** (1 023 000 M^{-1} cm^{-1} at 427 nm).

The corresponding zinc complexes, monomer **12** and dimer **5** have low luminescence quantum yield (around 5-7%), but bis zinc trimer **7** presents a quantum yield of 9%, which is relatively high when zinc complexes are present, higher than reference compound **ZnTPP** (3.3%) and parent compound **ZnTFP** (5%).[15] This can be related to the efficient energy transfer from the zinc complexes to the central free base. It should also be noticed that the quantum yield of trimer **7** is also higher than that of dimer **5** (5%), despite trimer **7** contains two zinc complexes for one single free base porphyrin instead of a one to one ratio for dimer **5**, which confirms that the energy transfer is more efficient in trimer **7** than in dimer **5**.

Porphyrin	**λ_{max} / nm$^{(a)}$ UV band**	**λ_{max} / nm$^{(b)}$ Soret band**	**λ_{max} / nm Q bands**	**λ_{em} / nm**	**Φ_f $^{(c)}$**
TPP (1)	-	417	513, 548, 589, 646	650, 714	0.12
Free Monomer (2)	**272**	**426**	**519, 557, 593, 649**	**661, 725**	**0.24**
OOFP(3)	263	423	516, 551, 592, 653	656, 721	0.13
SOFP (4)	270	423	517, 552, 590, 647	656, 721	0.14

Free 11	275	425	518, 555, 594, 649	657, 700	0.21
Zn (12)	273	426	554, 595	607, 655	0.07
diIodo (13)	288	422	513, 550, 590, 645	663, 728	0.02
Dimer (5)	281	428	513, 555, 597, 643	600, 657, 720	0.05
Free Dimer (6)	**268**	**426**	**521, 557, 595, 650**	**657, 720**	**0.17**
Trimer (7)	265	429	521, 555, 596, 649	609, 657, 722	0.09
Free Trimer (8)	**263**	**427**	**520, 557, 594, 649**	**658, 724**	**0.13**

(a) Wavelengths of the absorption maxima in the UV region (200-400 nm range)
(b) Wavelengths of the absorption maxima in the Soret or B band region (400-450 nm range)
(c) Fluorescence quantum yields using **TPP** in DCM as standard, following excitation into the Soret bands

Table 1: Photophysical properties of the fluorenyl porphyrins **1**, **2**, **3** and **4** in dilute CH_2Cl_2 solution at 298K, and of dimer**s 5, 6**, trimers **7** and **8**, zinc complex **12** and free base **11, 13**, under the same conditions for comparison.

3.3.5. Energy transfer from the fluorenes to the porphyrins

The efficiency of energy transfer from fluorenyl donors toward porphyrin acceptors will now be discussed. Excitation of trimers **7** and **8** in the fluorenyl *antennae* results in the red emission of porphyrins with a maximum at 657-658 nm in both cases. Actually, the blue fluorenyl emission is partly quenched for trimer **8** and almost completely quenched for free trimer **7**, and red emission is seen predominantly from the porphyrin (Figure 6b and c).

We have to notice that, when excited directly at the Soret band, trimer **7** shows a strong red emission, but the indirect excitation in the UV region shows as well an important red emission (Fig. 6b). For free trimer **8**, when exciting the Soret band, a strong red emission is observed in comparison to excitation in the UV region. But this is not evidence of inefficient energy transfer but of a more complex process.[34]

Thus for these trimer compounds, the luminescence can be modulated in a large range of excitation wavelengths from UV to red, to finally obtain the desired red emission particularly efficiently for trimer **7**.

4. Conclusions and outlook

In summary, a series of intermediate porphyrins bearing fluorenyl donor groups was presented. Successively, intermediate compounds **12** (bearing three fluorenyl arms), and **13** (bearing two fluorenyl groups and two iodides) have been synthesized. Starting from these building blocks, new trimers **7** and **8**, bearing in totally eight peripheral fluorenyl arms were finally synthesised and fully characterized.

We then compared the detailed luminescence properties of these trimers **7** and **8** with porphyrin dendrimers **3** and **4,** with corresponding dimers **5** and **6**, but also with **TFP** (**2**), which was the precursor model of this work. New bis zinc trimer **7** exhibits a relatively high luminescence quantum yield (9%), higher than reference compound **ZnTPP** (3.3%) and parent compound **ZnTFP** (5%).[15] It shows also an efficient energy transfer from the fluorenyl arms toward the porphyrins, as well as an efficient energy transfer from the zinc complexes toward the free base central porphyrin. New free trimer **8** exhibits a relatively high quantum yield (13%) and energy transfer from the fluorenyl arms toward the porphyrin core is also observed. Taking into account their large absorptivities, these assemblies of three porphyrins exhibit larger brightness than the corresponding dimers and monomers.

Perspectives of this work may be to change the bridge connecting the porphyrins of the assembly to optimize the luminescence properties and the efficiency of the energy transfer between porphyrins, and eventually extend this work to tetramers or pentamers. We can also consider grafting dendrons at the periphery of the new trimer, still in the idea of increasing the number of antennas around the core porphyrins for light collection.

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Highlights

►Synthesis of new porphyrin trimers within totally eight peripheral fluorenyl arms is are presented. ► New bis zinc trimer exhibits a relatively high luminescence quantum yield (9%), higher than reference compound **ZnTPP** (3.3%) and parent compound **ZnTFP** (5%).►

We report an efficient energy transfer from the fluorenyl arms toward the porphyrins, as well as from the zinc complexes toward the free base central porphyrin.