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Synthesis and photophysical properties of porphyrins with fluorenyl pendant arms

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ABSTRACT

Symmetrical-A_4-porphyrins bearing four fluorene donor moieties **TOFP** (5,10,15,20-tetra(4-(2 methyloxyfluorenyl)phenyl)porphyrin) as well as eight fluorene arms **OOFP** (5,10,15,20-octa(3,5-(2-methyloxyfluorenyl)phenyl)porphyrin) were synthesized and characterized. Preliminary photophysical properties are reported. In comparison to the reference tetraphenylporphyrin **TPP**, the luminescence properties are slightly improved. The fluorescence quantum yields of tetrafluorenylporphyrin **TOFP** (**1**) and octafluorenylporphyrin **OOFP** (**2**) are 0.10 and 0.13, respectively.

1. Introduction

Porphyrin systems, as energy acceptors, have been covalently linked to donor units like carotenoids[1,2] or anthracenes[3] to model photosynthetic systems and to develop efficient molecular devices. The porphyrin skeleton permits to attach easily four energy donor arms in the near periphery, and such a light-harvesting system can be expected to show an antenna effect. Antenna systems comprising a central porphyrin linked to four peripheral photon-harvesting hydrocarbon moieties have been reported. For example, naphthalene,[4] anthracene[5] or phenanthrene[6] groups have been linked directly to four *meso*-carbons of the porphyrin and more recently a series of star-shaped porphyrins bearing pendant linear oligofluorene arms have also been reported.[7,8] In the previous donor–acceptor (D–A) system described, the energy donors are linked directly to the porphyrin periphery. For antenna effect, it is better to have a multicomponent structure in which the donors and acceptors retain their individual characteristics. For a realistic description of the photosynthetic antenna function, a porphyrin-based model system should exhibit high local concentrations of the light-harvesting chromophores. All of these considerations indicate that a molecular pentad system, in which a porphyrin acceptor is linked, via spacers, to four donor hydrocarbons, forms a suitable choice for the antenna function. On the other hand, Fréchet[9] demonstrated that antenna effect was facilitated in dendritic case versus the corresponding linear case. Thus, more recently, light-harvesting donor two-photon absorbing chromophores (TPAC) with metalated porphyrin cores were synthesized in this group.[10] The same year, the synthesis of hyperbranched polymers containing porphyrin core possessing fluorene arms has been reported, for tuning the optical properties of hyperbranched polymers through the modification of the end groups.[11]

In our previous papers, we have reported the synthesis of a free macrocycle possessing four pendant fluorene arms directly connected at the *meso* positions (**TFP**) and evidenced that the ruthenium(II) complexes of this type are very efficient heterogeneous catalysts.[12–15] Recently, we focused on the photophysical properties of such porphyrins possessing four identical fluorene pendant arms.[16,17] These porphyrins exhibited high quantum yields (22%), so a complete family of relevant porphyrins was studied to investigate this high luminescence efficiency. It was demonstrated therein the good capacity of the fluorenyl units to enhance quantum yields by increasing the radiative process.[18]

The present report deals with the design of a new building block based on fluorenyl porphyrins with the aim to exploit this capacity to enhance quantum yields and to combine this advantage with Fréchet's style dendritic architecture in order to improve energy transfer. The target is to obtain highly luminescent

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organic compounds, by the design of porphyrins possessing fluorenyl arms using dendritic synthesis. In more detail, in this paper, we present the synthesis of systems in which a 5,10,15,20-tetraphenylporphyrin (**TPP**) is linked, via ether bridges, to four and eight fluorene donor moieties, compounds **1** and **2**, respectively (Fig. 1), and in a second part preliminary photophysical results are also reported.

2. Results and discussion

2.1. Synthesis

2-Hydroxyl-methyl-fluorene (**7**) was obtained by reduction of fluorene-2-carboxaldehyde with sodium borohydride in ethanol. After 1 h reaction time followed by extraction with dichloromethane,

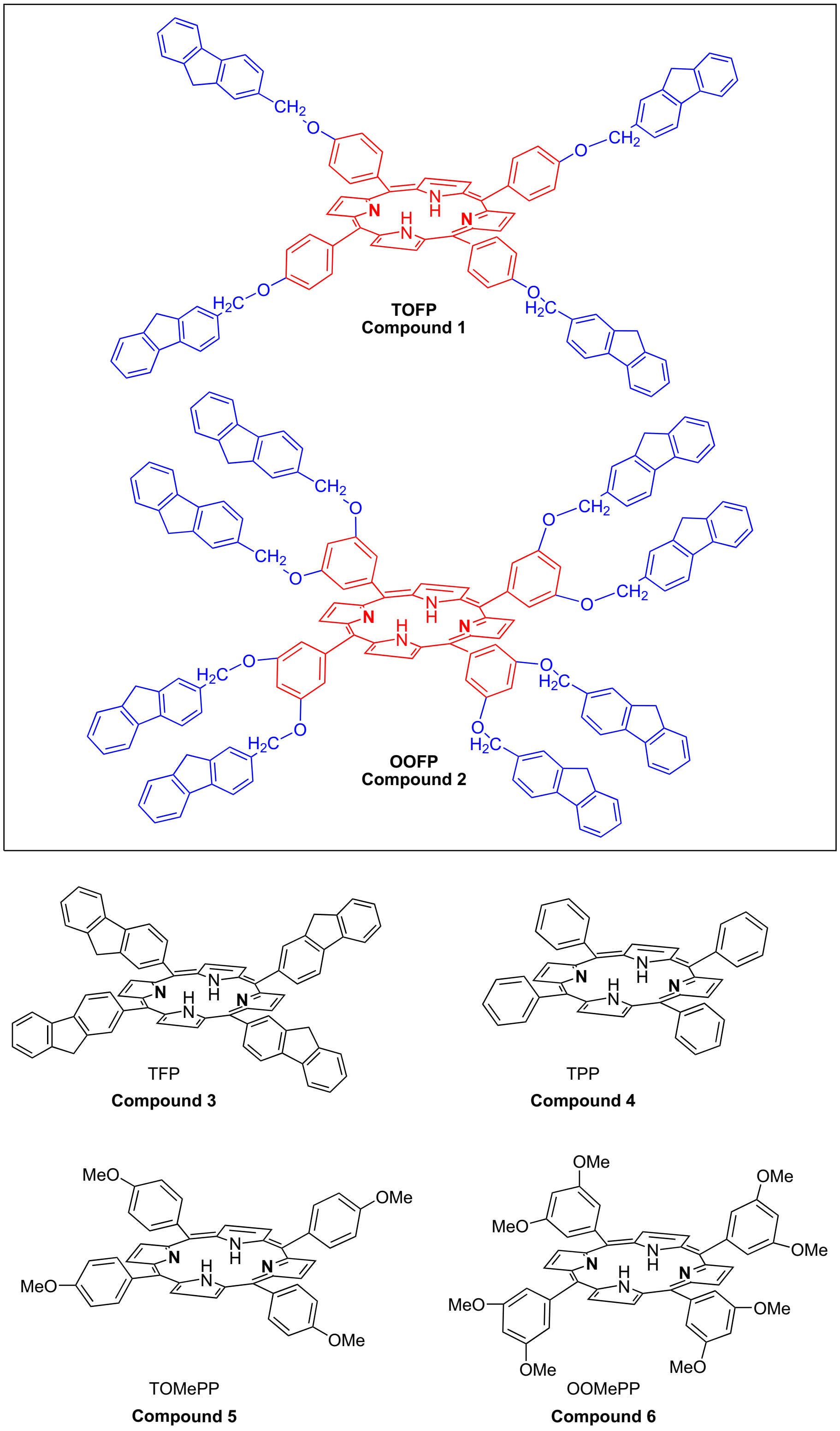
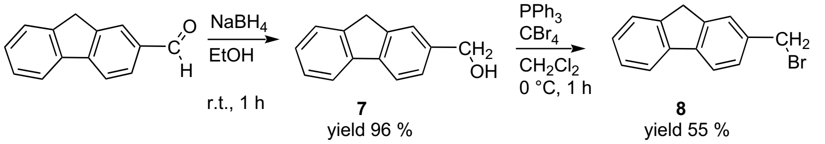


Figure 1. Compounds **1**, **2**, **3**, **4**, **5**, and **6**.



Scheme 1. Synthesis of compounds **7** and **8**.

the crude product was purified by column chromatography to yield **7** as a white solid (96%). This alcohol was then brominated with carbon tetrabromide in the presence of triphenylphosphine in dichloromethane. The mixture was stirred overnight, concentrated, and purified by column chromatography to give 2-bromomethyl-fluorene (**8**) as a white solid (55%) (Scheme 1).

The two intermediate porphyrins, **TOHPP** and **OOHPP**, were obtained from the methylated porphyrin analogs, porphyrin **5** (**TOMePP**) and **6** (**OOMePP**), respectively, by reaction with BBr_3.[19]

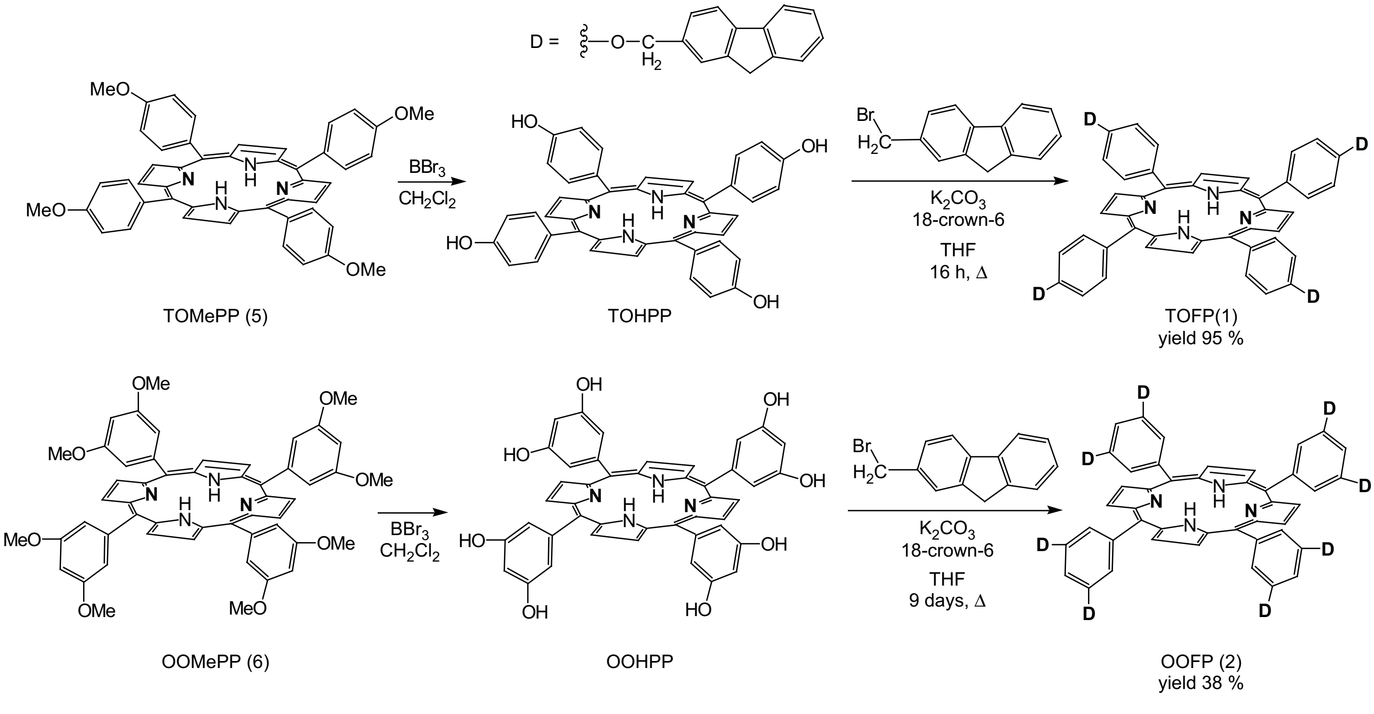
meso-(5,10,15,20-Tetra(4-(2-methyloxyfluorenyl)phenyl)porphyrin) **1** was obtained by condensation from the prepared bromide **8** (5 equiv) and **TOHPP** (1 equiv) in dry THF using potassium carbonate as base in the presence of 18-crown-6 (Scheme 2). This solution was stirred under argon at reflux for one day. The reaction time was monitored by UV spectroscopy. After purification by crystallization, the desired porphyrin **1** was obtained as a brown-violet solid (95%). *meso*-(5,10,15,20-Tetra(4-(3,5-dimethyloxyfluorenyl)phenyl)porphyrin) **2** was obtained by condensation from the prepared bromide **8** (10 equiv) and **OOHPP** (1 equiv) in dry THF using potassium carbonate as base in the presence of 18-crown-6 (Scheme 2). This solution was stirred under argon at reflux for nine days. Completion of the reaction time was monitored by UV spectroscopy. After purification by column chromatography on silica gel, the desired porphyrin **2** was obtained as a brown-violet solid (38%).

These new porphyrins **1** and **2** were characterized by NMR, UV–vis, and mass spectrometry. The hydrogen and carbon atom-labeling scheme for the porphyrin ligands **1** and **2** is shown in Figure 2.

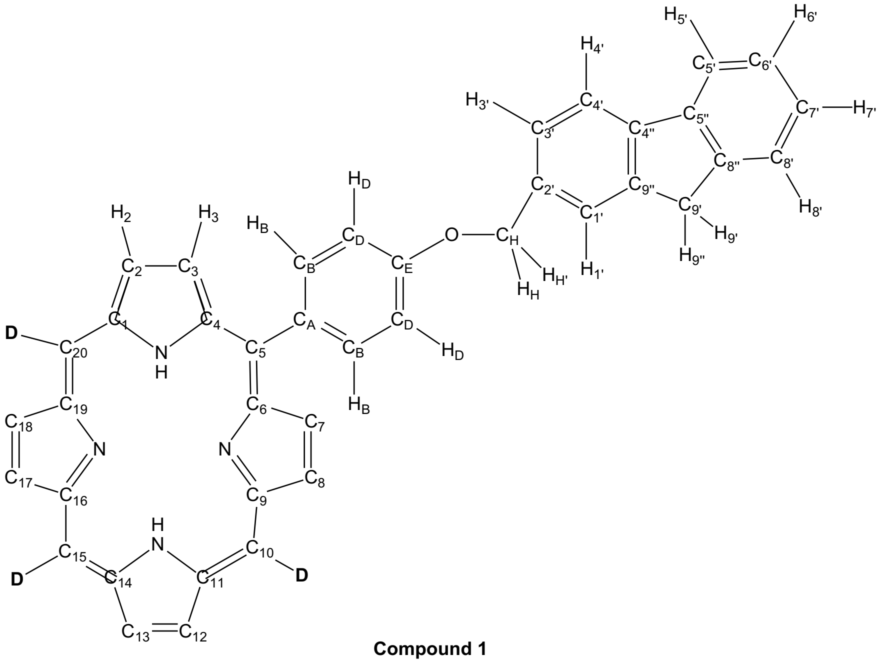
In the conditions used, the non-substituted fluorene arm is stable but often alkyl chains have been introduced on the position-9 of the fluorene units to increase the solubility.[8]

2.2. Optimized geometries

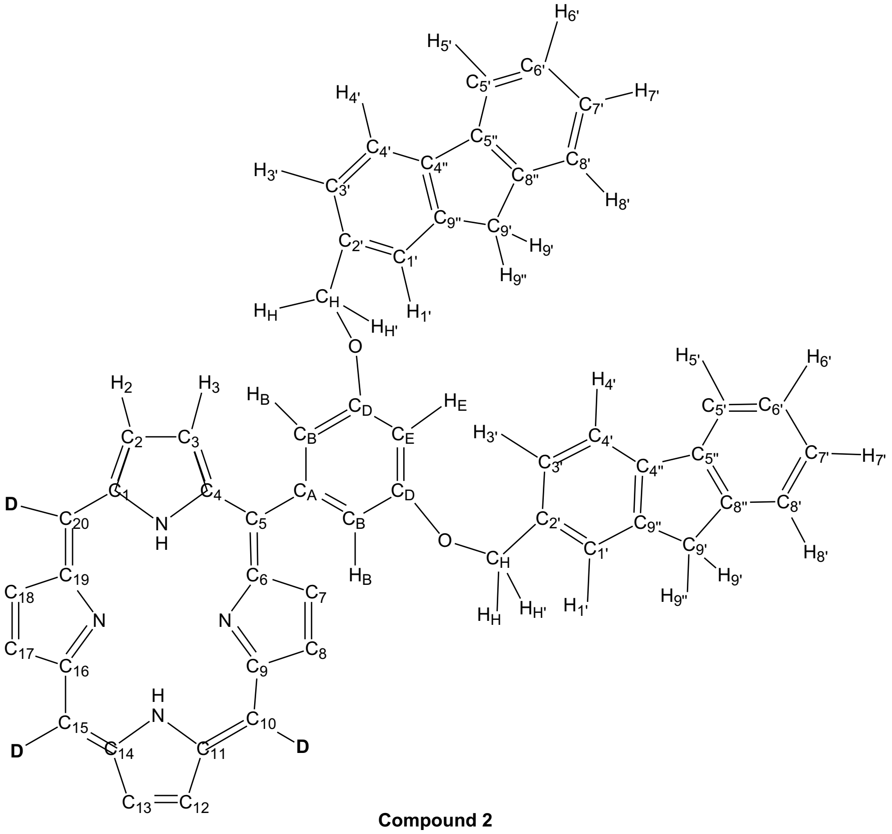
The calculated optimized geometries ('SPARTAN Pro, Molecular Mechanics and Quantum Chemical Calculations', PM3)[20] for porphyrin derivatives **1** and **2** are shown in Figure 3a and b, respectively. These molecular modeling data clearly show for the new compound **1** that the *trans* fluorenyl arms are on the same side of the porphyrin core, in a alternate way, whereas the macrocyclic core is essentially planar. Actually, it is known that the *meso*-aryl groups are not orthogonal to the porphyrin plane, but slightly tilted,[21] allowing the *meso* group to develop some conjugative interaction with the main porphyrin framework. Thus, in spite of the large dihedral angle between the plane of the phenyl ring and the porphyrin π system in the **TPP** series, conjugation exists to some extent and is affected by the substituents on the phenyl ring. This conjugative interaction of the aromatic *meso*-substituents can explain the color shift observed for various derivatives. Surprisingly, the calculated optimized geometries showed that the phenyl groups are almost perpendicular to the porphyrin core for **1**. Indeed, the dihedral angles between the phenyl groups and the porphyrin core are 89°, whereas for **TFP** this angle is 64°, and for **TPP** 60°. Similarly the fluorenyl arms are also perpendicular to the porphyrin core. This special arrangement gives to the monomer a wheel aspect. So the interactions between the porphyrin and fluorenyl will be enhanced



Scheme 2. Synthesis of A/**TOFP**: *meso*-(5,10,15,20-tetra(4-(4-methyloxyfluorenyl)phenyl)porphyrin **1**; B/**OOFP**: *meso*-(5,10,15,20-tetra(4-(3,5 dimethyloxyfluorenyl)phenyl)porphyrin **2**.



Compound 1



Compound 2

Figure 2. Hydrogen and carbon atom labeling for the porphyrin ligands **1** and **2**.

because the distance is relatively short, around 7–10 Å.[20] Similarly for **2**, the phenyl group appears also perpendicular to the porphyrin core, and the molecular modeling data clearly show for the new compound **2** that the four fluorenyl arms, on the same side of the porphyrin core, are disposed like a calix, so the entire molecule appears as a double calix. In this case the distance between the porphyrin and fluorenyl arms is short as well. These calculated conformations are only representative of the prevailing ones, given that these structures are certainly fluxional in solution. In consequence, other local energy minima might also exist in solution.

2.3. Photophysical properties

2.3.1. *Electronic spectra*

The UV–vis spectra of **1** and **2** exhibit an intense Soret band with a maximum absorption similar at around 423 nm (Fig. 4). This band

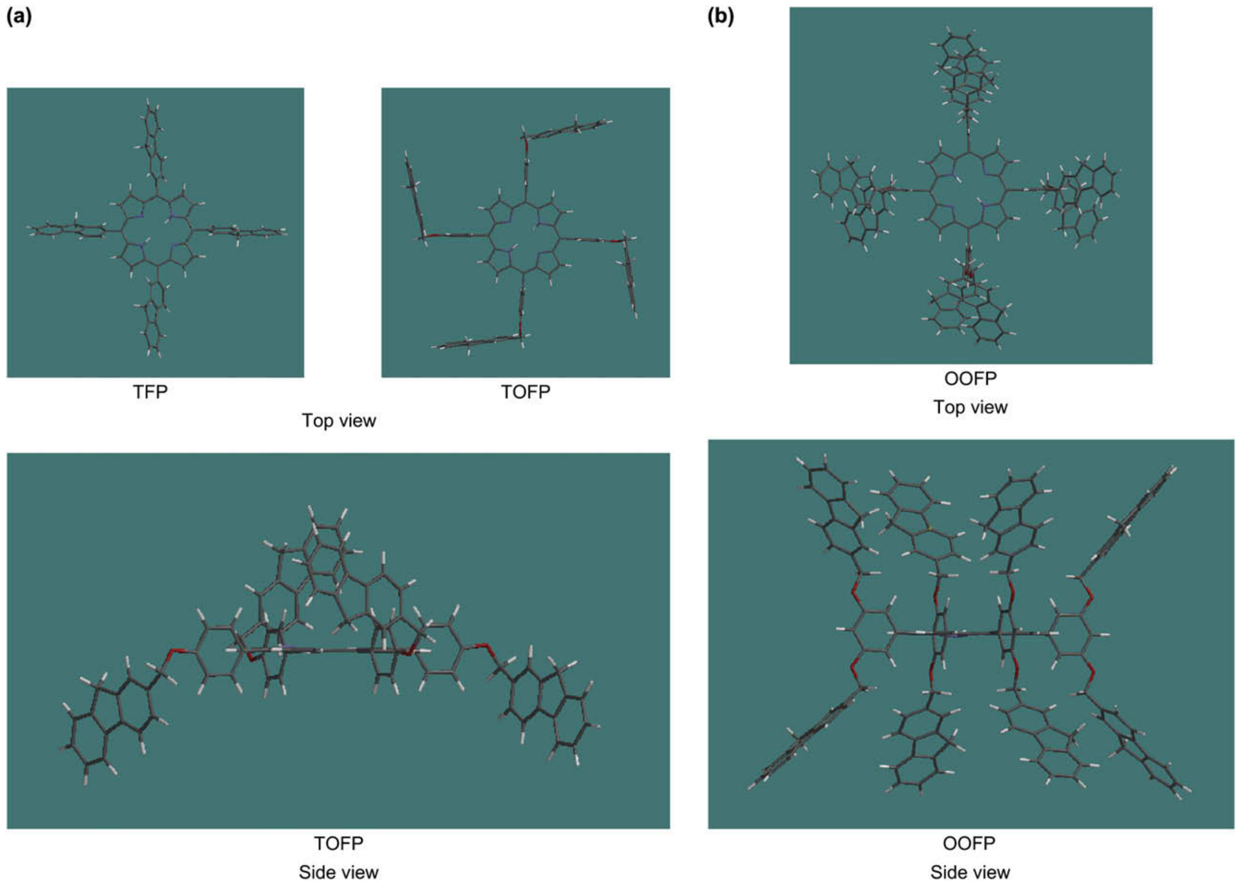


Figure 3. (a) Spartan plot of the molecular structure of **1** in comparison to compound **3**. (b) Spartan plot of the molecular structure of **2**.

is slightly red shifted compared to 417 nm for **TPP** (**4**), but not as much as for **TFP** (**3**) (426 nm). This tendency in red shifting is observed as well for the Q bands. The π–π* absorption in the UV range is clearly apparent, due to the presence of fluorene. For compound **1**, the four fluorene arms absorb in the UV range with a maximum absorption peak at 272 nm, for compound **2** possessing eight arms the absorption is stronger with a maximum at 263 nm. Finally we have the following shift for the absorption of the Soret band, for these compounds:

$$\lambda_{\mathbf{3}} > \lambda_{\mathbf{1}} = \lambda_{\mathbf{2}} > \lambda_{\mathbf{4}}$$

2.3.2. Emission

The emission spectrum of compound **1**, after excitation in the Soret band reveals a strong red fluorescence with a peak maximum at 663 nm and a weak shoulder at 728 nm (Fig. 5). Concerning the emission spectrum of compound **2**, after excitation in the Soret band, a strong red emission at 656 nm and a shoulder at 721 nm are observed (Fig. 5). After excitation in bounded-fluorene absorption (272 nm for compound **1** and 263 nm for compound **2**), the emission spectra reveal red fluorescence and almost no residual emission of the fluorene for both compounds. Thus, there is apparently a good energy transfer between fluorene and porphyrin, since essentially red emission of porphyrin is observed in comparison to blue emission of fluorene at around 300 nm. In fact, almost all the UV energy absorbed by the fluorine units is emitted by the porphyrin core.

The excitation spectra obtained after exciting in the strongest emission band at around 660 nm reveal an emission from the Soret state, the three first Q states, as well as from the fluorene. This indicates that excitation over all the 200–650 nm region leads to the population of all the fluorescent excited states of the porphyrin. Notably the fluorene chromophore involved in the UV absorption process becomes also strongly apparent under such excitation conditions. For comparison, the excitation spectra of compounds **1** and **2** are shown in Figure 5.

Thus for the new compounds **1** and **2**, the luminescence can be modulated in a large range of excitation wavelengths from UV to red, to finally obtain the desired red emission.

2.3.3. Fluorescence quantum yields

The fluorescence quantum yields of these compounds were next determined by comparing with a calibration standard of compound

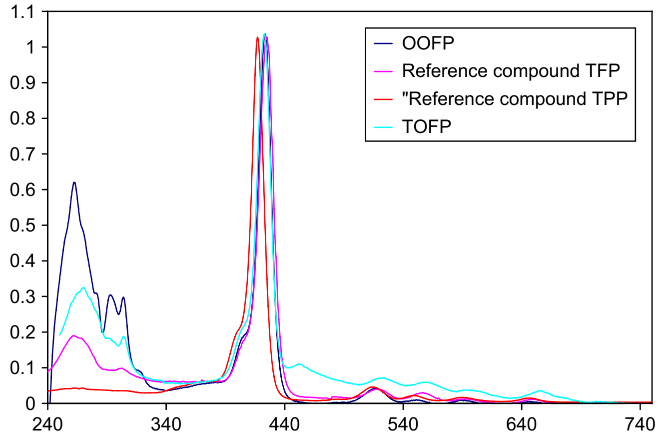


Figure 4. UV–vis absorption spectra for compounds **1**, **2**, **3**, and **4**, in CH_2Cl_2 at 25 °C (2.6×10^{-6} M for **TFP, 3** and normalized to the same absorbance for **1**, **2**, and **4**).

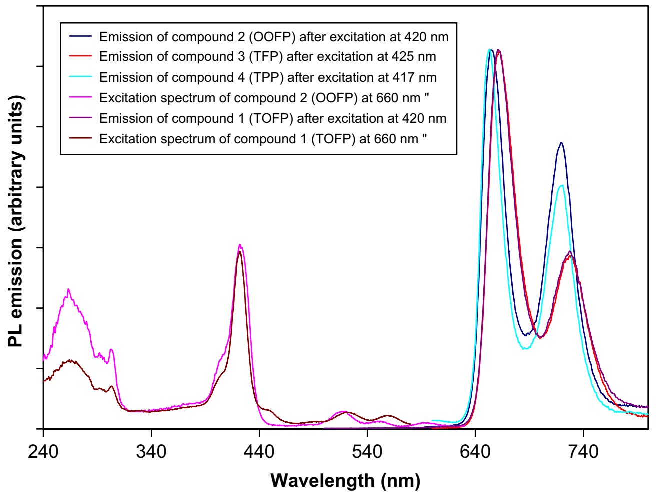


Figure 5. Photoluminescence spectra of free ligands **1**, **2**, **3**, and **4** (~1.0×10^{-6} M) in CH_2Cl_2 solution, at 25 °C, the emission spectra were cut above 800 nm. Excitation spectra of compounds **1** and **2**.

4 (**TPP**) in degassed toluene solution presenting a fluorescence quantum yield of 0.12,[22] preferentially to a benzene solution with a fluorescence quantum yield of 0.13[23] (in this latter case, different refractive indices of the solvents used in the standard and sample must be corrected).[24] In consequence the correction made for the difference in refractive indices of solvents is in this case not necessary. The quantum yield was calculated from the following equation:

$$\Phi_S = \Phi_{\mathbf{TPP}} \times (F_S/F_{\mathbf{TPP}}) \times (A_{\mathbf{TPP}}/A_S) \times (n_{\mathbf{TPP}}/n_S)^2$$

In the above expression, Φ_S is the fluorescent quantum yield of the new compound, F is the integration of the emission intensities, n is the index of refraction of the solution, and A is the absorbance of the solution at the exciting wavelength. The subscripts **TPP** and s denote the reference **TPP** and unknown samples, respectively.[25]

Values of quantum yield of free ligands **1**, **2**, **3** and **4** are reported in Table 1. All measurements were obtained under an argon atmosphere to limit photo-oxidative degradation (Table 1). Compound **2** presents a luminescence quantum yield (13%), which is similar to that of the reference **4** (12%). Apparently the high quantum yield (24%) observed for the compound possessing fluorene arms directly connected on the *meso* positions of **TFP** is not maintained when a phenyl intermediate substituted in positions 3 and 5 is introduced. So a system in which a 5,10,15,20-tetraphenylporphyrin (**TPP**) is linked, via ether bridges, to eight fluorene donor moieties in positions 3 and 5 presents the same luminescence efficiency as the parent **TPP** compound. Similarly, compound **1** presents a quantum yield of 10%. Further photophysical investigations will be undertaken to rationalize these results.[26]

Table 1
Photophysical properties of the fluorenyl porphyrins **1, 2, 3** and of **TPP**, **4**, for comparison

	Porphyrin			
	TOFP (**1**)	**OOFP** (**2**)	**TFP** (**3**)	**TPP** (**4**)
λ_{max}/nm[a] Soret band	423	423	426	417
λ_{em}/nm[a]	663, 728	656, 721	663, 730	653, 721
Φ_f[b]	0.10	0.13	0.22	0.12

[a] Wavelengths of the absorption and emission maxima in dilute CH_2Cl_2 solution at 298 K.
[b] Fluorescence quantum yields in toluene degassed solution, using **TPP** as standard, following excitation into the Soret bands.

3. Conclusion

In summary, we have synthesized and characterized two new porphyrins **TOFP**, **1**, and **OOFP**, **2**, bearing four and eight fluorenyl pendant arms at the *meso*-positions, respectively. These two porphyrins emit essentially red light after selective UV or visible irradiation. In the case of UV irradiation, these systems comprising a central porphyrin like **TPP** linked to peripheral photon-harvesting fluorene moieties have been shown to act as efficient antennas. Porphyrin **TOFP**, **1**, shows similar emission, in terms of solution-state fluorescence quantum yield, compared to the reference **TPP**, **4**, whereas compound **OOFP**, **2**, is slightly enhanced. These results suggest that a judicious choice of *meso*-aryl dendrons can allow the properties of porphyrins to be optimized for OLEDs, both in terms of efficiency and color tuning. Based on our recent results of anodic electropolymerization of monomers **3**,[12] **4**,[27] and **6**,[28] we now expect to obtain a polymeric 3D network after connections of the four or even eight fluorenyl pendant arms. This should allow growing a polymeric 3D structure from such macrocycle, possessing several connecting points for each monomer. Compounds **1** and **2** constitute therefore an interesting building block to access new emissive organic materials.

4. Experimental

4.1. General

All reactions were performed under argon and were magnetically stirred. Solvents were distilled from appropriate drying agent prior to use, CH_2Cl_2 from CaH_2, $CHCl_3$ from P_2O_5, and all other solvents were HPLC grade. Commercially available reagents were used without further purification unless otherwise stated. ^1H 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. Pyrrole and 2-fluorenecarboxaldehyde were purchased from Aldrich and were used as received. Reference: **TFP**=tetrafluorenylporphyrin, **TPP**=tetraphenylporphyrin. Purity of compounds **1** and **2** has been checked by GPC. Size exclusion chromatography (SEC) of compounds was performed in THF at 20 °C using a Polymer Laboratories PL-GPC 50 plus apparatus (PLgel 5 µm MIXED-C 300×7.5 mm, 1.0 mL min^{-1}, RI, and Dual angle LS detector (PL-LS 45/90)).

4.2. Synthesis of the arms

*4.2.1. Synthesis of 2-hydroxyl-methyl-fluorene (**7**)*
To a solution of the commercial fluorene-2-carboxaldehyde (500 mg, 2.57 mmol) in ethanol (40 mL) was added sodium borohydride (117 mg, 3.09 mmol) at 0 °C for a period of 10 min. The reaction mixture was stirred at room temperature for 1 h and then poured into water, followed by extraction with dichloromethane. The organic layer was washed with brine, dried over anhydrous $MgSO_4$, and the solvent was removed. The residue was purified by column chromatography on silica gel (1:1 CH_2Cl_2/pentane) to yield 476 mg of a white solid (96%). ^1H NMR (200 MHz, $CDCl_3$): 7.81 (d, $^3J_{HH}$=8.0 Hz, 2H), 7.58 (d, $^3J_{HH}$=8.0 Hz, 2H), 7.40 (d, $^3J_{HH}$=10.0 Hz, 2H), 7.33 (s, 1H), 4.80 (s, 2H, CH_2–OH), 3.94 (s, 2H, $CH_{2fluorene}$).

4.2.2. *Synthesis of 2-bromomethyl-fluorene (**8**)*

To a solution of alcohol **7** (0.5 g, 2.56 mmol) in dichloromethane (10 mL) was added carbon tetrabromide (936 mg, 2.82 mmol) followed by the portion-wise addition of triphenylphosphine (739 mg, 2.82 mmol). The mixture was stirred at 0 °C for 1 h and then at room temperature for overnight, concentrated, and purified by column chromatography on silica gel (9:1 pentane/CH_2Cl_2) to give 366 mg (55 %) of **8** as a white solid: ^1H NMR (200 MHz, $CDCl_3$): 7.81 (d, $^3J_{HH}=8.0$ Hz, 1H), 7.75 (d, $^3J_{HH}=7.7$ Hz, 1H), 7.59 (d, $^3J_{HH}=8.8$ Hz, 2H), 7.43 (d, $^3J_{HH}=7.9$ Hz, 1H), 7.38 (d, $^3J_{HH}=8.0$ Hz, 1H), 7.37 (s, 1H), 4.91 (s, 2H, CH_2–Br), 3.94 (s, 2H, $CH_{2\text{fluorene}}$).

4.3. Synthesis of the porphyrins

4.3.1. *Synthesis of porphyrin **1***

TOFP, *meso*-(5,10,15,20-tetra(4-(2methyloxyfluorenyl)phenyl)-porphyrin), **1**: 2-bromomethyl-fluorene (191 mg, 736 μmol), tetrakis (4-hydroxyphenyl)-porphyrin **TOHPP** (100 mg, 147 μmol), K_2CO_3 (162 mg, 1.18 mmol), and 18-crown-6 (40 mg, 67 μmol) were dissolved in 10 mL of dry THF and stirred under argon at reflux for 16 h. The reaction mixture was cooled to room temperature and the mixture was filtrated. The insoluble violet powder was washed with THF (100 mL), water (100 mL), and pentane (100 mL). The precipitate was dried over $MgSO_4$ and in oven (50 °C) under vacuum to yield a violet solid (95%). The purity of compound **1** has been checked by TLC plate and by GPC (SEC).

^1H NMR (solubilized by acidic deuterated TFA in $CDCl_3$): 8.54 (d, $^3J_{HH}=8.4$ Hz, 8H, H_B), 8.52 (s, 8H, pyrrole), 7.96 (d, $^3J_{HH}=7.8$ Hz, 4H, $H_{4'}$), 7.90 (d, $^3J_{HH}=7.4$ Hz, 4H, $H_{5'}$), 7.87 (s, 4H, $H_{1'}$), 7.68 (d, $^3J_{HH}=7.8$ Hz, 4H, $H_{3'}$), 7.65 (d, $^3J_{HH}=8.4$ Hz, 8H, H_D), 7.64 (d, $^3J_{HH}=7.3$ Hz, 4H, $H_{8'}$), 7.46 (t, $^3J_{HH}=7.6$ Hz, 4H, $H_{6'}$), 7.38 (t, $^3J_{HH}=7.4$ Hz, 4H, $H_{7'}$), 5.52 (s, 8H, $H_{H\text{-}H'}$), 4.06 (s, 8H, $H_{9'\text{-}9''}$).

^{13}C NMR (solubilized by acidic deuterated TFA in $CDCl_3$): 160.82 (C_E), 146.04 ($C_{1-4-6-9-11-14-16-19}$), 144.18 ($C_{9''}$), 143.31 ($C_{8''}$), 142.18 ($C_{4''}$), 141.13 ($C_{5''}$), 140.01 (C_B), 133.53 (C_A), 134.86 ($C_{2'}$), 127.84 ($C_{2-3-7-8-12-13-17-18}$), 127.03 ($C_{7'}$), 126.91 ($C_{6'}$), 126.69 ($C_{3'}$), 125.18 ($C_{8'}$), 124.69 ($C_{1'}$), 122.10 ($C_{5-10-15-20}$), 120.11 ($C_{5'}$), 120.20 ($C_{4'}$), 114.95 (C_D), 70.97 (C_H), 37.02 ($C_{9'}$).

Analysis: calcd for $C_{100}H_{70}N_4O_4\cdot 1.5CHCl_3$: C, 77.02; H, 5.32; N, 3.54; found: C, 77.44; H, 4.76; N, 3.37. MALDI TOF-MS: calcd for $C_{100}H_{70}N_4O_4$: 1390.5500 $[MH]^+$, found 1390.3650 [MH]. UV–vis (CH_2Cl_2): $\lambda_{max/nm}$ 263 (fluorene, $\varepsilon_{263}=74\,800$), 291 (fluorene, $\varepsilon_{291}=45\,000$), 304 (fluorene, $\varepsilon_{304}=53\,200$), 423 (Soret band, $\varepsilon_{423}=213\,600$), 516 ($Q_1$ band, $\varepsilon_{516}=14\,800$), 551 ($Q_2$ band, $\varepsilon_{551}=11\,400$), 590 ($Q_3$ band, $\varepsilon_{590}=8200$) and 647 nm (Q_4 band, $\varepsilon_{647}=11\,400$). UV–vis (0.02 mL **TFA**/1 L CH_2Cl_2): $\lambda_{max/nm}$ 263 (fluorene, $\varepsilon_{263}=105\,600$), 291 (fluorene, $\varepsilon_{291}=53\,200$), 304 (fluorene, $\varepsilon_{304}=63\,000$), 451 (Soret band, $\varepsilon_{51}=373\,000$), 682 ($Q_1$ band, $\varepsilon_{682}=58\,600$), 700 ($Q_3$ band, $\varepsilon_{700}=41\,000$).

4.3.2. *Synthesis of porphyrin **2***

OOFP, *meso*-(5,10,15,20-tetra(4-(3,5dimethyloxyfluorenyl)-phenyl)porphyrin), **2**: 2-bromomethyl-fluorene (157 mg, 606 μmol), tetrakis (3′,5′-dihydroxyphenyl)-porphyrin **OOHPP** (50 mg, 67 μmol), K_2CO_3 (149 mg, 1.07 mmol), and 18-crown-6 (18 mg, 67 μmol) were dissolved in 5 mL of dry THF and stirred under argon at reflux for 9 days. The reaction mixture was cooled to room temperature, and the mixture was poured in a separatory funnel containing 50 mL of CH_2Cl_2 and washed with water (100 mL) twice and brine (100 mL). The organic phase was dried over $MgSO_4$ and the solvent was removed. The residue was purified by column chromatography on silica gel (9:1 CH_2Cl_2/pentane) to yield 56 mg of a brown solid (38%). The purity of compound **2** has been checked by TLC plate after column chromatography and by GPC (SEC).

^1H NMR ($CDCl_3$): 8.83 (s, 8H, pyrrole), 7.81 (d, $^3J_{HH}=7.9$ Hz, 8H, $H_{4'}$), 7.80 (d, $^3J_{HH}=7.6$ Hz, 8H, $H_{5'}$), 7.72 (s, 8H, $H_{1'}$), 7.55 (d, $^3J_{HH}=7.4$ Hz, 8H, $H_{8'}$), 7.54 (s, 8H, H_B), 7.52 (d, $^3J_{HH}=8.0$ Hz, 8H, $H_{3'}$), 7.40 (t, $^3J_{HH}=7.2$ Hz, 8H, $H_{6'}$), 7.32 (t, $^3J_{HH}=7.2$ Hz, 8H, $H_{7'}$), 7.18 (t, $^3J_{HH}=2.2$ Hz, 4H, H_E), 5.33 (s, 16H, $H_{H-H'}$), 3.91 (s, 16H, $H_{9'-9''}$).

^{13}C NMR ($CDCl_3$): 157.997 (C_D), 147.08 ($C_{1-4-6-9-11-14-16-19}$), 143.939 (C_A), 143.73 ($C_{9''}$), 142.42 ($C_{8''}$), 141.78 ($C_{4''}$), 141.32 ($C_{5''}$), 135.28 ($C_{2'}$), 130.95 ($C_{2-3-7-8-12-13-17-18}$), 126.91 ($C_{6'}$), 126.86 ($C_{7'}$), 126.69 ($C_{3'}$), 125.18 ($C_{8'}$), 124.685 ($C_{1'}$), 120.033 ($C_{4'}$), 119.975 ($C_{5'}$), 119.79 ($C_{5-10-15-20}$), 115.275 (C_B), 102.87 (C_E), 70.752 (C_H), 36.904 ($C_{9'}$).

Analysis: calcd for $C_{156}H_{108}N_4O_8\cdot 2CH_3CO_2Et$: C, 84.08; H, 5.33; N, 2.39; found: C, 84.62; H, 6.03; N, 1.57, MALDI TOF-MS calcd for $C_{156}H_{108}N_4O_8$: 2166.550 $[MH]^+$, found 2166.596 $[MH]^+$. UV–vis (CH_2Cl_2): $\lambda_{max/nm}$ 270 (fluorene, $\varepsilon_{270}=141\,700$), 292 (fluorene, $\varepsilon_{2912}=64\,600$), 304 (fluorene, $\varepsilon_{304}=71\,000$), 423 (Soret band, $\varepsilon_{423}=245\,300$), 516 ($Q_1$ band, $\varepsilon_{516}=10\,700$), 551 ($Q_2$ band, $\varepsilon_{551}=2200$), 592 (Q_3 band, $\varepsilon_{592}=2200$) and 653 nm (Q_4 band, $\varepsilon_{653}=4600$).

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.02.015.

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