Tetrahedron 65 (2009) 10693–10700

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Fluorenyl dendrimer porphyrins: synthesis and photophysical properties

Samuel Drouet [a], Christine O. Paul-Roth [a,b,*]

[a] *Groupe Ingénierie Chimique & Molécules pour le Vivant, ICMV-SCR-UMR-CNRS 6226, Université de Rennes I, 35042 Rennes Cedex, France*
[b] *Institut National des Sciences Appliquées-INSA de Rennes, France*

ARTICLE INFO

Article history:
Received 8 September 2009
Received in revised form
8 October 2009
Accepted 12 October 2009
Available online 4 November 2009

Keywords:
Fluorescence
Porphyrins
Fluorene
Light harvesting
Red emission

ABSTRACT

New symmetrical dendrimeric type super-porphyrin bearing sixteen fluorenyl donor groups sixteen fluorenylporphyrin **SOFP** (**1**) have been synthesized and characterized. Preliminary photophysical properties are reported; in comparison to the references first generation dendrimer tetra-fluorenylporphyrin **TOFP** (**2**) bearing four peripheral fluorenyl and second generation dendrimer octa-fluorenylporphyrin **OOFP** (**3**) bearing eight peripheral fluorenyl, the luminescence properties are slightly improved. It is found that the excitation energy transfer occurs from the sixteen fluorenyl units to the porphyrin core, following what the porphyrin emits intense red light.

1. Introduction

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. Consequently, they present wide potential applications in different fields: such as, for instance, light harvesting, Organic Light-Emitting Diodes (OLEDs) or switches.

Light harvesting can be optimized by attaching four energy donor dendrons to the porphyrin skeleton, to obtain an antenna system comprising a central porphyrin unit linked to four peripheral photon-harvesting hydrocarbon moieties.[1–3] Recently a series of star-shaped porphyrins bearing pendant linear oligofluorene arms have been reported.[4,5] Indeed, Fréchet[6] had demonstrated that the antenna effect was facilitated in dendritic architectures versus the corresponding linear case and reported the synthesis of porphyrin systems with modified fluorenyl units as light-harvesting two-photon absorbing chromophores.[7,8] The same year, for tuning the optical properties of polymers, the synthesis of hyperbranched polymers containing porphyrin core possessing fluorenyl arms has also been reported.[9]

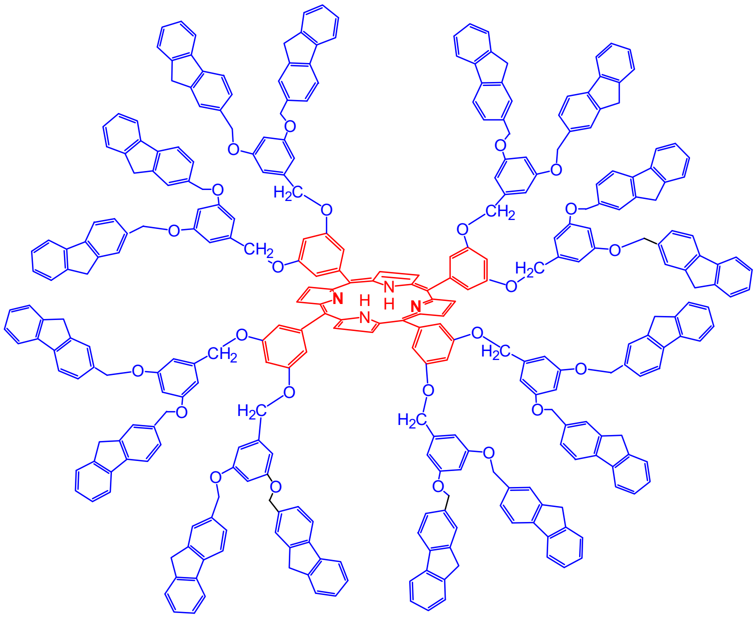
We have previously reported the synthesis of porphyrin possessing four fluorenyl arms directly connected at the *meso*-positions (**TFP** compound **4**) and demonstrated that the ruthenium(II) complexes are efficient catalysts.[10] More recently, we focused on the photophysical properties of such porphyrins[11,12] and a complete family of relevant porphyrins was studied in collaboration with Williams.[13] Surprisingly, this porphyrin **TFP** exhibited a high quantum yields (24%), demonstrating the good capacity of the fluorenyl units to enhance quantum yields by increasing the radiative process. By the fact that **TFP** exhibits good red chromaticity and enhanced emission efficiency, it is interesting to incorporate this compound in the fabrication of Organic Light-Emitting Diodes (OLEDs), this work is actually in progress.[14] In this view, very recently, a density functional theory (DFT) study on photophysical properties of the complete family of porphyrin bearing fluorenyl arms synthesized by Paul-Roth was accomplished.[15] This work, done by Ren et al., provides some useful information for the charge carrier transport properties of high efficiency red light-emitting material by theoretical investigations.

The aim of the present work was to exploit this capacity of the fluorenyl arms to enhance further fluorescence. So the synthesis of a super-porphyrin bearing sixteen peripheral fluorenyl groups is proposed and compared to the references first generation molecule bearing four units (**TOFP**) and second generation bearing eight units (**OFP**). The target is to obtain highly luminescent soluble organic compounds, by the design of porphyrin possessing fluorenyl arms using Fréchet's style dendritic strategy. In more details, in this paper, we present systems in which a 5,10,15,20-tetraphenylporphyrin (**TPP**) is linked, via ether bridges, to four, eight and sixteen fluorenyl donor moieties, compounds **2**, **3** and **1**, respectively (Fig. 1), and in a second part preliminary photophysical results are reported and compared to previous data of these compounds in order to understand better the energy transfer between the fluorenyl units and the macrocyclic core.

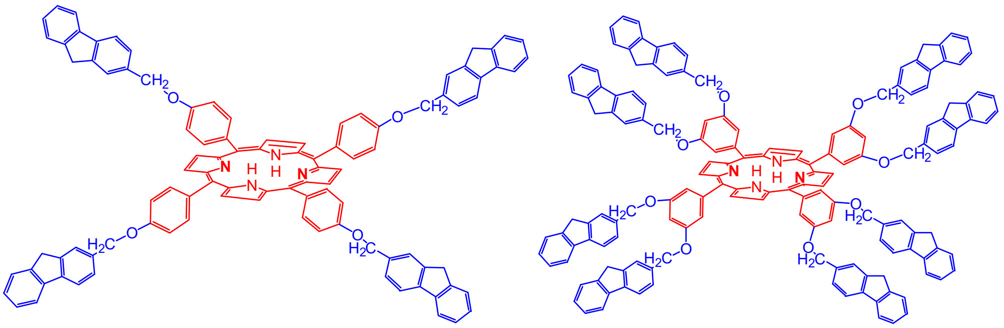
---

* Corresponding author. Tel.: +33 02 23 23 63 72; fax: +33 02 23 23 56 37.
E-mail addresses: christine.paul@univ-rennes1.fr, christine.paul@insa-rennes.fr (C.O. Paul-Roth).

0040-4020/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2009.10.043

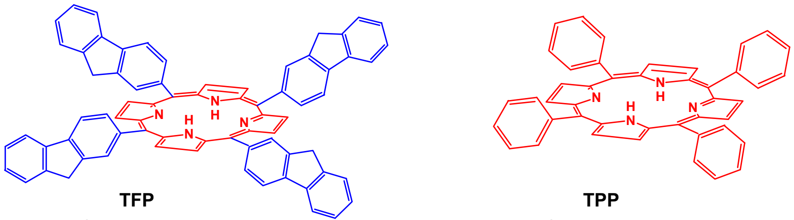


SOFP
Compound 1



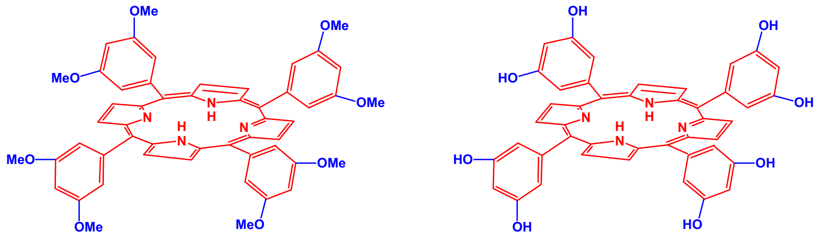
TOFP
Compound 2

OOFP
Compound 3



TFP
Compound 4

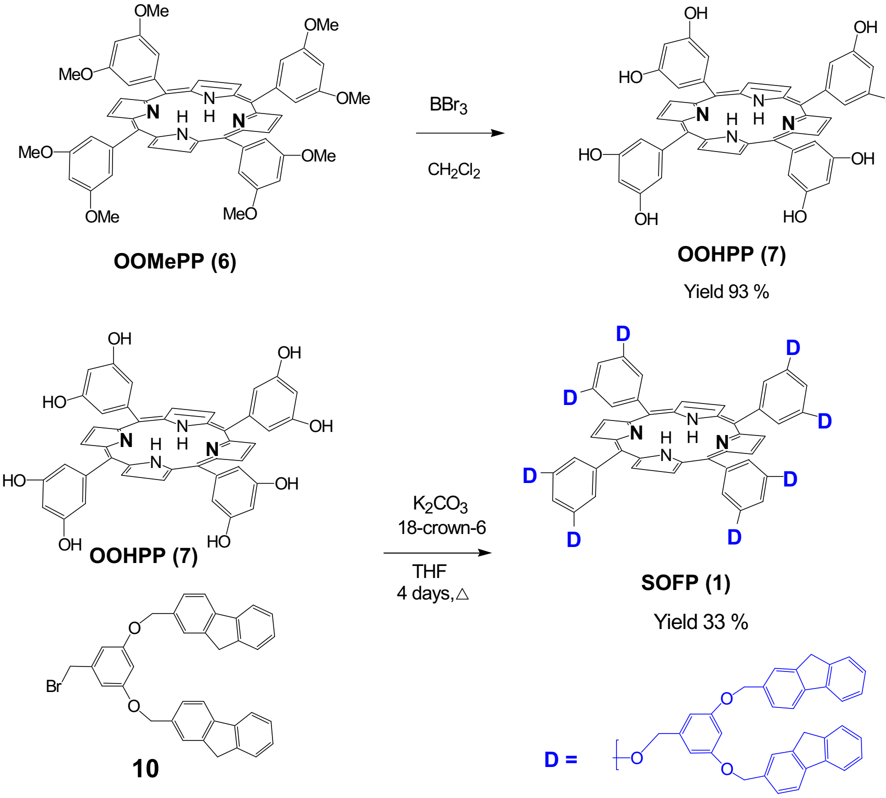
TPP
Compound 5



OOMePP
Compound 6

OOHPP
Compound 7

Figure 1. Compounds **1**, **2**, **3**, **4**, **5**, **6**, and **7**.



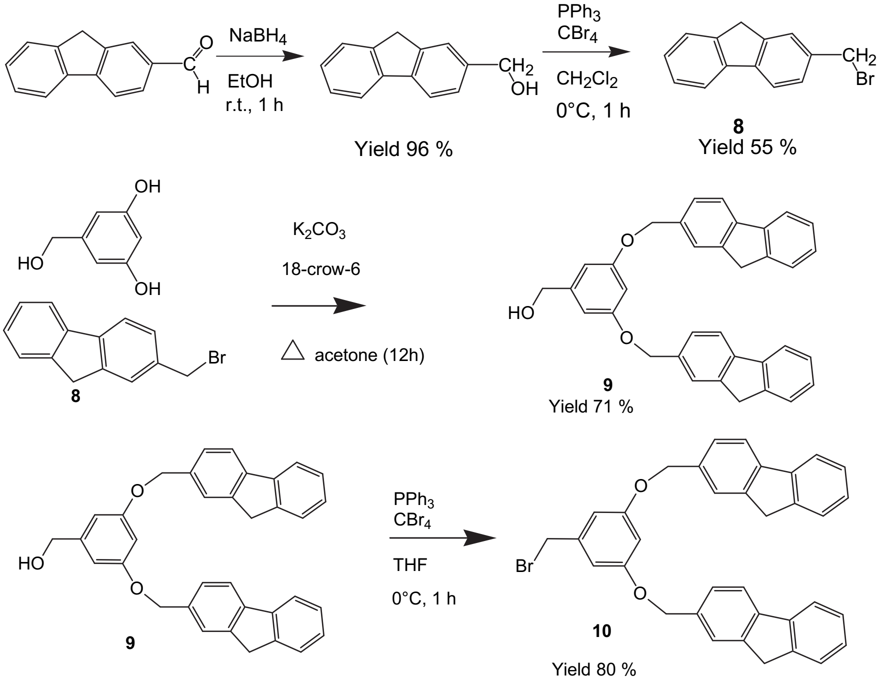
Scheme 1. Synthesis of porphyrins **6**, **7** and **SOFP 1**.

2. Results and discussion

2.1. Synthesis

The synthetic strategy developed for the preparation of these dendrimeric compounds is a Frechet's style condensation. First the porphyrin possessing eight anchoring points is synthesized as well as the new dendron **10**. In a second time, four of these dendrons are connected to the mother porphyrin core.

In more details, the intermediate porphyrin **7** (**OOHPP**), was obtained from the prepared methylated porphyrin analog, porphyrin **6** (**OOMePP**) by reaction with BBr_3 as illustrated in Scheme 1.[16]



Scheme 2. Synthesis of dendrons **9** and **10**.

The 2-hydroxyl-methyl-fluorene was obtained by reduction of commercial fluorene-2-carboxaldehyde and the corresponding alcohol was then brominated with carbon tetrabromide to obtain 2-bromomethyl-fluorene **8**. The detailed synthesis of these building blocks was described earlier.[17] First the alcoholic form of the dendron **9** was obtained by condensation from the previous prepared bromide **8** and from commercial 5-hydroxymethyl-benzen-1,3-diol in acetone using potassium carbonate as a base in presence of 18-crown-6 (Scheme 2). Finally, the intermediate dendron **9** was obtained pure as a white solid after purification in 71% yield. The alcohol **9** was then brominated with carbon tetrabromide in THF and the desired brominated dendron **10** was obtained pure as a white solid after flash chromatography in 80% yield.

The target super-porphyrin **1** (Fig. 1), containing 16 absorbing donor chromophores in a multivalent dendritic configuration was eventually synthesized from the prepared bromide dendron **10** (10 equiv) and **OOHPP 7** (1 equiv) in dry THF using potassium carbonate as a base in presence of 18-crown-6 (Scheme 2). The fixation of all 16 donor chromophores in compound **1** was confirmed by matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) as well as by NMR. Compound **1** is soluble in most organic solvents but can be purified by precipitation and is well-behaved on silica gel chromatography. The desired porphyrin **1** was thus obtained as a brown-violet solid (33%).

In the conditions used, the non-substituted fluorenyl arm is stable, but note that alkyl chains have often been introduced on the position-9 of the fluorenyl units by other researchers to increase their solubility. This is presently not necessary for compound **1**.[5]

2.2. Photophysical properties

2.2.1. Electronic spectra. The UV–visible spectra of **1**, **2**, and **3** exhibit an intense Soret band with a maximum absorption similar around 423 nm (Fig. 2). This band is slightly red shifted compared to 417 nm for **TPP** (**5**), but not as much as for **TFP** (**4**) (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 **2**, the four fluorene arms absorb in the UV range with a maximum absorption peak at 272 nm, while for compound **3** possessing eight arms the absorption is stronger with a maximum at 263 nm. These units were absorbing at 270 nm for new compound **1**. For the super-porphyrin **1**, we can notice that the absorption in the UV of the fluorenyl groups at 270 nm is as strong as the Soret band.

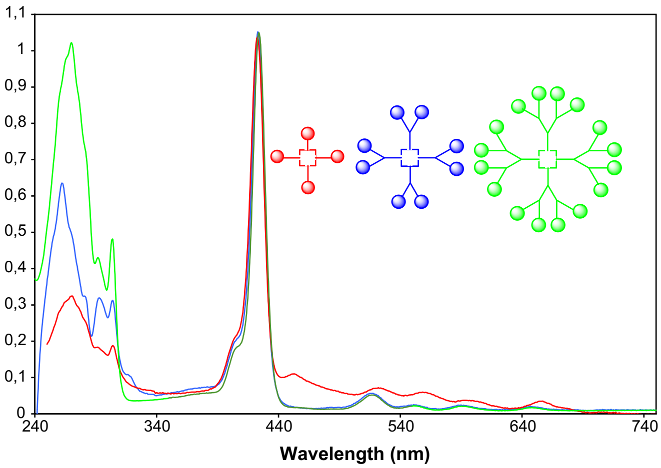


Figure 2. UV–visible absorption spectra for compounds **1** (green), **2** (red) and **3** (blue), in CH_2Cl_2 at 25 °C (~2.0×10^{-6} M for **1** and normalized to the same absorbance for **2** and **3**).

Figure 3 shows the absorption spectra of **1**, **6**, and **10**. The absorption spectrum of **1** shows the characteristic peaks at 280 and 300 nm of compound **10** in addition to the porphyrin Soret band at 423 nm and less intense Q-bands, the first of which appear at 513 nm for compound **6**. Obviously, the dendrons and the porphyrin core retain their individual characteristics. These considerations indicate that this molecular pentad **1**, in which the porphyrin acceptor is linked, via spacers, to four donor dendrons, forms a suitable choice for exploiting the *antennae* effect between peripheral units and the central core. Effectively, for this effect, it is better to have a multicomponent structure in which the donors and acceptors retain their individual characteristics. Elsewhere for a realistic description of the photosynthetic antenna function, a porphyrin-based model system should exhibit high local concentrations of the light-harvesting chromophores.

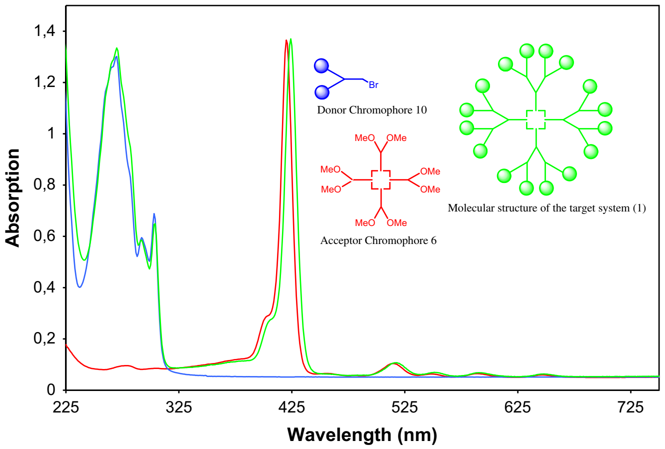


Figure 3. Absorption spectra of **6** (red), **10** (blue), and **1** (green) in chloroform at room temperature. The spectrum of **10** is normalized to the spectrum of **1** at 300 nm, while the height of the Soret band at 420 nm in the spectrum of **6** is normalized to the height of the Soret band of **1**.

2.2.2. Emission spectroscopy. The emission spectrum of compound **1**, after excitation in the Soret band reveals a strong red fluorescence with a peak maximum at 656 nm and a big shoulder at 721 nm (Fig. 4). For comparison, the emission spectrum of compound **2** is

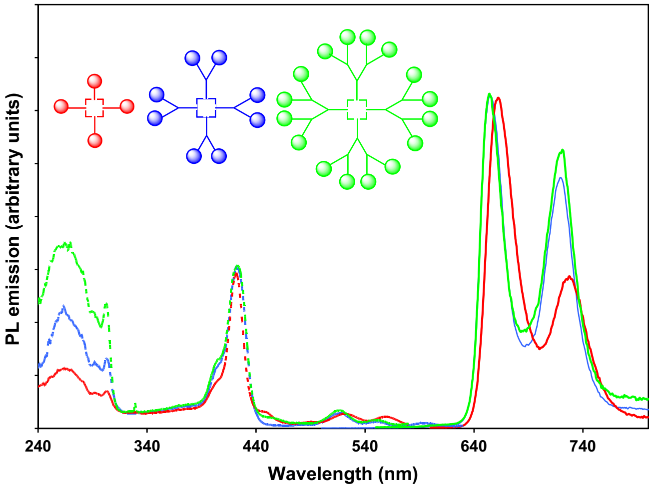


Figure 4. Photoluminescence spectra of free ligands **1** (plain green), **2** (plain red) and **3** (plain blue) in CH_2Cl_2 solution (~1.0×10^{-6} M), at 25 °C, the emission spectra were cut above 800 nm. Excitation spectra of compounds **1** (dashed green), **2** (dashed red) and **3** (dashed blue) at 660 nm.

also reported, after excitation in the Soret band, a strong red emission at 663 nm and a weaker shoulder at 728 nm are observed (Fig. 4). Concerning, compound **3**, after excitation in the Soret band, a strong red emission at 656 nm and a stronger shoulder at 721 nm are observed. The emission profile for compounds **1** and **3** are quite similar. The emission for compound **2** possessing only four fluorenyl groups in the *para* position, is slightly red shifted.

2.2.3. Energy transfer. The emission spectra of compound **1** show that the fluorenyl donors transfer energy with high efficiency to the porphyrin acceptor (Fig. 5). Excitation of **1** at 300 nm results mainly in the red emission of porphyrins with a maximum at 656 nm. It is noteworthy that the blue fluorenyl emission is almost completely quenched, and emission is seen predominantly from the porphyrin. Compound **1** shows nice red emission when excited at 300 nm or 423 nm. Efficiency of energy transfer in this complex process will be studied in details.[18]

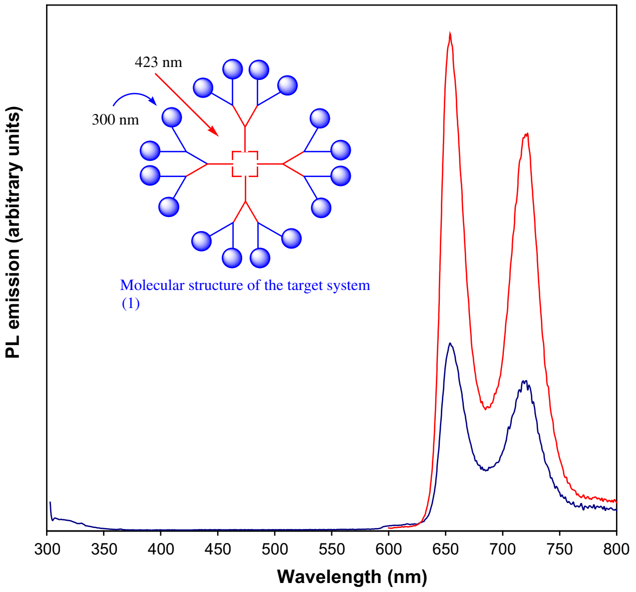


Figure 5. Fluorescence spectra of **1** in chloroform at room temperature under single photon excitation conditions. A near complete quenching of the donor emission is observed upon excitation of **1** at 300 nm (blue), resulting in a significant porphyrin emission from **1**, compared to direct emission of **1** at 423 nm (red).

The excitation spectrum of compound **1** around 660 nm reveals that the strong emission from the Soret state is populated when the fluorenyl band is excited. This indicates that excitation over all the 200–650 nm region leads to the population of the fluorescent excited states of the porphyrin, as the fluorene absorption becomes apparent under such excitation conditions. For comparison, the corresponding excitation spectra of compounds **1**, **2**, and **3** are shown in Figure 4, and we can see a nicely regular enhancement in the UV region due to the fluorenyl arms.

Thus for these compounds **1**, **2**, and **3**, the luminescence can be modulated in a large range of excitation wavelengths from UV to red, to finally obtain the desired red emission.

2.2.4. Fluorescence quantum yields. The fluorescence quantum yields of these compounds were next determined by comparing with a calibration standard of compound **5** (**TPP**) in degassed toluene solution presenting a fluorescence quantum yield of 0.12,[19] preferentially to a benzene solution with a fluorescence quantum yield of 0.13.[20] [In this latter case, different refractive indices of the solvents used in the standard and sample must be corrected.[21] 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:

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

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.[22]

Values of quantum yields of free ligands **1**, **2**, **3**, **4**, and **5** are reported in Table 1. All measurements were obtained under an argon atmosphere to limit photo-oxidative degradation (Table 1). Compounds **1**, **2** and **3** present a luminescence quantum yield (14, 10 and 13%, respectively), which is similar to that of the reference compound **5** (12%). Further photophysical investigations will be undertaken to rationalize these results.[18]

Table 1

Photophysical properties of the fluorenyl porphyrins **1**, **2**, and **3** in dilute CH_2Cl_2 solution at 298 K, and of **4** and **5**, under the same conditions for comparison

Porphyrin	**SOFP (1)**	**TOFP (2)**	**OOFP (3)**	**TFP (4)**	**TPP (5)**
λ_{max}/nm[a] Soret band	423	423	423	426	417
λ_{em}/nm	656, 721	663, 728	656, 721	663, 730	653, 721
Φ_f [b]	0.14	0.10	0.13	0.24	0.12

[a] Wavelengths of the absorption maxima in the Soret or B band region (400–450 nm range).

[b] Fluorescence quantum yields in degassed solution, using **TPP** in toluene as standard, following excitation into the Soret bands.

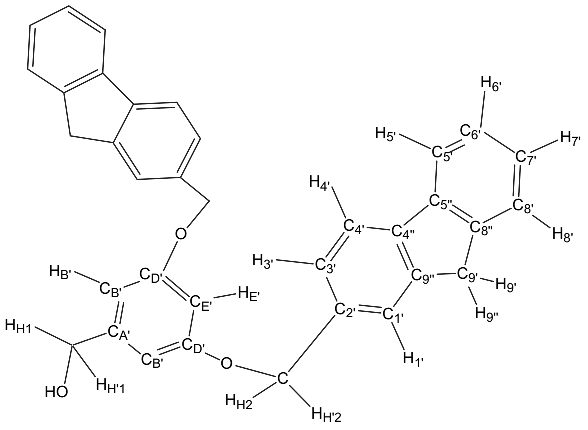
3. Conclusions

In summary, we have synthesized and characterized a new superporphyrin **1** bearing 16 fluorenyl pendant arms at the *meso*-positions. The photophysical properties are compared to the references first generation dendrimer bearing four units and second generation bearing eight units. These porphyrins emit essentially red light after selective UV or visible irradiation. In 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 *antennae*. Due to the flexibility of molecular design, dendritic architectures allow site-specific positioning of multiple chromophore units in three-dimensional space; we have found that a large, spherical third-generation dendrimer porphyrin, upon exposure to UV light, shows high energy transfer efficiency from the peripheral aromatic fluorenyl units to the porphyrin core. 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 **4**,[10] **5**[23], and **6**,[24,25] we now expect to obtain a polymeric 3D network composed of spherical chromophores after connections of the 16 fluorenyl pendant arms. This should allow growing a dendrimer-polymeric 3D structure from such macrocycles, possessing several connecting points for each monomer. This family of compounds constitutes therefore an interesting building block to access new red emissive organic materials.

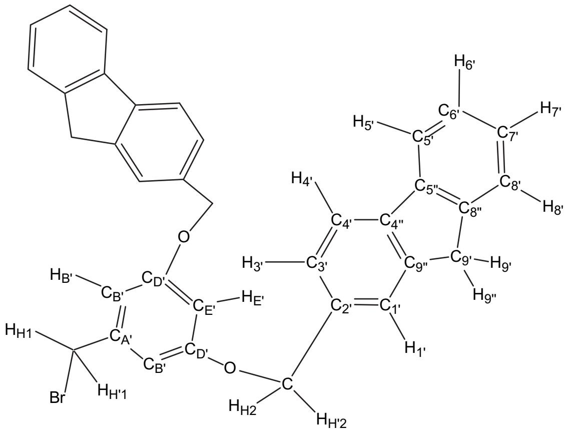
4. Experimental

4.1. General

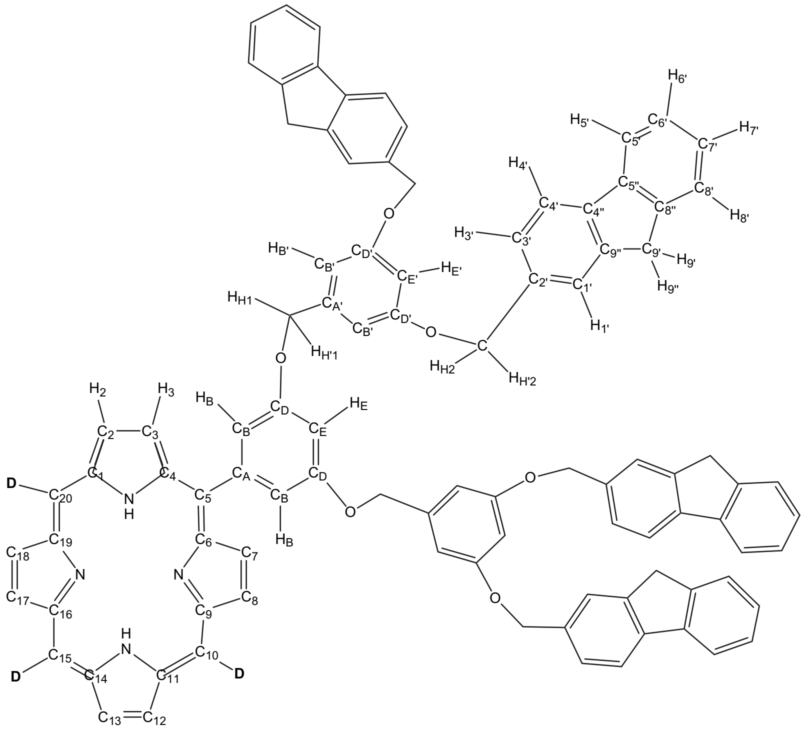
All reactions were performed under argon and were magnetically stirred. Solvents were distilled from appropriate drying agent prior to use, CH_2Cl_2 from CaH_2, $CHCl_3$ from P_2O_5 and all other solvents were HPLC grade. Commercially available reagents were used without further purification unless otherwise stated. ^1H NMR and



Compound 9



Compound 10



Compound 1

Figure 6. Hydrogen and carbon atom-labeling for dendrons **9**, **10** and for the porphyrin **1**.

^{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. References **TFP**=tetrafluorenylporphyrin, **TPP**=tetraphenylporphyrin. The hydrogen and carbon atom-labeling scheme for the porphyrin ligand **1** as well as for dendron **9** and **10** are shown in Figure 6.

4.2. Synthesis of the arms

*4.2.1. Synthesis of 2-bromomethyl-fluorene (**8**) from 2-hydroxylmethyl-fluorene was described earlier*[17]. ^{1}H NMR (200 MHz, $CDCl_3$): 7.81 (d, $^{3}J_{HH}$=8.0 Hz, 1H), 7.75 (d, $^{3}J_{HH}$=7.7 Hz, 1H), 7.59 (d, $^{3}J_{HH}$=8.8 Hz, 2H), 7.43 (d, $^{3}J_{HH}$=7.9 Hz, 1H), 7.38 (d, $^{3}J_{HH}$=8.0 Hz, 1H), 7.37 (s, 1H), 4.61 (s, 2H, $C\mathbf{H_2}$–Br), 3.94 (s, 2H, $C\mathbf{H_{2}}_{\text{fluorene}}$).

*4.2.2. Synthesis of alcool **9***. To a solution of the commercial 5-hydroxymethyl-benzen-1,3-diol (0.98 g, 7.02 mmol) and 2-bromomethyl-fluorene **8** (4.00 g, 15.44 mmol) in 20 mL of dry acetone was added K_2CO_3 (3.87 g, 28.0 mmol) and 18-crown-6 (1.85 g, 7.02 mmol). This solution is stirred under argon at reflux during 12 h. The reaction mixture was cooled at room temperature, filtered and evaporated to dryness. The crude product was partitioned between water and $CH_2Cl_{2,}$ and the organic phase was dried over $MgSO_4$ and evaporated to dryness. The residue was purified by column chromatography on silica gel (CH_2Cl_2) to yield 2.47 g of a white solid (71%).

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.81 (d, $^{3}J_{HH}$=7.5 Hz, 4H, $H_{4'-5'}$), 7.64 (s, 2H, $H_{1'}$), 7.57 (d, $^{3}J_{HH}$=7.1 Hz, 2H, $H_{8'}$), 7.46–7.26 (m, 6H, $H_{3'-6'-7'}$), 6.69 (br s, 2H, $H_{B'}$) 6.63 (br s, 1H, $H_{E'}$), 5.15 (s, 4H, $H_{2-2'}$), 4.68 (d, $^{3}J_{HH}$=3.7 Hz, 2H, $H_{1-1'}$), 3.95 (s, 4H, $H_{9'-9''}$).

*4.2.3. Synthesis of final dendron **10***. To a THF solution (100 mL) of alcohol **9** (1.60 g, 3.22 mmol) was added carbon tetrabromide (1.28 g, 38.7 mmol) followed by the portion-wise addition of triphenylphosphine (1.01 g, 38.7 mmol). The mixture was stirred at 0 °C for 1 h, and 2 h at room temperature. The crude product was partitioned between water (to neutralize CBr_4) and CH_2Cl_2 then the organic phase was dried over $MgSO_4$ and evaporated to dryness. The residue was purified by column chromatography on silica gel (5:1 pentane/CH_2Cl_2) to give 1.44 g (80%) of **10** as a white solid.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.81 (d, $^{3}J_{HH}$=7.5 Hz, 4H, $H_{4'-5'}$), 7.63 (s, 2H, $H_{1'}$), 7.57 (d, $^{3}J_{HH}$=7.1 Hz, 2H, $H_{8'}$), 7.45–7.26 (m, 6H, $H_{3'-6'-7'}$), 6.71 (d, $^{4}J_{HH}$=2.1 Hz, 2H, $H_{B'}$) 6.63 (t, $^{4}J_{HH}$=2.1 Hz, 1H, $H_{E'}$), 5.13 (s, 4H, $H_{2-2'}$), 4.46 (s, 2H, $H_{1-1'}$), 3.94 (s, 4H, $H_{9'-9''}$).

4.3. Synthesis of porphyrins

*4.3.1. Synthesis of porphyrin **6***. Tetrakis(3,5-dimethoxyphenyl)-porphyrin **6** (**OOMePP**) was prepared from pyrrole and the respective aromatic aldehyde using Adler–Longo condensation conditions.[26]

*4.3.2. Synthesis of porphyrin **7***. Tetrakis(3,5-dihydroxyphenyl)-porphyrin **7** (**OOHPP**) was prepared by boron tribromide deprotection of tetrakis(3,5-dimethoxyphenyl)porphyrin **6**.

*4.3.3. Synthesis of super-porphyrin **SOFP 1***. The bromide dendron, compound **10** (500 mg, 0.90 mmol), tetrakis (3,5-dihydroxyphenyl)-porphyrin, **7** (74 mg, 0.09 mmol), K_2CO_3 (219 mg, 1.59 mmol) and 18-crown-6 (26 mg, 0.01 mmol), were dissolved in 20 mL of dry THF and stirred under argon at reflux for four days. Then the reaction mixture was cooled to room temperature and evaporated to dryness. The crude product was partitioned between water (200 mL) and dichloromethane (200 mL), the aqueous layer was extracted with dichloromethane (200 mL), and the combined extracts were dried by $MgSO_4$ and evaporated to dryness. Purification by flash chromatography eluting with 4:6 pentane/dichloromethane gave the super-porphyrin **1**, as a violet powder (150 mg, yield 33%).

^{1}H NMR (assignments aided by COSY) ($CDCl_3$): δ 8.85 (s, 8H, pyrrole), 7.55 (d, $^{3}J_{HH}$=7.4 Hz, 16H, $H_{5'}$), 7.49 (d, $^{3}J_{HH}$=7.8 Hz, 16H, $H_{4'}$), 7.45 (d, $^{4}J_{HH}$=2.2 Hz, 8H, H_B), 7.35 (s, 16H, $H_{1'}$), 7.34 (d, $^{3}J_{HH}$=7.4 Hz, 16H, $H_{8'}$), 7.22 (t, $^{3}J_{HH}$=6.7 Hz, 16H, $H_{6'}$), 7.16 (t, $^{3}J_{HH}$=7.3 Hz, 16H, $H_{7'}$), 7.15, (d, $^{3}J_{HH}$=7.1 Hz, 16H, $H_{3'}$), 7.04 (t, $^{4}J_{HH}$=2.1 Hz, 4H, H_E), 6.70 (d, $^{4}J_{HH}$=2.1 Hz, 16H, $H_{B'}$), 6.59 (t, $^{4}J_{HH}$=2.1 Hz, 8H, $H_{E'}$), 5.07 (s, 16H, $H_{H1-H1'}$), 4.92 (s, 32H, $H_{H2-H2'}$), 3.66 (s, 32H, $H_{9'-9''}$), −2.72 (br s, 2H, NH).

^{13}C NMR ($CDCl_3$): δ 160.30 ($C_{D'}$), 157.91 (C_D), 143.54 ($C_{9''}$), 143.32 ($C_{4''}$), 143.00 (br s, $C_{1-4-6-9-11-14-16-19}$), 141.50 ($C_{8''}$), 141.19 ($C_{5''}$), 135.13 ($C_{2'}$), 131.00 (br s, $C_{2-3-7-8-12-13-17-18}$), 126.68 ($C_{7'}$), 126.65 ($C_{6'}$), 126.28 ($C_{3'}$), 124.94 ($C_{8'}$), 124.26 ($C_{1'}$), 119.86 ($C_{5'}$), 119.76 ($C_{4'}$), 115.36 (C_B), 106.45 ($C_{B'}$), 102.42 (C_E), 102.41 ($C_{5-10-15-20}$), 101.86 ($C_{E'}$), 70.38 (C_{H1}), 70.31 (C_{H2}), 36.67 ($C_{9'}$).

Anal. Calcd for $C_{324}H_{238}N_4O_{24}\cdot 3CHCl_3$: C, 79.67; H, 4.93; N, 1.14. Found: C, 79.50; H, 5.36; N, 0.29. MALDI-TOF MS calcd for $C_{324}H_{238}N_4O_{24}$: 4572.4645 $[MH]^+$, found 4575.9907 $[MH]^+$, 4398.4219 $[MH-\text{fluorenyl}]^+$, 4220.0283 $[MH-2\text{fluorenyl}]^+$, 4039.8440 $[MH-3\text{fluorenyl}]^+$. UV–vis (CH_2Cl_2): $\lambda_{\max/}$nm ($10^{-3}\epsilon$) 270 (421, fluorene), 304 (194, fluorene), 423 (433, Soret band), 517 (17, Q_1), 552 (6, Q_2), 590 (5, Q_3), 647 (3, Q_4).

Acknowledgements

The authors are grateful to S. Sinbandhit (CRMPO), G. Simonneaux and P. Le Maux (ICMV-UMR 6226) for their technical assistance and helpful discussions.

References and notes

1. Abraham, R. J.; Hawkes, G. E.; Hudson, M. F.; Smith, K. M. *J. Chem. Soc., Perkin. Trans. 2* **1975**, 204–211.
2. Fonda, H. N.; Gilbert, J. V.; Cormier, R. A.; Sprague, J. R.; Kamioka, K.; Connolly, J. S. *J. Phys. Chem.* **1993**, *97*, 7024–7033.
3. Toeibs, A.; Haeberle, N. *Justus Liebigs Ann. Chem.* **1968**, *718*, 183–187.
4. Li, B.; Xu, X.; Sun, M.; Fu, Y.; Yu, G.; Liu, Y.; Bo, Z. *Macromolecules* **2006**, *39*, 456–461.
5. Li, B.; Li, J.; Fu, Y.; Bo, Z. *J. Am. Chem. Soc.* **2004**, *126*, 3430–3431.
6. Harth, E. M.; Hecht, S.; Helms, B.; Malmstrom, E. E.; Fréchet, J. M.; Hawker, C. J. *J. Am. Chem. Soc.* **2002**, *124*, 3926–3938.
7. Dichtel, W. R.; Serin, J. M.; Edder, C.; Fréchet, J. M. *J. Am. Chem. Soc.* **2004**, *126*, 5380–5381.
8. Oar, M. A.; Serin, J. M.; Fréchet, J. M. *Chem. Mater.* **2006**, *18*, 3682–3692.
9. Sun, M.; Bo, Z. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *45*, 111–124.
10. Paul-Roth, C.; Rault-Berthelot, J.; Simonneaux, G. *Tetrahedron* **2004**, *60*, 12169–12175.
11. Paul-Roth, C. O.; Simonneaux, G. *Tetrahedron Lett.* **2006**, *47*, 3275–3278.
12. Paul-Roth, C. O.; Simonneaux, G. C. R. *Acad. Sci., Ser. IIb: Chim.* **2006**, *9*, 1277–1286.
13. Paul-Roth, C.; Williams, G.; Letessier, J.; Simonneaux, G. *Tetrahedron Lett.* **2007**, *48*, 4317–4322.
14. Drouet, S.; Paul-Roth, C.; Williams, J. A. G.; Fattori, V, in preparation.
15. Ren, X.; Ren, A.; Feng, J.; Sun, C. *J. Photochem. Photobiol. A: Chem.* **2009**, *203*, 92–99.
16. Jiang, D.-L.; Aida, T. *J. Am. Chem. Soc.* **1998**, *120*, 10895–10901.
17. Drouet, S.; Paul-Roth, C.; Simonneaux, G. *Tetrahedron* **2009**, *65*, 2975–2981.
18. Drouet, S.; Williams, J.A.G.; Paul-Roth, C, in preparation.
19. Owens, J. W.; Smith, R.; Robinson, R.; Robins, M. *Inorg. Chim. Acta* **1998**, *279*, 226–231.
20. Zang, X. H.; Xie, Z. Y.; Wu, F. P.; Zhou, L. L.; Wong, O. Y.; Lee, C. S.; Kwong, H. L.; Lee, S. T.; Wu, S. K. *Chem. Phys. Lett.* **2003**, *382*, 561–566.
21. Quimby, D. J.; Longo, F. R. *J. Am. Chem. Soc.* **1975**, *97*, 5111–5117.
22. Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991–1024.

23. Paul-Roth, C.; Rault-Berthelot, J.; Simonneaux, G.; Poriel, C.; Abdalilah, M.; Letessier, J. *J. Electroanal. Chem.* **2006**, *597*, 19–27.
24. Rault-Berthelot, J.; Paul-Roth, C.; Poriel, C.; Juillard, S.; Ballut, S.; Drouet, S.; Simonneaux, G. *J. Electroanal. Chem.* **2008**, *623*, 204–214.
25. Drouet, S.; Ballut, S.; Rault-Berthelot, J.; Turban, P.; Paul-Roth, C. *Thin Solid Films* **2009**, *517*, 5474–5481.
26. Kim, J. B.; Adler, A. D.; Longo, F. R. In *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, NY, 1978; Vol. 1, Part A, p 85.