Tetrahedron 68 (2012) 7901–7910

Contents lists available at SciVerse ScienceDirect

Tetrahedron

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

A family of fluorenyl dendrons for porphyrin dendrimers synthesis

Areej Merhi[a,b], Samuel Drouet[a], Nicolas Kerisit[a], Christine O. Paul-Roth[a,b,*]

[a] *Institut des Sciences Chimiques de Rennes, ISCR-UMR CNRS 6226, Université de Rennes 1, 35042 Rennes Cedex, France*
[b] *Institut National des Sciences Appliquées, INSA-ISCR, Université Européenne de Bretagne, 35043 Rennes Cedex, France*

ARTICLE INFO

Article history:
Received 4 May 2012
Received in revised form 6 July 2012
Accepted 8 July 2012
Available online 16 July 2012

ABSTRACT

A series of dendrons bearing various number of fluorenyl donor groups have been synthesized. First, the reference compound *2-(bromomethyl)-9H-fluorene* (***8***) with one fluorenyl unit, then dendron **10**, with two fluorenyl arms, and finally new generation dendrons, **11** and **12**, bearing four peripheral fluorenyl arms were synthesized and characterized. A series of different generations of porphyrin dendrimers, obtained from these dendrons are also presented. Preliminary results on higher generation dendrimers are reported as well. Under mild basic conditions, surprisingly, a new compound **1** incorporating a fluorenyl unit in the cycle and three pendant fluorenyl arms was obtained by an intramolecular reaction of brominated tetrapod dendron **12**.

1. Introduction

Porphyrin systems are very interesting because the peripheral substituent on the macrocyclic core can modulate the physical properties at will. Such systems present wide potential applications in different fields: such as for instance Organic Light Emitting Diodes (OLEDs), light-harvesting antenna or photonic switches. Light-harvesting can be optimized by connecting four energy donor dendrons to the porphyrin core, to obtain an antenna system.[1–3] Recently, following such a scheme, a series of porphyrins bearing pendant linear oligofluorenyl arms have been reported.[4,5] In this connection, 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, the synthesis of hyperbranched polymers containing porphyrin with fluorenyl arms has also been reported.[9]

On our side, we have previously reported the synthesis of porphyrin possessing four fluorenyl arms directly connected at the *meso*-positions (**TFP**, compound **5**).[10–13] More recently, a complete family of relevant porphyrins was studied in collaboration with Williams.[14] Surprisingly, **TFP** exhibited a remarkably high quantum yield (24%), demonstrating the capacity of the fluorenyl units to enhance quantum yields. Logically, we next tested the corresponding platinum(II) complex in the fabrication of red Organic Light Emitting Diodes (OLEDs).[15,16] Also, new supramolecular assemblies using these efficient building blocks have been prepared and studied by our group.[17]

In this report, another way to use fluorenyl-based antenna with systems like **TFP** will be considered. Earlier, we described efficient systems in with 5,10,15,20-tetraphenylporphyrin (**TPP**), linked, via ether bridges, to 4, 8 and 16 fluorenyl donor moieties, compounds **2**, **3**[18] and **4**,[19] respectively (Fig. 1). After the successful synthesis of these porphyrin-fluorenyl dendrimers, we wondered about higher generation compounds. Indeed, starting from new dendrons, a new dendrimer with 32 fluorenyl donor moieties (**32F**) can be designed. However, in this respect, the synthesis of higher generation dendrons was required. To this aim new dendrons with four peripheral fluorenyl groups (**11** and **12**) are described and compared to the dendrons with two units (**9** and **10**), reported earlier by our group.[18,19] Results are reported and compared to previous data in order to better understand the reactivity of the new brominated tetrafluorenyl dendron **12**.

2. Results and discussion

2.1. Synthesis

The synthetic strategy developed for the preparation of these porphyrin-fluorenyl dendrimers is a Frechet's style condensation.[20] First, we will present rapidly the already described synthesis of dendrons **8**, **9**, **10** and in more detail, the synthesis of new dendrons **11** and **12**. In a second time, the synthesis of an intermediate porphyrin **7**, possessing anchoring points is reported. Then, the previous dendrons **8** and **10** are connected to porphyrin macrocycle to obtain the dendrimeric porphyrins **2**, **3** and **4**, as described earlier

---

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

0040-4020/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tet.2012.07.018

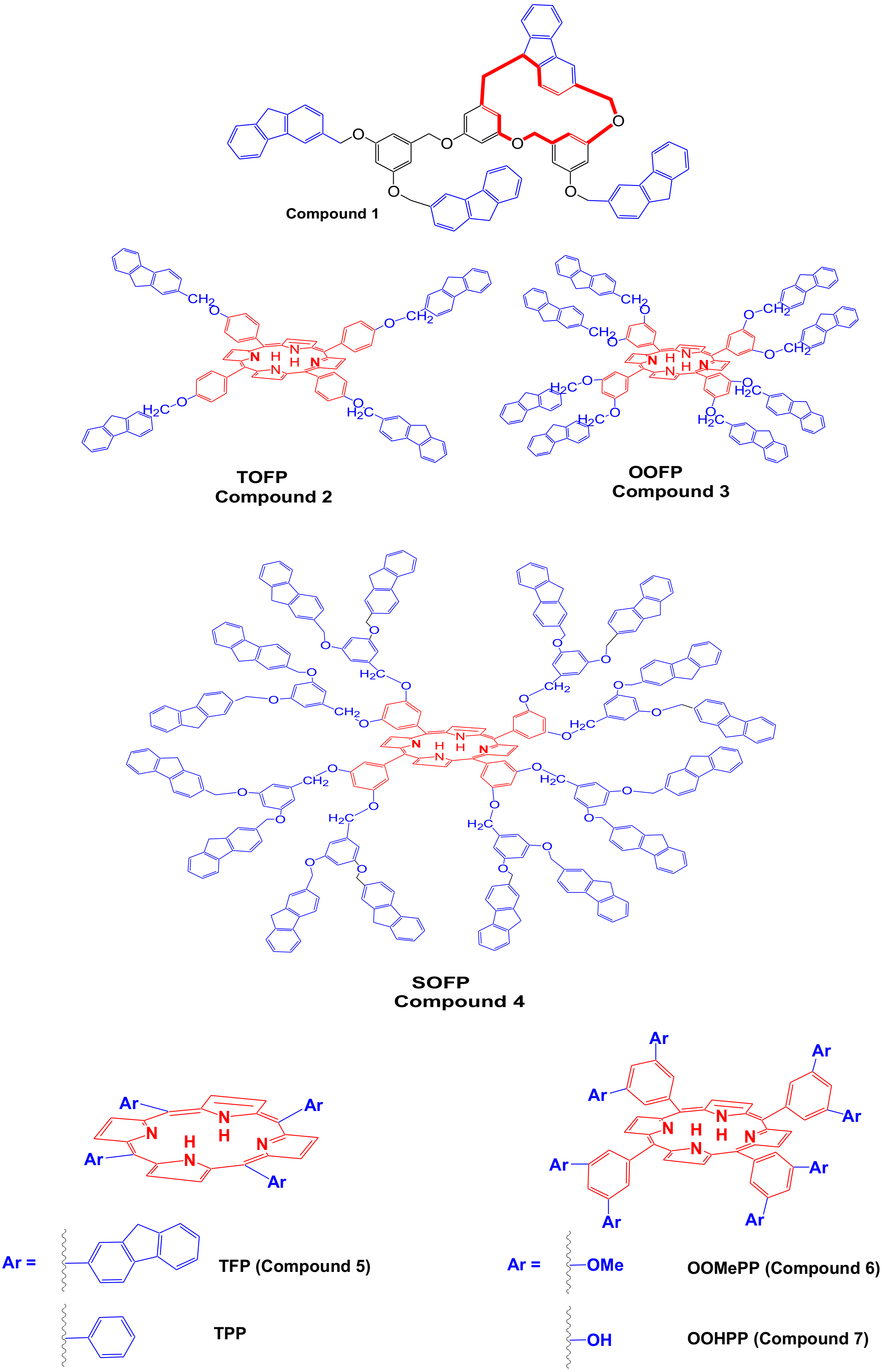
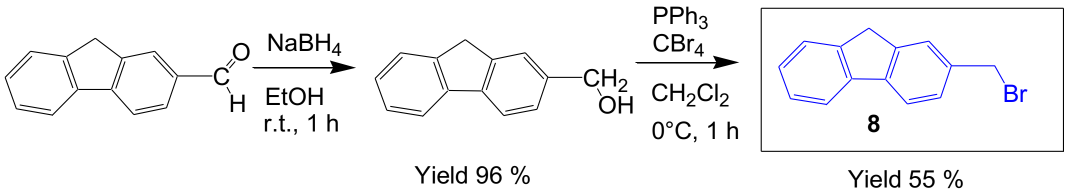


Fig. 1. Compounds **1**, **2**, **3**, **4**, **5**, **6** and **7**.

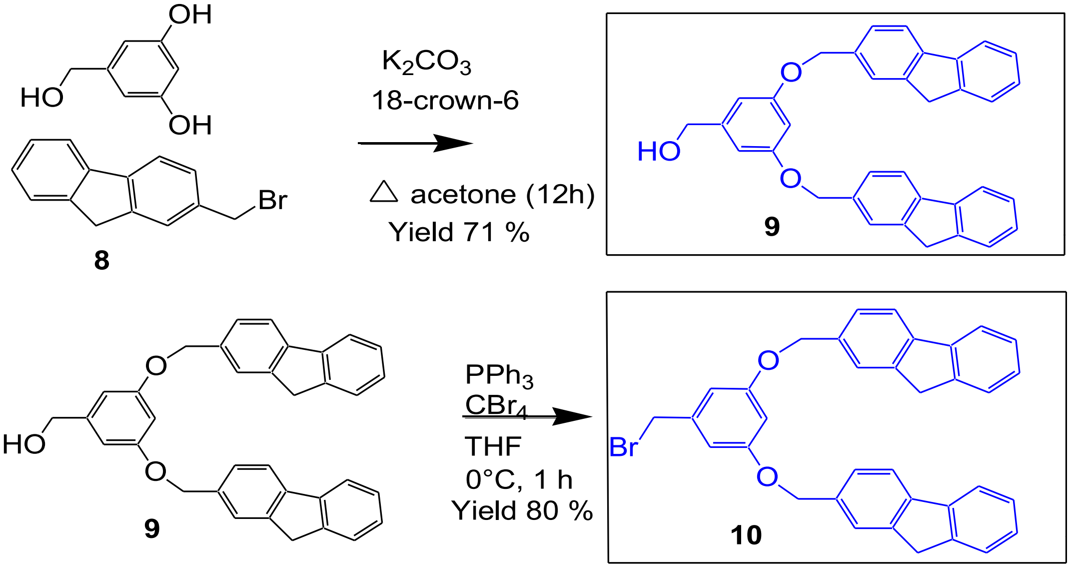
by our group.[18,19] Preliminary results on higher generation dendrimer syntheses are reported; in this case, eight of these new dendrons **12** are tried to be connected by Williamson reactions, to porphyrin **7**.

2.1.1. Synthesis of dendrons. 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** (Scheme 1).[18]

Next, the alcoholic form of the dendron **9** was obtained by condensation from the previous prepared bromide **8** and commercial 5-hydroxymethyl-benzen-1,3-diol, in basic conditions (Scheme 2).



Scheme 1. Synthesis of compound **8**.



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

Thus, the dendron **9** was obtained pure as a white solid after purification in 71% yield. This alcohol **9** was then brominated with carbon tetrabromide in THF and the final dendron **10** was obtained pure as a white solid after flash chromatography in 80% yield. The detailed synthesis of these building blocks was described earlier,[19] but for clarity characterization by NMR is reported; the hydrogen and carbon atom-labelling schemes for compounds **9** and **10** are shown in Fig. 2.

The new tetrapod dendron **11** was synthesized by condensation from the previous prepared bromide **10** and 5-hydroxymethyl-benzen-1,3-diol in acetone using potassium carbonate as a base in presence of 18-crown-6 (Scheme 3).

Finally, the dendron **11** was obtained pure as a white solid after purification in 70% yield. This alcohol **11** was then brominated with carbon tetrabromide in THF and the new desired dendron **12** was obtained pure as a white solid, after flash chromatography in 70% yield. New dendrons **11** and **12** were fully characterized, the hydrogen and carbon atom-labelling schemes for these dendrons **11** and **12** are shown in Fig. 3.

2.1.2. Synthesis of macrocycle. In this second part, different generations of porphyrin dendrimers are synthesized using convergent strategy. First, the intermediate porphyrin **7** (**OOHPP**), was obtained from the prepared methylated porphyrin analogue, porphyrin **6** (**OOMePP**) by reaction with BBr_3 as illustrated in Scheme 4.[21]

The small dendrimer **3**, generation G_1, containing eight absorbing donor chromophores was obtained by condensation from the prepared bromide **8** (10 equiv) and porphyrin **7** (1 equiv) in dry THF using potassium carbonate as base in presence of 18-crown-6. After purification, **3** was obtained as a brown-violet solid (38%) as already described.[18] For clarity, characterization by NMR is reported; the hydrogen and carbon atom-labelling scheme for this porphyrin **3** is shown in Fig. 4.

The larger dendrimer **4**, generation G_2, containing 16 chromophores was synthesized from dendron **10** (10 equiv) and porphyrin **7** (1 equiv) in the same conditions as before. Compound **4** was thus obtained as a brown-violet solid (33%) as described,[19] and for clarity, characterization by NMR is reported. The hydrogen and carbon atom-labelling scheme for this porphyrin **4** is shown in Fig. 5.

It should be noted that in the conditions used, the non-substituted fluorenyl arm is stable but alkyl chains have often been introduced on the position-9 of the fluorenyl units to increase their solubility.[5] This is presently not necessary for compounds **3** and **4**; they are very soluble and stable.

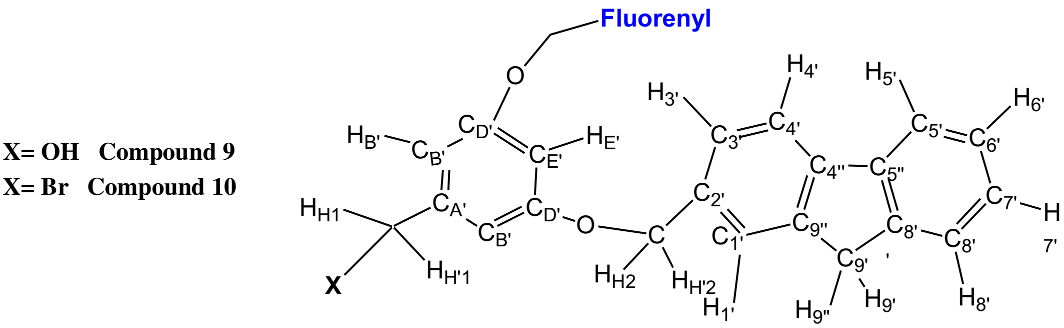
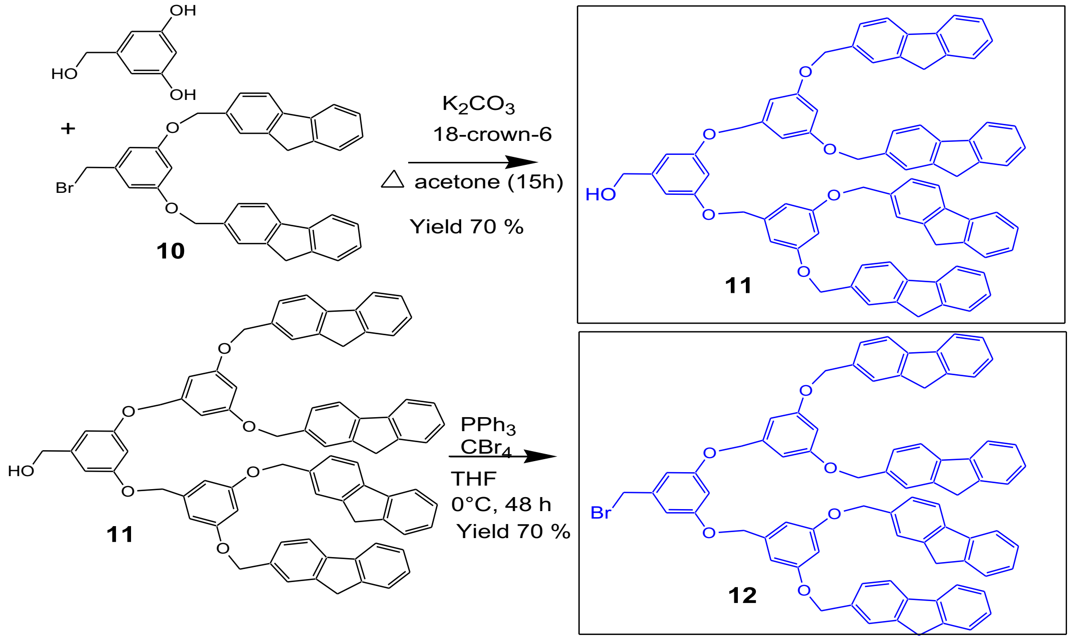


Fig. 2. Hydrogen and carbon atom-labelling for dendrons **9** and **10**.



Scheme 3. Synthesis of dendrons **11** and **12**.

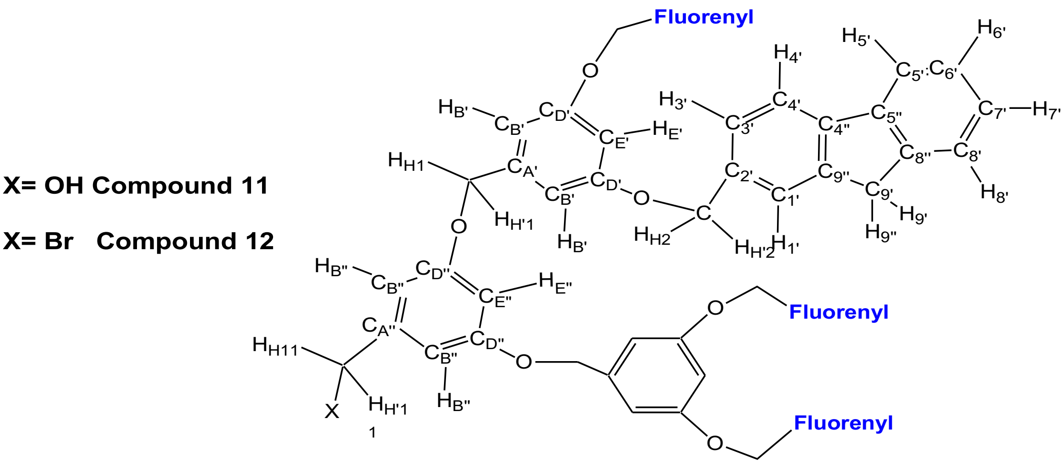
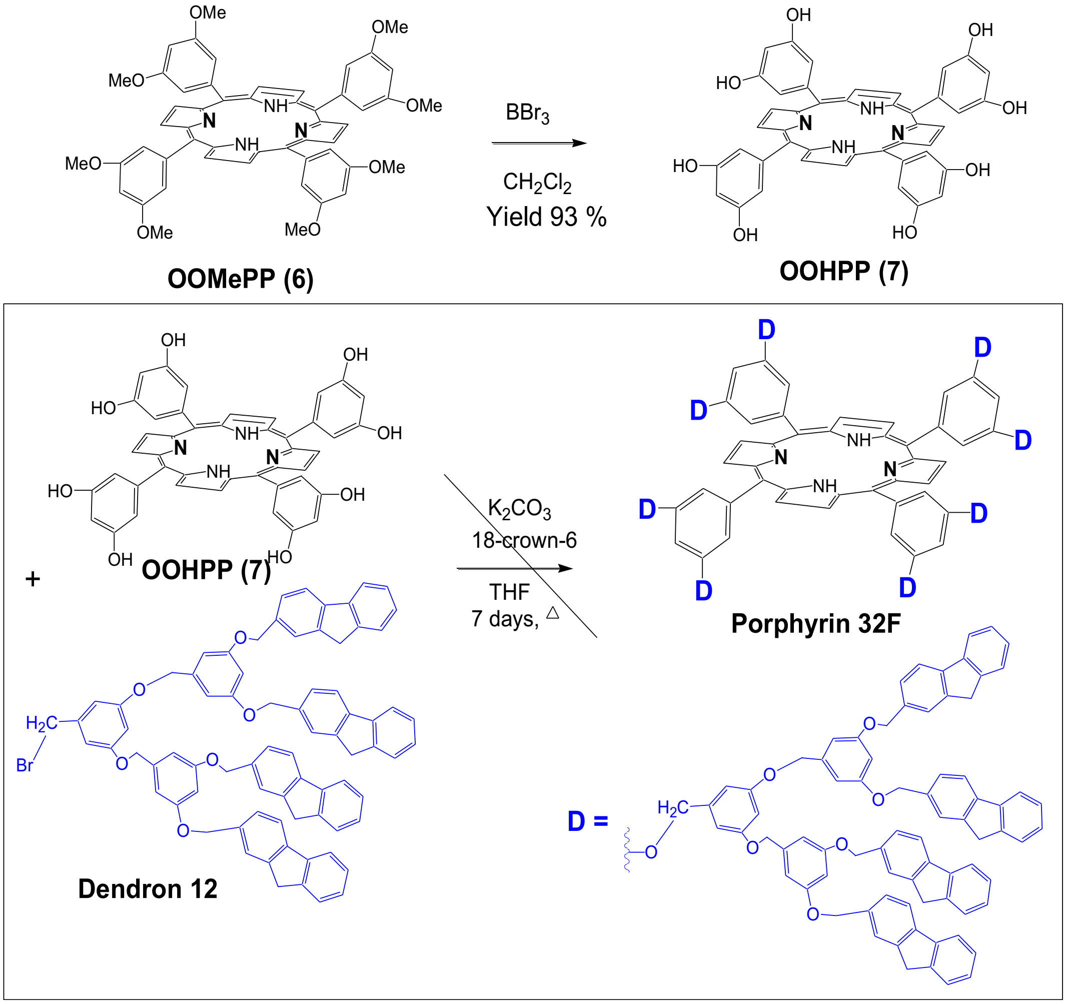


Fig. 3. Hydrogen and carbon atom-labelling for dendrons **11** and **12**.

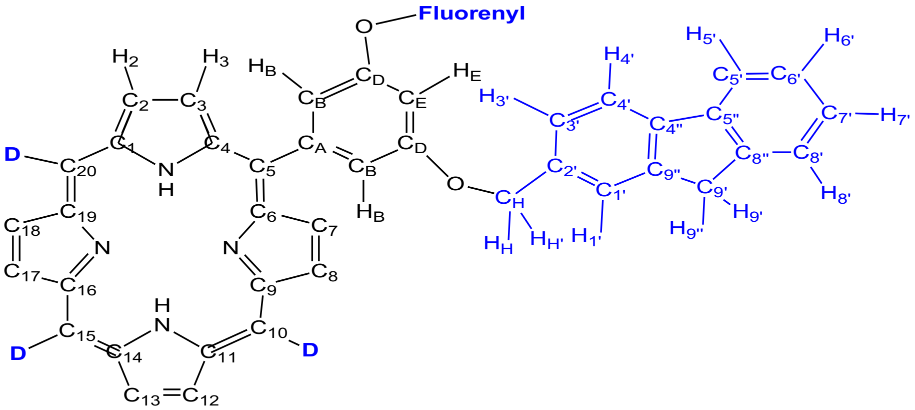
Preliminary results on the syntheses of a higher generation porphyrin dendrimer (G_3) are reported. Synthesis of **32F** (Scheme 4), containing thirty-two chromophores, was tried, and in this case, eight of new dendrons **12** should be attached to porphyrin **7**. For this synthesis, a mixture of 10 equiv of bromide **12** and 1 equiv of **7** in dry THF, using potassium carbonate as a base, in presence of 18-crown-6 was reacted (Scheme 4). Reaction progress is monitored by TLC, spotting directly from the



Scheme 4. Synthesis of porphyrin-intermediate **7** and attempt to synthesis porphyrin **32F**.

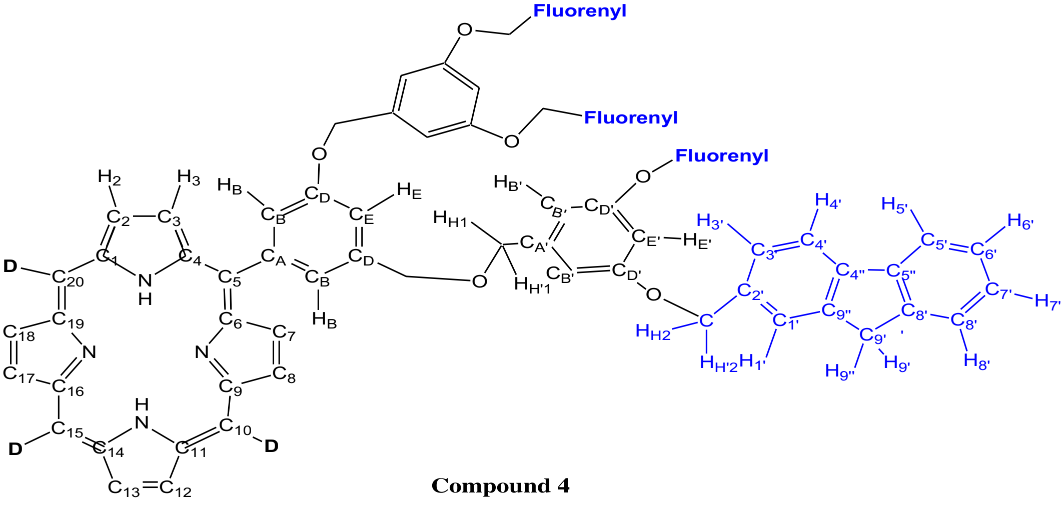
organic layer. The fixation of a various number of donor chromophores was confirmed by proton NMR, but total fixation of all eight donor chromophores **12** was not observed. The desired porphyrin **32F** was not extracted from the crude, only a mixture of differently substituted porphyrin dendrimers (yield around 40%).

It is known that above a certain dendrimer size, a limiting generation is reached beyond, which a dendrimer of perfect structure is no longer possible. Attainment of the limiting generation in dendrimer growth is considered as a result of the starburst limit effect, due to steric hindrance during formation of the dendrimer.[22] The starburst point occurs at a well-defined limit for each



Compound 3

Fig. 4. Hydrogen and carbon atom-labelling for porphyrin **3**.



Compound 4

Fig. 5. Hydrogen and carbon atom-labelling for porphyrin **4**.

dendrimer system,[23] in our case, this point is probably reached for dendrimer G_3.

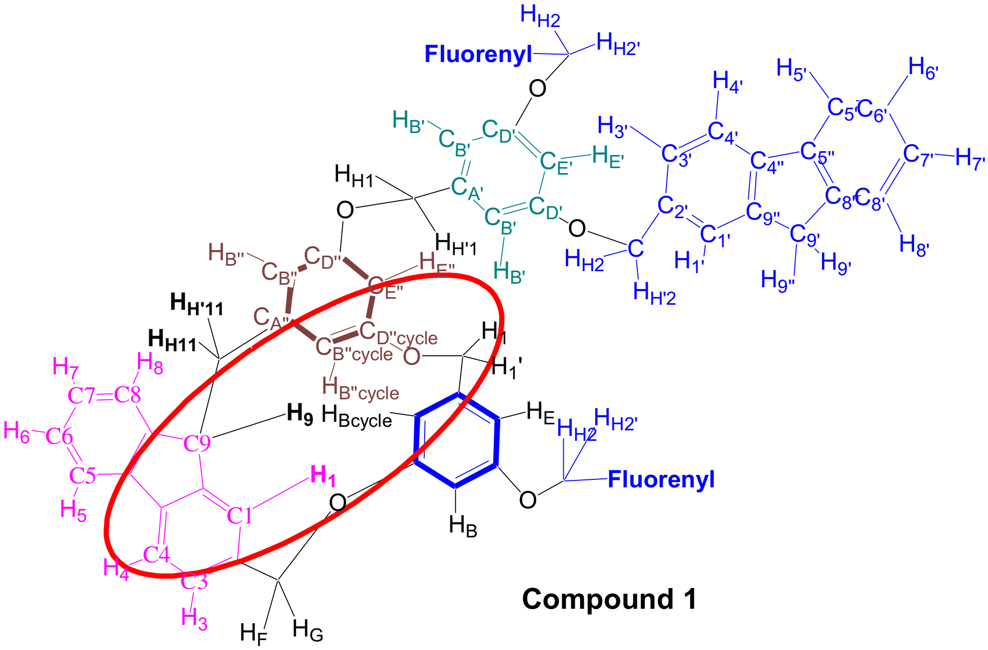
Nevertheless, we observed that in the basic conditions used (Scheme 4), one of the protons in position-9 of the non-substituted fluorenyl arms (compound **12**), can react. The non-protected carbon, in position-9, will in an intramolecular way, react with the bromomethyl group to form new compound **1** incorporating a fluorenyl unit in the cycle and three pendant fluorenyl arms. Compound **1** was obtained as a pale yellow solid (52%), very soluble in most organic solvents and can be purified by precipitation (THF, heptane). Compound **1** is well-behaved in silica gel chromatography and was fully characterized by usual solution spectroscopies (NMR and mass spectrometry) and microanalysis. For clarity, characterization by NMR is reported; the hydrogen and carbon atom-labelling scheme for compound **1** is shown in Fig. 6.

As reminded earlier, alkyl chains are often introduced in position-9 of the fluorenyl, to increase the solubility and stability of this unit. For our project, due to the encouraging results obtained for synthesis of lower generation dendrimers (G_0, G_1 and G_2), and a lack of space in the desired dendrimeric species **32F** (G_3), this was voluntary avoid. Surely, the presence of alkyl chains will prevent the formation of compound **1**,[5] but will not favour the formation of higher generation G_3.

2.2. NMR studies

The ^1H NMR signals obtained in deuterated chloroform for dendrons **11** and **12** are fine and well resolved. For these two dendrons, there is only a clear difference in shift for the protons in the CH_2 group for the bromide ligand **12**, CH_2–Br: δ=4.38 ppm and for and the corresponding alcohol **11**, CH_2–OH at δ=4.59 ppm. The other proton signals are quite similar.

The ^1H NMR signals obtained in deuterated chloroform for compound **1**, are fine and well resolved. A clear difference in shift is



Compound 1

Fig. 6. Hydrogen and carbon atom-labelling for new compound **1** incorporating a fluorenyl unit in the cycle (in pink) and three pendant fluorenyl arms (in blue).

observed for the tetrapodal ligand **12** when free and in the corresponding tripodal cyclic compound **1** (Fig. 7). The latter is induced by the very close proximity of the benzyl groups shielding cone of the proton in the newly formed cycle.

For example, the ^1H NMR spectrum of **1** reveals that the three ^1H resonances for proton in the position-9 of the fluorenyl ($\boldsymbol{H_9}$-triplet) and CH_2 units ($\boldsymbol{H_{H11}}$ and $\boldsymbol{H_{H'11}}$-doublet), are significantly up field of their positions in tetrapod ligand **12**, as expected for protons located within the shielding cone of benzyl groups (benzyl group in bold blue and brown, in Fig. 6). This effect is particularly important for $\mathbf{H_9}$ (bold in Fig. 6) with $\Delta\delta=-1.8$ but weaker for $\mathbf{H_{H11}}$ and $\mathbf{H_{H'11}}$ (bold in Fig. 6), with $\Delta\delta=-0.4$ and $\Delta\delta=-0.7$, these protons being on the CH_2 unit responsible for closing the cycle. These signals are also broader and less resolved, in line with the highly fluxional nature of the ligand at ambient temperature. Similar shift is observed for $\mathbf{H_{B''cycle}}$ (δ at 6.02 ppm) but not for $\mathbf{H_{Bcycle}}$ (δ at 6.39 ppm), this difference is probably due to proximity to shielding cone of benzyl groups in the cycle.

In addition, we can notice that all the seven peripheral protons on the three non-cyclized fluorenyl arms are equivalent, and in expected position: 7.80 ($H_{4'}$), 7.78 ($H_{5'}$), 7.59 ($H_{8'}$), 7.56 ($H_{3'}$), 7.33 ($H_{7'}$), 7.43–7.37 ($H_{1'}$ and $H_{6'}$). In the opposite, the proton $\mathbf{H_1}$ (bold in Fig. 6), on the cyclized fluorenyl group, is shifted to 6.44 ppm, so with an important up field of $\Delta\delta=-1.0$, as before, due to be located within the shielding cone of benzyl groups (benzyl group in bold blue and brown in Fig. 6). Whereas all the six other peripheral protons on the cyclized fluorenyl are in expected positions: 7.72–7.62 (m, 3H, H_{5-6-8}) and 7.44-7.36 (m, 3H, H_{3-4-7}).

2.3. Photophysical properties

2.3.1. Electronic spectra. The UV–visible spectra of **2**, **3** and **4** exhibit an intense Soret band with a maximum absorption similar

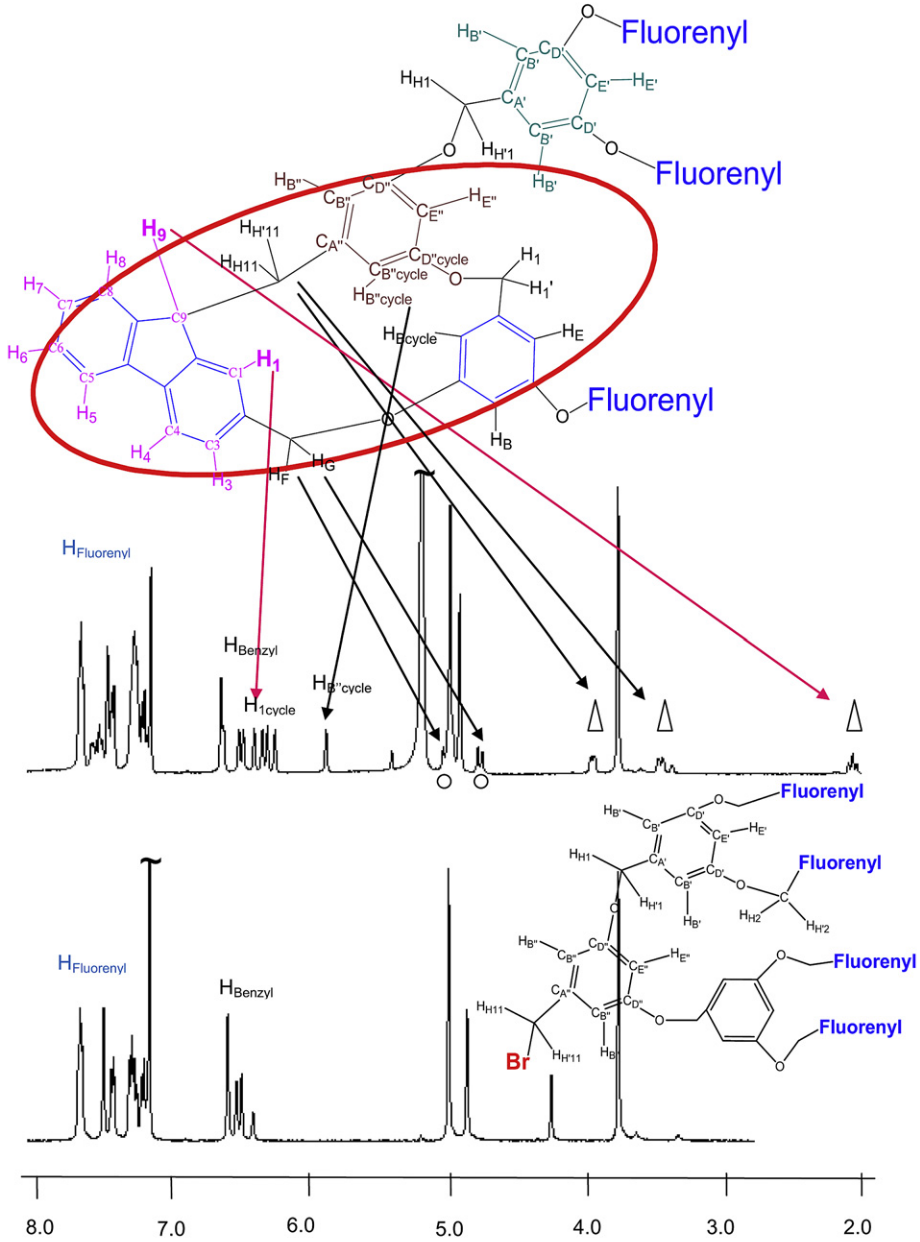


Fig. 7. ^1H NMR studies (in $CDCl_3$) of free dendron **12** in comparison to compound **1** (on the top with a CH_2Cl_2 pic), showing the shift for the cyclic fluorenyl as indicated by the arrows.

around 423 nm (Fig. 8a). This band is slightly red shifted compared to 417 nm for **TPP**, but not as much as for **TFP** (426 nm). This tendency in red shifting is observed as well for the Q-bands. The $\pi-\pi^*$ absorption in the UV range is clearly apparent, due to the presence of fluorenyl arms. For compound **2**, the four fluorenyls 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. For the generation G_2, super porphyrin **4**; we can notice that the absorption in the UV of the fluorenyl groups at 270 nm is as strong as the Soret band, as illustrated in Fig. 8a. Consequently, it is important for light-harvesting optimization to try to access to higher generation G_3, porphyrin dendrimer.

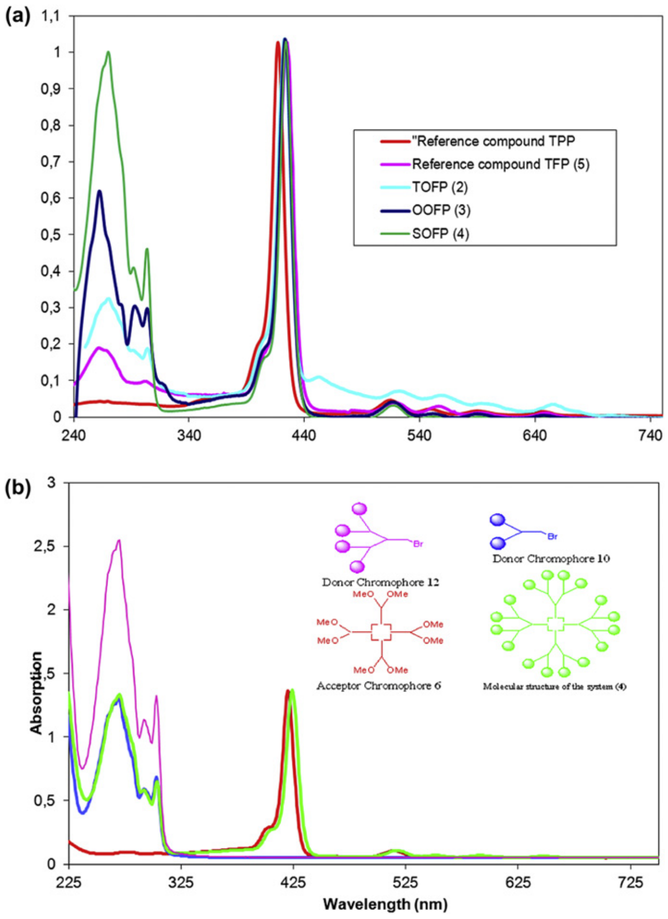


Fig. 8. (a) Absorption spectra of **TPP** (red), **5** (pink), **2** (blue), **3** (dark blue) and **4** (green) in chloroform at room temperature. All the spectra are normalized to the spectrum of *the reference* ***TPP*** at 417 nm (concentration $\sim 2.0\times10^{-6}$ M). (b) Absorption spectra of **6** (red), **10** (blue), **12** (pink) and **4** (green) in chloroform at room temperature. The spectrum of **10** is normalized to the spectrum of **4** 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**. The spectrum of **12** is at the same concentration as dendron **10** ($\sim 2.0\times10^{-6}$ M).

Fig. 8b shows the absorption spectra of dendron **10** possessing two fluorenyl units, the porphyrin core with 8 anchoring points, and the porphyrin possessing 16 fluorenyl arms **4** is again reported. The absorption spectrum of **4** shows the characteristic peaks at 280 and 300 nm of dendron **10** in addition to the porphyrin Soret band at 423 nm and less intense Q-bands, the first of which appears at 513 nm. Obviously, the dendron **10** and the porphyrin core retain their individual characteristics. These considerations indicate that this molecular pentad **4**, in which the porphyrin acceptor is linked, via spacers, to donor dendrons, forms a suitable choice for exploiting the antenna 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. Consequently, for an optimization of this photosynthetic antenna function, a higher generation porphyrin-based model system was tried. In this goal tetrapodal dendron **12** was synthesized. In the same conditions, and same concentration as dendron **10**, as expected, the absorption of new dendron **12** is strongly exalted in comparison to bipodal dendron **10** (Fig. 8b).

3. Conclusions

In summary, a series of dendrons bearing fluorenyl donor groups were presented. Successively, compound **8**: bearing one fluorenyl, compound **10**: with two fluorenyl units, and finally new dendrons **11** and **12**, bearing four peripheral fluorenyl arms were synthesized and fully characterized. Then, a series of porphyrin dendrimers (generation G_0, G_1 and G_2) bearing these fluorenyl dendrons are presented, namely: **2**, **3** and **4**. However, the synthesis of a higher generation porphyrin (G_3), bearing thirty-two fluorenyl arms (called **32F**), from the new tetrapod dendron **12** failed. Most likely the so called 'starburst limit effect' was reached here. Nevertheless, in the course of these trials, an interesting compound **1**, incorporating a fluorenyl unit in the cycle and three pendant fluorenyl arms, was obtained and fully characterized. It is probably formed by an intramolecular reaction of the brominated dendron **12**.

4. Experimental section

4.1. General procedures

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. Melting points were measured on Leica VMHB apparatus with a System Kofler. Pyrrole and 2-fluorenecarboxaldehyde were purchased from Aldrich and were used as received. References **TFP**=tetrafluorenylporphyrin and **TPP**=tetraphenylporphyrin.

4.2. Synthesis of the dendrons

*4.2.1. Synthesis of 2-(bromomethyl)-9H-fluorene (**8**).* Synthesis of 2-(bromomethyl)-9*H*-fluorene (**8**) from prepared 2-(hydroxymethyl)-9*H*-fluorene was described earlier.[18] ^1H NMR (200 MHz, $CDCl_3$, δ in ppm): 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), 4.61 (s, 2H, CH_2−Br), 3.94 (s, 2H, $CH_{2\,fluorene}$).

*4.2.2. Synthesis of alcohol **9**.* Synthesis of alcohol **9** from prepared 2-(bromomethyl)-9*H*-fluorene (**8**) was described earlier.[18] ^1H NMR (200 MHz, $CDCl_3$, δ in ppm): δ 7.81 (d, $^3J_{HH}$=7.5 Hz, 4H, $H_{4'-5'}$), 7.64 (s, 2H, $H_{1'}$), 7.57 (d, $^3J_{HH}$=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, $^3J_{HH}$=3.7 Hz, 2H, $H_{1-1'}$), 3.95 (s, 4H, $H_{9'-9''}$).

*4.2.3. Synthesis of bromide dendron **10**.* We describe here briefly the synthesis of bromide dendron **10** from alcohol (**9**).[18] 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, and 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 in ppm): 7.81 (d, $^3J_{HH}$=7.5 Hz, 4H, $H_{4'-5'}$), 7.63 (s, 2H, $H_{1'}$), 7.57 (d, $^3J_{HH}$=7.2 Hz, 2H, $H_{8'}$), 7.45–7.26 (m, 6H, $H_{3'-6'-7'}$), 6.71 (d, $^4J_{HH}$=2.1 Hz, 2H, $H_{B'}$), 6.63 (t, $^4J_{HH}$=2.1 Hz, 1H, $H_{E'}$), 5.13 (s, 4H, $H_{2-2'}$), 4.46 (s, 2H, $H_{1-1'}$), 3.94 (s, 4H, $H_{9'-9''}$).

*4.2.4. Synthesis of new tetrapod dendron **11**.* The brominated compound **10** (175 mg, 0.31 mmol) was placed in a three-necked flask under an argon atmosphere and then dissolved in distilled THF (20 mL). The commercial alcohol, 5-hydroxymethyl-benzen-1,3-diol (21 mg, 0.15 mmol) was added and then potassium carbonate (83 mg, 0.60 mmol) and finally 18-crown-6 ether (40 mg, 0.15 mmol). The three-necked flask was surmounted by a water condenser and the solution was heated to reflux for 15 h. The solution was left until cooled to room temperature and then filtered over a frit funnel. The filtrate was evaporated and the residue was dissolved in DCM and transferred into a separating funnel. The organic layer was washed two times with distilled water and one time with a saturated solution of sodium chloride. Aqueous layers were combined and extracted one time with DCM. Organic layers were combined and dried over $MgSO_4$, filtered and the solvent was evaporated. The oil obtained was subjected to column chromatography of silica with DCM as eluent. The expected compound **11** was obtained as a thin white powder (115 mg, 70%). ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 7.78, (d, 4H, $H_{4'}$, $^3J_{HH}$=7.5 Hz), 7.77 (d, 4H, $H_{5'}$, $^3J_{HH}$=7.5 Hz), 7.61 (s, 4H, $H_{1'}$), 7.55 (d, 4H, $H_{8'}$, $^3J_{HH}$=7.2 Hz), 7.41 (d, 4H, $H_{3'}$, $^3J_{HH}$=7.6 Hz), 7.39 (t, 4H, $H_{6'}$, $^3J_{HH}$=7.6 Hz), 7.32 (t, 4H, $H_{7'}$, $^3J_{HH}$=7.2 Hz), 6.73 (d, 4H, $H_{B'}$, $^3J_{HH}$=2.1 Hz), 6.65 (t, 2H, $H_{E'}$, $^3J_{HH}$=2.3 Hz), 6.59 (d, 2H, $H_{B''}$, $^3J_{HH}$=2.1 Hz), 6.55 (t, 1H, $H_{E''}$, $^3J_{HH}$=2.3 Hz), 5.12 (s, 8H, OCH_2, $H_{H2-H2'}$), 5.00 (s, 4H, OCH_2, $H_{H1-H1'}$), 4.59 (d, 2H, CH_2–OH, $H_{H11-H11'}$,$^3J_{HH}$=5.7 Hz), 3.90 (s, 8H, $CH_{2fluorene}$, $H_{9'-9''}$). Anal. Calcd for $C_{77}H_{60}O_7\cdot 1CH_2Cl_2$: C, 79.24; H, 5.29; N, 0.00. Found: C, 80.29; H, 5.56; N, 0.00. MALDI TOF-MS calcd for $C_{77}H_{60}O_7$: 1119.4339 $[MNa]^+$, found 1119.1800 $[MNa]^+$. Melting point: 130.1 °C.

*4.2.5. Synthesis of new tetrapod dendron **12**.* Alcohol **11** (75 mg, 0.07 mmol) was placed in a Schlenk tube under an argon atmosphere and then dissolved in distilled THF (1.5 mL). Carbon tetrabromide (37 mg, 0.11 mmol) was added and the reaction mixture was cooled to 0 °C with an ice bath, followed by the portion-wise addition of triphenylphosphine (29 mg, 0.11 mmol). The reaction mixture was stirred at 0 °C for 1 h. The ice bath was removed and the reaction mixture was stirred at room temperature for 3 h. Repetitive additions of 4 equiv of carbon tetrabromide, 1.5 mL of THF followed by addition of 4 equiv of triphenylphosphine were done twice every 12 h. Reaction progress is monitored by TLC, spotting directly from the organic layer. The solution was transferred in a separating funnel with distilled water. The aqueous layer was extracted three times with DCM. Organic layers were combined and dried over $MgSO_4$ and then the solvent was evaporated. The light brownish oil obtained was subjected to column chromatography over silica with DCM as eluent. The expected compound tetrafluorenyl dendron **12**, was obtained as a yellow powder to yield 60 mg (70%). This new dendron **12** was characterized by NMR, UV–visible, microanalysis and mass spectrometry. ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 7.79 (d, 4H, $H_{4'}$, $^3J_{HH}$=7.5 Hz), 7.77 (d, 4H, $H_{5'}$, $^3J_{HH}$=7.5 Hz), 7.61 (s, 4H, $H_{1'}$), 7.55 (d, 4H, $H_{8'}$, $^3J_{HH}$=7.2 Hz), 7.42 (d, 4H, $H_{3'}$, $^3J_{HH}$=7.6 Hz), 7.39 (t, 4H, $H_{6'}$, $^3J_{HH}$=7.6 Hz), 7.32 (t, 4H, $H_{7'}$, $^3J_{HH}$=7.2 Hz), 6.72 (d, 4H, $H_{B'}$, $^3J_{HH}$=2.1 Hz), 6.66 (t, 2H, $H_{E'}$, $^3J_{HH}$=2.3 Hz), 6.62 (d, 2H, $H_{B''}$, $^3J_{HH}$=2.1 Hz), 6.55 (t, 1H, $H_{E''}$, $^3J_{HH}$=2.3 Hz), 5.12 (s, 8H, OCH_2, $H_{H2-H2'}$), 4.98 (s, 4H, OCH_2, $H_{H1-H1'}$), 4.38 (d, 2H, CH_2–Br, $H_{H11-H11'}$, $^3J_{HH}$=5.7 Hz), 3.89 (s, 8H, $CH_{2fluorene}$, $H_{9'-9''}$). Anal. Calcd for $C_{77}H_{59}BrO_6\cdot 4CH_2Cl_2$: C, 64.97; H, 4.72; N, 0.00. Found: C, 65.72; H, 4.28; N, 0.00. MS (ESI): calcd for $C_{77}H_{59}BrO_6$: 1181.33927 $[MNa]^+$, found 1181.33860 $[MNa]^+$. Melting point: 126.0 °C.

4.3. Synthesis of porphyrins

*4.3.1. Synthesis of porphyrin **6**.* Tetrakis(3,5-dimethoxyphenyl) porphyrin (**OOMePP**) was prepared from pyrrole and the respective aromatic aldehyde using Adler–Longo condensation conditions.[24]

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

*4.3.3. Synthesis of porphyrin **2**.* Tetrakis(fluorenyl-4-hydroxyphenyl)porphyrin (**TOFP**) was described earlier.[18] ^{1}H NMR (300 MHz, solubilized by acidic deuterated TFA in $CDCl_3$, δ in ppm): 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, $H_{H-H'}$), 4.06 (s, 8H, $H_{9'-9''}$).

*4.3.4. Synthesis of octafluorenylporphyrin **OOFP** (**3**).* Synthesis of octafluorenylporphyrin **OOFP** (**3**) was described earlier.[18] ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 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, $H_{9'-9''}$).

*4.3.5. Synthesis of sixteenfluorenylporphyrin **SOFP** (**4**).* Synthesis of sixteenfluorenylporphyrin **SOFP** (**4**) was described earlier.[19] ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 8.85 (s, 8H, pyrrole), 7.55 (d, $^3J_{HH}$=7.4 Hz, 16H, $H_{5'}$), 7.49 (d, $^3J_{HH}$=7.8 Hz, 16H, $H_{4'}$), 7.45 (d, $^4J_{HH}$=2.2 Hz, 8H, H_B), 7.35 (s, 16H, $H_{1'}$), 7.34 (d, $^3J_{HH}$=7.4 Hz, 16H, $H_{8'}$), 7.22 (t, $^3J_{HH}$=6.7 Hz, 16H, $H_{6'}$), 7.16 (t, $^3J_{HH}$=7.3 Hz, 16H, $H_{7'}$), 7.15 (d, $^3J_{HH}$=7.1 Hz, 16H, $H_{3'}$), 7.04 (t, $^4J_{HH}$=2.1 Hz, 4H, H_E), 6.70 (d, $^4J_{HH}$=2.1 Hz, 16H, $H_{B'}$), 6.59 (t, $^4J_{HH}$=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 (300 MHz, $CDCl_3$, δ in ppm): δ 160.30 ($C_{D'}$), 157.91 (C_D), 143.54 ($C_{9''}$), 143.32 ($C_{4''}$), 143.00 (broad signal $C_{1-4-6-9-11-14-16-19}$), 141.50 ($C_{8''}$), 141.19 ($C_{5''}$), 135.13 ($C_{2'}$), 131.00 (broad signal $C_{2-3-7-8-12-13-17-18}$), 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 ($C_{9'}$).

*4.3.6. Attempt to synthesis porphyrin **32F**—formation of compound **1**.* The tetrakis (3,5-dihydroxyphenyl)-porphyrin **7** (3.6 mg, 4.8×10^{-6} mol) was placed in a Schlenk tube, under an argon atmosphere and then dissolved in distilled THF (3 mL). Potassium carbonate (11 mg, 7.7×10^{-5} mol), 18-crown-6 ether (1.3 mg,

4.8×10^{-6} mol) were added to this solution, and finally, the bromide dendron **12** (50 mg, 4.3×10^{-5} mol) was added. Then, the solution was stirred under argon and heated to reflux for 2 days. Repetitive additions of 16 equiv of K_2CO_3 (11 mg, 7.7×10^{-5} mol) and 18-crown-6 ether (1.3 mg, 4.8×10^{-6} mol) were done every 2 days. Reaction progress is monitored by TLC, spotting directly from the organic layer. Then, at the end of the reaction (eight days), the mixture was cooled to room temperature and THF was evaporated in vacuum. The residue was dissolved in DCM and transferred into a separating funnel. The organic layer was washed two times with distilled water and one time with a saturated solution of sodium chloride. Aqueous layers were combined and extracted one time with DCM. Organic layers were combined. The organic layer obtained was dried over $MgSO_4$, filtered and the solvent was evaporated. The brown product obtained was subjected to column chromatography over silica with 100% DCM as eluent and then a mixture of DCM/acetone gradient and finally, 100% acetone. Two products were obtained: compound **1** as a pale yellow product (24 mg, yield: 52%) and a dark red product; a mixture of differently substituted porphyrins (12 mg, yield around 40%). Separation of these porphyrins was unsuccessfully tried but compound **1** was isolated pure. This new compound **1** was characterized by NMR, microanalysis and mass spectrometry. ^{1}H NMR (assignments aided by COSY; 300 MHz, $CDCl_3$, δ in ppm): 7.80 (d, 3H, $H_{4'}$, $^{3}J_{HH}$==.3 Hz), 7.78 (d, 3H, $H_{5'}$, $^{3}J_{HH}$=7.3 Hz), 7.72-7.62 (m, 3H, H_{5-6-8}), 7.59 (d, 3H, $H_{8'}$, $^{3}J_{HH}$=5.1 Hz), 7.56 (d, 3H, $H_{3'}$, $^{3}J_{HH}$=5.1 Hz), 7.43–7.37 (m, 6H, $H_{1'-6'}$), 7.44–7.36 (m, 3H, H_{3-4-7}), 7.33 (t, 3H, $H_{7'}$, $^{3}J_{HH}$=7.0 Hz), 6.78 (d, $^{3}J_{HH}$=2.2 Hz, 2H, $2H_{B'}$), 6.75 (m, 1H, $H_{B''}$), 6.65 (t, $^{3}J_{HH}$=2.2 Hz, 1H, $H_{E'}$), 6.61 (t, $^{3}J_{HH}$=2.2 Hz, 1H, $H_{E''}$), 6.54 (m, 1H, H_E), 6.48 (t, $^{3}J_{HH}$=2.2 Hz, 1H, H_B), 6.44 (t, $^{3}J_{HH}$=2.2 Hz, 1H, H_9), 6.39 (m, 1H, H_{Bcycle}), 6.02 (m, 1H, $H_{B''cycle}$), 5.14 (d, 1H, H $_F$, $^{2}J_{HH}$=13.1 Hz), 5.12 (s, 6H, OCH_2, $H_{H2-H2'}$), 5.05 (s, 4H, OCH_2, $H_{H1-H1'}$), 4.91 (d, 1H, H $_G$, $^{2}J_{HH}$=13.1 Hz), 4.08 (dd, 1H, H_{H11}, $^{2}J_{HH}$=11.09 Hz, $^{3}J_{HH}$=4.1 Hz), 3.89 (s, 6H, $3CH_{2fluorene}$, $H_{9'-9''}$), 3.59 (dd, 1H, H $_{H11'\ (cycle)}$, $^{2}J_{HH}$=13.0 Hz, $^{3}J_{HH}$=4.7 Hz), 2.21 (dd, 1H, H_x, $^{2}J_{HH}$=13.1 Hz, $^{3}J_{HH}$=11.4 Hz). ^{13}C NMR (assignments aided by COSY; 300 MHz, $CDCl_3$, δ in ppm): 160.3 (C_q), 160.0 ($C_{D''}$), 159.8 (C_q), 159.4 ($C_{D''cycle}$), 158.9 (C_q), 147.3 (C_q), 145.3 ($C_{A''}$), 143.7, 143.6, 143.4, 142.2, 141.7, 141.6, 141.3 (C_q), 140.7 (C_2), 140.3, 139.8, 139.4 (C_q), 135.3, 135.2, 134.7, 127.8 (C_1), 127.4–127.3–127.1 (C_{5-6-8}), 126.8 ($C_{3'}$), 126.7 ($C_{4'}$), 126.4 ($C_{8'}$), 125.0 ($C_{7'}$), 124.4 ($C_{5'}$), 124.1 (C_{3-4-7}), 120.1, 120.0, 119.9, 119.8 (C_q), 108.9 ($C_{B''}$), 108.6 ($C_{B''cycle}$), 106.5, 105.45, 104.7, 103.9, 102.1 ($C_{E''}$), 101.6 (C_t), 70.50, 70.33, 70.1, 69.9, 69.1, 49.3 (C_9), 40.8 ($C_{H11-H11'}$), 36.8, 29.7, 29.3, 22.7. Anal. Calcd for $C_{77}H_{58}O_6\cdot Na$: C, 83.90; H, 5.30; N, 0.00. Found: C, 83.91; H, 6.02; N, 0.00. MS (ESI): calcd for $C_{77}H_{58}O_6$: 1101.41311 $[MNa]^+$, 1117.38705 $[MK]^+$; found: 1101.41150 $[MNa]^+$, 1117.37140 $[MK]^+$.

Acknowledgements

The authors are grateful to S. Sinbandhit (CRMPO-Rennes), G. Simonneaux and P. Le Maux (ICMV-ISCR-UMR 6226) for their technical assistance and helpful discussions. The authors are grateful to MRT for Ph.D. grant concerning S.D. and Region Bretagne for ARED grant for A.M.. Partial funding for the project was obtained from the 'Université Européenne de Bretagne' (UEB) and from FEDER by an EPT grant in the 'MITTSI' program from RTR BRESMAT.

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. Poriel, C.; Ferrand, Y.; Le Maux, P.; Paul-Roth, C.; Simonneaux, G.; Rault-Berthelot, J. *J. Electroanal. Chem.* **2005**, *583*, 92–103.
12. Paul-Roth, C. O.; Simonneaux, G. *Tetrahedron Lett.* **2006**, *47*, 3275–3278.
13. Paul-Roth, C. O.; Simonneaux, G. *C.R. Acad. Sci., Ser. IIb: Chim.* **2006**, *9*, 1277–1286.
14. Paul-Roth, C.; Williams, G.; Letessier, J.; Simonneaux, G. *Tetrahedron Lett.* **2007**, *48*, 4317–4322.
15. Drouet, S.; Paul-Roth, C. O.; Fattori, V.; Cocchi, M.; Williams, J. A. G. *New J. Chem.* **2011**, *35*, 438–444.
16. Ren, X.; Ren, A.; Feng, J.; Sun, C. *J. Photochem. Photobiol., A: Chem.* **2009**, *203*, 92–99.
17. Drouet, S.; Merhi, A.; Argouarch, G.; Paul, F.; Mongin, O.; Blanchard-Desce, M.; Paul-Roth, C. O. *Tetrahedron* **2012**, *68*, 98–105.
18. Drouet, S.; Paul-Roth, C.; Simonneaux, G. *Tetrahedron* **2009**, *65*, 2975–2981.
19. Drouet, S.; Paul-Roth, C. O. *Tetrahedron* **2009**, *65*, 10693–10700.
20. Fréchet, J. M. J.; Tomalia, D. A. In *Dendrimers and Other Dendritic Polymers*; John Wiley & Sons: Chichester, UK, 2001.
21. Jiang, D.-L.; Aida, T. *J. Am. Chem. Soc.* **1998**, *120*, 10895–10901.
22. Nicholson, J. W. *The Chemistry of Polymers*; Royal Society of Chemistry: Great Britain, 2006.
23. Vögtle, F.; Richardt, G.; Werner, N. *Dendrimer Chemistry: Concepts, Syntheses, Properties, Applications—Science*; Wiley: Weinheim, 2009.
24. 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.