New meso-tetrafluorenylethynyl porphyrin platform

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Graphical Abstract

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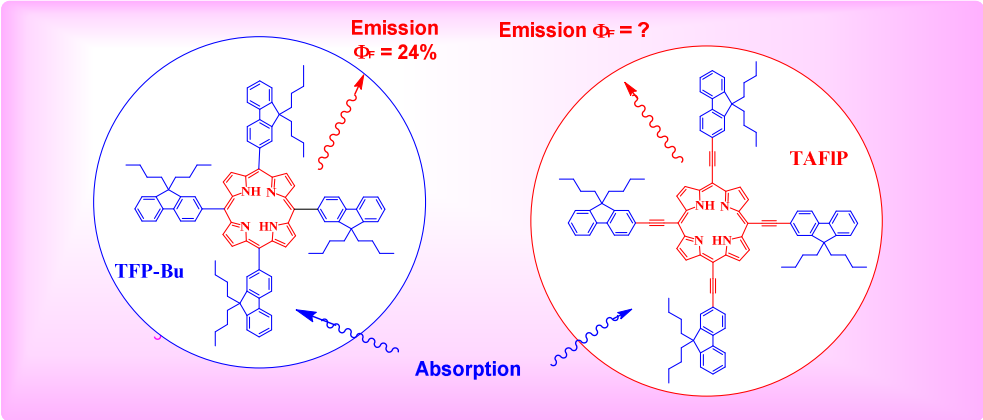

We have designed a new *meso*-alkynyl fluorenyl porphyrin (TAFlP) by introducing in the tetrafluorenyl porphyrin (TFP-Bu) an **ethynyl spacer** at the *meso* positions. We discuss the effect of this extra extension of the π-manifold on the optical properties.

New *meso*-tetrafluorenylethynyl Porphyrin platform

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"Dedicated to Dr Gérard Simonneaux for opening the door of the wonderful world of Porphyrins"

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ABSTRACT: To improve conjugation between a central porphyrin core and its peripheral fluorenyl *antennae*, we have introduced in the *meso*-tetrafluorenyl porphyrin (**TFP-Bu**) unit an **ethynyl spacer** at the *meso* positions. By this mean, we have synthesized and characterized a new *meso*-alkynyl fluorenyl porphyrin (**TAFlP**). We discuss the effect of this extra extension of the π-manifold on the optical properties. This enlarged porphyrin core, **TAFlP**, is foreseen as a key building block for the design of new dendrimers for theranostic applications. The constant improvement of porphyrin-based dendrimers featuring conjugated fluorenyl dendrons is recalled herein and demonstrates the important role of the central core structure in determining linear and nonlinear optical properties. Further improvement of these properties seems possible with **TAFlP**-like structures based on observations made for dendrimers recently obtained. This makes the exploration of new molecular architectures based on tetrafluorenyl ethynyl porphyrin appealing for PDT and related applications.

KEYWORDS: Porphyrin, fluorenyl, fluorescence, alkyne.

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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. Porphyrin-based systems are largely present nowadays, in many applied developments encompassing by far the numerous bio-related studies in which these macrocycles were initially involved.[1a]

Stimulated by the fact that the unique photochemical properties of the porphyrin core can be fine-tuned by modification of the peripheral substituents, intense research in fields more related to photophysics and material sciences has been undertaken these last decades. Symmetrical **A4** porphyrins type, substituted at the four *meso* positions, is particularly interesting because the molecules are easily accessible with good yields. Very appealing is also the synthetic expansion of such structures by introducing dendrons at these positions, and the modification of these *dendrons* for light harvesting. In this respect, many **porphyrin-based dendrimers** have been synthesized these last decades. Their light-harvesting properties could be optimized by connecting highly absorbing dendrons to the central porphyrin core, the former acting as energy donors to the second, overall behaving like an antenna system.[1b] In particular, some porphyrins bearing pendent linear oligofluorene arms have been reported in this context,[1c] and for such assemblies, Fréchet[1d] demonstrated that the antenna effect was facilitated in dendritic architectures *versus* linear ones. More recently, hyperbranched polymers containing porphyrin with fluorenyl arms have also been synthesized for light harvesting,[1e] while the group of Okada and Kozaki investigated the use of series of multi-porphyrin arrays in conjugated networks as light-harvesting antenna.[1f] In this field, we also have recently reported efficient light-harvesting systems in which 5,10,15,20-tetraphenylporphyrin (**TPP**) was linked, *via* flexible ether bridges, to fluorenyl donor moieties.[1g,h] One may wonder why such an interest for the **porphyrin-fluorenyl** combinations. Actually, as we have discovered, in collaboration with J.A.G. Williams, 5,10,15,20-tetrafluorenylporphyrin (**TFP**) exhibits a high quantum yield (24%), demonstrating the capacity of 2-fluorenyl units to strongly enhance the emission quantum yield of the porphyrin core.[1i] Our aim was then to exploit further this capacity and a series of **super porphyrins** based on the small **TPP**-core was targeted. In the first family, the dendrons were linked *via* ether bridges to the central core. Four, eight and sixteen fluorenyl donor moieties were included in these dendrons. Then, we wondered about improving the light-harvesting mechanism by preserving some π-overlap between the peripheral fluorenyl arms and the central core.[1j] Indeed, porphyrin-based dendrimers containing π-conjugated dendrons are expected to present better energy transfer properties than systems for which π-conjugation is completely disrupted, as indicated by the work of Burn and Samuel on porphyrin dendrimers with stilbene dendrons for instance.[1k] The *meso*-phenyl units of the **TPP**-core molecule have two positions easy to functionalize (*para* and *meta*), so the corresponding dendrimers were then synthesized. The optical properties of these porphyrin-based

dendrimers, featuring 2-fluorenyl containing dendrons with extended π-manifolds on these positions, were then studied (Fig. 1). Such systems present increasing numbers of terminal fluorenyl units at their periphery, going from 4 to 8 to 16 (**TPP1**, **TPP2** and **TPP3**, respectively). We have shown that the conjugation between the **TPP** porphyrin core and the unsaturated dendrons is more effective in the *para*-functionalized systems than in the *meta*-ones. This better conjugation improves the photophysical properties of the *para-substituted* compounds (**TPP1**) over the *meta-substituted* ones (**TPP2**, **TPP3**),[11] encouraging us to consider, the **2,7-fluorenyl** unit as a new spacer, in replacement of the **1,4-phenyl** unit.

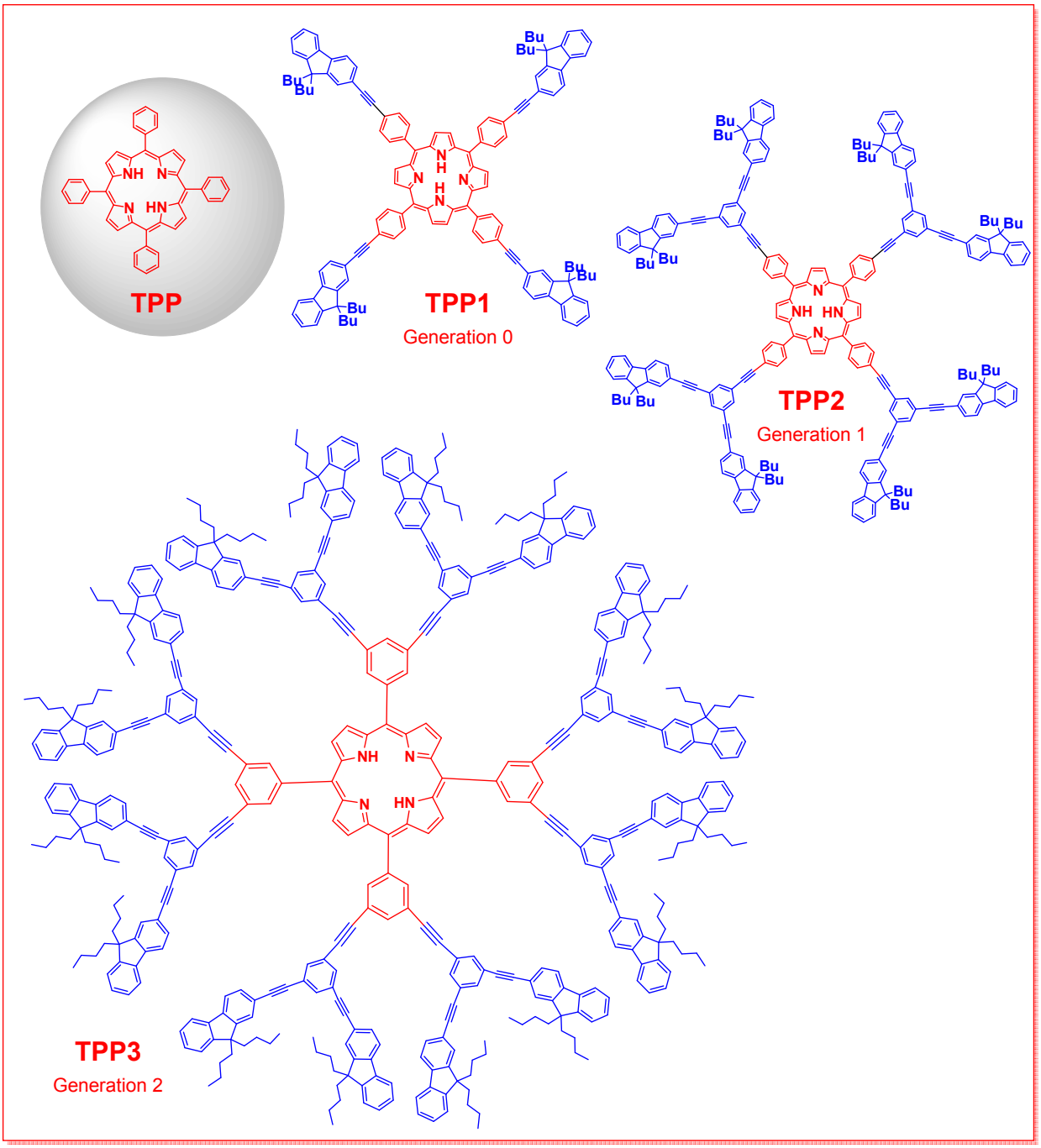


Fig. 1. Molecular structures of **TPP**-cored porphyrin dendrimers **TPP1**-**TPP3** and their reference **TPP**

A series of related compounds in which 2,7-fluorenyl groups was connected directly to the *meso* positions of the central porphyrin core (*i.e.* a dendritic architecture featuring **TFP** instead of **TPP** as a central core) and still possessing fully conjugated peripheral arms incorporating fluorene units at both *terminal* and *internal* positions was then developed.

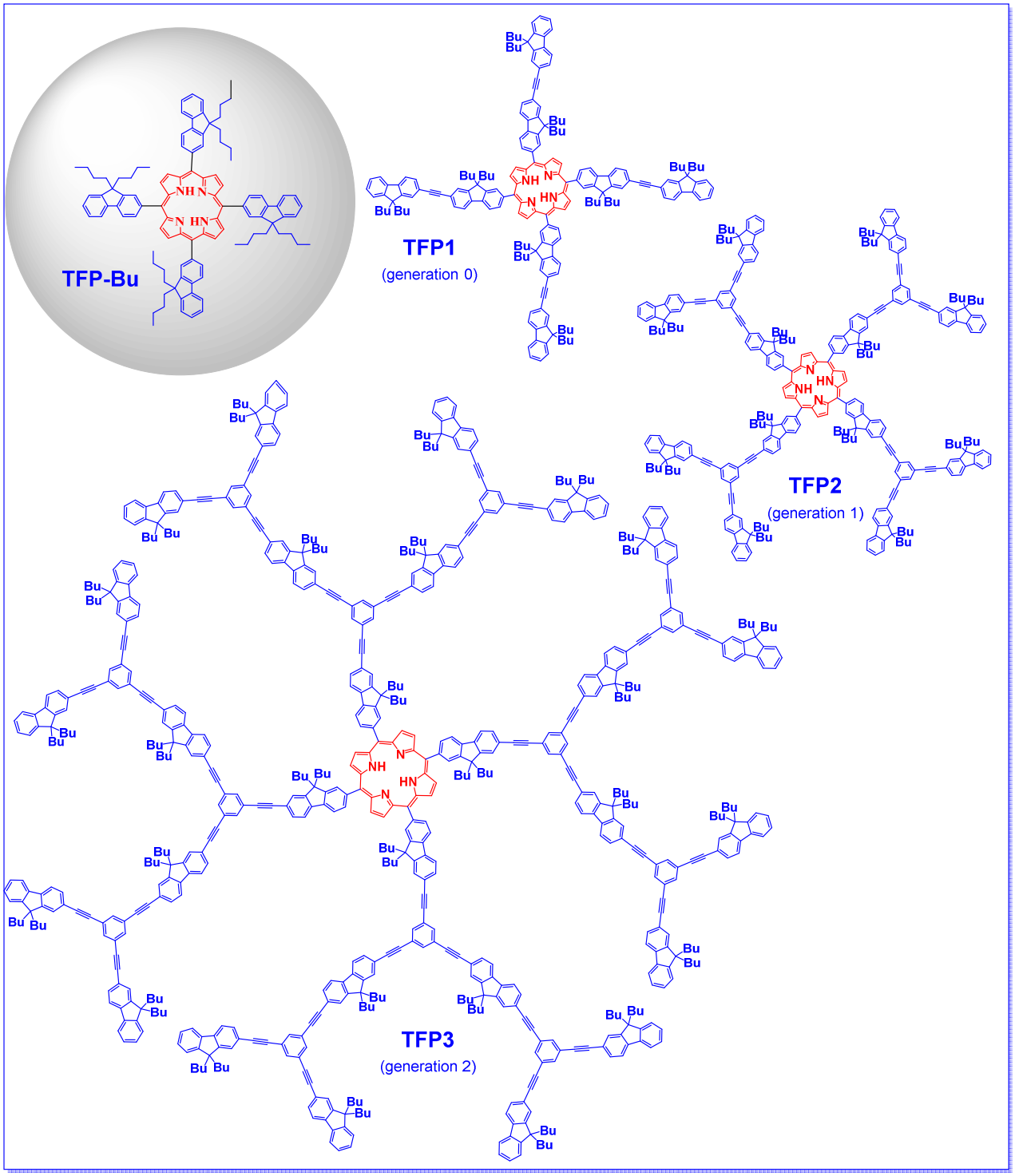


Fig. 2. TFP-cored porphyrin dendrimers **TFP1**, **TFP2** and **TFP3** and the corresponding reference compound **TFP-Bu**

A versatile synthetic protocol allowed us to easily introduce fluorenyl units as internal chromophores (behaving also as *antennae*). The effect of this structural variation on the photophysical properties of the resulting dendrimers was then explored. The dendrimers with increasing generations going from 1 to 3, were called **TFP1**, **TFP2** and **TFP3**, respectively (represented in Fig. 2).[1m] In terms of photophysical properties, this **TFP** series exhibit

remarkably high luminescence quantum yields (20-24%) again thanks to a very efficient energy transfer (ET) from the peripheral fluorenyl units toward the central porphyrin core. This process is plainly apparent for dendrimers **TFP1** and **TFP2**, but contrasts with the dual emission (blue and red) observed for the big **TFP3** compound featuring the largest dendrons at the *meso* positions. Such a size-limit to the ET was expected considering the **tilted conformation** adopted by the inner *meso*-fluorenyl groups bearing the peripheral dendrons. In spite of that non-optimal π-conjugation, the one-photon brightness of these compounds increases almost linearly with the number of fluorenyl groups in the peripheral arms, in line with the existence of the antenna effect previously mentioned.[1m] To improve further the photophysical performance of such dendrimeric systems, with the aryl groups tilted conformations should be replaced by another unit permitting to achieve co-planarity between the central core and aromatic system of the peripheral dendrons. In particular, this can be done by using a *meso*-substituted tetra **alkynyl** porphyrin as the central unit. We therefore turned our interest toward *meso*-ethynylporphyrins.

The first porphyrins of this kind, substituted by one or two alkynyl groups, were initially targeted as precursors for the elaboration of conducting polymers,[2-3] non-linear optical (NLO) materials,[4,5] photosynthetic models[6,7] and enzyme mimics.[8-10] Most of these alkynyl-*meso* substituted porphyrins contained only one or two ethynyl moieties. These macrocycles turned out to present a strong bathochromic shift of their first absorptions relative to tetraphenylporphyrin.[11-15] This is due to the direct conjugation of the 18π-electronic system of the macrocycle over the alkynyl group to the terminal aromatic moieties. As a result, the Soret (B-) band and Q-bands are significantly altered.[11] In consequence, the color of these porphyrins in solution turns to a brilliant green departing from the typical red color of tetraphenylporphyrin. Hence the trivial name of **Chlorphyrins** was given for arylethynyl-*meso*-substituted porphyrins.[12-15] In the tetralkynyl series, in 1992, Anderson reported a tetra-substituted derivative: 5,10,15,20-tetra-trimethylsilylethynyl-porphyrin (H_2**1**) (see Fig. 3) which was isolated in moderate yield (14%).[11] The same year, Hevesi obtained a closely related compound (H_2**2**), but with methyl endgroups substituent rather than TMS ones. This new tetra-alkynylporphyrin was isolated with an even low yield (around 1%).[16] Finally, the corresponding aryl-ethynyl derivative (5,10,15,20-tetra-phenylethynyl)-porphyrin (H_2**3-R**) was also reported the same year, with a yield of 2%.[16] Subsequently, Milgrom reported the synthesis of related compounds with octyl or nonyloxy chains appended in the *para* positions of the four phenyl groups (H_2**3-R**) to increase the solubility of these compounds.[12] These last

porphyrins (H_2**2** and H_2**3-R**) were synthesized with the aim of developing highly conjugated porphyrin polymers and arrays by assembling these building blocks together.[12,16]

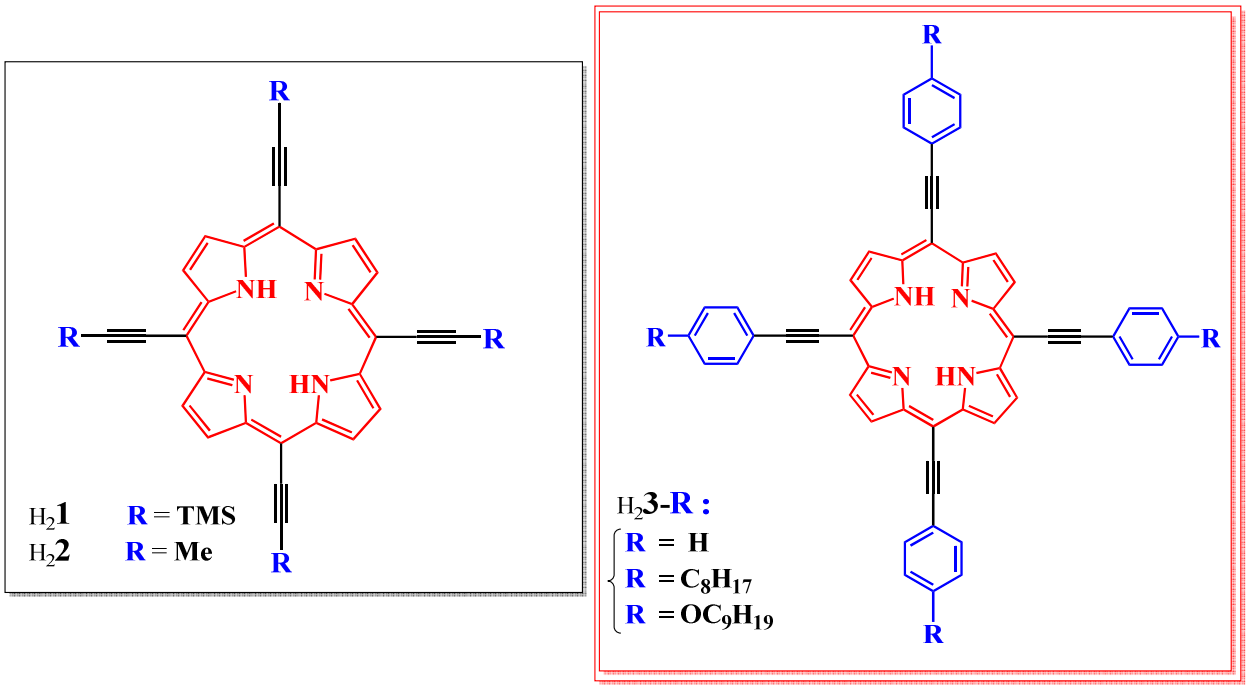


Fig. 3. Molecular structures of reported *meso*-alkynyl porphyrins (H_2**1,** H_2**2** and H_2**3-R**)

Based on these tetra-alkynyl *meso*-substituted precursors, we believe that the related *meso*-tetra-alkynyl fluorenyl porphyrin (**TAFlP**) composed of one central porphyrin substituted at its *meso* positions by four alkynylfluorenyl units could constitute an interesting platform for designing new dendrimers for theranostics (Fig. 4). Indeed expending the π-manifold should increase the 2PA and bring about a red shift in emission and absorption. We have therefore synthesized **TAFlP** porphyrin as a model compound to study its optical properties and compare them to those of **TFP-Bu** taken as reference. **TAFlP** porphyrin will also be compared to the known tetraalkynyl porphyrins H_2**1,** H_2**2** and H_2**3-R** (R = H, C_8H_{17}, OC_9H_{19}). This molecular assembly might (i) possess the remarkable fluorescence yield and brightness of **TFP**[1i] precursor, (ii) present a fully conjugated and extended π-manifold which will favour the 2PA and also redshift the 2PA and the emission. As usual (see Fig. 1, 2) butyl chains will be connected to the peripheral fluorenyl units (in the 9 position) to improve the solubility of the compound in organic solvents.

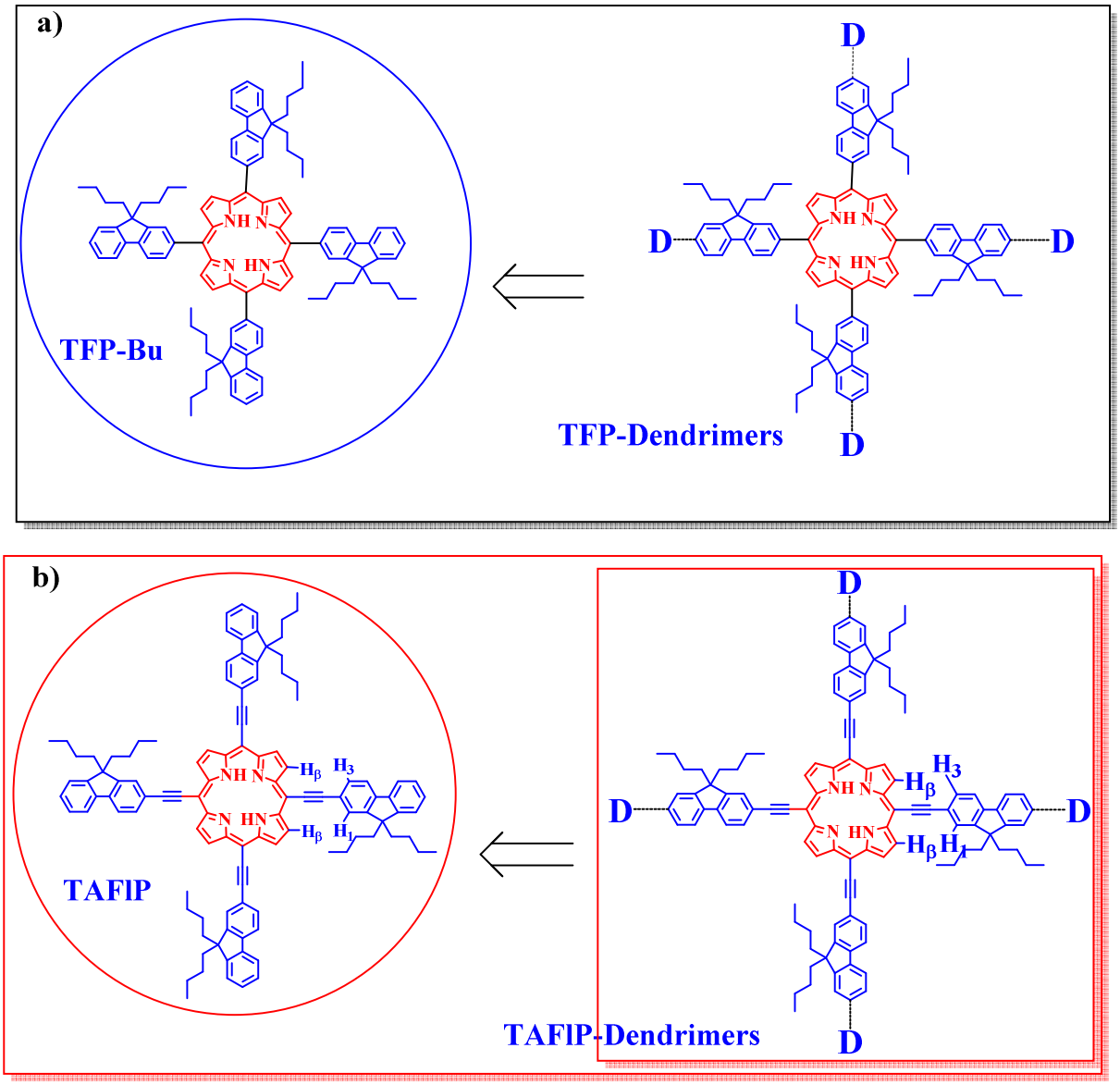


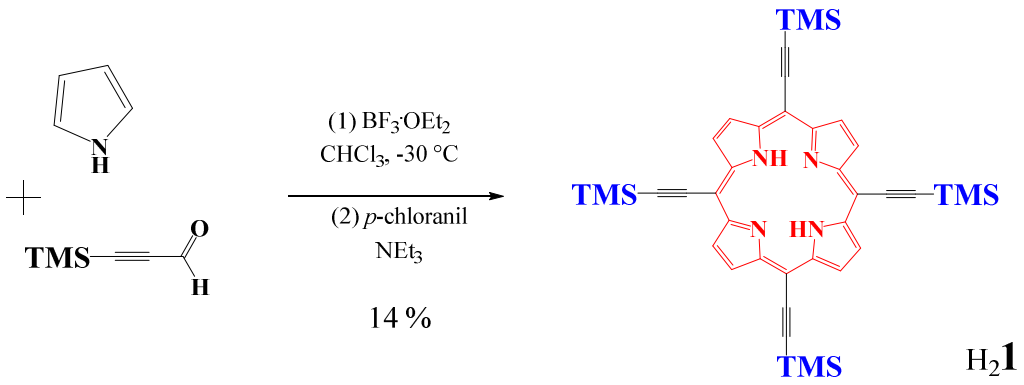
Fig. 4. a) Structure of reference compound **TFP-Bu** and corresponding **TFP** based dendrimers; b) target compound: new *meso*-alkynyl fluorenyl porphyrin **TAFlP** allowing the design of new **TAFlP**-based dendrimers

RESULTS AND DISCUSSION

Synthesis and characterization

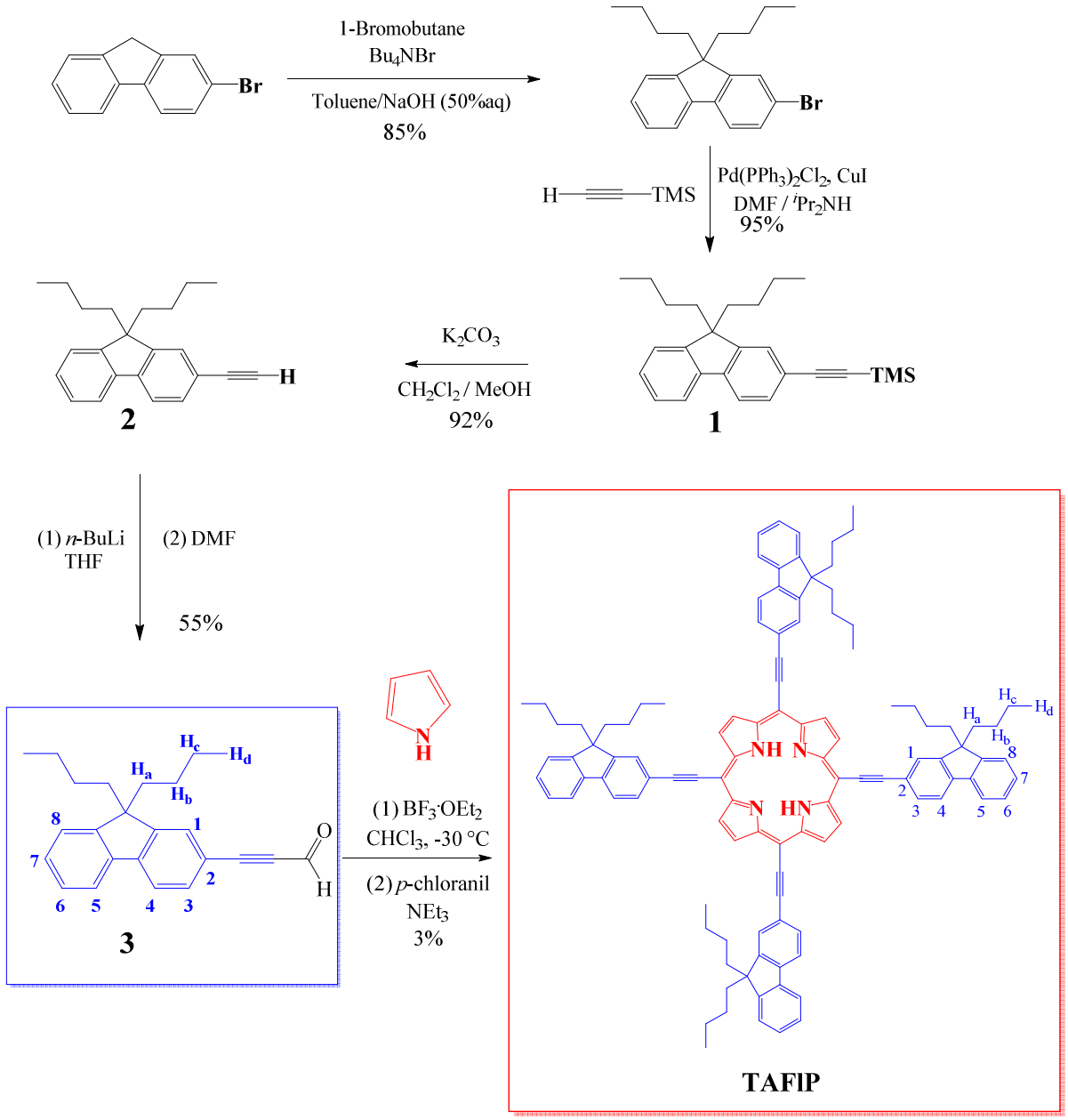
To synthesize **TAFlP**, two different ways were tested. A first trial at isolating this molecule was done *via* H_2**1**.[2a] As shown in Scheme 1: one equivalent of the commercial 3-(trimethylsilyl)-2-propynal and pyrrole were dissolved in distilled $CHCl_3$ under argon. The reaction was conducted by adapting the reaction protocol given by Anderson in the literature

for H_2**1**,[11] and it allowed the isolation of H_2**1** with a low yield (14%).[11] Considering the large quantity of H_2**1** required for the next step and also the high price of the starting material (3-(trimethylsilyl)-2-propynal); this approach was eventually not pursued, and a second approach was tested.



Scheme 1. Syntheses of intermediate H_2**1**, following Anderson's work up[11]

In the second approach, 9,9-dibutyl-fluorenyl-2-propiolaldehyde **3** was synthesised first as a precursor and then assembled to obtain the desired **TAFlP** under Lindsey's conditions (Scheme 2). The intermediate alkyne **2** was prepared in three steps as described earlier,[11] giving the precursor **3** by exchange of the terminal proton and carboxylation.[17] The desired new *meso*-alkynyl fluorenyl porphyrin **TAFlP** was finally isolated albeit with a low yield (3%). This second synthetic approach (Scheme 2), using for each step well known reactions and leading to isolation of the precursor **3** in good yields was eventually selected, in spite of its comparatively final low yield, mostly for practical and cost-related reasons.



Scheme 2. Synthesis of the new 9,9-dibutyl-fluorenyl-2-propiolaldehyde **3** and of *meso*-alkynyl fluorenyl porphyrin **TAFlP**

The new compounds were characterized by usual methods. The ^{1}H NMR spectra of the known 9,9-dibutyl-fluorenyl-2-carboxaldehyde and of the new (9,9-dibutyl-fluorenyl)-2-propiolaldehyde (**3**) are shown in Fig. 5. We observe that the aldehyde proton of new compound **3**, at 9.46 ppm, is shifted to higher field (+0.62 ppm) upon the introduction of the alkynyl function. The multiplets corresponding to aromatic, as well as *n*-butyl protons, present similar shifts for **3** compared to 9,9-dibutyl-fluorenyl-2-carbaldehyde, but of lower magnitude.

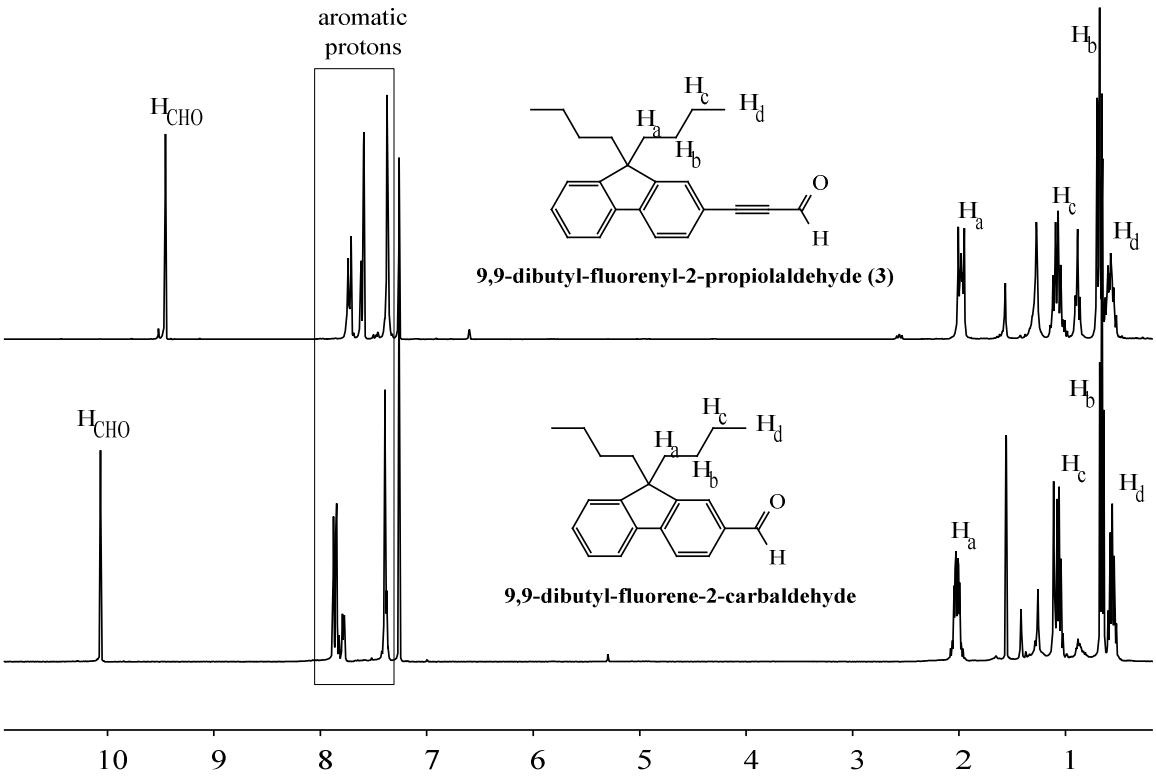


Fig. 5. Comparison of complete ^{1}H NMR spectra of 9,9-dibutyl-fluorenyl-2-carbaldehyde and new (9,9-dibutyl-fluorenyl)-2-propiolaldehyde (**3**)

The corresponding *meso*-alkynyl fluorenyl porphyrin (**TAFlP**) was also characterized by ^{1}H NMR. The partial spectrum is compared to reference **TFP-Bu** in CD_2Cl_2 (Fig. 6). As shown, the singlet at 9.69 ppm, corresponding to eight β-pyrrolic protons is shifted to lower field compared to the corresponding signal of **TFP-Bu** at 8.92 ppm. This can be because these β-pyrrolic protons are further removed from ring currents field of the aromatic units in the arms. An alternative explanation is that they experience a smaller ring current from the porphyrin cycle. The second explanation is also supported by the fact that the singlet at -1.36 ppm of NH protons is strongly shifted to lower field compared to that at -2.57 ppm for **TFP-Bu**. Thus it seems that the combination of the alkynyl bridges and fluorenyl units also causes a decreased electron density at the porphyrin ring. On the contrary, the electron density of fluorenyl arms seems to be partially increased, leading to signals for aromatic protons ($\mathbf{H_{1\text{-}5}}$) at higher field for **TAFlP** than for **TFP-Bu.**

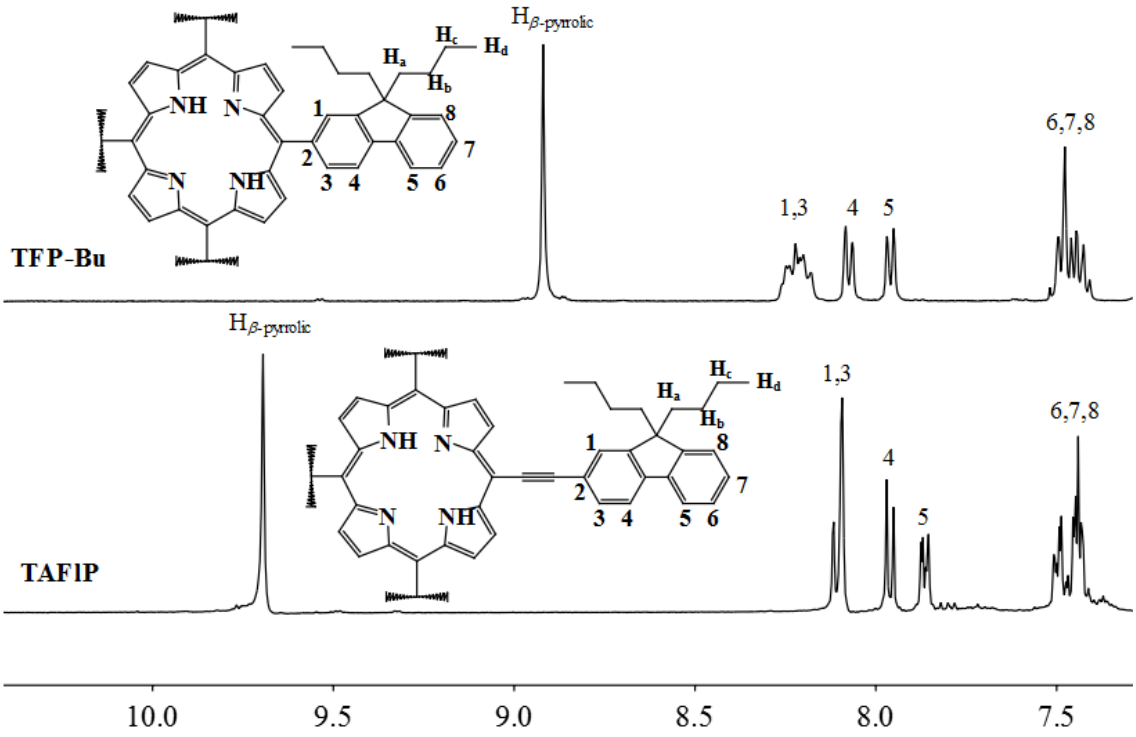


Fig. 6. The partial ^{1}H NMR spectra of new *meso*-alkynyl fluorenyl porphyrin **TAFlP** compared to reference **TFP-Bu**

UV-visible absorption and emission spectra were next recorded for the new porphyrin (**TAFlP)** in CH_2Cl_2 solution (HPLC level) at room temperature. Molecules with similar structures, such as H_2**1**, H_2**2** and H_2**3-R** reported previously (Fig. 3)[9,11-16] and **TPP**, **TFP-Bu** were chosen as references to analyze the influence of the triple bond introduction on the optical properties. When compared to *meso*-tetra-alkynylporphyrins, the fluorenyl rings of **TAFlP** extend the π-manifold of the chromophore, resulting in a bathochromic shift of all the absorption bands compared to H_2**1**, H_2**2** and H_2**3-R**, but also compared to **TFP-Bu**. **TAFlP** has several characteristic features in the UV-visible region (Fig. 7): (i) an intense Soret-band around 479 nm with a shoulder at 486 nm and two red shifted Q-bands at 661 and 748 nm, characteristic of the porphyrin macrocycle, and (ii) an extra absorption due to alkynylfluorenyl antennae (**AFl**), around 250-400 nm ($\lambda_{Dendron}$ = 319 nm) which corresponds to a π*← π transition of the conjugated dendron. This strong absorption, largely fluorenyl-based, is absent for reference **TFP-Bu**, suggesting that the unconjugated *meso*-fluorenyl groups of **TFP-Bu** absorb above 270 nm,[1m] whereas those of **TAFlP**, conjugate with the porphyrin core appear strongly red shifted and show up more intense.

Table 1. Photophysical data of new *meso*-alkynyl fluorenyl porphyrin **TAFlP** and reported H_2**1,** H_2**2** and H_2**3-R** and references **TFP-Bu**, **TPP**

	UV-visible absorption /nm		**Emission** /nm		Φ_{fl} / %	τ /ns
	λ_{Soret}	$\lambda_{Q\text{-}bands}$	excited at λ_{Soret}			
			Q (0,0)	Q (0,1)		
TPP	419	515, 548, 592, **647**, ,	653	721	11	8,6
TFP-Bu	426	520, 557, 593, **650**, ,	663	730	24	8,0
H_2**1**[a]	451	567, 606, **646**, 710	660	724	20	8.2
H_2**2**[a]	446	517, 563, 602, **647**, 708,	760	-	-	-
H_2**3**$_H$[a]	463	621, , 717				
H_2**3**$_{C8H17}$	466	599, **642**, 673, **737**				
H_2**3**$_{OC9H19}$	472	600, **653**, , **744**				
TAFlP	**479 (486)**	**661, , 748**				

[a] data from lit. [11-16]

When going from reference **TFP-Bu** to new porphyrin **TAFlP**, a strong red shift (Δλ = 53 nm) can be clearly observed on the normalized absorption spectra for the porphyrin based bands due to the alkynyl bridges (Soret-band and Q-bands in Figure 7). It should also be noticed that generally, free based porphyrins have four obvious Q-bands, but for **TAFlP**, only two coalesced Q-bands with and hyperchromic effect are observed in the visible region. In addition, there is a marked increase in the main Q band absorption (661 nm) relative to that of the B band (479 nm), and the second Q band (748 nm) appears as a smaller band on the right-side of this main Q band absorption.

We can notice that the derivative H_2**3-H**, which possess similar ethynylaryl structures than **TAFlP**, presents similar spectral profiles and show only two Q-band absorptions. In contrast, the para octyl substituted derivate of H_2**3-R** presents four Q-bands but very strongly red shifted and in this case, this red shift is even larger, going up to Δλ = 79 nm. The porphyrin H_2**2** also presents four classical Q-bands in the visible region.[12,16] Likewise, the aryl rings of the tetra-phenylethynylporphyrin (H_2**3-H**) by extending the porphyrin chromophore

result in a bathochromic shift for the B- and Q- absorption bands compared to those of porphyrin. Thus, compared to short tetra-phenylporphyrin (**TPP**), the B band of porphyrin H_2**1** is red-shifted to 451 nm. Also, by replacing TMS groups of H_2**1** with aryl groups (H_2**3-R**), increases the B- and Q- band red shifts even further.

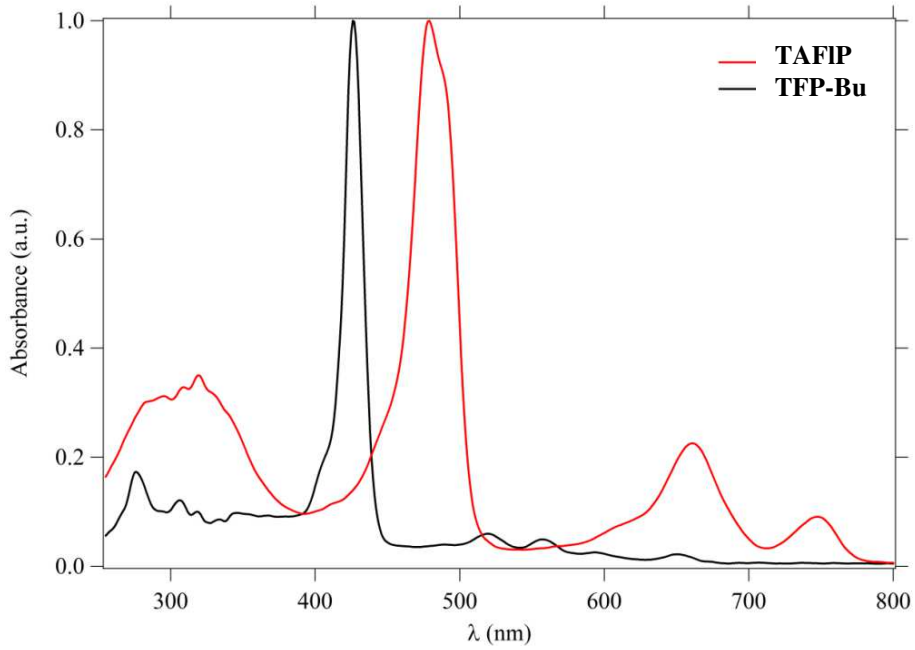


Fig. 7. Normalized absorption UV-visible spectra of **TAFlP** and reference **TFF-Bu** in CH_2Cl_2 (HPLC grade) at room temperature.

The emission spectra of **TAFlP** and the reference compound **TFP-Bu** were measured in CH_2Cl_2 (HPLC grade) at room temperature. Upon excitation in their Soret-band, they both exhibit the characteristic porphyrin emission peaks Q(0,0) (Fig. 8). The lowest energy Q-band absorption is at 748 nm, while the corresponding fluorescence band appears at 760 nm. The new tetra-fluorenylethynylporphyrin spectra are also characterized by small Stokes shifts (~12 nm) but slightly larger than for **TFP-Bu** derivatives (~10 nm)[19] similar to the shift reported in 1998, for 5,10,15,20 tetra-arylethynyIporphyrinato zinc(II) complexes (13 nm).[18] The proximity of these two bands indicates that the nuclear configurations of the ground and excited states of **TAFlP** are nearly similar. Whereas reference **TFP-Bu** emits a typical red luminescence, with two Q bands (660 and 724 nm), for new **TAFlP** only a strong single band Q(0,0) could be detected in the visible region with a maximum at 760 nm with a large red shift ($\Delta\lambda$ = 100 nm) compared to **TFP-Bu.** This intense Q(0,0) emission band has a part of its emission located in near infrared region (shadowed on Fig. 8). Thus, as for absorption, the

presence of the four ethynyl groups results in a significant red shift in the fluorescence peak maxima relative to **TPP** and **TFP-Bu** derivatives, resulting in emission located partly in the near infra-red region of the spectrum. The detector of the Edinburgh FS920 Fluorimeter (Xe900) can only collect the signal at the maximum wavelength of 900 nm, so for the moment eventually weaker emission band Q(0,1) could not be detected and in consequence, the quantum yield of this new porphyrin **TAFlP** is calculated but maybe under evaluate. The fluorescence quantum yields, measured in CH_2Cl_2 for this new porphyrin **TAFlP** is found to be 24% albeit similar to **TFP** (24%), and higher then **TFP-Bu** (20%). In agreement with what had already been noted earlier about fluorescence. Indeed it was proofed that fluorescence quantum yield values are significantly higher for the arylethynyl derivatives (ϕ_{fl} > 20%) and are among the highest values observed for porphyrinic species.[19] So measurement must be repeated on a fluorimeter allowing detection further in the near IR range.

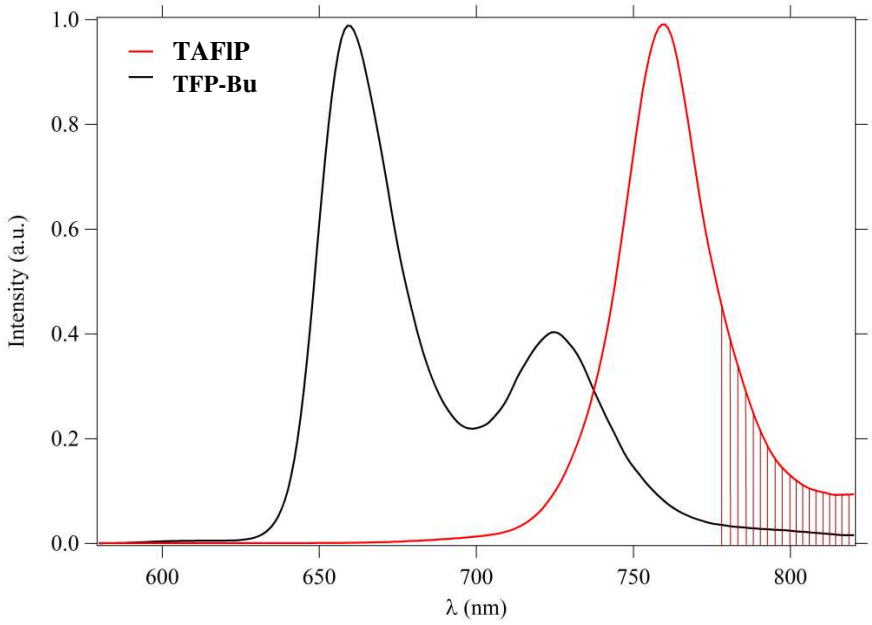


Fig. 8. Comparison of emission spectra of **TAFlP** and reference **TFP-Bu** in the visible region, upon excitation in their Soret-band

EXPERIMENTAL

Materials

Unless otherwise stated, all solvents used in reactions were distilled using common

purification protocols,[20] except DMF and $^{i}Pr_2NH$, which were dried on molecular sieves (3 Å). Compounds were purified by chromatography on silica gel using different mixtures of eluents as specified. ^{1}H and ^{13}C NMR spectra were recorded on BRUKER Ascend 400 and 500 at 298 K. The chemical shifts are referenced to internal tetramethylsilane. High-resolution mass spectra were recorded on different spectrometers: a Bruker MicrOTOF-Q II, a Thermo Fisher Scientific Q-Exactive in ESI positive mode and a Bruker Ultraflex III MALDI Spectrometer at CRMPO (centre regional de mesures physiques de l'Ouest) in Rennes. Reagents were purchased from commercial suppliers and used as received. Compounds 9,9-dibutyl-7-((trimethylsilyl)ethynyl)-fluorene-2-carboxaldehyde and 2-ethynyl-9,9-dibutyl-fluorene (**2**), were synthesized as described earlier.[11,1m]

Spectroscopic Measurements

All photophysical properties have been performed with freshly-prepared air-equilibrated solutions at room temperature (298 K). UV-Vis absorption spectra were recorded on a BIO-TEK instrument UVIKON XL spectrometer or on a Jasco V-570 spectrophotometer. Steady-state fluorescence measurements were performed on dilute solutions (*ca.* 10^{-6} M, optical density < 0.1) contained in standard 1 cm quartz cuvettes using an Edinburgh Instrument (FLS920) spectrometer in photon-counting mode. Fully corrected emission spectra were obtained, for each compound, after excitation at the wavelength of the absorption maximum, with $A_{\lambda ex} < 0.1$ to minimize internal absorption.

Synthesis

9,9-dibutyl-fluorenyl-2-propargylaldehyde (3): In a Schlenk tube, a mixture of 9,9-dibutyl-2-ethynyl-fluorene (**2**) (1.03 g, 3.41 mmol, 1 equiv) was dissolved in dried THF (10 mL). The reaction medium was degassed by freeze-pump-thaw for three times and cooled to -78 ^{o}C in a liquid nitrogen-acetone bath. At -78 °C, *n*-BuLi (2.60 mL, 4.09 mmol, 1.2 equiv) was injected dropwise to the previous mixture over 30 min. Then the system was kept stirring at -78 ^{o}C for more than 3 h. Subsequently dry DMF (0.53 mL) was injected in the medium and the reaction was maintained under stirring at -78 ^{o}C for another hour. The reaction was then taken away from cooling bath and stirred overnight at room temperature. At last, saturated NH_4Cl (aq.) was injected (for quenching the reaction). The mixture was extracted with ethyl acetate/water mixtures. After evaporation of the volatiles, the residue was purified by silica chromatography using heptane/CH_2Cl_2 (5:1) as eluent. The desired compound 9,9-dibutyl-fluorenyl-2-propiolaldehyde (**3**) was isolated as a white powder (623 mg, 55% yield).

^{1}H NMR (400 MHz; $CDCl_3$) : δ_H, ppm 9.44 (s, 1H, H_{CHO}), 7.77-7.75 (m, 2H, $H_{1,3}$), 7.64-7.62 (m, 2H, $H_{4,5}$), 7.41-7.35 (m, 3H, $H_{6,7,8}$), 2.03-1.99 (m, 4H, H_a), 1.13-1.04 (m, 4H, H_c), 0.67 (t, J = 7.2 Hz, 6H, H_d), 0.60-0.52 (m, 4H, H_b). ^{13}C{^{1}H}NMR (400 MHz, CD_2Cl_2, ppm): δ = 176.6 (CHO), 151.5, 151.1, 144.6, 139.7, 132.5, 128.5, 127.9, 127.1, 123.1, 120.5, 119.9, 117.2, 96.3, 88.8, 55.2, 39.9, 25.9, 23.0, 13.5. HRMS-ESI for $C_{24}H_{27}O$: m/z = 331.2060 $[M]^+$ (calcd: 331.20619); for $C_{24}H_{26}O$: m/z = 330.1990 $[M]^+$ (calcd: 330.19837).

***Meso-alkynyl fluorenyl porphyrin (TAFlP)**:* In a two-neck flask, a mixture of 9,9-dibutyl-fluorenyl-2-propiolaldehyde (**3**) (300 mg, 0.91 mmol, 1 equiv) and distilled pyrrole (0.06 mL, 0.91 mmol, 1 equiv) were dissolved in dried chloroform (60 mL) under argon. After degassing the mixture with argon bubbling for 30 min, BF_3**.**OEt_2 (0.02 mL, 0.16 mmol, 0.25 equiv) was injected and the reaction was stirred in dark for 1 h under argon at -30 °C. Then *p*-chloranil (315 mg, 1.28 mmol, 0.75 equiv) was added as oxidant, and the reaction was continued at room temperature. for another hour. At last, NEt_3 (2 mL) was injected, and the reaction medium was kept stirring for several minutes. After evaporation of the volatiles, purification of the residual solid was done by silica chromatography using THF/heptane (1:10) mixtures as eluents. **TAFlP** was collected as green powder (10 mg, 3% yield). ^{1}H NMR (400 MHz; $CDCl_3$) : δ_H, ppm 9.69 (s, 8H, $H_{\beta\text{-pyrrolic}}$), 8.11 (d, 8H, J = 10.5 Hz,$H_{1,3}$), 7.96 (d, 4H, J = 7.6 Hz, H_4), 7.88-7.85 (m, 4H, H_5), 7.51-7.43 (m, 12H, $H_{6,7,8}$), 2.30-2.15 (m, 16H, H_a), 1.25-1.17 (m, 16H, H_c), 0.78 (t, 24H, J = 7.3 Hz H_d), 0.75-0.62 (m, 16H, H_b), -1.36 (s, 2H, NH). ^{13}C{^{1}H}NMR (400 MHz, CD_2Cl_2, ppm): δ = 151.3, 151.2, 142.4, 140.5, 131.1, 127.9, 127.0, 126.1, 123.1, 121.7, 120.1, 103.1, 55.4, 40.3, 29.7, 26.2, 23.2, 13.7. UV-vis (λ_{max}, CH_2Cl_2, nm): 319, 479, 661, 748. HRMS-ESI for $C_{112}H_{111}N_4$: m/z = 1511.8797 $[M+H]^+$ (calcd: 1511.88033).

CONCLUSIONS

We have successfully synthesized and characterized the new *meso* tetra-fluorenylethynylporphyrin derivative (**TAFlP**). Linear optical measurements reveal better conjugation between the porphyrin core and the peripheral fluorenyl-containing antennae, than in the **TFP-Bu** core. This results from the presence of an yne linkage at the *meso* positions which allows more planar conformations. We now look forward to use similar central platforms for the design of new families of dendrimers. We hope that the extended and

more conjugated π-manifold, besides providing a desirable red-shift for theranostic and high fluorescence for imaging will also enhance the 2PA of the central core allowing for more efficient photosensitizers to be accessed. For the moment, extensive studies of the NLO properties of **TAFlP** are in progress to verify this point.

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