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New Highly Fluorescent Phthalocyanines Dendrimers with Fluorenyl-based Connectors vs Phenyl-based Connectors

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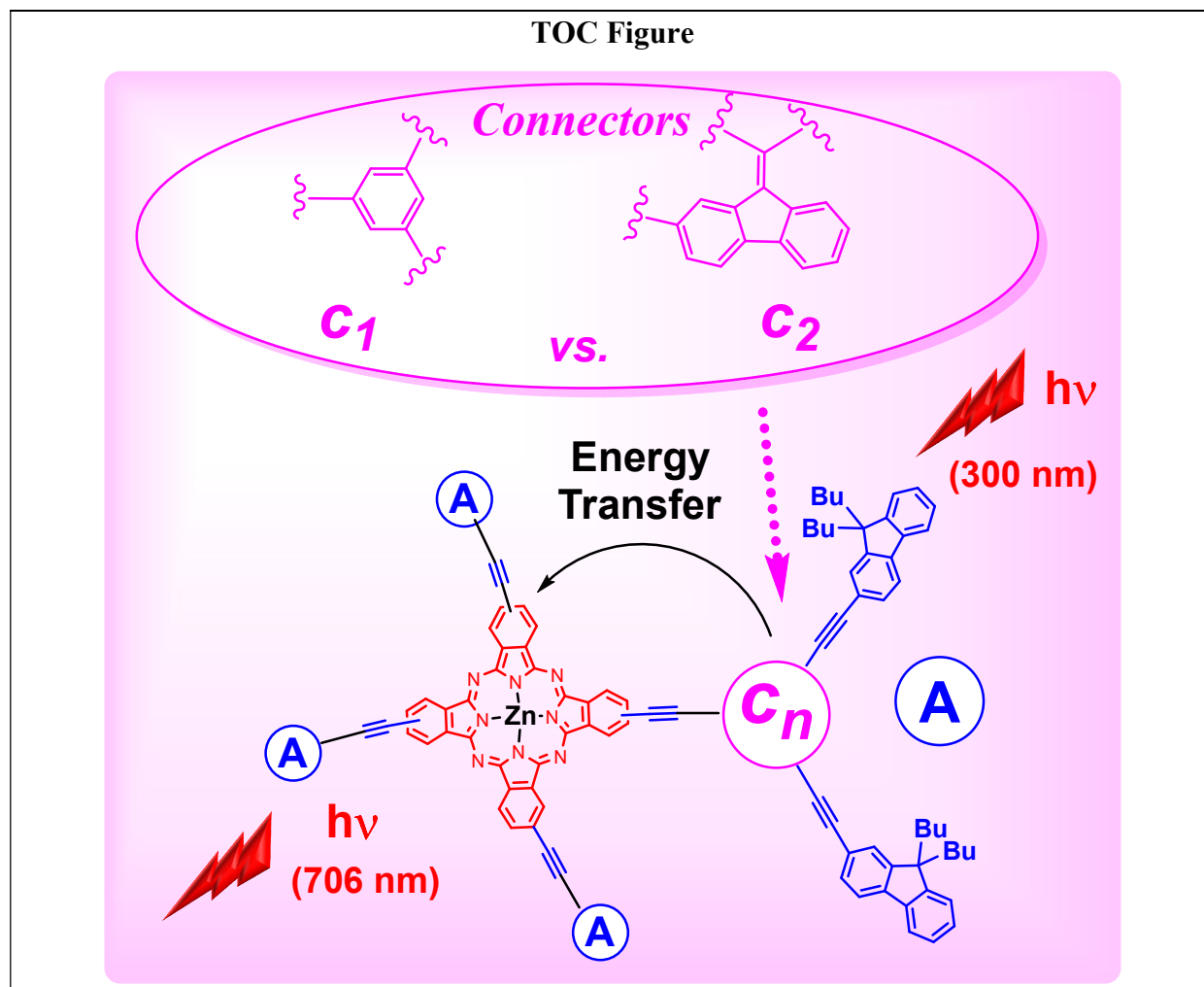
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ABSTRACT

The design of dendrimers featuring conjugated fluorenyl dendrons *via* new connectors allows evaluating the importance of the role of these junctions and the nature of the core, on the optical properties of interest. In the continuation of our sustained interest for dendrimers and their use as luminescent labels for bioimaging, we wondered about the effect of changing the central **porphyrin core** for a **phthalocyanine one** in these macromolecular structures. Thus, a related phthalocyanine-based dendrimer possessing up to eight conjugated 9,9-dibutyl-2-fluorenyl endgroups was designed, and for the first time, these endgroups are linked to the central **phthalocyanine core** by new **fluorenyl-based connectors C2** instead of the more classic 1,3,5-phenylene one **C1**. This original dendrimer was characterized and studied and as for porphyrin analogues, it was found that an efficient energy transfer occurs from the peripheral fluorenyl units to the central phthalocyanine core, leading to an intense red light emission. The luminescence is improved compared to that of their porphyrin-cored analogues for bioimaging, evidencing the key role played by the **central core** in this respect and the nature of the **connector Cn**. The impact of the structural changes of the core in relation with the impact resulting from the changes in dendron connectors is discussed.

Keywords:

Phthalocyanine • Fluorenyl • Dendrimers • Fluorescence • Energy Transfer • Porphyrin • Node

1. Introduction

Nowadays, following the remarkable works of Vogtle,¹ Tomalia,² Newkome³ and Fréchet,⁴ dendrimers form a wonderful class of molecules in the molecular world. In this respect, Fréchet and coworkers⁴ have reported porphyrin systems with fluorene-containing oligoether-type dendrons as efficient one- and two-photon light-harvesting units and demonstrated that such an “antenna effect” was facilitated in dendritic architectures *versus* linear ones. More recently, related star-shaped porphyrins with fully conjugated oligofluorene arms have also been reported by Bo and co-workers and shown to behave as a remarkable light-harvesting systems.⁵ In these assemblies, dendrons can work as efficient “**light-harvesting antenna**” in selected porphyrin-based dendrimers presenting molecular architectures recalling those collecting natural light in various photosystems.^{6,7} These systems are foreseen as key building blocks which can be fine-tuned at will, by modification of the peripheral substituents and this for many recent applied developments. In this respect, impressive fundamental research based on porphyrins has been undertaken in fields related to material sciences and information

treatment these last decades,^{8,9} but also in fields related to health, such as photodynamic therapy (PDT) for instance.¹⁰ Their use for PDT is particularly promising because the photosensitizers can be also fluorescent probes, allowing to perform curing and bioimaging at the same time in a so-called theranostic approach.^{11,12}

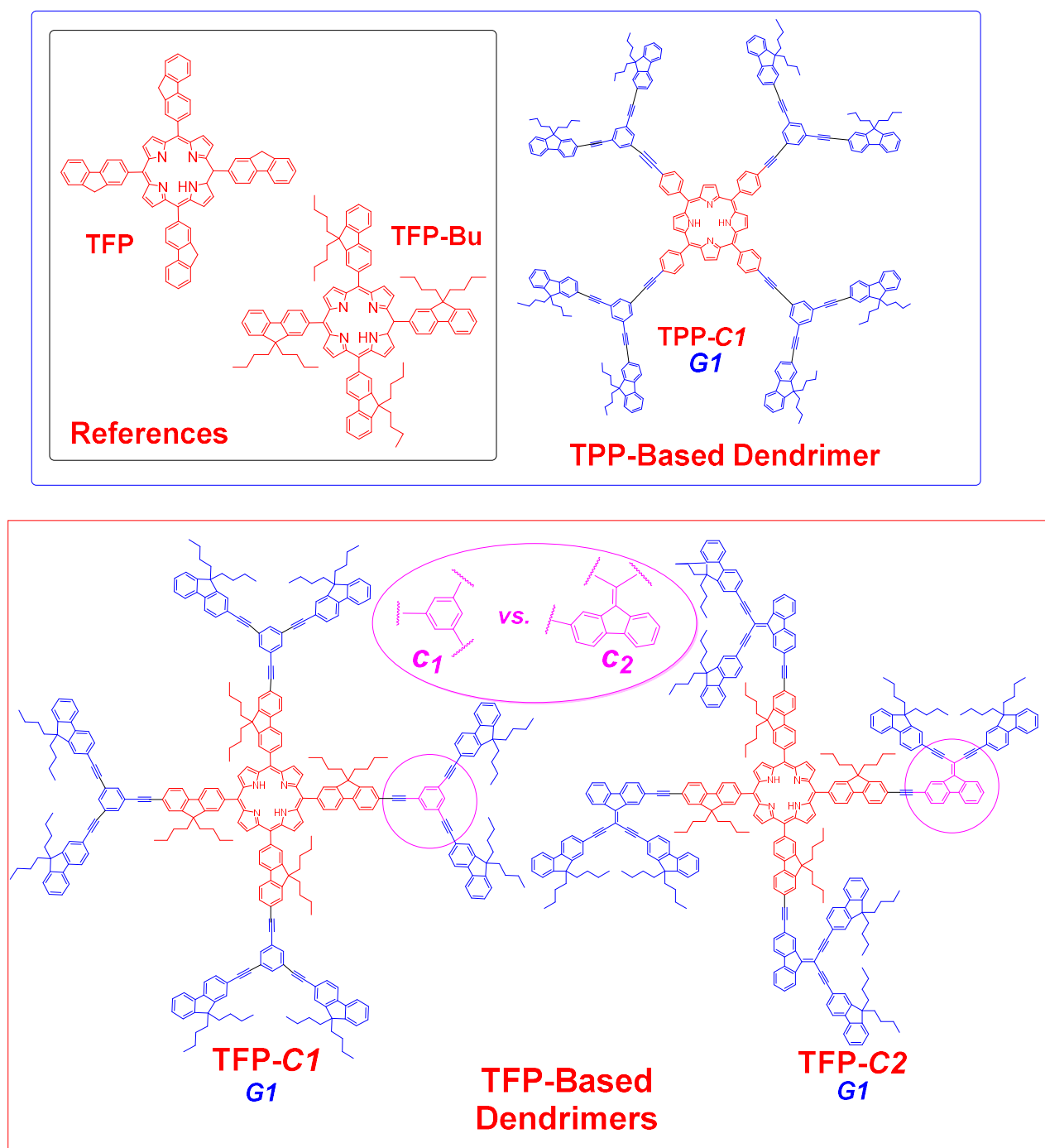


Fig. 1 Molecular structures of TPP- and TFP-cored porphyrin dendrimers with *conjugated* peripheral fluorenyl arms along with the reference compounds TFP and TFP-Bu.

Given that tetraphenylporphyrin (**TPP**) or related derivatives (**TPP-*C*₁** in Figure 1) are only modestly fluorescent in their free base form, most of the investigations in this field, relied on porphyrin conjugates featuring an expanded π -manifold, in order to enhance among others their absorption and so their one-photon absorption (OPA) brightness ($\epsilon \times \Phi_F$). Moreover, our group reported earlier, the synthesis of a simple porphyrin possessing four fluorenyl arms named tetrafluorenylporphyrin (**TFP** in Figure 1).¹³ Surprisingly, **TFP** exhibited a remarkably high quantum yield (24%) compared to the reference **TPP**, demonstrating thereby the capacity of the **fluorenyl** units to enhance fluorescence quantum yields (Φ_F). Likewise, to **TFP**, *n*-butyl groups were added in position 9 on the terminal fluorene groups (**TFP-Bu**) to improve the overall solubility of the porphyrin **TFP** and the corresponding dendrimers. Then, we could recently show with various families of *non-conjugated*^{14,15} or *conjugated* dendrimeric porphyrins,^{16,17} that by appending **fluorenyl-containing dendrons** at the periphery of a central tetra-arylporphyrin core, fluorescent photosensitizers with significantly enlarged one-photon brightnesses could be obtained upon increasing the dendrimer generation **G**.¹⁸

Furthermore, when fully unsaturated dendrons were used, a partial disruption of the π -manifold takes place at the *meso* positions in the most stable conformers. These twisted conformations adopted by the *meso* aryl groups allow the peripheral dendrons to behave as efficient **light-harvesting antennae**.¹⁸ Their optical properties studies reveal that among the members of the different dendrimer families, the **TFP**-cored dendrimers are always the most efficient.^{17,18} Recently, in order to improve further these fluorescent probes, we explored a new node and so replaced the classic **1,3,5-phenylene unit** (**C₁**; Figure 1) by a **fluorenyl-based unit** (**C₂**; Figure 1) in the dendrons. Thus, **TFP**-based dendrimer **TFP-C₂**, the analogue of dendrimer **TFP-C₁** featuring these innovative connectors, was studied.¹⁹ In *generation one* (**G1**) dendrimer **TFP-C₂**, contrary to what is happening with classic connector **C₁**, the 2-alkynylfluorenyl units on **C₂** are no more connected to topologically orthogonal positions²⁰ and there is probably a better electronic communication between the various fluorenyl subunits.¹⁸ The **C₂** fluorenyl connector, substituted in the position 9 by a double bond linked to two (2-ethynyl)fluorenyl groups, allows electronic conjugation between the four fluorenyl

groups of the dendron. The large dendrons in **TFP-C₂**, with rigid and entirely planar *termini* (except for the four butyl chains), adopt probably a propeller-shaped conformation around the central porphyrin core.¹⁹

Motivated by further enhancing the efficiency of our systems and inspired by the phthalocyanine-cored dendrimers reported by Kimura^{21,22} and others,²³⁻³² we recently wondered about the impact of replacing the central free-base *meso*-tetrafluorenylporphyrin (**TFP-Bu**) by zinc(II) phthalocyanine (**ZnPc**). Thus, we first synthesized the *non-conjugated* zinc(II) phthalocyanines series, decorated with fluorenyl arms connected by flexible ether linkers,³³ and then a *conjugated* zinc(II) phthalocyanine dendrimers series.³⁴ For this last one, we obtained successive generations of **ZnPc-C₁** type compounds (Fig. 2) and probed their photonic properties.³⁴ In details, we first synthesized the star shaped zinc(II) phthalocyanine (**ZnPcFI** in Figure 2), decorated with four fluorenyl arms, and then *higher generations* zinc(II) phthalocyanine dendrimers (*generation 1* and *2*), based on **ZnPc-C₁** model (Figure 2).³⁴ The idea behind this structural variation was to enhance the emission of these photosensitizers by using (i) a more luminescent central core than **TFP**, (ii) and the classic **1,3,5-phenylene node C₁**, for all these series. This goal was perfectly reached with this phthalocyanines series since all these compounds are more fluorescent than porphyrins dendrimers (with luminescence quantum yields around 29-37%). For these phthalocyanines, the comparison with the naked **ZnPc** complex (Fig. 2) also demonstrated the critical role of the peripheral fluorenyl-containing antenna on the optical properties.

Phthalocyanine Dendrimers

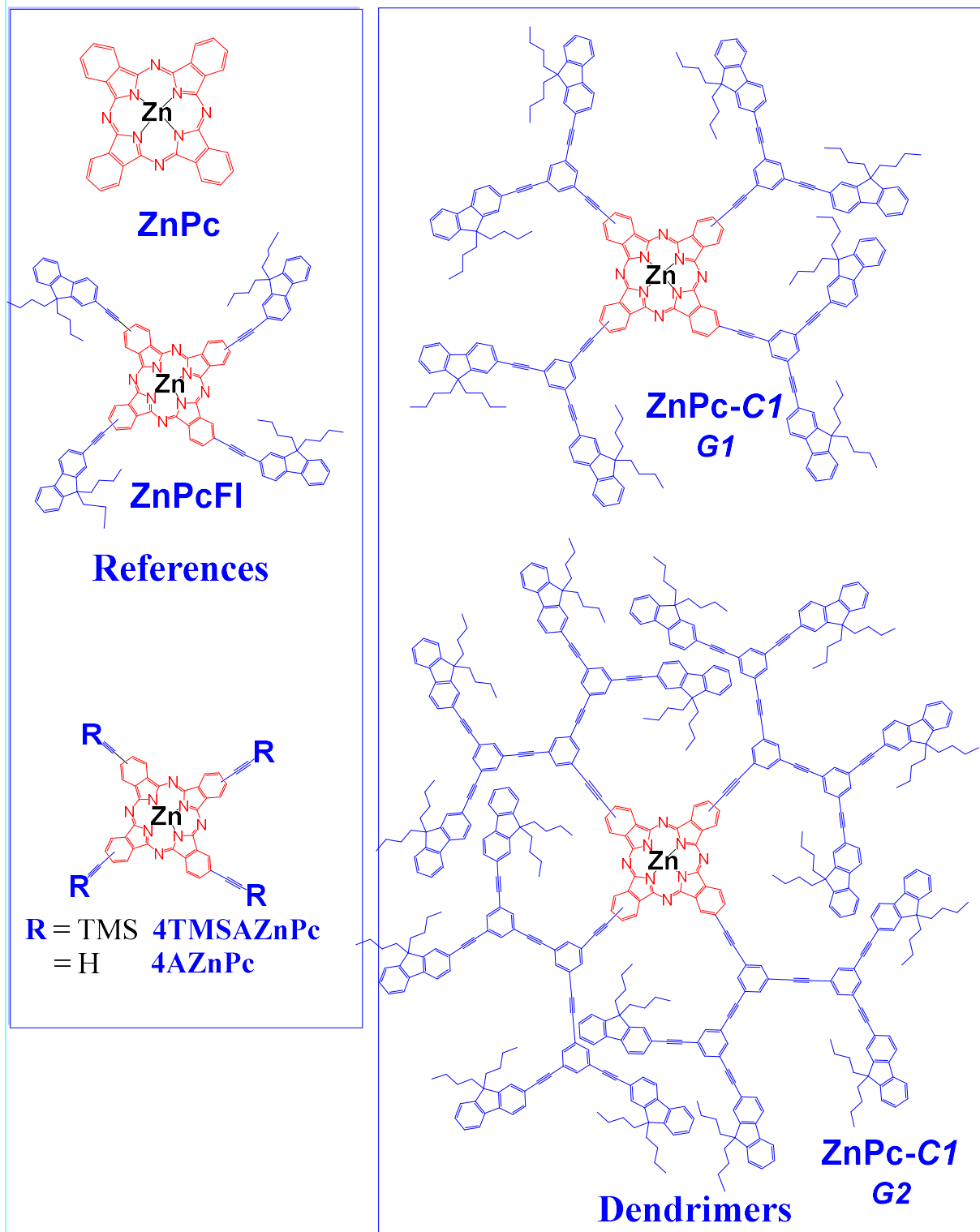


Fig. 2 Molecular structures of zinc(II) phthalocyanines dendrimers **ZnPc** previously synthesized with *conjugated* peripheral fluorenyl arms along with the reference compounds **ZnPc** and **ZnPcFI** and intermediates (**4TMSAZnPc** and **4AZnPc**).

In this project, we will now combine the most efficient core and the dendron with the best connector **C2**. So, in the following, we will describe (i) synthesis of useful fluorenyl dendrons with **C2** connector; (ii) synthesis of substituted **ZnPc** core; (iii) the synthesis and characterization of the targeted **ZnPc**-based dendrimer **ZnPc-C2**, featuring these units as components and last (iv) the study of the linear optical properties. Their optical properties as well as their energy transfer behavior will then be compared with parent phthalocyanine dendrimer **ZnPc-C1** and discussed in the light of previous results.^{17,33, 34}

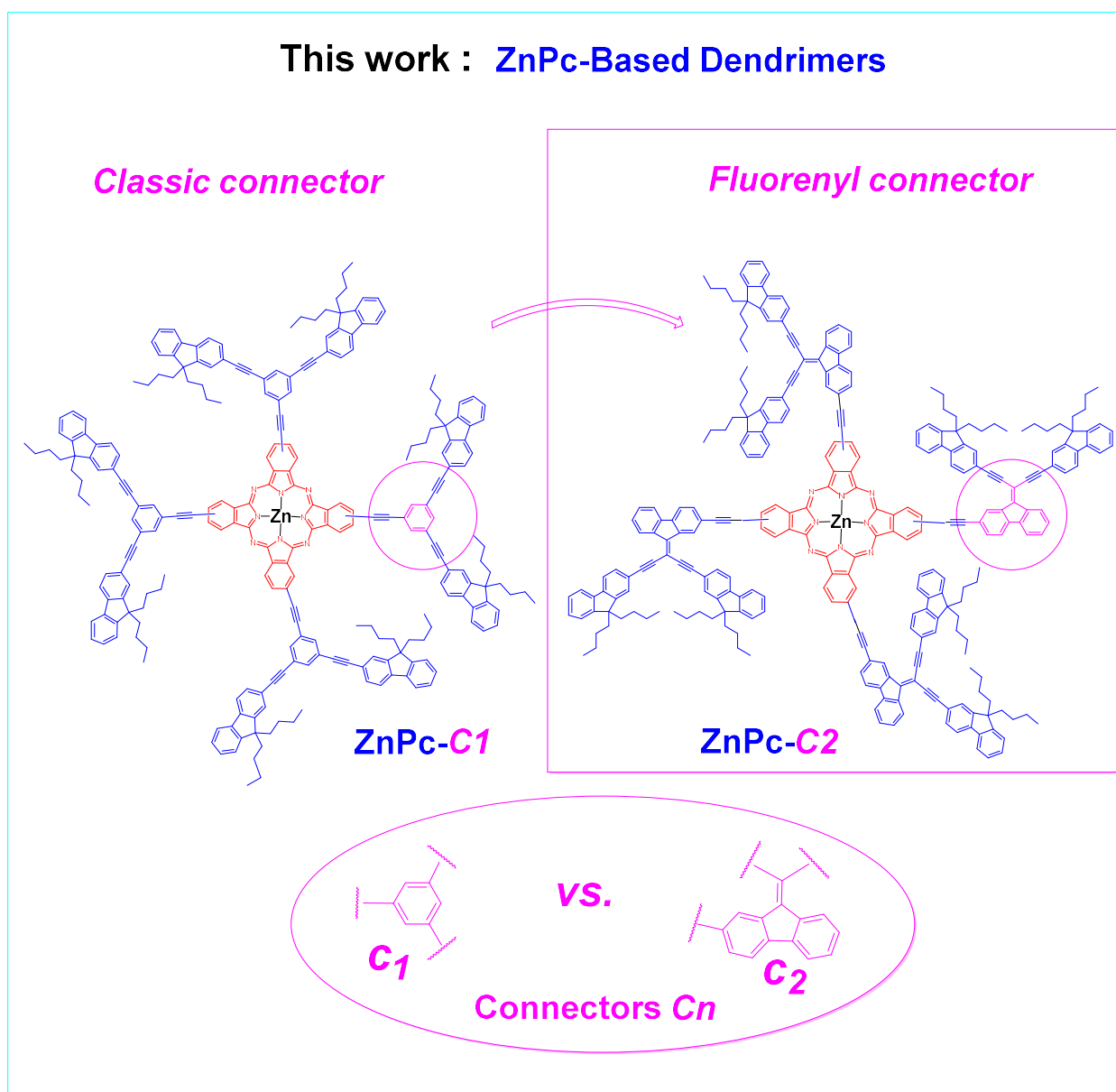


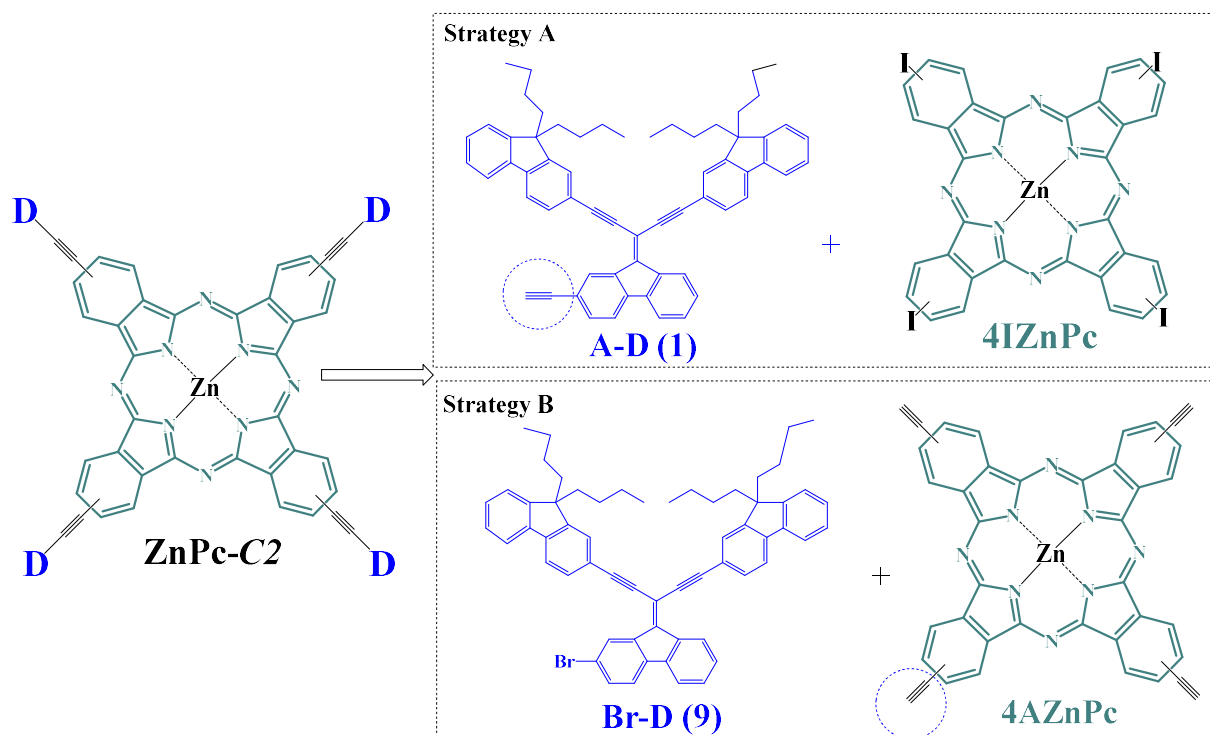
Fig. 3 Molecular structures of zinc(II) phthalocyanines dendrimers with *conjugated peripheral fluorenyl arms* with different connectors **Cn**.

2. Results and discussion

2.1. Synthesis

To synthetically access the new dendrimer **ZnPc-C2**, two reverse **Strategies A** and **B** in three steps each, can be envisioned (Scheme 1). For **Strategy A**, *i.e.* (i) Synthesis of Zn(II) tetraiodophthalocyanine **4IZnPc**, standing for **ZnPc**-cored precursor, (ii) Synthesis of the alkynyl-terminated dendron precursors **A-D** (**1**) and finally, (iii) Connection of Zn(II) phthalocyanine to the dendrons **A-D** (**1**) by Sonogashira coupling reactions.³⁵

For the second **Strategy B**, (i) Synthesis of the tetra-alkynyl Zn(II) phthalocyanine **4AZnPc**, standing for **ZnPc**-cored precursor (ii) Synthesis of the bromo-dendron precursors **Br-D** (**9**) and finally, (iii) Connection of Zn(II) phthalocyanine to the dendrons **Br-D** (**9**) by Sonogashira coupling reactions.³⁵

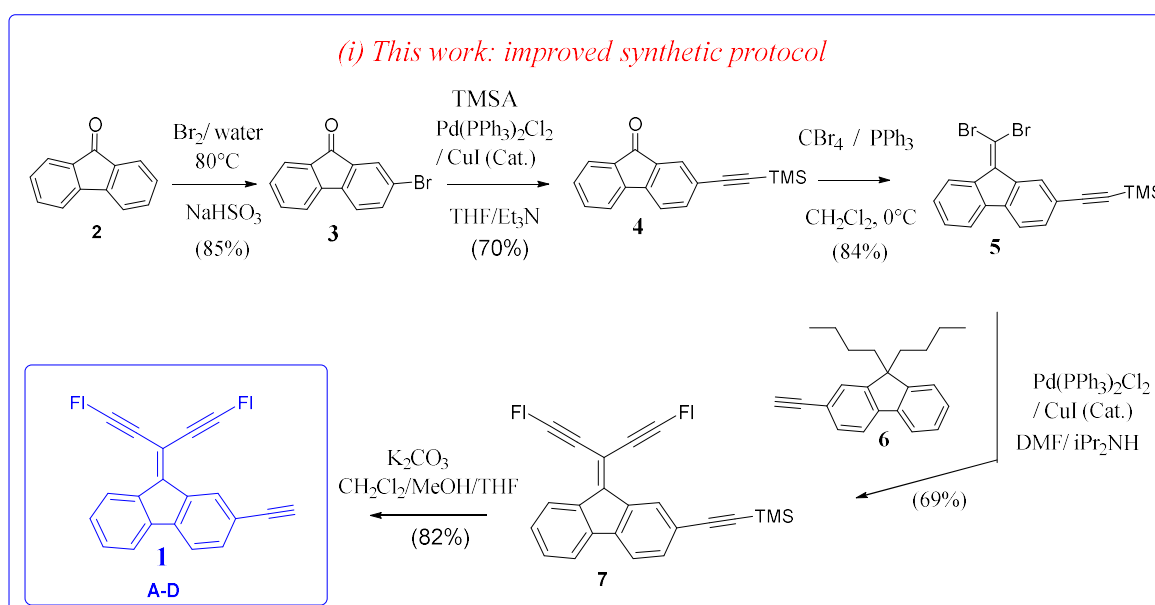


Scheme 1. Two Retrosynthetic **Strategies** proposed to access to the phthalocyanine dendrimer **ZnPc-C2**.

To obtain new dendrimer **ZnPc-C2**, two reverse **Strategies A** and **B** will now be considered, we will first discuss the **Strategy A** :

Conjugated Dendron 1. This Dendron was obtained from commercial fluorenone (**2**) in a few steps (Scheme 2) following two different approaches (i) *the improved synthetic protocol* described in this work and (ii) *the synthetic protocol used previously* in our group.¹⁹ We will now describe in details the first approach (i).

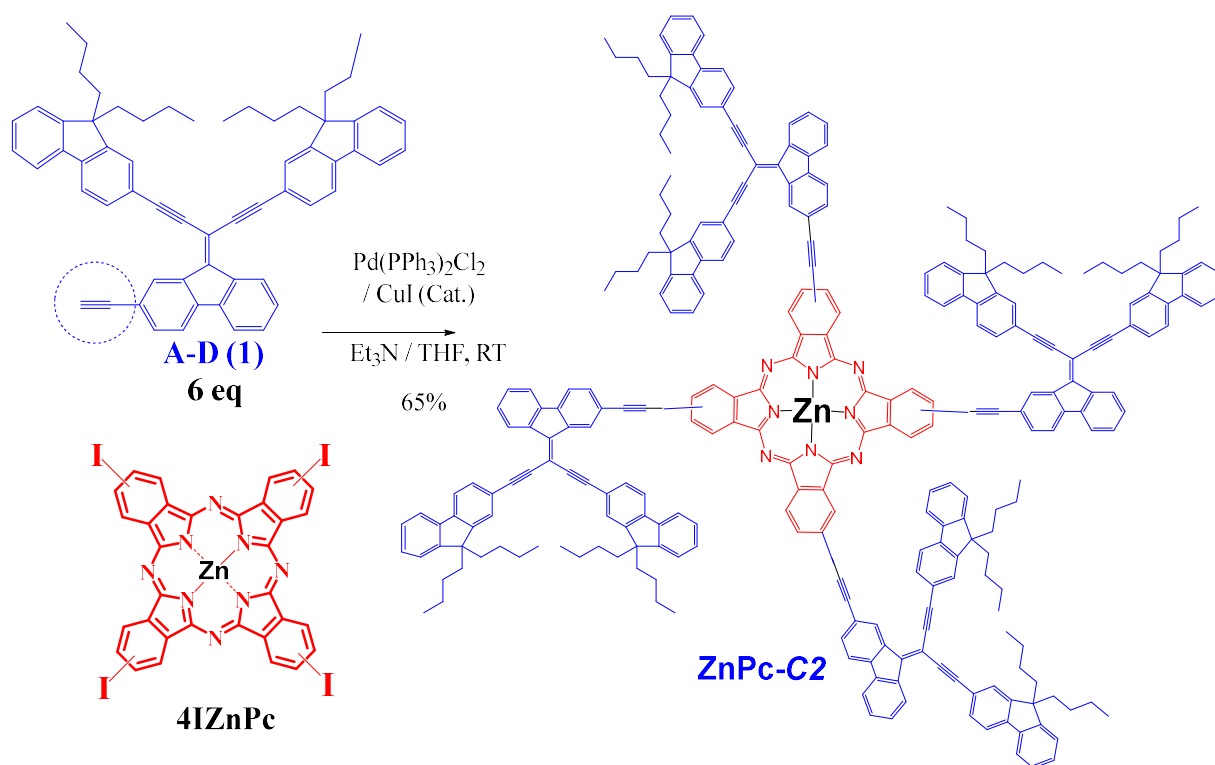
(i) *In the improved synthetic protocol*, the 2-bromofluorenone **3** was obtained from the commercial fluorenone **2** using dibromide in water, then, we introduced a trimethylsilylacetylene (TMSA) group by Sonogashira reaction.³⁵ Compound **4** was reacted with carbon tetrabromide and triphenylphosphine offering the *gem*-dibromo derivative **5**. After, we insert two **9,9-dibutyl-2-ethynyl-9H-fluorene** antennae by using two equivalents of **6**. This alkyne **6** was previously synthesized from commercial **2-bromo-9,9-dibutyl-fluorene** as described recently.^{16,17} The TMS protected dendron **7** was deprotected under basic condition (K_2CO_3) to give the terminal alkyne **1** with a global yield of 33% from intermediate **3** which is already higher than the yield obtained in the second approach (ii). This synthetic path is around three time more efficient than path (ii) *In the synthetic protocol already reported*.¹⁹



Scheme 2. Syntheses of the conjugated dendron precursor **A-D (1)** following new approach (i) *the improved synthetic protocol*.

Desired **dendron 1** and corresponding intermediates **3**, **4**, **5** and **7** were characterized by ^1H NMR in CDCl_3 (as shown in SI Fig. S3b and for intermediate **8** and dendron **9** see SI Fig. 1, 2 and 3a). We can observe that by exchanging the bromine, present in 2-bromofluorenone **3**, by a TMS group, a new peak appears around 0.26 ppm for the three methyl groups for compound **4** (still present for **5** and **7**). Then fluorenone **4** is transformed to **5** by exchanging oxygen for CBr_2 , and the presence of these two bromo atoms causes a large shift to low field from 7.6 to 8.5 ppm for the very close protons H_1 and H_8 .

The connection of two extra fluorenyl *antennae* provided compound **7**, and a little shift to lower field was again observed for H_1 and H_8 . In fact, for non-symmetric compounds such as intermediate **7** or **9**, a singlet at 9.15 ppm (H_1) and doublet at 8.8 ppm (H_8) are seen at low field (Fig. 4 and SI Fig. 3). This peculiar ^1H NMR signal can therefore be used as a convenient NMR marker to assess the presence of dendrons like **1** in final dendrimers (only if there is no overlap in this low field region). The aliphatic protons of n-butyl chains appear around 2.1-0.7 ppm and global aromatic fluorenyl protons between 7.2 and 9.1 ppm. The final dendron **1** was clearly identified by the presence of the terminal alkynyl proton around 3.2 ppm.



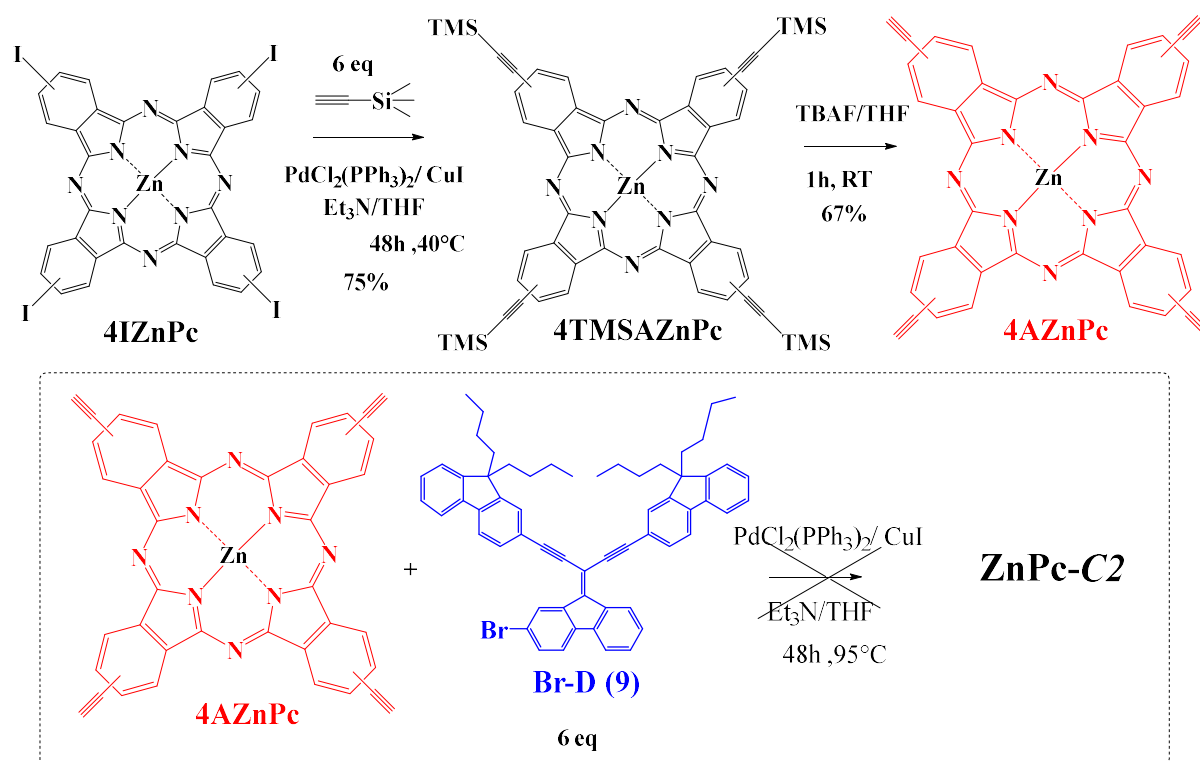
Scheme 3. Syntheses of the new conjugated dendrimer **ZnPc-C2**, by **Strategy A**.

Synthesis of dendrimer (ZnPc-C2). The synthesis of Zn(II) tetraiodophthalocyanine (**4IZnPc**) is obtained following the method described by Torres.³⁶ The targeted dendrimer **ZnPc-C2** was obtained by coupling prepared **4IZnPc** with 6 equiv. of deprotected dendron **1**, under Sonogashira conditions.³⁵ This dendrimer **ZnPc-C2** was then obtained as a green solid in 65% yield (Scheme 3). This new dendrimer was characterized by NMR, elemental analysis and MALDI MS. In ¹H NMR spectrum (400 MHz, using THF-d₈ as a solvent; see ESI Fig; 8), the large multiplets between 9.5-8 ppm are corresponding to the aromatic protons (H α , H α' and H β) of the phthalocyanine core, between 8 and 7 ppm, we observe large multiplets corresponding to the aromatic proton peaks, of the twelve fluorenyl units. The four large peaks in region of 2.3 to 0.3 ppm are corresponding to the protons of the sixteen butyl chains from the eight external fluorenyl groups.

After having detailed successful **Strategy A**, to obtain new dendrimer **ZnPc-C2**, we will now rapidly consider reverse **Strategy B**, we can notice that this last path was used earlier to obtain similar *generation G1* dendrimer **TFP-C2**¹⁹ based on a porphyrin core rather than on a phthalocyanine acceptor

Bromo Dendron 9. This synthesis has already been described above, in **Strategy A**, as an intermediate in (ii) *the synthetic protocol already reported*,¹⁹ and obtained in three steps from 2-bromofluorenone **3** (scheme 2).

Phthalocyanine-based dendrimer ZnPc-C2. For this second **Strategy B**, the synthesis of the tetra-alkynyl Zn(II) phthalocyanine **4AZnPc** (see Scheme 2), standing for **ZnPc**-cored precursor, is necessary. This tetra-alkynyl phthalocyanine **4AZnPc** was obtained in two steps as a green solid, in 50% yield (Scheme 4). First by coupling **4IZnPc** with 6 equiv. of ethynyltrimethylsilane (TMSA), under Sonogashira conditions,³⁵ to obtain protected **4TMSZnPc** (yield 75 %). Then, the TMS protection groups were removed by treatment with tetra-n-butyl ammonium fluoride (TBAF) in THF, so **4AZnPc** containing four terminal alkynyl groups was obtained with a yield of 67 % as described by Torres.³⁶ Finally, the connection of dendrons **9** to central Zn(II) phthalocyanine **4AZnPc** core was tried several times, by Sonogashira coupling reactions, in different conditions. Unfortunately, we could only obtain dark polymers, probably produced by the homo-coupling of the tetra-alkynyl phthalocyanine **4AZnPc**. As previously stated, this **Strategy B** was followed earlier to obtain the porphyrin based dendrimer **TFP-C2**, but in this case the rigid **fluorenyl node** is further from the central core, so there is less steric hindrance and the Sonogashira coupling is more favorable although the reported coupling efficiency is only around 20%.¹⁹



Scheme 4. Try to obtain new dendrimer **ZnPc-C2**, by reverse **Strategy B**.

These phthalocyanine precursors were characterized by ^1H NMR (400 MHz) using THF- d_8 as solvent (SI Fig. 4). For **4TMSAZnPc** and deprotected form (**4AZnPc**), the large peaks at low field (between 9.2-8 ppm) are corresponding to the twelve aromatic protons of the phthalocyanine core (H_α , $\text{H}_{\alpha'}$ and H_β). For phthalocyanine **4TMSAZnPc**, the singlet at 0.62 ppm is corresponding to the protons of the four TMS groups, and by reaction with TBAF, this peak disappeared and a new singlet at 4.07 ppm arises, attributed to the four alkynyl protons of deprotected phthalocyanine **4AZnPc**. To conclude, we succeed by following **Strategy A**, with **4IZnPc** as an acceptor and alkyne **dendron 1** as a donor, rather than following reversed **Strategy B**, using tetra alkynyl **4AZnPc** with bromo-dendron **9**.

2.2 Photophysical properties

2.2.1. Absorption and emission spectra in solution

The normalized UV-visible (abs) and emission (em) spectra of the **new dendrimer ZnPc-C2** using bare zinc phthalocyanine **ZnPc** as reference, were measured in THF solution at room temperature (Figures 5 and 6) and compared to those of the known compounds **ZnPcFl**,³⁴ and **ZnPc-C1**,¹⁹ decorated with four and eight fluorenyl units, respectively (see Fig. 2). The former phthalocyanine **ZnPc-C1**, used classical *connector C1*, whereas for new **dendrimer ZnPc-C2**, fluorenyl *connector C2* is used with a zinc phthalocyanine **ZnPc** core, for the first time.

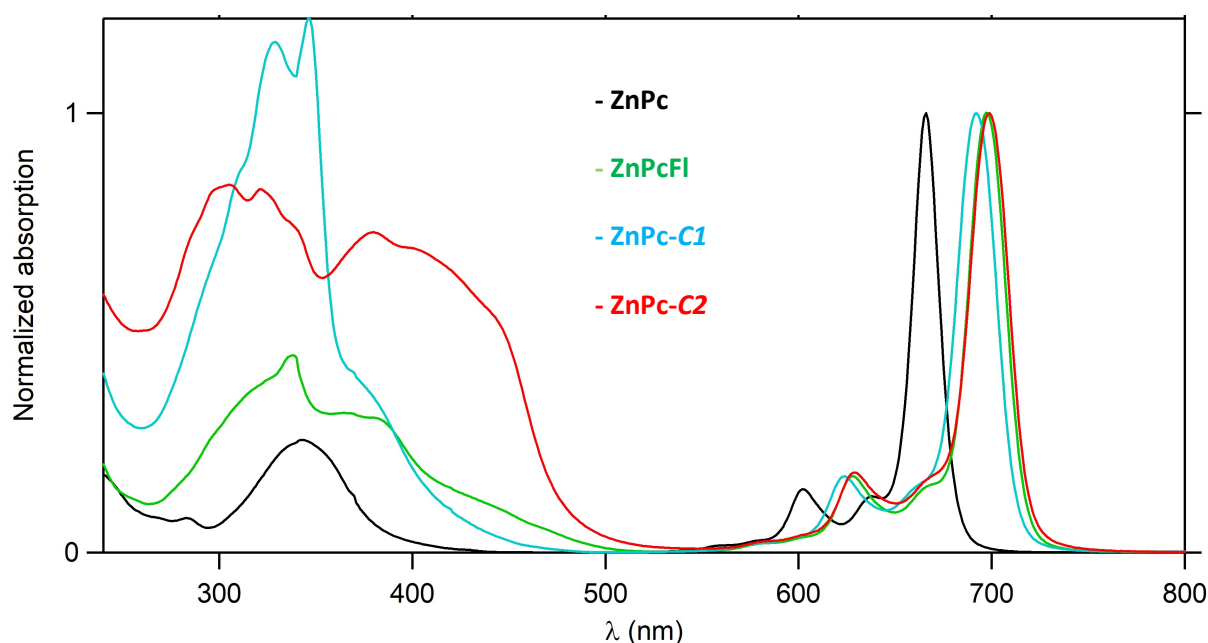


Fig. 5. The UV-visible absorption spectra of the series **ZnPcFl**, **ZnPc-C1** and **ZnPc-C2** and **ZnPc** used as a reference in THF.

The UV/Vis absorption spectra of all these phthalocyanines were recorded between 250 and 800 nm (Figure 5). The new **dendrimer ZnPc-C2** features the characteristic absorption bands of phthalocyanines already seen on the spectra of **ZnPc**,^{34,37} which are: (i) the Q-bands, corresponding to main absorption bands, detected in the visible range between 650 and 750 nm, and resulting from π - π^* transitions from the HOMO to the LUMO and LUMO+1 with a vibronic sub-band around 630 nm; (ii) the Soret band, corresponding to a

wide band between 300 and 500 nm and resulting from π - π^* transitions from deeper lying MOs to the LUMO and LUMO+1, and finally, (iii) the N band, a less intense and narrower band centered around 280-300 nm. The latter still corresponds to a set of more energetic π - π^* transitions within the phthalocyanine core.³⁴ These last two absorption bands can not be detected for **ZnPcFl**, **ZnPc-C1** and **ZnPc-C2** because they are overlapped by another intense absorption band, absent in **ZnPc**, which grows in intensity when progressing from **ZnPcFl** to **ZnPc-C1** and then to **ZnPc-C2** (Figure 5) *i.e.* roughly with the increasing size of the conjugated π -manifold within the arms when going from four to eight and finally twelve fluorenyl units, respectively. This broad band, going from 250 nm to 500 nm, which becomes more important than the Q-band for the two dendrimers (**ZnPc-C1** and **ZnPc-C2**), can be confidently attributed to dendron-centered π - π^* transitions.^{13,34} This extra absorption, around 300-400 nm, largely fluorenyl-based, is absent for the bare reference **ZnPc**. For new dendrimer **ZnPc-C2**, this extra absorption is even larger and more red-shifted (going to 450-500 nm) and more intense, to what had been previously observed with **ZnPc-C1**.³⁴ Moreover, when this fluorenyl-based absorption is compared to these previously observed around 300 nm with phthalocyanines presenting non-conjugated dendrons, such as reported earlier by our group³³ a bathochromic shift is stated for it in **ZnPcFl**, **ZnPc-C1** and **ZnPc-C2**. This shift reflects at least in part the better π -conjugation existing between the peripheral arms and core in these compounds.

On the other hand, a bathochromic shift is experienced by the main Q-band following roughly the same order. Thus, this maximum shifts towards the red, from 671 to 706 nm, along the order: **ZnPc** < **ZnPc-C1** < **ZnPcFl** \approx **ZnPc-C2**. The star-shaped phthalocyanine **ZnPcFl** presenting roughly the similar Q-band (706 nm) as corresponding dendrimer **ZnPc-C2**. Again, this shift reflects the importance of the π -manifold present on the peripheral dendrons, conjugating with the central core.

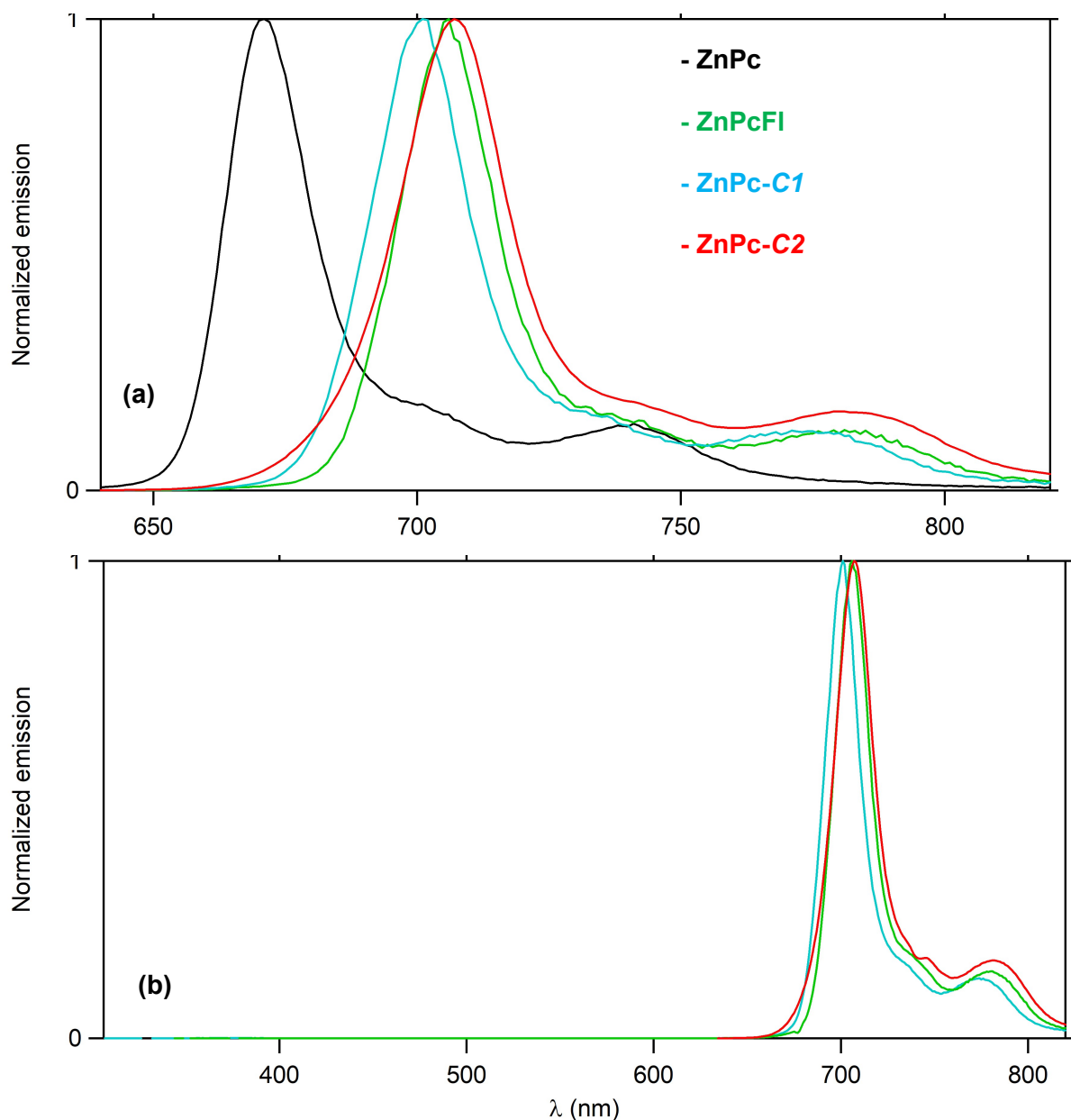


Fig. 6. a) Normalized emission spectra of the series **ZnPcFl**, **ZnPc-C1** and **ZnPc-C2** and **ZnPc** used as a reference in THF, after excitation at 606 nm; b) Normalized emission spectra of these phthalocyanines under similar conditions after excitation at the arm (300 nm).

Figure 6a shows the emission spectra of dendrimers **ZnPcFl**, **ZnPc-C1** and **ZnPc-C2** in THF, as well as that of **ZnPc** used as bare reference. After excitation at 606 nm *i.e.* in the Q vibronic sub-band, a strong red emission between 650 and 850 nm, characteristic of the phthalocyanine core, is observed. As for one-photon absorption, these dendrimers present a red-shifted emission relative to that of **ZnPc**. Without surprise, the wavelength ordering

between the dendrimers follows that previously observed in absorption for the Q-band: **ZnPc** < **ZnPc-C1** < **ZnPcFl** \approx **ZnPc-C2**. Then, to probe the efficiency of the energy transfer process (ET) between the peripheral dendrons, as energy donors **D** and the central phthalocyanine, as energy acceptor **A**, we have excited the dendrimers in their specific π - π^* band, at about 300 nm (Figure 6b). By doing so, we observed no residual emission of the dendrons in the 350-450 nm range,^{19,33,34} but only the characteristic emission band from the phthalocyanine core (between 650 and 850 nm) which proves an efficient ET process.

Table 1. Photophysical data of *generation G1* dendrimers **ZnPc-C1**, **ZnPc-C2** and bare **ZnPc** used as a reference, and **ZnPcFl** in THF at R.T.

Compound	λ_{abs} (arm) (nm)	λ_{abs} (Pc) (nm)	ϵ_{max} (M ⁻¹ cm ⁻¹) at $\lambda_{\text{Q}}^{\text{max}}$	λ_{em} (nm)	Φ_{F}^a
ZnPc	-	343, 602, 666	234000	671, 741	0.26
ZnPcFl	338	628, 697	398000	706, 781	0.29
ZnPc-C1	329, 346	624, 692	393000	701, 774	0.32
ZnPc-C2	305, 380	629, 699	272000	706, 781	0.35

^a Fluorescence quantum yield determined relative to (py)ZnPc in toluene / pyridine 99:1 ($\Phi_{\text{F}} = 0.30$, *J. Chem. Phys.*, **1971**, 55, 4131), upon excitation at 606 nm.

As previously done with phthalocyanines **ZnPcFl** and **ZnPc-C1**,^{33,34} the fluorescence quantum yields (Φ_{F}) were determined by comparison with **ZnPc** in a toluene/pyridine mixture (99:1). Compared to this standard **ZnPc** ($\Phi_{\text{F}} = 26\%$), all quantum yields found for these compounds are higher than this value (Table 1). We noticed earlier that among the dendrimer series, based on **ZnPc** core with connector **C1**, there is a regular increase in their fluorescence quantum yield with increasing generations ($29\% < 32\% < 36\%$), suggesting that the increase of the π -manifold on the peripheral dendrons favors the non-radiative deactivation of the phthalocyanine core.³⁴ In this work, when *generation G1* dendrimers with different connectors **C1** and **C2**, meaning reported **ZnPc-C1** and new **ZnPc-C2**, are compared, a better quantum yield (35%) is found for **ZnPc-C2**, possibly in line with better conjugation for **C2**.

When compared to the fluorescence quantum yield of zinc complexes previously investigated by our group (29-37%),^{33,34} these quantum yields cover an almost similar range of values, but only the yield found for the largest compound **ZnPc-C2** compares to that previously obtained (37%), which was the most luminescent compound among our complete series.^{33,34} The efficiency of the ET between the dendrons **D** and the phthalocyanine **A**, was also tested by exciting the dendrons at about 300 nm (Figure 6b) and, as observed before, only the phthalocyanine emission band (between 650 - 850 nm), with similar fluorescence quantum yields to that is seen when the compounds are excited in their Q-bands. This reveals again that for compound **ZnPc-C2**, the energy absorbed by the four large dendrons is almost quantitatively transferred to the central core, with an optimal process ($\Phi_{\text{ET}} \sim 100\%$).

3. Conclusions

To summarize, in this work we investigate the impact of the structural change of the central core of **dendrimers**, going from **porphyrin** to **phthalocyanine**, in relation with the impact resulting from the changes in dendron **connectors**. A new *conjugated* dendrimer **ZnPc-C2** has been synthesized and characterized. For this dendrimer the peripheral fluorenyl units are linked to the central **ZnPc** core by original fluorene-based connectors **C2** instead of the more classic 1,3,5-phenylene **C1** previously used in related compounds. Comparison of absorption, emission and ET studies of these dendrimers **ZnPc-C1** and **ZnPc-C2** are discussed here. In contrary to what is happening with classic connector **C1**, the 2-alkynylfluorenyl units on **C2** are no longer connected to orthogonal positions^{19,20} and therefore there is a better electronic communication between the three fluorenyl subunits of the dendron. In consequences, their absorption bands are strongly red shifted and enlarged compared to that of bare **ZnPc**. In fact, these large dendrons in **ZnPc-C2**, with rigid and entirely planar *termini* (except for the four butyl chains), adopt probably a propeller-shaped conformation around the central **ZnPc** core. During these investigations, we observed again that rigid and conjugated fluorenyl-based connector **C2** leads to higher performances than the 1,3,5-phenylene spacer **C1** as observed earlier with central porphyrin core.¹⁹ This original connector ameliorates the electronic communication within the dendrimeric branches without affecting the fluorescence

performances. For this reason, this connector should now be used in the future when designing dendrimers of higher generation based on phthalocyanines.

4. Experimental Section

4.1. General

Unless otherwise stated, all solvents used in reactions were distilled using common purification protocols,³⁸ except DMF and $i\text{Pr}_2\text{NH}$ which were dried on molecular sieves (3 Å). Compounds were purified by chromatography on silica gel using different mixtures of eluents as specified. ^1H and ^{13}C NMR spectra were recorded on BRUKER Ascend 400 and 500 at 298 K. The chemical shifts (in ppm) 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 2-ethynyl-9,9-dibutyl-fluorene (**6**),^{16,17} was synthesized as described earlier. The zinc tetraiodophthalocyanine complex **I₄ZnPc**, the protected **4TMSAZnPc** intermediate and the zinc tetraalkynyl-phthalocyanine complex **4AZnPc** were obtained as previously described in the literature by Torres.³⁶

4.2. Synthesis

(i) Improved synthetic protocol

2-((trimethylsilyl)ethynyl)-9H-fluoren-9-one (4). To a mixture of 2-bromo-fluoren-9-one **3** (8 g, 30.9 mmol, 1 equiv), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (1.08 g, 1.54 mmol, 5% equiv) and CuI (0.29 mg, 1.54 mmol, 5% equiv) were successively added THF (60 mL), Et_3N (60 mL) and ethynyltrimethylsilane (8.54 mL, 61.7 mmol, 2 equiv) under argon atmosphere. The system

was degassed by freeze-pump-thaw twice and heated for 24 h at 80 °C. The reaction mixture was poured into saturated NH₄Cl and extracted with DCM, the combined organic layers were dried with MgSO₄. Volatiles were evaporated and the residue was further purified by silica chromatography using heptane as eluent to give title compound **4** as a yellow solid (6.0 g, 70%). ¹H NMR (400 MHz, CDCl₃) δ = 7.73 (dd, *J* = 1.5, 0.7 Hz, 1H), 7.65 (d, *J* = 7.3 Hz, 1H), 7.57 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.53 – 7.46 (m, 2H), 7.47 – 7.42 (m, 1H), 7.30 (ddd, *J* = 7.4, 5.9, 2.6 Hz, 1H), 0.26 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ = 192.9, 143.9, 138.0, 134.8, 134.3, 134.0, 129.4, 127.7, 124.4, 124.0, 120.6, 120.1, 104.0, 96.2, 0.1.

((9-(dibromomethylene)-9H-fluoren-2-yl)ethynyl)trimethylsilane (5). In a Schlenk tube, a mixture of fluoren-2-yl ethynyl trimethylsilane-9-one **4** (5.7 g, 20.6 mmol, 1 equiv) and PPh₃ (10.81 g, 41.2 mmol, 2 equiv) in dry CH₂Cl₂ (240 mL) was cooled to 0 °C in ice-water bath under argon protection. Then, CBr₄ (13.67 g, 41.2 mmol, 2 equiv) was added into Schlenk and the mixture was kept stirring at low temperature for 2 min. The bath was removed and the solution was stirred overnight at room temperature. After evaporation of volatiles, the residue was adsorbed into silica and further purified by chromatography using heptane/CH₂Cl₂ (9:1) as an eluent system. Compound **5** was obtained as a yellow powder (7.5 g, 84% yield). ¹H NMR (400 MHz, CDCl₃) δ = 8.70 (s, 1H), 8.60 (d, *J* = 8.0 Hz, 1H), 7.64 (dt, *J* = 7.6, 1.0 Hz, 1H), 7.61 – 7.56 (m, 1H), 7.52 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.41 (t, *J* = 6.9 Hz, 1H), 7.31 (td, *J* = 7.7, 1.3 Hz, 1H), 0.29 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ = 140.3, 139.7, 138.7, 138.3, 137.8, 133.2, 129.4, 127.7, 125.9, 121.9, 119.8, 119.3, 105.6, 94.5, 91.8, 0.05.

((9-(1,5-bis(9,9-dibutyl-9H-fluoren-2-yl)penta-1,4-diyn-3-ylidene)-9H-fluoren-2-yl)ethynyl) trimethylsilane (7). In a Schlenk tube, to a mixture of ((9-(dibromomethylene)-9H-fluoren-2-yl)ethynyl)trimethylsilane **5** (0.5 g, 1.15 mmol, 1 equiv), 9,9-dibutyl-2-ethynyl-9H-fluorene **6** (1.0 g, 3.47 mmol, 3 equiv), Pd(PPh₃)₂Cl₂ (4.9 mg, 0.007 mmol, 0.6% equiv) and CuI (1.32 mg, 0.007 mmol, 0.6% equiv) were successively added DMF (14 mL), ⁱPr₂NH (14 mL) and under argon. The system was degassed by freeze-pump-thaw twice and heated for 2 days at 95 °C. After evaporation of volatiles, the residue was further purified by chromatography (heptane), and intermediate **7** was obtained as an orange powder (0.7 g,

69%). ^1H NMR (400 MHz, CDCl_3) δ = 9.14 (d, J = 1.3 Hz, 1H), 8.94 – 8.84 (m, 1H), 7.90 (dd, J = 8.0, 1.4 Hz, 1H), 7.83 – 7.73 (m, 8H), 7.70 (d, J = 7.8 Hz, 1H), 7.61 – 7.56 (m, 1H), 7.47 – 7.36 (m, 8H), 2.16 – 1.98 (m, 8H), 1.15 (m, 8H), 0.72 (q, J = 7.3 Hz, 20H), 0.37 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ = 151.3, 151.2, 151.1, 143.8, 142.5, 140.4, 140.3, 140.1, 139.6, 138.1, 137.6, 132.9, 130.9, 130.9, 129.5, 129.4, 127.9, 127.1, 127.0, 126.5, 126.4, 125.6, 123.0, 122.0, 120.9, 120.3, 120.1, 120.1, 119.9, 119.5, 106.1, 102.7, 100.1, 99.7, 94.1, 89.5, 89.3, 55.3, 55.2, 54.9, 40.3, 40.2, 31.9, 29.0, 29.1, 26.00, 23.1, 22.8, 14.2, 13.9, 0.3.

Dendron A-D: **2,2'-(3-(2-ethynyl-9H-fluoren-9-ylidene)penta-1,4-diyne-1,5-diyl)bis(9,9-dibutyl-9H-fluorene) (1).** Intermediate **7** (200 mg, 0.23 mmol, 1 equiv) was added into a mixture of CH_2Cl_2 (18 mL), MeOH (6 mL), THF (6 mL), together with K_2CO_3 (94 mg, 0.68 mmol, 3 equiv). The mixture was stirred overnight at room temperature. After being evaporated, residue was further purified by chromatography using heptane/ CH_2Cl_2 (4:1) as an eluent system, getting desired **Dendron A-D (1)** as an orange powder (150 mg; 82% yield). ^1H NMR (400 MHz, CDCl_3): δ = 9.17 (s, 1H), 8.86 (d, J = 7.5 Hz, 1H), 7.91 – 7.65 (m, 10H), 7.59 (d, J = 7.8 Hz, 1H), 7.48 – 7.32 (m, 8H), 3.22 (s, 1H), 2.08 (dq, J = 10.7, 5.4 Hz, 8H, $\text{CH}_2\text{-Bu}$), 1.23 – 1.07 (m, J = 7.2 Hz, 8H, $\text{CH}_2\text{-Bu}$), 0.81 – 0.55 (m, 20H, CH_2 & $\text{CH}_3\text{-Bu}$). ^{13}C NMR (100 MHz, CDCl_3): δ = 151.3, 151.2, 151.1, 143.5, 142.6, 142.5, 140.4, 140.3, 139.5, 138.1, 137.6, 133.0, 131.2, 130.9, 129.5, 129.5, 128.0, 127.9, 127.1, 127.0, 126.4, 126.1, 125.6, 123.0, 120.9, 120.8, 120.3, 120.1, 119.9, 119.5, 102.9, 100.0, 99.8, 89.3, 89.2, 84.6, 55.3, 55.3, 40.3, 40.2, 29.8, 26.0, 23.2, 23.1, 14.2, 13.9. HRMS-ESI (m/z): for $\text{C}_{62}\text{H}_{58}$: m/z = 802.456 $[\text{M}]^+$ (calcd: 802.4533). Anal. Calcd. (%) for $\text{C}_{62}\text{H}_{58}$: C, 92.72; H, 7.28. Found: C, 92.25; H, 7.57.

Phthalocyanine dendrimer ZnPc-C2 (1). In a Schlenk tube, to a mixture of zinc tetraiodophthalocyanine complex **4IZnPc** (10 mg, 0.97 mmol, 1 equiv), **Dendron 1** (47 mg, 5.9 mmol, 6 equiv), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (4.2 mg, 6×10^{-3} mmol, 6% equiv) and CuI (1.14 mg, 6×10^{-3} mmol, 6% equiv) were added THF (4 mL) and NEt_3 (4 mL) under argon. Then, the system was degassed by freeze-pump-thaw twice and stirred overnight at room temperature. After being evaporated, the suspension was poured into cold methanol. The dark green precipitate was then filtered off and washed with hot methanol. The crude product was purified by column chromatography on silica gel using heptane/THF (9:1) as eluent. Desired compound

ZnPc-C2 was obtained as a green solid (24 mg, 65% yield). ^1H NMR (400 MHz, $\text{THF-}d_8$) δ = 9.54 -8.07 (m, 12H, Pc), 8.09 – 7.57 (m, 42H), 7.54 – 6.87 (m, 42H), 2.10 (m, 32H, $\text{CH}_2\text{-Bu}$), 1.24 – 0.97 (m, 32H, $\text{CH}_2\text{-Bu}$), 0.85 – 0.41 (m, (32+48H), CH_2 & $\text{CH}_3\text{-Bu}$). **Dendrimer ZnPc-C2** is not soluble enough for trying a ^{13}C NMR. HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ ($\text{C}_{280}\text{H}_{241}\text{N}_8\text{Zn}$): m/z = 3778.842 (calcd: 3778.8390).

4.3. 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 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 $A_{\lambda_{\text{ex}}} < 0.1$ to minimize internal absorption.

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