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New Luminescent Extended Linear Dimer based on *meso*-Tetrafluorenylporphyrins

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ABSTRACT

A series of porphyrin monomers bearing four *n*-butyl substituted fluorenyl donor groups is presented; successively, intermediate compounds **1** (TMS protected), **2** (possessing an acetylene group) and corresponding zinc complex **3** have been synthesized. Starting from these building blocks, new extended **Dimer,** with in totally 9 fluorenyl groups, has been obtained and fully characterized. For the first time two highly luminescent tetrafluorenylporphyrin units (**TFP**) are connected to form a linear geometry and in addition, a rigid 2,7-fluorenyl linker was selected to connect these building blocks. The luminescence properties were compared with **TFP** monomer, dimer and trimer described earlier by our group.

Keywords: Porphyrin * fluorenyl * fluorescence * energy transfer * dimer*

1. Introduction

Porphyrins are well known as light absorber in photosynthesis: chlorophyll, using very elaborate light harvesting systems to capture dilute sunlight and funnel this energy to the reaction center through rapid and efficient transfer processes.[1] Based on great interest in understanding porphyrin photophysical properties, chemists have designed amount of

synthetic porphyrins and their complexes in different application fields: light-emitting diodes,[2] artificial photosynthetic systems,[3] and organic frameworks.[4] In particular, for all the applications mentioned, enhancing the absorption of porphyrins is also very important as well as the emission. These decades, Many chemists have prepared some polymers,[5] oligomers[6] and some porphyrin assemblies,[7a-e] by taking porphyrin unit as light-harvesting group. One of the first examples, in 1976, was the synthesis of diporphyrins and triporphyrins bridged by an ester bond.[7f] Later in 1983, porphyrins connected by flexible ether bond were used for light collecting.[7g] Few years later,; Therien published porphyrin dimers and trimers linked at *meso* position by two rigid triple bonds.[7h] Assemblies in which the porphyrins are directly connected by a single bond, at the *meso* positions, have been prepared by Smith's group.[7i] Later, the synthesis of dimers and trimers linked by ethynyl bond at positions like *meso-meso* were proposed.[7f]

Previously in our group, we have reported the synthesis of a porphyrin monomer possessing four fluorenyl arms (**TFP**).[8a-b] Surprisingly, **TFP** exhibited a remarkably high quantum yield (24%), compared to the reference tetraphenylporphyrin (**TPP**) demonstrating the capacity of the fluorenyl units to enhance quantum yields.[8c-e] Then, to exploite this capacity, a series of porphyrin dendrimers bearing fluorenyl dendrons was prepared.[9] In more details, we synthesized two series of substituted *meso*-porphyrin dendrimers with terminal fluorenyl arms, taking **TPP** as dendrimers' core: (i) non-conjugated family with ether group[9a-c] and recently (ii) conjugated one with alkynyl bridge.[9d-e]

Recently, assemblies of fluorenyl-porphyrins linked by rigid alkyne-aryl bond were reported by our group.[10] The synthesis of smaller systems possessing 6 fluorenyl arms like dimers **AB** were synthesised successfully,[10a] then we synthesized longer trimers like **ACA** substituted by eight fluorenyls units in the *meso* position (see Figure 1A).[10b] The optical properties for dimer and trimer were studied,[11] encouraged by these results, we will now investigate a conjugated linear dimer bridged by a supplementary fluorenyl unit (Figure 1B).

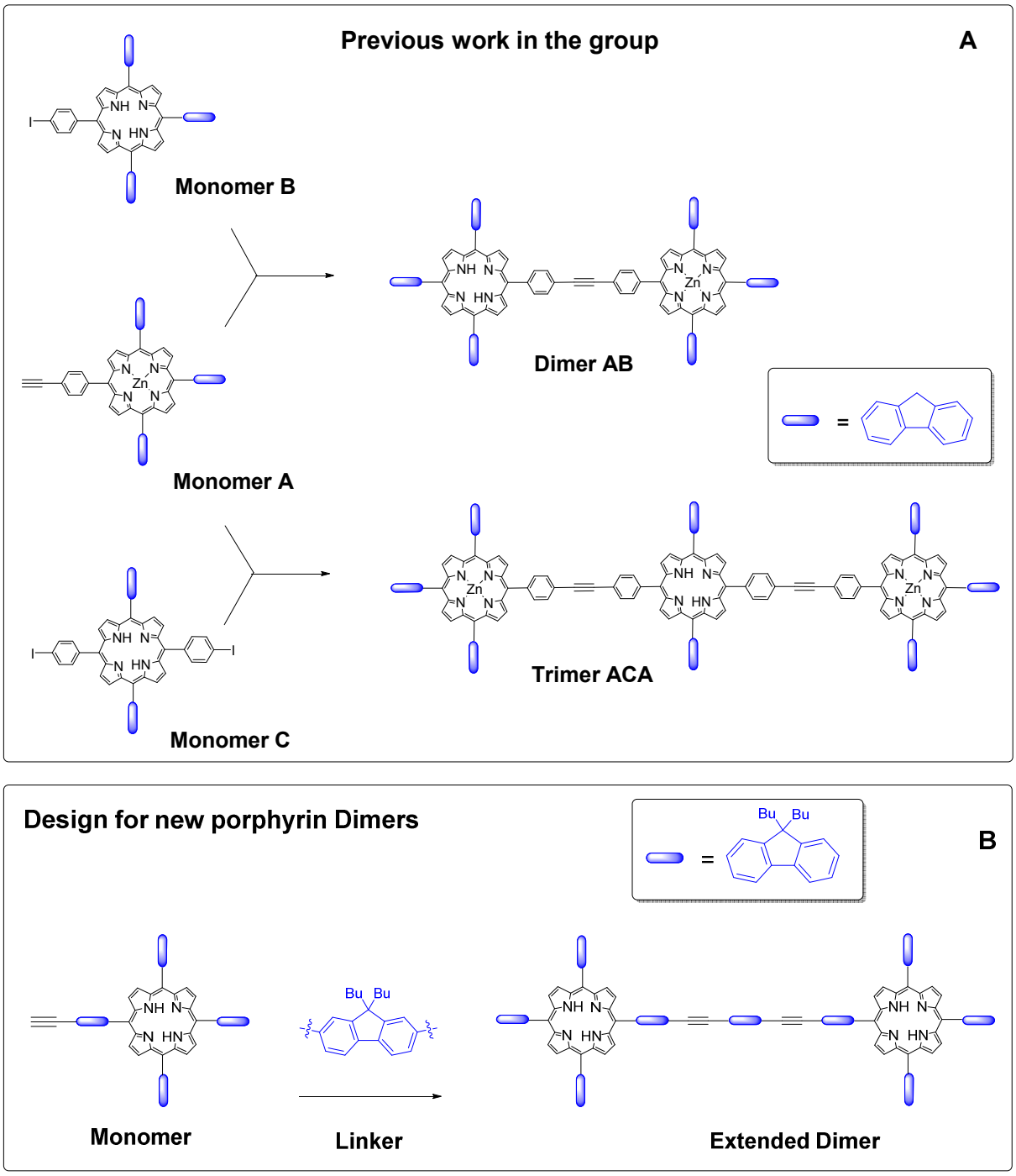


Figure 1. Previous work (A) and new design (B) for porphyrin Extended Dimer.

For the design of this new molecule, we chose efficient mono substituted TFP-core, expecting to keep high quantum yield as parent **TFP**.[8] This assembly will present three advantages: (i) more fluorenyls as light absorbers can be inserted in this dimer; (ii) the possibility of byproducts is decreased, because this coupling will be done by using only one type of monomer; (iii) to gain in solubility, we propose to add *n*-butyl chains on all fluorenyl

units. For the new dimer, 2,7-fluorenyl linker is chosen to form linear conjugated conformation with in totally 9 substituted fluorenyls: one bridged and 8 cored fluorenyls (see Figure 2).

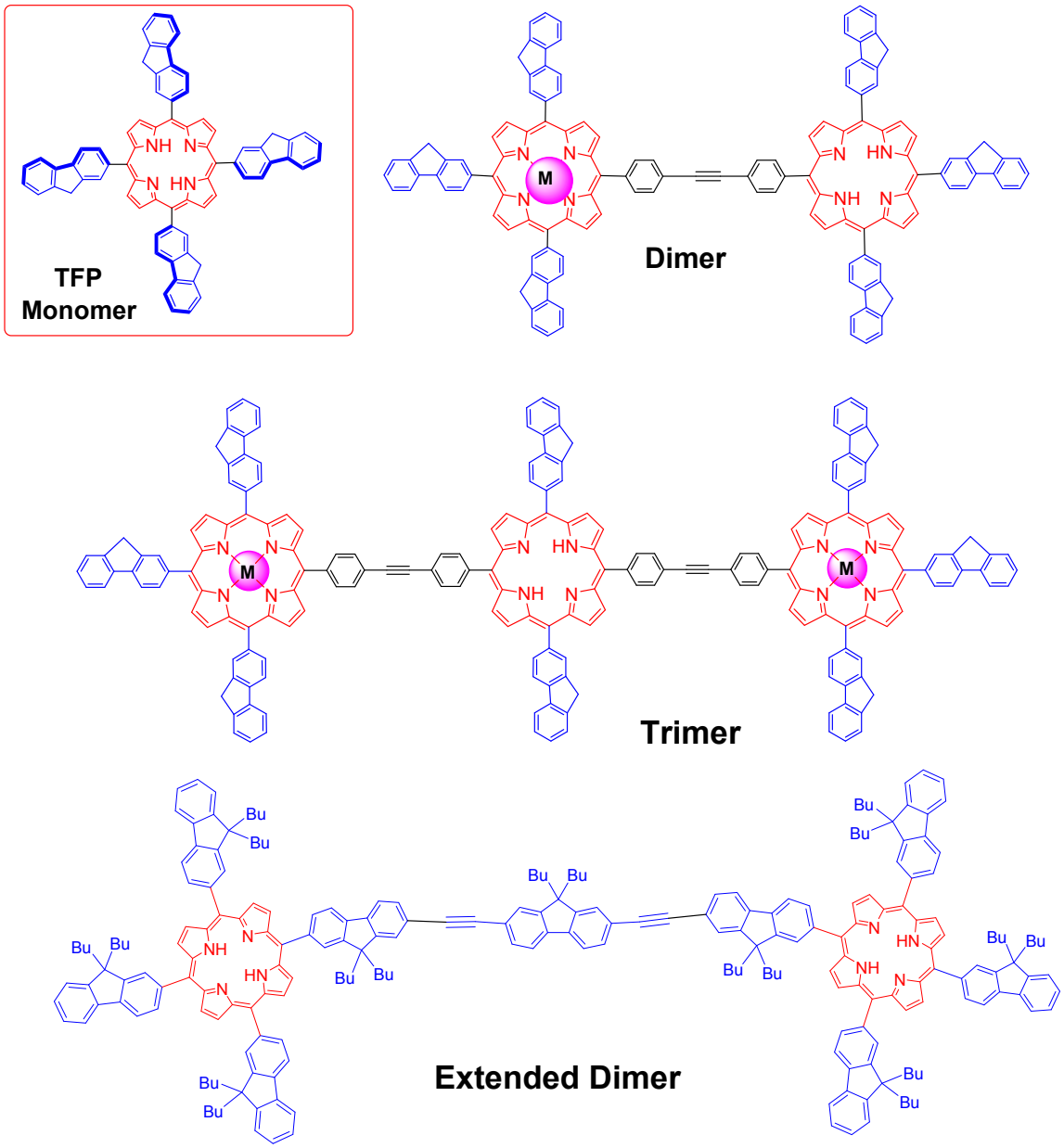


Figure 2. Monomer **TFP**, **Dimer**, **Trimer** and target extended **Dimer**.

Preliminary photophysical results are reported; For new dimer, eigth fluorenyl antennas are linked by direct *meso* connection to the porphyrin macrocycles and an extra fluorenyl unit is used as a bridge. These results are compared to monomer **TFP**,[8c-e] to porphyrin dimer[10a] and trimer[10b] in order to better understand the effect on luminescence when the system is elongated. The spectroscopic properties will be discussed from absorption and fluorescence

spectra, and relative quantum yield will be presented.

2. Results and discussion

2.1. Synthesis

2.1.1. Objectives - The aim of this work consists in the synthesis of an extended porphyrin dimer composed of only one type of porphyrin: substituted at three positions by *meso* fluorenyl units and a fourth one possessing an extra acetylenic group for future linkage by a central **fluorenyl** bridge. The synthesis is based on the coupling of two metallized **A_3B** porphyrins.

First, we will describe the synthesis of the intermediate porphyrins **Monomer** and **Zn-Monomer** possessing one anchoring point. In a second time, previous intermediate porphyrins are connected to obtain the dimer zinc complex porphyrins and finally by dematallation : free desired **Dimer** will be obtained.

It should be noted that in the conditions used, the non-substituted methylene in the fluorenyl unit is stable but alkyl chains have been introduced on the position-9 of this unit to increase the solubility,[12] in this work we will only considere the soluble substituted compounds.

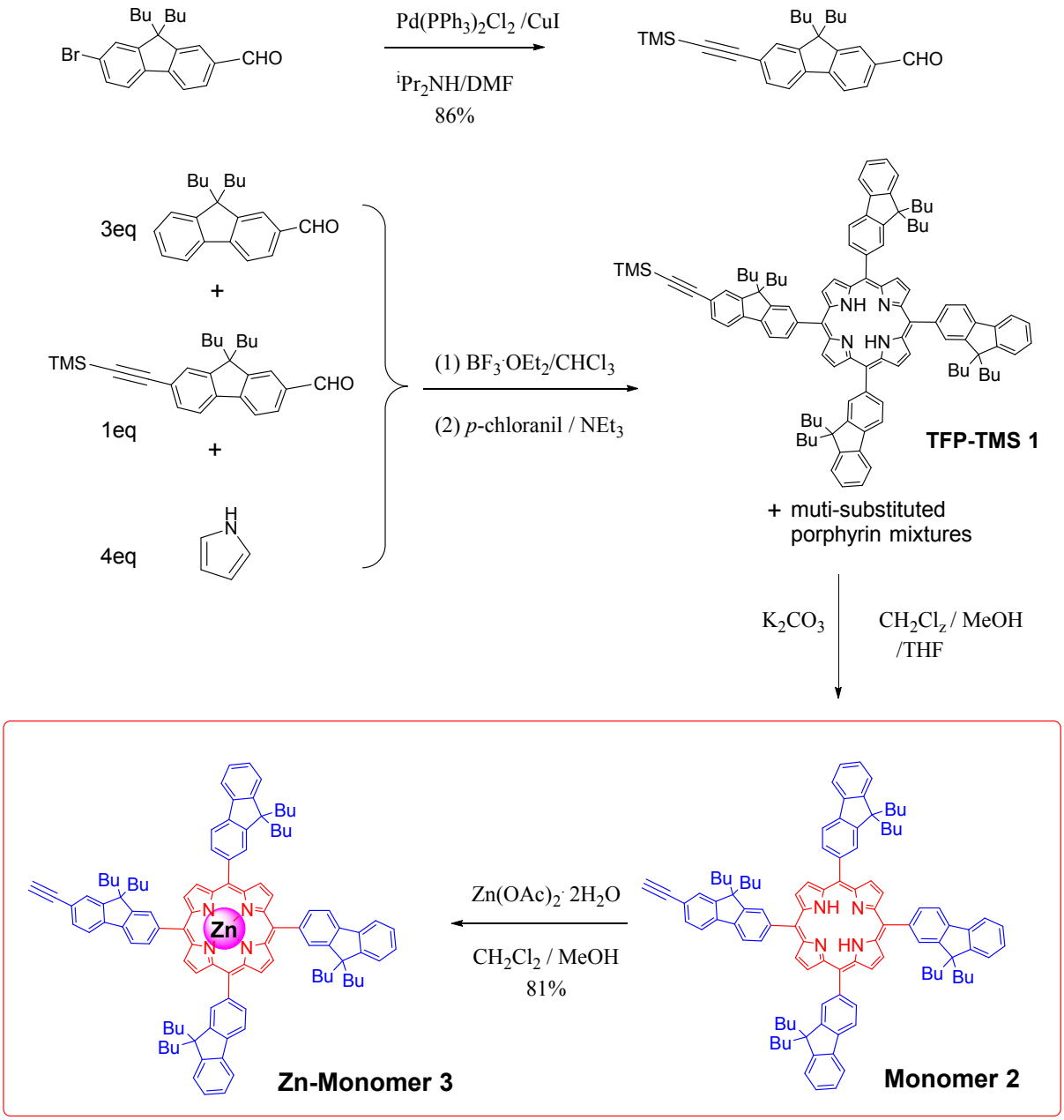
2.1.2. Monomer formation **-** Nowadays, two methods are the most used to synthesize porphyrin core: Adler-Longo[13a-b] and Lindsey,[13c] which are both efficient for synthesizing porphyrins substituted at the *meso* position. However, we noticed that our target porphyrins could be obtained easily under Lindsey conditions; the synthetic method used for porphyrin monomers is described in Scheme 1.

Consequently, to form the **A_3B**-type asymmetric porphyrin named **TFP-TMS (1)**, we adopted Lindsey conditions: (1) In the first step, starting materials were added in stoichiometric ratio of 3 : 1 : 4, and dissolved in distilled $CHCl_3$; After degassing the system with argon for 30 min, Lewis acid $BF_3{\cdot}OEt_2$ was injected to start the reaction and the mixture was stirred in dark for 3 h, under argon protection. (2) In the second step, oxidant *p*-chloranil

was added to quench the cyclization of porphyrinogen, the system was refluxing for another 2 h without argon protection. After cooling to room temperature, controlled amount of base (NEt_3) was injected to neutralize the protonated porphyrin. Chromatography had been tried to purify the product, but unfortunately, porphyrin mixtures were collected simultaneously because of their similar polarities, showing 68% yield as red powders.

Subsequently, deprotection of TMS was achieved directly in a mixture of CH_2Cl_2 and MeOH using excess of K_2CO_3, and then to dissolve all the porphyrins, controlled amount of THF was added. The reaction mixture was heated at 45 ^oC for 30 h and followed by TLC monitoring. Then chromatography was used to isolate free **Monomer (2)**: different eluents were tried, showing that a mixture of heptane and THF (4 : 1) could separate every component by TLC. Lower polar eluent (heptane : THF = 10 : 1) was adopted in column chromatography, giving pure mono-substituted product **Monomer 2** as red powder (15% yield for two steps).

We have to notice that, for the previous porphyrin mixtures (before deprotection of TMS), separation could not be possible by using this eluent (heptane : THF = 4 : 1) on TLC. Otherwise, during Sonogashira catalytically coupling,[14] to avoid copper ion insertion, metallization was done in advance to protect the heart of porphyrin by introducing zinc ion. in In a mixture of solvents (CH_2Cl_2 /MeOH), zinc salt: $Zn(OAc)_2$ will react with **Monomer** at 45 ^oC overnight, and after purification by precipitation (diethyl ether) , we could obtain 81% yield of corresponding **Zn-Monomer** (**3**) as a purple powder.

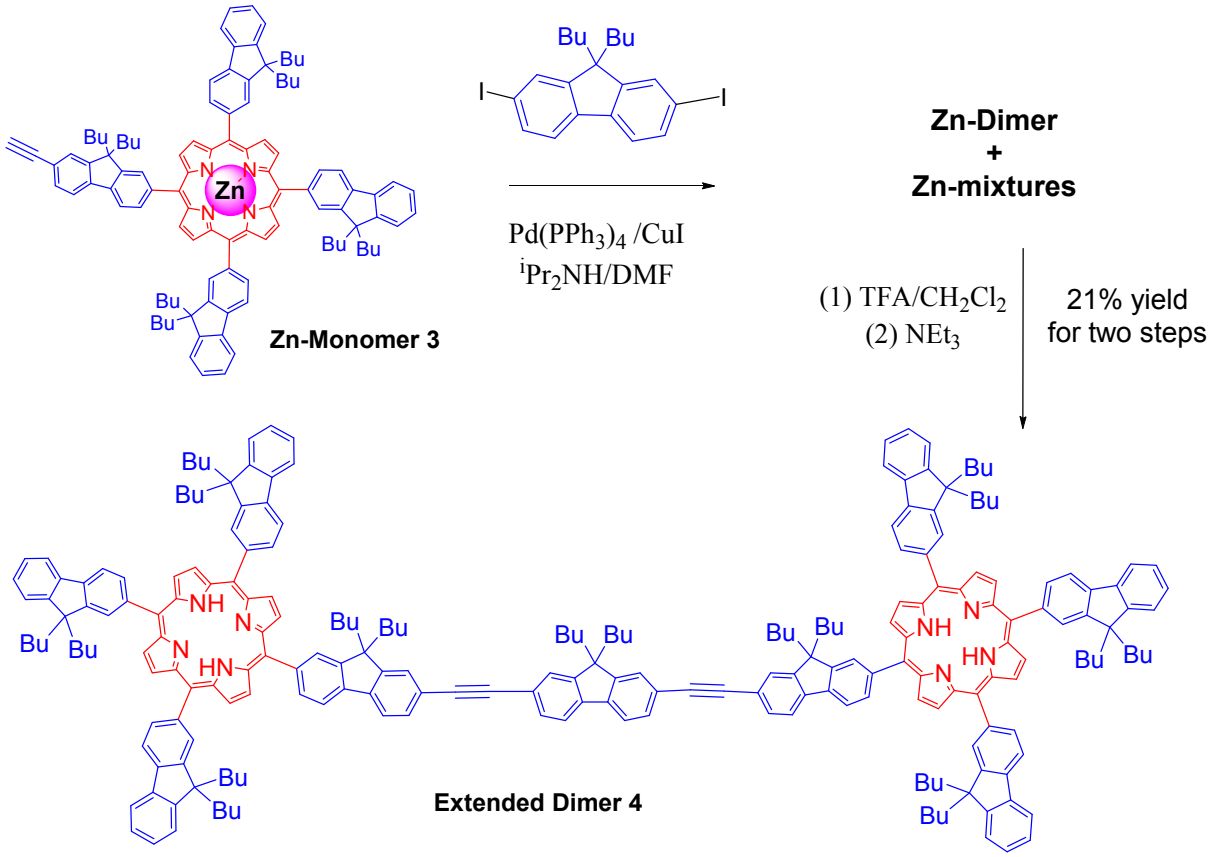


Scheme 1. Synthesis of new $\mathbf{A_3B}$-type asymmetric porphyrins: **Monomer 2** and **Zn-Monomer 3**.

2.1.3. Dimer formation - The optimized synthetic method to obtain porphyrin dimer is described in Scheme 2. By considering the large rigid building block: **Zn-Monomer**, more active catalysts $Pd(PPh_3)_4$/CuI were used in the Sonogashira coupling,[14] and the proportion of solvents DMF and $^{i}Pr_2NH$ was chosen as 10:1 to increase the solubility of starting materials and products. The reaction time and temperature were optimized: so heating the reaction for 70 h at 140 ^{o}C was finally adopted. After reaction, a porphyrin mixture was obtained: starting material, mono-substituted byproduct, homo-coupling byproduct and target

product, etc. Likewise, Zn porphyrin derivatives had the same difficulties to be separated because of their similar polarities.

Then, demetallation was done in two steps: (1) an excess of TFA (Trifluoroacetic Acid) was added drop wise in a CH_2Cl_2 solution of a Zn complexes mixture, showing the color of solution changing from red to green gradually. The formation of protonated porphyrins was observed in UV-visible absorption spectrum. We kept the protonation reaction stirring at room temperature overnight to be sure all the porphyrins are demetallized. (2) Then controlled amount of NEt_3 was added to neutralize the protonated porphyrin derivatives, and the color of solution changed progressively from green to red-brown. After 1 h of neutralization, CH_2Cl_2 was evaporated under reduced pressure, and enough MeOH was added subsequently to precipitate all the neutral porphyrin derivatives. We filtered this MeOH solution and did further purification of the obtained residue by column chromatography using as eluent a mixture of heptane and THF (4 : 1). We could finally obtain desired free dimeric compound **4** as a red powder, with a yield of 21%.



Scheme 2. Synthesis of new extended **Dimer 4**.

2.2. NMR studies

The **^{1}H-NMR** signals obtained in deuterated chloroform for porphyrins intermediates **2** and **3** and free **Dimer 4**, carried out at room temperature, are fine and well resolved.

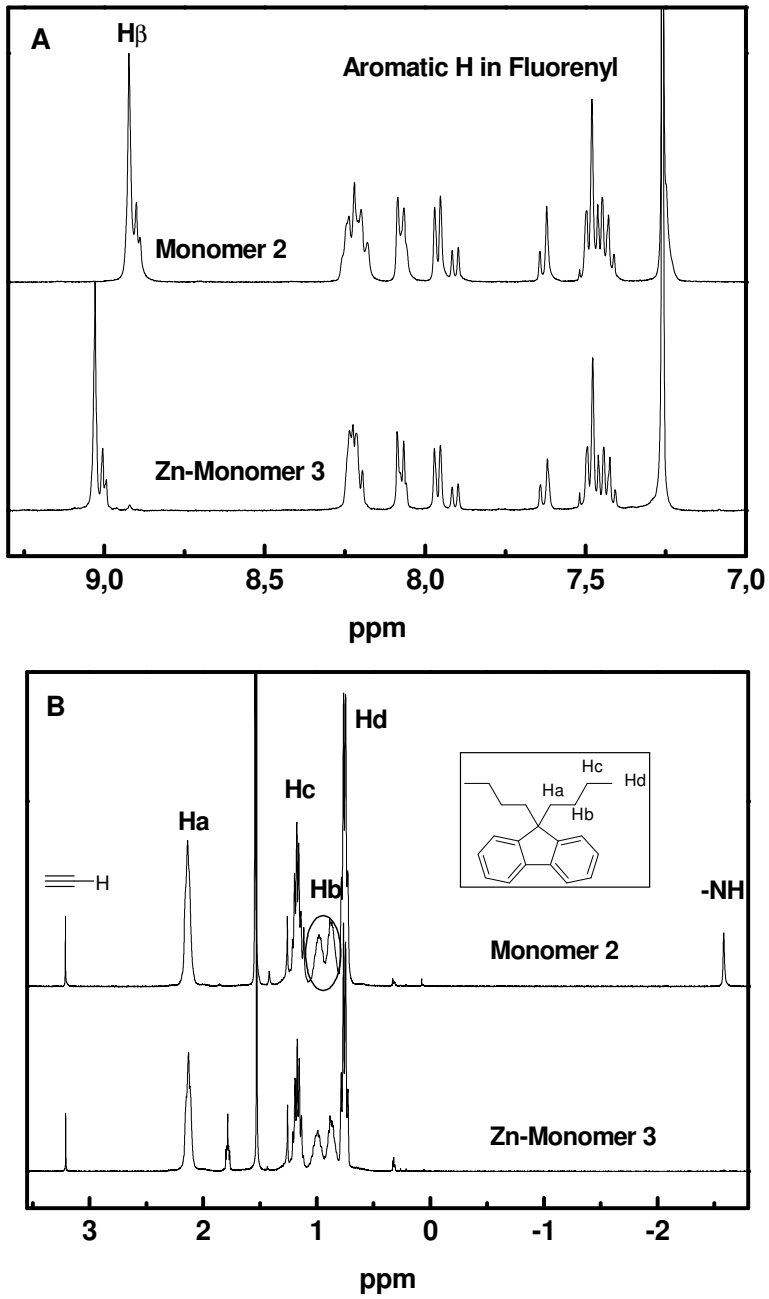


Figure 3. Comparison of ^{1}H NMR spectra of intermediates: **Monomer 2** and **Zn-Monomer 3**

*^{1}H NMR spectra of **Monomer 2** and **Zn-Monomer 3-*** Figure 3 exhibits full ^{1}H NMR spectra of these porphyrin intermediates in two parts (A: 9.5-7 ppm and B: 3.5-(-3.0) ppm) in $CDCl_3$. For free **Monomer 2** we observe: (i) a large peak corresponding to eight protons of porphyrin ring Hβ located around 9 ppm; (ii) many peaks corresponding to twenty-seven protons, around 8.3-7.4 ppm, are assigned to aromatic protons of fluorenyl groups; (iii) a peak for the alkynyl proton lies at 3.21 ppm; (iv) many peaks for *n*-butyl protons $H_{a,b,c,d}$ could be identified very well from 2.2 to 0.7 ppm, particularly sixteen protons of H_c are separated into two broad peaks with the same integrations (8/peak); (v) a peak at -2.58 ppm, for two -NH protons in the porphyrin heart.

After the Zn ion insertion, corresponding **Zn-Monomer 3** still keeps same peaks and same integrations of protons as free **Monomer**: peaks for aromatic protons in fluorenyl, alkynyl protons and *n*-butyl protons. We can notice that **Zn-Monomer** presents a slight shift to lower field for the peak for Hβ of porphyrin ring. Around -3 ppm, the two protons carried by the nitrogen atoms of the porphyrin-free base are not observed because of zinc chelation in porphyrin ring.

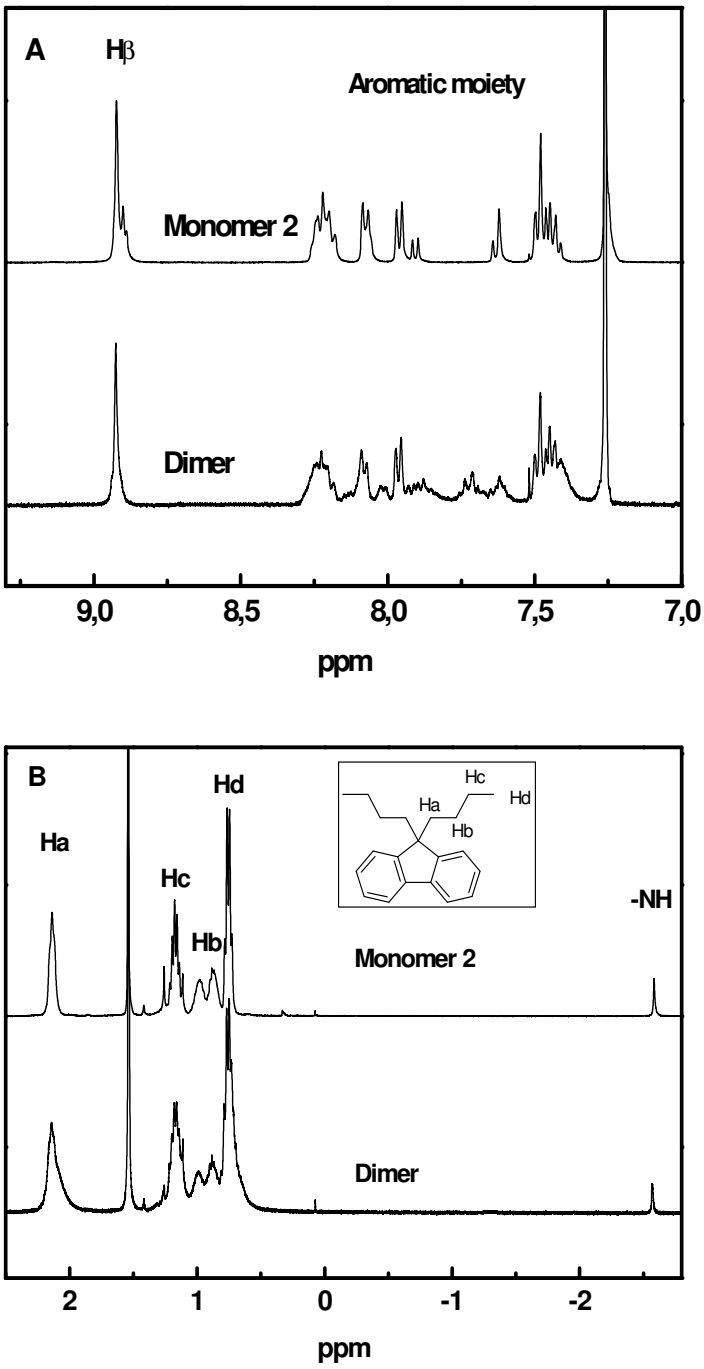


Figure 4. Comparison of ^{1}H NMR spectra of precursor **Monomer 2** and new **Dimer 4**.

^{1}H-NMR spectra of ***Dimer 4-*** Figure 4 shows ^{1}H NMR spectra of free **Dimer** compared to free-based **Monomer** precursor. In Figure 4.A, the peaks for pyrrolic protons of these two compounds are located around 8.92 ppm; the aromatic fluorenyl protons peaks mainly distribute from 8.3 to 7.4 ppm. Some multiplets of **Dimer** are obviously similar to parent

Monomer but with slight differences in integration. For parent **Monomer 2**, the peak for the alkynyl proton lies at 3.21 ppm, and for **Dimer** this peak disappears. In Figure 4.B, the signals of *n*-butyl protons and -NH protons in high field could be very well identified and the peaks for **Dimer** correspond to these of **Monomer**.

2.3. Optical properties

UV-visible absorption and photoluminescence spectroscopy measurements for porphyrin **Dimer** in toluene (HPLC) were performed at room temperature, as well as for **Monomer** as reference, on Edinburg FS920 Fluorimeter (Xe900) and BIO-TEK instrument UVIKON XL spectrometer at room temperature, respectively. Their relative optical data are summarized in Table 1.

2.3.1 Absorption and Emission Properties - Normalized absorption spectra of free **Monomer 2** and **Dimer 4** are shown in details, in Figure 5. These compounds present two intrinsic absorption regions of porphyrin: Soret-band located at 428 nm and four Q-bands distributed from 519 to 653 nm. From **2** to **4**, no shift is observed for the Soret-band, but for Q-bands, the last one presents a small red shift compared to **Monomer 2**. After normalizing at Soret-band, **Dimer** presents slightly more intense Q-bands absorption compared to **Monomer**, especially for the Q band at 653 nm.

For these compounds, measurements at different concentrations were performed; a more concentrated solution is used to display the absorption and a less concentrated for the emission spectra. All the dilute toluene solutions were prepared with similar Soret-band intensity (near to 0.1 on UV-visible spectrometer), while measuring, their emission spectra also exhibited similar intensity at Q(0,1) peaks, therefore, the emission spectra of **2** and **4** are also summarized at normalizing the intensities of Q(0,1). In Figure 5, the emission peaks Q(0,0) present similar change tendency as Qx(0,0) at 653 nm, and from **2** to **4**, the intensities of Q(0,0) increase obviously. It suggests that, with the numbers of terminal porphyrin increasing, Q(0,0) of **Dimer** becomes the predominant red-lighting emission.

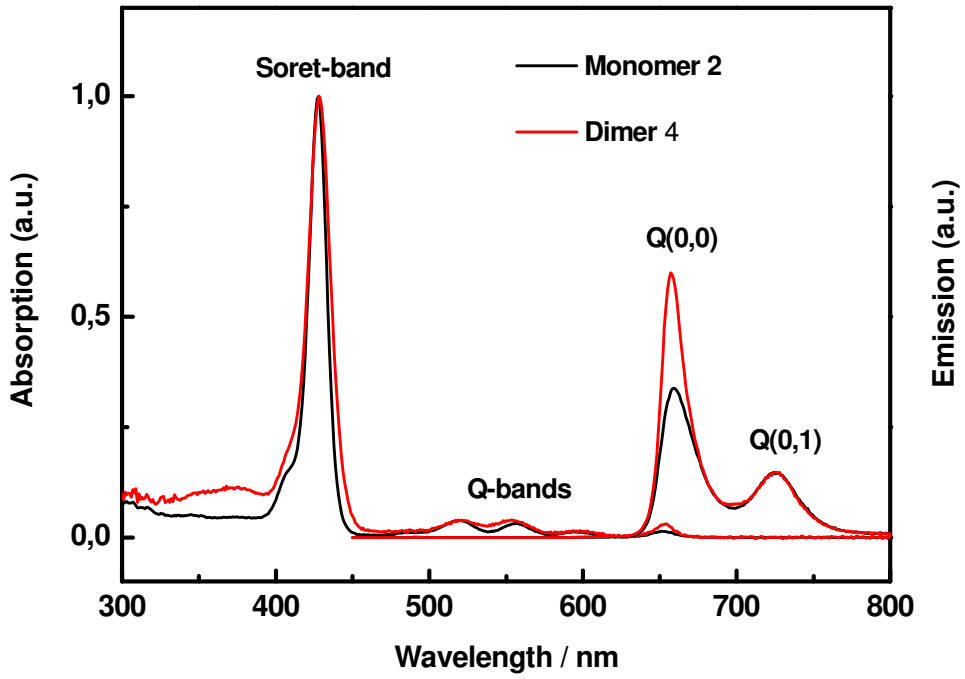


Figure 5. UV-visible absorption and emission spectra of **Monomer** precursor **2** and **Dimer 4**.

2.3.2 Quantum yield - The fluorescence quantum yields of these compounds were listed in Table 1, taking **TPP** (Φ = 11% in toluene) as reference. Porphyrin **2** shows 20% quantum yield, the same as to parent **TFP-Bu** without one alkynyl unit. Similarly new **Dimer 4,** with two terminal porphyrins, shows about 20% quantum yield. This value is still higher than for shorter Dimer **5**, studied earlier, which shows 17% quantum yield,[10a] suggesting that introducing an extended bridge is also an important factor for quantum yield. Therefore, along this line, it will encourage us in future, to design 2D or 3D expanded conjugated oligomers with terminal **TFP** porphyrin.

Table 1. Optical data of porphyrin Monomers, Dimers and **Trimer**.

		Absorption[a]		Emission		
	UV band	**Soret-band**	**Q-bands**	**Q(0,0)**	**Q(0,1)**	**Quantum yield[b] (%)**
TPP	-	419	514,548,590,649	652	719	11
TFP	272	426	519,557,593,649	661	725	24
TFP-Bu	≤ 300	427	519,555,596,652	659	725	20
Free Monomer 2	-	428	519,556,596,652	659	726	20
Free Dimer 5[10a]	268	426	521,557, 595, 650	657	720	17
Trimer[10b]	263	427	520,557, 594, 649	658,	724	13
New Dimer 4	**-**	**428**	**521,554,598,653**	**657**	**726**	**20**

[a]·Experiments were achieved in toluene (HPLC level) with the UV-visible absorption region from 287 to 800 nm and emission region from 450 to 800 nm.

[b]·Experiments for fluorescence quantum yields were achieved in toluene (HPLC level) using TPP (Φ =11%) as standard, by Soret-band excitation.

3. Conclusions and outlook

In summary, a series of intermediate porphyrins bearing *n*-butyl substituted fluorenyl donor groups is presented. Successively, intermediate compounds **1** (TMS protected), **2** (bearing four fluorenyl groups, with one possessing an acetylene group) and corresponding zinc complex **3** have been synthesized. Starting from these building blocks, new extended linear **Dimer 4**, bearing in totally nine fluorenyl groups in the architecture, was successfully obtained and characterized.

By considering this new extended **Dimer** with two **TFP** terminal units, we can observe that elongation of the bridge, shows important effect on the optical properties of the final dual porphyrin system. For this elongated **Dimer 4**, enhanced quantum yield is observed compared to shorter dimer **5** previously synthesized in the group (17 %). New free **Dimer 4**, exhibits a relatively high quantum yield (20 %) similar to precursor **Monomer 2** (20 %), but we have to

consider the larger absorptivity of this molecule, so this assembly of two porphyrins exhibit larger brightness than corresponding monomers.

Perspectives of this work may be to extend the bridge connecting the **TFP** porphyrins of the assembly to optimize the luminescence properties, and eventually extend this work to trimer or tetramers. Further studies are going on and optimization will be undertaken to increase efficiency.

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, DCM and $CHCl_3$ from CaH_2 and THF was distilled using sodium/benzophenone system. The other solvents used were of HPLC grade. Commercially available reagents were used without further purification unless otherwise stated. Pyrrole and 2-fluorenecarboxaldehyde were purchased from Aldrich and were used as received. References **TFP** = tetrafluorenylporphyrin, **TPP** = tetraphenylporphyrin.

^{1}H and ^{13}C NMR spectra were recorded on BRUKER Ascend 400 and 500 at 298K. 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. 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. *Steady-state fluorescence* measurements were performed at room temperature (R. T.) with dilute solutions (ca. 10^{-6}M) using an Edinburgh Instruments (FLS 920) spectrometer working in photon-counting mode, equipped with a calibrated quantum counter for excitation correction. Fluorescence quantum yields were measured using standard methods; **TPP** in DCM ($\Phi = 0.12$ at $\lambda_{ex} = 417$ nm) was used as a reference. The reported fluorescence quantum yields are

within ± 10%.

4.2. Synthesis of the Monomers

9,9-dibutyl-7-((trimethylsilyl)ethynyl)-fluorene-2-carbaldehyde. In a Schlenk tube, a mixture of prepared 7-bromo-9,9-dibutyl-9*H*-fluorene-2-carbaldehyde[9e] (2.07 g, 5.37 mmol, 1 eq), $Pd(PPh_3)_2Cl_2$ (23 mg, 0.032 mmol, 0.6% eq) and CuI (3 mg, 0.016 mmol, 0.3% eq) were dissolved in DMF (5 mL), $^iPr_2NH$ (5 mL) and ethynyltrimethylsilane (1.15 mL, 8.06 mmol, 1.5 eq) under argon, successively. The mixture was degassed by freeze-pump-thaw twice and heated for 2 days at 95 ^oC. After evaporation of the solvents, the residue was absorbed on silica and further purified by chromatography using heptane as eluant, and yellow white powder was obtained (1.86 g, 86% yield). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 10.06 (s, 1H), 7.87-7.85 (m, 2H), 7.82-7.80 (m, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 8 Hz, 1H), 7.47 (s, 1H), 2.07-1.94 (m, 4H), 1.11-1.02 (m, 4H), 0.65 (t, *J* = 8.0 Hz, 6H), 0.60-0.44 (m, 4H), 0.29 (s, 9H).

Porphyrin TFP-TMS 1. In a two-neck flask, a mixture of 9,9-dibutyl-fluorene-2-carbaldehyde (2.05 g, 6.71 mmol, 3 eq), 9,9-dibutyl-7-((trimethylsilyl)ethynyl)-fluorene-2-carbaldehyde (900 mg, 2.23 mmol, 1 eq) and pyrrole (0.62 mL, 8.94 mmol, 4 eq) were dissolved in dry chloroform (550 mL) under argon. After degassing the mixture with argon for 30 min, $BF_3{\cdot}OEt_2$ (0.2 mL) was injected and the reaction was stirred in dark for 3 h under argon at room temperature. Then oxidant *p*-chloranil (1.5 g) was added, and the reaction was heated at 60 ^oC for another 2 h without argon protection. After cooling the reaction to room temperature, NEt_3 (2 mL) was added to the mixture and then continue stirred for 10 min. After evaporation of the solvents, the residue was absorbed on silica and further purified by chromatography using the mixture (CH_2Cl_2 : heptane = 1 : 3) as eluant, and a porphyrin mixture was obtained as red powder (2.3 g, 68% yield).

Free Porphyrin Monomer 2. In a mixture solvents of CH_2Cl_2 (300 mL), MeOH (100 mL) and THF (60 mL), previous porphyrin mixture TFP-TMS (2.3 g, 1.52 mmol, 1 eq) was added

together with K_2CO_3 (840 mg, 6.08 mmol, 4 eq). The mixture was stirred at 45 ^oC for 30 h. After filtering excess of K_2CO_3, the residue was washed by CH_2Cl_2. After evaporation of the solvents, the residue was absorbed on silica and further purified by chromatography using a mixture of (heptane : THF = 10 : 1) as eluant, and pure target porphyrin **2** was obtained as a red powder (470 mg, 15% yield for two steps). ^1H NMR (400MHz, $CDCl_3$, ppm): δ 8.92-8.89 (m, 8H), 8.24-8.18 (m, 8H), 8.08-8.07 (m, 4H), 7.96 (d, *J* = 8.0 Hz, 3H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.64-7.62 (m, 2H), 7.52-7.41 (m, 9H), 3.21 (s, 1H), 2.14 (m, broad, 16H), 1.21-1.14 (m, 16H), 0.98 (m, broad, 8H), 0.88 (m, broad, 8H), 0.78-0.73 (m, 24H), -2.58 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 151.2, 149.5, 149.2, 141.8, 141.7, 141.0, 140.9, 140.7, 139.8, 133.8, 133.6, 131.5, 129.4, 127.4, 127.0, 126.7, 123.0, 120.8, 120.6, 120.4, 120.1, 118.3, 117.8, 84.8, 55.3, 40.3, 40.2, 26.3, 23.1, 14.0, 13.8. HRMS-ESI: *m/z* calcd for $C_{106}H_{111}N_4$: 1439.88033 $[M+H]^+$; found 1439.8804 and *m/z* calcd for $C_{106}H_{112}N_4$: 720.44380 $[M+2H]^{++}$; found 720.4438.

Porphyrin Zn-Monomer 3. Previously prepared free **Monomer 2** (270 mg, 0.19 mmol, 1 eq) and $Zn(OAc)_2{\cdot}2H_2O$ (123 mg, 0.75 mmol, 4 eq) were added into a mixture solvents of CH_2Cl_2 (90 mL) and MeOH (30 mL). The reaction was stirred overnight at 45 ^oC. After evaporating the solvents, the residue was farther purified by silica chromatography (heptane : CH_2Cl_2 = 1 : 1), collecting the desired **Zn-Monomer 3** as a red powder (228 mg, 81% yield). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 9.03-8.99 (m, 8H), 8.24-8.20 (m, 8H), 8.09-8.06 (m, 4H), 7.96 (d, *J* = 8.0 Hz, 3H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.64-7.62 (m, 2H), 7.52-7.41 (m, 9H), 3.21 (s, 1H), 2.13 (m, broad, 16H), 1.21-1.13 (m, 16H), 0.99 (m, broad, 8H), 0.88 (m, broad, 8H), 0.78-0.73 (m, 24H).

4.3. Synthesis of Porphyrin Dimers

Zn-Dimer. In a Schlenk tube, to a mixture of 9,9-dibutyl-2,7-diiodo-fluorene (13 mg, 0.024 mmol, 1 eq), previously prepared **Zn-Monomer** complex **3** (80 mg, 0.053 mmol, 2.2 eq), $Pd(PPh_3)_4$ (12 mg, 0.011 mmol, 45% eq) and CuI (2 mg, 0.011 mmol, 45% eq) was added successively DMF (10 mL) and $^iPr_2NH$ (1 mL) under argon. The system was degassed by

freeze-pump-thaw twice and heated at 140 ^{o}C for 70 h. After being evaporated, residue was farther purified by chromatography (heptane : THF = 4 : 1 to 2 : 1), and then porphyrin mixtures of Zn complexes were obtained as a red powder.

Free Dimer (4). In a flask, the previous obtained mixture, containing Zn complexes, was dissolved in CH_2Cl_2. A slight excess of TFA was added dropwise into the flask until the color of solution changes from red to green gradually. This protonation reaction was stirred at room temperature overnight. Then, base NEt_3 was added dropwise into the solution until the color changes from green to red-brown, and the neutralization was kept for another 1 h at room temperature. After evaporation of all the CH_2Cl_2 under reduced pressure, and leaving a minimum volume of solvents with high boiling temperature, then MeOH was added subsequently to precipitate all the porphyrin derivatives. A red residue was obtained after filtration of this MeOH solution. This red precipitate will be further purified by chromatography (heptane : THF = 4 : 1). After column chromatography, pure free **Dimer 4** was collected as red powder (16 mg, 21% yield from **Zn-Monomer**). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.93 (s, 8H), 8.25-8.19 (m, 11H), 8.15-8.07 (m, 6H), 8.01 (d, *J* = 8.0 Hz, 2H), 7.96 (d, *J* = 8.0 Hz, 5H), 7.93-7.83 (m, 6H), 7.76-7.67 (m, 5H), 7.65-7.56 (m, 4H), 7.52-7.39 (m, 21H), 2.14 (m, broad, 36H), 1.22-1.11 (m, 36H), 0.99-0.70 (m, 90H), -2.57 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 151.4, 151.2, 149.2, 141.0, 140.9, 140.7, 133.6, 131.0, 130.8, 129.4, 127.4, 127.3, 127.0, 126.1, 126.0, 123.1, 123.0, 120.9, 120.1, 119.9, 118.2, 117.8, 55.4, 55.3, 40.3, 29.7, 26.3, 26.0, 23.1, 14.1, 14.0, 13.9. HRMS-ESI: *m/z* calcd for $C_{233}H_{243}N_8$: 3152.92553 $[M+H]^+$; found 3152.9255 and *m/z* calcd for $C_{233}H_{244}N_8$: 1576.9664 $[M+2H]^+$; found 1576.9671. HRMS-MALDI: *m/z* calcd for $C_{233}H_{243}N_8$: 3152.92553 $[M+H]^+$; found 3152.925 and *m/z* calcd for $C_{466}H_{485}N_{16}$: 3154.94118 $[M_2+H]^{++}$; found 3154.945.

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