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Synthesis and characterization of new ferrocene, porphyrin and C_{60} triads, connected by triple bonds

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ABSTRACT

The 2,12 pyrrole positions of *meso*-tetraphenylporphyrin were functionalized through triple carbon–carbon bonds by ferrocene and C_{60} giving new electron donor-acceptor triads which have been characterized and studied by photophysical methods.

Introduction

Electron and energy transfer are important topics in the chemistry of biological and artificial systems and have been extensively studied over the past twenty years [1]. Photosynthesis in plants and bacteria is based on chemical reactions induced by the electron-transfer phenomena between natural tetrapyrrolic pigments, such as chlorophyls and related molecules, and quinones, both embedded in a protein matrix [2]. The entire process is not yet well understood and more information can be obtained by the use of synthetic models [3]. In this area, the difficulties of obtaining new useful models were slowly overcome applying methods based on the catalytic activity of palladium complexes [4]. The Suzuki and Sonogashira reactions have been used for building new porphyrin derivatives able to give charge separation (CS) processes under irradiation with high efficiency and long lifetime [5].

The discovery of fullerenes, new allotropic forms of carbon, has disclosed the possibility to explore the electron-transfer processes using, for example, C_{60} as the final destination of the negative charge in the synthetic models [6]. During our studies on the possibility to use molecular wires to connect to the beta-pyrrole positions of the porphyrins one C_{60} unit through the assembling of one or more triple bonds, we found that it was very convenient and important to have a large delocalization of the π electrons between the donor and the acceptor moieties of the models [7]. Anderson and coworkers reported similar models but with the ferrocene and C_{60} connected to the *meso*-positions of the porphyrin obtaining long-range charge separated states when photoexcited. The rates of long-range charge recombination in such compounds, are remarkably fast and not depending from the distance [6c].

Results and discussion

Recently we have reported the *beta* functionalization of H_2TPP by one or two ferrocene molecules in the 2 and 3 positions through ethynyl or phenylethynyl groups, applying a new approach of the Sonogashira reaction, never used before in the case of porphyrins [8].

Some other groups have recently reported on the synthesis and characterization of different tetraphenylporphyrins bearing ferrocene at *beta, meso* or 4-phenyl positions [9].

In this paper we report on the synthesis of four new triads, useful as a model for investigating the electron-transfer processes, connecting ferrocene and C_{60} to the 2,12 pyrrole positions of H_2TPP through ethynyl bonds.

In Figs. 1 and 2 the structures of compound **1** and **8** and their zinc complexes **2** and **9** are reported.

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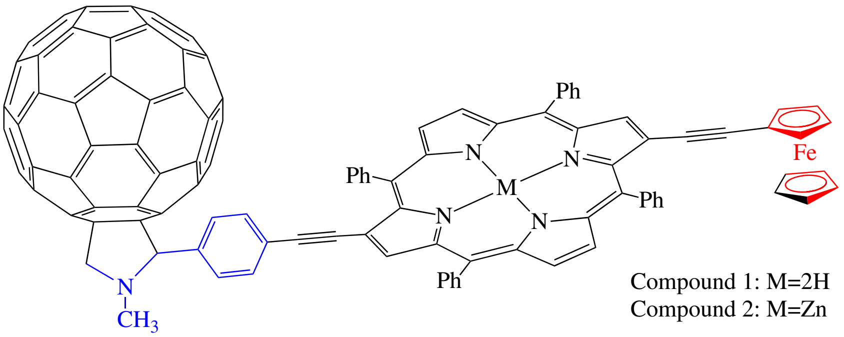


Compound 1: M=2H
Compound 2: M=Zn

Fig. 1. The structure of compounds **1** and **2**.

The synthetic pathways for obtaining the new porphyrin free bases are reported in Scheme 1.

The starting compound **3**, for the synthesis of the triads, the 2,12-dibromo-tetraphenylporphyrin, was obtained as reported in the literature [10]. The correct stereochemistry of compound **3** was recently elucidated by another group [11]. Ethynylferrocene was commercially available while phenylethynylferrocene was synthesized as reported in the literature [8].

The first step of the synthetic pathway involved the Sonogashira coupling of compound **3** with the 1.5 equivalent of the ethylene acetal derivative of 4-ethynylbenzaldehyde, **4** in 40% of yield after chromatographic purification. We found that the protection of the aldehyde function gives a better result in the coupling reaction, comparing with the simple 4-ethynylbenzaldehyde.

The following step was again a Sonogashira coupling between compound **5** and 2 equivalent of ethynylferrocene or phenylethynylferrocene giving, after hydrolysis of the dioxolane protective group, the intermediates **6** or **7** in 70% of yield. Finally these last compounds were used in the Prato and Maggini reaction [12] affording the final compounds **1** and **8** in 60–65 % of yield.

Looking at the positions of the Soret bands of compound **1** and H_2TPP, a red shift of 18 nm can be found. In a previous paper [8] we reported for the 2,3-diethynylferrocene-tetraphenylporphyrin, a Soret band red-shifted by 20 nm, a value close to that for compound **1** which shows the presence of two triple bonds connected on the 2 and 12 beta-positions of the macrocycle.

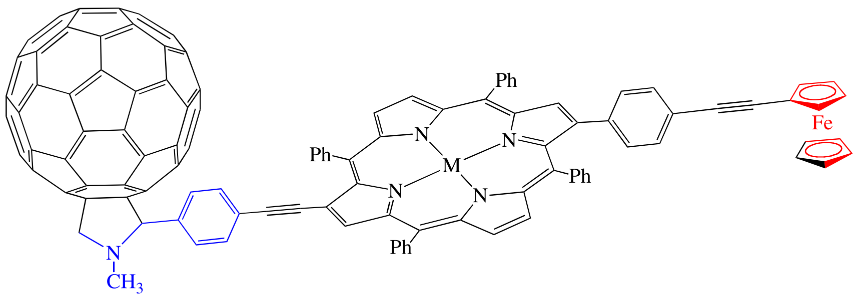
Compounds **1** and **8** were also converted to the zinc derivatives **2** and **9** by standard procedures. In Table 1 the UV–visible data of all the compounds are reported.

The ^{1}H NMR spectrum of triad **1**, (see ESI) shows a pattern with the typical signals at 2.74, 3.99, 4.77 and 4.65 ppm of the fulleropyrrolidine ring and two singlets centered at 4.25 and 4.36 ppm which can be assigned to the ferrocene residue [6]. The ^{1}H NMR spectra of triad **8** shows a different pattern, with the signals of the ferrocene splitted into three singlets at 4.70, 4.38 and 4.08 ppm (see ESI). This situation has been previously reported for similar compounds bearing an ethynylferrocene or an ethynylphenylferrocene on the *beta*-position of H_2TPP [8]. Fig. 3 shows the emission spectra of the triads **1** compared with the partial related reference compounds (i.e. H_2TPP-C_{60}, H_2TPP-Fc) in THF solutions [7,8].

The emission spectra of the reference compounds, i.e. H_2TPP is also reported. In Fig. 4 the structures of the related reference compounds free bases are also reported.

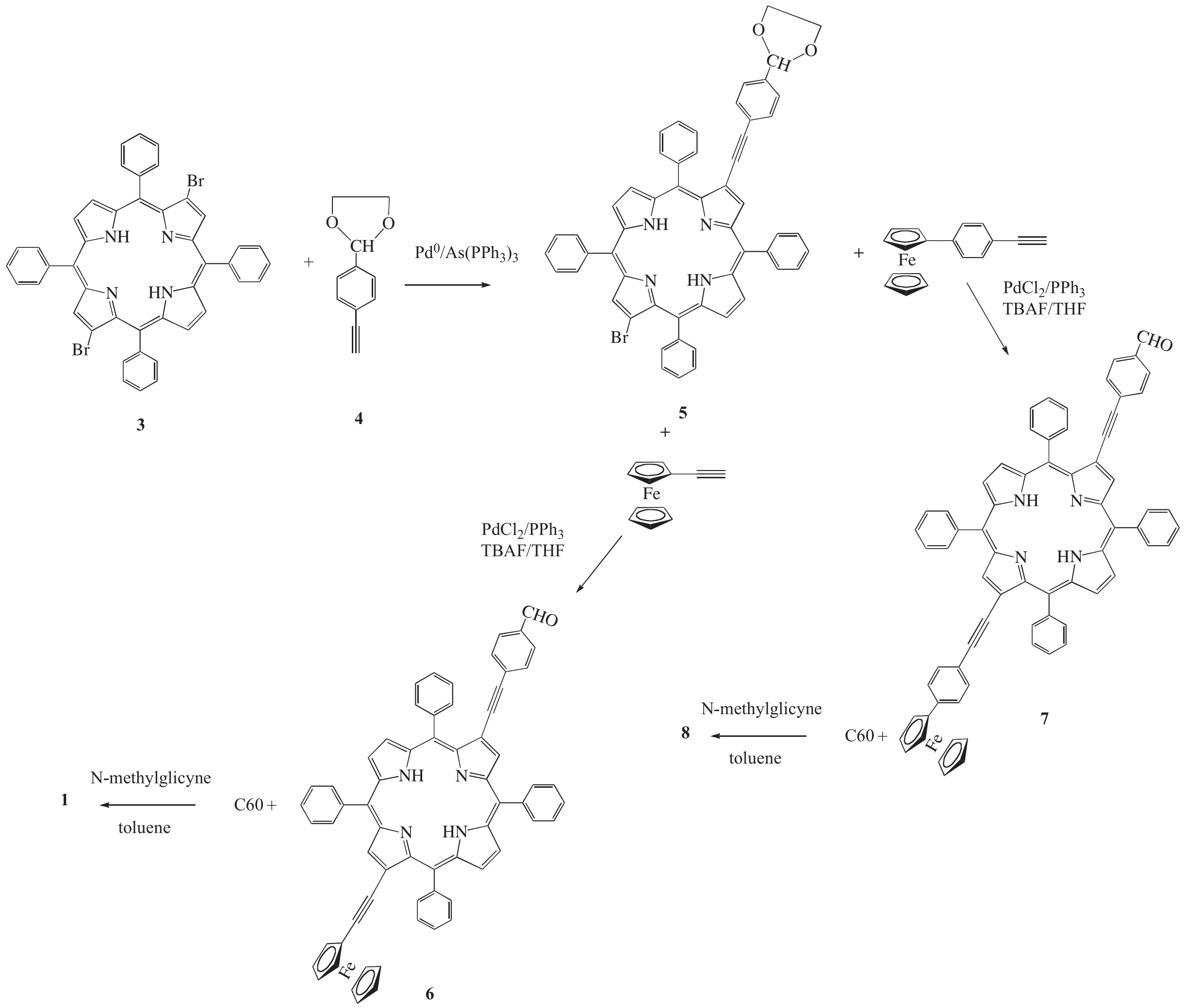
The excitation wavelength was $\lambda_{ex} = 430$ nm for all the compounds. The spectra are normalized by the optical density at excitation wavelength, so that they can be compared to each other and the PL intensity is an estimate of the relative quantum efficiency. As the most striking feature of the emission spectra, we note that the functionalization with either C_{60} or ferrocene, or with both groups, strongly decreases the emission intensity of the reference compounds. In our opinion, this fact can be due to a complete charge delocalization along the carbon–carbon bond that links the ethynylenephenylene subunit and the tetrapyrrole ring [6c].

In fact, the magnitude of the optical quantum efficiency is of the order of $\Phi \cong 10^{-3}$ for H_2TPP derivatives and $\Phi \cong 10^{-4}$ for ZnTPP derivatives (see ESI). However, the singlet excited-state nature and the spectral distribution of the emitted energy is not significantly altered. Specifically, the fluorescence spectra of both the related partial compounds and the triads greatly resemble those of the relative reference compounds, with two main bands in the range between 600 and 750 nm. The relative intensities of the two peaks are also substantially retained. On the other hand, a small red shift is observed as a result of the progressive degree of functionalization, mainly with the addition of ferrocene, up to 10 nm for the triad **1** and to 20 nm for the triad **2**. This behaviour is in agreement with the typical trend found for the polycyclic compounds when a



Compound 8: M=2H
Compound 9: M=Zn

Fig. 2. The structure of compounds **8** and **9**.



Scheme 1. Synthetic pathways for obtaining compounds **1** and **8.**

functionalization is performed with either electron-withdrawing and electron-donating groups [13].

Such spectral characteristics are also found in the emission spectra of the triads **8** and **9** (see ESI) but some small differences, yet meaningful, can be observed. A small red shift (i.e. ≈10 nm) can be observed in both the emission bands of all the compounds with an additional phenyl ring spacer. This fact can be reasonably attributed to their greater conjugation effect. The PL quenching effect produced by the addition of the ferrocene subunit is much weaker in this case than that observed in triads **1** and **2**. This observation is consistent with the greater distance from the porphyrin macrocycle and the lower effect of the additional phenyl ring as a conjugated spacer.

Table 1
UV–visible spectral data of all the new compounds in dichloromethane.

Porphyrin	Soret	Visible abs bands λ, nm($\varepsilon \times 10^{-4}$)			
1	434(14.10)	527(3.90)	580(0.65)	616(0.41)	670(0.51)
2	449(22.90)		574(2.34)	613(2.21)	
3	424(28.85)	520(1.78)	554(0.40)	596(0.48)	651(0.45)
5	430(17.09)	526(1.58)	561(0.43)	601(0.40)	659(0.37)
6	431(19.15)	526(1.86)	567(0.83)	603(0.77)	659(0.44)
7	433(15.40)	530(1.88)	573(1.06)	608(0.78)	664(0.39)
8	435(16.85)	532(2.35)	574(1.61)	609(1.01)	666(0.48)
9	438(15.82)		570(0.57)	612(0.41)	

Finally, as a common characteristic of the two series of compounds, it should be noted that the same spectral profile was obtained at concentration from 10^{-6} to 10^{-3} M in THF, which

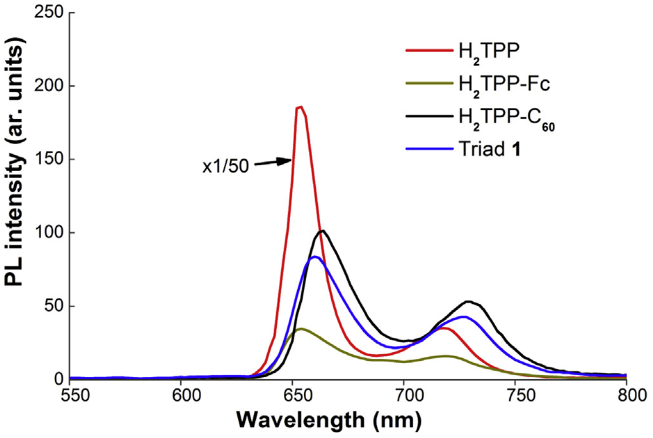
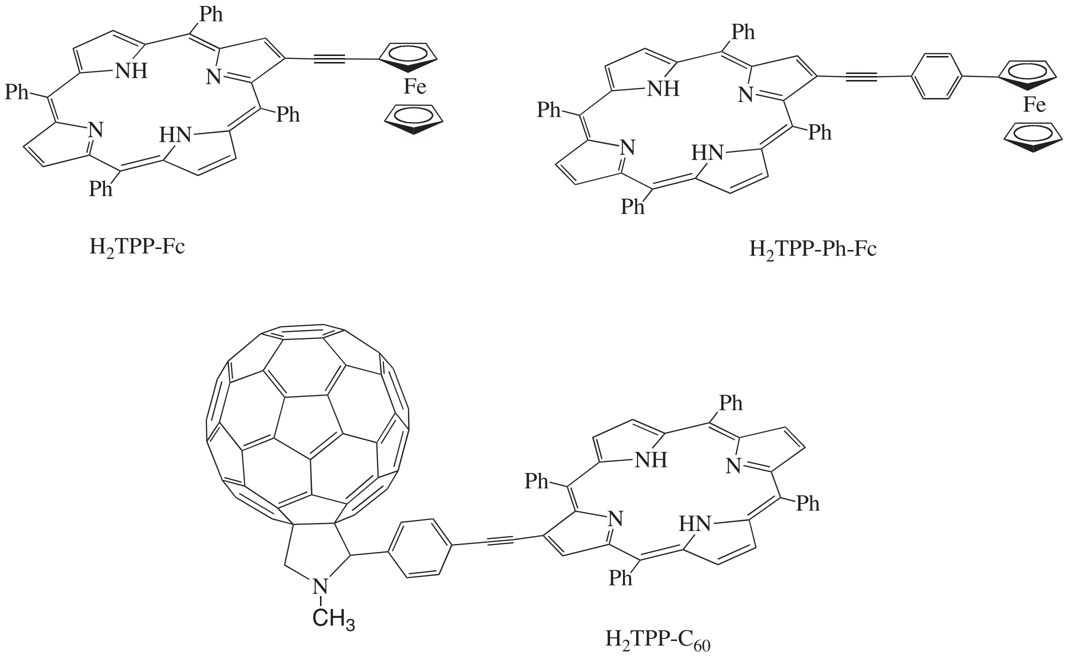


Fig. 3. Emission spectra of Triad **1** and the partial reference compounds in THF.



H_2TPP-Fc

H_2TPP-Ph-Fc

H_2TPP-C_{60}

Fig. 4. The structures of the partial reference compounds.

suggests that the concentration-dependent aggregation phenomena are not present in this solvent. In the case of the data reported by Anderson [6], the steady state fluorescence measurements gave a very high degree of quenching of the porphyrin emission (>99%) of the triad. However, when the reference system containing only the ferrocene and porphyrin was examined, it was found that the porphyrin fluorescence was also quenched very efficiently by ferrocene as we report for our similar compound H_2TPP-Ph-Fc(see SI).

Conclusions

In summary we have reported on the synthesis and characterization of four new porphyrin-ferrocene-fullerene triads connected each other by ethynyl bonds. The reported procedures for obtaining the compounds are very promising for extending them to other similar molecules and the work in this field is presently in progress.

Experimental section

General methods

^{1}H NMR spectra were recorded as $CDCl_3$ solutions on a Bruker AM-300 instrument using residual solvent signal as an internal standard (7.27 ppm). Chemical shifts are given as δ values. FAB mass spectra were measured on a VG-4 spectrometer using m-nitrobenzyl alcohol (NBA) as a matrix. UV/vis spectra were recorded on a Varian Cary 50 Scan spectrophotometer in dichloromethane solution.

Photoluminescence (PL) emission spectra were recorded on a standard laboratory set-up equipped with a 200-W continuous Hg(Xe) discharge lamp (Oriel Corp.), an excitation 25-cm monochromator (PMI), an emission 25-cm monochromator (Oriel Cornerstone 260) and a Hamamatsu R3896 photomultiplier. The spectra of diluted solutions were recorded using spectroscopic THF as solvent, with an absorbance <0.1 in the range 250–400 nm, by using conventional 90° geometry on fused-silica cuvettes with an optical length of 10 mm. The typical excitation wavelength of $\lambda_{ex} = 430$ nm was used. The curves were fully corrected for the spectral response of the apparatus that was calibrated over the spectral range from 300 nm to 800 nm with a reference black-body lamp and standard-fluorophore solutions. A spectral band-pass of 2.5 nm was used for both the excitations and emission monochromators.

Chemicals

Silica gel 60 (70–230 and 230–400 mesh, Merck) was used for column chromatography. High-purity-grade nitrogen gas was purchased from Rivoira. C_{60} was purchased from Term-USA. All the reagents and solvents were from Fluka Chem. Co., Aldrich Chem. Co. or Carlo Erba and were used as received. All the compounds gave satisfactory elemental analysis.

Synthesis

4-trimethylsylyethynylbenzaldehyde ethylene acetal. 5 g of 4-trimethylsylylethynyl benzaldehyde, (0.9 mmol) were dissolved in 200 ml of dry toluene. 5 ml of ethylene glycol and 0.1 g of 4-toluenesulfonic acid were added and the solution was refluxed under nitrogen, eliminating the water by-product using a Dean–Stark apparatus. The final organic solution was washed with a sat. $NaHCO_3$ and dried on anhydrous Na_2SO_4. The residue was recrystallized from hexane at low temperature giving 5.78 g of the final compound. Yield 95%. Mass (EI): 246(M)$^+$; ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 7.49 (d, 2H, J = 9 Hz), 7.43 (d, 2H, J = 9 Hz), 5.81 (s, 1H), 4.12 (d, 2H, J = 2 Hz), 4.05 (d, 2H, J = 2 Hz), 0.27 (s, 9H). Anal. Calcd. for $C_{14}H_{18}SiO_2$: C, 68.24; H, 7.36; Found: C, 68.42; H, 7.21.

4-ethynylbenzaldehyde ethylene acetal **4**. 5.78 g (0.023 mmol) of 4-trimethylsylyethynylbenzaldehyde ethylene acetal were dissolved in 250 ml of methanol and 1 g of anhydrous K_2CO_3 was added with stirring under nitrogen. After 12 h the solution was diluted with water and extracted three times with diethyl ether. The organic solution was dried with anhydrous Na_2SO_4 and evaporated under vacuum. The residue was recrystallyzed from pentane at low temperature giving 4.75 g of the final compound. Yield 100%.

Mass(EI): 173 $(M - H)^+$; ^1H NMR (300 MHz, $CDCl_3$): δ(ppm) 7.53 (d, 2H, J = 9 Hz), 7.45 (d, 2H, J = 9 Hz), 5.82 (s, 1H), 4.13 (d, 2H, J = 4 Hz), 4.03 (d, 2H, J = 4 Hz), 3.13 (s, 1H). Anal. Calcd. for $C_{11}H_{10}O_2$: C, 75.84; H, 5.78; Found: C, 75.62; H, 5.71.

2-bromo-12-(ethynyl-4′-benzaldehyde ethylene acetal)-5,10,15,20-tetraphenylporphyrin **5**. 2,12-dibromo-5,10,15,20-tetraphenylporphyrin, **3**, 200 mg, (0.26 mmol), was dissolved in 150 ml of 5:1 mixture of dry toluene/triethylamine under nitrogen and 56 mg of **4** (0.31 mmol) were added. 110 mg, (0.36 mmol) of $AsPh_3$ were added and the solution was deareated by argon bubbling for 10 min 30 mg (0.052 mmol) of bis(dibenzylideneacetone)palladium were added and after 20 min of argon bubbling, the solution was kept at 60 ° C for 12 h under nitrogen. The resulting mixture was evaporated under vacuum and the residue chromatographed on a silica gel column, eluting with toluene, affording 175.3 mg (0.091 mmol) of the desired compound in 60% of yield. MS(FAB): 867$(M + H)^+$; ^1H NMR (300 MHz, $CDCl_3$): δ(ppm) 9.09 (d, 1H, J = 2 Hz), 8.79 (m, 5H), 8.10 (m, 8H), 7.80 (d, 2H, J = 4 Hz), 7.71 (m, 10H), 7.43 (d, 2H, J = 9 Hz), 7.39 (d, 2H, J = 9 Hz), 5.85 (s, 1H), 4.19 (s, 2H), 4.15 (s, 2H), -2.78 (s, 2H); UV/vis (CH_2Cl_2): λ_{max} (nm): 430, 526, 561, 601, 659. Anal. Calcd. for $C_{55}H_{37}N_4O_2Br$: C, 76.29; H, 4.30; N, 6.47. Found: C, 75.92; H, 4.21; N, 6.32.

2-ferrocenylethynyl-12-(4′-formylphenylethynyl)-5,10,15,20-tetraphenylporphyrin **6**. Compound **5** (108 mg, 0.124 mmol) was dissolved in 50 ml of dry THF under nitrogen and 0.35 ml of tetrabutylammonium fluoride (TBAF), 10% THF solution, were added. The solution was deareated by argon bubbling for 10 min after that ethynylferrocene, (46 mg, 0.220 mmol) were added with further argon bubbling of 10 min 40 mg of $Pd(PPh_3)_2Cl_2$ were added and after 20 min of argon bubbling, the solution was kept at 80 ° C for 12 h under nitrogen. The resulting mixture was evaporated under vacuum and redissolved in 100 ml of THF/H_2O under nitrogen. 0.1 ml of conc. HCl was added and after 4 h the mixture was diluted with water and extracted with $CHCl_3$. The solvent was evaporated and the residue chromatographed on a silica gel column, eluting with toluene, affording 55 mg (0.055 mmol) of the desired compound in 45% of yield. MS(FAB): 952$(M + H)^+$; ^1H NMR (300 MHz, $CDCl_3$): δ(ppm) 10.04 (s, 1H), 9.09 (d, 1H, J = 2.9 Hz), 8.87 (d, 1H, J = 2.9 Hz), 8.87 (s, 1H), 8.84 (t, 1H, J = 5.9 Hz), 8.78 (t, 1H, J = 5.9 Hz), 8.76 (s, 1H), 7.83 (m, 8H), 7.68 (m, 12H), 7.67 (m, 2H), 7.50 (d, 2H, J = 9 Hz), 4.37 (s, 3H), 4.26 (s, 6H), -2.65 (s, 1H), -2.68 (s, 1H); UV/vis (CH_2Cl_2): λ_{max} (nm): 431, 526, 567, 603, 659. Anal. Calcd. for $C_{65}H_{42}N_4FeO$: C, 82.10; H, 4.45; N, 5.89. Found: C, 81.98; H, 4.65; N, 5.56.

2-phenylethynylferrocenyl-12-(4′-formylphenylethynyl)-5,10,15,20-tetraphenylporphyrin **7**. Compound **5** (108 mg, 0.124 mmol) was dissolved in 50 ml of dry THF under nitrogen and 0.35 ml of tetrabutylammonium fluoride (TBAF), 10% THF solution, were added. The solution was deareated by argon bubbling for 10 min after that phenylethynylferrocene, (63 mg, 0.220 mmol) were added with further argon bubbling of 10 min 40 mg of $Pd(PPh_3)_2Cl_2$ were added and after 20 min of argon bubbling, the solution was kept at 80 ° C for 12 h under nitrogen. The resulting mixture was evaporated under vacuum and redissolved in 100 ml of THF/H_2O under nitrogen. 0.1 ml of conc. HCl was added and after 4 h the mixture was diluted with water and extracted with $CHCl_3$. The solvent was evaporated and the residue chromatographed on a silica gel column, eluting with toluene, affording 62 mg (0.06 mmol) of the desired compound in 48% of yield. MS(MALDI-TOF):1028.51$(M + H)^+$; ^1H NMR (300 MHz, $CDCl_3$): δ(ppm) 10.05 (s, 1H), 9.07 (d, 2H, J = 1.5 Hz), 8.87 (m, 4H), 8.23 (m, 8H), 7.87 (m, 12H), 7.51 (m, 6H), 7.26 (d, 2H, J = 2.1 Hz), 4.73 (s, 2H), 4.40 (s, 2H), 4.10 (s, 5H), -2.61 (s, 2H); UV/vis (CH_2Cl_2): λ_{max} (nm): 433, 530, 573, 608, 664. Anal. Calcd. for $C_{71}H_{46}N_4FeO$: C, 83.03; H, 4.51; N, 5.45. Found: C, 82.98; H, 4.60; N, 5.59.

Triad **1**. 100 mg of **6**, (0.1 mmol), were dissolved in 50 ml of dry toluene under nitrogen and 180 mg, (0.25 mmol) of C_{60} and 26 mg, (0.30 mmol) of N-methylglycine were added. The solution was refluxed for 48 h and then evaporated under vacuum. The residue was chromatographed on a silica gel column eluting with toluene. The second fraction containing the desired compound was evaporated under vacuum and recrystallized from toluene/hexane affording 70 mg, (0.041 mmol). Yield 41%. MS(MALDI-TOF): 1699.32 $(M + H)^+$; ^1H NMR (300 MHz, $CDCl_3$): δ(ppm) 9.04 (s, 1H), 8.99 (s, 1H), 8.91 (t, 1H, J = 2.9 Hz), 8.87 (t, 1H, 2.9 Hz), 8.84 (s, 1H), 8.78 (t, 1H, J = 5.9 Hz), 8.13 (m, 8H), 7.85 (m, 10H), 7.81 (m, 2H), 7.78 (m, 2H), 4.77 (d, 1H, J = 8.3 Hz), 4.65 (s, 1H), 4.36 (s, 3H), 4.24 (s, 6H), 3.99 (d, 1H, J = 8.3 Hz) 2.74 (s, 3H), -2.65 (s, 1H), -2.69 (s, 1H); UV/vis (CH_2Cl_2): λ_{max} (nm): 434, 527, 580, 616, 670. Anal. Calcd. for $C_{127}H_{47}N_5Fe$: C, 89.80; H, 2.78; N, 4.12. Found: C, 90.08; H, 2.65; N, 4.26.

Triad **8**. 100 mg of **7**, (0.097 mmol), were dissolved in 50 ml of dry toluene under nitrogen and 180 mg, (0.25 mmol) of C_{60} and 26 mg, (0.30 mmol) of N-methylglycine were added. The solution was refluxed for 48 h and then evaporated under vacuum. The residue was chromatographed on a silica gel column eluting with toluene. The second fraction containing the desired compound was evaporated under vacuum and recrystallized from toluene/hexane affording 60 mg, (0.033 mmol). Yield 35%. MS(MALDI-TOF): 1775.35, $(M + H)^+$; ^1H NMR (300 MHz, $CDCl_3$): δ(ppm) 9.02 (s, 1H), 8.92 (d, 1H, J = 1.9 Hz)), 8.77 (m, 4H), 8.21 (m, 8H), 7.78 (m, 12H), 7.59 (m, 2H), 7.47 (m, 6H), 4.90 (d, 1H, J = 1.3 Hz), 4.81 (s, 1H), 4.70 (s, 2H), 4.38 (s, 2H), 4.14 (d, 1H, J = 1.2 Hz) 4.08 (s, 5H), 2.81 (s, 3H), -2.65 (s, 2H); UV/vis (CH_2Cl_2): λ_{max} (nm): 435, 532, 574, 609, 666. Anal. Calcd. for $C_{133}H_{51}N_5Fe$: C, 90.01; H, 2.89; N, 3.94. Found: C, 90.08; H, 2.75; N, 3.76.

General procedure for zinc insertion

To a solution of starting compound in chloroform, a saturated solution of $Zn(AcO)_2$ in methanol was added and the mixture was left to react at room temperature under nitrogen for 2 h. The solvent was evaporated and the product was purified using a plug of silica gel, eluting with toluene.

Zn-Triad **2**. Yield: 97%. MS(MALDI-TOF), m/z: 1041.41, $[M\text{-}C60]^+$; ^1H NMR (300 MHz, $CDCl_3$): δ(ppm) 9.18 (s, 1H), 9.12 (s,1H), 8.90 (m, 2H), 8.82 (m, 1H), 8.67 (s, 1H), 8.18 (m, 8H), 7.82 (m, 12H), 7.57 (m, 4H), 7.41 (d, 2H, J = 9.2 Hz), 4.80 (d, 1H, J = 9 Hz), 4.66 (s, 1H), 4.39 (s, 3H), 4.26 (s, 6H), 4.03 (d, 1H, J = 9.2 Hz), 2.80 (s, 3H); UV/vis (CH_2Cl_2): λ_{max} (nm): 449, 574, 613. Anal. Calcd. for $C_{127}H_{45}N_5FeZn$: C, 86.57; H, 2.57; N, 3.97. Found: C, 85.99; H, 2.25; N, 3.80.

Zn-Triad **9**. Yield: 98%. MS(MALDI-TOF), m/z: 1117.05, $[M\text{-}C60]^+$; ^1H NMR (300 MHz, $CDCl_3$): δ(ppm) 9.06 (s, 1H), 9.01 (s, 1H), 8.90 (m, 2H), 8.82 (m, 1H), 8.67 (s, 1H), 8.21 (m, 8H), 7.78 (m, 12H), 7.57 (m, 4H), 7.39 (m, 2H), 7.03 (d, 2H, J = 6.2 Hz); 4.84 (d, 1H, J = 9 Hz), 4.73 (s, 1H), 4.40 (s, 3H), 4.10 (s, 6H), 4.03 (d, 1H, J = 9.2 Hz), 2.77 (s, 3H); UV/vis (CH_2Cl_2): λ_{max} (nm): 438, 572, 612. Anal. Calcd. for $C_{133}H_{49}N_5FeZn$: C, 86.90; H, 2.68; N, 3.81. Found: C, 86.99; H, 2.75; N, 3.90.

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