Spectral and redox properties of zinc porphyrin core dendrimers with triarylamines as dendron[†]

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The first and second generation of zinc porphyrin core dendrimers (**3** and **4**) with triarylamine as dendron have been synthesized *via* Ullmann coupling reaction. Their absorption and emission spectra indicate that there are strong interactions between zinc porphyrin core and triarylamine dendrons. Zinc porphyrin links with triarylamine causes Soret band broadening and Q band shift as compared with **ZnTPP**. Because of the antenna effect on these dendrimers, the fluorescence quantum yields were strongly enhanced when more triarylamine moieties were linked. Cyclic voltammetry and spectroelectrochemical methods were used to investigate the redox properties of dendrimers. Axial ligation of zinc porphyrin with *N*-methylimidazole is useful in differentiating the oxidation site of dendrimers. For the first generation dendrimer (**3**), porphyrin ring oxidation potential shifts cathodically because the periphery dendrons are strong electron-donating groups. On the other hand, the dendrons of the second generation (**4**) are oxidized first and generate an atmosphere of eight positive charges. The porphyrin ring core is then oxidized with an anodic shift in potential due to the electron-withdrawing effect of the oxidized substituents.

Introduction

Porphyrin is a π -conjugated macromolecular with unique photophysical and electrochemical properties. These properties can be fine tuned and controlled by bonding with proper functional groups at the *meso* and β positions on the macrocycle.¹ In the past decades, artificial metalloporphyrins have played an important role in biological applications, for example, to mimic the catalytic reactions of cytochromes.² Subsequently, metalloporphyrin core dendrimers have been synthesized, which show reversible O₂ binding,³ good regioselectivity for the substrate and a more stable catalytic active center in the catalytic reaction.⁴ Moreover, porphyrin core dendrimers with a large number of chromophores at the branches or periphery are appropriate to mimic the antenna effect of light-harvesting photosynthetic complexes.⁵

Triphenylamine (TPA)-based derivatives are widely investigated in the application to optoelectronic materials such as hole transporting materials in organic light emitting diode (OLED),⁶ dyes in dye-sensitized solar cells (DSSCs)⁷ and electrochromic polymer.⁸ Recently, hybridization of porphyrin and TPA have attracted much attention.⁹⁻¹² Cheng's group first reported the electrochemistry of triarylamine-porphine hybrid conjugates.⁹ Yeh's group is engrossed in the porphyrin-triarylamine conjugates link *via* ethynyl linkage to enhance the electronic interaction.¹⁰⁻¹¹ Both of their investigations show strong electronic interactions between two entities, including the decrease in HOMO–LUMO gap, the potential shift of porphyrin ring oxidation and the charge transfer from triarylamine to porphyrin. We report here the study of porphyrin-triarylamine dendrimers. The spectral and electrochemical properties of first and second generation (3 and 4) are analyzed. As compared to the previous study in porphyrin-carbazole dendrimers,¹³ porphyrin-triarylamine dendrimers show stronger electronic interactions between porphyrin and dendrons, and the intramolecular energy transfer from dendrons to the zinc porphyrin core is observed.

Scheme 1



Scheme 1 Zinc porphyrin core dendrimers and relative compounds.

Results and discussion

Spectral properties

Absorption spectra of zinc porphyrins are shown in Fig. 1. Zinc porphyrin core dendrimers **3** and **4** exhibit very different shapes of the spectra as compare to **ZnTPP**. These observations

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Table 1 Absorption spectral λ_{max} (nm), full width at half maximum height
(fwhm, cm⁻¹) and oscillator strength $(f)^a$ of zinc porphyrins in CH₂Cl₂

Compound	Soret band λ_{\max} , fwhm, <i>f</i>	$\begin{array}{l} Q(0,1)\\ \lambda_{\max}, \text{fwhm}, f \end{array}$	Q(0,0) λ_{max} , fwhm, f	Q band $f_{\text{total}^{b}}$
ZnTPP 3 4	419, 573, 1.98 445, 3684, 1.33 419, 1132, 1.54	548, 704, 0.079 558, 993, 0.050 561, 1347, 0.058	586, 614, 0.009 604, 903, 0.051 610, 1047, 0.070	0.088 0.101 0.128

^{*a*} Oscillator strength (f). $f = 4.319 \times 10^{-9} A/n$, where A = integrated area of peak and n = reflection index of solvent. Using the plot of (*c* vs. cm⁻¹) to obtain each absorption peak's integrated area (A) in the spectrum. ^{*b*} $f_{\text{total}} = f_{Q(0,1)} + f_{Q(0,0)}$.



Fig. 1 Absorption spectra of 2.0×10^{-6} M ZnTPP, 3 and 4 in CH₂Cl₂.

include the specific absorption of dendrons in UV region, the broadening and splitting of Soret bands, and bathochromic shift of Q bands. These phenomena indicate that there is strong electronic interaction between dendron and zinc porphyrin. The results are similar to the previous studies in triarylamine-porphyrin conjugates.⁹⁻¹⁰ Maximum absorption wavelength (λ_{max}), full width at half maximum height (fwhm) and oscillator strength (f) of peaks are summarized in Table 1. In this study, the Q band oscillator strength becomes more intense as more electron-donating groups bond with porphyrin. We find the dendritic zinc porphyrin 4 has the most intense Q band in these three zinc porphyrins. According to the four-orbital-model theory,14 the intensity of Q band depends on the energy difference between a_{2u} and a_{1u} orbitals. Previous studies have indicated that the energy of a_{2u} is higher than a_{1u} in tetraphenylporphyrin.^{14,15} The bonding of electron-donating group at the meso position of porphyrin ring will raise the energy of a_{2u} orbital, and then result in a larger energy difference between a_{2u} and a_{1u} .

The fluorescence spectra of **ZnTPP** and **1–4** are shown in Fig. 2, where **1** and **2** were excited at 301 and 313 nm respectively. The emission peaks are at 389 nm for **1** and 423 nm for **2**, respectively. When dendritic zinc porphyrin **3** is excited at wavelength of Soret band, it exhibits one emission peak at 635 nm. Interestingly, while **3** is excited at 301 nm, there is no peak found in the region of 350– 550 nm and instead, it emits at 635 nm. Similar results also can be found in **2** and **4**, where the emission peak of **4** is at 632 nm. These phenomena indicate that an intramolecular energy transfer occurs between dendron and zinc porphyrin core. The antenna effect of triphenyamine bound zinc porphyrin has been reported before.⁹ In this study, the quantum efficiency of **3** and **4** are also measured by using H₂TPP as standard. The quantum yield of H₂TPP was

Table 2 Half-wave potentials $(E_{1/2} \text{ vs. Ag/AgCl(saturated)})^{e}$ and peak potentials (E_p) of zinc porphyrins and dendrons

Compour	nd Ox 4	Ox 3	Ox 2	Ox 1	Red 1	Red 2
ZnTPP	_	_	+1.13	+0.82	-1.31	-1.82^{a}
1			$+1.42^{a}$	+0.78	_	
3	$+1.35^{a}$	+0.96	$+0.87^{b}$	$+0.66^{b}$	-1.36	-1.81^{a}
2		$+1.42^{a}$	+0.71	+0.38		
4	$+1.43^{a}$	+1.00	$+0.73^{b}$	$+0.42^{b}$	-1.36	-1.84^{a}

^{*a*} Peak potential of an irreversible wave. ^{*b*} Multiple electrons transfer involved. ^{*c*} $E_{1/2}$ of Fc/Fc⁺ is +0.54 V vs. Ag/AgCl(saturated).



Fig. 2 Fluorescence spectra of compounds. ZnTPP, 1 and 3 were excited at 419, 301, 301 nm in CH₂Cl₂ respectively. 2 and 4 were excited at 313 nm in toluene. The concentration of 1 and 2 were 8.0×10^{-6} M, 3 and 4 were 2.0×10^{-6} M.

set to 0.11.¹⁶ Values obtained for **ZnTPP**, **3** and **4** are 0.037, 0.130 and 0.163 respectively.¹⁷ It shows an enhanced quantum efficiency when triarylamine dendrons are bonded to the zinc porphyrin core.

Cyclic voltammetry

Cyclic voltammograms (CV) and half-wave potentials ($E_{1/2}$) of **ZnTPP** and **1–4** are shown and listed in Fig. 3 and Table 2. **ZnTPP** can undergo two ring oxidations to radical cation and dication at $E_{1/2} = +0.82$ and +1.13 V, respectively. Compound **1** can reversibly be oxidized at $E_{1/2} = +0.78$ V, followed by an irreversible oxidation wave at $E_{pa} = +1.42$ V. There is a new and small oxidative wave



Fig. 3 Cyclic voltammograms of ZnTPP and 1–4 in CH_2Cl_2 containing 0.1 M TBAP. Scan rate: 0.1 V s⁻¹. Molar concentrations of compounds: 1.0×10^{-3} M.

at about +1.00 V in the second cyclic scan when scan potential is over +1.42 V. The new wave is suggested to be the oxidation of the carbazole derivative, which is generated from an unstable $1^{2+.18}$ It can be observed in Fig. 3 that there are multiple redox couples overlapping in the potential range of +0.5 to +1.2 V in the CV of **3**. According to the structural relations and oxidation potentials between **ZnTPP**, **1** and **3**, it is reasonable to predict that the CV of **3** could have total $6e^-$ oxidations involved.

The literature has reported that axial ligation to zinc porphyrin could tune the redox potentials of zinc porphyrin.¹⁹ Imidazole ligation would cause a cathodic shift in potential for first zinc porphyrin oxidation and an anodic shift for the second oxidation. In this study, we use N-methylimidazole (N-MeIm) as the axial ligand to deconvolute the overlapping oxidation waves. Fig. 4(A)is the CV of 3 in the presence of N-MeIm. In the potential range of +0.5 to +0.8 V, as N-MeIm is added to the solution, one redox couple at $E_{pa} = +0.56$ V appears while other redox waves have little change in potential. It gradually separated into two redox couples when the concentration of N-MeIm reaches one equivalent of 3 (Fig. 4(A)(e)). According to the axial ligation effect on zinc porphyrin, the first oxidation of 3 is thus assigned to the oxidation at the porphyrin ring, and the second one is assigned to one of the four triarylamines. During the N-MeIm titration, the redox reactions in the region of +0.8 to +1.2 V were getting closer and became one redox with a peak-to-peak separation of 0.19 V. The results suggest that 4e⁻ transfer is involved in this redox including 1e- oxidation of porphyrin radical cation to dication and 3e⁻ oxidation of three triarylamine moieties. Further confirmation will be conducted by spectroelectrochemical method.



Fig. 4 Cyclic voltammograms of zinc porphyrins (A) **3**; (B) **4** in CH₂Cl₂ containing 0.1 M TBAP. Scan rate: 0.1 V s⁻¹. Molar concentrations of **3** and **4** are both 1.0×10^{-3} M; [*N*-MeIm]: (a) 0; (b) 2.5×10^{-4} ; (c) 5.0×10^{-4} ; (d) 7.5×10^{-4} ; (e) 1.0×10^{-3} M.

The CV of **2** exhibited two reversible redox reactions at $E_{1/2}$ = +0.38 and +0.71 V and a subsequent irreversible oxidative wave at +1.42 V. It is noteworthy that there is a new wave produced at +1.12 V in the second cyclic scan when the scan potential is over +1.42 V. The new wave is assigned as the oxidation of benzidine, which is the dimerization product of 2^{3+} . This phenomenon is similar to the dimerization of triphenylamine and oligo(*N*-phenyl-*m*-aniline)s.²⁰ There are four reversible redox reactions in the CV of **4** and may have nine electrons involved in the three oxidative couples. The redox couple at $E_{1/2} = -1.36$ V (Red 1) is a 1e⁻ reduction of the porphyrin ring. Peak current (i_p) and peak-to-

Table 3 Half-wave potentials $(E_{1/2})$, peak-to-peak separations (ΔE_p) and peak currents (i_p) of each redox in the cyclic voltammogram of zinc porphyrin **4**

Zinc porphyrin (4)	Ox 3	Ox 2	Ox 1	Red 1
$\frac{E_{1/2}/V}{\Delta E_{p}/V}$	+1.00 0.13	$+0.73^{b}$ 0.23	$+0.42^{b}$ 0.22	-1.36 0.12
$i_{\rm p}/\mu {\rm A}^a$	8.6	37.1	37.0	9.2

^{*a*} These values are referring to anodic and cathodic peak currents for oxidative and reductive reactions respectively. ^{*b*} Multiple electrons transfer involved.

peak separation (ΔE_p) of Red 1 are 9.2 μ A and 0.12 V respectively. As compared with Red 1, the first and second oxidative redox reactions (Ox 1 and Ox 2) have larger i_p and ΔE_p (Table 3). The third oxidative redox (Ox 3) has about the same current value with Red 1 can be assigned as a 1e⁻ transfer electrochemical reaction. The i_p of Ox 3 is smaller than that of Red 1 by about 6%. The large positive charge (9+) apparently exhibits significant effect in association with electrolyte during the diffusion process. As shown in Table 3, the values of i_p and ΔE_p in Ox 1 and Ox 2 are almost equal. So we infer that both Ox 1 and Ox 2 involved 4e⁻ transfers. Using N-MeIm as axial ligand to probe the oxidation sites of 4. The CV of 4 in the presence of N-MeIm is shown in Fig. 4(B). Only Ox 3 was cathodically shifted by 0.06 V when N-MeIm ligated to 4. It indicates that Ox 3 is the porphyrin ring oxidation of 4. It is interesting to note that the dendrons at the periphery of 4 bearing 8+ charges causes the porphyrin ring to be harder to oxidize by 0.18 V as compared with ZnTPP, and that imidazole ligation makes the porphyrin ring oxidation easier by 0.06 V.

In the discussion above, we conclude the Ox 1 and Ox 2 of 4 are the removal of the first and second electron from each of the four dendrons to form 4^{4+} and 4^{8+} , respectively. Subsequently, Ox 3 is the first porphyrin ring oxidation to form 4^{9+} .

UV/Vis/NIR spectroelectrochemistry

The studies of electron interaction between dendron and zinc porphyrin core and further confirmation of the oxidative sites on zinc porphyrins were carried out by UV/Vis/NIR spectroelectrochemistry. The spectral changes upon applied potentials of 1 and 3 are in Fig. 5. The radical cation of compound 1 exhibits absorption peaks at 372, 582 and 756 nm. Owing to the overlapped multiple redox reactions in CV, the spectroelectrochemical investigation of 3 were performed by small increments of potential from +0.45 to +1.04 V. According to the trend of spectral change, the spectra were divided into five diagrams (Fig. 5(B)-(F)). In Fig. 5(B), the diminished Soret band at 445 nm indicates that the porphyrin ring is oxidized. This result is consistent with what we inferred from cyclic voltammetry (Fig. 4(A)). It is worth noting that during the process of 3 to 3^+ , the absorption band of triarylamine moieties at 301 nm also decreases, accompanied by forming new bands at 780 and 1418 nm, which are due to the specific absorption of triarylamine radical cation and the charge transfer between triarylamines and zinc porphyrin core.9-10 A reasonable explanation for this phenomenon is that electronrich triarylamines transfer its electrons to the porphyrin ring, which lacks an electron after 1e⁻ removal. Fig. 5(C) represents the formation of 3^{2+} , which is assigned as the oxidation of one



Fig. 5 Spectral changes of 1 and 3 in CH₂Cl₂ containing 0.1 M TBAP at various applied potentials.

triarylamine moiety. The absorbance of triarylamine decreases and the charge transfer band at NIR region continues to grow.

Fig. 5(D)–(F) are the spectra at applied potentials from +0.78 to +1.04 V, as we inferred in cyclic voltammetry that there should be a total of 4e⁻ oxidations within this potential region. In Fig. 5(D), the absorption of neutral triarylamine is totally diminished and the extinction coefficient (ε) of the new absorption band formed at 756 nm is about three times as compared with that of 1⁺. It indicates the four triarylamines were all oxidized to radical cations at +0.90 V. The oxidation state in here is assigned as 3⁵⁺, including 1e⁻ removed from the porphyrin ring and 4e⁻ from the triarylamine moieties. Because all redox centers in this molecule were oxidized, there is only small absorbance

present in NIR region. Furthermore, one band with a high ε value (150000 dm³ mol⁻¹ cm⁻¹) and a quite narrow bandwidth appeared at 430 nm. This band is like a Soret band of neutral porphyrin. This "Soret band-like" absorption probably resulted from the resonance of electrons from four triarylamine radical cations to the periphery of porphyrin ring, and then causes an increased electron density in porphyrin ring. The spectral changed at +0.90 V to +1.02 V become more irregular and more complicated (Fig. 5(E) and (F)). The potential applied at +1.04 V leads to the decomposition of the zinc porphyrin.

During the process of 2 oxidized to 2^+ , three new bands appeared at 438, 768 and 1356 nm (Fig. 6(A)). The bands in NIR are known as intervalence charge transfer (IVCT) band. The spectral pattern



Fig. 6 Spectral changes of 2 and 4 in CH₂Cl₂ containing 0.1 M TBAP at various applied potentials

of 2^+ is similar to the triamine radical cation in the previous study.²¹ Because the electron-donating effect of methoxy groups on 2^+ , the new peaks were located at lower energy (22 831, 13 016, 7375 cm⁻¹) as compared to the peaks of triamine radical cation (23 040, 14 350, 8117 cm⁻¹).²¹ The intensity of the IVCT band is increased and blue shift to 1182 nm during the oxidation process of 2^+ to 2^{2+} (Fig. 6(B)). Moreover, absorption bands at 294 and 438 nm were diminished and one band appeared at 590 nm. The spectral recoveries are both quantitative for monocation 2^+ and dication 2^{2+} , when they returned to their former oxidation state. It shows that these two oxidation products are very stable.

The first oxidative redox in the CV of 4 was examined by spectroelectrochemistry with applied potentials from 0.00 V to +0.55 V. In Fig. 6(D), the spectral shape in 650 to 2200 nm at +0.55 V is similar to the spectrum of 2^+ , and no other new bands appear in this region. The ε of the IVCT band at 1354 nm is almost four times as large as that of 2⁺ at 1356 nm. Furthermore, the number of electrons transferred in this oxidation process is about 1 for each dendron.²² This evidence indicates that there is no charge transfer from the dendron moieties to the zinc porphyrin core. The electrochemical behaviour of dendrons are independent and the intervalence charge transfer occurs within each of four single dendron moieties. Because of the spectral overlapping, the Soret band has a red shift from 419 to 426 nm with increased absorbance by about 18%. Furthermore, the spectrum of 4^{4+} at +0.55 V is very similar to the sum of the spectrum of neutral state of ZnTPP and four times of 2^+ (Fig. 6(C)). Similar phenomena are occurring at the process of the oxidation of 4^{4+} to 4^{8+} , where the ε of the band at 1172 nm is also almost four times to that of 2^{2+} at 1182 nm (Fig. 6(E)). During the process of 4^{8+} to 4^{9+} , the Soret band at 426 nm and the Q band at 554 nm are decreasing and is accompanied by an increasing of absorbance in 550-700 nm (Fig. 6(F)). This is a typical absorption spectrum of the formation of porphyrin radical cation.²³ Absorption band at NIR region just has slightly changed in absorbance, which shows there has quite small amount of charge transfer between dendron and zinc porphyrin core via the phenyl bridging.

Conclusions

The first synthesis of porphyrin-triarylamine conjugated dendrimers is reported here. As compared with those porphyrincarbazole dendrimers,¹³ bonded triarylamine dendrons greatly affect the electronic configuration of porphyrin. These phenomena are reflected in the electronic spectra of **3** and **4**. In the emission spectroscopy study, the intramolecular energy transfer is found in both **3** and **4**. Dendrons absorb the UV light and then transfer the energy to the porphyrin core. Fluorescence in the visible region subsequently is emitted from porphyrin. Due to the antenna effect found in these dendrimers, **3** and **4** exhibit an enhancement in quantum efficiency.

From cyclic voltammetry and spectroelectrochemistry studies, we have analyzed the electron transfer reactions for each redox couples of **3** and **4**. Owing to the strong electron-donating N,N-di-(p-methoxyphenyl)amino groups bonded to the zinc porphyrin, the potential of the first porphyrin ring oxidation of **3** was cathodic shifted about 0.20 V as compared to **ZnTPP**.³⁰ It is worth noting that the same substituent effect on **4** is not observed because the dendrons of **4** are easier to oxidize than

ZnTPP. Consequently an electron-lacking environment around the porphyrin ring was therefore created. The oxidized dendrons just like electron-withdrawing groups, which causes an anodic shift in potential of the first porphyrin ring oxidation of **4**. The charge transfer bands which appeared in NIR in the oxidation process of **3** indicates the significant interaction between dendrons and zinc porphyrin core. In the oxidation process of **4**, the IVCT bands are resulted from the charge transfer between nitrogen atoms within each dendron substituent, not through the zinc porphyrin bridge. Further studies in catalytic reactions by using these two macrocycles with electro-active metals are in progress.

Experimental

General

¹H and ¹³C NMR spectra were obtained from Varian Unity Inova 300 WB spectrometers. Varian Cary-50 scanning UV/Vis spectrometer was used to determine extinction coefficients of zinc porphyrins and to obtain absorption spectra with 1 cm cuvette. Mass spectra were obtained with Applied Biosystem Voyager-DETM Pro spectrometer. Fluorescence spectra, excitation spectra and fluorescence quantum yields measurement were finished with Varian Cary Eclipse spectrometer. For electrochemical studies, CHI 700A electroanalytical workstation was used in cyclic voltammetry and conducted with a three-electrode cell. Glassy carbon electrode (area = 0.07 cm^2) was used as working electrode. The auxiliary and reference electrodes were platinum wire and Ag/AgCl(KCl saturated) respectively. Spectroelectrochemistry was performed with JASCO V-570 UV/Vis/NIR spectrometer and Bioanalytical System Model SP-2 potentiostat. Platinum gauze, platinum wire and Ag/AgCl(KCl saturated) were used as working, auxiliary and reference electrode respectively in a spectroelectrochemical cell with an 1 mm optical path length.

Materials

Zinc tetraphenylporphyrin (ZnTPP) and zinc *meso*-tetra(p-aminophenyl)porphyrin (ZnTAPP) were synthesized from literature methods,^{24,25} and follow by metallating with zinc acetate dihydrate in CH₂Cl₂–CH₃OH. *N*,*N*-Di-(4-methoxyphenyl)phenylamine (1) and *N*,*N*-di-(4-methoxy-phenyl)-4'iodophenylamine (I-TPA-(OCH₃)₂) were obtained according to the literature methods.^{26,27} Other chemicals were all commercially available. Organic solvents that were used in electrochemical studies were dried and distilled before use. Tetra-*n*-butylammonium perchlorate (TBAP) were recrystallized twice from ethyl acetate and dried before use.

4,4'-Di-[N,N-di(4-methoxyphenyl)amino]triphenylamine (2)³¹

The precursor 4,4'-diaminotriphenylamine was synthesized by modifying the literature method,²⁸ in which 3,4-dimethylaniline was replaced by aniline. Compound **2** was obtained by reacting 4,4'-diaminotriphenylamine and 4-iodoanisole with Ullmann coupling reaction. 4,4'-Diaminotriphenylamine (0.39 g, 1.42 mmol) and 4-iodoanisole (6.80 g, 29.05 mmol) were dissolved in 1,2-dichlorobenzene (10 ml) containing K_2CO_3 (1.57 g, 11.36 mmol), Cu powder (0.72 g, 11.36 mmol) and 18-crown-6 (1.13 g,

4.26 mmol). The reaction mixture was heated to reflux with stirring for 48 h. When the mixture was cooled to room temperature, 50 ml CH₂Cl₂ was added and then filtrated. The filtrate was passed through a silica gel column with CH₂Cl₂ as eluent. Yield: 0.35 g, 35%. UV/Vis λ_{max} (CH₂Cl₂)/nm 313 (ε /dm³ mol⁻¹ cm⁻¹ 38 600), ¹H NMR $\delta_{\rm H}$ (300 MHz, d_6 -DMSO) 7.19 (2 H, t, *J* 7.6, Ar–H), 6.97 (8 H, d, *J* 8.8, Ar–H), 6.87 (15 H, m, Ar–H), 6.74 (4 H, d, *J* 8.8, Ar–H), 3.71 (12 H, s, OCH₃); EA found: N, 5.70; C, 78.55; H, 6.10. Calc. for C₄₆H₄₁N₃O₄: N, 6.00; C, 78.95; H, 5.91%.

Zinc *meso*-tetra-4-[*N*,*N*-di(4-methoxylphenyl)amino]phenyl-porphyrin (3)

Compound 3 was synthesized by modifying the literature method.²⁹ ZnTAPP (0.15 g, 0.20 mmol) and 4-iodoanisole (3.80 g, 16.30 mmol) were dissolved in 1,2-dichlorobenzene (2 ml) containing K₂CO₃ (2.25 g, 16.30 mmol), Cu powder (1.04 g, 16.30 mmol) and 18-crown-6 (0.16 g, 0.60 mmol). The reaction mixture was heated to reflux with stirring for 24 h. When the mixture was cooled to room temperature, 50 ml CH₂Cl₂ was added and then filtrated. The filtrate was passed through a silica gel column with CH₂Cl₂ as eluent. Yield: 0.25 g, 78%. UV/Vis λ_{max} (CH₂Cl₂)/nm $301 \ (\epsilon/dm^3 \ mol^{-1} \ cm^{-1} \ 69\ 800), \ 408 \ (82\ 500), \ 445 \ (123\ 000), \ 558$ (15 900), 604 (17 000); ¹H NMR $\delta_{\rm H}$ (300 MHz, CDCl₃) 9.09 (8 H, s, pyrrolic-H), 8.01 (8 H, d, J 8.5, Ar-H), 7.36 (16 H, d, J 9.0, Ar-H), 7.31 (8 H, d, J 8.5, Ar-H), 6.96 (16 H, d, J 9.0, Ar-H), 3.84 (24 H, s, OCH₃); ¹³C NMR $\delta_{\rm C}$ (75.47 MHz, CDCl₃) 156.0, 150.4, 148.1, 141.2, 135.3, 134.9, 131.8, 126.9, 121.1, 118.3, 114.9, 55.5; MS(MALDI-TOF): m/z calcd for C₁₀₀H₈₀N₈O₈Zn: 1587.14, found: 1587.17.

Zinc meso-tetra-4-[N',N'-di-4-[(N,N-di(4-methoxylphenyl)-amino)phenyl]amino]phenylporphyrin (4)

The synthetic method of 4 is similar to 3. ZnTAPP (0.065 g, 0.09 mmol) and I-TPA-(OCH₃)₂ (3.04 g, 7.04 mmol) were dissolved in 1,2-dichlorobenzene (2 ml) containing K_2CO_3 (0.97 g, 7.04 mmol), Cu powder (0.45 g, 7.04 mmol) and 18-crown-6 (0.07 g, 0.26 mmol). The reaction mixture was heated to reflux with stirring for 96 h. When the mixture was cooled to room temperature, 50 ml CH₂Cl₂ was added and then filtrated. The filtrate was passed through a column (silica gel) with CH₂Cl₂ as eluent to carry out unreacted reactants and 1,2-dichlorobenzene. Then $CH_2Cl_2: EA = 1:1$ was used as eluent to get the target compound. Yield: 0.19 g, 68%. UV/Vis λ_{max} (CH₂Cl₂)/nm 313 $(\varepsilon/dm^3 \text{ mol}^{-1} \text{ cm}^{-1} 140\,800), 332 (133\,800), 419 (247\,900), 561$ (16 800), 610 (20 700); ¹H NMR $\delta_{\rm H}$ (300 MHz, CDCl₃) 9.06 (8 H, s, pyrrolic-H), 8.03 (8 H, d, J 8.1, Ar-H), 7.40 (8 H, d, J 7.8, Ar-H), 7.25 (16 H, d, overlap with solvent peak, Ar-H), 7.11 (32 H, d, J 8.6, Ar-H), 7.01 (16 H, d, J 8.6, Ar-H), 6.84 (32 H, d, J 8.7, Ar–H), 3.78 (48 H, s, OCH₃); ¹³C NMR $\delta_{\rm C}$ (75.47 MHz, CDCl₃) 155.7, 150.5, 147.9, 144.6, 141.5, 141.3, 135.5, 135.4, 132.0, 127.1, 126.2 122.6, 121.2, 119.4, 114.8, 55.6; MS(MALDI-TOF): m/z calc. for C₂₀₄H₁₆₈N₁₆O₁₆Zn: 3165.00, found: 3165.17.

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