DOI: 10.1002/ejic.201101033

# A Systematic Study of Electrochemical and Spectral Properties for the **Electronic Interactions in Porphyrin–Triphenylamine Conjugates**

## Chih-Yen Huang,<sup>[a]</sup> Chao-Yen Hsu,<sup>[a]</sup> Luo-Yi Yang,<sup>[a]</sup> Chia-Jung Lee,<sup>[a]</sup> Te-Fang Yang,<sup>[a]</sup> Chia-Chan Hsu,<sup>[a]</sup> Chung-Hsiu Ke,<sup>[a]</sup> and Yuhlong Oliver Su\*<sup>[a,b]</sup>

Keywords: Electrochemistry / Electron transfer / Charge transfer / Energy transfer / Luminescence / Zinc / Porphyrinoids / Antenna effect

A series of mono-, di-, tri-, and tetra-triphenylamine (TPA)substituted porphyrinatozinc complexes have been synthesized to investigate their spectral and electrochemical properties. The varied shapes of absorption spectra of porphyrintriphenylamine (Por-TPA) conjugates in comparison with tetramesitylporphyrinatozinc (ZnTMP) indicate that there are strong interactions between porphyrin and TPA moieties. In general, the electron-donating capability of a substituent on TPA and the number of TPA derivatives that bond with porphyrin would cause Soret band broadening and intensification of the Q(0,0) band. Due to the antenna effect of these conjugates, the fluorescence quantum yields were enhanced

## Introduction

Porphyrin molecules have unique electrochemical and photophysical properties, which can be easily controlled by functionalization with specific groups at the *meso* and  $\beta$ positions.<sup>[1]</sup> Recently, the hybridization of porphyrins and photoelectronic molecules such as triphenylamine (TPA) has attracted much attention.<sup>[2-6]</sup> TPA-based derivatives are widely investigated for the application of dye-sensitized solar cells,<sup>[7]</sup> organic light-emitting diodes,<sup>[8]</sup> and electrochromic polymers.<sup>[9]</sup> Cheng's and Yeh's groups reported the spectral and electrochemical properties of porphyrin-triphenylamine hybrid conjugates.<sup>[2-4]</sup> Both of their studies showed an obvious bathochromic shift in the Soret and Q bands; the potential shift of porphyrin-ring oxidation and the charge-transfer band appeared in the near-IR region of

- [b] Department of Materials Science and Engineering, National Chung Hsing University, 250 Kuo Kuang Rd., Taichung 402, Taiwan
- Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201101033.

when more TPA moieties were linked. Cyclic voltammetry and spectroelectrochemical methods revealed the redox properties of Por-TPA conjugates. Axial ligation of porphyrinatozinc with N-methylimidazole was useful in differentiating the oxidation site of Por-TPA conjugates. The first one-electron oxidations of these conjugates are at the porphyrin ring. The charge-transfer bands present in the near-IR region in the absorption spectra of Por-TPA radical cations are evidence of an electronic interaction between porphyrin and TPA. The electron-donating strength of the TPA group and the symmetry of the Por-TPA conjugate affect the intensity of the charge-transfer band.

the absorption spectrum as the porphyrin ring was oxidized. These phenomena indicated that there were strong electronic interactions between the porphyrin core and TPA moieties.

Recently, we published a spectral and electrochemical investigation of porphyrin-triphenylamine dendrimers<sup>[6]</sup> because of their interesting behavior in spectroscopy and electrochemistry. It is worth studying how each TPA group interacts with porphyrinatozinc and to establish the knowledge of the electronic properties of the Por-TPA conjugate. Thus the mono-, di-, tri-, and tetra-TPA-substituted Por-TPA conjugates were synthesized. Early work on the electronic effects of unsymmetrical phenyl substitution on the  $\pi$ -electron system of a porphyrin ring has been carried out by Walker and co-workers.<sup>[10]</sup> As shown in Figure 1, we report here a series of Por-TPA conjugates bound to one to four TPA derivatives and with different substituents at the *para* position of TPA in an investigation of the electronic interactions between a porphyrin core and the TPA moiety. Due to the solubility problem of a tetrakis(TPA-NO<sub>2</sub>)-substituted porphyrin, conjugate 4 with four TPA-Cl was used instead. In this work, we have studied two kinds of effects on the spectral and electrochemical properties of Por-TPA conjugates. The first is the number of TPA derivatives bound with porphyrinatozinc, and the second is the functional group substituted at the para position of TPA.

<sup>[</sup>a] Department of Applied Chemistry, National Chi Nan University, 1, University Rd., Puli, Nantou County 545, Taiwan

Fax: +886-49-2917956 E-mail: yosu@ncnu.edu.tw



Figure 1. Structures of ZnTMP and Por-TPA conjugates.

### **Results and Discussion**

Figure 2 shows the absorption spectra of **ZnTMP** and Por–TPA conjugates with different numbers of bound TPA-OCH<sub>3</sub> groups. The mono- to tetra(TPA-OCH<sub>3</sub>)-substituted porphyrinatozinc complexes 13-16 exhibit very different



Figure 2. Absorption spectra of ZnTMP and 13–16 in  $CH_2Cl_2$ . Cyan: ZnTMP, black: 13, red: 14, blue: 15, green: 16.

shapes of spectra relative to **ZnTMP**. As the number of bound TPA-OCH<sub>3</sub> groups increased from one to four, the absorption spectra exhibited an intense specific absorption of TPA at around 300 nm. On the other hand, the Soret band absorption decreased in its molar extinction coefficient ( $\varepsilon$ ) and broadened. Both Q bands exhibited bathochromic shifts and a significant increase in the  $\varepsilon$  of Q(0,0) band. These observations indicate that there are strong electronic interactions between TPA-OCH<sub>3</sub> and porphyrinatozinc. The absorption maxima ( $\lambda_{abs}$ ) and molar extinction coefficients of **ZnTMP** and Por–TPA conjugates are summarized in Table 1. In general, more TPA bound with por-

Table 1. Absorption maximum ( $\lambda_{abs}$ ) [nm] with molar extinction coefficient ( $\epsilon$ ) [10<sup>4</sup> mol<sup>-1</sup> dm cm<sup>-1</sup>] in parenthesis, emission maximum ( $\lambda_{em}$ ) [nm], and quantum yields of **ZnTMP** and Por–TPA conjugates in CH<sub>2</sub>Cl<sub>2</sub>.

	-	-							
			Absorption			Emission		Antenna effect	
Porphyrins	TPA band	Soret band	Q(0,1)	Q(0,0)	$\varepsilon_{Q(0,0)}/\varepsilon_{Q(0,1)}$	$\lambda_{\rm em}^{[a]}$	Quantum yield <sup>[b]</sup>	$\lambda_{\rm em}^{[c]}$	Emission peak area <sup>[c,d]</sup>
ZnTMP	_	421 (74.82)	550 (2.63)	587 (0.25)	0.10	592, 644	0.044	_	_
1	_[e]	422 (45.03)	550 (1.86)	589 (0.25)	0.13	597, 646	0.021	598, 648	$0.07 \times 10^{5}$
2	_[e]	423 (25.93)	551 (1.60)	593 (0.49)	0.31	599, 647	0.021	601, 650	$0.05 \times 10^{5}$
3	_[e]	426 (43.63)	551 (2.19)	593 (0.65)	0.30	601, 650	0.028	601, 650	$0.24 \times 10^{5}$
4	311 (7.79)	436 (18.80)	555 (1.65)	597 (1.03)	0.62	614	0.093	621	$1.62 \times 10^{5}$
5	305 (3.68)	422 (33.79)	551 (2.34)	588 (0.44)	0.19	600, 648	0.060	601, 649	$0.61 \times 10^{5}$
6	307 (5.76)	424 (29.07)	552 (2.56)	595 (0.87)	0.34	606, 651	0.077	602, 653	$0.98 \times 10^{5}$
7	306 (7.77)	432 (23.30)	554 (2.47)	596 (1.31)	0.53	613, 653	0.081	606, 655	$1.20 \times 10^{5}$
8	305 (8.71) <sup>[f]</sup>	438 (18.60) <sup>[f]</sup>	555 (2.24) <sup>[f]</sup>	599 (1.76) <sup>[f]</sup>	0.79	618	0.100	616	$1.60 \times 10^{5}$
9	308 (3.90)	422 (37.64)	552 (2.51)	592 (0.51)	0.20	602, 648	0.070	601, 649	$0.57 \times 10^{5}$
10	307 (4.86)	423 (19.05)	553 (2.10)	595 (0.89)	0.42	609, 652	0.088	603, 652	$0.96 \times 10^{5}$
11	305 (6.67)	429 (13.50)	555 (1.85)	599 (1.19)	0.64	617	0.091	619	$1.70 \times 10^{5}$
12	305 (9.45) <sup>[f]</sup>	442 (16.60) <sup>[f]</sup>	557 (2.15) <sup>[f]</sup>	602 (1.99) <sup>[f]</sup>	0.93	625	0.100	624	$1.99 \times 10^{5}$
13	307 (3.93)	421 (37.16)	553 (2.64)	593 (0.59)	0.22	605, 650	0.059	601, 649	$0.66 \times 10^{5}$
14	305 (5.90)	420 (23.04)	554 (2.71)	597 (1.34)	0.49	613	0.078	614	$0.61 \times 10^{5}$
15	302 (5.02)	425 (14.20)	556 (1.67)	600 (1.06)	0.63	621	0.088	622	$1.22 \times 10^{5}$
16	301 (6.98) <sup>[g]</sup>	445 (12.30) <sup>[g]</sup>	558 (1.59) <sup>[g]</sup>	604 (1.70) <sup>[g]</sup>	1.07	636 <sup>[g]</sup>	0.130 <sup>[g]</sup>	637	$3.04 \times 10^{5}$

[a] **ZnTMP** and all the Por–TPA conjugates were excited at the Soret band. [b] Using  $H_2TPP$  as standard. The quantum yield of  $H_2TPP$  was set to  $0.11^{[13]}$ . [c] The Por–TPA conjugates were excited at the TPA moiety. In the spectra of conjugates **4–16**, the emission peak was overlapped with excitation overtone. [d] Plotting fluorescence spectra in the form of intensity versus wavenumber. The emission peak area was obtained by integration from 17857 to 12500 cm<sup>-1</sup> (560 to 800 nm). For conjugates **1–3**, the areas were integrated from 17857 to 13888 cm<sup>-1</sup> (560 to 720 nm). [e] The absorption maximum of TPA-NO<sub>2</sub> is at 417 nm in CH<sub>2</sub>Cl<sub>2</sub>. [f] Data from the literature<sup>[2]</sup>. [g] Data from the literature<sup>[6]</sup>.

phyrinatozinc further causes a redshift of both Soret and Q bands, an increase in  $\varepsilon$  value of the TPA and Q(0,0) bands, and a decrease in the  $\varepsilon$  value of the Soret band. For example, the Q(0,0) band of tetrakis(TPA-OCH<sub>3</sub>) porphyrinatozinc 16 is redshifted by 11 and 17 nm relative to porphyrinatozinc 13 and ZnTMP, respectively. The enhancement in the  $(\varepsilon_{Q(0,0)}/\varepsilon_{Q(0,1)})$  ratio of 16 is about 5 and 11 times more than that of 13 and ZnTMP, respectively. We also found that the substituent effect at the TPA moieties is relatively small. The Q(0,0) band of the tetrakis(TPA- $OCH_3$ ) porphyrinatozinc 16 is redshifted only by 5 nm relative to the tetrakis(TPA)-substituted zinc complex 8. Although the nitro group is strongly electron-withdrawing, zinc complexes 1-3 bound with TPA-NO<sub>2</sub> group still exhibit redshifts of Q bands relative to ZnTMP. Apparently, these phenomena suggest that the number of TPA derivatives bound with porphyrinatozinc is the major effect on the ground-state electronic configuration of the porphyrin as the result of  $\pi$ -conjugation expansion. The strongly enhanced Q(0,0) band should be due to the enlarged energy difference between a<sub>2u</sub> and a<sub>1u</sub> orbitals of porphyrin. From the four-orbital-model theory,[11] TPA derivatives bound at the meso position of the porphyrin ring can interact with the a<sub>2u</sub> orbital of porphyrinatozinc and the strong electrondonating group, then raise the energy of the  $a_{2u}$  orbital.<sup>[12]</sup>

The fluorescence spectra and emission maximum ( $\lambda_{em}$ ) of Por–TPA conjugates are shown and listed in Figure 3 and Table 1. In comparison with **ZnTMP**, the emission maximum of tetra-TPA-bonded Por–TPA conjugates **4**, **8**, **12**, and **16** were largely redshifted by 22, 26, 33, and 44 nm, respectively.



Figure 3. Normalized fluorescence spectra of Por–TPA conjugates in  $CH_2Cl_2$ . All of the conjugates were excited at the Soret band. The black, red, blue, and green lines indicate mono-, di-, tri-, and tetra(TPA-X)-substituted conjugates, respectively. (a) TPA-NO<sub>2</sub> (green line: TPA-Cl); (b) TPA; (c) TPA-CH<sub>3</sub>; (d) TPA-OCH<sub>3</sub>-substituted Por–TPA conjugates.

However, for mono-TPA-bonded conjugates 1, 5, 9, and 13, the redshifts in  $\lambda_{em}$  were less than 13 nm. It again demonstrated that the number of bound TPA has a major effect on the electronic configuration of porphyrinatozinc as the

result of  $\pi$ -conjugation expansion. This is consistent with what we inferred from the absorption spectra. On the other hand, the quantum efficiency of conjugates was measured by using H<sub>2</sub>TPP as standard in which the quantum yield of H<sub>2</sub>TPP was set to 0.11.<sup>[13]</sup> Values obtained for Por-TPA conjugates are listed in Table 1. An enhancement in quantum efficiency was observed when TPA derivatives were bound to the zinc complex except for conjugates with strong electron-withdrawing nitro groups. Cheng's group and ours have reported the antenna effect of triphenylamine-bound porphyrinatozinc before.<sup>[2,6]</sup> In this study, we also examine the antenna effect of the Por-TPA conjugates by exciting at their corresponding TPA moieties (Figure S15 in the Supporting Information). All the fluorescence spectra of these conjugates are similar to those emitted by porphyrin with Soret-band excitation, thereby indicating an intramolecular energy transfer from TPA to porphyrinatozinc. The relaxation from the S1 of porphyrin to  $S_0$  was then observed. The  $\lambda_{em}$  obtained from TPA excitation are listed in Table 1. In the molecular structures of Por-TPA conjugates, the TPA moieties act as antennas to absorb radiation. Consequently, the fluorescence intensity was increased as more TPA bonded with porphyrinatozinc. This phenomenon is reflected in the increased emission peak area (Table 1). The typical emission peak of TPA can be observed slightly in the spectra of tri-TPA-bound conjugates only. At its simplest, it may due to the low symmetry of tri-TPA-bound conjugates. Further confirmation of the antenna effect was performed by recording the excitation profiles of Por-TPA conjugates (Figures S16 and S17 in the Supporting Information).

#### **Electrochemical Properties**

Cyclic voltammetry (CV) and spectroelectrochemistry were used to investigate the electrochemical behavior of Por-TPA conjugates. It can be expected that there would be multiple oxidations, including two steps of one-electron ring oxidation of porphyrinatozinc and the oxidation of the nitrogen atom of TPA in the cyclic voltammograms of Por-TPA conjugates in which several TPA groups were bound with porphyrinatozinc. Figure 4 shows the CVs of ZnTMP and zinc complexes 13-16 with different numbers of TPA-OCH<sub>3</sub>. As only one TPA-OCH<sub>3</sub> group is bound to porphyrinatozinc, the CV of 13 exhibits three redox couples in oxidation. Subsequently, as more TPA-OCH<sub>3</sub> groups are bonded, 14–16 exhibit multiple and overlapping oxidation waves in their CVs. It is interesting to study the electrochemical behavior of each redox in the CVs of Por-TPA conjugates even though the CVs become more complex as the number of TPA increases. Hence, in the following discussion, we focus on the effect of the first-electron oxidation (Ox1) of conjugates after TPA derivatives were bound. The electrochemical data obtained from CV are summarized in Table 2. As more TPA groups bonded with porphyrinatozinc, the conjugates were easier to oxidize, as reflected in the cathodic shift in their onset potentials ( $E_{onset}$ ). Basically,

TPA is an electron-donating group. Conjugate 1 and 2 show almost no difference in  $E_{\text{onset}}$  relative to ZnTMP. The results indicate a diminished electronic interaction by the nitro groups bound at TPA, whereas conjugate 16 with four TPA-OCH<sub>3</sub> exhibits a large cathodic shift of 0.19 V. Obviously, the  $E_{\text{onset}}$  values of these conjugates are dominated by electron-donating capability.



Figure 4. Cyclic voltammograms of (a) **ZnTMP**, (b) **13**, (c) **14**, (d) **15**, and (e) **16** in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP). Scan rate: 0.1 V s<sup>-1</sup>. Molar concentrations of compounds:  $1.0 \times 10^{-3}$  M.

Table 2. Half-wave potentials  $[E_{1/2}$  versus Ag/AgCl (saturated)]<sup>[a]</sup> and peak potentials  $(E_p)$  of ZnTMP and 1–16.

	Ox5	Ox4	Ox3	Ox2	Ox1	Eonset	Ox1' <sup>[b]</sup>
ZnTMP	_	_		+1.12	+0.80	+0.71	+0.63
1	_	_	+1.66	+1.14	+0.82	+0.72	+0.72
2	_	_	$+1.46^{[e]}$	+1.13	+0.83	+0.72	+0.76
3	_	_	_	$+1.61^{[e]}$	+0.84	+0.67	$+0.80^{[e]}$
4	_	+1.51 <sup>[e]</sup>	+1.32 <sup>[d]</sup>	+0.94	+0.74	+0.65	+0.66
5	_	_	+1.36 <sup>[e]</sup>	+1.07	+0.79	+0.68	+0.65
6	_	_	$+1.29^{[e]}$	+0.91	+0.73	+0.66	+0.60
7	_	_	$+1.38^{[d,d]}$	$^{e]}+0.92$	+0.73	+0.65	+0.59
8	_	_	+1.30 <sup>[d,d</sup>	<sup>e]</sup> +0.84	+0.71	+0.63	+0.59
9	_	+1.79 <sup>[e]</sup>	+1.25	+1.00	+0.75	+0.66	+0.64
10	$+1.70^{[e]}$	+1.26	+1.09	+0.95	+0.70	+0.63	+0.60
11	_	+1.33	$+1.09^{[d]}$	+0.87	+0.71	+0.61	+0.58
12	$+1.68^{[e]}$	+1.33	$+1.08^{[d]}$	+0.76	+0.65	+0.60	+0.57
13	_	$+1.44^{[e]}$	+1.20	+0.88	+0.74	+0.64	+0.60
14	$+1.47^{[e]}$	+1.23	+0.93	+0.82	+0.68	+0.63	+0.58
15	_	$+1.43^{[e]}$	$+0.92^{[c]}$	$+0.83^{[c]}$	$+0.70^{[c]}$	+0.59	+0.57
16	+1.35 <sup>[e]</sup>	+0.96	$+0.87^{[d]}$	$+0.69^{[c]}$	$+0.62^{[c]}$	+0.52	+0.50

[a]  $E_{1/2}$  of Fc<sup>+</sup>/Fc is +0.54 V versus Ag/AgCl (saturated). [b] The  $E_{1/2}$  of Ox1 of five-coordinate porphyrinatozinc. [c] Estimated half-wave potential by deconvoluting the overlapped CV. [d] Multiple electron transfer involved. [e] Peak potential of an irreversible wave.



In our previous study of the porphyrinatozinc core dendrimers, we were able to deconvolute the overlapping CV by introducing N-methylimidazole (N-MeIm) as an axial ligand.<sup>[6]</sup> Imidazole is a strong nitrogenous base that, ligated with porphyrinatozinc, would cause a cathodic shift in the potential for first porphyrinatozinc oxidation.<sup>[14]</sup> Thus, N-MeIm is useful to differentiate the oxidation site of Por-TPA conjugates. After ligating with electron-rich N-MeIm, the CVs of Por-TPA conjugates all exhibit a cathodic shift in the first oxidation potential (Ox1' in Table 2; Figures S22 and S23 in the Supporting Information). The observation indicates that the Ox1 of four-coordinate Por-TPA conjugates belongs to the first ring oxidation of porphyrins. For example, Figure 5 is the CV of 13 in the presence of N-MeIm. As N-MeIm is added to the solution, the half-wave potentials exhibit a cathodic shift for Ox1 and an anodic shift for Ox3. Ox2, however, remains unchanged in potential. These observations indicate that Ox1 and Ox3 are due to the porphyrin-ring oxidations and that Ox2 is the oxidation at TPA. The first half-wave potentials of N-MeImligated TPA-Por conjugates (Ox1') are summarized in Table 2.



Figure 5. Cyclic voltammograms of Por–TPA conjugate **13** in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M TBAP. Scan rate: 0.1 V s<sup>-1</sup>. Molar concentration of **13** is  $1.0 \times 10^{-3}$  M; [*N*-MeIm]: (a) 0, (b)  $2.5 \times 10^{-4}$ , (c)  $5.0 \times 10^{-4}$ ; (d)  $7.5 \times 10^{-4}$ , and (e)  $1.0 \times 10^{-3}$  M.

The effects of the substituent at TPA on the oxidation potential of Por–TPA conjugates were also examined by CV. In Figure 6, the CVs of mono-TPA-bound conjugates 1, 5, 9, and 13 clearly show three redox couples in their oxidations, including two electrons removed from the porphyrin ring and one electron removed from the nitrogen atom of TPA derivatives. For the above compounds, the first oxidation potentials are at +0.82, +0.79, +0.75, and +0.74 V, respectively. Addition of *N*-MeIm causes the potential shifts to +0.72, +0.65, +0.64, and +0.60 V, respectively. It is thus inferred that the first oxidation sites of Por–TPA conjugates 1, 5, 9, and 13 are all at the porphyrin ring.

The second oxidation potentials of compounds 5, 9, and 13 remain unchanged upon *N*-MeIm addition and are thus assigned as their respective TPA oxidation. However, the second oxidation of compound 1 shifts concurrently to a more anodic potential, the third oxidation of which remains unchanged. Thus, the Ox1 and Ox2 of conjugate 1 are attributed to the first and second porphyrin-ring oxidations. Namely, the strong electron-withdrawing nitro groups attached to the *para* positions of TPA cause the TPA group to be more difficult to oxidize than porphyrin ring. Clearly,



Figure 6. Cyclic voltammograms of mono-substituted Por–TPA conjugates (a) 1, (b) 5, (c) 9, and (d) 13 in  $CH_2Cl_2$  containing 0.1 M TBAP. Scan rate: 0.1 Vs<sup>-1</sup>. Molar concentrations of conjugates:  $1.0 \times 10^{-3}$  M.

the nature of substituent at the *para* positions of TPA directly affects the oxidation potential of TPA more than that of porphyrinatozinc. Electron-donating methyl and methoxy groups of conjugates **9** and **13** cause both the first ring oxidation of porphyrin and nitrogen atom to be easier to oxidize than conjugate **5**, whereas the strong electron-withdrawing nitro group of conjugate **1** has the opposite effect.

In the studies of Por–TPA conjugates, we found that both substituent effect and the number of bound TPA derivatives significantly affect the oxidation potentials of TPA and the porphyrin ring. Generally, the porphyrinatozinc ring is oxidized first, and the electron-donating substituents at the *para* position of TPA cause a cathodic shift in potential of Ox1, whereas electron-withdrawing groups cause the opposite effect. Furthermore, since triphenylamine itself is an electron-donating group, the presence of methoxy groups will enhance the effect on oxidation potential in the same direction. However, the presence of electron-withdrawing groups such as Cl and NO<sub>2</sub> will decrease the electron-donating capability of triphenylamine. For example, conjugate **4** is harder to oxidize by 0.06 V than conjugate **8**, but it is easier to oxidize than **ZnTMP** (Table 2).

Based on the results of cyclic voltammetry and absorption spectra discussed above, the Por–TPA conjugate 16, which has four TPA-OCH<sub>3</sub> groups bound to porphyrinatozinc, would have the strongest electrochemical interaction between the porphyrinatozinc core and the TPA groups.



Figure 7. Spectral changes of (a) 13, (b) 14, (c) 15, and (d) 16 in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M TBAP at various applied potentials.

#### Spectroelectrochemistry

The studies of electron interaction between TPA derivatives and porphyrinatozinc were carried out by UV/Vis/ NIR spectroelectrochemistry. The spectral changes of 13–16 upon applied potentials to form their corresponding radical cation are shown in Figure 7. In Figure 7A, the diminishing Soret band at 421 nm and the formation of a specific absorption band of the porphyrin radical cation at 500-700 nm indicate that the porphyrin ring is oxidized. This result is consistent with that inferred from cyclic voltammetry. During the process of 13 oxidation to  $13^{+-}$ , the absorbance of TPA-OCH<sub>3</sub> at 307 nm decreased slightly. New bands at 754 and 1298 nm were formed and are assigned as the specific absorption of triarylamine radical cation and the intramolecular charge transfer from TPA-OCH<sub>3</sub> moiety to porphyrinatozinc, respectively.<sup>[3,6]</sup> The porphyrin ring was oxidized first and the Por-TPA conjugate thus became an electron donor-acceptor complex in which the electronrich TPA-OCH<sub>3</sub> moiety would transfer its electron cloud to the porphyrin ring, which lacks an electron after oxidation. The new charge-transfer band at the NIR region is evidence of the electronic interaction between the porphyrinatozinc radical cation and the TPA-OCH<sub>3</sub> moiety. Similar phenomena were also observed in the absorption spectra of conjugates 14-16 upon oxidation (Figure 7, B-D). The spectroscopic data of charge-transfer bands of the radical cation spectra of Por-TPA conjugates are summarized in Table 3. In the radical cation spectra of mono- and bis(TPA-NO<sub>2</sub>)bound zinc complexes 1 and 2, there are no charge-transfer bands in the region of 900-2200 nm. Apparently, the presence of strong electron-donating methoxy groups can pro-

Table 3. Absorption maximum  $(\lambda_{abs})$  [nm] with molar extinction coefficients ( $\epsilon$ ) [mol<sup>-1</sup>dm<sup>3</sup>cm<sup>-1</sup>], full width at half-maximum height (fwhm) [cm<sup>-1</sup>], and oscillator strength (f)<sup>[a]</sup> of the radical cation spectra of Por–TPA conjugates in CH<sub>2</sub>Cl<sub>2</sub>.

	G 1	2		C 1	
	meso-Substituents	$\lambda_{\rm abs}$	3	fwhm	$f^{[a]}$
1	$(TPA-NO_2)_1$	_[b]	_[b]	_[b]	_[b]
2	$(TPA-NO_2)_2$	_[b]	_[b]	_[b]	_[b]
3	$(TPA-NO_2)_3$	994	6196	3818	0.077
4	(TPA-Cl) <sub>4</sub>	1226	23435	3131	0.243
5	(TPA) <sub>1</sub>	1254	5086	3680	0.045
6	$(TPA)_2$	1262	10530	3537	0.102
7	(TPA) <sub>3</sub>	1190	11044	2398	0.077
8	$(TPA)_4$	1243	24063	3137	0.240
9	(TPA-CH <sub>3</sub> ) <sub>1</sub>	1338	6757	2910	0.057
10	$(TPA-CH_3)_2$	1290	15534	2753	0.145
11	(TPA-CH <sub>3</sub> ) <sub>3</sub>	1264	8459	2984	0.076
12	(TPA-CH <sub>3</sub> ) <sub>4</sub>	1296	30093	3673	0.340
13	(TPA-OCH <sub>3</sub> ) <sub>1</sub>	1298	7766	5681	0.106
14	$(TPA-OCH_3)_2$	1350	18252	2877	0.173
15	(TPA-OCH <sub>3</sub> ) <sub>3</sub>	1610	9524	4116	0.116
16	(TPA-OCH <sub>3</sub> ) <sub>4</sub>	1418	40107	4715	0.530

[a] Taken from the literature<sup>[15]</sup>. Oscillator strength  $(f) = 4.319 \times 10^{-9}$  A/n, for which A = integrated area of peak and n = refractive index of CH<sub>2</sub>Cl<sub>2</sub>. Using the plot of  $\varepsilon$  versus cm<sup>-1</sup> to obtain the integrated area (A) of each absorption peak in the spectrum. [b] No absorption band present in the region of 900–2200 nm.

mote the charge-transfer process, and methyl groups or hydrogen atoms have less effect on it. On the other hand, the strong electron-withdrawing nitro groups would pull the electron cloud of the nitrogen atom of TPA away from the porphyrin ring and make it more difficult for charge transfer to proceed.

The oscillator strengths<sup>[15]</sup> (f) of charge-transfer bands of that tri-TPA-substituted conjugates are much less than those of di- and tetra-TPA-substituted conjugates in their respective radical cation forms. These results may be attributed to their low symmetry. Conjugate **4** has a high f value of 0.243 even though chlorine possesses electron-with-drawing property. This could interpret that the number of bonded TPA groups is the major effect on the electronic properties of porphyrinatozinc again.

### Conclusion

A series of Por-TPA conjugates have been synthesized and characterized by spectral and electrochemical methods. The absorption spectra of Por-TPA conjugates exhibit broadening of Soret band, intensifying of the O(0,0) band, and redshifting of both Soret and Q bands as more TPA derivatives bond to porphyrinatozinc. These phenomena indicate the strong electronic interaction between porphyrin and triphenylamine moieties. In the emission spectroscopy study, the intramolecular energy transfer was found in all Por-TPA conjugates. When TPA moieties were excited, they would transfer energy to the porphyrinatozinc core from which fluorescence occurred. Due to the antenna effect found in these conjugates, an enhancement in quantum efficiency can be observed as the number of TPA derivatives increases. In cyclic voltammetry, more TPA groups in the Por-TPA conjugate cause more oxidation centers to be present in the molecular structure. We have characterized the Ox1 of each Por-TPA conjugate as the oxidation site. The porphyrin-ring oxidation has been identified by utilizing the N-MeIm ligation effect and spectroelectrochemical methods. In the radical cation absorption spectra of Por-TPA conjugates, the oscillator strength describes the intensity of charge-transfer bands in the NIR region. The Por-TPA conjugate that has a higher symmetry, more bound TPA groups, and stronger electron-donating at the para position of TPA would have a more intense charge-transfer band, which accounts for a stronger interaction.

#### **Experimental Section**

**General:** <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained with a Bruker Avance-III 300 spectrometer. A Varian Cary-50 scanning UV/Vis spectrometer was used to determine extinction coefficients of Por– TPA conjugates and to obtain absorption spectra with a 1 cm cuvette. Mass spectra were obtained with Applied Biosystem Voyager-DETM Pro spectrometer. Emission spectra, excitation profiles, and fluorescence quantum yield measurements were completed with a Varian Cary Eclipse spectrometer. For electrochemical studies, a CHI 700A electroanalytical workstation was used for cyclic voltammetry and conducted with a three-electrode cell. Glassy carbon

electrode (area: 0.07 cm<sup>2</sup>) was used as working electrode. The auxiliary and reference electrodes were platinum wire and Ag/AgCl (aqueous satd. KCl), 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 (aqueous satd. KCl) were used as working, auxiliary, and reference electrodes, respectively, in a spectroelectrochemical cell with an 1 mm optical path length.

Materials: Tetramesitylporphyrinatozinc (ZnTMP),<sup>[16]</sup> 5-(4-aminophenyl)-10,15,20-trimesitylporphyrinatozinc [Zn(AP)(mesityl)<sub>3</sub>P],<sup>[17]</sup> 5,15-bis(4-aminophenyl)-10,20-dimesitylporphyrinatozinc [Zn-(AP)<sub>2</sub>(mesityl)<sub>2</sub>P],<sup>[18]</sup> and tetrakis(4-aminophenyl)porphyrinatozinc (ZnTAPP)<sup>[19]</sup> were synthesized according to literature methods, the metalation was performed with zinc acetate dihydrate in CH<sub>2</sub>Cl<sub>2</sub>/ CH<sub>3</sub>OH. N,N-Bis(4-methoxyphenyl)phenylamine (TPA-OCH<sub>3</sub>) was obtained from the literature method.<sup>[20]</sup> N,N-Bis(4-nitrophenyl)phenylamine (TPA-NO<sub>2</sub>) was synthesized by modifying the literature method,<sup>[21]</sup> in which 3,4-dimethylaniline was replaced by aniline. Except for nitro-containing compounds, N,N-bis(4-methylphenyl)phenylamine (TPA-CH<sub>3</sub>),<sup>[22]</sup> N,N-bis(4-chlorophenyl)phenylamine (TPA-Cl),<sup>[23]</sup> and Por-TPA derivatives were obtained by means of the Ullmann reaction.<sup>[24]</sup> Other chemicals were all commercially available. Organic solvents used in electrochemical studies were dried and distilled before use. TBAP was recrystallized twice from ethyl acetate (EA) and dried before use.

General Procedures in Synthesis of Por-TPA Conjugates: The synthetic routes of Por-TPA are shown in Scheme 1. Generally, the amino compound and the corresponding iodo compound were added into a reaction vessel that contained copper powder, potassium carbonate, 18-crown-6, and o-dichlorobenzene (2-3 mL). The reaction mixture was heated to reflux with stirring for 24 h under N2 atmosphere. After the reaction was complete, the mixture was cooled to room temperature, then filtered and washed with CH<sub>2</sub>Cl<sub>2</sub>. The filtrate was passed through a silica gel column. In general, hexane was used as the first eluent to elute o-dichlorobenzene. Next, hexane/CH<sub>2</sub>Cl<sub>2</sub> mixed solvent was used to obtain each target compound. For tri-TPA-substituted Por-TPA conjugates, CH<sub>2</sub>Cl<sub>2</sub>/ EA was necessary to use as final eluent. Nitro-containing Por-TPA conjugates were synthesized by treating 4-fluoronitrobenzene with the corresponding amino compound in the presence of cesium fluoride (CsF) in DMSO (5 mL). The reaction was performed at 140 °C for 24 h under N<sub>2</sub>. The reaction mixture was cooled, poured into chilled water, and stirred for 2 h with an ice bath. The crude product was then collected by filtration and dried in vacuo. Further purifications are described individually in the following sections.

**5,10,15-Tris(4-aminophenyl)-20-mesitylporphyrinatozinc** [Zn(AP)<sub>3</sub>-(mesityl)P]: The precursor 5-mesityl-10,15,20-tris(4-nitrophenyl)-porphyrin free base was obtained from the condensation of mesityl-aldehyde (0.37 g, 2.50 mmol) and 4-nitrobenzaldehyde (1.14 g, 7.50 mmol) with pyrrole (0.70 mL, 10.00 mmol) by using the same



Scheme 1. Synthetic routes for Por-TPA conjugates.



reaction conditions of H<sub>2</sub>TMP.<sup>[16]</sup> The crude solid first underwent soxhlet extraction with MeOH to wash the black substance away. Then acetone was used to wash H<sub>2</sub>TMP, mono- and di-nitrophenyl-substituted porphyrin free base out of the crude solid. The tri- and tetra-nitrophenylporphyrin free bases remained in the thimble. These nitrophenylporphyrin mixtures were then reduced directly by using stannous chloride.<sup>[19]</sup> The resulting mixtures of aminophenylporphyrins were dissolved in CH<sub>2</sub>Cl<sub>2</sub> and chromatographed by silica gel column with CH2Cl2/EA mixed solvent as eluent. 5,10,15-Tris(4-aminophenyl)-20-mesitylporphyrin free base [H<sub>2</sub>(AP)<sub>3</sub>(mesityl)P] was obtained; yield 0.23 g, 13%. Zn(AP)<sub>3</sub>(mesityl)P was obtained by metalating H<sub>2</sub>(AP)<sub>3</sub>(mesityl)P with zinc acetate dihydrate in CH<sub>2</sub>Cl<sub>2</sub>/MeOH; yield 0.20 g, 78%. <sup>1</sup>H NMR (300 MHz,  $[D_6]DMSO$ ):  $\delta = 8.82-8.80$  (a singlet overlapping with a doublet, 6 H, pyrrolic H), 8.50 [d, J(H,H) = 4.5 Hz, 2 H, pyrrolic H], 7.79 [d, J(H,H) = 7.8 Hz, 6 H, Ar–H], 7.29 (s, 2 H, Ar–H), 6.94 [d, J(H,H) = 8.0 Hz, 6 H, Ar-H], 5.46 (s, 6 H, NH<sub>2</sub>), 2.57 (s, 3 H, CH<sub>3</sub>), 1.76 (s, 6 H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (75 MHz, [D<sub>6</sub>]-DMSO):  $\delta = 149.87, 149.73, 148.69, 147.99, 139.49, 138.47, 136.71,$ 135.18, 132.13, 131.37, 130.34, 130.21, 129.47, 127.57, 121.37, 120.72, 116.94, 112.98, 112.27, 109.59, 21.54, 21.10 ppm. MS (FAB<sup>+</sup>): *m*/*z* calcd. for C<sub>47</sub>H<sub>37</sub>N<sub>7</sub>Zn: 763.24; found 763.3.

5-[4-{Bis(4-nitrophenyl)amino}phenyl]-10,15,20-trimesitylporphyrinatozinc (1): Zn(AP)(mesityl)<sub>3</sub>P (50.0 mg, 0.061 mmol), 4fluoronitrobenzene (34.6 mg, 0.245 mmol), CsF (185.5 mg, 1.221 mmol). The crude product was dissolved and passed through a silica gel column. The final product can be obtained by using hexane and CH<sub>2</sub>Cl<sub>2</sub> mixed solvent as eluent; yield 0.04 g, 64%. <sup>1</sup>H NMR (300 MHz,  $CD_2Cl_2$ ):  $\delta = 8.99$  [d, J(H,H) = 4.6 Hz, 2 H, pyrrolic H], 8.81 [d, J(H,H) = 4.6 Hz, 2 H, pyrrolic H], 8.72 (s, 4 H, pyrrolic H), 8.33-8.29 [dd, J(H,H) = 8.4 and 9.2 Hz, 6 H, Ar-H], 7.59 [d, J(H,H) = 8.3 Hz, 2 H, Ar–H], 7.51 [d, J(H,H) = 9.2 Hz, 4 H, Ar-H], 7.31 and 7.30 (two overlapping singlets, 6 H, Ar-H), 2.63 and 2.62 (two overlapping singlets, 9 H, CH<sub>3</sub>), 1.85 (s, 18 H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>): *δ* = 152.54, 150.41, 150.18, 150.06, 144.69, 143.44, 142.03, 139.54, 139.31, 139.23, 138.00, 136.65, 132.11, 131.57, 131.47, 131.03, 128.02, 125.99, 125.42, 123.30, 119.40, 119.00, 21.78, 21.74, 21.55 ppm. MS (FAB<sup>+</sup>): *m*/*z* calcd. for C<sub>65</sub>H<sub>53</sub>N<sub>7</sub>O<sub>4</sub>Zn: 1059.35; found 1060.6.

**5,15-Bis[4-{bis(4-nitrophenyl)amino}phenyl]-10,20-dimesitylporphyrinatozinc (2):** Zn(AP)<sub>2</sub>(mesityl)<sub>2</sub>P (70.0 mg, 0.088 mmol), 4fluoronitrobenzene (500.0 mg, 3.544 mmol), CsF (810.0 mg, 5.332 mmol). The crude was washed by acetone and CH<sub>2</sub>Cl<sub>2</sub> until yellow filtrate became reddish brown. The solid maintain on filter paper is the final product; yield 0.02 g, 18%. <sup>1</sup>H NMR (300 MHz, [D<sub>7</sub>]DMF):  $\delta$  = 8.99 [d, *J*(H,H) = 4.7 Hz, 4 H, pyrrolic H], 8.71 [d, *J*(H,H) = 4.4 Hz, 4 H, pyrrolic H], 8.43–8.36 [dd, *J*(H,H) = 9.1 and 8.1 Hz, 12 H, Ar–H], 7.79 [d, *J*(H,H) = 7.8 Hz, 4 H, Ar–H], 7.72 [d, *J*(H,H) = 9.3 Hz, 8 H, Ar–H], 7.40 (s, 4 H, Ar–H), 2.65 (s, 6 H, CH<sub>3</sub>), 1.88 (s, 12 H, CH<sub>3</sub>) ppm. MS (FAB<sup>+</sup>): *m/z* calcd. for C<sub>74</sub>H<sub>54</sub>N<sub>10</sub>O<sub>8</sub>Zn: 1274.34; found 1276.3. Due to the solubility problem, we could not obtain a <sup>13</sup>C spectrum.

**5,10,15-Tris[4-{bis(4-nitrophenyl)amino}phenyl]-20-mesitylporphyrinatozinc (3):** Zn(AP)<sub>3</sub>(mesityl)P (75.0 mg, 0.098 mmol), 4fluoronitrobenzene (186.0 mg, 1.318 mmol), CsF (980.0 mg, 6.451 mmol). The crude product was dissolved and passed through a silica gel column. The final product can be obtained by using CH<sub>2</sub>Cl<sub>2</sub> as eluent; yield 0.04 g, 24%. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 9.12 (s, 4 H, pyrrolic H), 9.04 [d, *J*(H,H) = 4.7 Hz, 2 H, pyrrolic H], 8.87 [d, *J*(H,H) = 4.7 Hz, 2 H, pyrrolic H], 8.34–8.29 (m, 18 H, Ar–H), 7.64–7.59 (m, 6 H, Ar–H), 7.54–7.49 (m, 12 H, Ar–H), 7.34 (s, 2 H, Ar–H), 2.66 (s, 3 H, CH<sub>3</sub>), 1.84 (s, 6 H, CH<sub>3</sub>) ppm. MS (FAB<sup>+</sup>): m/z calcd. for  $C_{83}H_{55}N_{13}O_{12}Zn$ : 1489.34; found 1490.2. Due to the solubility problem, we could not obtain a <sup>13</sup>C spectrum.

**5,10,15,20-Tetrakis**[**4-{bis(4-chlorophenyl)amino}phenyl]**porphyrinatozinc (**4**): Zn(AP)<sub>4</sub>P (0.10 g, 0.135 mmol), 1-chloro-4iodobenzene (2.58 g, 10.837 mmol), Cu (0.69 g, 10.837 mmol),  $K_2CO_3$  (1.31 g, 9.450 mmol), [18]crown-6 (0.11 g, 0.410 mmol); yield 0.12 g, 53%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.08 (s, 8 H, pyrrolic H), 8.11 [d, *J*(H,H) = 8.4 Hz, 8 H, Ar–H], 7.45–7.31 (m, 40 H, Ar–H) ppm. <sup>13</sup>C NMR (75 MHz, [D<sub>7</sub>]DMF):  $\delta$  = 150.67, 147.23, 147.10, 139.09, 136.56, 132.25, 130.47, 128.30, 126.52, 122.84, 120.87 ppm. MS(MALDI-TOF): *m/z* calcd. for C<sub>92</sub>H<sub>56</sub>N<sub>8</sub>O<sub>8</sub>Zn: 1621.14; found 1621.59.

**5-[4-(Diphenylamino)phenyl]-10,15,20-trimesityporphyrinatozinc (5):** Zn(AP)-(mesityl)<sub>3</sub>P (20.0 mg, 0.024 mmol), iodobenzene (15.3 mg, 0.075 mmol), Cu (4.8 mg, 0.075 mmol), K<sub>2</sub>CO<sub>3</sub> (6.9 mg, 0.050 mmol), [18]crown-6 (6.6 mg, 0.025 mmol); yield 0.02 g, 70%. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 9.02 [d, *J*(H,H) = 4.7 Hz, 2 H, pyrrolic H], 8.76 [d, *J*(H,H) = 4.6 Hz, 2 H, pyrrolic H], 8.68 (s, 4 H, pyrrolic H), 8.08 [d, *J*(H,H) = 8.3 Hz, 2 H, Ar–H], 7.44–7.39 (m, 10 H, Ar–H), 7.30 (s, 6 H, Ar–H), 7.12 [t, *J*(H,H) = 4.3 Hz, 2 H, Ar–H], 2.62 (s, 9 H, CH<sub>3</sub>), 1.83 (s, 18 H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 150.06, 149.80, 149.75, 149.68, 147.98, 147.08, 143.34, 139.30, 137.25, 137.14, 135.70, 135.30, 132.04, 131.19, 130.94, 130.41, 129.71, 129.41, 128.73, 127.57, 127.16, 124.67, 123.04, 121.78, 121.48, 119.84, 118.88, 118.57, 118.22, 21.67, 21.45 ppm. MS (FAB<sup>+</sup>): *m*/*z* calcd. for C<sub>65</sub>H<sub>55</sub>N<sub>5</sub>Zn: 969.37; found 970.4.

**5,15-Bis[4-(diphenylamino)phenyl]-10,20-dimesitylporphyrinatozine** (**6**): Zn-(AP)<sub>2</sub>(mesityl)<sub>2</sub>P (150.0 mg, 0.189 mmol), 4-iodobenzene (385.0 mg, 1.887 mmol), Cu (150.0 mg, 2.360 mmol), K<sub>2</sub>CO<sub>3</sub> (260.0 mg, 1.881 mmol), [18]crown-6 (16.0 mg, 0.061 mmol); yield 0.09 g, 42%. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 9.04 [d, *J*(H,H) = 3.9 Hz, 4 H, pyrrolic H], 8.78 [d, *J*(H,H) = 3.7 Hz, 4 H, pyrrolic H], 8.08 [d, *J*(H,H) = 7.9 Hz, 4 H, Ar–H], 7.44–7.40 (m, 20 H, Ar–H), 7.31 (s, 4 H, Ar–H), 7.13 (t, 4 H, Ar–H), 2.64 (s, 6 H, CH<sub>3</sub>), 1.83 (s, 12 H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 150.29, 149.85, 147.94, 147.22, 139.29, 139.10, 137.42, 136.70, 135.30, 132.33, 130.67, 129.45, 127.63, 124.77, 123.14, 121.39, 120.09, 119.19, 21.61, 21.48 ppm. MS (FAB<sup>+</sup>): *m/z* calcd. for C<sub>74</sub>H<sub>58</sub>N<sub>6</sub>Zn: 1094.4; found 1096.3.

**5,10,15-Tris**[4-(diphenylamino)phenyl]-20-mesitylporphyrinatozinc (7): Zn-(AP)<sub>3</sub>(mesityl)P (140.0 mg, 0.183 mmol), iodobenzene (12.0 g, 0.059 mol), Cu (0.8 g, 0.013 mol), K<sub>2</sub>CO<sub>3</sub> (1.54 g, 0.011 mol), [18]crown-6 (44.4 mg, 0.168 mmol); yield 0.09 g, 41%. <sup>1</sup>H NMR (300 MHz, [D<sub>6</sub>]DMSO):  $\delta$  = 8.91–8.87 (a singlet overlapping with a doublet, 6 H, pyrrolic H), 8.59 [d, *J*(H,H) = 4.6 Hz, 2 H, pyrrolic H], 8.06 [d, *J*(H,H) = 8.2 Hz, 6 H, Ar–H], 7.47–7.31 (m, 32 H, Ar–H), 7.15 [t, *J*(H,H) = 7.1 Hz, 6 H, Ar–H], 2.58 (s, 3 H, CH<sub>3</sub>), 1.77 (s, 6 H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 150.26, 149.89, 147.87, 147.18, 139.27, 139.04, 137.41, 136.85, 136.70, 135.43, 135.37, 132.43, 131.85, 130.76, 129.45, 127.64, 124.73, 123.11, 121.44, 121.36, 120.93, 120.47, 119.11, 21.73, 21.50 ppm. MS (FAB<sup>+</sup>): *m*/*z* calcd. for C<sub>83</sub>H<sub>61</sub>N<sub>7</sub>Zn: 1219.43; found 1221.3.

**5-[4-(Ditolylamino)phenyl]-10,15,20-trimesitylporphyrinatozinc (9):** Zn-(AP)(mesityl)<sub>3</sub>P (50.0 mg, 0.061 mmol), 4-iodotoluene (106.4 mg, 0.488 mmol), Cu (31 mg, 0.488 mmol), K<sub>2</sub>CO<sub>3</sub> (56.2 mg, 0.407 mmol), [18]crown-6 (16.1 mg, 0.061 mmol); yield 0.05 g, 78%. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 9.03 [d, *J*(H,H) = 4.6 Hz, 2 H, pyrrolic H], 8.75 [d, *J*(H,H) = 4.6 Hz, 2 H, pyrrolic H], 8.04 [d, *J*(H,H) = 8.5 Hz, 2 H, Ar–H], 7.37–

7.20 (m, 16 H, Ar–H), 2.63 and 2.61 (two singlet overlapped, 9 H, CH<sub>3</sub>), 2.38 (s, 6 H, CH<sub>3</sub>), 1.84 and 1.83 (two singlet overlapped, 18 H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 150.19, 149.85, 149.75, 149.69, 147.53, 145.48, 139.30, 139.13, 139.01, 137.33, 135.80, 135.14, 132.77, 132.24, 131.02, 130.45, 130.06, 127.60, 125.01, 120.28, 120.16, 118.70, 118.30, 21.73, 21.66, 21.47, 20.90 ppm. MS (FAB<sup>+</sup>): *m*/*z* calcd. for C<sub>67</sub>H<sub>59</sub>N<sub>5</sub>Zn: 997.41; found 998.6.

**5,15-Bis**[4-(ditolylamino)phenyl]-10,20-dimesitylporphyrinatozinc (10):  $Zn(AP)_2(mesityl)_2P$  (150.0 mg, 0.189 mmol), 4-iodotoluene (410.0 mg, 1.880 mmol), Cu (150.0 mg, 2.360 mmol), K<sub>2</sub>CO<sub>3</sub> (260.0 mg, 1.881 mmol), [18]crown-6 (16.0 mg, 0.061 mmol); yield 0.09 g, 41%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.03 [d, *J*(H,H) = 4.7 Hz, 4 H, pyrrolic H], 8.78 [d, *J*(H,H) = 4.6 Hz, 4 H, pyrrolic H], 8.04 [d, *J*(H,H) = 8.5 Hz, 4 H, Ar–H], 7.38 [d, *J*(H,H) = 8.5 Hz, 4 H, Ar–H], 7.20 [d, *J*(H,H) = 8.3 Hz, 8 H, Ar–H], 2.65 (s, 6 H, CH<sub>3</sub>), 2.39 (s, 12 H, CH<sub>3</sub>), 1.84 (s, 12 H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 150.36, 149.79, 147.58, 145.48, 139.30, 139.15, 137.37, 135.68, 135.18, 132.80, 132.36, 130.57, 130.07, 127.61, 125.05, 120.26, 120.12, 119.09, 21.61, 21.48, 20.90 ppm. MS (FAB<sup>+</sup>): *m*/z calcd. for C<sub>78</sub>H<sub>66</sub>N<sub>6</sub>Zn: 1150.46; found 1151.4.

**5,10,15-Tris[4-(ditolylamino)phenyl]-20-mesitylporphyrinatozinc** (11): Zn-(AP)<sub>3</sub>(mesityl)P (0.12 g, 0.157 mmol), 4-iodotoluene (2.70 g, 0.013 mol), Cu (0.69 g, 0.011 mol), K<sub>2</sub>CO<sub>3</sub> (1.32 g, 9.551 mmol), [18]crown-6 (0.04 g, 0.144 mmol); yield 0.10 g, 48%. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 9.12 (s, 4 H, pyrrolic H), 9.06 [d, *J*(H,H) = 4.7 Hz, 2 H, pyrrolic H], 8.78 [d, *J*(H,H) = 4.7 Hz, 2 H, pyrrolic H], 8.78 and 8.5 Hz, 6 H, Ar-H], 7.40–7.21 (m, 32 H, Ar–H), 2.64 (s, 3 H, CH<sub>3</sub>), 2.38 (s, 18 H, CH<sub>3</sub>), 1.84 (s, 6 H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 150.70, 150.16, 148.03, 145.77, 139.52, 137.89, 136.07, 135.95, 135.65, 135.58, 133.38, 132.73, 132.10, 130.83, 130.40, 127.96, 125.44, 121.46, 121.03, 120.30, 119.31, 21.76, 21.54, 20.96 ppm. MS (FAB<sup>+</sup>): *m/z* calcd. for C<sub>89</sub>H<sub>73</sub>N<sub>7</sub>Zn: 1303.52; found 1304.4.

5-[4-{Bis(4-methoxyphenyl)amino}phenyl]-10,15,20-trimesitylporphyrinatozinc (13): Zn(AP)(mesityl)<sub>3</sub>P (50.0 mg, 0.061 mmol), 4iodoanisole (114.2 mg, 0.488 mmol), Cu (31.0 mg, 0.488 mmol), K<sub>2</sub>CO<sub>3</sub> (56.2 mg, 0.407 mmol), [18]crown-6 (16.1 mg, 0.061 mmol); yield 0.05 g, 74%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.01 [d, J(H,H) = 4.6 Hz, 2 H, pyrrolic H], 8.77 [d, J(H,H) = 4.6 Hz, 2 H, pyrrolic H], 8.69 (s, 4 H, pyrrolic H), 8.00 [d, J(H,H) = 8.4 Hz, 2 H, Ar-H], 7.35 [d, J(H,H) = 8.9 Hz, 4 H, Ar-H], 7.30-7.26 (a doublet and a singlet overlapping with solvent peak, 8 H, Ar-H),  $6.95 \text{ [d, } J(\text{H},\text{H}) = 8.9 \text{ Hz}, 4 \text{ H}, \text{ Ar-H]}, 3.84 \text{ (s, } 6 \text{ H}, \text{ OCH}_3), 2.64$ and 2.62 (two singlets overlapped, 9 H, CH<sub>3</sub>), 1.85 (s, 18 H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 156.02, 150.30, 149.87, 149.76, 148.09, 141.19, 139.33, 139.19, 139.05, 137.32, 135.11, 134.81, 132.28, 130.99, 130.40, 127.61, 126.90, 120.47, 118.68, 118.32, 114.89, 114.20, 55.55, 21.72, 21.65, 21.46 ppm. MS (FAB<sup>+</sup>): m/z calcd. for C<sub>67</sub>H<sub>59</sub>N<sub>5</sub>O<sub>2</sub>Zn: 1029.4; found 1029.6.

**5,15-Bis[4-{bis(4-methoxyphenyl)amino}phenyl]-10,20-dimesitylporphyrinatozinc (14):**  $Zn(AP)_2(mesityl)_2P$  (100.0 mg, 0.126 mmol), 4-iodoanisole (275.0 mg, 1.175 mmol), Cu (96.0 mg, 1.511 mmol), K<sub>2</sub>CO<sub>3</sub> (139.5 mg, 1.009 mmol), [18]crown-6 (16.0 mg, 0.061 mmol); yield 0.05 g, 31%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.02 [d, *J*(H,H) = 4.6 Hz, 4 H, pyrrolic H], 8.77 [d, *J*(H,H) = 4.7 Hz, 4 H, pyrrolic H], 8.01 [d, *J*(H,H) = 8.5 Hz, 4 H, Ar–H], 7.35 [d, *J*(H,H) = 8.9 Hz, 8 H, Ar–H], 7.30–7.27 (a doublet overlapping with a singlet, 8 H, Ar–H), 6.95 [d, *J*(H,H) = 8.9 Hz, 8 H, Ar–H], 3.84 (s, 12 H, OCH<sub>3</sub>), 2.65 (s, 6 H, CH<sub>3</sub>), 1.83 (s, 12 H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 156.02, 150.44, 149.74, 148.08, 141.14, 139.31, 139.20, 137.35, 135.15, 134.63, 132.38, 130.50, 127.60, 126.94, 120.37, 119.01, 118.22, 114.87, 55.54, 21.61, 21.48 ppm. MS (FAB<sup>+</sup>): m/z calcd. for  $C_{78}H_{66}N_6O_4Zn$ : 1214.44; found 1214.4.

**5,10,15-Tris[4-{bis(4-methoxyphenyl)amino}phenyl]-20-mesitylporphyrinatozinc (15):** Zn(AP)<sub>3</sub>(mesityl)P (0.12 g, 0.157 mmol), 4iodoanisole (2.97 g, 0.013 mol), Cu (0.69 g, 0.011 mol), K<sub>2</sub>CO<sub>3</sub> (1.32 g, 9.551 mmol), [18]crown-6 (0.04 g, 0.144 mmol); yield 0.07 g, 33%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.09 (s, 4 H, pyrrolic H), 9.04 [d, *J*(H,H) = 4.6 Hz, 2 H, pyrrolic H], 8.78 [d, *J*(H,H) = 4.7 Hz, 2 H, pyrrolic H], 8.01 [d, *J*(H,H) = 8.4 Hz, 6 H, Ar–H], 7.37–7.28 (m, 20 H, Ar–H), 6.95 [d, *J*(H,H) = 8.9 Hz, 12 H, Ar– H], 3.83 (s, 18 H, OCH<sub>3</sub>), 2.65 (s, 3 H, CH<sub>3</sub>), 1.84 (s, 6 H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 155.95, 150.39, 150.35, 150.29, 149.78, 148.05, 141.10, 139.31, 139.16, 137.33, 135.27, 135.22, 134.85, 134.68, 132.41, 131.78, 130.53, 127.59, 126.93, 121.23, 120.69, 118.78, 118.22, 118.17, 114.84, 55.52, 21.69, 21.48 ppm. MS (FAB<sup>+</sup>): *m*/*z* calcd. for C<sub>89</sub>H<sub>73</sub>N<sub>7</sub>O<sub>6</sub>Zn: 1399.49; found 1400.7.

**Supporting Information** (see footnote on the first page of this article): <sup>1</sup>H NMR spectra, absorption spectra, excitation profiles, and cyclic voltammograms of Por–TPA conjugates are shown in the Supporting Information. The emission spectra obtained from the study of antenna effect and the absorption spectra of the radical cation of Por–TPA conjugates are also shown.

## Acknowledgments

This work was supported by the National Science Council of the Republic of China (97-2113-M-260-005-MY3). We also thank Prof. Cheng for providing conjugates **8** and **12**.

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Received: September 30, 2011

Published Online: January 30, 2012