Contents lists available at SciVerse ScienceDirect





Electrochimica Acta

# journal homepage: www.elsevier.com/locate/electacta

# Unusual spectral and electrochemical properties of azobenzene-substituted porphyrins

Kuo Yuan Chiu<sup>a</sup>, Yi-Jung Tu<sup>a</sup>, Chia-Jung Lee<sup>a</sup>, Te-Fang Yang<sup>a,\*\*\*</sup>, Long-Li Lai<sup>a</sup>, Ito Chao<sup>b,\*\*</sup>, Yuhlong Oliver Su<sup>a,c,\*</sup>

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

<sup>b</sup> Institute of Chemistry, Academia Sinica, 128, Academia Road Sec. 2, Nankang, Taipei 115, Taiwan

<sup>c</sup> Department of Materials Science and Engineering, National Chung Hsing University, 250 Kuo Kuang Rd., Taichung 402, Taiwan

#### ARTICLE INFO

Article history: Received 4 October 2011 Received in revised form 15 November 2011 Accepted 17 November 2011 Available online 14 December 2011

Keywords: Azobenzene–porphyrin Cyclic voltammetry Spectroelectrochemistry DFT calculation

#### ABSTRACT

A series of azobenzene-substituted porphyrin derivatives, MPA<sub>n</sub> (M=H<sub>2</sub>, Zn; *n* = 1, 2, 4), has been prepared. These compounds were characterized by spectral and electrochemical methods. The Soret and Q bands of ZnPA<sub>n</sub> were red-shifted along with the increase of Q-band intensity ratio ( $\varepsilon_{\alpha}/\varepsilon_{\beta}$ ) as the substitution of azobenzene increased. Addition of imidazole towards ZnPA<sub>n</sub> caused a significant increase in Q band intensity ratio. A noteworthy characteristic is that the Q band intensity ratio was reversed (>1.0) by imidazole ligation for ZnPA<sub>4</sub>. Additionally, cyclic voltammetry of H<sub>2</sub>PA<sub>n</sub> exhibited anodic shift of the first oxidation potential but cathodic shift for the second oxidation potential for porphyrin free bases as azobenzene number increased. According to DFT calculation, the unusual features in UV-vis spectra and redox potentials arised mainly due to the intramolecular  $\pi$ -conjugation between porphyrin and azobenzene.

© 2011 Elsevier Ltd. All rights reserved.

# 1. Introduction

The design and synthesis of molecular devices have been the foci of intense research in recent years. Porphyrins and metalloporphyrins are commonly chosen as a basic component in electronic materials because their outstanding electrochemical and spectral properties have an amazing range for modulation via the alteration of the central metal and the peripheral substituents [1–4]. Moreover, the interaction between porphyrin and substituents influences the efficiency of energy or electron transfer so that the selection of substituents has become an important issue. A great deal of recent research has been devoted to the investigation of chromophore-linked metalloporphyrin dyads [5–8] with the hope for the construction of artificial redox and photosynthetic systems. With this objective, porphyrins are commonly functionalized with a number of redox-active chromophores, such as fullerenes [5], quinones [6], ferrocenes [7], and other porphyrins [8].

Azobenzene, one of the most important dyes, behaves in theory as an electron-withdrawing group [9] but there is no investigation using this group as an electron acceptor in molecular electronics since the original feature of azobenzene can be changed by the intramolecular electronic communication between azo group and adjacent chromophores. In contrast, azobenzenes are widely used as photoresponsive linkers [10,11] between chromophores since the E/Z photoisomerization of azobenzenes has been shown to be a useful way to regulate molecular motion in numerous photoswitchable devices [12,13]. To our knowledge, there are some reports on the physical properties of the azobenzene-substituted porphyrins [9,14,15], in which the fluorescence quenching have been observed, whereas other fundamental characteristics for these compounds have not been thoroughly studied.

We report herein the characterization of a new class of modified porphyrins, the azobenzene-linked free base porphyrins and the corresponding zinc complexes (Fig. 1). Azobenzene is covalently connected to the *meso*-positions of the porphine ring to form mono-, di- and tetra-substituted porphyrins. The spectral and electrochemical characteristics of the azobenzene–porphyrins have been studied using UV–vis absorption and cyclic voltammetry (CV). These results are expected to provide more comprehensive information on their chemical properties. The chemical structure of the porphyrin complexes and their abbreviations are shown in Fig. 1.

<sup>\*</sup> Corresponding author. Tel.: +886 49 2910960x4150.

<sup>\*\*</sup> Corresponding author Tel: +886 2 27898530.

<sup>\* \* \*</sup>Corresponding author Tel: +886 49 2910960x4946.

*E-mail addresses*: tfyang@ncnu.edu.tw (T.-F. Yang), ichao@chem.sinica.edu.tw (I. Chao), yosu@ncnu.edu.tw (Y.O. Su).

<sup>0013-4686/\$ -</sup> see front matter © 2011 Elsevier Ltd. All rights reserved. doi:10.1016/j.electacta.2011.11.061



MTMP  $R_1 = R_2 = R_3 = R_4$  = Mesityl



**Fig. 1.** Chemical structure of metalloporphyrins containing azobenzene and azobenzene derivative;  $M = H_2$ , Zn.

#### 2. Experimental

#### 2.1. Synthesis

In order to aid the solubility of porphyrins, the long-chain alkoxyl moiety was used on the end of the azobenzene substituent. Porphyrin free bases were prepared following Lindsey's methods [16,17]. Metallation was achieved by heating the porphyrin free base with excess zinc acetate in DMF for 2h under nitrogen [18]. Completion of the reaction was checked by the shift of the Q bands spectrophotometrically. The solution was evaporated and further purified by column chromatography on silica gel with CH<sub>2</sub>Cl<sub>2</sub>. 4-Methoxylazobenzene (CH<sub>3</sub>OAz) was prepared according to a literature method [19]. All the porphyrins were characterized by UV-vis, FAB<sup>+</sup>-HRMS, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and elemental analysis. The formation constant of five-coordinated zinc porphyrins were calculated by plot of  $\log [(A_i - A_{obs})/(A_{obs} - A_f)]$  vs. log[HIm]. Azobenzene exists possibly in E and Z forms. The E isomer is more stable and can be switched to Z form by exciting with a UV light source [14]. In order to minimize the change, the synthesis and electrochemical experiments were performed in the dark. We presumed that all of our azobenzene-porphyrins were in the E form. Even if small amount of Z-azobenzene moiety was generated during our experiments, it would thermally relax to the E form via isomerization.

#### 2.1.1. 4-(4-Hexyloxyphenylazo)benzaldehyde [20]

4-Aminobenzoaldehyde (50.0 mmol) was added to fluoroboric acid (50 wt% in H<sub>2</sub>O, 50 mL) and then sodium nitrite (60.0 mmol) was added slowly at 0 °C. The resulting mixture was kept at 0 °C and stirred for 1 h; the precipitated diazonium salt was filtered off and dried.

Phenol (10 mmol) in aqueous potassium hydroxide (KOH: 0.62 g,  $H_2O$ : 5 mL) was added to the salt (11.0 mmol) in EtOH, the solution was stirred for 3 h at room temperature. Hydrochloric acid (10%, 50 mL) was added and the solid was filtered off and chromatographed on silica gel to give 4-(4-hydoxyphenylazo)benzaldehyde.

In a sealed tube with potassium carbonate (1.0 mmol), 4-(4-hydoxyphenylazo)-benzaldehyde (1.0 mmol), DMF (6 mL) and 1-bromohexane (1.2 mmol) were added subsequently. The mixture was stirred for 20 h at 110–120 °C, aqueous sodium hydroxide solution (NaOH: 0.10 g, H<sub>2</sub>O: 50 mL) was added. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined extracts were dried (MgSO<sub>4</sub>), the solvent was removed at reduced pressure. The residue was chromatographed on silica gel to give 4-(4-hexyloxyphenylazo)benzaldehyde (yield = 53%).

#### 2.1.2. H<sub>2</sub>PA<sub>1</sub>

solution 4-(4-hexyloxyphenylazo)benzaldehyde А of (0.5 mmol), mesitylaldehyde (1.5 mmol) and pyrrole (2 mmol) in 200 mL CHCl<sub>3</sub> (7.5% EtOH) was purged with N<sub>2</sub> for 10 min, then BF<sub>3</sub>•OEt<sub>2</sub> (24 mmol) was then added. The solution was stirred for 1 h at room temperature then DDQ (1.6 mmol) was added. The mixture was stirred for an addition 1 h and then the solvent was removed. Column chromatography afforded the porphyrin as the second moving band (yield = 13%). UV/vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}/nm$ : 352, 420, 516, 551, 592, 648; HRMS (FAB<sup>+</sup>): *m*/*z* 945.5226 (M<sup>+</sup>); <sup>1</sup>H NMR (CDCl<sub>3</sub>/ppm):  $\delta$  8.815 (2H, d), 8.677 (2H, d), 8.616 (4H, s), 8.313 (2H, d), 8.223 (2H, d), 8.063 (2H, d), 7.256 (6H, s), 7.078 (2H, d), 2.603 (13H, s), 1.835 (27H, d), -2.571 (2H, s). <sup>13</sup>C NMR(CDCl<sub>3</sub>/ppm): 161.9, 152.2, 147.1, 144.2, 139.4, 138.3, 138.1, 137.7, 135.2, 127.7, 125.0, 120.8, 118.3, 118.17, 117.9, 114.8, 68.4, 31.6, 29.7, 29.2, 25.7, 22.6, 21.8, 21.7, 21.5, 14.1. Anal. Calc'd for C<sub>65</sub>H<sub>64</sub>N<sub>6</sub>O:C, 82.59; H, 6.82; N, 8.89; O, 1.69. Found:C, 82.55; H, 6.82; N, 8.88; O, 1.65.

# 2.1.3. ZnPA1

ZnPA<sub>1</sub> was obtained by metallation of H<sub>2</sub>PA<sub>1</sub> with excess zinc acetate under nitrogen in DMF for 2 h at 150 °C. Completion of the reaction was checked by the shift of the Q bands spectrophotometrically. The solution was evaporated and further purified by column chromatography on silica gel with CH<sub>2</sub>Cl<sub>2</sub>. yield = 88%. UV/vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$ /nm: 352, 421, 550, 589; HRMS (FAB<sup>+</sup>): *m*/*z* 1007.4373 (M<sup>+</sup>); <sup>1</sup>H NMR(CDCl<sub>3</sub>/ppm):  $\delta$  8.896 (2H, d), 8.751 (2H, d), 8.688 (4H, s), 8.335 (2H, d), 8.225 (2H, d), 8.063 (2H, d), 7.254 (6H, s), 7.079 (2H, d), 2.606 (13H, s), 1.838 (27H, d).

# 2.1.4. H<sub>2</sub>PA<sub>2</sub>

Pyrrole (250 mmol) and mesitaldehyde (10 mmol) were added to a dry 250-mL round-bottomed flask and degassed with a stream of  $N_2$  for 10 min.  $BF_3$ •OEt<sub>2</sub> (1 mmol) was then added, and the solution was stirred under N<sub>2</sub> at room temperature for 1 h. CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was then added, and the organic phase was washed with diluted water (500 mL) and dried (Na<sub>2</sub>SO<sub>4</sub>). The solvent was removed under vacuum to give a black oil and then cyclohexanes (100 mL) were added to precipitate a yellow solid that was filtered giving 5-mesityldipyrromethane (yield = 45%). A solution of 4-(4-hexyloxyphenylazo)benzaldehyde (4 mmol) and 5-mesityldipyrromethane (4 mmol) in 1000 mL CHCl<sub>3</sub> (7.5% EtOH) was purged with N<sub>2</sub> for 20 min, then  $BF_3 \circ OEt_2$  (100 µL) was then added. The solution was stirred for 1 h at room temperature then DDQ (6 mmol) was added. The mixture was stirred for an addition 1 h and then the solvent was removed. The solid was washed by methanol and give H<sub>2</sub>PA<sub>2</sub> (yield = 30%). UV/vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}/nm$ : 352, 422, 517, 554, 593, 649; HRMS (FAB<sup>+</sup>): *m*/*z* 1107.6010 (M<sup>+</sup>); <sup>1</sup>H NMR (CDCl<sub>3</sub>/ppm): δ 8.846 (4H, d), 8.704 (4H, d), 8.346 (4H, d), 8.237 (4H, d), 8.066 (4H, d), 7.256 (4H, d), 7.081 (4H, d), 2.609 (18H, s), 1.833 (26H, d), -2.606 (2H, s). <sup>13</sup>C NMR (CDCl<sub>3</sub>/ppm): 162.0, 152.2, 147.1, 144.1, 139.4, 138.3, 137.8, 135.3, 127.8, 125.0, 120.8, 118.6, 114.8, 68.4, 31.6, 29.7, 29.2, 25.7, 22.6, 21.6, 21.5, 14.1. Anal. Calc'd for C<sub>74</sub>H<sub>74</sub>N<sub>8</sub>O<sub>2</sub>: C, 80.26; H, 6.74; N, 10.12; O, 2.89. Found: C, 80.27; H, 6.73; N, 10.12; O, 2.79.

I aDIC I	Та	bl	e	1
----------	----	----	---	---

Absorption data and molar extinction coefficients  $\varepsilon$  (10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup>) in parentheses of azobenzene-substituted porphyrins in CH<sub>2</sub>Cl<sub>2</sub>.

	Azo	Porphyrin	
		B band	Q band
CH <sub>3</sub> OAz <sup>b</sup>	347 (2.7),433 (0.1) <sup>a</sup>		
$H_2TMP$		418 (40)	514 (1.5), 547 (0.4), 591 (0.6), 647 (0.3)
H <sub>2</sub> PA <sub>1</sub>	352 (3.2)	420 (34)	516 (1.9), 551 (0.8), 592 (0.6), 648 (0.6)
H <sub>2</sub> PA <sub>2</sub>	352 (4.7)	422 (29)	517 (1.9), 554 (1.4), 593 (0.7), 649 (1.1)
$H_2PA_4$	352 (7.9)	430 (30)	520 (2.2), 558 (1.7), 593 (0.7), 651 (0.8), 690 (0.5)
ZnTMP		421 (67)	550 (2.2), 587 (0.09)
ZnPA <sub>1</sub>	352 (2.1)	421 (31)	550 (1.7), 589 (0.3)
ZnPA <sub>2</sub> <sup>b</sup>	352 (2.4)	423 (17)	550 (1.1), 592 (0.3)
ZnPA <sub>4</sub>	352 (7.6)	431 (32)	552 (2.7), 593 (1.2)
(HIm)ZnTMP		431 (69)	567 (2.0), 606 (0.9)
(HIm)ZnPA <sub>1</sub>	352 (2.4)	432 (36)	567 (2.5), 609 (1.4)
(HIm)ZnPA <sub>2</sub>	352 (2.8)	434 (18)	567 (1.8), 614 (1.3)
(HIm)ZnPA <sub>4</sub>	352 (9.1)	441 (31)	570 (2.6), 614 (2.8)

<sup>a</sup> Shoulder.

<sup>b</sup> ZnPA<sub>2</sub> was slightly soluble in CH<sub>2</sub>Cl<sub>2</sub>.

#### 2.1.5. ZnPA<sub>2</sub>

Yield = 90%. UV/vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}/nm$ : 352, 423, 550, 592; HRMS (FAB<sup>+</sup>): m/z 1169.5156 (M<sup>+</sup>); <sup>1</sup>H NMR (CDCl<sub>3</sub>/ppm):  $\delta$  8.934 (4H, d), 8.787 (4H, d), 8.361 (4H, d), 8.237 (4H, d), 8.067 (4H, d), 7.257 (4H, d), 7.081 (4H, d), 2.612 (18H, s), 1.833 (26H, d).

#### 2.1.6. H<sub>2</sub>PA<sub>4</sub>

A solution of 4-(4-hexyloxyphenylazo)benzaldehyde (2 mmol) and pyrrole (2 mmol) in 200 mL CHCl<sub>3</sub> (7.5% EtOH) was purged with N<sub>2</sub> for 10 min, then BF<sub>3</sub>•OEt<sub>2</sub> (24 mmol) was then added. The solution was stirred for 1 h at room temperature then DDQ (1.6 mmol) was added. The mixture was stirred for an addition 1hr and then the solvent was removed. Column chromatography afforded the porphyrin as the first moving band (yield = 40%). UV/Vis(CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}/nm$ : 352, 430, 520, 558, 593, 651, 690; HRMS (FAB<sup>+</sup>): *m/z* 1431.7605 (M<sup>+</sup>); <sup>1</sup>H NMR (CDCl<sub>3</sub>/ppm):  $\delta$  8.959 (8H, s), 8.376 (8H, d), 8.280 (8H, d), 8.079 (8H, d), 7.099 (8H, d), 4.103 (8H, t), 1.871 (8H, m), 1.523, (36H, m) -2.677 (2H, s). <sup>13</sup>C NMR (CDCl<sub>3</sub>/ppm): 162.0, 152.3, 147.1, 144.1, 135.4, 125.0, 120.9, 119.7, 114.8, 68.4, 31.6, 29.2, 25.7, 22.6, 14.1. Anal. Calc'd for C<sub>92</sub>H<sub>94</sub>N<sub>12</sub>O<sub>4</sub>: C, 77.17; H, 6.62; N, 11.74; O, 4.47. Found: C, 77.20; H, 6.64; N, 11.77; O, 4.45.

#### 2.1.7. ZnPA<sub>4</sub>

Yield = 90%. UV/vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}/nm$ : 352, 433, 556, 599; HRMS (FAB<sup>+</sup>): m/z 1510.1109 (M<sup>+</sup>); <sup>1</sup>H NMR (CDCl<sub>3</sub>/ppm):  $\delta$  9.046 (8H, s), 8.378 (8H, d), 8.273 (8H, d), 8.079 (8H, d), 7.090 (8H, d), 4.101 (8H, t), 1.551 (44H, m).

# 2.1.8. CH<sub>3</sub>OAz [19]

Anal. Calc'd for C<sub>13</sub>H<sub>12</sub>N<sub>2</sub>O: C, 73.56; H, 5.70; N, 13.20; O, 7.54. Found: C, 73.59; H, 5.70; N, 13.25; O, 7.45.

# 2.2. Instrument

Electrochemistry was performed with a CHI Model 700 series electroanalytical workstation. Absorption spectra were measured with a HP-8453 UV/vis spectrophotometer. <sup>1</sup>H NMR spectra were obtained with a Varian Unity Inova 300 WB spectrometer.

## 2.3. Electrodes

Cyclic voltammetry was conducted with the use of a three-electrode cell in which a BAS glassy carbon electrode (area =  $0.07 \text{ cm}^2$ ) was used as working electrode. The glassy carbon electrode was polished with  $0.05 \,\mu\text{m}$  alumina on Buehler felt pads and was ultrasonicated for 2 min to remove the alumina residue.

The auxiliary electrode is a platinum wire and the reference electrode is a homemade Ag/AgCl, KCl(sat'd) reference electrode. The spectroelectrochemical cell was composed of a 1 mm cuvette, a platinum gauze thin layer as working electrode, a platinum wire as auxiliary electrode, and an Ag/AgCl, KCl(sat'd) reference electrode.

# 3. Theoretical calculations

All calculations have been carried out using density functional theory (DFT) method in the Gaussian program [21]. The geomteries were optimized using the B3LYP functional with 6-31G(d) basis set for C, H, N, O atoms and LANL2DZ for Zn atom since this theory level has been successfully applied in the electronic structures of porphyrins and metalloporphyrins [22,23]. For the reason of computational efficiency, we compute a series of model compounds by replacing the bulky  $OC_6H_{13}$  group with the OCH<sub>3</sub> group, labeled as MPA<sub>n</sub>-OCH<sub>3</sub> and (HIm)MPA<sub>n</sub>-OCH<sub>3</sub>. All fully optimized geometries were confirmed to be local minima by frequency analysis. Molecular orbitals (MO) of the optimized structures were obtained with the program Gauss View (version 4.1.2) [24].

#### 4. Results and discussion

#### 4.1. Absorption spectra studies

The UV-vis absorption spectral data of azobenzene-containing porphyrins ( $H_2PA_n$ ; n = 1, 2, 4) and their zinc complexes ( $ZnPA_n$ ; n = 1, 2, 4) are summarized in Table 1. The absorption spectra of H<sub>2</sub>PA<sub>n</sub> and ZnPA<sub>n</sub> in CH<sub>2</sub>Cl<sub>2</sub> are basically given by the superimposition of the spectra of the individual porphyrin and azobenzene. The meso-azobenzenes do not markedly affect the absorption characteristic of prophyrins; the Soret and O bands of porphyrins are just shifted bathochromically by a few nanometers upon the substitution of each azobenzene. In comparison with the UV-vis absorption spectra of H<sub>2</sub>TMP and ZnTMP, both the Soret and Q band regions are shifted to longer wavelengths with the increasing substituent number of azobenzene. In particular, H<sub>2</sub>PA<sub>4</sub> display a 12 nm red shift in comparison with H<sub>2</sub>TMP in the Soret band. A slight increase in the relative intensity of the  $Q_{\alpha}$  band occurs as the number of azobenzene increases. The ratio of Q-band intensity  $(\varepsilon_{\alpha}/\varepsilon_{\beta})$  increases in the order  $ZnPA_1 < ZnPA_2 < ZnPA_4$ .

The UV–vis spectra for ZnPA<sub>1</sub>, ZnPA<sub>2</sub>, and ZnPA<sub>4</sub> are also changed upon addition of imidazole [25]. The original Q bands decreased in absorbance and new bands appeared at longer wavelength. In addition, the intensity ratio of  $Q_{\alpha}$  and  $Q_{\beta}$  band ( $\varepsilon_{\alpha}/\varepsilon_{\beta}$ ) is dramatically enhanced from 0.18–0.44 for four-coordinate ZnPA<sub>n</sub> to 0.56–1.07 for five-coordinate (HIm)ZnPA<sub>n</sub> (Table 2).

The ratio of Q-band intensity ( $\varepsilon_{\alpha}/\varepsilon_{\beta}$ ) for zinc porphyrins, and the formation constants ( $K_f$ ) for imidazole ligation to zinc porphyrins.

Compound	$\varepsilon_{\alpha}/\varepsilon_{\beta}^{a}$	$K_{f}$	$\varepsilon_{\alpha}/\varepsilon_{\beta}{}^{\mathrm{b}}$
ZnTMP	0.13	$1.9\times10^4$	0.48
ZnPA <sub>1</sub>	0.18	$1.1  imes 10^5$	0.56
ZnPA <sub>2</sub>	0.27	$2.0  imes 10^5$	0.75
ZnPA <sub>4</sub>	0.44	$3.2\times10^5$	1.07

<sup>a</sup> Four-coordinate zinc porphyrin.

<sup>b</sup> Four-coordinate zinc porphyrin.

The Q-band intensity ratios for imidazole ligation increase in the order (HIm)ZnPA<sub>1</sub> < (HIm)ZnPA<sub>2</sub> < (HIm)ZnPA<sub>4</sub>. The most noteworthy feature is that the absorbance ratio of  $Q_{\alpha}$  at 614 nm and  $Q_{\beta}$  at 570 nm bands is larger than 1 for (HIm)ZnPA<sub>4</sub> (Fig. 2). To our knowledge, such intensity inversion of the Q bands is unusual in *meso*-substituted porphyrins since the Q-bands usually follow the order of relative intensities  $Q_{\beta} > Q_{\alpha}$ .

It has been reported that the intensity of  $Q_{\beta}$  bands is mainly derived from vibronic coupling with the intense Soret band, so the  $Q_{\beta}$  intensity is not easily affected by peripheral substituents and ligands [26]. This indicates that the variation in Q-band intensity ratios mainly resulted from the intensity of  $Q_{\alpha}$  band. A larger Q-band ratio originates from a larger  $Q_{\alpha}$  band. Based on the Gouterman four-orbital model, the intensity of  $Q_{\alpha}$  band is dependent on the energy gap between porphyrin  $a_{1u}$  and  $a_{2u}$  orbitals [26,27]. If the two porphyrin orbitals,  $a_{2u}$  and  $a_{1u}$ , are nearly degenerative, the  $Q_{\alpha}$  band will be small, and vice versa. It is also the reason why four-coordinate porphyrins usually exhibit very small Q-band ratio. Therefore, the energy gap between HOMO and HOMO-1 can be used to reflect the Q band intensity ratio. The orbital energies of HOMO and HOMO-1 of the model compounds, ZnPA<sub>n</sub>–OCH<sub>3</sub> and (HIm)ZnPA<sub>n</sub>-OCH<sub>3</sub>, are displayed in Fig. 3. As can be seen, the HOMO and HOMO-1 are a<sub>2u</sub> and a<sub>1u</sub>-like MO, respectively, and the trend of energy gap between HOMO and HOMO-1 is in agreement with experimental trend for the Q band intensity ratio.

We first scrutinize the MOs of  $ZnPA_n$ –OCH<sub>3</sub> to comprehend the influence of *meso*-azobenzene substituents. As the number of azobenzene increases, the energy level of HOMO-1 shifts slightly to a more negative value from -5.15 eV to -5.17 eV. Conversely, the  $a_{2u}$ -like HOMO shifts positively from -4.95 eV to -4.89 eV. The reverse behavior seen for  $a_{2u}$ -like HOMO can be understood from the inspection of the MO patterns in Fig. 3. Although the HOMO and HOMO-1, respectively, remain as  $a_{2u}$  and  $a_{1u}$ -like orbitals with the increasing number of azobenzene,  $a_{2u}$ -like HOMO shows



Fig. 2. Absorption spectral change of ZnPA<sub>4</sub>  $(4\times 10^{-5}\,M)$  in  $CH_2Cl_2$  in the presence of various concentration of imidazole.

some  $\pi$ -electron on *meso*-azobenzene, which expands the extent of  $\pi$ -conjugation of HOMO (Fig. 3). Because more extended  $\pi$ conjugation will raise the energy of HOMO, the energy-stabilization effect of electron-withdrawing azobenzene on HOMO is canceled. Consequently, the energy of HOMO increases with increasing number of azobenzene. In contrast to the HOMO, the extent of  $\pi$ -conjugation of HOMO-1 always remains unchanged so that the energy of HOMO-1 follows the stabilizing effect of electronwithdrawing azobenzene. Because the two opposite behaviors of HOMO and HOMO-1 cause the increased energy gap and  $Q_{\alpha}$  intensity, it can be found in Table 2 that the Q-band intensity ratio slightly increases as the extent of substitution of azobenzene increases.

In the presence of axial imidazole, both the HOMO and HOMO-1 of (HIm)ZnPA<sub>n</sub>-OCH<sub>3</sub> are greatly destabilized by electron donated from imidazole to porphyrin ring through central Zn and the conformational distortion of porphyrin ring. For (HIm)ZnPA<sub>1</sub>-OCH<sub>3</sub>, the HOMO are raised from -4.95 eV to -4.57 eV, and the HOMO-1 are increased from -5.15 eV to -4.85 eV in comparison with ZnPA<sub>1</sub>-OCH<sub>3</sub>. On the  $a_{2u}$ -like HOMO, there is  $\pi$ -electron distributed on the central N atoms, but this is not the case for the a<sub>1u</sub>-like HOMO-1 (Fig. 3). Therefore, the electron-donating effect of imidazole is more prominent in HOMO than in HOMO-1 and an increase in the energy gap between HOMO and HOMO-1 is observed for (HIm)ZnPA<sub>n</sub>-OCH<sub>3</sub> when compared to ZnPA<sub>n</sub>-OCH<sub>3</sub> in Fig. 3. For ZnPA<sub>1</sub>–OCH<sub>3</sub> and (HIm)ZnPA<sub>1</sub>–OCH<sub>3</sub>, the energy gap increases from 0.20 eV to 0.28 eV. Similar changes in the energy gap of HOMO and HOMO-1 are also observed for ZnPA2-OCH3 and  $(HIm)ZnPA_2-OCH_3$  (0.22  $\rightarrow$  0.30 eV), and  $ZnPA_4-OCH_3$  and  $(HIm)ZnPA_4 - OCH_3 (0.28 \rightarrow 0.33 \text{ eV}).$ 

In the above discussion, we have presented that the relative energies of HOMO and HOMO-1 of azobenzene-substituted porphyrins can be increased with the substitution of azobenzene and ligation of imidazole and are associated with the increase in Q-band intensity ratio. Since (HIm)ZnPA<sub>4</sub>–OCH<sub>3</sub> has four *meso*-azobenzenes and one axial imidazole, the energy of HOMO is much more destabilized than HOMO-1. Not surprisingly, the unusual high ratio in the Q band ( $\varepsilon_{\alpha}/\varepsilon_{\beta} > 1$ ) is then observed.

### 4.2. Electrochemical studies of 4-methoxylazobenzene

CH<sub>3</sub>OAz (4-methoxylazobenzene) exhibited one redox couple at  $E_{pc} = -1.52$  V (Fig. 4(a)) in CH<sub>2</sub>Cl<sub>2</sub>. The reduction potential for CH<sub>3</sub>OAz was not affected by 1-methylimidazole (MeIm), indicating no specific interaction between CH<sub>3</sub>OAz and MeIm. On the other hand, the current of the original redox couple for CH<sub>3</sub>OAz gradually decreased and a new reduction wave at  $E_{pc} = -1.38$  V appeared as the original peak when imidazole (HIm) was added to the solution (Fig. 4). Therefore, we presume that CH<sub>3</sub>OAz<sup>-•</sup> would quickly form hydrogen bonding with HIm after CH<sub>3</sub>OAz was reduced [28].

# 4.3. Electrochemcial and spectroelectrochemical studies of free-base porphyrins

#### 4.3.1. Cyclic voltammetry

Fig. 5(a) shows the cyclic voltammogram of H<sub>2</sub>PA<sub>1</sub> in CH<sub>2</sub>Cl<sub>2</sub>. In the oxidation part, two reversible redox couples could be observed at  $E_{1/2}$  = +1.05 and +1.43 V. In the reduction part, an overlapping wave at  $E_{pc}$  = -1.38 V and one reversible redox couple at  $E_{1/2}$  = -1.66 V could be observed.

Upon addition of HIm, an irreversible reduction wave split away from the overlapping wave and the peak potential occurs at  $E_{pc} = -1.27$  V, more anodically than the original reduction reaction (Fig. 6A). The first irreversible reduction wave was thus attributed to the hydrogen bond formation of imidazole with the azobenzene anion radical (Scheme 1) and the second and third redox couples were due to porphyrin ring reduction. Furthermore, the third



Fig. 3. MO diagrams of four-coordinate ZnPA<sub>n</sub>-OCH<sub>3</sub> and five-coordinate (HIm)ZnPA<sub>n</sub>-OCH<sub>3</sub> calculated by a DFT method at the B3LYP/6-31G(d) level.

reduction potential started shifting anodically when more than 1.0 equivalent of HIm was added. The third reduction potential shifted by about +0.1 V as [HIm] reaches two equivalents of  $[H_2PA_1]$ , indicating that the extra HIm forms hydrogen bonding with the doubly reduced state of porphyrin ring (Scheme 2) [28]. As the concentration of HIm increased, the current of the oxidation wave at ~0V also increased (Fig. 6(a)–(e)). It suggested that the reduced form  $H_2PA_1$  would undergo chemical reaction with HIm to produce a new compound which was oxidized at ~0V.

To probe the solvent effect [29], the redox behaviors are measured for  $H_2PA_1$  under the same experimental conditions in DMF (Fig. 6B). DMF is a polar solvent and can stabilize the reduced porphyrin in the electrochemical experiment. In DMF, the reductions of  $H_2PA_1$  and azobenzene were resolved as compared with those in  $CH_2Cl_2$ . The reduction of  $H_2PA_1$  exhibited three resolvable reduction waves, namely one irreversible reduction wave at  $E_{pc} = -1.29$  V and two redox couples at  $E_{1/2} = -0.99$  and -1.51 V, respectively. Upon addition of HIm, the current of the second reduction wave decreased and the reduction peak potential moved to -1.06 V. The first and third redox couples are thus assigned to porphyrin ring and the second wave is azobenzene reduction. The effect of imidazole towards the third redox couple of  $H_2PA_1$  is similar to that in  $CH_2Cl_2$ . When imidazole concentration was higher than one equivalent of  $H_2PA_1$ , the third redox couple shifted potential anodically (Scheme 3). However, the shift (about +0.07 V) in  $E_{1/2}$  for the H<sub>2</sub>PA<sub>1</sub><sup>-2/-3</sup> wave in the presence of HIm is smaller than that in CH<sub>2</sub>Cl<sub>2</sub> even though three reductions in DMF are resolvable.

There are two special features in the redox chemistry of free bases H<sub>2</sub>PA<sub>1</sub>, H<sub>2</sub>PA<sub>2</sub>, and H<sub>2</sub>PA<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> (Fig. 5). Firstly, the azobenzene moieties were reduced at a potential close to that of the porphyrin ring. The current ratio for azobenzene moieties versus porphyrin reduction were about 2.0 and 4.0 for H<sub>2</sub>PA<sub>2</sub> and H<sub>2</sub>PA<sub>4</sub>, respectively. It appears that H<sub>2</sub>PA<sub>2</sub> and H<sub>2</sub>PA<sub>4</sub> could undergo multiple electron reduction in a step. Secondly, the potential of the first oxidation wave is slightly more positive as the number of *meso*-azobenzene increases, in line with the electron-withdrawing nature of the azo group. The second oxidation, however, exhibits a more negative potential as the number of *meso*-azobenzene increases (Table 3). The difference in oxidation potential ( $\Delta E^{\text{ox}}$ ) thus becomes smaller concurrently.

In order to interpret these unusual tendencies, we continued to seek help from DFT calculations. We examined the MO for all charge states, and found the patterns of the highest occupied MO (HOMO) of the neutral state and  $\alpha$ -HOMO of the cation radical state to be very different (Fig. 7). For the neutral H<sub>2</sub>PA<sub>n</sub>–OCH<sub>3</sub>, the dihedral angle between azobenzene and porphyrin ring ( $\phi_1$ ) is in the range of 64.9–66.6° (Table 4). The two phenyl rings of *meso*-azobenzene is about coplanar ( $\phi_2 \pm \phi_3 < 5^\circ$ ) and the mesityl



**Fig. 4.** Cyclic voltammograms of  $1.0 \times 10^{-3}$  M CH<sub>3</sub>OAz in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M TBAP and various concentrations of HIm. [HIm] = (a) 0.00; (b) 0.50; (c) 1.00; (d) 1.50; and (e)  $2.0 \times 10^{-3}$  M. Scan rate: 0.1 V/s.

groups are perpendicular to porphyrin ring ( $\phi_4 \approx 90^\circ$ ). The HOMO of the neutral state, which is related to the first oxidation, closely resembles Gouterman's  $a_{2u}$  orbital and there is only a glimmer of  $\pi$ -electron delocalized on *meso*-azobenzene (Fig. 7). This situation remains no matter how many *meso*-azobenzene are present. The dihedral angle  $\phi_1$  decrease from 64.9° to 66.6° at neutral state to 54.1–58.5° at cation state. At the cation radical state, the dihedral angles  $\phi_2$ ,  $\phi_3$ , and  $\phi_4$  are not significantly changed (Table 4). The



Fig. 5. Cyclic voltammograms of  $1.0 \times 10^{-3}$  M (a)  $H_2PA_1$ ; (b)  $H_2PA_2$ ; (c)  $H_2PA_4$  in  $CH_2CI_2$  containing 0.1 M TBAP. Scan rate: 0.1 V/s.

reduction of dihedral angle  $\phi_1$  upon first oxidation afford stronger  $\pi$ -conjugation between porphyrin and *meso*-azobenzenes. Therefore, the  $\alpha$ -HOMO of the cation radical state, which is related to the second oxidation, shows  $\pi$ -electron delocalization over the whole molecule. The extent of electron delocalization in  $\alpha$ -HOMO is very different as the number of azobenzene increases. As more extended  $\pi$ -conjugation will raise the energy of HOMO, it is not surprising that the orbital energies of  $\alpha$ -HOMO of cation radical H<sub>2</sub>PA<sub>1</sub>–OCH<sub>3</sub>, H<sub>2</sub>PA<sub>2</sub>–OCH<sub>3</sub>, and H<sub>2</sub>PA<sub>4</sub>–OCH<sub>3</sub> are rising (Fig. 7), thus counteracting the energy-lowering effect of the electron-withdrawing azo group and affording a more negative potential for second oxidation as the number of  $\pi$ -electron delocalization among HOMOs of neutral H<sub>2</sub>PA<sub>n</sub>–OCH<sub>3</sub> explains why the electron-withdrawing effect of the azo group can still be observed for the first oxidation.

#### Table 3

Half-wave potentials (V vs. Ag/AgCl) of free-base porphyrins in CH<sub>2</sub>Cl<sub>2</sub>/TBAP (Fc <sup>0/+</sup> = +0.56 V).

	0.11.1.1				<b>D</b> 1 (1 )			
	Oxidation <sup>a</sup>			Reduction <sup>a</sup>				
	$\Delta E^{\mathrm{ox}}$	$E_2^{\text{ox}}$	$E_1^{\text{ox}}$	$\Delta E$	$E_1^{\rm red}$	$E_2^{\rm red c}$	$E_3^{\rm red}$	$\Delta E^{red}$
CH <sub>3</sub> OAz					-1.44			
$H_2TMP$	0.44	+1.48	+1.04	2.37	-1.33		-1.68	0.35
$H_2PA_1$	0.38	+1.43	+1.05	2.43	-1.38 <sup>b,d</sup>	-1.38 <sup>b,d</sup>	-1.60	0.22
H <sub>2</sub> PA <sub>2</sub> <sup>e</sup>	0.32	+1.40	+1.08	2.36	-1.28 <sup>b</sup>	-1.42 <sup>b</sup>	-1.64	0.36
$H_2PA_4^e$	0.20	+1.29	+1.09	2.24	-1.15	-1.27	-1.57	0.42

<sup>a</sup>  $\Delta E^{OX} = E_2^{OX} - E_1^{OX}$  (difference between the first and second oxidation potential),  $\Delta E = E_1^{OX} - E_1^{red}$ ,  $\Delta E_1^{red} = E_1^{red} - E_3^{red}$ .

<sup>b</sup> Peak potential.

<sup>c</sup> The reduction of azobenzene moiety.

<sup>d</sup> The overlapping wave.

<sup>e</sup> The  $E_{1/2}$  was obtained from differential pulse voltammetry.



$$H_{2}P-A_{1} \xrightarrow{+e^{-}} H_{2}P-\overrightarrow{A_{1}} - H-N \swarrow N \xrightarrow{+e^{-}} H_{2}\overrightarrow{P} - \overrightarrow{A_{1}} - H-N \swarrow N$$

$$\xrightarrow{+e^{-}} H_{1}M \longrightarrow N - H - H_{2}P^{2-} \overrightarrow{A_{1}} - H - N \swarrow N$$
Scheme 2.

The LUMO and LUMO+1 energy levels of  $H_2PAn$  were obtained by the DFT calculation and the values were listed in Table 5. The energy of the LUMO and LUMO+1 decreased with increasing number of azobenzene moiety. It indicated that the azobenzene substituent was an electron-withdrawing group.

#### 4.3.2. Spectroelectrochemistry

Fig. 8(a) shows the absorption spectra of  $H_2TMP$  in  $CH_2Cl_2$  at various applied potentials. When  $E_{appl.} = +0.85$  to +1.21 V, the Soret band (418 nm) and three of Q bands (514, 547 and 591 nm) of  $H_2TMP$  decreased. The corresponding  $H_2TMP^{+\bullet}$  exhibit a strong absorption peak at 437 nm and the other Q band (634 nm) increased in absorbance.

In the potential range of  $E_{appl.} = +0.00$  to +1.15 V, the spectra of H<sub>2</sub>PA<sub>1</sub> under various potentials were obtained (Fig. 8(b)). As the potential shifted anodically, the characteristic absorption of azobenzene substituent at 352 nm and the Soret band (420 nm) gradually decreased while a new peak at 446 nm grew. The absorbance at 516 nm gradually decreased and a new peak at 647 nm grew concurrently.

Fig. 8(c) was the spectroelectrochemical results of  $H_2PA_2$  and the pattern of spectral change was similar to  $H_2PA_1$ . In the potential range of  $E_{appl.} = +0.00$  to +1.20 V, the equilibrium spectra of  $H_2PA_2$ under various potentials were obtained. As the potential shifted anodically, the characteristic absorption of azobenzene substituent at 352 nm and the Soret band (422 nm) gradually decreased while a new peak at 453 nm grew. The Q band absorbance at 517 and 554 nm gradually decreased and a new peak at 658 nm grew concurrently.

#### Table 4



The dihedral angles ( $\phi$ ) of optimized H<sub>2</sub>PA<sub>n</sub>-OCH<sub>3</sub> (n = 0, 1, 2, 4) at the neutral and



Table 5

The LUMO and LUMO+1	energy	levels of	$H_2$ PAn.
---------------------	--------	-----------	------------

Compound	МО	Energy (eV)
H <sub>2</sub> PA <sub>1</sub>	LUMO LUMO+1	-2.26373 -2.18074
$H_2PA_2$	LUMO LUMO+1	-2.32251 -2.18482
H <sub>2</sub> PA <sub>4</sub>	LUMO LUMO+1	-2.32441 -2.28686

Fig. 8(d) shows the absorption spectra of  $H_2PA_4$  in  $CH_2CI_2$  at various applied potentials. In the potential range of  $E_{appl.} = +0.00$  to +1.18 V, the equilibrium spectra of  $H_2PA_4$  under various potentials were obtained. As the potential was moved anodically, the characteristic absorption of azobenzene substituent at 352 nm, and the Soret band (430 nm) gradually decreased while a new peak at 475 nm grew. The Q band absorbance at 520 nm gradually decreased and a new peak at 689 nm grew concurrently.

Fig. 9 was the absorption spectra of H<sub>2</sub>TMP and H<sub>2</sub>PA<sub>n</sub> of which the reduction potentials  $(E_{appl.})$  were applied at their respective onset potentials. When  $E_{appl.} = -1.33 V$  (Fig. 9(a)), the Soret band (418 nm) and one Q band (514 nm) of H<sub>2</sub>TMP decreased and the other three Q band (547, 595 and 652 nm) increased, corresponding to the anion radical formation. The spectral changes of H<sub>2</sub>PA<sub>n</sub> were similar to that of H<sub>2</sub>TMP. When each E<sub>appl.</sub> was at onset reduction potential, the characteristic absorbance of azobenzene moiety (352 nm). Soret band and first two O bands decreased significantly. and the other Q bands increased. Noteworthily, the azobenzene peak and Soret band decreased concurrently. We used the DFT calculation results (Fig. 7) to explain the phenomena. In the cation radical state, stronger  $\pi$ -conjugation was observed between porphyrin and meso-azobenzenes. Conjugation was also applied to in the anion radical, and both the azobenzene peak and Soret band decreased in absorbance at the same time indicated that the charge delocalized between the porphyrin ring and azobenzene moiety.

# 4.4. Electrochemcial and spectroelectrochemical studies of zinc porphyrins

#### 4.4.1. Cyclic voltammetry

The electrochemical results of ZnPA<sub>n</sub> are similar to that of H<sub>2</sub>PA<sub>n</sub>. Fig. 10(a) shows the cyclic voltammogram of ZnPA<sub>1</sub> in CH<sub>2</sub>Cl<sub>2</sub>. Two reversible redox couples could be observed at  $E_{1/2}$  = +0.79 and +1.11 V in the oxidation part. An overlapping wave at  $E_{pc}$  = -1.43 V (a shoulder at  $E_{pc}$  = -1.34 V) and one reversible redox couples could be observed at  $E_{1/2}$  = -1.59 V in the reduction part. The current ratios for azobenzene moieties versus zinc porphyrin reduction were also about 2.0 and 4.0 for ZnPA<sub>2</sub> and ZnPA<sub>4</sub>, respectively. The results were the similar to H<sub>2</sub>PA<sub>n</sub>. The peak current of ZnPA<sub>2</sub> was not as clear as the others because of its low solubility in CH<sub>2</sub>Cl<sub>2</sub>. The peak potentials of ZnPA<sub>n</sub> were summarized in Table 6.

With the imidazole coordinating onto a zinc porphyrin, the first oxidation wave shifts cathodically but the second one shifts anodically. The first reduction wave of zinc porphyrin shifts cathodically [30]. The formation constant of imidazole with zinc porphyrin is about  $10^4$ – $10^5$ . Upon addition of Melm (Fig. 11), the first oxidation wave shifted cathodically by +0.10 V. The second one, however, shifted anodically and was irreversible [30]. The first overlapping irreversible reduction wave became a single wave (the shoulder reduction wave shifted cathodically) and the reduction wave at  $E_{\rm pc} = -1.43$  V did not shift (the peak current increased). The second reduction wave  $(E_{1/2} = -1.59$  V) remained unchanged. The binding constant between the zinc porphyrin and Melm is ~ $10^4$  M<sup>-1</sup> [30,33]. Melm coordinated to the anions of zinc porphyrin with



Fig. 6. Cyclic voltammograms of  $1.0 \times 10^{-3}$  M H<sub>2</sub>PA<sub>1</sub> in (A) CH<sub>2</sub>Cl<sub>2</sub> and (B) DMF containing 0.1 M TBAP and various concentrations of HIm. [HIm] = (a) 0.00; (b) 0.50; (c) 1.00; (d) 1.50; and (e)  $2.00 \times 10^{-3}$  M. Scan rate: 0.1 V/s.



**Fig. 7.** MO diagrams of the  $H_2PA_n$ -OMe (n = 0, 1, 2, 4) for neutral and cation radical states.

# Table 6 Half-wave potentials (V vs. Ag/AgCl) of zinc porphyrins in CH<sub>2</sub>Cl<sub>2</sub>/TBAP (Fc <sup>0/+</sup> = +0.56 V).

	Oxiadtion <sup>a</sup>			Reduction <sup>a</sup>				
	$\Delta E^{\mathrm{ox}}$	$E_2^{\text{ox}}$	$E_1^{\text{ox}}$	$\Delta E$	E <sub>1</sub> <sup>red</sup>	$E_2^{\rm red c}$	$E_2^{\rm red}$	$\Delta E^{red}$
CH <sub>3</sub> OAz					-1.44			
ZnTMP	0.32	+1.11	+0.79	2.27	-1.48			
ZnPA <sub>1</sub>	0.33	+1.14	+0.81	2.24	-1.34 <sup>b</sup>	-1.43 <sup>b</sup>	-1.59	0.25
ZnPA <sub>2</sub>	0.31	+1.14	+0.83	2.14	-1.31 <sup>b</sup>	$-1.42^{b}$	-1.58	0.27
ZnPA <sub>4</sub>	0.29	+1.16	+0.87	2.11	-1.24 <sup>b</sup>	-1.35	-1.62	0.38

<sup>a</sup>  $\Delta E^{OX} = E_2^{ox} - E_1^{ox}$  (difference between the first and second oxidation potential),  $\Delta E = E_1^{ox} - E_1^{red}$ ,  $\Delta E_1^{red} = E_1^{red} - E_3^{red}$ . <sup>b</sup> Peak potential.

<sup>c</sup> The reduction of azobenzene moiety.



**Fig. 8.** Spectral changes of (a)  $H_2TMP 5.0 \times 10^{-5}$  M and (b)  $H_2PA_1 2.5 \times 10^{-5}$  M; (c)  $H_2PA_2 2.5 \times 10^{-5}$  M; (d)  $H_2PA_4 2.5 \times 10^{-5}$  M in  $CH_2CI_2$  containing 0.1 M TBAP at various applied potentials.



Fig. 9. Spectral changes of  $2.5 \times 10^{-5}$  M (a)  $H_2$ TMP; (b)  $H_2$ PA<sub>1</sub>; (c)  $H_2$ PA<sub>2</sub>; and (d)  $H_2$ PA<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M TBAP at onset reduction potentials.



Fig. 10. Cyclic voltammograms of (a)  $ZnPA_1$   $1.0\times10^{-3}$  M; (b)  $ZnPA_2$   $6.0\times10^{-4}$  M; (c)  $ZnPA_4$   $1.0\times10^{-3}$  M in  $CH_2Cl_2$  containing 0.1 M TBAP. Scan rate: 0.1 V/s.



**Fig. 11.** Cyclic voltammetry of  $1.0 \times 10^{-3}$  MZnPA<sub>1</sub> in the presence of MeIm in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M TBAP. [MeIm] = (a)0.00; (b)0.50; (c)1.00; and (d)1.50  $\times 10^{-3}$  M. Working electrode: glassy carbon. Scan rate:0.1 V/s.

smaller formation constants (about  $10^2-10^3 \text{ M}^{-1}$ ) than the neutral species [30]. It suggested that the MeIm was de-ligated from (MeIm)ZnPA<sub>1</sub> (Scheme 4) [30]. According to the results, we presume that the shoulder ( $E_{pc} = -1.34 \text{ V}$ ) of the overlapping reduction wave in Fig. 11(a) was attributed to the porphyrin ring reduction. The azobenzene moiety was reduced at  $E_{pc} = -1.43 \text{ V}$ , and  $E_{1/2} = -1.59 \text{ V}$  corresponds to the second reduction potential of porphyrin ring.





**Fig. 12.** Cyclic voltammetry of  $1.0 \times 10^{-3}$  M ZnPA<sub>1</sub> in the presence of HIm in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M TBAP. [HIm] = (a) 0.00; (b) 0.50; (c) 1.00; (d)  $1.50 \times 10^{-3}$  M. Working electrode: glassy carbon. Scan rate: 0.1 V/s.

When the additive was HIm (Fig. 12), it not only coordinated with zinc porphyrin but also formed hydrogen bonding with reduced azobezene moiety. As HIm was added to the ZnPA<sub>1</sub> solution stepwise, the first oxidation wave shifted cathodically and the second one shifted anodically. There were two new waves at  $E_{pc} = -1.18$  and -1.35 V in the reduction part. The anodic shift of first zinc porphyrin ring reduction from -1.34 V to -1.18 V was due to HIm coordinated on ZnPA<sub>1</sub> and azobenzene moiety interacted with HIm was  $E_{pc} = -1.43$  V to -1.35 V. The zinc porphyrin ring reduction wave shifted cathodically (from  $E_{1/2} = -1.59$  to -1.67 V).

#### 4.4.2. Spectroelectrochemistry

Fig. 13 shows the spectroelectrochemical results of ZnTMP and ZnPA<sub>n</sub> under various oxidation potentials. When the potential was moved anodically (Fig. 13(a)), the Soret band (421 nm) of ZnTMP gradually decreased while a shoulder peak at 436 nm grew. The Q band absorbance at 550 nm gradually decreased and a broad band at 600-700 nm grew concurrently. As the number of meso-azobenzene increases, the absorbance of azobenzene substituent at 352 nm increases and the Soret band of  $ZnPA_n$  is red-shifted (Table 1). In the first oxidation step of each ZnPAn, the Soret band and Q band gradually decreased while the peak at 352 nm and a broad band between 600 and 950 nm grew concurrently. The broad band was suggested that the charge transfer between porohyrin ring and azobenzene moiety [31-33]. The broad bands were intra-molecular charge transfer bands. The results exhibited the typical metal porphyrin ring oxidized spectrum.

ZnTMP was used as model compound. When  $E_{appl.} = -1.48 \text{ V}$  (Fig. 14(a)), the Soret band (420 nm) gradually decreased while a new peak at 435 nm grew. The absorbance at 550 nm gradually decreased and two new peaks at 570 and 612 nm grew concurrently. The anion radical spectrum of ZnTMP was then obtained. In order to further identify the reduction site on the ZnPA<sub>n</sub>, we set the  $E_{appl.}$  at onset reduction potential and monitored the spectral changes by spectroelectrochemical method. As E = -1.20 V was applied (Fig. 14(b)), the Soret band (421 nm) and Q band (550 nm) of ZnPA<sub>1</sub> decreased while a shoulder peak at 435 nm and two new peak between 600 and 700 nm increased in absorbance. But at this potential, the characteristic peak (352 nm) of azobenzene moiety has no significant change. In order to understand this phenomenon,



**Fig. 13.** Spectral changes of (a) ZnTMP  $5.0 \times 10^{-5}$  M; (b) ZnPA<sub>1</sub>  $1.88 \times 10^{-5}$  M and (c) ZnPA<sub>2</sub>  $2.5 \times 10^{-5}$  M; (d) ZnPA<sub>4</sub>  $2.5 \times 10^{-5}$  M in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M TBAP at various applied potentials.



Fig. 14. Spectral changes of (a) ZnTMP  $2.5 \times 10^{-5}$  M; (b) ZnPA<sub>1</sub>  $2.5 \times 10^{-5}$  M; (c) ZnPA<sub>2</sub>  $1.5 \times 10^{-5}$  M; (d) ZnPA<sub>4</sub>  $2.5 \times 10^{-5}$  M in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M TBAP at onset reduction potentials.

the results of the conjugation between porphyrin ring and azobenzene moiety in the oxidation was used. Compared with the  $\Delta E^{\text{ox}}$  of  $H_2PA_n$  (Table 3) and the  $\Delta E^{ox}$  of ZnPA<sub>n</sub> (Table 6), it was observed that the  $\Delta E^{\text{ox}}$  of H<sub>2</sub>PA<sub>n</sub> decreased obviously with the increasing number of azobenzene because of the stronger  $\pi$ -conjugation between porphyrin ring and meso-azobenzenes (Fig. 7). When the onset reduction potentials were applied, Soret band and azobenzene peak (352 nm) decreased concurrently (Fig. 9). These results revealed that the electron delocalization between porphyrin ring and meso-azobenzenes also could be obtained in the reduction part. But the  $\Delta E^{\text{ox}}$  of ZnPA<sub>n</sub> has slightly decreased as azobenzene number increased. It indicated that only a glimmer of  $\pi$ -electron delocalized between *meso*-azobenzene and porpyrin ring. The azobenzene peak (352 nm) was not significantly changed at  $E_{appl.} = -1.20 \text{ V}$  (Fig. 14). With the results, we could further confirm that the first reduction wave of  $ZnPA_1$  at  $E_{pc} = -1.34$  V was due to the porphyrin ring reduction. When  $E_{appl.}$  was at onset reduction potential, the spectral change patterns of ZnPA<sub>2</sub> and ZnPA<sub>4</sub> were similar, the soret and Q band decreasing and azobenzene peak having no change. According to the spectroelectrochemical results, it is thus inferred that the first reduction sites of  $ZnPA_n$  were at the prophyrin ring.

#### 5. Conclusions

This work displays several idiosyncratic features of absorption spectra and electrochemistry for the azobenzene-containing porphyrins. (1) The Q-band intensity ratios ( $\varepsilon_{\alpha}/\varepsilon_{\beta}$ ) for ZnPA<sub>n</sub> slightly increase with the increase number of meso-azobenzene. Upon addition of imidazole, the Q band ratio for (HIm)ZnPA4 is even larger than 1. (2) The reduction of free base  $H_2PA_n$  to various charge states would create a specific interaction with imidazole. (3) The azobenzene moieties were reduced at a potential close to that of the porphyrin ring, and it was observed that the current for the first overlapping wave dramatically increase with the increase number of meso-azobenzene. (4) The potential of the first oxidation wave of  $H_2PA_n$  is slightly more positive but the second oxidation exhibits a reverse shift as the number of meso-azobenzene increases. (5) The first reduction wave of ZnPA<sub>n</sub> is at the zinc porphyrin ring reduction and spectroelectrochemistry also reveal this results. Based on MO analysis, points (1) and (4) have been rationalized. Further investigations by replacing the azo group with imine or alkene links and by variation of positions of the linkers will be undertaken in future to see if those unusual features can also be observed.

#### Acknowledgment

This research is supported by the National Science Council of the Republic of China (NSC 97-2113-M-260-005-MY3, NSC 99-2811-M-260-006) and the National Center for High-performance Computing for computer time and facilities.

#### References

- [1] F. Li, S.I. Yang, Y. Ciringh, J. Seth, C.H. Martin III, D.L. Singh, D. Kim, R.R. Birge, D.F. Bocian, D. Holten, J.S. Lindsey, J. Am. Chem. Soc. 120 (1998) 10001.
- 2] D. Holten, D.F. Bocian, J.S. Lindsey, Acc. Chem. Res. 35 (2002) 57.
- [3] B.M.J.M. Suijkerbuijk, R.J.M. Klein Gebbink, Angew. Chem. Int. Ed. 47 (2008) 7396.
- [4] H. Imahori, T. Umeyama, S. Ito, Acc. Chem. Res. 42 (2009) 1809.
- [5] S. Fukuzumi, K. Ohkubo, H. Imahori, J. Shao, Z. Ou, G. Zheng, Y.R. Chen, K. Pandey, M. Fujitsuka, O. Ito, K.M. Kadish, J. Am. Chem. Soc. 123 (2001) 10676.
- [6] A.N. Macpherson, P.A. Liddell, S. Lin, L. Noss, G.R. Seely, J.M. DeGraziano, A.L. Moore, T.A. Moore, D. Gust, J. Am. Chem. Soc. 117 (1995) 7202.
- [7] Y. Kashiwagi, H. Imahori, Y. Araki, O. Ito, K. Yamada, Y. Sakata, S. Fukuzumi, J. Phys. Chem. A 107 (2003) 5515.
- [8] J.K. Park, J. Chen, H.R. Lee, S.W. Park, H. Shinokubo, A. Osuka, D. Kim, J. Phys. Chem. C 113 (2009) 21956.
- [9] M. Autret, M. Le Plouzennec, C. Moinet, G. Simonneaux, J. Chem. Soc. Chem. Commun. (1994) 1169.
- [10] S. Tsuchiya, J. Am. Chem. Soc. 121 (1999) 48.
- [11] T. Yamamura, A. Momotakeb, T. Arai, Tetrahedron Lett. 45 (2004) 9219.
- [12] A. Aemissegger, V. Kräutler, W.F. van Gunsteren, D. Hilvert, J. Am. Chem. Soc. 127 (2005) 2929.
- [13] I. Tomatsu, A. Hashidzume, A. Harada, J. Am. Chem. Soc. 128 (2006) 2226.
- [14] C.A. Hunter, L.D. Sarson, Tetrahedron Lett. 37 (1996) 699.
- [15] M.V. Peters, R. Goddard, S. Hecht, J. Org. Chem. 71 (2006) 7846.
- [16] J.S. Lindsey, W. Wagner, J. Org. Chem. 54 (1989) 828.
- [17] C.H. Lee, J.S. Lindsey, Tetrahedron 50 (1994) 11427.
   [18] A.D. Adler, F.R. Longo, F. Kamas, J. Kim, J. Inorg. Nucl. Chem. 32 (1970)
- 2443. [19] J. March, Advanced Organic Chemistry, 4th ed., Wiley, New York, 1992,
- p. 1280.
   [20] Y.C. Lin, K.L. Cheng, W.S. Tzeng, C.L. Su, LJ. Lee, LY. Wang, C.M. Yang, L.L. Lai,
- [20] Y.C. Lin, K.L. Cheng, W.S. Izeng, C.L. Su, L.J. Lee, L.Y. Wang, C.M. Yang, L.L. Lai Liq. Cryst. 33 (2006) 289.
- [21] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, T. Vreven Jr., K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, GAUSSIAN 03 Revision E. 01;, Gaussian Inc, Wallingford, CT, 2004.
- [22] R. Ma, P. Guo, H. Cui, X. Zhang, M.K. Nazeeruddin, M. Grätzel, J. Phys. Chem. A 113 (2009) 10119.
- [23] Y. Nakamura, N. Aratani, H. Shinokubo, A. Takagi, T. Kawai, T. Matsumoto, Z.S. Yoon, D.Y. Kim, T.K. Ahn, D. Kim, A. Muranaka, N. Kobayashi, A. Osuka, J. Am. Chem. Soc. 128 (2006) 4119.
- [24] R. Dennington II, T. Keith, J. Millam, K. Eppinnett, W.L. Hovell, R. Gilliland, Gauss View, Version 4.1.2, Semichem, Inc., Shawnee Mission, KS, 2007.
- [25] M. Nappa, J.S. Valentine, J. Am. Chem. Soc. 100 (1978) 5075.
   [26] J.L. Retsek, C.J. Medforth, D.J. Nurco, S. Gentemann, V.S. Chirvony, K.M. Smith,
- D. Holten, J. Phys. Chem. B 105 (2001) (2001) 6396. [27] P.J. Spellane, M. Gouterman, A. Antipas, S. Kim, Y.C. Liu, Inorg. Chem. 19 (1980)
- 386.
- [28] J. Bu, N.D. Lilienthal, J.E. Woods, C.E. Nohrden, K.T. Hoang, D. Truong, D.K. Smith, J. Am. Chem. Soc. 127 (2005) 6423.
- [29] F. Barrire, W.E. Geiger, J. Am. Chem. Soc. 128 (2006) 3980.
- [30] C.L. Lin, M.Y. Fang, S.H. Cheng, J. Electroanal. Chem. 531 (2002) 155.
- [31] J.C. Chang, C.J. Ma, G.H. Lee, S.M. Peng, C.Y. Yeh, Dalton Trans. (2005) 1504.
- [32] C.W. Huang, K.Y. Chiu, S.H. Cheng, Dalton Trans. (2005) 2417.
- [33] K.Y. Chiu, Y.O. Su, Chem. Commun. (2009) 2884.