六种酞菁锌配合物:交叉聚合法合成、分离、光谱和电化学性质

柏 铭* 张 岩 万培红 张崇禧

(山东大学(威海)海洋学院,威海 264209)

摘要:使用 2 种前驱体 **1** 和 **2**(**1**=4,5-二(4-甲酯基)酚氧取代邻苯二甲腈,**2**=4-二缩三乙二醇单甲醚取代邻苯二甲腈)与 Zn(OAc)$_2$·2H$_2$O 在 DBU(1,8-二氮杂双环[5.4.0]十一碳-7-烯)催化下,在正戊醇中进行酯交换及交叉聚合反应得到 6 种酞菁锌配合物。通过简单的硅胶柱色谱,可以将这 6 种配合物 Zn[Pc(BP)$_4$](**3**), Zn[Pc(BP)$_3$(TEG)](**4**), Zn[Pc(BP)$_2$(TEG)$_2$]-opp(**5**), Zn[Pc(BP)$_2$(TEG)$_2$]-adj(**6**), Zn[Pc(BP)(TEG)$_3$](**7**)和 Zn[Pc(TEG)$_4$](**8**)进行分离。对合成的 6 种化合物进行了质谱,元素分析,紫外-可见吸收光谱,核磁共振谱表征。另外,对这些化合物的电化学性质也进行了研究。

Six Phthalocyaninato Zinc(II) Complexes: Synthesis via Cross-Condensation of Two Phthalonitriles, Spectroscopy and Electrochemistry

BAI Ming* ZHANG Yan WAN Pei-Hong ZHANG Chong-Xi

(*Marine College, Shandong University, Weihai*, 264209)

Abstract: Cross-condensation of two different phthalonitriles, namely 4,5-bis [(4-methyloxycarbonyl)phenoxy] phthalonitrile (**1**) and 4-{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}phthalonitrile(**2**), in the presence of Zn(OAc)$_2$·2H$_2$O and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) followed by transesterification in refluxing *n*-pentanol afforded six phthalocyaninato zinc(II) complexes modulated with different numbers of pentyloxycarbonyl and/or triethylene glycol monomethyl ether groups. Simple silica-gel column chromatography leads to the successful separation of all these six compounds, namely Zn[Pc(BP)$_4$](**3**), Zn[Pc(BP)$_3$(TEG)](**4**), Zn[Pc(BP)$_2$(TEG)$_2$]-opp(**5**), Zn[Pc(BP)$_2$(TEG)$_2$]-adj(**6**), Zn[Pc(BP)(TEG)$_3$](**7**), and Zn[Pc(TEG)$_4$](**8**). In addition, the six complexes have been characterized with elemental analysis, MALDI-TOF mass, UV-Vis spectroscopy, ^{1}H NMR, and 2D COSY spectroscopy. The electrochemical properties have also been investigated.

Key words: cross-condensation; esterification; phthalocyanines; NMR spectroscopy; electrochemical property

0 Inrtoduction

Phthalocyanines (Pcs) as versatile functional dyes have attracted long term of continuous research interest because of their applications in the fields of organic semiconductors, nonlinear optical and optical limiting materials, chemosensors, organic photovoltaics, catalysis, and photosensitisers for photodynamic therapy [1-4]. Their physicochemical, electrochemical, and spectroscopic properties as well as intermolecular interactions can be modulated through modifying the species and number of the

peripheral substituents and/or the nature of the π-conjugation system. For special applications, phthalocyanines containing different species and number of substituents with low molecular symmetry have been highly desired for a long time[5]. These low symmetrical phthalocyanine compounds were usually prepared via cross-condensation of two different kinds of phthalonitrile precursors. Separation of the whole series of six compounds obtained in the same reaction with AAAA, AAAB, AABB-opp, ABAB-adj, ABBB, and BBBB type has been the key problem since the first synthesis using such procedure. Usually, the AAAB or ABBB type phthalocyanine derivative could be relatively easily separated from the reaction mixture in particular when the ratio of two kinds of phthaloycanine precursors was controlled [6] or two precursors with large different steric hindrance effect were employed [7]. Actually subphthalocyanine approach[8-9] and polymer supported method [10-11] were also utilized to prepare the AAAB or ABBB type phthalocyanine derivatives. To the best of our knowledge, successful separation over the whole series of six phthalocyanine compounds obtained by cross-condensation of two different kinds of precursors still remains extremely rare. Except the case that a tetraazaporphyrin precursor and a phthalocyanine precursor [12-18] as well as a phthalocyanine precursor and a naphthalocyanine precursor were simultaneously employed [12,19-22], which results in the phthalocyanine analogues with the π-system itself possessing a lower symmetry than D_{4h}, only several examples have been reported thus far for the separation of six phthalocyanine derivatives with the π-system itself maintaining the D_{4h} symmetry[23-30].In the present paper, cross-condensation of 4,5-bis [(4-methyloxycarbonyl) phenoxy]phthalonitrile (**1**) and 4-{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}phthalonitrile (**2**) in the presence of Zn (OAc)$_2$ ·2H$_2$O and 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU) followed by transesterification[31-32] in refluxing n-pentanol afforded the whole series of six phthalocyaninato zinc (II) complexes, namely Zn[Pc(BP)$_4$] (**3**), Zn[Pc(BP)$_3$(TEG)] (**4**), Zn[Pc(BP)$_2$(TEG)$_2$]-opp (**5**), Zn[Pc(BP)$_2$(TEG)$_2$]-adj (**6**), Zn[Pc(BP)(TEG)$_3$](**7**), and Zn[Pc(TEG)$_4$] (**8**), which were separated through simple silica-gel column chromatography.

1　Experimental

1.1　General Remarks

n-Pentanol and dimethylformamide (DMF) were distilled under an inert atmosphere by using sodium and anhydrous MgSO$_4$, respectively. Dichloromethane was distilled by using LiAlH$_4$. Column chromatography was carried out on a silica gel column (Qingdao Haiyang, 200 ~325 mesh (74 ~44 μm) with the indicated eluents. [Bu$_4$N][ClO$_4$] was prepared in this method: a solution of 50 mL Bu$_4$N·Cl (1.0 mol·L^{-1}) was added dropwise into 500 mL NaClO$_4$ (0.1 mol·L^{-1}) solution, while the temperature of the mixture was kept at 70~80 ℃. Stirring was continued for 0.5 h to complete the reaction. The reaction mixture was cooled. The crude product was filtered by suction and washed with H$_2$O. The product was recrystalized in acetone/H$_2$O (1∶1, V/V) and dried in vacuo. Other reagents and solvents were used as received.

^{1}H NMR spectra were recorded on a Bruker DPX 400 spectrometer (^{1}H: 400 MHz) in CDCl$_3$ unless otherwise stated. Spectra were referenced internally using the residual solvent resonance (δ=7.260 for ^{1}H NMR) relative to SiMe$_4$ (δ=0). ^{13}C NMR spectra were referenced internally by using the solvent resonance (δ =77.00 for CDCl$_3$). Electronic absorption spectra were recorded on a Hitachi U-4100 spectrophotometer. MALDI-TOF mass spectra were taken on a Bruker BIFLEX Ⅲ ultrahigh resolution Fourier Transform Ion cyclotron resonance (FT-ICR) mass spectrometer with R-cyano-4-hydroxycinnamic acid as a matrix. Electrochemical measurements were carried out with a BAS CV-50W voltammetric analyzer. The cell comprised inlets for a glassy carbon disk working electrode of 3.0 mm in diameter and a silver-wire counter electrode. The reference electrode was Ag/Ag$^+$ (0.01 mol·L^{-1}), which was connected to the solution by a Luggin capillary whose tip was placed close to the working electrode. It was corrected for junction potentials by being referenced internally

to the ferrocenium/ferrocene (Fc$^+$/Fc) couple [E$_{1/2}$(Fc$^+$/Fc)=0.50 V vs. SCE]. Typically, a 0.1 mol·L^{-1} solution of [Bu$_4$N][ClO$_4$] in CH$_2$Cl$_2$ containing 0.5 mmol·L^{-1} of sample was purged with nitrogen for 10 min, then the voltammograms were recorded at ambient temperature. The scan rate was 20 and 10 mV·s^{-1} for CV and DPV, respectively.

1.2　Synthesis of 4, 5-bis [(4-methyloxycarbonyl) phenoxy]phthalonitrile 1

A mixture of 4,5-dichlorophthalonitrile (1.0 g, 5.1 mmol), methyl 4-hydroxybenzoate (1.86 g, 12.2 mmol), and potassium carbonate (3.53 g, 25.5 mmol) in DMF (60 mL) was heated at 70 ℃ overnight. Then the solvent was removed in vacuo. The residue was purified by silica-gel chromatography using CHCl$_3$ as eluent. The product was obtained as a white solid (1.33 g, 61%). ^{1}H NMR (CDCl$_3$) 8.080 (d, J=8.8 Hz, 4H, ArH), 7.371 (s, 2H, ArH), 7.015 (d, J=8.8 Hz, 4H, ArH), 3.915 (s, 6 H, COOCH$_3$). ^{13}C NMR (CDCl$_3$) δ 165.84, 158.11, 150.79, 132.16, 127.33, 124.50, 118.34, 114.41, 112.04, 52.27.

1.3　Synthesis of 4-{2-[2-(2-methoxyethoxy)ethoxy] ethoxy}phthalonitrile 2

A mixture of 4-nitrophthalonitrile (1.72 g, 0.01 mol), 2-(2-(2-methoxyethoxy)ethoxy)ethanol (1.64 g, 0.01 mol), and potassium carbonate (13.90 g, 0.1 mol) in DMF (80 mL) was heated at 80 ℃ overnight. Then the reaction mixture was poured into ice water. After filtration, the solid product was purified by silica-gel chromatography using CH$_2$Cl$_2$ as eluent to give a white solid product (2.09 g, 72%). ^{1}H NMR (CDCl$_3$) 7.194 (d, 1H, J=8.8 Hz, ArH), 7.302 (d, 1H, J=2.8 Hz, ArH), 7.219 (dd, 1H, J=8.8 Hz, J=2.4 Hz, ArH), 4.218 (t, 2H, J=4.6 Hz, -OCH$_2$-), 3.876 (t, 2H, J=4.4 Hz, -OCH$_2$-), 3.698~3.720 (m, 2H, -OCH$_2$-), 3.617~3.665 (m, 4H, -OCH$_2$-), 3.537 (t, 2H, J=2.0 Hz, -OCH$_2$-), 3.521 (s, 3H, -OCH$_3$). ^{13}C NMR (CDCl$_3$) δ 162.00, 153.11, 119.81, 119.53, 117.32, 115.62, 115.21, 107.36, 71.87, 70.91, 70.60, 70.56, 107.38, 52.91.

1.4　Synthesis of phthalocyaninato zinc complexes (3~8)

A mixture of 4,5-bis [(4-methyloxycarbonyl) phenoxy]phthalonitrile (1) (0.1 mmol), 4-{2-[2-(2-

methoxyethoxy)ethoxy]ethoxy}phthalonitrile (2) (0.1 mmol), Zn (OAc)$_2$·2H$_2$O (110 mg, 0.05 mmol), and DBU (0.5 g) in n-pentanol (15 mL) was heated at 140 ℃ overnight under a slow stream of nitrogen. After cooling, the solvent was removed in vacuo. The residue was purified by silica-gel column chromatography using CH$_2$Cl$_2$-MeOH as eluent. Six fractions were collected.

Zn[Pc(BP)$_4$] (3). Mobile phase: CH$_2$Cl$_2$. ^{1}H NMR (CDCl$_3$) δ 8.964 (s, 8H, PcH$_\alpha$), 8.029 (d, 16H, J=8.8 Hz, ArH), 7.167 (d, 16H, J=8.8 Hz, ArH), 4.297 (t, 16H, J=6.8 Hz, -COOCH$_2$-), 1.729~1.781 (m, 16H, -CH$_2$-), 1.374~1.435 (m, 32H, -CH$_2$-), 0.921 (t, 24H, J=7.0 Hz, -CH$_3$).

Zn [Pc (BP)$_3$ (TEG)] (4). Mobile phase: CH$_2$Cl$_2$-MeOH from 0.3% to 0.5% (V/V). H NMR (CDCl$_3$) 8.921 (d, 1H, J=8.0 Hz, PcH$_\alpha$), 8.899 (s, 1H, PcH$_\alpha$), 8.615~8.639 (m, 3H, PcH$_\alpha$), 8.573 (s, 1H, PcH), 8.503 (s, 1H, PcH$_\alpha$), 8.424 (s, 1H, PcH$_\alpha$), 7.972~8.069 (m, 12H, ArH), 7.661 (dd, 1H, J=8.4 Hz, J=2.0 Hz, PcH$_\beta$), 7.165~7.282 (m, 12H, ArH), 4.652 (s, 2H, -OCH$_2$-), 4.238~4.307 (m, 12H, -COOCH$_2$-), 4.019 (s, 2H, -CH$_2$O-), 3.839 (t, 2H, J=4.8 Hz, -OCH$_2$-), 3.740 (t, 2H, J=4.6 Hz, -CH$_2$O-), 3.678 (t, 2H, J=4.6 Hz, -OCH$_2$-), 3.543 (t, 2H, J=4.6 Hz, -CH$_2$O-), 3.340 (s, 3H, -OCH$_3$), 1.670~1.737 (m, 12H, -CH$_2$-), 1.302~1.368 (m, 24H, -CH$_2$-), 0.831~0.878 (m, 18H, -CH$_3$).

Zn[Pc(BP)$_2$(TEG)$_2$]-opp (5). Mobile phase: CH$_2$Cl$_2$ containing MeOH from 0.8% to 1.0% (V/V). ^{1}H NMR (CDCl$_3$) 8.847 (d, 2H, J=8.4 Hz, PcH$_\alpha$), 8.783~8.828 (m, 2H, PcH$_\alpha$), 8.637 (s, 1H, PcH$_\alpha$), 8.618 (s, 1H, PcH$_\alpha$), 8.353 (s, 1H, PcH$_\alpha$), 8.310 (s, 1H, PcH$_\alpha$), 8.021~8.081 (m, 8H, ArH), 7.583 (d, 2H, J=8.4 Hz, PcH$_\beta$), 7.233~7.292 (m, 8H, ArH), 4.519 (br s, 4H, -OCH$_2$-), 4.263 (t, 8H, J=6.6 Hz, -COOCH$_2$-), 4.076 (br s, 4H, -CH$_2$O-), 3.842 (t, 4H, J=4.8 Hz, -OCH$_2$-), 3.731 (t, 4H, J=4.8 Hz, -CH$_2$O-), 3.658 (t, 4H, J=4.8 Hz, -OCH$_2$-), 3.515 (t, 4H, J=4.6 Hz, -CH$_2$O-), 3.307 (s, 3H, -OCH$_3$), 1.683~1.752 (m, 8H, -CH$_2$-), 1.297~1.407 (m, 32H, -CH$_2$-), 0.855~0.876 (m, 24H, -CH$_3$).

Zn[Pc(BP)$_2$(TEG)$_2$]-adj (6). Mobile phase: CH$_2$Cl$_2$-MeOH(V/V from 99:1 to 98.8:1.2). ^{1}H NMR (CDCl$_3$) δ 9.058(d, J=8.4, PcH$_\alpha$), 8.924(d, J=8.4, PcH$_\alpha$), 8.857(d,

J =8.0, PcH$_\alpha$), (total 2H), 8.810 (s, PcH$_\alpha$), 8.784 (s, PcH$_\alpha$), 8.531(s, PcH$_\alpha$), 8.575(s, PcH$_\alpha$), 8.403(s, PcH$_\alpha$), 8.462 (s, PcH$_\alpha$), 8.434 (s, PcH$_\alpha$), (total 4H), 8.447(s, PcH$_\alpha$), 8.403(s, PcH$_\alpha$), (total 2H), 8.010~8.100(m, 8H, ArH), 7.671(d, 1H, J=8.4 Hz, PcH$_\alpha$),7.650(d, 1H, J=8.0 Hz, PcH$_\beta$), 7.215~7.337 (m, 8H, ArH), 4.493~4.572 (m, 4H, -OCH$_2$-), 4.232~4.303 (m, 8H, -COOCH$_2$-), 4.052~4.120 (m, 4H, -CH$_2$O-), 3.842~3.910 (m, 4H, -OCH$_2$-), 3.738~3.781(m, 4H, -CH$_2$O-), 3.670~3.707 (m, 4H, -OCH$_2$-), 3.532~3.578 (m, 4H, -CH$_2$O-), 3.337~3.355(m, 3H, -OCH$_3$), 1.693~1.759(m, 8H, -CH$_2$-), 1.317~1.381(m, 32H, -CH$_2$-), 0.844~0.896 (m, 24H, -CH$_3$).

Zn [Pc (BP) (TEG)$_3$] (**7**). Mobile phase: CH$_2$Cl$_2$-MeOH(98.5:1.5, V/V). ^{1}H NMR (CDCl$_3$) δ 8.976(d, J=8.4, PcH$_\alpha$) δ 8.929 (d, J=8.0, PcH$_\alpha$) δ 8.920 (d, J=8.4, PcH$_\alpha$) 8.909 (d, J=8.0, PcH$_\alpha$) 8.899 d, J=8.4, PcH$_\alpha$), 8.854 (d, J=7.6, PcH$_\alpha$) 8.844 (d, J=7.2, PcH$_\alpha$), (total 3H), 8.813 (s, PcH$_\alpha$), 8.690 (s, PcH$_\alpha$), 8.496 (s, PcH$_\alpha$), 8.478 (s, PcH$_\alpha$), 8.451 (s, PcH$_\alpha$), (total 2H), 8.401 (s, PcH$_\alpha$), 8.364 (s, PcH$_\alpha$), 8.359 (s, PcH$_\alpha$), (total 3H), 8.078~8.159 (m, 4H, ArH), 7.571~7.631 (m, 3H, PcH$_\beta$), 7.274~7.373 (m, 4H, ArH), 4.598 (br s, 6H, -OCH$_2$-), 4.282~4.309 (m, 4H, -COOCH$_2$-), 4.139 (br s, 6H, -CH$_2$O-), 3.883~3.921 (m, 6H, -OCH$_2$-), 3.770~3.817 (m, 6H, -CH$_2$O-), 3.705~3.739 (m, 6H, -OCH$_2$-), 3.550~3.597 (m, 6H, -CH$_2$O-), 3.350~3.371 (m, 9H, -OCH$_3$), 1.717~1.767 (m, 4H, -CH$_2$-), 1.380 (br s, 8H, -CH$_2$-), 0.874~0.902 (m, 6H, -CH$_3$).

Zn [Pc (TEG)$_4$] (**8**). Mobile phase: CH$_2$Cl$_2$-MeOH (98:2, V/V). H NMR (CDCl$_3$) δ 8.924 (br s, 4H, PcH$_\alpha$), 8.470 (br s, 4H, PcH$_\alpha$), 7.545(br s, 4H, PcH$_\beta$), 4.689 (s, 8H, -OCH$_2$-), 4.178 (br s, 8H, -CH$_2$O-), 3.936 (br s, 8H, -OCH$_2$-), 3.820 (br s, 8H, -CH$_2$O-), 3.740 (br s, 8H, -OCH$_2$-), 3.598 (t, 8H, J=4.2 Hz, -CH$_2$O-), 3.385 (s, 12H, -OCH$_3$).

2 Results and discussion

2.1 Synthesis

4,5-Bis [(4-methyloxycarbonyl)phenoxy]phthalonitrile (**1**) was prepared by treating 4,5-dichlorophthalonitrile, methyl 4-hydroxybenzoate, and potassium carbonate in DMF, while 4-{2-[2-(2-methoxyethoxy) ethoxy]ethoxy}phthalonitrile (**2**) was obtained using 4-nitrophthalonitrile, triethylene glycol monomethyl ether, and potassium carbonate in DMF. As shown in Scheme 1, phthalocyaninato zinc (Ⅱ) complexes are obtained as a mixture of six components by the mix-cyclisation of the two kinds of precursors in the presence of DBU and Zn (OAc)$_2$ ·2H$_2$O followed by transesterification in refluxing n-pentanol. In particular, the whole series of six phthalocyanine compounds **3**~**8** have been completely separated by simple silica-gel column chromatography and eluted in
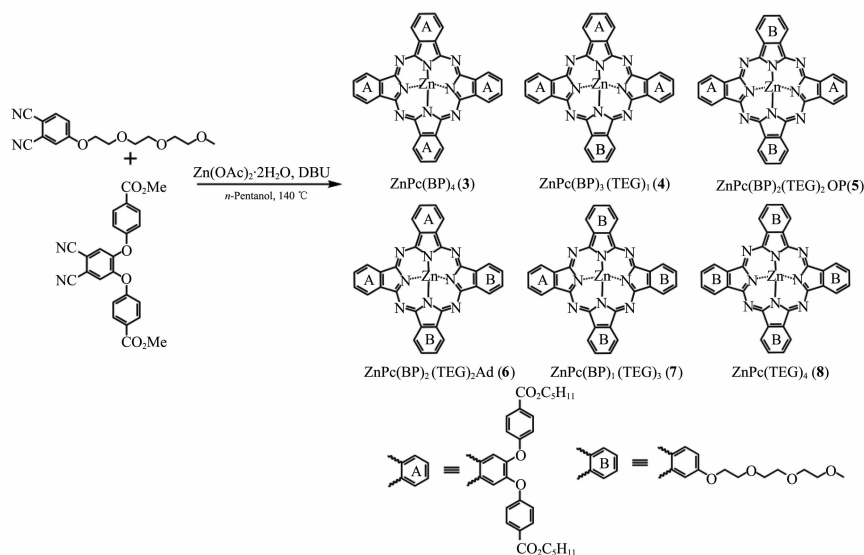
Scheme 1　Synthesis of phthalocyaninato zinc(Ⅱ) complexes 3~8

the order from **3** to **8** along with increasing the polarity of the eluent. Satisfactory elemental analysis results are obtained after column chromatography followed by recrystallization (see Table 1). Interestingly, the six phthalocyanine compounds are isolated with the yield from 4% to 18%, which is in line with the statistical distribution expected with the ratio of 1:4:2:4:4:1 from **3** to **8**.

These phthalocyanine compounds have also been characterized by MALDI-TOF mass spectrometry, ^{1}H NMR, 2D COSY, and UV-Vis spectroscopy. Their MALDI-TOF mass spectra clearly show intense signals of molecular ions (M[+]/MH[+]) (Table 1). The isotopic patterns closely resemble the simulated ones as exemplified by the spectrum of $Zn[Pc(BP)_2(TEG)_2]$-opp (**5**)[Figure S1 (Supporting information)].

<p align="center">Table 1　Yields, mass spectroscopic and elemental analysis data for compounds 3~8 [a]</p>

Compound	Molecular formula	Yield / %	M[+]/MH[+](m/z)	Elemental analysis / %		
				C	H	N
$Zn[Pc(BP)_4]$ (**3**)	$ZnC_{128}H_{128}N_8O_{24}$	4	2 226.844(2 225.837)	68.73(69.01)	5.76(5.79)	5.01(5.03)
$Zn[Pc(BP)_3(TEG)]$ (**4**)	$ZnC_{111}H_{114}N_8O_{22}$	14	1 976.082(1 975.737)	66.73(67.42)	5.78(5.81)	5.63(5.67)
$Zn[Pc(BP)_2(TEG)_2]$-opp (**5**)	$ZnC_{94}H_{100}N_8O_{20}$	6	1 726.040(1 725.638)	64.52(65.37)	5.83(5.84)	6.35(6.49)
$Zn[Pc(BP)_2(TEG)_2]$-adj (**6**)	$ZnC_{94}H_{100}N_8O_{20}$	17	1 726.235(1 725.638)	65.01(65.37)	5.77(5.84)	6.44(6.49)
$Zn[Pc(BP)(TEG)_3]$ (**7**)	$ZnC_{77}H_{86}N_8O_{18}$	18	1 474.778(1 474.535)	62.13(62.62)	5.79(5.87)	7.46(7.59)
$Zn[Pc(TEG)_4]$ (**8**)	$ZnC_{60}H_{72}N_8O_{16}$	5	1 224.830(1 224.436)	58.17(58.75)	5.84(5.92)	8.95(9.13)

[a] Calculated values are given in parentheses

2.2　NMR spectra studies

^{1}H NMR and 2D COSY spectra of all the six compounds have been recorded in $CDCl_3$ with a drop of pyridine[d5], which reduces the aggregation of the compounds. As shown in Fig.1 and summarized in Table 2, all the signals especially for compounds **4~6** can be assigned unambiguously through the correlations established in this two dimensional NMR
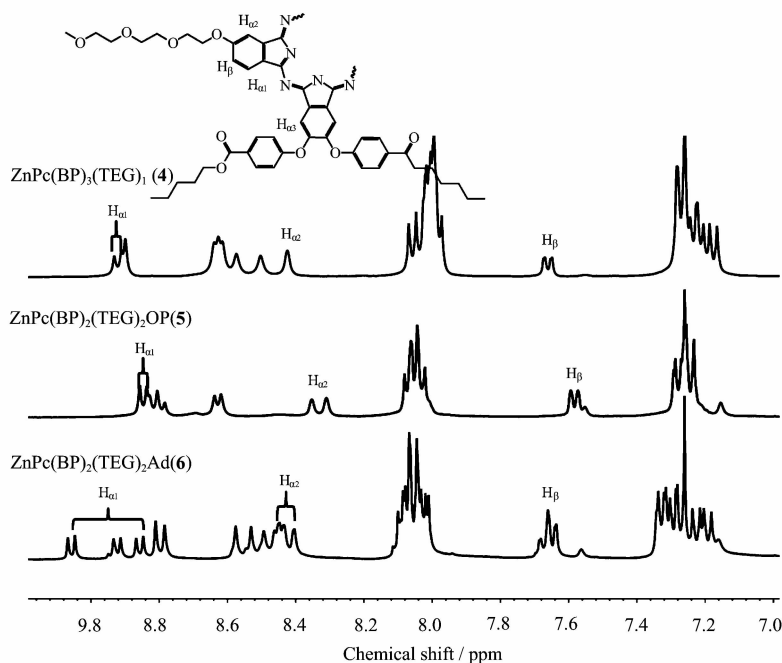

<p align="center">Fig.1　^{1}H NMR spectra of compounds Zn[Pc(BP)₃(TEG)] (4), Zn[Pc(BP)₂(TEG)₂]-opp (5), and Zn[Pc(BP)₂(TEG)₂]-adj (6) in CDCl₃ with a drop of pyridine[d5]</p>

Table 2　Chemical shift(ppm) of aromatic protons in 3~8

| Compound	$H_{\alpha1}$	$H_{\alpha2}$	$H_{\alpha3}$	H_{β}	H_{Ar}
3			8.964		8.029, 7.167
4	8.921	8.424	8.899, 8.639, 8.626, 8.615, 8.573, 8.503	7.661	7.972~8.06, 7.165~7.282
5	8.847	8.353, 8.310	8.828, 8.805, 8.783, 8.637, 8.618	7.583	8.021~8.081, 7.233~7.292
6	9.058, 8.924, 8.857	8.447, 8.403	8.810, 8.784, 8.531, 8.575, 8.403, 8.462, 8.434	7.671, 7.650	8.010~8.100, 7.215~7.337
7	8.976, 8.929, 8.920, 8.909, 8.899, 8.854, 8.844	8.401, 8.364, 8.359	8.813, 8.690, 8.496, 8.478, 8.451	7.545~7.631	8.078~8.159, 7.274~7.373
8	8.924	8.470		7.545	
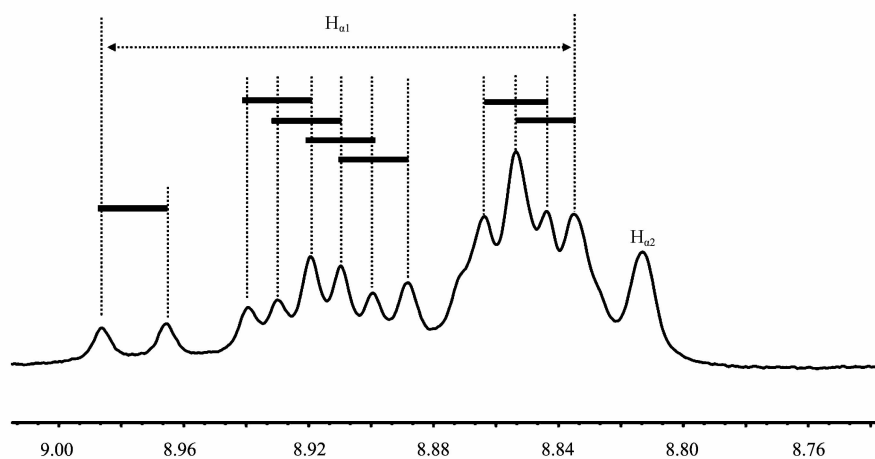
Fig.2　^{1}H NMR spectrum of $Zn[Pc(BP)(TEG)_3]$ (**7**) in CDCl$_3$ with a drop of pyridine[d5]

spectra (Figures S4~S9 (Supporting information)). The α-position protons H_1, H_2, and $H_{\alpha3}$ of phthalocyanine ring resonate at δ 8.310~9.058, while their β-position protons resonate at δ 7.545~7.661. When comparing the chemical shifts of $H_{\alpha1}$, $H_{\alpha2}$, and $H_{\alpha3}$, the signals of H_2 and $H_{\alpha3}$ lie in the higher field since they suffer electronic and shielding effects of the substituents from adjacent position. The remaining signals arise from the protons of substituents. The signals at δ 7.972~8.159 and 7.165~7.373 are assigned to the aromatic protons of phenoxy groups, the signals at δ 4.297~4.689 and 4.238~4.309 are attributed to the -position aliphatic protons of triethylene glycol groups and pentyloxycarbonyl groups, respectively, and the signals at δ 3.307~4.178 and 0.844~1.781 are separately assigned to the rest aliphatic protons of

triethylene glycol and alkoxycarbonyl side chains with correct integration. Interestingly, although there is no isomer for compound $Zn[Pc(BP)_3(TEG)]$ (**4**), its six H_3 protons exhibit six singlets ranging from δ 8.503 to 8.899, which may attribute to the surrounding environment of different H_3 protons. It can also be observed that the number of peaks for $H_{\alpha1}$, $H_{\alpha2}$ and $H_{\alpha3}$ is different between $Zn[Pc(BP)_2(TEG)_2]$-opp (**5**) and $Zn[Pc(BP)_2(TEG)_2]$-adj (**6**), which can be interpreted by the different isomers arising from disposition of the triethylene glycol groups. As shown in Figure S2 (Supporting information), there are two possible isomers for compound $Zn[Pc(BP)_2(TEG)_2]$-opp (**5**). The environment of the two kinds of H_1 keeps almost the same, resulting in only a doublet signal. For compound $Zn[Pc(BP)_2(TEG)_2]$-adj (**6**), three possible

Table 3　Electronic absorption data for 3~8 in CHCl₃

Compound	λ_{max} / nm (lgε/(L·mol⁻¹·cm⁻¹))		
Zn[Pc(BP)₄] (**3**)	357(4.87)	613(4.49)	680(5.28)
Zn[Pc(BP)₃(TEG)] (**4**)	359(5.07)	612(4.64)	681(5.36)
Zn[Pc(BP)₂(TEG)₂]-opp (**5**)	356(5.01)	611(4.51)	637(4.56)
		672(5.13)	692(5.19)
Zn[Pc(BP)₂(TEG)₂]-adj (**6**)	355(5.01)	614(4.63)	680(5.33)
Zn[Pc(BP)(TEG)₃] (**7**)	354(5.05)	614(4.62)	683(5.26)
Zn[Pc(TEG)₄] (**8**)	355(5.08)	614(4.72)	680(5.39)
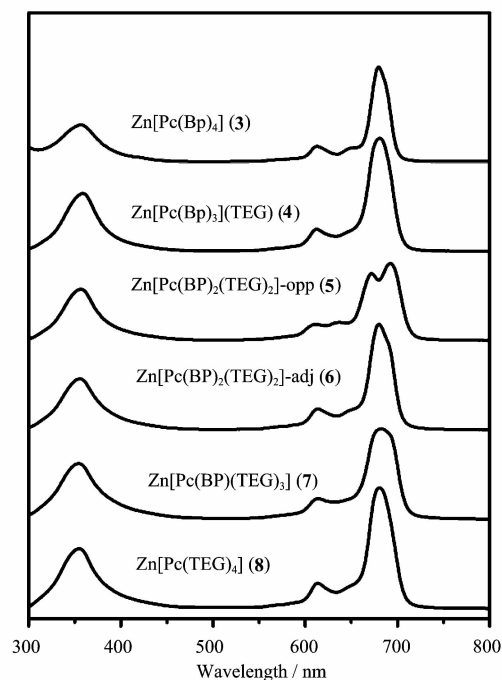
The concentration was fixed at 5×10⁻⁶ mol·L⁻¹

Fig.3　UV-Vis spectra of compounds **3~8** in CHCl₃

isomers give four kinds of H₁ and therefore three doublet signals at δ 9.058, 8.924, 8.857 are detected (Figure 1). For Zn[Pc(BP)(TEG)₃] (**7**), although it contains four isomers, the disposition of the three

triethylene glycol groups yields ten kinds of H₁ due to the same reason. Seven sets of doublet signals are observed in the region of 8.844 ~8.976 with the coupling constant about 8.0 [Figure 2, Figure S11 (Supporting information)]. Other protons of phthalocyanine ring $H_{\alpha2}$, $H_{\alpha3}$ and H_{β} can be also interpreted by the same procedure based on the above-mentioned isomers.

2.3　Electronic absorption studies

The data for electronic absorption spectra of compounds **3~8** are summarized in Table 3. As can be seen in Figure 3, all the absorption spectra show a typical broad Soret band at 354 ~359 nm, which involves a couple of electronic transitions related to the third occupied HOMO and the first LUMO, and a typical Q band at 680~683 nm with a vibronic band at 612 ~614 nm except Zn [Pc (BP)₂ (TEG)₂]-opp (**5**) bearing splitting Q and vibration bands due to the decreased molecular symmetry of this compound [26]. Similar to the previous reports about low symmetry Pcs[30], the absorption positions of the Q bands seem to bear no relationship to the number of two kinds of substituents.

Table 4　Half-wave redox potentials of 3~8 in CH₂Cl₂ containing 0.1 mol·L⁻¹ TBAP

Compound	Oxd₂	Oxd₁	Red₁	Red₂	Red₃	$\Delta E_{1/2}^{0}$ [a]
Zn[Pc(BP)₄] (**3**)	1.35	0.80	−1.03	−1.20	−1.43	1.83
Zn[Pc(BP)₃(TEG)] (**4**)	1.33	0.70	−0.85	−1.08	−1.48	1.55
Zn[Pc(BP)₂(TEG)₂]-opp (**5**)	1.37	0.69	−0.87	−1.12	−1.38	1.56
Zn[Pc(BP)₂(TEG)₂]-adj (**6**)	1.32	0.63	−0.98	−1.23		1.61
Zn[Pc(BP)(TEG)₃] (**7**)	1.30	0.56	−1.12	−1.52		1.68
Zn[Pc(TEG)₄] (**8**)	1.29	0.54	−0.88	−1.16		1.42

[a] $\Delta E^{0}_{1/2}$ is the potential difference between the first oxidation and first reduction processes, that is, the HOMO-LUMO gap of corresponding molecule

2.4 Electrochemical properties studies

The electrochemical behavior of the whole series of compounds **3~8** was examined by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in CH_2Cl_2. As detailed in Table 4 and Figure S13-18 (Supporting information), all these six compounds show two quasi-reversible one-electron oxidations. However, compounds **3 ~5** exhibit three quasi-reversible one-electron reductions, while only two quasi-reversible one-electron reductions are found for **6~8**. All the redox processes are ligand-based since the divalent zinc metal ion can not be redoxed in this range. The first oxidation potentials gradually decrease along with increasing the number of triethylene glycol substituents from **3** to **8**. The potential differences of first oxidation and first reduction, which reflects the HOMO-LUMO gap, are between 1.42 and 1.83 V for **3~8**.

3　Conclusions

We have prepared a whole series of six phthalocyaninato zinc(Ⅱ) complexes from cross-condensation reaction between 4,5-bis [(4-methyloxycarbonyl) phenoxy] phthalonitrile and 4-{2-[2-(2-methoxyethoxy) ethoxy]ethoxy}phthalonitrile. All these six compounds have been separated by simple silica-gel column chromatography. Their spectroscopic and electrochemical properties have also been studied.

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