



Synthesis and separation of the constitutional isomers of 1(4),8(11),15(18),22(25)-tetrakis[(pentyloxycarbonyl)phenoxy]-phthalocyaninato zinc(II) complexes

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ABSTRACT

Cyclic tetramerization of 3-[(methyloxycarbonyl)phenoxy]phthalonitrile (**1a–1c**) in the presence of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) followed by transesterification in refluxing *n*-pentanol afforded 1(4),8(11),15(18),22(25)-tetrakis[(pentyloxycarbonyl)phenoxy]phthalocyaninato zinc(II) complexes (**2a–2c**) as a mixture of four constitutional isomers. Simple silica-gel column chromatography leads to the successful separation of pure isomers with the C_{4h} and D_{2h} symmetry together with a section containing the C_{2v} and C_s isomers, which have been characterized with a wide range of spectroscopic methods including MALDI-TOF mass, electronic absorption, ^1H NMR, and 2D COSY spectroscopy. Synthesis yields in combination with the NMR spectroscopic results reveal that the distribution of the four isomers in the final product for **2a–2c** does not strictly follow that expected according to statistical calculation with the ratio of $C_{4h}:C_{2v}:C_s:D_{2h} = 1:2:4:1$, indicating the effect of steric hindrance of substituents on the formation of various constitutional isomers.

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1. Introduction

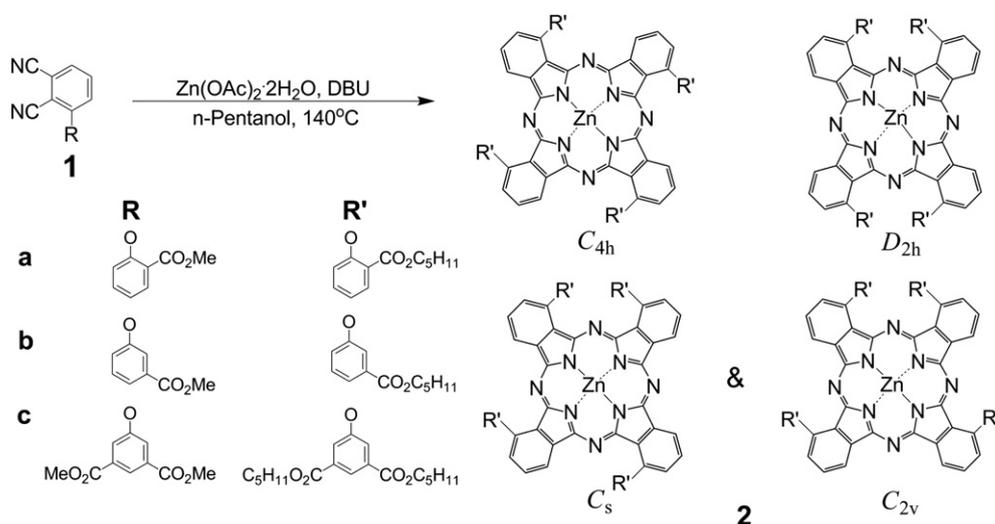
Phthalocyanines as versatile functional dyes have got a wide range of applications in the fields of organic semiconductors, nonlinear optical and optical limiting materials, chemosensors, organic photovoltaics, catalysis, and photosensitisers for photodynamic therapy [1–7]. Their physicochemical, electrochemical, and spectroscopic properties, and intermolecular interactions can be modulated by rational modification of the metal center and the substituents of phthalocyanines. In line with this idea, lowering the molecular symmetry of phthalocyanine derivatives through suitable modification on the peripheral substituents and/or the nature of the π -conjugation system has been attracting increasing research interests [8]. Among the low symmetry phthalocyanines, isolation of constitutional isomers arising from cyclic tetramerization of one unsymmetrical precursor such as 3-substituted-phthalonitrile has been common but extremely difficult. However, quite a few constitutional isomers of corresponding low symmetry phthalocyanine compounds have been successfully isolated by means of HPLC technique or TLC method [9]. Separation of constitutional isomers depending on simple silica-gel column

chromatography was still rarely reported, to the best of our knowledge. In 2004, the C_{4h} and C_{2v} isomers of phthalocyaninato metal complexes of Zn and Pb were prepared from cyclic tetramerization of 3-(2,4-dimethyl-3-pentyloxy)phthalonitrile and separated by column chromatography on silica gel [10a], while the other two isomers with D_{2h} and C_s symmetry were not detected. In a similar manner, a trace amount of D_{2h} isomer was isolated from the mixture of four constitutional isomers of tetrahexyl phthalocyaninato vanadium(IV) oxide complex [10b]. Very recently, three of the four constitutional isomers with the C_{4h} , C_s , and C_{2v} symmetry (except the D_{2h} one) for the triazolo-fused azaphthalocyanine synthesized from 3-substituted 8-(diethylamino)-[1,2,4]triazolo[4,3-a]-pyrazine-5,6-dicarbonitrile were successfully isolated [10c]. However, it should be mentioned that the C_{4h} isomer of phthalocyanine derivatives with bulky substituents at the 1,8,15,22-positions usually could be obtained and isolated by controlling the reaction at relatively low temperature condition [11,12].

In the presented paper, a series of 1(4),8(11),15(18),22(25)-tetrakis[(pentyloxycarbonyl)phenoxy]phthalocyaninato zinc(II) complexes **2a–2c**, which are a mixture of four constitutional isomers, were synthesized by the cyclic tetramerization of 3-[(methyloxycarbonyl)phenoxy]phthalonitrile (**1a–1c**) and the transesterification of substituents in the presence of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in refluxing *n*-pentanol.

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Scheme 1. Synthesis of constitutional isomers of complexes **2a–2c**.

Most importantly, the constitutional isomers with the C_{4h} and D_{2h} symmetry together with a mixture containing the C_{2v} and C_s isomers have been successfully separated by simple silica-gel column chromatography.

2. Experimental section

2.1. General remarks

n-Pentanol and dimethylformamide (DMF) were distilled from sodium and anhydrous $MgSO_4$, respectively. Column chromatography was carried out on a silica-gel column (Qingdao Haiyang, 200–300 mesh) with the indicated eluents. All of the other reagents and solvents were used as received.

1H NMR spectra were recorded on a Bruker DPX 400 spectrometer (1H : 400 MHz) in $CDCl_3$ solution unless otherwise stated. Spectra were referenced internally using the residual solvent resonances ($\delta = 7.26$ for 1H NMR) relative to $SiMe_4$ ($\delta = 0$ ppm). ^{13}C NMR spectra were referenced internally by using the solvent resonances ($\delta = 77.0$ ppm 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.

2.2. Synthesis of 3-substituted-phthalonitriles (**1a–1c**)

A mixture of 3-nitrophthalonitrile (1.72 g, 0.01 mol), methyl hydroxybenzoate (0.01 mol), and potassium carbonate (13.90 g, 0.1 mol) in DMF (80 mL) was heated at 80 °C overnight. Then the reaction mixture was poured into ice water. After filtration, the solid product was purified by silica-gel chromatography using CH_2Cl_2 as eluent to give a white solid product.

2.2.1. 3-(2-Methoxycarbonylphenoxy)phthalonitrile (**1a**)

Yield: 80%. 1H NMR ($CDCl_3$) δ 8.069(dd, 1H, $J = 7.6$ Hz, $J = 1.6$ Hz, ArH), 7.655(ddd, 1H, $J = 7.6$ Hz, $J = 7.6$ Hz, $J = 1.6$ Hz, ArH), 7.513(dd, 1H, $J = 8.4$ Hz, $J = 8.2$ Hz, ArH), 7.425(dd, 1H, $J = 7.6$ Hz, $J = 7.6$ Hz, ArH), 7.427(d, 1H, $J = 7.6$ Hz, ArH), 7.198(d, 1H, $J = 8.4$ Hz, ArH), 6.854(d, 1H, $J = 8.4$ Hz, ArH), 3.781(s, 3H, $-COOCH_3$). ^{13}C NMR ($CDCl_3$) δ 164.67, 161.59, 152.57, 134.70, 134.35, 132.92, 126.92, 126.69, 124.09, 123.51, 119.22, 117.30, 115.32, 112.84, 105.53, 52.56.

2.2.2. 3-(3-Methoxycarbonylphenoxy)phthalonitrile (**1b**)

Yield: 76%. 1H NMR ($CDCl_3$) δ 7.973(d, 1H, $J = 7.6$ Hz, ArH), 7.745(dd, 1H, $J = 2.0$ Hz, $J = 1.6$ Hz, ArH), 7.600(dd, 1H, $J = 8.0$ Hz, $J = 8.0$ Hz, ArH), 7.548(dd, 1H, $J = 8.0$ Hz, $J = 8.0$ Hz, ArH), 7.506(d, 1H, $J = 7.6$ Hz, ArH), 7.330(dd, 1H, $J = 8.0$ Hz, $J = 2.4$ Hz, ArH), 7.096(d, 1H, $J = 8.8$ Hz, ArH), 3.927(s, 6H, $-COOCH_3$). ^{13}C NMR ($CDCl_3$) δ 165.67, 160.16, 154.04, 134.82, 132.73, 130.71, 127.65, 127.09, 124.74, 121.04, 121.00, 117.31, 115.02, 112.54, 106.46, 52.46.

2.2.3. 3-[3,5-Bis(methoxycarbonyl)phenoxy] phthalonitrile (**1c**)

Yield: 75%. 1H NMR ($CDCl_3$) δ 8.583(s, 1H, ArH), 7.940–7.944(m, 2H, ArH), 7.639(dd, 1H, $J = 8.4$ Hz, $J = 8.2$ Hz, ArH), 7.554(d, 1H, $J = 8.0$ Hz, ArH), 7.124(d, 1H, $J = 8.4$ Hz, ArH), 3.958(s, 6H, $-COOCH_3$). ^{13}C NMR ($CDCl_3$) δ 165.10, 159.70, 154.57, 134.85, 133.36, 128.26, 128.02, 125.17, 121.42, 117.94, 114.94, 112.32, 107.38, 52.91.

2.3. Synthesis of phthalocyanines (**2a–2c**)

A mixture of phthalonitrile **1** (0.1 mmol), $Zn(OAc)_2 \cdot 2H_2O$ (110 mg, 0.05 mmol), and DBU (0.5 g) in *n*-pentanol (15 mL) was heated at 140 °C 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_2Cl_2 containing MeOH as eluent. Three fractions were collected.

2.3.1. Phthalocyanine **2a**

Mobile phase: CH_2Cl_2 containing MeOH from 0.3% to 1.5% (V/V). C_{4h} isomer: 1H NMR ($CDCl_3$) δ 8.850(d, 4H, $J = 7.6$ Hz, PcH_α),

Table 1
Yields of isolated isomers and mass spectroscopic data for compound **2a–2c**.^a

Compound	Isomer	Total yield (%)	Yield (%)	M^+ (m/z)
2a	C_{4h}	23.2	6.0	1400.119
	C_{2v} & C_s		15.6	1400.892
	D_{2h}		1.6	1400.992
2b	C_{4h}	74.3	13.8	1400.521
	C_{2v} & C_s		49.5	1400.454
	D_{2h}		10.9	1400.343
2c	C_{4h}	37.5	10.4	1858.491
	C_{2v} & C_s		22.4	1858.250
	D_{2h}		4.7	1858.263

^a Calculated values for $Zn_{C_{80}H_{72}N_8O_{12}}$ (**2a** and **2b**) [M^+] 1400.456; $Zn_{C_{104}H_{112}N_8O_{20}}$ (**2c**) [M^+] 1857.732.

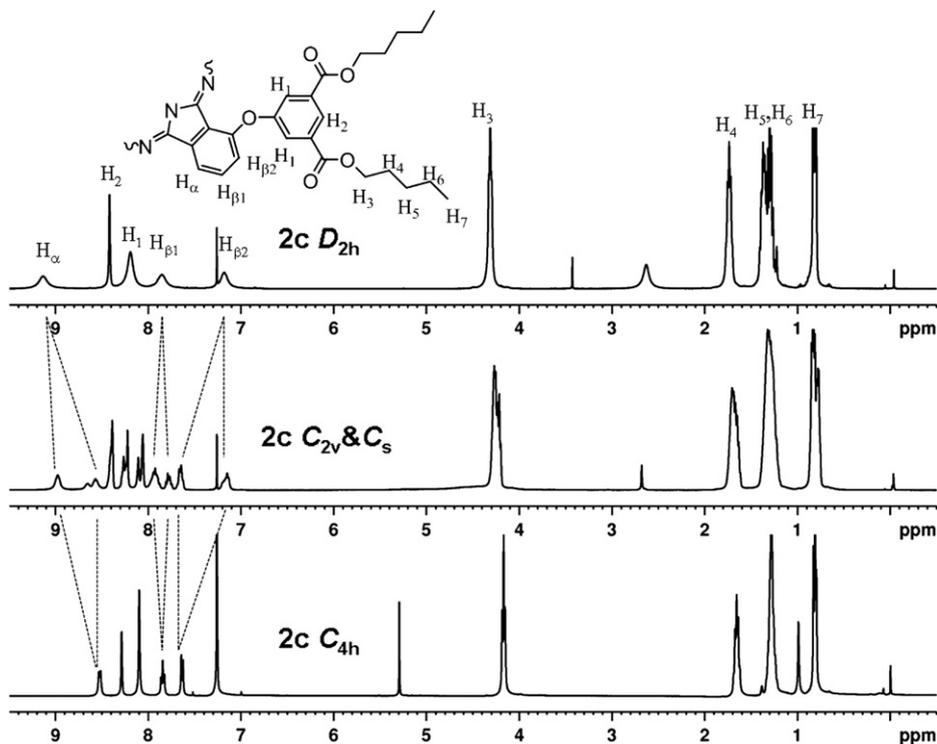


Fig. 1. ^1H NMR spectra of $\text{C}_{4\text{h}}$ (in CDCl_3), C_s & $\text{C}_{2\text{v}}$, and $\text{D}_{2\text{h}}$ isomers of compound **2c** (in CDCl_3 with a drop of pyridine- D_5).

8.221(dd, 4H, $J = 7.6$ Hz, $J = 1.6$ Hz, ArH), 7.955(dd, 4H, $J = 7.6$ Hz, $J = 7.6$ Hz, PcH_β), 7.610(d, 4H, $J = 7.6$ Hz, PcH_β), 7.282(ddd, 4H, $J = 8.0$ Hz, $J = 7.6$ Hz, $J = 6.2$ Hz, $J = 1.2$ Hz, ArH), 7.193(d, 4H, $J = 7.6$ Hz, ArH), 7.178(d, 4H, $J = 7.6$ Hz, ArH), 4.301(t, 8H, $J = 6.8$ Hz, $-\text{COOCH}_2-$), 1.471–1.542(m, 8H, $-\text{CH}_2-$), 1.130–1.206(m, 8H, $-\text{CH}_2-$), 0.848–0.941(m, 8H, $-\text{CH}_2-$), 0.434(t, 12H, $J = 7.2$ Hz, $-\text{CH}_3$). $\text{D}_{2\text{h}}$ isomer: ^1H NMR (CDCl_3 with a drop of pyridine- D_5) δ 9.100(d, 4H, $J = 6.8$ Hz, PcH_α), 7.897(dd, 4H, $J = 8.0$ Hz, $J = 7.6$ Hz, PcH_β), 7.806(d, 4H, $J = 7.6$ Hz, ArH), 7.355(dd, 4H, $J = 8.0$ Hz, $J = 5.2$ Hz, ArH), 7.333(d, 4H, $J = 7.2$ Hz, ArH), 7.141–7.160(m, 4H, ArH; 4H, $J = 7.6$ Hz, PcH_β), 3.813(t, 8H, $J = 6.2$ Hz, $-\text{COOCH}_2-$), 0.974(br s, 8H, $-\text{CH}_2-$), 0.739(br s, 8H, $-\text{CH}_2-$), 0.533(br s, 8H, $-\text{CH}_2-$), 0.197(br s, 12H, $-\text{CH}_3$).

Table 2
Chemical shifts of protons on phthalocyanines **2a–2c** rings.^a

Compound	Isomer	H_α	$\text{H}_{\beta 1}$	$\text{H}_{\beta 2}$
2a	$\text{C}_{4\text{h}}$	8.850 (4)	7.955 (4)	7.610 (4)
	$\text{C}_{2\text{v}}$ & C_s	9.351 (1.42) [C_s]	8.091 [C_s]	7.661 [C_s]
		9.151 (0.58) [$\text{C}_{2\text{v}}$]	7.891 [$\text{C}_{2\text{v}}$]	7.178 [$\text{C}_{2\text{v}}$]
		8.883 (0.58) [$\text{C}_{2\text{v}}$]	7.955 [$\text{C}_{2\text{v}}$]	7.606 [$\text{C}_{2\text{v}}$]
		8.678 (0.71) & 8.652 (0.71) [C_s]	7.756 [C_s]	7.076 [C_s]
	$\text{D}_{2\text{h}}$	9.110 (4)	7.897 (4)	7.151 (4)
2b	$\text{C}_{4\text{h}}$	8.769 (4)	7.923 (4)	7.637 (4)
	$\text{C}_{2\text{v}}$ & C_s	8.982 (2) [$\text{C}_{2\text{v}}$ & C_s]		
		8.604 (0.73) [$\text{C}_{2\text{v}}$]		
		8.579 (0.73) [C_s]		
	$\text{D}_{2\text{h}}$	8.105 (0.54) [C_s]		
	8.972 (4)	7.847 (4)	7.169 (4)	
2c	$\text{C}_{4\text{h}}$	8.523 (4)	7.843 (4)	7.635 (4)
	$\text{C}_{2\text{v}}$ & C_s	8.974 (2) [$\text{C}_{2\text{v}}$ & C_s]		
		8.654 (0.65) [$\text{C}_{2\text{v}}$]		
		8.570 (1.35) [C_s]		
	$\text{D}_{2\text{h}}$	9.136 (4)	7.855 (4)	7.181 (4)

^a The integration values given in parentheses. The assignment of the isomers mixture given in bracket.

2.3.2. Phthalocyanine **2b**

Mobile phase: CH_2Cl_2 containing MeOH from 0.1% to 0.5% (V/V). $\text{C}_{4\text{h}}$ isomer: ^1H NMR (CDCl_3 with a drop of pyridine- D_5) δ 8.769(d, 4H, $J = 7.6$ Hz, PcH_α), 8.211(br s, 4H, ArH), 7.923(dd, 4H, $J = 7.6$ Hz, $J = 7.6$ Hz, PcH_β), 7.799(d, 4H, $J = 7.6$ Hz, ArH), 7.637(d, 4H, $J = 7.6$ Hz, PcH_β), 7.524–7.550(ddd, 4H, $J = 8.0$ Hz, $J = 2.6$ Hz, $J = 2.4$ Hz, ArH), 7.412(dd, 4H, $J = 8.0$ Hz, $J = 8.0$ Hz, ArH), 4.261(t, 8H, $J = 6.8$ Hz, COOCH_2-), 1.654–1.724(m, 8H, $-\text{CH}_2-$), 1.226–1.372(m, 16H, $-\text{CH}_2-$), 0.807(t, 12H, $J = 7.2$ Hz, $-\text{CH}_3$). $\text{D}_{2\text{h}}$ isomer: ^1H NMR (CDCl_3 with a drop of pyridine- D_5) δ 8.972(br s, 4H, PcH_α), 8.039(s, 4H, ArH), 7.847(dd, 4H, $J = 7.6$ Hz, PcH_β), 7.813(d, 4H, $J = 7.6$ Hz, ArH), 7.463(d, 4H, $J = 7.6$ Hz, ArH), 7.327(dd, 4H, $J = 8.0$ Hz, $J = 7.6$ Hz, ArH), 7.169(br s, 4H, PcH_β), 4.329(t, 8H, $J = 6.6$ Hz, $-\text{COOCH}_2-$), 1.726–1.795(m, 8H, $-\text{CH}_2-$), 1.279–1.441(m, 16H, $-\text{CH}_2-$), 0.848(t, 12H, $J = 7.2$ Hz, $-\text{CH}_3$).

2.3.3. Phthalocyanine **2c**

Mobile phase: CH_2Cl_2 containing MeOH from 0.1% to 0.5% (V/V). $\text{C}_{4\text{h}}$ isomer: ^1H NMR (CDCl_3 with a drop of pyridine- D_5) δ 8.523(d,

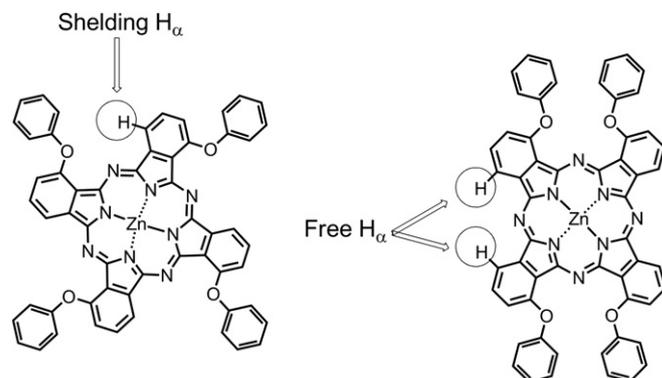


Fig. 2. Definition of “free H_α ” and “shielding H_α ”.

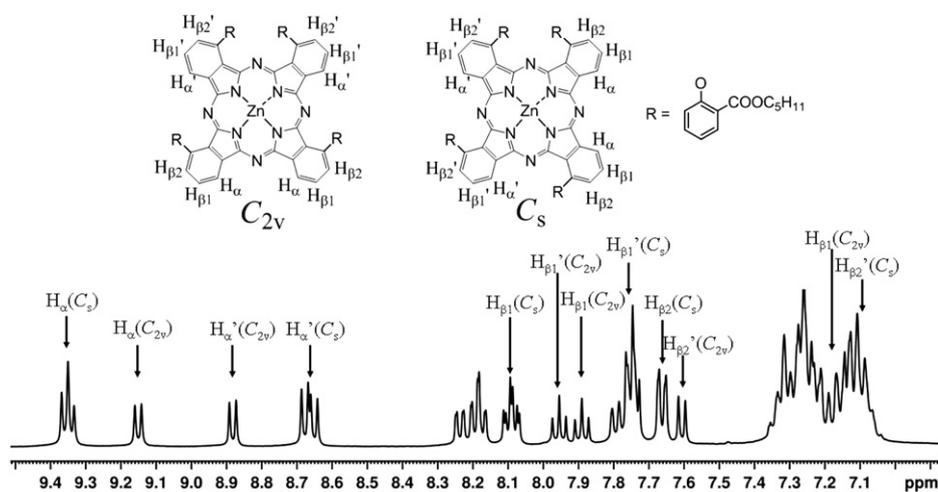


Fig. 3. ^1H NMR spectrum (δ 6.9–9.5 ppm) of C_5 & C_{2v} mixture of compound **2a** in CDCl_3 with a drop of pyridine[D_5].

4H, $J = 6.8$ Hz, PcH_α), 8.286(s, 4H, ArH), 8.097(s, 8H, ArH), 7.843(dd, 4H, $J = 7.6$ Hz, $J = 7.2$ Hz, PcH_β), 7.635(d, 4H, $J = 7.6$ Hz, PcH_β), 4.168(t, 16H, $J = 6.6$ Hz, COOCH_2 –), 1.622–1.673(m, 16H, $-\text{CH}_2$ –), 1.278–1.286(br m, 32H, $-\text{CH}_2$ –), 0.812(t, 24H, $J = 6.8$ Hz, $-\text{CH}_3$). D_{2h} isomer: ^1H NMR (CDCl_3 with a drop of pyridine[D_5]) δ 9.136(br s, 4H, PcH_α), 8.417(s, 4H, ArH), 8.191(s, 8H, ArH), 7.855(br s, 4H, PcH_β), 7.181(br s, 4H, PcH_β), 4.311(t, 16H, $J = 5.8$ Hz, COOCH_2 –), 1.719–1.753(m, 16H, $-\text{CH}_2$ –), 1.263–1.407(m, 32H, $-\text{CH}_2$ –), 0.815(t, 24H, $J = 7.2$ Hz, $-\text{CH}_3$).

3. Results and discussion

As shown in Scheme 1, 3-substituted phthalonitriles (**1a–1c**) was afforded by treating 3-nitrophthalonitrile with methyl hydroxybenzoate (methyl 2-hydroxybenzoate, methyl 3-hydroxybenzoate, and methyl 3,5-dihydroxybenzoate) and K_2CO_3 in DMF. Cyclisation of **1a–1c** followed by transesterification in the presence of DBU and $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ in refluxing *n*-pentanol led to the formation of 1(4),8(11),15(18),22(25)-tetrakis[(pentylloxycarbonyl)phenoxy]phthalocyaninato zinc(II) complexes **2a–2c** as a mixture of four constitutional isomers [7a]. The C_{4h} and D_{2h} isomers of all the three phthalocyanine compounds could be separated by simple silica-gel column chromatography in the first and third fraction respectively, while the C_{2v} and C_s isomers were collected as a mixture in the second fraction. As summarized in Table 1, the phthalocyanine **2b** was obtained with the highest yield among the series of three phthalocyanine compounds due to the relatively less steric hindrance arising from only one alkyloxycarbonyl group attached at the *meta*-position of the phenoxy moieties in comparison with the same alkyloxycarbonyl group attached at the *ortho*-position for **2a** and two alkyloxycarbonyl groups for **2c**. Due to the same reason, the distribution of the constitutional isomers obtained from **2b** shows the most consistency ($\text{C}_{4h}:\text{C}_{2v}$ & $\text{C}_s:D_{2h} = 1:3.6:0.8$) with the statistical expected yields ($\text{C}_{4h}:\text{C}_{2v}$ & $\text{C}_s:D_{2h} = 1:6:1$).

The phthalocyanine compounds including the mixed isomers with C_{2v} and C_s symmetry have been characterized by MALDI-TOF mass and electronic absorption spectroscopy in addition to elemental analysis. The MALDI-TOF mass spectra of these compounds clearly showed intense signals of molecular ions (M) $^+$ (Table 1). The isotopic pattern closely resembled the simulated one as exemplified by the spectrum of C_{4h} isomer of **2a**, Fig. S1 (Supplementary material).

^1H NMR and 2D COSY spectra of all the single isomers were recorded in CDCl_3 with a drop of pyridine[D_5] except the one with

C_{4h} symmetry for **2c** only in CDCl_3 . The nature of the C_{4h} and D_{2h} isomers of **2a–2c** can be easily distinguished by their NMR spectra, Fig. 1 and S2–11 (Supplementary material) and Table 2. Fig. 1 displays the ^1H NMR spectra of the single C_{4h} and D_{2h} as well as the mixed C_{2v} and C_s isomers of compound **2c**. The spectrum of C_{4h} isomer shows a doublet at 8.523 ppm, an overlapping doublet of doublets at 7.843 ppm, and a doublet at 7.635 ppm, which are assigned to the three protons of H_α , $\text{H}_{\beta 1}$, and $\text{H}_{\beta 2}$ at the phthalocyanine ring, respectively. Compared with the chemical shift of protons in the spectrum of C_{4h} isomer, the peak of H_α (free H_α) for D_{2h} isomer shifts to low field at 9.153 ppm owing to no shielding effect of substituent arising from the benzene ring of opposite side (Fig. 2), while the peak of $\text{H}_{\beta 2}$ for D_{2h} shifts to high field at 7.201 ppm because it suffers bigger shielding from the pentylloxycarbonylphenoxy group of adjacent position, which is excluded to closer position of $\text{H}_{\beta 2}$ by the other pentylloxycarbonylphenoxy group at a face-to-face position. Meanwhile, the interaction of two substituents in the D_{2h} isomer also make the chemical shifts of phenoxy protons (H_1 , H_2) and aliphatic protons (H_3 to H_7) move to high field to some extent in comparison with those peaks related to the C_{4h} isomer.

Interestingly, although C_{2v} and C_s isomers cannot be separated by column chromatography, their ratio in the product can be estimated

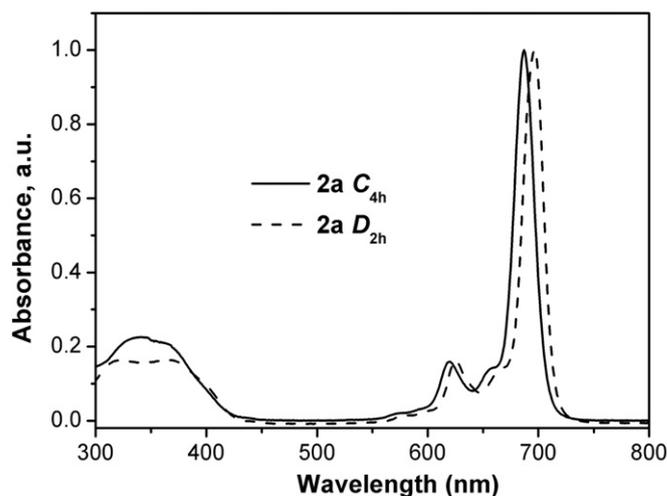


Fig. 4. Electronic absorption spectra of C_{4h} (full) and D_{2h} (dotted) isomers of compound **2a** in THF. Spectra were normalized to the same absorbance at Q-band.

Table 3

Electronic absorption data for isolated C_{4h} and D_{2h} isomers of compounds **2a–2c** in THF.

Compound	Isomer	λ_{max}/nm		
2a	C_{4h}	341	620	687
	D_{2h}	365	625	697
2b	C_{4h}	343	616	683
	D_{2h}	366	623	693
2c	C_{4h}	348	615	681
	D_{2h}	366	621	691

through NMR spectroscopic data based on the integration of peaks especially from the H_{α} signals of phthalocyanine with the help of 2D COSY spectra. It can be seen that there exist two free H_{α} and two shielding H'_{α} in both the C_{2v} and C_s isomers. As a typical example, the 1H NMR spectrum of mixed C_{2v} and C_s isomers of **2a** is displayed in Fig. 3, and the data are summarized in Table 2. The signals at 9.151 and 8.883 ppm are assigned to the free H_{α} and shielding H'_{α} of the C_{2v} isomer, respectively, while the peaks at 9.351 and 8.678 ppm attributed to the free H_{α} and shielding H'_{α} of the C_s isomer. Accordingly, the ratio of integration of the α protons (1:2.44) corresponds to the distribution of C_{2v} and C_s isomers in this mixture, which is almost in consistent with the statistical expected yield (1:2). For the compounds **2b** and **2c**, the signals of the free H_{α} for the C_{2v} and C_s isomers are overlapped, but the shielding H'_{α} can be used to reveal their distribution in the mixture (1:1.74 for **2b**, 1:2.08 for **2c**, Table 2 and Fig. 1 and Figs. S14–16 (Supplementary material).

The electronic absorption spectra of the C_{4h} and D_{2h} isomers of **2a–2c** have been recorded in THF. As can be seen in Fig. 4, S17, and S18 (Supplementary material), Table 3, both isomers of these compounds show typical electronic absorption spectra of the phthalocyaninato metal complexes [1a]. The absorption spectra of C_{4h} isomers show a Soret band at 341–348 nm, an intense and sharp Q band at 681–687 nm, and a vibronic band at 615–620 nm, while the spectra of D_{2h} isomers exhibit a 10 nm red-shift in the Q-band and 5–7 nm in the vibronic band probably due to the non-planarity of the macrocycle in these sterically stressed isomers [10c].

4. Conclusions

We have prepared a series of 1(4),8(11),15(18),22(25)-tetrakis [(pentylloxycarbonyl)phenoxy]phthalocyaninato zinc(II) complexes as a mixture of four constitutional isomers. Their C_{4h} and D_{2h} isomers have been successfully separated using simple column chromatography on silica gel and are spectroscopically characterized. The yields in combination with the NMR spectroscopic results reveal that the distribution of the four isomers in the final product for **2a–2c** does not strictly follow that expected according to statistical calculation with the ratio of $C_{4h}:C_{2v}:C_s:D_{2h} = 1:2:4:1$, indicating the effect of the steric hindrance of substituents on the formation of various constitutional isomers.

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Appendix A. Supplementary data

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