Synthesis and Characterization of Several Soluble Tetraphenoxy-Substituted Copper and Zinc Phthalocyanines

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Received 18 October 2004; revised 17 November 2004

Abstract: Synthesis of copper and zinc phthalocyanines (Pcs) bearing phenoxy-substituents is described. Precursors required for the preparation of Pcs **9**–**16** are prepared by a nucleophilic aromatic substitution reaction between a sterically hindered phenol derivative and 4-nitrophthalonitrile (**1**) or 3-nitrophthalonitrile (**2**). Cyclotetramerization of the resulting precursor phthalonitriles in DMAE or in pentan-1-ol catalyzed by DBU gives desired Pcs, which are well soluble in common organic solvents, such as chloroform and dichloromethane. Each of these Pcs are composed of four constitutional isomers and are characterized by ^{1}H NMR, UV/Vis, IR and mass spectra, as well as elemental analysis, which are consistent with the proposed structures.

Key words: phthalocyanines, zinc, copper, synthesis, phenols

Phthalocyanines (Pcs) and their derivatives have demonstrated their commercial value as industrial dyes and pigments and photoconductors in xerography. Additionally, their potential applications in material science, such as nonlinear optics,[1] chemical sensors, liquid crystals, Langmuir–Blodgett films,[2–4] sensitizers for photodynamic therapy of cancer,[5,6] among others, have been attracting chemists worldwide for the exploitation of fascinating properties of Pcs over the past few decades. Due to intermolecular interactions between the macrocycles, peripherally unsubstituted metallophthalocyanines are practically insoluble in common organic solvents, thereby minimizing their applications.[7] The solubility can be improved by introduction of substituents on the periphery that, to some extent, increases the distance between the 18p electron conjugated systems of Pcs and facilitates the solubility. A considerable effort has been applied to generate novel Pc derivatives possessing enhanced properties, e.g. higher solubility in common organic solvents.[8,9]

Generally, tetrasubstituted phthalocyanines possess higher solubility than the symmetrically octasubstituted ones, which bear eight same substituents. The outstanding solubility of some tetrasubstituted phthalocyanines is derived not only from the steric bulk of the substituents preventing aggregation, but also from the presence of the very similar isomers.[10] Thus, a mixture of similar isomers may practically be more useful than a single, less soluble isomer.[11,12]

Tetrasubstituted phthalocyanines are usually obtained as a mixture of four constitutional isomers, which are formed in different proportions (D_{2h}:C_s:C_{2v}:C_{4h} = 1:4:2:1). These constitutional isomers were separated by chromatographic methods (MPLC, HPLC) using special modified silica gels.[13,14]

A commonly used synthetic route to soluble tetrasubstituted Pcs involves the aromatic nucleophilic substitution reaction between 4-nitrophthalonitrile or 3-nitrophthalonitrile and a suitable oxygen, nitrogen or sulfur nucleophile followed by cyclotetramerization of the resultant phthalonitrile derivatives, e.g. 4-(cumylphenoxy)phthalonitrile[15] and 4-(neopentoxy)phthalonitrile.[16]

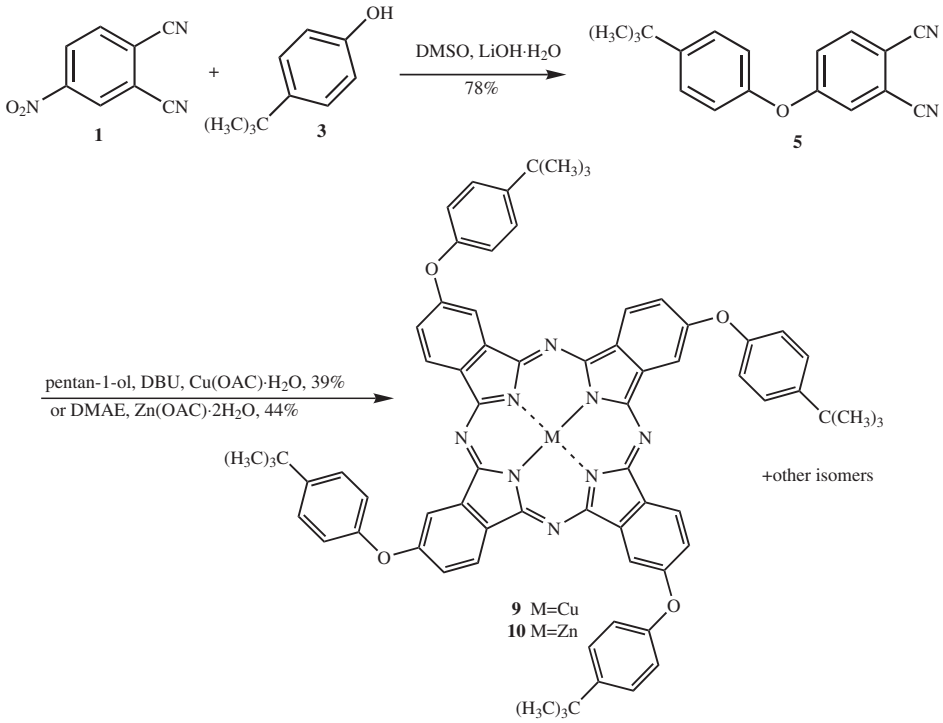
We report here synthesis and characterization of new Pcs **9**–**16** and four Pc precursors **5**–**8** (Schemes 1– 4) using the above mentioned synthetic strategy.

We chose phthalonitriles **1**, **2**, 4-*tert*-butylphenol (**3**), and 2-isopropyl-5-methylphenol (**4**) as starting materials. In DMSO, under alkaline conditions, anion of phenol **3** or **4** displaced the nitro group of **1** or **2** to generate a phthalonitrile derivative. A modified procedure according to the previous literature[17] was adopted to prepare **5**. Treatment of **3** and **1** in the presence of LiOH and anhydrous DMSO at room temperature afforded the expected **5** (Scheme 1) in good yield (79%), which was purified by column chromatography on silica gel with petroleum ether–diethyl ether as the mobile phase. Upon treatment with zinc acetate in refluxing dimethylaminoethanol (DMAE) or copper acetate in the presence of DBU and pentan-1-ol under nitrogen, phthalonitrile **5** was converted to Pcs **9** and **10**, which could be purified by chromatography on silical gel as a blue-green powder. Their UV/Vis spectra showed the characteristic Q-band and B-band.

Similar to **5**, compound **6** was also prepared in good yield and excellent purity and converted to Pcs **11** and **12** as shown in Scheme 2.

As expected, under the same strategy, compound **3** was reacted with **2** to prepare the analogous 3-substituted phthalonitrile **7** (Scheme 3) as colorless crystals in pretty good yield (78%). The good yields of phthalonitriles **5** and **7** seems to suggest that the position of nitro group in 3-

SYNTHESIS 2005, No. 5, pp 0741–0748
Advanced online publication: 09.02.2005
DOI: 10.1055/s-2005-861795; Art ID: F14704SS

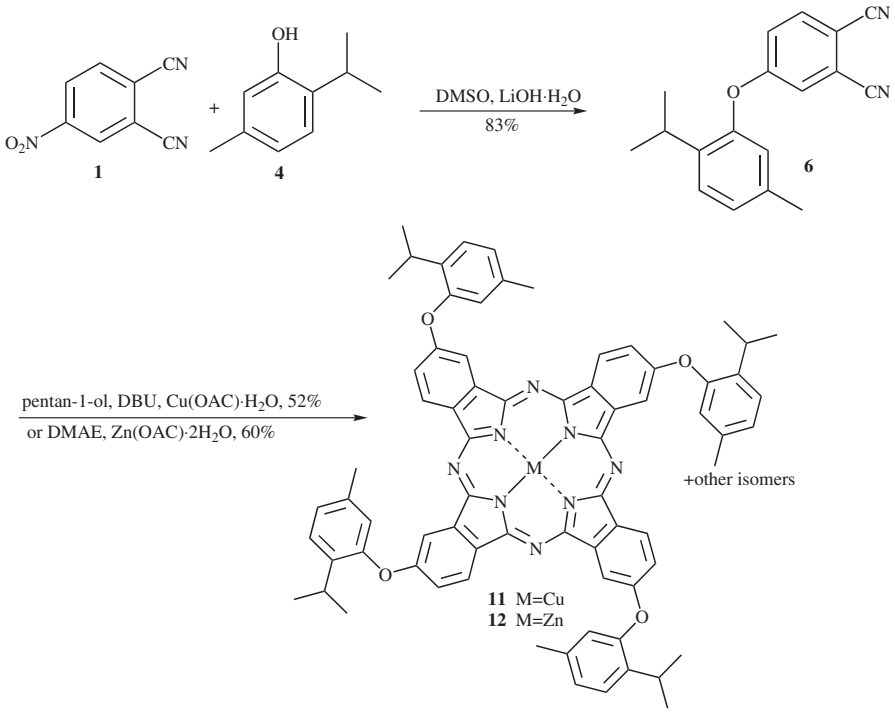


Scheme 1

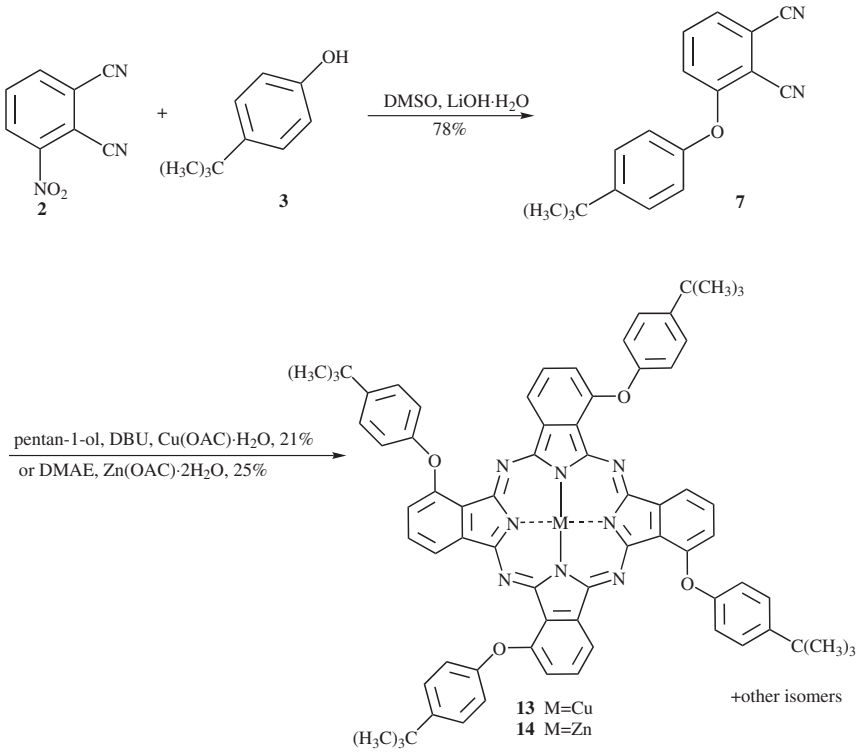
and 4-nitrophthalonitriles has little influence on the yield of the corresponding phenoxy-substituted phthalonitrile derivatives, which is different from the reported result.[18]

Compound **7** was used as the precursor for the preparation of Pcs **13** and **14** under the well-established synthetic routes. Compound **8** is a white flocculent solid, which was converted to Pcs **15** and **16** in reasonable yields and superior purity (Scheme 4).

Compared to Pcs **9**–**12**, Pcs **13**–**16** have relatively better solubility in certain organic solvents, such as pentan-1-ol and DMAE, most possibly due to the result of the position of substituents in the phthalonitriles **3** and **4** leading to the correspondingly substituted Pc ring. We also found that

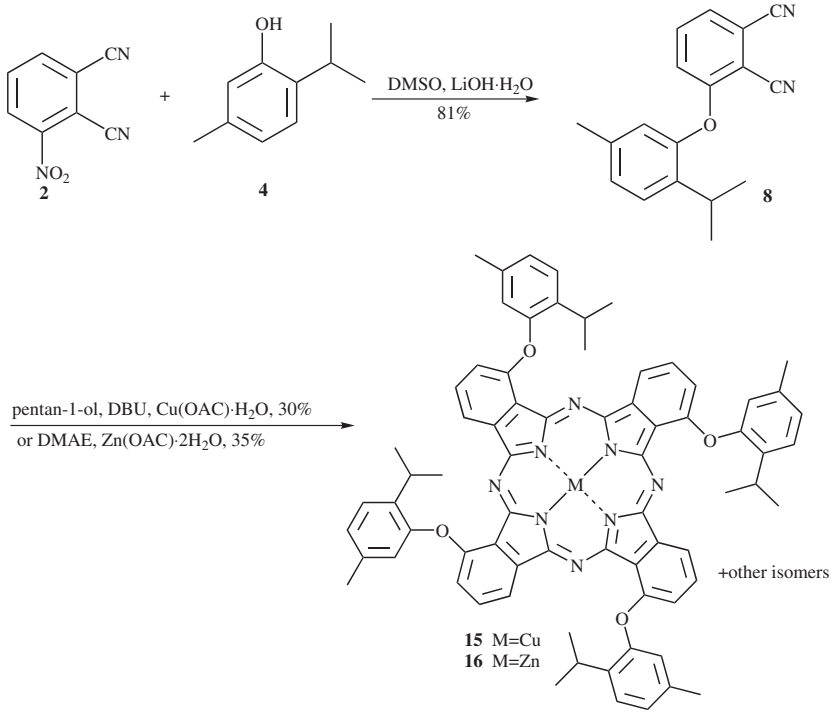


Scheme 2



Scheme 3

Pcs **9**–**16** display excellent solubility in chloroform or dichloromethane. However, in acetone, while copper Pcs **9**, **11**, **13**, and **15** are almost insoluble, zinc Pcs **10**, **12**, **14**, and **16** still have solubility just as good as that in chloroform or dichloromethane. Pcs **9**–**16** are hardly soluble in certain polar solvents, such as DMF, DMSO and attempts to obtain ^{1}H NMR spectra of Pcs **9**–**16** in DMSO-d_6 were not successful. The difference of steric hindrance derived from position of bulky substituents in Pcs **9**–**16** can account for the relatively poor yield of Pcs **13**–**16** as compared to Pcs **9**–**12**.



Scheme 4

It is well known that cyclotetramerization of monosubstituted phthalonitriles leads to the formation of four constructional isomers. It could be deduced from the broadening of absorption peaks of ^{1}H NMR, and TLC analysis that metal Pcs **9**–**16** are a mixture of four isomers. The conclusions of this paper do not depend on having a pure isomer, thus no further purification was attempted. To the best of our knowledge, there is no literature presently that reports the successful separation of these four isomers with ordinary column chromatography. Our attempts to separate these isomers by column chromatography were not successful. However, Hanack and coworkers separated all four isomers of two different tetrasubstituted Pcs by HPLC.[19,20]

All the new Pcs were characterized by elemental analysis and adequate spectroscopic means including ^{1}H NMR, TOF-MS, UV/Vis and IR, all of which were compatible with the proposed structures. The ^{1}H NMR spectra (500 MHz, $CDCl_3$) of the four precursors **5**–**8** and Pcs **10**, **12**, **14**, and **16** did not display signals of impurities. ^{1}H NMR measurements of Pcs **9**, **11**, **13**, and **15** were precluded owing to paramagnetic nature of the copper(II) ion in a square planar environment. Table 1 gives the chemical shifts of the aromatic hydrogen atoms of **1**,**2** and **5**–**8**. The resonances shifts of H_a, H_b and H_c of **5**–**8** shift to upfield due to the influence of electron-donating phenoxyl group. It is noteworthy that the chemical shifts of H_a and H_b of **6** is unusually smaller than those of H_a and H_b of **5** (Table 1), which can be interpreted.

Based on the studies of previous researchers,[18,21,22] compound **6** should be a 'H-inside' conformation (Figure 1), which can be judged readily from the ^{1}H NMR spectra analysis. For diphenyl ethers such as the representative structure in Figure **1**, if two large groups *ortho* to the oxygen linkage exist in one of the phenyl rings, they prefer to adopt the 'H-inside' conformation. Certain electron-withdrawing groups, e.g. nitrile groups, augment this tendency.[23] The H-inside conformation makes the resonances of the *ortho*-hydrogens appear in unusually shielded positions. Although compound **6** only contains one relatively bulky group, namely isopropyl, it still adopts the 'H-inside' conformation.

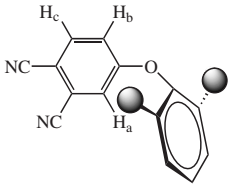
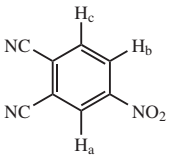
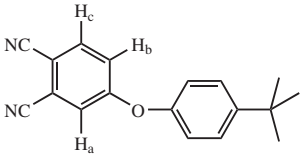
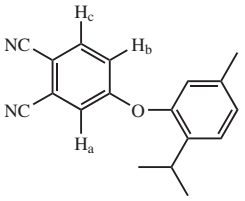
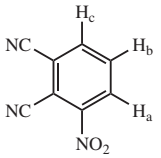
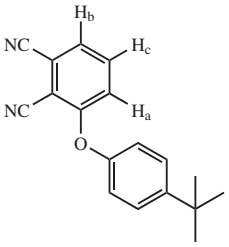
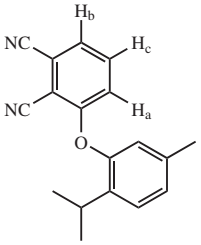


Figure 1 Representative 'H-inside' conformation of diphenyl ethers. The balls represent bulky substituents.

In TOF-MS spectra of Pcs **9**–**16**, their peaks of singly charged molecular ions in the range of $m/z = 0$ to 3000 are obvious and peaks of impurities can hardly be found. We did not find the dimer peaks in the mass spectra measured in the LDI-1700 TOF mass spectrometer of Pcs **9**–**16** (Figure 2), all of which are in the range of $m/z = 0$ to 3000 (exact molecular mass of Pcs **9**–**16** are 1168.4 or 1167.4). For certain monosubstituted metal Pcs bearing some relatively small substituents, such as NH_2 group,[24] its dimer peak in MS measured in the same mass spectrometer could be readily found.

The characteristic absorptions B-band and Q-band could be observed in UV/Vis spectra of Pcs **9**–**16**. UV/Vis spectrum of Pc **10** measured in $CHCl_3$ shows the intense Q-band absorption origining from $\pi \rightarrow \pi^*$ transitions at 682 nm. There is also a weak band at slightly higher energy in this spectrum. B-band of Pcs arising from the deeper π-

Table 1 ^{1}H NMR Signals (δ) of Some Compounds

Compound	H_a	H_b	H_c
	8.678	8.604	8.084
	7.464	7.477	7.711
	7.218	7.295	7.708
	8.580	8.164	8.083
	7.093	7.427	7.551
	7.286	7.425	7.543

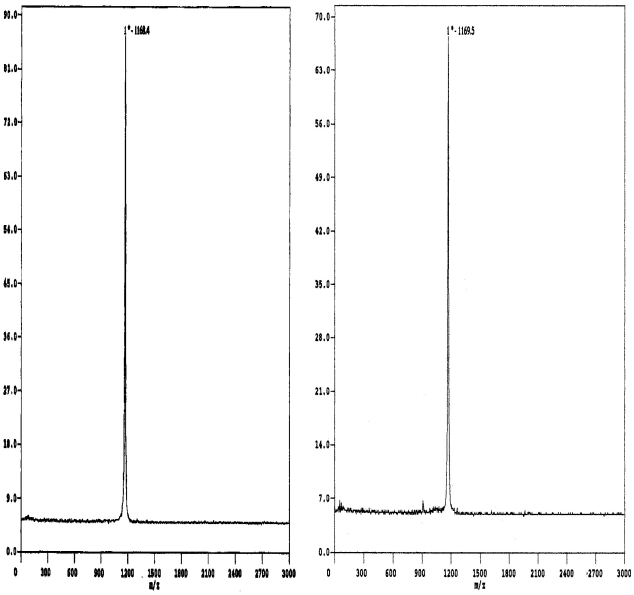


Figure 2 Scanned pictures of mass spectra of Pcs **11** and **12**.

levels → LUMO transitions is observed in the UV region at 357 nm (Figure 3).

The UV-Vis spectra of other Pcs obtained at the concentration of 1.2–3.6 × 10^{-6} M are shown in Figure 4.

UV-Vis spectra of **14** and **16** are peculiar and worth mentioning. Besides the Q-bands at about 700 nm, additional absorption bands emerged at 744 and 748 nm, respectively (Figure 5). The similar phenomena were also observed previously for Mg(II) and Zn(II) complexes of 1,8,15,22-tetrakis(3-pentyloxy)phthalocyanine and the longest wavelength band was tentatively attributed to a slipped face to-face dimer.[25] To reveal the origin of this band, the concentration dependency of the absorption spectra of **14** and **16** was studied. For both compounds in $CHCl_3$, the intensity of the 'monomer' bands at about 700 nm increased dramatically while the so-called 'dimer' bands at around 740 nm could hardly be observed at concentration as high as 1.2 × 10^{-5} M or 1.5 × 10^{-5} M (Figure 6). This suggests

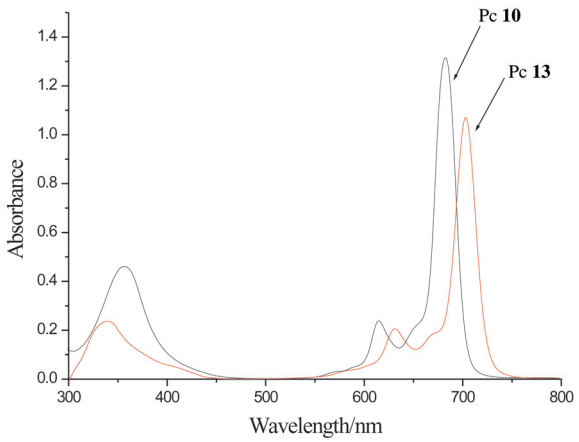


Figure 3 UV/Vis spectra of Pc **10** and **13** in $CHCl_3$ (10^{-5} M).

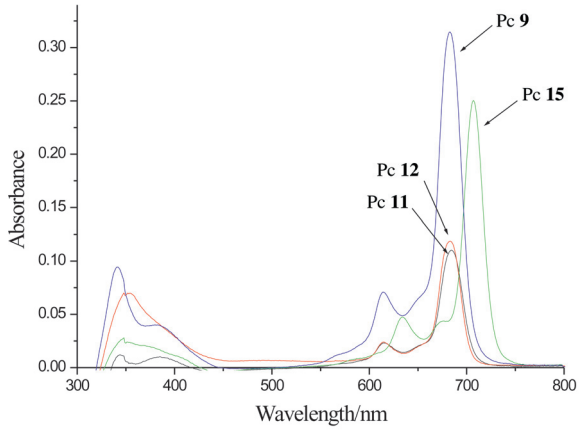


Figure 4 UV/Vis spectra of Pcs.

that the longer wavelength absorption may not be due to a co-facial dimer which is expected to be dominant in higher concentrations as in the cases of zinc(II)[26] and aluminum(III)[27] complexes of tetrasulfonatophthalocyanine in MeCN–H_2O and aqueous alcohol, respectively, which were also assumed to adopt a dimeric structure with a face-to-face slipped or tilted conformation. Thus, the exact nature of these bands is not clear and needs to be explored further, which is compatible with one previous result.[28]

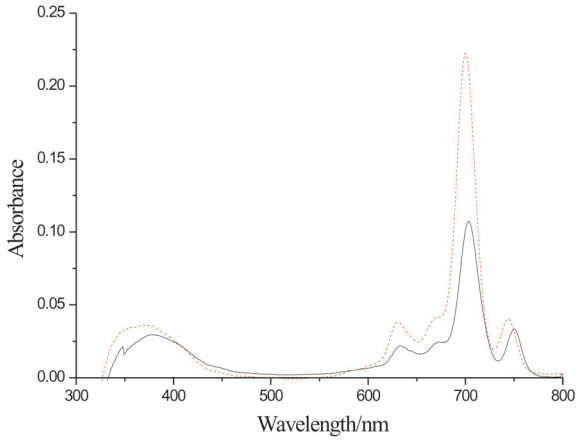


Figure 5 UV/Vis spectra of **14** (1.5 × 10^{-6} mol/L, dashed line) and **16** (1.3 × 10^{-6} mol/L, solid line) in $CHCl_3$.

Aggregation in phthalocyanine systems is readily detected from optical absorption studies resulting in a decrease of the maximum extinction coefficient and a blue shift of the Q-band.[29] When the UV/Vis spectrum of compound **16** was measured in $CHCl_3$ at concentrations as high as 1.2 × 10^{-4} M, the peak corresponding to the monomer at 703 nm is still evident.[30] Pcs **9**–**15** also show the analogous phenomena as **16**. These non-aggregation behavior could have important advantages not only for studying intermolecular processes in compounds but also for the application of these compounds in photodynamic therapy.[31,32]

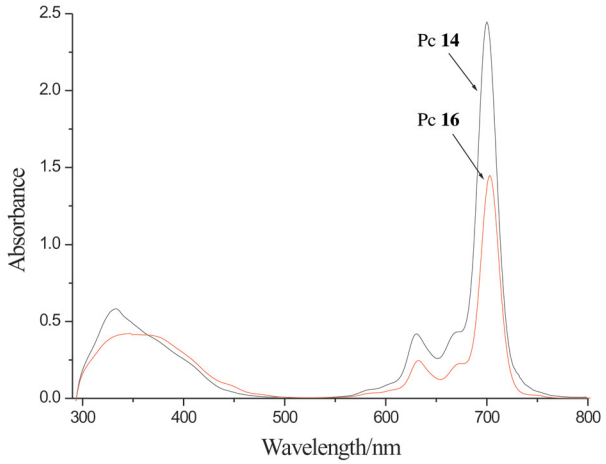


Figure 6 UV/Vis spectra of Pc **14** (1.5×10^{-5} M) and **16** (1.2×10^{-5} M) in $CHCl_3$.

From IR spectra we could find the stretching vibration peaks of C≡N (usually at ca. 2230 cm^{-1}) and C–O–C stretching vibration peaks (usually in the rang from 1050 to 1250 cm^{-1}) of **5**–**8**.

In summary, we have synthesized copper Pcs **9**, **11**, **13**, and **15** and zinc Pcs **10**, **12**, **14**, and **16** from phthalonitriles **1**, **2**, **3** and **4** as the starting materials. All of them were sufficiently characterized by ^{1}H NMR, TOF-MS, UV/Vis, IR spectra, and elemental analyses, which are consistent with the proposed structures. The bulky phenoxy substituents in the peripheral moieties will not only decrease the molecular aggregation in solution but also expand the Pc π-electron conjugated system to generate new photoelectric properties for Pcs **9**–**16**. Excellent solubility for Pcs **9**–**16** in common organic solvents, such as chloroform or dichloromethane, is advantageous in the establishment of molecular order systems and helpful in the investigation of physical and chemical properties of molecular order systems.

Pentan-1-ol was distilled from Na prior to use. DMSO was predried over BaO and distilled under reduced pressure. Column chromatography purifications were preformed on silica gel unless otherwise stated. All other reagents and solvents are commercial available and used without further purification. Petroleum ether used had bp 60–90 °C.

High-resolution ^{1}H NMR spectra were recorded on a Varian Unity 500 spectrometer unless otherwise stated. IR spectra were measured on a Magna 560 FT-IR spectrometer. UV/Vis spectra were taken on a Cary 500 UV-VIS-NIR spectrophotometer. MS spectra were obtained on a QUSTAR-TOF mass spectrometer or a LDI-1700-TOF mass spectrometer. Elemental analyses were performed on a Flash EA1112 Elemental Analyzer.

4-Substituted Phthalonitriles; 4-(2-Isopropyl-5-methylphenoxy)phthalonitrile (6); Typical Procedure

To anhyd DMSO (30 mL) were added **1** (1.73 g, 10 mmol) and **4** (1.5 g, 10 mmol) at r.t. The reaction mixture was stirred and LiOH (0.60 g, 25mmol) was added over a 2 h period and the mixture was then stirred for 2 days. The progress of the reaction was monitored by TLC analysis. The mixture was then poured into H_2O (400 mL) and stirred till a grey solid appeared. The product was collected by vacuum filtration. The crude product was purified by column chromatography with petroleum ether–anhyd Et_2O (9:1) as the mobile phase to afford colorless crystals of **6**; yield: 229 mg (83%).

IR (KBr): 2229 m (C≡N), 1246 vs cm^{-1} (C–O–C).

^{1}H NMR (500 MHz,$CDCl_3$): δ = 7.708 (d, 1 H, *J* = 8.5 Hz, ArH), 7.295 (d, 1 H, *J* = 8.5 Hz, ArH), 7.219 (s, 1 H, ArH), 7.189 (d, 1 H, *J* = 8 Hz), 7.109 (d, 1 H, *J* = 8 Hz, ArH), 6.745 (s, 1 H, ArH), 2.958 (m, 1 H, CH), 2.331 (s, 3 H, ArCH_3), 1.154 [d, 6 H, *J* = 6.5 Hz, 2 $CH(CH_3)_2$].

MS (QUSTAR-TOF): *m*/*z* calcd for [M + Na^+]: 299.1160; found: 298.9497 (an isotopic cluster peak) [M + Na^+] .

UV/Vis ($CHCl_3$): λ_{max} = 261, 297, 306 nm.

4-(4-*tert*-Butylphenoxy)phthalonitrile (5)

Yield: 217 mg (79%).

IR (KBr): 2230 m (C≡N), 1244 vs cm^{-1} (C–O–C).

^{1}H NMR (500 MHz,$CDCl_3$): δ = 1.358 (s, 9 H, *t*-C_4H_9), 6.994 (q, 2 H, *J* = 2 Hz, Ar H), 7.248 (q, 2 H, *J* = 2 Hz, ArH), 7.464 (s, 1 H, ArH), 7.477 (d, 1 H, *J* = 2 Hz, ArH), 7.711 (d, 1 H, *J* = 2 Hz, ArH).

MS (QUSTAR-TOF): *m*/*z* calcd for [M + Na^+]: 299.1160; found: 298.9504 (an isotopic cluster peak) [M + Na^+].

UV/Vis ($CHCl_3$): λ_{max} = 264, 306 nm.

3-Substituted Phthalonitriles; 3-(4-*tert*-Butylphenoxy)phthalonitrile (7); Typical Procedure

A mixture of **3** (1.50 g, 10 mmol), **2** (1.73 g, 10 mmol), and LiOH (10 g, 25 mmol) in anhyd DMSO (30 mL) was stirred at r. t. for 48 h. The progress of the reaction was monitored by TLC analysis. The mixture was poured into H_2O (400 mL) and stirred till a slightly yellow solid appeared. The crude product was collected and purified by chromatography with Et_2O–petroleum ether (1:9) to afford colorless crystals of **7**.

Yield: 215 mg (78%).

IR (KBr): 2230 m (C≡N), 1236 w cm^{-1} (C–O–C).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.342 (s, 9 H, *t*-C_4H_9), 7.022 (d, 2 H, *J* = 9 Hz, Ar H), 7.093 (d, 1 H, *J* = 8 Hz, ArH), 7.451 (d, 2 H, *J* = 9 Hz, ArH), 7.427 (d, 1 H, *J* = 8 Hz, ArH), 7.551 (dd, 1 H, *J* = 8 Hz, ArH).

MS (QUSTAR-TOF): *m*/*z* calcd for [M + Na^+]: 299.1160; found: 299.0608 (an isotopic cluster peak) [M + Na^+]

UV/Vis ($CHCl_3$): λ_{max} = 321 nm.

3-(2-Isopropyl-5-methylphenoxy)phthalonitrile (8)

Yield: 223 mg (81%).

IR (KBr): 2229 m (C≡N), 1242 w cm^{-1} (C–O–C).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.543 (dd, 1 H, *J* = 8 Hz, ArH), 7.425 (d, 1 H, *J* = 8 Hz, ArH), 7.286 (d, 1 H, *J* = 8 Hz, ArH), 7.091 (d, 1 H, *J* = 9 Hz, ArH), 6.971 (d, 1 H, *J* = 9 Hz, ArH), 6.769 (s, 1 H, ArH), 3.023 (m, 1 H, CH), 2.320 (s, 3 H, ArCH_3), 1.182 [d, 6 H, *J* = 6.5 Hz, $CH(CH_3)_2$].

MS (QUSTAR-TOF): *m*/*z* calcd for [M + Na^+]: 299.1160; found: 299.0597 (an isotopic cluster peak) [M + Na^+].

UV/Vis ($CHCl_3$): λ_{max} = 321 nm.

Phthalocyaninatocopper; Copper 2,9(10),16(17),23(24)-Tetra(4-*tert*-butylphenoxy)phthalocyanine (9); Typical Procedure

Phthalonitrile **5** (1.104 g, 4 mmol) and $Cu(OAc)_2$ (0.20 g, 1 mmol) were added under stirring to pentan-1-ol (10 mL) in a 25 mL one-neck round-bottomed flask equipped with an air condenser. Then, a catalytic amount of DBU was added, and the mixture was stirred and heated at 135 °C under N_2 over 12 h. After cooling under N_2,

pentan-1-ol was removed under reduced pressure. The collected solid was purified by column chromatography with $CHCl_3$ and subsequently with a mixture of $CHCl_3$–MeOH (90:1) as eluents to afford **9**; yield: 455 mg (39%).

IR (KBr): 1238 vs cm^{-1} (C–O–C).

MS (LDI-1700-TOF): *m/z* calcd for [M + H^+]: 1168.4; found: 1168.6 [M + H^+].

UV/Vis ($CHCl_3$): λ_{max} (log ε) = 341 (4.68), 614 (4.56), 683 nm (5.21).

Anal. Calcd for $C_{72}H_{64}CuN_8O_4$ (1168.4): C, 73.87; H, 5.51; N, 9.57. Found: C, 73.85; H, 5.86; N, 9.43.

Copper 2,9(10),16(17),23,(24)-Tetra(2-isopropyl-5-methylphenoxy)phthalocyanine (11)
Yield: 607 mg (52%).

MS (LDI-1700-TOF): *m/z* calcd for 1168.4 [M + H^+]; found: 1168.4 [M + H^+].

UV/Vis ($CHCl_3$): λ_{max} (log ε) = 344 (3.57), 385 (3.49), 615 (3.85), 684 nm (4.53).

Anal. Calcd for $C_{72}H_{64}CuN_8O_4$ (1168.4): C, 73.87; H, 5.51; N, 9.57. Found: C, 73.54; H, 5.70; N, 9.23.

Copper 1,8(11),15(18),22(25)-Tetra(4-*tert*-butylphenoxy)phthalocyanine (13)
Yield: 245 mg (21%).

MS (LDI-1700-TOF): *m/z* calcd for [M + H^+]: 1168.4; found: 1168.5 [M + H^+].

UV/Vis ($CHCl_3$): λ_{max} (log ε) = 340 (5.09), 630 (5.03), 703 nm (5.75).

Anal. Calcd for $C_{72}H_{64}CuN_8O_4$ (1168.4): C, 73.87; H, 5.51; N, 9.57. Found: C, 73.47; H, 5.38; N, 9.37.

Copper 1,8(11),15(18),22(25)-Tetra(2-isopropyl-5-methylphenoxy)phthalocyanine (15)
Yield: 350 mg (30%).

MS (LDI-1700-TOF): *m/z* calcd for [M + H^+]: 1168.4; found: 1168.4 [M + H^+].

UV/Vis ($CHCl_3$): λ_{max} (log ε) = 348 (4.21), 634 (4.45), 707 nm (5.16).

Anal. Calcd for $C_{72}H_{64}CuN_8O_4$ (1168.4): C, 73.87; H, 5.51; N, 9.57. Found: C, 73.70; H, 5.90; N, 9.32

Phthalocyaninatozinc; Zinc 2,9(10),16(17),23,(24)-Tetra(4-*tert*-butylphenoxy)phthalocyanine (10); Typical Procedure
Phthalonitrile **5** (1.104 g, 4 mmol) and $Zn(OAc)_2$ (0.220 g, 1 mmol) were added under stirring to DMAE (10 mL) in a 25 mL one-neck round-bottomed flask equipped with an air condenser and heated at 135 °C under N_2 for 12 h. After cooling under N_2, DMAE was removed under reduced pressure. The collected solid was purified twice by column chromatography with Et_2O–petroleum ether (1:3) as the mobile phase to give pure **10**; yield: 514 mg (44%).

IR (KBr): 1235 vs cm^{-1} (C–O–C).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.359–7.469 (m, 12 H, ArH), 7.139–7.243 (m, 16 H, ArH), 1.361–1.555 (m, 36 H, 4 *t*-C_4H_9).

MS (LDI-1700-TOF): *m/z* calcd for [M + H^+]: 1169.4; found: 1169.5 [M + H^+].

UV/Vis ($CHCl_3$): λ_{max} (log ε) = 357 (4.53), 615 (4.42), 682 nm (5.30).

Anal. Calcd for $C_{72}H_{64}N_8O_4Zn$ (1168.4): C, 73.98; H, 5.52; N, 9.59. Found: 73.64; H, 5.87; N, 9.24

Zinc 2,9(10),16(17),23,(24)-Tetra(2-isopropyl-5-methylphenoxy)phthalocyanine (12)
Yield: 701 mg (60%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.340 (br s, 12 H, ArH), 7.044 (br s, 12 H, ArH), 3.452 (br s, 4 H, 4 CH), 2.300 (br s, 12 H, 4 ArCH_3), 1.394 [br s, 24 H, 4 CH(CH_3)$_2$].

MS (LDI-1700-TOF): *m/z* calcd for [M + H^+]: 1169.4; found: 1169.5 [M + H^+].

UV/Vis ($CHCl_3$): λ_{max} (log ε) = 348 (4.28), 352 (4.28), 615 (3.82), 683 nm (4.52).

Anal. Calcd for $C_{72}H_{64}N_8O_4Zn$ (1168.4): C, 73.98; H, 5.52; N, 9.59. Found: C, 73.62; H, 5.26; N, 9.30.

Zinc 1,8(11),15(18),22(25)-Tetra(4-*tert*-butylphenoxy)phthalocyanine (14)
Yield: 292 mg (25%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.305–7.389 (m, 12 H, ArH), 6.857–7.031 (m, 16 H, ArH), 1.290–1.347 (m, 36 H, 4 *t*-C_4H_9).

MS (LDI-1700-TOF): *m/z* calcd for [M + H^+]: 1169.4; found: 1169.3 [M + H^+].

UV/Vis ($CHCl_3$): λ_{max} (log ε) = 368 (4.38), 630 (4.40), 700 (5.18), 744 nm (4.43).

Anal. Calcd for $C_{72}H_{64}N_8O_4Zn$ (1168.4): C, 73.98; H, 5.52; N, 9.59. Found: C, 73.74; H, 5.40; N, 9.46.

Zinc 1,8(11),15(18),22(25)-Tetra-(2-isopropyl-5-methylphenoxy)phthalocyanine (16)
Yield: 409 mg (35%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.309–7.622 (m, 12 H, ArH), 6.912–7.065 (m, 12 H, ArH), 3.538 (br s, 4 H, 4 CH), 2.145–2.227 (m, 12 H, 4 ArCH_3), 1.187–1.340 [m, 24 H, 4 CH(CH_3)$_2$].

MS (LDI-1700-TOF): *m/z* calcd for [M + H^+]: 1169.4 found: 1169.5 [M + H^+] .

UV/Vis ($CHCl_3$): λ_{max} (log ε) = 348 (4.51), 632 (4.27), 703 (5.04), 748 nm (4.30).

Anal. Calcd for $C_{72}H_{64}N_8O_4Zn$ (1168.4): C, 73.98; H, 5.52; N, 9.59. Found: C, 73.82; H, 5.33; N, 9.80.

Acknowledgment

Financial support of this project was provided by NSFC (60307002). We also wish to thank Shukun Yu for the purification of Pcs **9**–**16**.

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