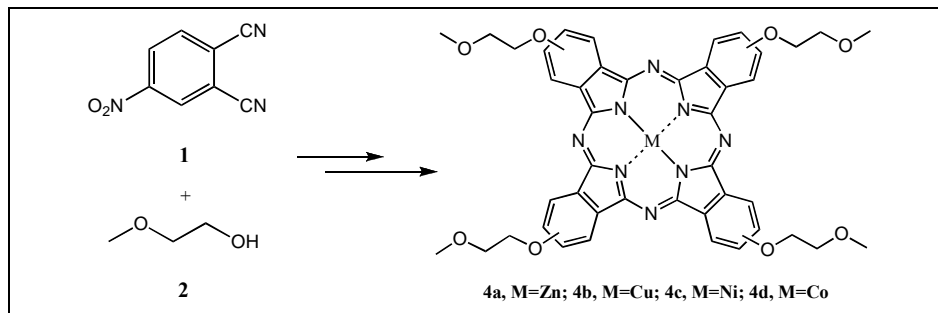


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Four soluble tetra(2-methoxyethoxy)metallophthalocyanines **4a-4d** were, in two steps, synthesized from phthalonitrile **1** and 2-methoxyethanol **2**, and characterized by MS, <sup>1</sup>H NMR, UV-vis, IR and elemental analysis, as well as Cyclic voltammetry.

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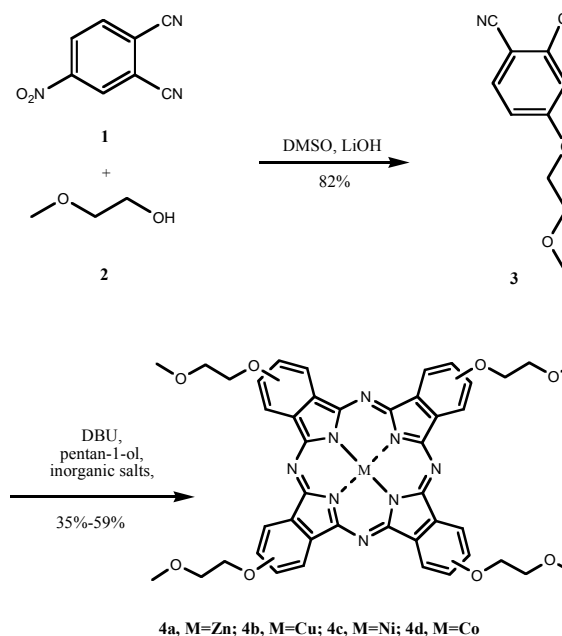
## INTRODUCTION

Phthalocyanine (Pc) compounds have significant application in many areas such as catalysis [1], photochemistry [2], electrochemistry [3], nonlinear optics [4], information storage [5] and photodynamic therapy [6], etc. So the worldwide chemists have been pursuing the study on synthesis and property of this kind of heterocyclic compounds since the first metal Pc (MPcs) was found in 1907 [7]. Because the various functions of MPcs are almost based on an electron transfer reaction occurred on the Pc ring or at the center metal [8], and the reaction can be adjusted by the introduction of peripheral substituents so as to optimize their physical and chemical properties [9]. So, it is critical for practical applications to study the synthesis and property of new MPc derivatives.

But, many MPcs are practically insoluble in common organic solvents due to the intermolecular interactions from 18- $\pi$  electron conjugated structure, which disturbs the investigation on them [10]. However, the solubility can be improved by introduction of suitable substituents on the periphery that, to some extent, increases the distance between the 18- $\pi$  electron conjugated systems and facilitates the solubility. On the basis of this, a considerable effort has been made to generate new Pc derivatives possessing enhanced solubility in common organic solvents [11], which are derived from the steric bulk and the solvent affinity of the substituents preventing aggregation [12]. Thus, the MPcs bearing lipophilic/hydrophilic substituents have been synthesized and used to understand their properties [13].

In this paper we described the synthesis of several soluble tetra(2-methoxyethoxy)metallophthalocyanines (TMPcs) **4a-4d** at 135°C lower than classic condition at > 150°C. They are characterized by MS, <sup>1</sup>H NMR, UV-vis, IR and elemental analysis, *etc.* Further their solubility, photostability and electrochemical properties were studied.

### Scheme 1

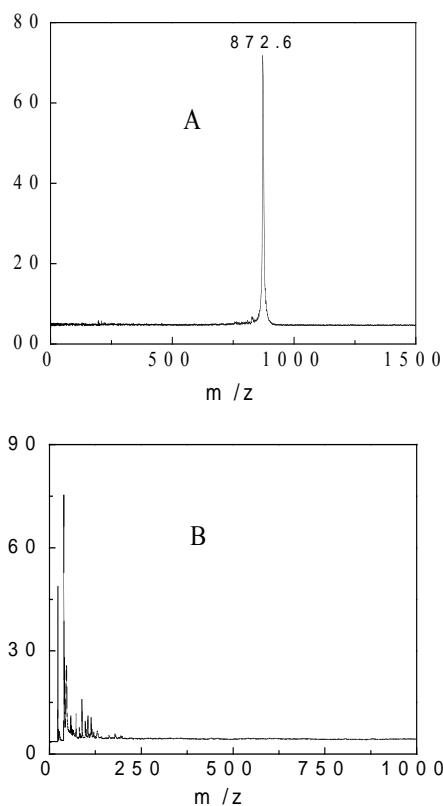


**4a**, M=Zn; **4b**, M=Cu; **4c**, M=Ni; **4d**, M=Co

## RESULTS AND DISCUSSION

A general synthetic route to soluble tetra-substituted MPcs involves the aromatic nucleophilic substitution reaction between nitrophthalonitriles and a suitable oxygen, nitrogen or sulfur nucleophile followed by cyclotetramerization of the resultant phthalonitrile derivatives [14]. Using the synthetic strategy, we report here the synthesis and characterization of new TMPcs **4a-4d** and their precursor **3** (Scheme 1). We chose 4-nitrophthalonitrile **1** and 2-methoxyethanol **2** as starting materials to synthesize **3** with good yield in the presence of LiOH and anhydrous DMSO at room temperature by using a modified procedure according to the literature [15]. Upon treatment with Zn(Ac)<sub>2</sub>, Cu(Ac)<sub>2</sub>, NiCl<sub>2</sub> or CoCl<sub>2</sub> in refluxing pentan-1-ol with DBU as catalyst under nitrogen, **4a-4d** were synthesized from **3**, which could be further purified by column chromatography.

Compounds **4a-4d** were characterized by <sup>1</sup>H NMR, MS, UV-vis, IR and elemental analysis, which were consistent with the proposed structures. The <sup>1</sup>H NMR spectra of the **4b-4d** were precluded because of the paramagnetic nature of the Cu (II), Ni (II) and Co (II) in a square planar environment, which phenomenon can be seen in our previous investigations [16]. In their TOF-MS, the peaks of singly charged molecular ions are obvious and the



**Figure 1** Mass spectra of **4a** in chloroform untreated (A) and treated (B) more than 30 min under midday sunlight.

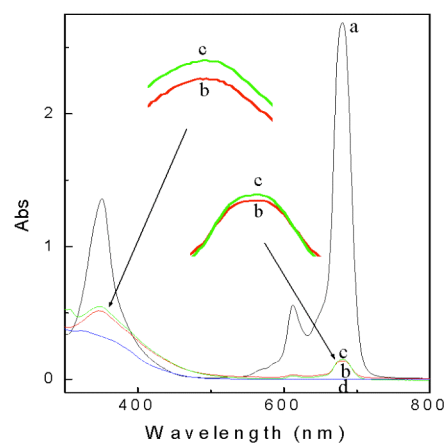
**Table 1**

UV-vis spectra of **4a-4d** in CHCl<sub>3</sub> (1.5×10<sup>-4</sup> mol/L)

λ (nm)	<b>4a</b>	<b>4b</b>	<b>4c</b>	<b>4d</b>
Q	682	681	672	672
B	351	338	300	326

peaks of impurities can hardly be found, e.g. mass spectrum of **4a** (Figure 1 A), which show the excellent purity. From the UV-vis spectrum of **4a** (Figure 2 a), the characteristic absorption bands, Q band and B band, were found at 682 nm and 351 nm, respectively, which means that the Pc ring exists in molecule. All parameters of UV-vis spectra on **4a-4d** are listed in Table 1, from which the impact of M (II) on UV-vis spectra can be found. The Q band wavelength of **4a-4d** follows Zn (II) ≈ Cu (II) > Ni (II) ≈ Co (II), which reveals that the impacts of Zn (Ni) and Cu (Co) on Q bands are similar. The lesser difference among them, namely that the Q band wavelength decreases slightly from Zn to Co in the above order, should be that the less and less *d* electron number in the four metals causes the electron-pulling powers of metals in the center of Pc ring increase and accordingly the electron cloud in Pc ring decrease, which does not favor the red shift of Q band [16a]. So there is the aforementioned order for the Q band wavelength of **4a-4d**.

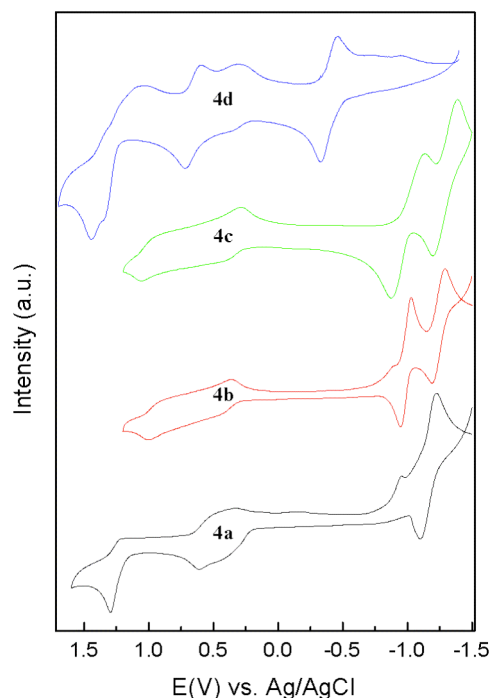
The **4a-4d** all present excellent solubility in CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, pyridine and quinoline, but they are hardly soluble in acetone and methanol. Both **4a** and **4d** dissolve in DMF and DMSO, but in which the solubility of **4b** and **4c** is poor. The good solubility of them in certain organic solvents is attributed to the steric hindrance and the solvent affinity of peripheral 2-methoxyethoxyls, which make the molecules of **4a-4d** hard aggregate. Their



**Figure 2** UV-vis spectra of **4a** in CHCl<sub>3</sub> (1.5×10<sup>-4</sup> mol/L) after radiated under midday sunlight for 0 min (a), 15 min (b) and 30 min (d); UV-vis spectrum of **4a** in CHCl<sub>3</sub> (1.5×10<sup>-4</sup> mol/L) after deoxygenated *via* bubbling dry nitrogen for 30 min and then radiated under midday sunlight for 15 min (c).

solubility facilitates not only the characterization, but also the study on properties.

However, the stability of them in solutions is not as good as in solid state. It is found that they can be quickly degraded by sunlight in  $\text{HCCl}_3$ , especially **4a**. Under midday sunlight, the UV-vis spectra of **4a** displayed that the Q band obviously decreased after 15 min and completely vanished after 30 min (Figure 2 b, d), and accordingly the solution color converts from blue-green to slight yellow. The mass spectrum of color-changed solution showed that the peaks of some charged fractions distributed from 22 to 134, which implied that **4a** had been thoroughly degraded (Figure 1 B). The solution color of **4b** showed change after two days and the solution color of **4c** and **4d** did not show any remarkable change even after one week. The poor stability of **4a** in solution may be ascribed to the photocatalysis of MPc containing non-transition metals, especially Zn (II), which monomer in solution is efficient photocatalyst for phenols and itself to degrade, according to the previous investigation [17]. A Type II mechanism assumed that, as a photosensitiser, MPc was excited to its triplet state, and then transfers the energy to ground-state triplet oxygen  $\text{O}_2 (^3\Sigma_g)$  forming the excited-state singlet oxygen  $\text{O}_2 (^1\Delta_g)$  to attach and decay Pc molecule [17b]. In another investigation, it was found that the decomposition rate of MPc in solution degassed *via* bubbling dry nitrogen for 30 min was enhanced greatly, which meant that oxygen played a role in the deactivation of the excited state of the dye [17c]. In order to find the difference between the systems with and without oxygen, a control experiment was performed by using the solution of **4a** in  $\text{HCCl}_3$ , which first was deoxygenated *via* bubbling dry nitrogen for 30 min and detected on a Cary 500 UV-VIS-NIR spectrophotometer after radiated under midday sunlight for 15 min. The result shows that no obvious difference for the UV-vis spectra of two systems (Figure 2 b, c). Comparing with the aforesaid two results reported in literatures [17b,c],



**Figure 3** Cyclic voltammograms of TMPcs **4a-4d** (scanning rate  $v$ : 50mV/s).

the different finding in our experiments may be owing to the varieties of Pc compounds or other factors, *e.g.* solvents and lifetime of singlet oxygen, which need to be given further special investigation in the future.

The reduction and oxidation of MPc derivatives are due to the interaction between the Pc ring and the central metal. According to Lever *et al.* [18], for Ni, Cu and Zn Pcs, redox processes take place on the Pc ring. In our experiment, it is found that **4b-4c** have similar curves, but **4a** has an irreversible reduction peak at  $-0.96$  V and an irreversible oxidation peak at  $0.61$  V, respectively (Figure 3 **4a-4c**). According to Sakamoto *et al.* [19], for Co Pcs,

**Table 2**  
Reduction and oxidation potential of TMPcs **4a-4d**

Compound	$E_{1/2}$ [a] / $\Delta E$ [b]				
	Oxidation		Reduction		
<b>4a</b>	1.26	0.61 [c]	0.44	-0.96 [c]	-1.17
	0.07		0.08		0.12
<b>4b</b>	0.95		0.39	-0.99	-1.25
	0.10		0.06	0.08	0.11
<b>4c</b>	1.02		0.34	-1.01	-1.29
	0.10		0.09	0.26	0.18
<b>4d</b>	1.44 [c]	1.05 [c]	0.32	-0.40	-0.97 [c]
			0.12	0.06	0.13

[a] Potential of reversible wave is midpoint potential of anodic and cathodic peaks for each couple (V, vs Ag/AgCl). [b] The anodic to cathodic peak separation for reversible couple. [c] Irreversible peak.

**Table 3**The  $i_a/i_c$ , anodic to cathodic peak current ratio of a reversible couple, of TMPcs **4a-4d**.

Compound	$i_a/i_c$ (scanning rate v: 20, 50, 100 and 200 mV/s, respectively)															
	Oxidation				Reduction											
<b>4a</b>	0.27	0.17	0.15	0.11	0.45	0.42	0.40	0.41	9.67	9.13	4.89	2.12				
<b>4b</b>	0.11	0.08	0.08	0.07	1.09	1.07	1.09	1.04	3.00	3.17	1.81	1.24	32.1	11.0	9.25	3.73
<b>4c</b>	0.13	0.13	0.12	0.13	1.08	1.05	0.95	0.88	1.53	1.25	1.31	1.15	10.7	6.21	5.60	4.05
<b>4d</b>	0.66	0.63	—	—	2.13	1.67	—	—	1.34	1.23	—	—				

the irreversible redox processes take place at the center metal. It can be found that the curve of **4d** is obviously different from that of **4a-4c** (Figure 3 **4d**). All in all, it is the center metals that generate the differences of their cyclic voltammograms. In Figure 3, the splitting of the redox couples, the redox processes occurred *via* multi-electron transfers [20], was not clearly observed for all of them, at the same potential, so the electrochemical reactions are single-electron processes. The cyclic voltammogram data of **4a-4d** are summarized in Table 2 and Table 3, respectively.  $\Delta E$  and  $i_a/i_c$  indicate that the aforementioned reactions of redox couples were less quasi-reversible processes.

## EXPERIMENTAL

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

<sup>1</sup>H NMR spectra were recorded on a Varian Unity 300 spectrometer or a Bruker AV 600 spectrometer. 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 LDI-1700-TOF mass spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 Elemental Analyzer. Cyclic voltammetry: LK98B Electrochemical Analyzer. In a lightproof room, the electrochemical data were recorded by a conventional three-electrode cell: a glassy carbon electrode (diameter: 3mm) as the working electrode; a platinum wire as the counter electrode and an Ag/AgCl as the reference electrode. The detected solutions of TMPcs in CH<sub>2</sub>Cl<sub>2</sub> (1.0×10<sup>-3</sup> mol/L, with 0.1 mol/L TBAP) were pre-deoxygenated by purging with nitrogen for 30 min.

**4-(2-Methoxyethoxy) phthalonitrile (3)**. 6.92 g **1** (40 mmol) and 3.04 g **2** (40 mmol) were added to 100 mL anhydrous DMSO at room temperature. The reaction mixture was stirred and 2.4 g LiOH (100 mmol) was interfused over a 2 h period and the mixture was then stirred for 1 day. The reaction was monitored by the way of TLC. The mixture was then poured into 10% NaCl solution and stirred till precipitate appeared. The product was collected and further purified by flash column (petroleum ether–ethyl ether 1:1) to afford adhered and light yellow **3**, 6.63 g (82%), mp 80–82°C; uv (CHCl<sub>3</sub>): 261, 297, 306 nm; ir (KBr): CN 2230, COC 1240 cm<sup>-1</sup>; <sup>1</sup>H nmr (CDCl<sub>3</sub>, 300MHz):  $\delta$  7.71 (d, 1 H,  $J = 8.7$  Hz, ArH), 7.31 (d, 1 H,  $J = 2.5$  Hz, ArH), 7.24 (f, 1 H,  $J = 8.8, 2.6$  Hz, ArH), 4.22 (t, 2 H,

ArOCH<sub>2</sub>), 3.78(t, 2 H, CH<sub>2</sub>O), 3.45(s, 3 H, OCH<sub>3</sub>); ms (CHCl<sub>3</sub>):  $m/z$  225.4 (M + Na<sup>+</sup>). *Anal.* Calcd for C<sub>11</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>: C, 65.34; H, 4.98; N, 13.85. Found: C, 65.25; H, 4.83; N, 13.90.

**TMPcs (4a-4d)**. Typical procedure. 0.81 g Phthalonitrile **3** (4.0 mmol) and 0.20 g Zn(Ac)<sub>2</sub> (1.0 mmol) were added under stirring to pentan-1-ol (10 mL) with a catalytic amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in a 25 mL one-neck round-bottomed flask equipped with an air condenser. The mixture was stirred and heated at 135 °C under N<sub>2</sub> for 24 h. After cooling under N<sub>2</sub>, the black cyan solution was poured into methanol, stirred and collected by vacuum filtration to afford the crude product. After dried, it was washed with methanol by Soxhlet extraction to remove unreacted **3** and other remnants. In the end, the collected solid was purified by column chromatography with chloroform–methanol (10:1) as the mobile phase to give pure blue-green solid.

**4a**, 0.52 g (59%); ir (KBr): COC 1240 cm<sup>-1</sup>; <sup>1</sup>H nmr (600MHz, CDCl<sub>3</sub>):  $\delta$  7.71-7.30 (m, 4H, ArH), 7.18-6.25 (m, 8H, ArH), 3.41 (m, 12H, CH<sub>3</sub>), 3.19 (m, 16H, 4OCH<sub>2</sub>CH<sub>2</sub>O); ms (CHCl<sub>3</sub>):  $m/z$  872.6 [M<sup>+</sup>]. *Anal.* Calcd for C<sub>44</sub>H<sub>40</sub>N<sub>8</sub>O<sub>8</sub>Zn: C, 60.45; H, 4.61; N, 12.82. Found: C, 61.05; H, 4.63; N, 12.85.

**4b**, 0.56 g (44%) $\mu$ ; ir (KBr): COC 1241 cm<sup>-1</sup>; ms (CHCl<sub>3</sub>):  $m/z$  871.4 [M<sup>+</sup>]. *Anal.* Calcd for C<sub>44</sub>H<sub>40</sub>N<sub>8</sub>O<sub>8</sub>Cu: C, 60.58; H, 4.62; N, 12.84. Found: C, 60.29; H, 4.47; N, 12.26.

**4c**, 0.44 g (35%); ir (KBr): COC 1244 cm<sup>-1</sup>; ms (CHCl<sub>3</sub>):  $m/z$  866.8 [M<sup>+</sup>]. *Anal.* Calcd for C<sub>44</sub>H<sub>40</sub>N<sub>8</sub>O<sub>8</sub>Ni: C, 60.92; H, 4.65; N, 12.92. Found: C, 60.69; H, 4.49; N, 12.60.

**4d**, 0.48 g (38%); ir (KBr): COC 1242 cm<sup>-1</sup>; ms (CHCl<sub>3</sub>):  $m/z$  867.8 [M<sup>+</sup>]; *Anal.* Calcd for C<sub>44</sub>H<sub>40</sub>N<sub>8</sub>O<sub>8</sub>Co: C, 60.90; H, 4.65; N, 12.91. Found: C, 60.89; H, 4.57; N, 12.83.

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