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Novel Pathway to Synthesize Unsymmetrical 2,3,9,10,16,17,23-heptakis(alkoxyl)-24-mono(dimethylaminoalkoxyl)phthalocyanines

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A new pathway by means of transetherification has been developed to synthesize novel unsymmetrical 2,3,9,10,16,17,23-heptakis(alkoxyl)-24-mono(dimethylaminoalkoxyl)phthalocyanine compounds. Cyclic tetramerization of 4,5-di-(alkoxyl)phthalonitrile in refluxing dimethylamino-alcohol with high boiling point such as dimethylaminoethanol (DMAE) and 1-dimethylamino-2-propanol in the presence of lithium and pyrazino[2,3-*f*][1,10]phenanthroline-2,3-dicarbonitrile followed by treatment with acetic acid led to the isolation of a series of unsymmetrical metal free 2,3,9,10,16,17,23-heptakis(alkoxyl)-24-mono(dimethylaminoalkoxyl)phthalocyanine compounds $H_2\{Pc(OR)_7[OR'N(CH_3)_2]\}$ [$R = C_4H_9$, C_5H_{11}, C_8H_{17} and $R' = C_2H_4$; $R = C_4H_9$ and $R' = CH(CH_3)CH_2$] (**1**−**4**). Metal insertion into unsymmetrical metal free phthalocyanines (Pc's) using $Cu(OAc)_2 \cdot H_2O$ in dimethylformamide (DMF) at 140 °C easily afforded corresponding unsymmetrical phthalocyaninato copper complexes $Cu\{Pc(OR)_7[OR'N(CH_3)_2]\}$ (**5**−**8**) in good yields. These novel unsymmetrical phthalocyanine compounds have been characterized by a series of spectroscopic methods including ^1H NMR, electronic absorption, IR, and mass spectroscopy in addition to elemental analysis. Their electrochemistry was also studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) methods. The present result will be helpful for designing and preparing unsymmetrical phthalocyanines with potential applications in dye-sensitized solar cells.

Introduction

Phthalocyanines (Pc's) have been an important class of dyes and pigments with extensive applications in paint, printing, and textile industries ever since their serendipitous discovery at the beginning of the past century.[1] Their metal complexes as exemplified by phthalocyanine cobalt are well-known catalysts for numerous chemical reactions including the sulfur removing reaction in gasoline fractions.[2] More recently, these macrocyclic molecular materials have found important applications in electrophotography and ink jet printing as well as photoconductors in photocopying devices.[3] The fields for which important potential applications have been revealed for phthalocyanines include medicine,[4] optical storage,[5] photocatalysis,[6] and molecular-based nanoelectronic devices.[7,8] In particular, very lately these artificial tetrapyrrole derivatives together with their naturally occurring analogues, porphyrins, have stimulated great research interest in organic heterojunction solar cells and dye-sensitized solar cells associated with their excellent semiconducting properties and photophysical characteristics.[9]

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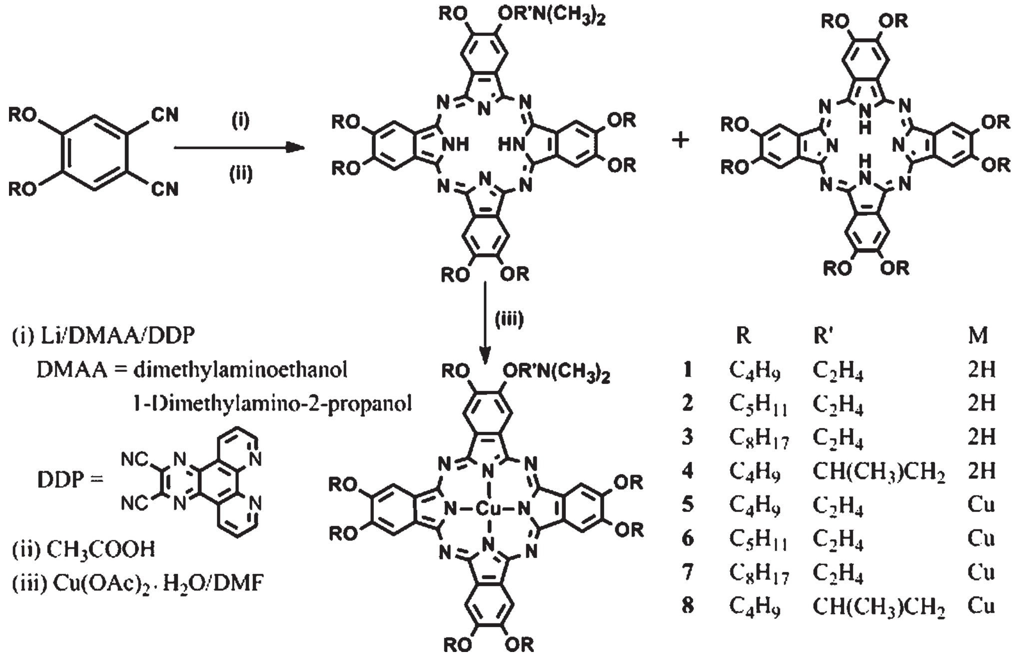
Scheme 1. Synthesis of Unsymmetrical Metal Free and Copper 2,3,9,10,16,17,23-Heptakis(alkoxyl)-24-mono(dimethylaminoalkoxyl)-phthalocyanine Compounds



(i) Li/DMAA/DDP
DMAA = dimethylaminoethanol
1-Dimethylamino-2-propanol
DDP =
(ii) CH_3COOH
(iii) $Cu(OAc)_2 \cdot H_2O$/DMF

	R	R'	M
1	C_4H_9	C_2H_4	2H
2	C_5H_{11}	C_2H_4	2H
3	C_8H_{17}	C_2H_4	2H
4	C_4H_9	$CH(CH_3)CH_2$	2H
5	C_4H_9	C_2H_4	Cu
6	C_5H_{11}	C_2H_4	Cu
7	C_8H_{17}	C_2H_4	Cu
8	C_4H_9	$CH(CH_3)CH_2$	Cu

For the purpose of being employed in the electro- and photoinduced energy- and electron-transfer process-based systems such as dye-sensitized solar cells, novel unsymmetrical phthalocyanine compounds simultaneously possessing peripheral electron-donating groups and electron-withdrawing groups, which not only lends corresponding phthalocyanines good solubility and less degree of aggregation but more importantly the directionality in the excited state,[10] should therefore be developed at the first step. However, despite the reports of quite a large number of various kinds of phthalocyanine compounds, unsymmetrical phthalocyanines simultaneously containing two different species of substituents still remain rare because of the limited pathways developed to prepare such kinds of unsymmetrical phthalocyanine derivatives. Since 1982, mixed cyclic tetramerization using two different kinds of phthalonitriles as starting materials has been utilized to prepare unsymmetrical phthalocyanine compounds, leading to a statistical mixture.[11,12] In 1990, a ring expansion reaction of subphthalocyanine was developed for the preparation of unsymmetrical A_3B-type phthalocyanines.[13] Very lately, a series of unsymmetrical phthalocyaninato copper complexes containing different numbers of 15-crown-ether moieties were prepared from corresponding heteroleptic bis(phthalocyaninato) europium complexes.[14] This method, however, appears not to be easy for further wide range of utilization in preparing unsymmetrical phthalocyanines. As a consequence, developing new pathways with a general sense toward preparing unsymmetrical phthalocyanine compounds still remains a great challenge for the phthalocyanine chemists.

In the present paper, we describe a new pathway developed for the synthesis of a series of novel unsymmetrical 2,3,9,10,16,17,23-heptakis(alkoxyl)-24-mono(dimethylaminoalkoxyl)-phthalocyanine compounds. Cyclic tetramerization of 4,5-di(alkoxyl)phthalonitrile in refluxing dimethylamino-alcohol with high boiling point in the presence of lithium and pyrazino[2,3-*f*]-[1,10]phenanthroline-2,3-dicarbonitrile followed by treatment with acetic acid led to the isolation of metal free 2,3,9,10,16,17,23-heptakis(alkoxyl)-24-mono(dimethylaminoalkoxyl)-phthalocyanine compounds $H_2\{Pc(OR)_7[OR'N(CH_3)_2]\}$ [R = C_4H_9, C_5H_{11}, C_8H_{17} and R′ = C_2H_4; R = C_4H_9 and R′ = $CH(CH_3)CH_2$] (**1**−**4**), Scheme 1. Reaction of these metal free phthalocyanines with $Cu(OAc)_2 \cdot H_2O$ in dimethylformamide (DMF) at 140 °C provided corresponding unsymmetrical phthalocyaninato copper complexes $Cu\{Pc(OR)_7[OR'N(CH_3)_2]\}$ (**5**−**8**). These compounds appear to represent the first example of unsymmetrical phthalocyanines that were isolated and unambiguously characterized through transetherification during the cyclic tetramerization of 4,5-di(alkoxyl)phthalonitrile, to the best of our knowledge.

Results and Discussion

Synthesis. There are generally two synthetic pathways for unsymmetrical phthalocyanines with different substituents at the four isoindole rings. The first method involves a mixed cyclic tetramerization of two species of phthalonitriles. As expected, it is very hard to separate the statistical mixtures of A_4-, A_3B-, A_2B_2-, ABAB-, AB_3-,

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and B_4-type phthalocyanines yielded by such kind of direct cyclic tetramerization of two precursors.[15] Actually, tedious column chromatography including preparative thin layer chromatography usually led to the isolation of small amount of limited species of corresponding unsymmetrical phthalocyanine derivatives. The second pathway involves the ring-expansion reaction of the subphthalocyanine composed of three isoindole units. Treatment of subphthalocyanine with a second species of phthalonitrile (actually 1,3-di-iminoisoindoline) gave the desired metal free unsymmetrical A_3B-type phthalocyanine compound.[13,15] However, limitation of this method for the synthesis of unsymmetrical phthalocyanines containing peripheral alkoxyl substituents retarded its further wide range of utilization. In the present case, a series of novel unsymmetrical metal free 2,3,9,10,16,17,23-heptakis(alkoxyl)-24-mono(dimethylaminoalkoxyl)phthalocyanines $H_2\{Pc(OR)_7[OR'N(CH_3)_2]\}$ whose π-system itself still maintains the D_{4h} symmetry were isolated in relatively good yield from the cyclic tetramerization of 4,5-di(alkoxyl)phthalonitrile in refluxing dimethylamino-alcohol with high boiling point $HOR'N(CH_3)_2$ in the presence of lithium and pyrazino[2,3-*f*][1,10]phenanthroline-2,3-dicarbonitrile followed by treatment with acetic acid. Transetherification before the cyclic tetramerization of 4,5-di(alkoxyl)phthalonitrile procedure occurring in the present reaction condition was considered to play a key role for the isolation of unsymmetrical metal free phthalocyanines in addition to the main product of symmetrical metal free 2,3,9,10,16,17,23,24-octakis(alkoxyl)phthalocyanines.[16] It is worth noting that actually phthalocyanine analogues whose π-system possesses the symmetry lower than D_{4h} were intended to be prepared from the mixed cyclic tetramerization of 4,5-di(butyloxy)phthalonitrile and pyrazino[2,3-*f*][1,10]phenanthroline-2,3-dicarbonitrile in the presence of lithium using dimethylaminoethanol (DMAE) as solvent. However, any such kind of phthalocyanine analogue including the symmetrical one containing isoindole subunit(s) with extended conjugation was not detected and isolated from the reaction mixture. Instead this reaction produced a relatively good yield of unsymmetrical metal free 2,3,9,10,16,17,23-heptakis(butyloxy)-24-mono(dimethylaminoethyloxy)-phthalocyanine $H_2\{Pc(OC_4H_9)_7[OC_2H_4N(CH_3)_2]\}$ (**1**) besides the main product of symmetrical metal free phthalocyanine $H_2Pc(OC_4H_9)_8$. Nevertheless, $H_2\{Pc(OC_4H_9)_7[OC_2H_4N(CH_3)_2]\}$ (**1**) could be easily separated from $H_2Pc(OC_4H_9)_8$ by simple silica gel chromatography probably because of the intrinsic difference in polarity between butyloxy and dimethylaminoethyloxy groups. It is noteworthy that unsymmetrical metal free phthalocyanine containing six butyloxy groups and two dimethylaminoethyloxy groups was also isolated in very low yield, which however was proved to be a mixture containing different isomers according to the ^1H NMR spectroscopic result. In addition, despite the detection by matrix-assisted laser desorption/ionization-time-of-flight (MALDI-TOF) mass spectroscopy, unsymmetrical metal free phthalocyanine containing five butyloxy groups and three dimethylaminoethyloxy groups could not be separated because of the trace amount of production. It is also worth noting that either pyrazino-[2,3-*f*][1,10]phenanthroline-2,3-dicarbonitrile or lithium plays an important role for the transetherification (actually the exchange between butyloxy and dimethylaminoethyloxy groups) during the cyclic tetramerization of 4,5-di(butyloxy)-phthalonitrile. Without the addition of pyrazino[2,3-*f*]-[1,10]phenanthroline-2,3-dicarbonitrile, reaction of 4,5-di(butyloxy)phthalonitrile in refluxing DMAE in the presence of lithium followed by treatment with acid led to the isolation of symmetrical 2,3,9,10,16,17,23,24-octakis-(butyloxy)phthalocyanine $H_2Pc(OC_4H_9)_8$ as the sole product. In the absence of lithium as template, cyclic tetramerization of 4,5-di(butyloxy)phthalonitrile under the present experimental condition did not occur.

For the purpose of verifying the generality of this method in synthesizing such kind of unsymmetrical phthalocyanines, the above-mentioned reaction using other 4,5-di-(alkoxyl)phthalonitrile like 4,5-di(pentyloxy)phthalonitrile and 4,5-di(octyloxy)phthalonitrile than 4,5-di(butyloxy)-phthalonitrile was conducted under the completely same reaction condition. The corresponding unsymmetrical metal free 2,3,9,10,16,17,23-heptakis(alkoxyl)-24-mono(dimethylaminoethyloxy)phthalocyanines $H_2\{Pc(OR)_7[OC_2H_4N(CH_3)_2]\}$ ($R = C_5H_{11}$, C_8H_{17}) (**2, 3**) were also isolated in relatively good yields in addition to the main product $H_2Pc(OR)_8$ ($R = C_5H_{11}$, C_8H_{17}). Nevertheless, reaction of 4,5-di(butyloxy)phthalonitrile conducted in refluxing 1-dimethylamino-2-propanol instead of DMAE led to the isolation of unsymmetrical metal free 2,3,9,10,16,17,23-heptakis(butyloxy)-24-mono(1-dimethylamino-2-propyloxy)phthalocyanine $H_2\{Pc(OC_4H_9)_7[OCH(CH_3)CH_2N(CH_3)_2]\}$ (**4**) in addition to $H_2Pc(OC_4H_9)_8$. At the end of this section, it is worth pointing out that despite the frequent claims of transetherification during the synthesis of alkoxyl-substituted phthalocyanine compounds when high boiling point alcohol was employed as reaction solvent, the present result seems to represent the first unsymmetrical phthalocyanine examples that were prepared and isolated using this reaction mechanism, to the best of our knowledge.

The above-mentioned reaction in the presence of metal salt like $Cu(OAc)_2\cdot H_2O$ was expected to provide corresponding unsymmetrical 2,3,9,10,16,17,23-heptakis(alkoxyl)-24-mono(dimethylaminoalkoxyl)phthalocyaninato copper complexes. However, practical trial failed to give any $Cu\{Pc(OR)_7[OR'N(CH_3)_2]\}$ probably because of the rapid coordination reaction between pyrazino[2,3-*f*][1,10]phenanthroline-2,3-dicarbonitrile and $Cu(OAc)_2\cdot H_2O$. Corresponding unsymmetrical phthalocyaninato copper complexes $Cu\{Pc(OR)_7[OR'N(CH_3)_2]\}$ (**5**−**8**) were actually easily obtained in good yields by metal insertion into unsymmetrical metal free phthalocyanines **1**−**4** using $Cu(OAc)_2\cdot H_2O$ in DMF at 140 °C. Satisfactory elemental analysis results have been obtained for both newly prepared unsymmetrical metal free phthalocyanines and their metal complexes after repeated column chromatography and recrystallization, Table 1.

Spectroscopic Characterization. Both unsymmetrical metal free 2,3,9,10,16,17,23-heptakis(alkoxyl)-24-mono(dimethylaminoalkoxyl)phthalocyanines $H_2\{Pc(OR)_7[OR'N(CH_3)_2]\}$ (**1**−**4**) and their metal complexes $Cu\{Pc(OR)_7[OR'N(CH_3)_2]\}$ (**5**−**8**) were well characterized by a series of

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Table 1. Analytical and Mass Spectroscopic Data for the Unsymmetrical 2,3,9,10,16,17,23-heptakis(alkoxyl)-24-mono(dimethylaminoalkoxyl)phthalocyanine Derivatives M{Pc(OR)$_7$[OR′N(CH$_3$)$_2$]} (M = 2H, Cu) (**1**−**8**)[a]

			analysis(%)		
compound	molecular formula	M$^+$/(M+H)$^+$ (*m*/*z*)	C	H	N
1	$C_{64}H_{83}N_9O_8$	1105.7 (1105.5)[b]	61.67 (61.20)[c]	6.65 (6.62)[c]	9.37 (9.80)[c]
2	$C_{71}H_{97}N_9O_8$	1204.9 (1204.7)[b]	66.77 (66.59)	7.38 (7.61)	9.58 (9.70)[d]
3	$C_{92}H_{139}N_9O_8$	1499.7 (1499.1)[b]	74.19 (73.71)	9.78 (9.35)	8.54 (8.41)
4	$C_{65}H_{85}N_9O_8$	1121.2 (1120.7)[b]	61.63 (61.46)	7.28 (6.71)	9.21 (9.70)[c]
5	$CuC_{64}H_{81}N_9O_8$	1167.7 (1166.5)[b]	61.53 (61.85)	6.49 (6.55)	9.51 (10.02)[d]
6	$CuC_{71}H_{95}N_9O_8$	1266.5 (1265.7)[b]	63.94 (63.57)	7.00 (7.12)	9.67 (9.30)[d]
7	$CuC_{92}H_{137}N_9O_8$	1561.0 (1560.0)[b]	66.77 (66.49)	8.58 (8.28)	7.38 (7.50)[e]
8	$CuC_{65}H_{83}N_9O_8$	1181.9 (1181.6)[b]	66.39 (66.05)	7.28 (7.08)	9.99 (10.66)

[a] Calculated values given in parentheses. [b] The value corresponds to the most abundant isotopic peak of the molecular ion (M$^+$) or (M+H)$^+$. [c] Contain 1.5 equiv of solvated CHCl$_3$. [d] Contain 0.75 equiv of solvated CHCl$_3$. [e] Contain 1.0 equiv of solvated CHCl$_3$.

Table 2. Electronic Absorption Data for Unsymmetrical Phthalocyanine Compounds M{Pc(OR)$_7$[OR′N(CH$_3$)$_2$]} (M = 2H, Cu) (**1**−**8**) in CHCl$_3$

compound	λ_{max}/nm (log ε)					
1	349 (5.00)	426 (4.62)	603 (4.50)	646 (4.75)	665 (5.16)	702 (5.23)
2	349 (4.95)	426 (4.61)	603 (4.47)	646 (4.71)	664 (5.09)	702 (5.17)
3	350 (5.04)	422 (4.70)	603 (4.58)	645 (4.80)	665 (5.16)	701 (5.22)
4	349 (5.06)	424 (4.69)	604 (4.56)	645 (4.78)	665 (5.17)	700 (5.26)
5	341 (4.42)	416 (4.03)	613 (4.15)		680 (4.79)	
6	341 (4.81)	417 (4.44)	612 (4.53)		680 (5.23)	
7	340 (4.72)	418 (4.38)	613 (4.52)		680 (5.09)	
8	340 (4.74)	416 (4.36)	613 (4.46)		680 (5.13)	

spectroscopic methods including MALDI-TOF mass, ^{1}H NMR, electronic absorption, and IR spectroscopy. The MALDI-TOF mass spectra of these compounds clearly showed intense signals for the molecular ion (M)$^+$ or (M+H)$^+$, Table 1. The isotopic pattern closely resembled the simulated one as exemplified by the spectrum of **1** given in Figure S1 (see the Supporting Information).

The electronic absorption spectra of these unsymmetrical phthalocyanine compounds **1**−**8** were recorded in CHCl$_3$, and the data are summarized in Table 2. Figure 1 shows the electronic absorption spectra of the metal free compound **1** and the copper complex **5** as a typical representative for respective series of unsymmetrical metal free phthalocyanines and phthalocyaninato copper complexes. As shown in Figure 1a, similar to other symmetrical metal free phthalocyanines like H$_2$Pc(OR)$_8$ (R = C$_4$H$_9$, C$_5$H$_{11}$, C$_8$H$_{17}$), this unsymmetrical metal free phthalocyanine compound in CHCl$_3$ shows a typical nonaggregated molecular electronic absorption spectrum with the Soret band at 349 nm and split Q bands at 665 and 702 nm with two shoulders at 603 and 646 nm, respectively. The weak band appearing at 426 nm is attributed to the n→π* transitions arising from the oxygen lone pairs of electrons.[17] Upon coordination with copper metal ion, the increase in the molecular symmetry from D_{2h} for the central Pc unit of **1**−**4** to D_{4h} for **5**−**8** induces change in the electronic absorption spectra from typical feature for metal free phthalocyanine to that for typical phthalocyaninato metal species, Table 2. As shown in Figure 1b, the phthalocyanine Soret band is observed at 341 nm and the Q absorption appears at 680 nm as a very strong band with a weak vibronic shoulder at 613 nm for **5** in CHCl$_3$. The weak absorption at 416 nm is due to an *n*→π* transition.

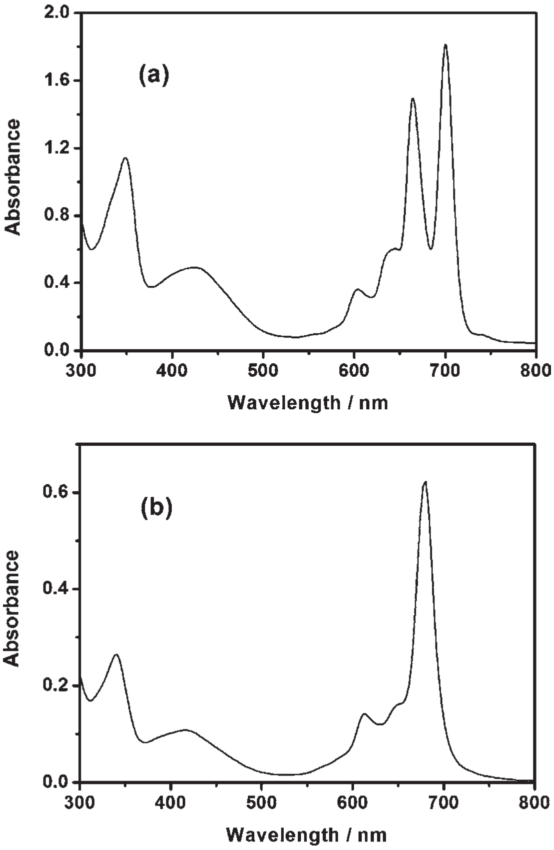

Figure 1. Electronic absorption spectra of (a) H$_2${Pc(OC$_4$H$_9$)$_7$[OC$_2$H$_4$N(CH$_3$)$_2$]} (**1**) and (b) Cu{Pc(OC$_4$H$_9$)$_7$[OC$_2$H$_4$N(CH$_3$)$_2$]} (**5**) in CHCl$_3$ (1.0 × 10^{-5} mol dm^{-3}).

Because of the paramagnetic nature of the divalent copper in Cu{Pc(OR)$_7$[OR′N(CH$_3$)$_2$]} (**5**−**8**), ^{1}H NMR

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Table 3. ^{1}H NMR data (δ) for Unsymmetrical Metal Free Phthalocyanines $H_2\{Pc(OR)_7[OR'N(CH_3)_2]\}$ (**1**−**4**) Recorded in $CDCl_3$

	Pc H_α	OCH_2(R)	CH_2 (R)	CH_3 (R)	OCH_2(R′)	CH (R′)	CH_2 (R′)	CH_3 (R′)	N−H
1	8.48 (s, 8 H)	4.57 (t, 14 H)	2.15−2.20 (m,14 H) 1.79−1.85 (m,14 H)	1.21 (t, 21 H)	4.63 (t, 2 H)		3.13 (t, 2 H)	2.60 (s, 6 H)	−2.40 (b, 2 H)
2	8.71 (s, 8 H)	4.60 (t, 14 H)	2.18−2.21 (m,14 H) 1.75−1.79 (m,14 H) 1.59−1.64 (m,14 H)	1.10 (t, 21 H)	4.70 (t, 2 H)		3.16 (t, 2 H)	2.62 (s, 6 H)	−1.69 (b, 2 H)
3	8.62 (s, 8 H)	4.57 (t, 14 H)	2.16 (m, 14 H) 1.75 (m, 14 H) 1.40−1.58 (m, 56H)	0.95 (t, 21 H)	4.67 (t, 2 H)		3.14 (t, 2 H)	2.61 (s, 6 H)	−2.16 (b, 2 H)
4	8.60 (s 8 H)	4.60 (t, 14 H)	2.17−2.20 (m, 14H) 1.82−1.84 (m,14 H)	1.22 (t, 21 H)	4.62 (t, 2 H)	3.14 (m, 1 H)		1.78−1.80 (m, 3 H) 2.55 (s, 6 H)	−1.97 (b, 2 H)

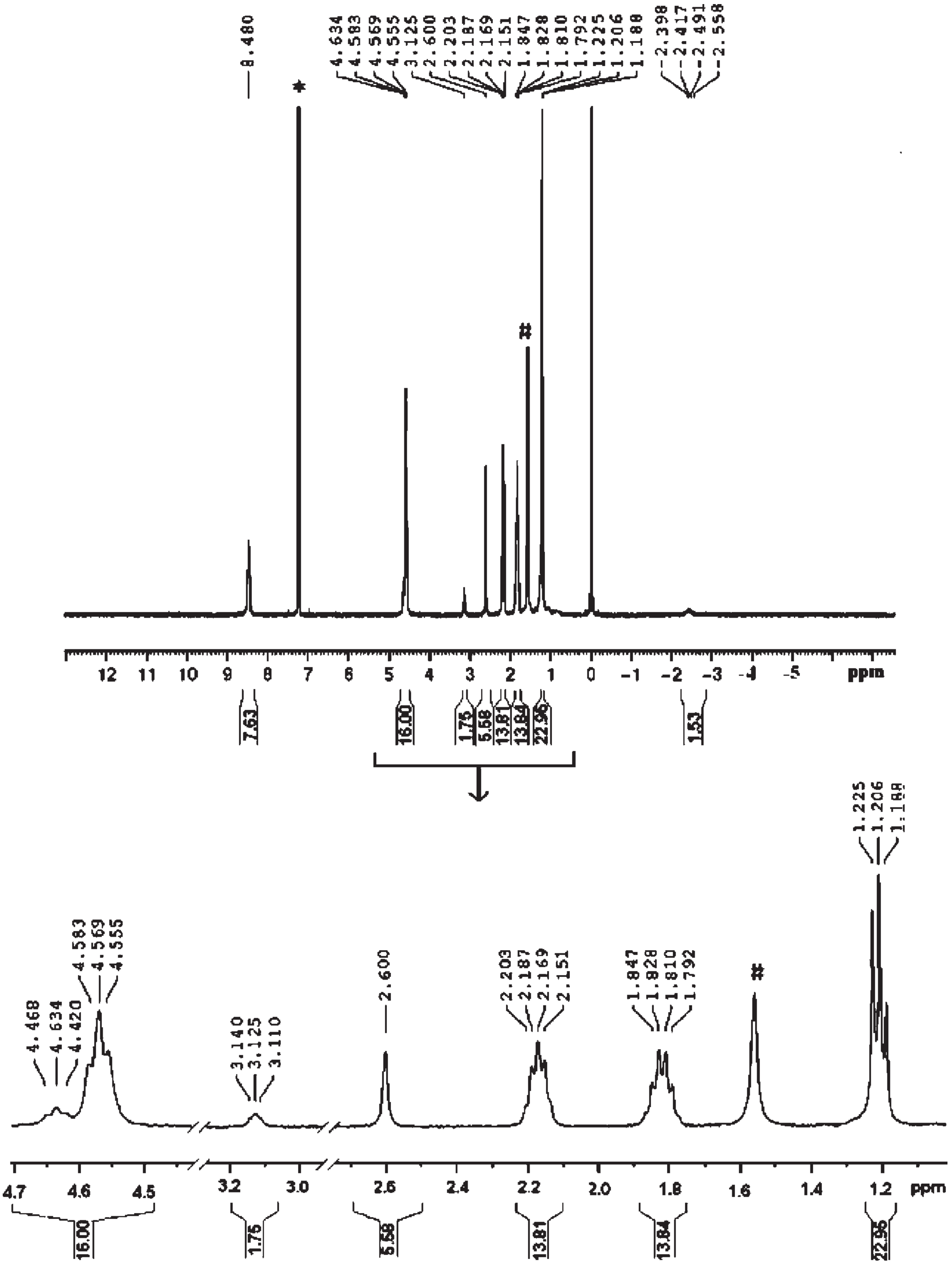

Figure 2. ^{1}H NMR spectrum for $H_2\{Pc(OC_4H_9)_7[OC_2H_4N(CH_3)_2]\}$ (**1**) in $CDCl_3$. The signals due to residue $CHCl_3$ and H_2O are denoted as * and #, respectively.

spectra only for metal free phthalocyanines $H_2\{Pc(OR)_7[OR'N(CH_3)_2]\}$ (**1**−**4**) were recorded in $CDCl_3$ at room temperature, Table 3. Figure 2 shows the ^1H NMR spectrum of **1** in $CDCl_3$ as a typical representative of this series of compounds. The assignment of the spectrum for this unsymmetrical metal free phthalocyanine compound is straightforward because of the resolved multiplicity in the signals for the alkyl chain protons and the availability of $H_2Pc(OC_4H_9)_8$ spectrum, Figure S2 (Supporting Information). The signal at δ 8.48 is due to the α ring protons of $Pc(OC_4H_9)_7[OC_2H_4N(CH_3)_2]$. While the seven butyloxy groups resonate at δ 4.56−4.58 (t, $\mathbf{OCH_2}$), 2.15−2.20 (m, $OCH_2\mathbf{CH_2}$), 1.79−1.85 (m, $OCH_2CH_2\mathbf{CH_2}$), and 1.19−1.23 (t, $OCH_2CH_2CH_2\mathbf{CH_3}$), the one dimethylaminoethyloxy side chain resonates at δ 4.62−4.65 (t, $\mathbf{OCH_2}$), 3.11−3.14 (t, $OCH_2\mathbf{CH_2}$), and 2.60 [s, $OCH_2CH_2N(\mathbf{CH_3})_2$]. In a similar manner, assignments of the ^1H NMR spectra for the remaining metal free phthalocyanines **2**−**4** are also reached, Table 3.

It has been proven that vibrational spectroscopy is a versatile technique for studying the intrinsic properties of phthalocyanine compounds. In the IR spectra of **1**−**8**, Figures S3 and S4 (Supporting Information), in addition to the absorption bands contributed from the central aromatic Pc macrocycle including the wagging and torsion vibrations of C−H groups, isoindole ring stretching vibrations, and the C═N aza group stretching vibrations,[18] the common absorptions observed at 2955−2958, 2932−2933, and 2860−2870 are attributed to the asymmetric and symmetric C−H stretching vibrations, while those at 1276−1277 and 1091 cm^{-1} to the asymmetric and symmetric C−O−C stretching vibrations of the butyloxy and dimethylaminoalkoxyl groups. In the IR spectrum of metal free phthalocyanine compounds **1**−**4**, Figure S3 (Supporting Information), a weak absorption at about 3290 cm^{-1} is obviously due to the asymmetrical N−H stretching vibration according to our previous calculations.[19] This point is supported by the disappearance of this band in the IR spectra of $Cu\{Pc(OR)_7[OR'N(CH_3)_2]\}$ (**5**−**8**) after insertion of the copper metal ion, Figures S4 (Supporting Information).

Electrochemical Properties. The redox behavior of unsymmetrical 2,3,9,10,16,17,23-heptakis(alkoxyl)-24-mono-(dimethylaminoalkoxyl)phthalocyanine derivatives **1**−**8** was studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in CH_2Cl_2. For the purpose of comparative studies, $H_2Pc(OC_5H_{11})_8$ and $Cu[Pc(OC_4H_9)_8]$ have also been electrochemically investigated. The data for $H_2Pc(OC_5H_{11})_8$ is in good agreement with that reported previously for the same compound.[20] Within the electrochemical window of CH_2Cl_2, all these newly prepared unsymmetrical phthalocyanine compounds as well as $Cu[Pc(OC_4H_9)_8]$ exhibited two quasi-reversible or irreversible one-electron oxidations and two quasi-reversible or irreversible one-electron reductions, all of which can be attributed to ligand-based redox processes. The half-wave potentials are summarized in Table 4. A representative cyclic voltammogram for $H_2\{Pc(OC_8H_{17})_7[OC_2H_4N(CH_3)_2]\}$ (**3**) is displayed in Figure 3.

Table 4. Half-Wave Redox Potentials of Unsymmetrical Phthalocyanine Compounds $M\{Pc(OR)_7[OR'N(CH_3)_2]\}$ (M = 2H, Cu) (**1**−**8**) (V vs SCE) in CH_2Cl_2 Containing 0.1 M TBAP

compound	oxd_2	oxd_1	red_1	red_2	$\Delta E°_{1/2}$[a]
1	+1.25	+0.77	−0.97	−1.28	1.74
2	+1.33	+0.81	−0.96	−1.32	1.77
3	+1.35	+0.77	−0.96	−1.27	1.73
4	+1.41	+0.81	−0.94	−1.36	1.75
$H_2Pc(OC_5H_{11})_8$[b]	+1.19	+0.72	−0.97	−1.25	1.69
5	+1.24	+0.74	−1.06	−1.34	1.80
6	+1.30	+0.73	−1.08	−1.36	1.81
7	+1.21	+0.73	−1.07	−1.36	1.80
8	+1.25	+0.71	−1.12	−1.40	1.83
$Cu[Pc(OC_4H_9)_8]$	+1.18	+0.71	−1.07	−1.41	1.78

[a] $\Delta E°_{1/2}$ is the potential difference between the first oxidation and first reduction processes. [b] Cited from reference 19.

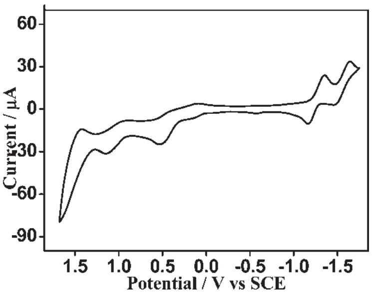

Figure 3. CV of $H_2\{Pc(OC_8H_{17})_7[OC_2H_4N(CH_3)_2]\}$ (**3**) in CH_2Cl_2 containing 0.1 M $[NBu_4][ClO_4]$ at scan rate of 20 mV s^{-1}.

Comparison of the redox behavior between the 2,3,9,10,16,17,23,24-octakis(alkoxyl)phthalocyanines and 2,3,9,10,16,17,23-heptakis(alkoxyl)-24-mono(dimethylaminoalkoxyl)phthalocyanine derivatives, namely, $H_2Pc(OC_5H_{11})_8$ and $H_2\{Pc(OR)_7[OR'N(CH_3)_2]\}$ (**1**−**4**) or $Cu[Pc(OC_4H_9)_8]$ and $Cu\{Pc(OR)_7[OR'N(CH_3)_2]\}$ (**5**−**8**), reveals that substitution of one of the eight peripheral alkoxyl groups by a dimethylaminoalkoxyl group at the phthalocyanine ring does not induce a significant shift in the half-wave potentials, Table 4, revealing the quite similar electron-donating property of the alkoxyl group and the dimethylaminoalkoxyl group attached onto the peripheral positions of phthalocyanine ring. It is worth noting that the very much similar potential difference between the first oxidation and first reduction of metal free $H_2Pc(OC_5H_{11})_8$ in comparison with that for $H_2\{Pc(OR)_7[OR'N(CH_3)_2]\}$ (**1**−**4**) is in good agreement with the almost no shift in the Q absorption bands of the former species relative to the latter ones. This is also true for the phthalocyaninato copper complexes.

Conclusion

Briefly summarizing, a new method by means of transetherification during the cyclic tetramerization of 4,5-di(alkoxyl)phthalonitrile in refluxing dimethylamino-alcohol with high boiling point in the presence of lithium and

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pyrazino[2,3-*f*][1,10]phenanthroline-2,3-dicarbonitrile has been developed for the synthesis of a series of novel unsymmetrical 2,3,9,10,16,17,23-heptakis(alkoxyl)-24-mono(dimethylaminoalkoxyl)phthalocyanines. The generality of this pathway has been verified by the preparation of a series of phthalocyanine compounds including $H_2\{Pc(OR)_7(OR')\}$ and $Cu\{Pc(OR)_7(OR')\}$ [$R = C_4H_9$, C_5H_{11}, C_8H_{17} and $R' = C_2H_4$; $R = C_4H_9$ and $R' = CH(CH_3)CH_2$]. The present result will be helpful for developing new pathways for unsymmetrical phthalocyanine derivatives with potential applications in dye-sensitized solar cells.

Experimental Section

General Remarks. DMAE and 1-dimethylamino-2-propanol were distilled from K_2CO_3. DMF was distilled from anhydrous $MgSO_4$. Dichloromethane was freshly distilled from CaH_2 under nitrogen. Column chromatography was carried out on silica gel column (Merck, Kieselgel 60, 70−230 mesh) with the indicated eluents. The electrolyte $[Bu_4N][ClO_4]$ was recrystallized twice from tetrahydrofuran. All other solvents and reagents such as $Cu(OAc)_2 \cdot H_2O$ were used as received. The compounds 4,5-di(alkoxyl)phthalonitrile and pyrazino[2,3-*f*][1,10]phenanthroline-2,3-dicarbonitrile were prepared according to the published procedure.[21,22]

^1H NMR spectra were recorded on a Bruker DPX 400 spectrometer in $CDCl_3$. Spectra were referenced internally using the residual solvent resonance (δ = 7.26 for ^1H NMR) relative to $SiMe_4$. Electronic absorption spectra were recorded on a Hitachi U-4100 spectrophotometer. IR spectra were recorded as KBr pellets using a Bruker Tensor 37 spectrometer with 2 cm^{-1} resolution. MALDI-TOF mass spectra were taken on a Bruker BIFLEX III ultrahighresolution Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer with alpha-cyano-4-hydroxycinnamic acid as matrix. Elemental analyses were performed on an Elementar Vavio El III.

Electrochemical measurements were carried out with a BAS CV-50W voltammetric analyzer. The cell comprised inlets for a glassy carbon disk working electrode of 2.0 mm in diameter and a silver-wire counter electrode. The reference electrode was Ag/Ag^+ {a solution of 0.01 M $AgNO_3$ and 0.1 M $[NBu_4][ClO_4]$ in acetonitrile}, which was connected to the solution by a Luggin capillary whose tip was placed close to the working electrode. Results were corrected for junction potentials by being referenced internally to the ferrocenium/ferrocene (Fe^+/Fe) couple [$E_{1/2}(Fe^+/Fe) = +0.50$ V vs SCE]. Potentials in this paper are referenced to the SCE. Typically, a 0.1 M solution of $[NBu_4][ClO_4]$ in CH_2Cl_2 containing 0.5 M of sample was purged with nitrogen for 10 min, and then the voltammograms were recorded at ambient temperature. The scan rate was 20 and 10 mV s^{-1} for CV and DPV, respectively.

Preparation of Unsymmetrical Metal Free 2,3,9,10,16,17,23-Heptakis(butyloxy)-24-mono(dimethylaminoethyloxy)phthalocyanine $H_2\{Pc(OC_4H_9)_7[OC_2H_4N(CH_3)_2]\}$ (1). A mixture of 4,5-di(butyloxy)phthalonitrile (272 mg, 1.0 mmol), pyrazino[2,3-*f*][1,10]phenanthroline-2,3-dicarbonitrile (56.4 mg, 0.2 mmol), and lithium (30 mg, 4.3 mmol) in DMAE (3 mL) was heated to reflux under nitrogen for 10 h. After being cooled to room temperature, the resulting green solution was poured into methanol (100 mL) containing 2 mL of CH_3COOH. The precipitate was collected by filtration and chromatographed on a silica gel column using $CHCl_3$ as eluent. A green band containing symmetrical 2,3,9,10,16,17,23,24-octakis(butyloxy)phthalocyanine $H_2Pc(OC_4H_9)_8$ was eluted first. Then $CHCl_3/CH_3OH$ (98:2) developed a second green band which was collected and rotary evaporated. Repeated chromatography followed by recrystallization from $CHCl_3$ and MeOH gave pure symmetrical and unsymmetrical metal free phthalocyanine compounds $H_2Pc(OC_4H_9)_8$ (96 mg, 35%) and $H_2\{Pc(OC_4H_9)_7[OC_2H_4N(CH_3)_2]\}$ (**1**) as dark-green powder (33 mg, 12%), respectively.

Preparation of Unsymmetrical Metal Free 2,3,9,10,16,17,23-Heptakis(pentyloxy)-24-mono(dimethylaminoethyloxy)phthalocyanine $H_2\{Pc(OC_5H_{11})_7[OC_2H_4N(CH_3)_2]\}$ (2). By employing the procedure described above using 4,5-di(pentyloxy)phthalonitrile (300 mg, 1.0 mmol) instead of 4,5-di(butyloxy)phthalonitrile as starting material, unsymmetrical metal free phthalocyanine compound $H_2\{Pc(OC_5H_{11})_7[OC_2H_4N(CH_3)_2]\}$ (**2**) (27 mg, 9%) was obtained in addition to $H_2Pc(OC_5H_{11})_8$ (96 mg, 32%).

Preparation of Unsymmetrical Metal Free 2,3,9,10,16,17,23-Heptakis(octyloxy)-24-mono(dimethylaminoethyloxy)phthalocyanine $H_2\{Pc(OC_8H_{17})_7[OC_2H_4N(CH_3)_2]\}$ (3). By utilizing the procedure described above using 4,5-di(octyloxy)phthalonitrile (384 mg, 1.0 mmol) instead of 4,5-di(butyloxy)phthalonitrile as starting material, unsymmetrical metal free phthalocyanine compound $H_2\{Pc(OC_8H_{17})_7[OC_2H_4N(CH_3)_2]\}$ (**3**) (35 mg, 9.4%) was obtained in addition to $H_2Pc(OC_8H_{17})_8$ (111 mg, 29%).

Preparation of Unsymmetrical Metal Free 2,3,9,10,16,17,23-Heptakis(butyloxy)-24-mono(1-dimethylamino-2-propyloxy)phthalocyanine $H_2\{Pc(OC_4H_9)_7[OCH(CH_3)CH_2N(CH_3)_2]\}$ (4). By employing the procedure described above using 1-dimethylamino-2-propanol (3 mL) instead of DMAE (3 mL) as starting material, unsymmetrical metal free phthalocyanine compound $H_2\{Pc(OC_4H_9)_7[OCH(CH_3)CH_2N(CH_3)_2]\}$ (**4**) (36 mg, 13%) was obtained in addition to $H_2Pc(OC_4H_9)_8$ (72 mg, 26%).

Preparation of 2,3,9,10,16,17,23-Heptakis(alkoxyl)-24-mono(dimethylaminoalkoxyl)phthalocyaninato Copper Complexes $Cu\{Pc(OR)_7[OR'N(CH_3)_2]\}$ [$R = C_4H_9$, C_5H_{11}, C_8H_{17} and $R' = C_2H_4$; $R = C_4H_9$ and $R' = CH(CH_3)CH_2$] (5−8). A mixture of $H_2\{Pc(OR)_7[OR'N(CH_3)_2]\}$ (0.03 mmol) and $Cu(OAc)_2 \cdot H_2O$ (24 mg, 0.12 mmol) in DMF (3 mL) was heated at 140° for 4 h under nitrogen. After being cooled to room temperature, the mixture was evaporated under reduced pressure, and the residue was chromatographed on a silica gel column using $CHCl_3/CH_3OH$ (98:2) as eluent. The dark-green band containing the target 2,3,9,10,16,17,23-heptakis(alkoxyl)-24-mono(dimethylaminoalkoxyl)phthalocyaninato copper complexes $Cu\{Pc(OR)_7[OR'N(CH_3)_2]\}$ [$R = C_4H_9$, C_5H_{11}, C_8H_{17}; $R' = C_2H_4$, $CH(CH_3)CH_2$] (**5**−**8**) was developed. Repeated chromatography followed by recrystallization from $CHCl_3$ and MeOH gave dark-green powder (43−91% yield).

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Supporting Information Available: Experimental and simulated isotopic pattern for the molecular ion of $H_2\{Pc(OC_4H_9)_7[OC_2H_4N(CH_3)_2]\}$ (**1**) shown in the MALDI-TOF mass spectrum; ^1H NMR spectrum of $H_2[Pc(OC_4H_9)_8]$ in $CDCl_3$; IR spectra of $H_2\{Pc(OR)_7[OR'N(CH_3)_2]\}$ (**1**−**4**) in the region of 400−4000 cm^{-1} with 2 cm^{-1} resolution; and IR spectra of $Cu\{Pc(OR)_7[OR'N(CH_3)_2]\}$ (**5**−**8**) in the region of 400−4000 cm^{-1} with 2 cm^{-1} resolution. This material is available free of charge via the Internet at http://pubs.acs.org.

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