

Phthalocyanine formation using metals in primary alcohols at room temperature

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ABSTRACT: Lithium metal added to a solution of 4-neopentoxypthalonitrile in 1-octanol or other long-chain primary alcohols at room temperature resulted in phthalocyanine formation at a reasonable rate in good yield, while preformed lithium 1-octanoate under the same conditions gave 2,9,16,23-tetraneopentoxypthalocyanine, but in lower yield at a slower rate. The use of lower-molecular-weight alcohols slowly gave a phthalocyanine in lower yields. Reverse micelle formation when using long-chain alcohols is proposed as a possibility for enhanced phthalocyanine formation at room temperature. 2,9,16,23-Tetrasubstituted phthalocyanines and metallated phthalocyanines were prepared at room temperature from 4-neopentoxypthalonitrile, 4-bis(4-methoxyphenyl)methoxyphthalonitrile, 4-[1-(4-ethoxy-3-methoxyphenyl)-1-phenyl]-methoxyphthalonitrile and phthalonitrile using lithium 1-octanoate in 1-octanol or by the addition, to a solution of the phthalonitrile in ethanol, of calcium turnings or, to a solution of the phthalonitrile in methanol, of magnesium, zinc, iron or copper powder. The tetrasubstituted phthalocyanines produced exhibited a non-statistical distribution of regioisomers, indicating that electronic effects become important in room-temperature cyclotetramerization of phthalonitriles to phthalocyanines. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: 2,9,16,23-tetrakis[bis(4-methoxyphenyl)methoxy]phthalocyaninato zinc(II); 2,9,16,23-tetrakis[1-(4-ethoxy-3-methoxyphenyl)-1-phenyl]methoxyphthalocyaninato zinc(II); metal catalysis

INTRODUCTION

The synthesis of phthalocyanines readily occurs by the condensation of phthalic anhydride derivatives at 200–300 °C [1–5] or by refluxing phthalonitriles with lithium 1-pentanoate in 1-pentanol at 135 °C [6, 7]. Lower-temperature syntheses have been demonstrated [8–15], but unusual substrates, complex approaches and poorer yields have inhibited their widespread use. In a recent communication [16] it was shown that phthalonitriles, the normal substrate for phthalocyanine formation, can give phthalocyanines (Pcs) at room temperature simply by changing the solvent to 1-octanol and using lithium 1-octanoate. We felt that this rather unusual result merited further studies and

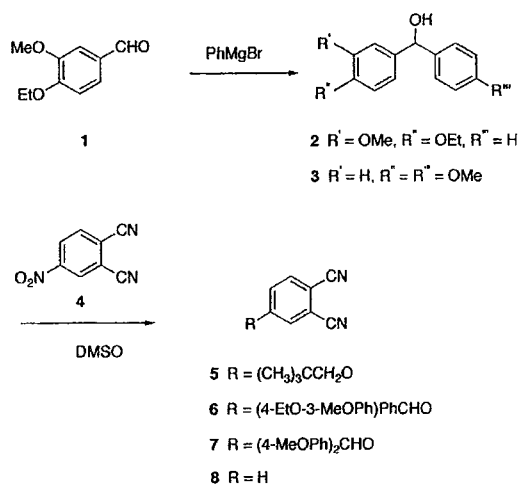
decided to examine the room-temperature condensation of some 4-substituted phthalonitriles and phthalonitrile itself under various conditions and expanding the type of solvents used. In particular we not only examined the use of other long-chain lithium alcohols but also the use of lithium and other *metals* in low- and higher-molecular-weight alcohols as media for Pc formation.

RESULTS AND DISCUSSION

Treatment of 4-ethoxy-3-methoxybenzaldehyde (1) with phenyl magnesium bromide gave 4-ethoxy-3-ethoxybenzhydrol (2) in 68% yield. Nucleophilic aromatic substitution reactions of neopentyl alcohol, 2 and 4,4'-dimethoxybenzohydrol (3) with 4-nitrophthalonitrile (4) and K₂CO₃ in evacuated DMSO [17] yielded 4-neopentoxypthalonitrile (5) [18], 4-[1-(4-ethoxy-3-methoxyphenyl)-1-phenyl]methoxyphthalonitrile (6) and 4-bis(4-methoxyphenyl)methoxyphthalonitrile (7) respectively (Scheme 1), while phthalonitrile (8) is readily available.

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Scheme 1.

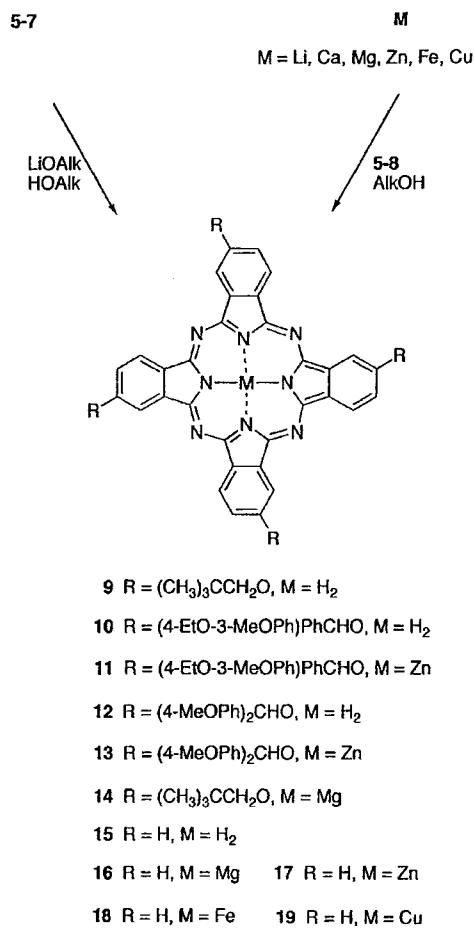
Condensation of **5–7** with lithium alcoholates in their respective alcohols at room temperature slowly gave phthalocyanines **9–13**. The phthalocyanine zinc(II) compounds **11** and **13** were obtained by conversion of the dilithium Pcs with $\text{Zn}(\text{OAc})_2$ *in situ*.

Phthalocyanines have been prepared from phthalonitriles and free metals [1–6, 19, 20] using high-temperature fusion reactions and more recently in an

electrochemical cell [14, 15]. We thought that the addition of a metal to a phthalonitrile dissolved in an alcohol would present, as the metal reacted with the alcohol, a clear metal activated surface to the phthalonitrile for Pc formation at lower temperatures. Lithium was rolled under argon to thin ribbons in a plastic bag, calcium was used as turnings, while magnesium, zinc, iron and copper were used as fine powders. Consequently, when rolled lithium was added to a solution of 4-neopentoxypthalonitrile (**5**) in C_1 to C_{10} primary alcohols, 3-methyl-1-butanol, 2-*N,N*-dimethylaminoethanol (DMAE), 2-pentanol or cyclohexanol, 2,9,16,23-tetraneopentoxypthalocyanine (**9**) was produced at varying rates. Reactions in the secondary alcohols 2-pentanol and cyclohexanol were very slow, while no reaction occurred in the tertiary alcohol, 2-methyl-2-butanol. Calcium metal was sufficiently reactive only in ethanol and hence addition of calcium to **5–7** in ethanol at room temperature proceeded slowly to give phthalocyanines **9, 10** and **12** respectively. Magnesium in methanol was sufficiently reactive, so magnesium was added to **5** in methanol to yield 2,9,16,23-tetraneopentoxypthalocyaninato magnesium(II) (**14**). Similarly, calcium, magnesium, zinc, iron or copper was added at room temperature to phthalonitrile (**8**) in ethanol (for calcium) or methanol to give phthalocyanines **15–19** respectively in low yields (Table 1, Scheme 2). Work-

Table 1. Room-temperature formation of phthalocyanines **9–19** using different metals

Phthalonitrile	Solvent	Time (days)	Metal	Phthalocyanine	Yield (%)
5	Ethanol	2	Ca (turnings)	9	28
5	Methanol	16	Mg (powder)	14	20
5	1-Octanol	2	Li (metal)	9	60
6	Ethanol	18	Ca (turnings)	10	10
6	1-Octanol	18	LiOAlk	10	18
6	1-Octanol	20	LiOAlk/ $\text{Zn}(\text{OAc})_2$	11	10
7	Ethanol	18	Ca (turnings)	12	12
7	1-Octanol	18	LiOAlk	12	7
7	1-Octanol	20	LiOAlk/ $\text{Zn}(\text{OAc})_2$	13	14
8	Ethanol	20	Ca (turnings)	15	9
8	Methanol	25	Mg (powder)	16	12
8	Methanol	20	Zn (powder)	17	12
8	Methanol	26	Fe (powder)	18	8
8	Methanol	25	Cu (powder)	19	<1



Scheme 2.

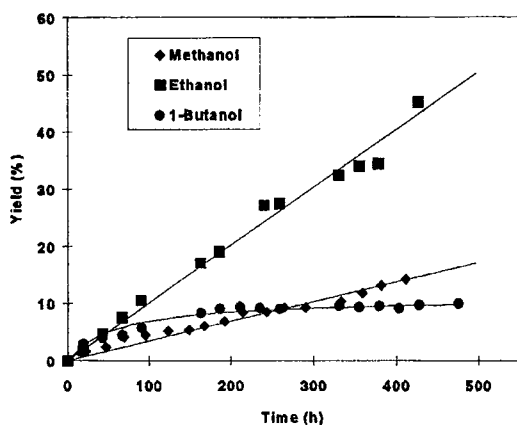


Fig. 1. Formation of 9 in lower-molecular-weight alcohols in presence of lithium metal.

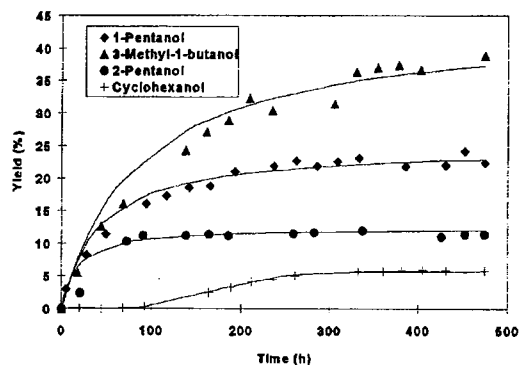


Fig. 2. Formation of 9 in secondary and reference primary alcohols in presence of lithium metal.

up of calcium Pcs always entailed loss of calcium to give the metal-free Pcs.

Examination of the data outlined in Figs 1–5 reveals some rather important information on phthalocyanine formation at room temperature. Firstly, phthalocyanine formation of 9 *does* occur with lithium alkoxides at room temperature in low-molecular-weight alcohols such as ethanol or even methanol, but the rate of reaction is slow, taking up to 400 h to achieve yields of ~20% in methanol and 30% in ethanol.

Adding lithium metal to solutions of 5 in low-molecular-weight alcohols does give phthalocyanine formation, but at similar rates (Fig. 1) to preformed lithium alkoxides. Secondly, reaction of 5 with lithium metal or lithium alkoxides in secondary alcohols occurs very slowly in low yield (5%–10%) and not at all in tertiary alcohols (Fig. 2). This is perhaps not unusual in that formation of Pcs requires the oxidation of an alcohol to an aldehyde or ketone to account for the reduction of some Pc intermediate. Thirdly, the reaction of 5 using lithium 1-octanolate in 1-octanol to give 9 was about twice as rapid and gave 9

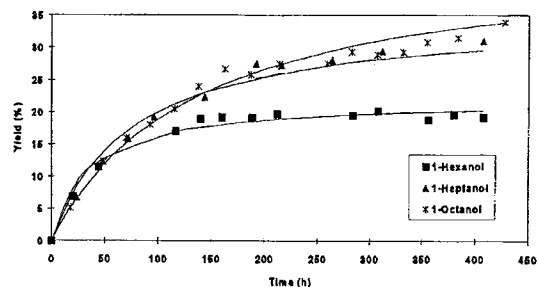


Fig. 3. Formation of 9 in higher-molecular-weight alcohols in absence of lithium metal.

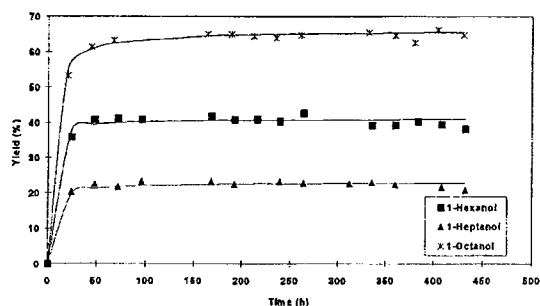


Fig. 4. Formation of 9 in higher-molecular-weight alcohols in presence of lithium metal.

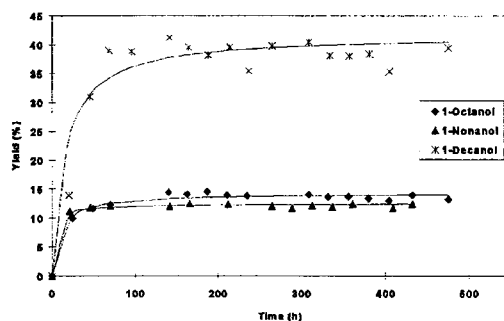


Fig. 5. Formation of 9 in higher-molecular-weight alcohols at dilute concentration in presence of lithium metal.

in higher yield than similar reactions in 1-pentanol (Fig. 3).

Fourthly, reaction of 5 with lithium metal in 1-octanol and other long-chain alcohols at room temperature was complete relatively rapidly (48 vs 400 h), giving Pc 9 in up to 60% yield (Table 1), almost double that under the other conditions (Figs 4 and 5). Fifthly, the direct reaction of 4-neopentoxophthalonitrile (5) with Mg in methanol gave MgPc 14 or with Ca in ethanol gave Pc 9 in higher yields than Li in these solvents (Table 1). Sixthly, phthalonitriles 6 and 7 gave Pcs 10–13 in lower yields at room temperature when reacted with lithium 1-octanolate in 1-octanol or with calcium in ethanol. Finally, phthalonitrile (8) did react at room temperature with calcium, magnesium, zinc, iron and copper slowly over 500 h to give phthalocyanine (15) and metallated Pcs (16–18) in lower yield, with only a trace of PcCu (19) being formed, showing that a variety of metals can be used to form metallated Pcs at room temperature but perhaps more activated forms of some metals are required. Indeed, in one example, ultrasound was used in conjunction with dissolving lithium metal but no rate enhancements or higher yields were noted.

A major question to be answered from the above observations involves the high yield and quicker rate of Pc formation at room temperature when lithium metal in long-chain alcohols was used. It could be that the local concentration of alkoxide or the temperature at the surface of the dissolving metal is high even though the bath solution remains at room temperature. The fact that lithium in the lower-molecular-weight alcohols does not exhibit high rates or yields of Pcs appears to negate this possibility. Of course, one must keep in mind that, especially in methanol, ethanol and DMAE, dissolution of the metal was rapid (0.5 h), so

Pc formation with alkoxide or lithium in these alcohols was, of necessity, essentially the same. Still, dissolution of lithium in 1-pentanol was much slower and rates were still slow and yields lower. It could be that alkoxide strength is modest [21] and could affect Pc formation, since lithium 1-octanolate is more effective than lithium 1-pentanolate, but the difference in alkoxide strength is modest [21] and is unlikely to be sufficient to cause this effect, and another explanation (see below) is more likely. We originally thought that electron transfer reactions [22] involving lithium or other metals would be important and that reduction of the phthalonitrile moiety to an *o*-cyanobenzaldehydimine as a precursor to Pc formation would be important. Since the imine would readily hydrolyze to *o*-cyanobenzaldehyde under the work-up conditions, we examined aliquots of the solution from the lithium in 1-octanol reaction for *o*-cyanobenzaldehyde by both thin layer chromatography (TLC) and high-performance liquid chromatography (HPLC) against a commercial sample. No *o*-cyanobenzaldehyde was observed. In addition, since lithium in the lower alcohols did not enhance rates or yields of Pcs, the electron transfer hypothesis was abandoned. Finally, we considered reverse micelle formation [23].

We had noticed that dissolution of lithium in 1-octanol or 1-decanol did give cloudy solutions of lithium 1-octanolate or lithium 1-decanolate. Pc formation in these solutions was enhanced. Pc formation was enhanced further if the phthalonitrile was first dissolved in the long-chain alcohol before lithium was added. It is possible that under both conditions reverse micelles are formed, but that reverse micelle formation might be more rapid or give more stable reverse micelles as the lithium

dissolves, so that conditions in which lithium is added after the phthalonitrile give the highest yields at the highest rates. Indeed, 1-octanol is a favored substrate in reverse micelle formation. If we accept the possibility of reverse micelle formation enhancing Pc formation, it still remains to speculate on the mechanism of enhanced Pc formation at room temperature. At least two possibilities come to mind. Intercalation of one phthalonitrile group in a micelle might enhance reaction to form a monomeric alkoxyisoindole intermediate [24–26], or four or more phthalonitrile units may intercalate into the reverse micelle giving enhanced rates and yields due to a template effect. Resolution of these and other possibilities remains for further studies.

Since lithium in 1-octanol converted **5** to **9** in good yield at room temperature, we wished to see if the use of other metals would enhance Pc formation at room temperature. As shown above (Scheme 2, Table 1), phthalonitrile (**8**) could only react with metals other than lithium in the lower alcohols. Even though yields were low, we were encouraged that Pc formation occurred at all. We had previously noted that some 4-substituted phthalonitriles gave Pcs at room temperature and that the isomer distribution was non-statistical [16, 27]. In attempts to form one-isomer Pcs from 4-substituted phthalonitriles, we used electron-donating alkoxyphenyl-substituted phthalonitriles **6** and **7** in an attempt to influence the direction of Pc formation and form one isomer. It turned out that **6** and **7** were not that stable to metallic lithium (perhaps owing to the reactive benzylic proton) but that condensation with calcium in ethanol or with magnesium in methanol did give Pcs **10** and **12** in modest yield, again in a non-statistical distribution, but not as a single isomer. The use of calcium in ethanol at room temperature may prove to be valuable in the formation of Pcs at room temperature in some instances.

CONCLUSION

It has been shown that lithium reacting in 1-octanol or other long-chain alcohols is a recommended medium for enhancing phthalocyanine formation in good yield from 4-neopentoxypthalonitrile at room temperature. It is speculated that reverse micelle formation may have a role in this rate enhancement. Other alkoxydiphenylmethoxy-substituted phthalonitriles or phthalonitriles gave Pcs at room temperature with calcium in ethanol or with magnesium in methanol, while phthalonitrile also reacted with zinc or iron in

methanol to give Pcs in lower yield at room temperature.

EXPERIMENTAL

All organic solvents were dried by appropriate methods and distilled before use. All reagents were freshly distilled or recrystallized and then dried under reduced pressure before use. Zinc acetate ($\text{Zn}(\text{AcO})_2 \cdot 2\text{H}_2\text{O}$) was finely ground, dried at 110°C under vacuum for 36 h and then stored in sealed vials. Unless otherwise noted, Praxair high-purity argon was used to maintain inert atmosphere conditions, and magnetic stirring methods were utilized during distillation and reaction processes. Thin layer chromatography (TLC) was performed using silica gel G as the stationary phase. Flash chromatography was performed using silica gel of particle size 20–45 μm . Melting points (m.p.) were determined using a Kofler hot-stage melting point apparatus and are uncorrected. IR spectra were recorded on a Pye Unicam SP3-200 or a Perkin-Elmer infrared spectrophotometer, and FT-IR spectroscopy was performed on a Unicam Mattson 3000 FT-IR spectrometer using KBr disks. UV-vis spectra were recorded on a Hewlett-Packard HP8451A diode array spectrophotometer. Mass spectrometry (MS) was performed by Dr B. Khouw (York University, Toronto, Ontario, Canada) and mass spectra were recorded at 70 eV on a Kratos MS-50 triple-analyzer mass spectrometer in EI mode. FAB mass spectra were obtained with a Kratos MS-50 triple-analyzer mass spectrometer equipped with a FAB ion source of standard Kratos design and an Ion Tech atom gun. Microanalyses were performed by Guelph Chemical Laboratories Ltd (Guelph, Ontario, Canada). Nuclear magnetic resonance (^1H NMR) spectra for protons and carbons were recorded on a Bruker ARX400 high-field Fourier transform instrument. ^{13}C NMR resonances are reported as the proton-decoupled chemical shifts, and in most cases the JMOD or/and DEPT ^{13}C NMR technique was used to differentiate carbons.

UV-vis Spectroscopic Analysis

2,9,16,23-Tetraneopentoxypthalocyanine (**9**) (100 mg, 0.116 mmol) was dissolved in THF (7 mL), and lithium wire (32 mg, 4.61 mmol) was added. The reaction mixture was heated to 50°C and the metallation process was monitored using UV-vis spectroscopy. After 3 days the excess lithium metal

was removed by filtration. Subsequent evaporation of the solvent under reduced pressure gave lithiated **9** (92 mg, 91%) as a dark blue solid, which was used directly to make standard solutions. Solutions containing various concentrations ((1.16, 1.41, 1.59, 1.76, 1.85, 1.95, 2.12, 2.30, 2.35, 2.43, 2.47, 2.92, 3.28, 3.29) $\times 10^{-5}$ M) of the dilithium compound of **9**, dissolved in ethanol, were independently prepared and examined by UV-vis spectroscopy. A calibration curve was constructed by plotting the absorbance measured at λ_{\max} (the Q band absorption maximum) versus the corresponding concentration. The concentration of the dilithium derivative of **9** present in the reaction mixtures at the various time intervals was determined by extracting a known volume of the reaction mixture, diluting it by a known factor and measuring the absorbance at λ_{\max} using UV-vis spectroscopy. The absorbance values were used to extrapolate the concentration of the dilithium compound of **9** in the sample from the calibration curve, which in turn was used to calculate the amount of the dilithium compound of **9** present in the reaction mixture.

General Procedure for the Formation of **9** Using Lithium Alkoxide in the Corresponding Alcohol

Lithium (30 mg, 4.61 mmol) was dissolved in the respective alcohols (6 mL). For the alcohols with a molecular weight equal to or greater than that of 1-pentanol, heat was required for the dissolution of lithium. To the alkoxide solution, cooled to room temperature, was added 4-neopentoxyphthalonitrile (**5**) (550 mg, 2.57 mmol) dissolved in THF (1 mL). The reaction mixtures were stirred at room temperature for a time period varying between 400 and 475 h. At various intervals throughout this time period, aliquots of the reaction mixtures were diluted with ethanol and analyzed using UV-vis spectroscopy as described above.

General Procedure for the Formation of **9** in the Various Alcohols in the Presence of Lithium Metal

4-Neopentoxyphthalonitrile (**5**) (550 mg, 2.57 mmol) was added to the respective alcohols (7 mL). Lithium (30 mg, 4.32 mmol) was rolled into a foil in an argon-flushed polyethylene bag and added to the reaction mixture. The reaction mixtures were stirred at room temperature for a time period varying between 400 and 475 hours. At various intervals throughout this time period, aliquots of the reaction mixtures were diluted

with ethanol and analyzed using UV-vis spectroscopy as described above.

General Procedure for the Condensation of Phthalonitrile (**8**) Using Different Metals

Phthalonitrile (**8**) (256 mg, 2.00 mmol) was added to the alcohol (3 mL). The metal (2.20 mmol) (Ca, 88 mg as turnings; Mg, 53 mg as a powder (325 mesh); Zn, 143 mg as a powder (300 mesh); Fe, 168 mg as a powder (350 mesh)) was added and the reaction mixture was stirred at room temperature for a time period varying between 20 and 26 days. Tetrahydrofuran (5 mL) was added and the reaction mixture was subjected to flash column chromatography on silica gel using THF as eluent. The product was dispersed in ethanol-water (1:1) and collected by centrifugation. The precipitate was successively washed with acetonitrile and ethanol and collected by centrifugation. Metallated Pcs **15–18** were produced in 8%–12% yields after reaction for 20–26 days, while PcCu (**19**) was formed but in less than 1% yield.

4-Ethoxy-3-methoxybenzohydrol (**2**)

Phenyl magnesium bromide was prepared by the slow addition of a solution of bromobenzene (5.32 g, 34 mmol) in ether (18 mL) to dry magnesium turnings (800 mg, 34 mmol) with vigorous stirring. Once the addition was complete, the mixture was refluxed for 15 min, cooled to room temperature and used immediately. A stirred solution of 4-ethoxy-3-methoxybenzaldehyde (**1**) (2.7 g, 15 mmol) in THF (10 mL) was added dropwise to the phenyl magnesium bromide. The reaction mixture was refluxed for 15 min, cooled to room temperature and poured onto crushed ice. The reaction mixture was acidified with 5 M aqueous HCl and extracted three times with ether, then the combined extracts were washed with water and dried over anhydrous magnesium sulfate. Evaporation of the solution yielded an oily product which was crystallized from hexane to obtain **2** (2.65 g, 68%) as a white crystalline solid. M.p. 56°C. IR: 3350, 3268, 3090–3020, 2975–2836, 1603, 1586, 1513, 1478, 1390, 1237, 1135, 1032 cm^{-1} . ^1H NMR (CDCl_3): δ (J in Hz) 7.42–7.35 (m, 4H), 7.31 (d, 1H, $J=8$), 6.96 (s, 1H), 6.87–6.81 (m, 2H), 5.81 (s, 1H), 4.12 (q, 2H, $J=6.5$), 3.86 (s, 3H), 2.32 (s, 1H), 1.49 (t, 3H, $J=6.5$). ^{13}C NMR (CDCl_3): δ 149.38, 147.81, 143.94, 136.54, 128.45, 127.49, 126.47, 119.01, 112.47, 110.14, 76.02, 64.37, 55.92, 14.84. EI-MS: m/z (%) 258 (M^+ , 100), 241 (50), 229 (35), 213 (75),

181 (70), 153 (80), 141 (35), 125 (55), 115 (25), 105 (75), 93 (25), 77 (35). Anal. calc. for $C_{16}H_{18}O_3$: C 74.42, H 6.98, O 18.60; found: C 73.50, H 6.68, O 18.68.

4-[1-(4-Ethoxy-3-methoxyphenyl)-1-phenyl]methoxyphthalonitrile (6)

4-Ethoxy-3-methoxybenzohydrol (**2**) (2.36 g, 9.66 mmol) and potassium carbonate (1.0 g, 7.25 mmol) were added to a solution of 4-nitrophthalonitrile (**4**) (2.0 g, 11.6 mmol) in DMSO (40 mL). The mixture was stirred for 96 h. Three portions of potassium carbonate (1.0 g, 7.25 mmol) were then added to the mixture at 20 h intervals and pumped under vacuum for 10 min at 10 h intervals throughout the reaction. The reaction was monitored by TLC using THF-hexane (3:7) as eluent until all the starting material was consumed. The reaction mixture was poured onto ice (500 g). The resulting precipitate was collected by filtration, washed with cold water and dried. The crude product was subjected to column chromatography on silica gel using THF-hexane (7:13) as eluent. The product was recrystallized from ethanol to obtain a white crystalline solid (1.85 g, 50%). M.p. 125–126°C. IR: 3075, 3034, 2893–2976, 2226 (CN), 1591, 1522, 1489, 1418, 1315, 1247, 1140, 1085, 1035 cm^{-1} . 1H NMR ($CDCl_3$): δ (J in Hz) 7.65 (d, 1H, $J=8$), 7.41–7.32 (m, 6H), 7.27–7.23 (m, 1H), 6.90–6.85 (m, 3H), 6.23 (s, 1H), 4.10 (q, 2H, $J=6.5$), 3.83 (s, 3H), 1.47 (t, 3H, $J=6.5$). ^{13}C NMR ($CDCl_3$): δ 161.16, 149.77, 148.74, 139.05, 135.15, 131.09, 128.99, 128.56, 126.66, 121.11, 120.71, 119.62, 117.36, 115.62, 115.25, 112.55, 110.25, 107.55, 83.00, 64.39, 56.07, 14.77. EI-MS: m/z (%) 384 (M^+ , 45), 241 (100), 213 (88), 181 (65), 165 (50), 152 (70), 144 (50), 115 (45). Anal. calc. for $C_{24}H_{20}O_3N_2$: C 75.00, H 5.21, N 7.29; found: C 74.73, H 5.05, N 7.22.

4-Bis(4-methoxyphenyl)methoxyphthalonitrile (7)

4,4'-Dimethoxybenzohydrol (**3**) (2.36 g, 9.66 mmol) and potassium carbonate (1.0 g, 7.25 mmol) were added to a solution of 4-nitrophthalonitrile (**4**) (2.0 g, 11.6 mmol) in DMSO (40 mL). The mixture was stirred for 96 h. Three portions of potassium carbonate (1.0 g, 7.25 mmol) were then added to the mixture at 20 h intervals and pumped under vacuum for 10 min at 10 h intervals throughout the reaction. The reaction was monitored by TLC using THF-hexane (3:7) as eluent until all the starting material was consumed.

The reaction mixture was poured onto ice (500 g). The resulting precipitate was collected by filtration, washed with cold water and dried. The crude product was subjected to column chromatography on silica gel using THF-hexane (3:7) as eluent. The product was recrystallized from THF/hexane. A white crystalline product (1.55 g, 43%) was obtained. M.p. 146–148°C. IR: 3072, 3010, 2975, 2941, 2845, 2224 (CN), 1598, 1512, 1300, 1247, 1177, 1094, 1023 cm^{-1} . 1H NMR ($CDCl_3$): δ (J in Hz) 7.62 (d, 1H, $J=9$), 7.29–7.20 (m, 6H), 6.89 (d, 4H, $J=8$), 6.21 (s, 1H), 3.90 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 661.21, 159.71, 135.10, 131.15, 128.15, 121.09, 120.76, 117.32, 115.67, 115.28, 114.38, 107.39, 82.52, 55.34. EI-MS: m/z (%) 370 (M^+ , 50), 241 (75), 227 (100), 213 (70), 197 (65), 183 (60), 169 (68), 144 (80), 114 (70), 97 (28), 89 (47), 63 (30). Anal. calc. for $C_{23}H_{18}N_2O_3$: C 74.59, H 4.86, N 7.57; found: C 74.33, H 4.71, N 7.51.

2,9,16,23-Tetraneopentoxypthalocyanine (9)

Compound **5** (214 mg, 1.00 mmol) was dissolved in ethanol (3 mL). Calcium metal (200 mg, 5.00 mmol), cut into small turnings, was added to the reaction mixture. The reaction mixture was stirred at room temperature for 2 days. The reaction mixture was diluted with ethanol-water (1:1) and the crude product was collected by centrifugation. The precipitate was subjected to flash column chromatography on silica gel using THF as eluent. Final purification involved the reprecipitation of the phthalocyanine from ethanol/water. The precipitate was collected by centrifugation and washed successively with water and acetonitrile. The product was further purified by flash column chromatography on silica gel using THF-benzene (1:19) as eluent. The reaction gave **9** (105 mg, 28%) as a dark blue solid.

2,9,16-23-Tetra{[(4-ethoxy-3-methoxyphenyl)-1-phenyl]methoxy}phthalocyanine (10) (Method I)

The same procedure (method I) was followed as described above for compound **9**, but compound **6** (770 mg, 2.00 mmol) was used as the precursor molecule. The reaction gave compound **10** (77 mg, 10%) as a dark blue solid. M.p. 222–225°C. UV-vis: λ_{max} (THF) ($\log \epsilon$) 706 (5.13), 668 (5.03), 638 (4.54), 610 (4.38), 388 (4.50), 344 nm (4.80). 1H NMR ($CDCl_3$): δ (J in Hz) 8.35–8.17 (m, 8H), 7.75–7.69 (m, 6H), 7.51–7.44 (m, 6H), 7.34–7.25 (m, 8H), 7.23–7.13 (m, 12H), 6.91–6.86 (m, 4H), 6.68–6.61 (m, 4H), 4.03–4.00 (t, 8H, $J=6$), 3.84–3.75 (m, 12H), 1.20–

1.09 (m, 12H), -3.68 (s, 1H), -4.09 (s, 1H). FAB-MS: m/z (%) 1539 ($M^+ + 1$, 100), 1299 (68), 1058 (40), 816 (100), 579 (88). Anal. calc. for $C_{96}H_{82}N_8O_{12}$: C 74.90, H 5.33, N 7.28; found: C 74.64, H 5.10, N 7.25.

2,9,16,23-Tetra[(4-ethoxy-3-methoxyphenyl)-1-phenyl]methoxy}phthalocyanine (10) (Method II)

The same procedure (method II) was followed as described below for compound **12**, but compound **6** (770 mg, 2.00 mmol) was used as the precursor molecule. The reaction gave compound **10** (138 mg, 18%) as a dark blue solid.

2,9,16,23-Tetra[(4-ethoxy-3-methoxyphenyl)-1-phenyl]methoxy}phthalocyaninato Zinc (II) (11)

The same procedure was followed as described below for compound **13**, but compound **6** (770 mg, 2.00 mmol) was used as the precursor molecule. The crude product was subjected to flash column chromatography on silica gel using ethyl acetate-benzene (2:3) as eluent. The reaction gave compound **11** (85 mg, 10%) as a dark blue solid. M.p. 215–220°C. UV-vis: λ_{max} (THF) (log ϵ) 673 (5.10), 656 (4.49), 612 (4.38), 352 (4.74), 290 nm (4.61). 1H NMR (DMSO- d_6): δ (J in Hz) 9.15–9.10 (m, 4H), 8.89 (s, 4H), 7.93–7.89 (m, 4H), 7.82 (t, 8H, $J=8$), 7.53–7.49 (m, 12H), 7.36 (t, 16H, $J=8$), 7.27 (t, 4H, $J=8$), 7.12–7.10 (m, 4H), 7.03–7.00 (m, 4H), 4.01–3.97 (m, 8H), 3.90–3.88 (m, 12H), 1.28 (t, 12H, $J=7$). FAB-MS: m/z (%) 1603 ($M^+ + 1$, 90), 1362 (45), 1120 (25), 789 (30), 649 (100). Anal. calc. for $C_{96}H_{80}N_8O_{12}$ Zn: C 71.91, H 4.99, N 6.99; found: C 71.05, H 5.02, N 6.66.

2,9,16,23-Tetra[bis(4-methoxyphenyl)methoxy]-phthalocyanine (12) (Method I)

Compound **7** (740 mg, 2.00 mmol) was added to ethanol (3 mL). Calcium metal (88 mg, 2.20 mmol), cut into small turnings, was added and the reaction mixture was stirred at room temperature for 18 days. The reaction mixture was monitored by TLC using THF-hexane (1:2) as eluent. The reaction mixture was then diluted with THF and the insoluble components of the reaction mixture were removed by centrifugation. The filtrate was evaporated under reduced pressure and the resulting phthalocyanine was reprecipitated from ethanol/water. The precipitate was collected by centrifugation and successively washed with acetonitrile and ethanol. The phthalocyanine was

subjected to flash column chromatography on silica gel using THF-benzene (1:19) as eluent. Compound **12** (46 mg, 12%) was obtained as a dark blue solid. M.p. 168–172°C. UV-vis: λ_{max} (THF) (log ϵ) 708 (5.06), 672 (4.99), 644 (4.55), 610 (4.39), 392 (4.50), 344 nm (4.78). 1H NMR ($CDCl_3$): δ 8.48–8.14 (m, 6H), 7.70–7.63 (m, 4H), 3.82–3.75 (m, 24H), -3.31 to -3.76 (br, d, 2H). FAB-MS: m/z (%) 1483 ($M^+ + 1$, 100), 1258 (45), 1128 (55), 1096 (58), 1043 (100), 1025 (38), 955 (40), 881 (45), 820 (100), 631 (80). Anal. calc. for $C_{92}H_{74}N_8O_{12}$: C 74.49, H 5.01, N 7.56; found: C 74.28, H 5.65, N 7.26.

2,9,16,23-Tetra[bis(4-methoxyphenyl)methoxy]-phthalocyanine (12) (Method II)

Lithium (30 mg, 4.32 mmol) was rolled into a foil in an argon-flushed polyethylene bag and dissolved in 1-octanol (2 mL) at 120°C. To the alkoxide solution, cooled to room temperature, was added compound **7** (740 mg, 2.00 mmol) dissolved in THF (1.5 mL). The reaction mixture was stirred at room temperature for 18 days and monitored by TLC using THF-hexane (1:2) as eluent. The reaction mixture was then diluted with ethanol-water (3:1) and the resulting precipitate was collected by centrifugation. The precipitate was successively washed with acetonitrile and ethanol and collected by centrifugation. The crude product was subjected to flash column chromatography on silica gel using THF-benzene (1:19) as eluent. Compound **12** (51 mg, 7%) was obtained as a dark blue solid.

2,9,16,23-Tetra[bis(4-methoxyphenyl)methoxy]-phthalocyaninato Zinc(II) (13)

Lithium (30 mg, 4.32 mmol) was rolled into a foil in an argon-flushed polyethylene bag and dissolved in 1-octanol (2 mL) at 120°C. To the alkoxide solution, cooled to room temperature, was added compound **7** (740 mg, 2.00 mmol) dissolved in THF (1.5 mL). The reaction mixture was stirred at room temperature for 8 days. Zinc acetate (183 mg, 1.00 mmol) was then added and the reaction mixture was stirred at room temperature for an additional 12 days. The reaction was monitored by TLC using THF-hexane (1:2) as eluent. The reaction mixture was then diluted with ethanol-water (3:1) and the resulting precipitate was collected by centrifugation. The precipitate was successively washed with water, acetonitrile and ethanol and collected by centrifugation. The crude product was subjected to flash column chromatography on silica gel using THF-benzene (1:4) as eluent.

Compound **13** (111 mg, 14%) was obtained as a dark blue solid. M.p. 177–181 °C. UV-vis: λ_{max} (THF) (log ϵ) 684 (5.04), 614 (5.02), 352 (4.58), 286 (4.04), 272 (4.20), 238 nm (4.78). ^1H NMR (pyridine- d_5): δ J (in Hz) 9.59–9.56 (m, 3H), 9.52 (s, 3H), 8.09–8.07 (d, 4H, $J=8$), 7.86–7.84 (d, 16H, $J=8$), 7.22–7.06 (m, 18H), 6.65 (s, 2H), 3.63–3.36 (m, 24H). FAB-MS: m/z (%) 1547 ($\text{M}^+ + 1$, 100), 1472 (30), 1323 (50), 1241 (20), 1095 (30), 863 (25), 766 (20). Anal. calc. for $\text{C}_{92}\text{H}_{72}\text{N}_8\text{O}_{12}\text{Zn}$: C 71.46, H 4.66, N 7.25; found: C 70.76, H 5.07, N 7.23.

Tetraneopentoxophthalocyaninato Magnesium(II) (**14**)

Compound **5** (400 mg, 1.87 mmol) was dissolved in methanol (3 mL). Magnesium powder (53 mg, 2.18 mmol) was added to the reaction mixture. The reaction mixture was stirred at room temperature for 16 days and monitored by TLC using THF–benzene (1:4) as eluent. Tetrahydrofuran (50 mL) was added and the reaction mixture was filtered through celite to remove excess magnesium powder. Evaporation of the solvent under reduced pressure gave the phthalocyanine which was reprecipitated from ethanol/water. The product was collected by centrifugation and washed with acetonitrile. The product was then subjected to flash column chromatography on silica gel using THF–benzene (1:19) as eluent. Compound **14** (83 mg, 20%) was obtained as dark blue solid. M.p. 204–208 °C. UV-vis: λ_{max} (THF) (log ϵ) 676 (5.04), 656 (4.45), 610 (4.37), 356 (4.76), 288 nm (4.40). ^1H NMR (acetone- d_6): δ J (in Hz) 9.32–9.28 (t, 4H, $J=17$), 8.93–8.90 (d, 4H, $J=12$), 7.79 (s, 4H), 4.26–4.25 (d, 8H, $J=4$), 1.31 (s, 36H). FAB-MS: m/z (%) 881 ($\text{M}^+ + 1$, 100), 810 (45), 725 (25), 572 (25). Anal. calc. for $\text{C}_{52}\text{H}_{56}\text{N}_8\text{O}_4\text{Mg}$: C 70.91, H 6.36, N 12.73; found: C 69.22, H 6.67, N 10.65.

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