Metallophthalocyanine dimers incorporating five-atom covalent bridges

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Metal-free copper and cobalt(II) binuclear phthalocyanines, in which the two phthalocyanine nuclei are covalently linked through five-atom bridges, have been prepared and characterized. Some new metal-free, copper, cobalt(II), and zinc 2,9,16,23-tetraalkoxyphthalocyanines, some of which are extremely soluble in organic solvents, are described.

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On a préparé et caractérisé une série de phtalocyanines, libres ou complexées par du cuivre ou du cobalt(II), dans lesquelles les deux noyaux de phtalocyanines sont liés d'une manière covalente par des ponts de cinq atomes. On décrit quelques nouvelles tétraalkoxy-2,9,16,23 phtalocyanines, libres ou complexées avec du cuivre, du cobalt(II) ou du zinc, qui sont extrèmement solubles dans les solvants organiques.

The use of cobalt phthalocyanine as a catalyst for the electro-reduction of oxygen has been known for some time (1) and extensive research efforts have shown that porphyrins and phthalocyanines can act as potential catalysts for energy conversion processes (2—4). It is well known that iron(II) porphyrins decompose oxygen through a mechanism involving two porphyrins acting on one oxygen molecule (5). Binuclear porphyrins (6—9) have been prepared and used in the 4-electron reduction of molecular oxygen to water. Under operating conditions, however, binuclear porphyrins lose catalytic activity with time (7) and it may be that the porphyrin nucleus itself is not sufficiently stable to be used as a long term photocatalyst. For this reason, we envisioned that binuclear photocatalysts based on the thermally (10) and photochemically stable phthalocyanine nucleus would be worthwhile molecules to synthesize and examine in electrochemical and photocatalytic studies.

Using a solid phase method of synthesis we have recently prepared some unsymmetrical phthalocyanines which are very soluble in organic solvents (11, 12), compared with most phthalocyanines which are notoriously insoluble. These soluble, unsymmetrical, mononuclear phthalocyanines contained the necessary handle, a hydroxy functional group, which could be used to attach the phthalocyanine to electrodes (13, 14). The synthesis of a very soluble mononuclear phthalocyanine in our earlier studies (11, 12) and the development of chromatographic methods for the separation of phthalocyanines in general (12) has enabled us to contemplate the syntheses of the hitherto unknown binuclear phthalocyanines.

Although we believed that a solid phase approach could be advantageously used in the synthesis of binuclear phthalocyanines, as a first experiment, prior to adopting solid phase methodology, we tried to synthesize a binuclear phthalocyanine in solution. As shown below, binuclear phthalocyanines *can* be separated chromatographically from mononuclear phthalocyanines using our unusual eluting solvent mixture
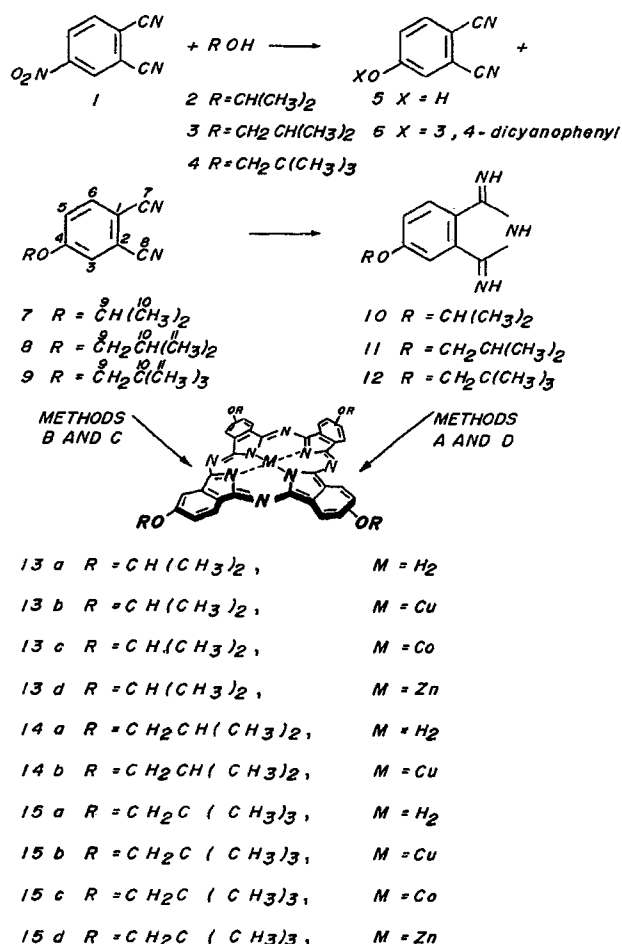
(12), and hence the more elaborate scheme using polymer supports was unnecessary.

Synthesis of mononuclear phthalocyanines, soluble in organic solvents

Treatment of 4-nitrophthalonitrile (1) with 2-propanol (2), 2-methyl-1-propanol (3), and 2,2-dimethyl-1-propanol (4) with potassium carbonate in dimethylformamide (DMF) in a useful modification (15) of published procedures (16, 17) gave in some instances at high temperatures the unwanted by-products 4-hydroxyphthalonitrile (5) (18) and bis(3,4-dicyanophenyl)-ether (6), but at room temperature (15) the desired 4-isopropoxyphthalonitrile (7) (11, 15), 4-isobutoxyphthalonitrile (8), and 4-neopentoxyphthalonitrile (9) respectively in 69 to 87% yield. Phthalonitriles 7—9 were readily converted, using gaseous ammonia and sodium methoxide in methanol (19, 20), to 5-isopropoxy-1,3-diiminoisoindoline (10), 5-isobutoxy-1,3-diiminoisoindoline (11), and 5-neopentoxy-1,3-diiminoisoindoline (12) respectively. The solvent was evaporated and compounds 10—12 were next used without further purification. We have previously reported the condensation of 10 in 2-*N,N*-dimethylaminoethanol (Method A) (19) to give the metal-free 2,9,16,23-tetraisopropoxyphthalocyanine (13a) (12), but had not described any metallated derivatives of 13a. In fact, several methods exist for the direct condensation of phthalonitriles to metallated phthalocyanines without the necessity of forming isoindolines. Thus, treatment of 7 with CuCN in DMF (Method B) (20) or with CuCl₂ and diaza-bicyclononane (DBN) in ethanol (Method C) (21) gave 2,9,16,23-tetraisopropoxyphthalocyaninato copper (13b) in 34 and 49% yield respectively (Table 1). Compound 7 was similarly converted to 2,9,16,23-tetraisopropoxyphthalocyaninato cobalt(II) (13c) and 2,9,16,23-tetraisopropoxyphthalocyaninato zinc (13d) using Methods B and C (Table 1; Scheme 1).

Isoindoline 11 was converted to the metal-free 2,9,16,23-tetraisobutoxyphthalocyanine (14a) by Method A and 14a was converted to 2,9,16,23-tetraisobutoxyphthalocyaninato copper (14b) by simple treatment of 14a with cupric acetate in toluene (Method D) (19), in this example (Table 1). Similarly, isoin-

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Scheme 1

1

2 R = CH(CH₃)₂
3 R = CH₂CH(CH₃)₂
4 R = CH₂C(CH₃)₃

$$1 \quad 2\ R=CH(CH_3)_2$$
$$3\ R=CH_2CH(CH_3)_2$$
$$4\ R=CH_2C(CH_3)_3$$

5 X = H
6 X = 3,4-dicyanophenyl

7 R = $\overset{9}{C}H\overset{10}{(}CH_3)_2$ 10 R = CH(CH₃)₂
8 R = $\overset{9}{C}H_2\overset{10}{C}H(CH_3)_2$ 11 R = CH₂CH(CH₃)₂
9 R = $\overset{9}{C}H_2\overset{10}{C}(CH_3)_3$ 12 R = CH₂C(CH₃)₃

METHODS B AND C   METHODS A AND D

13 a R = CH(CH₃)₂ ,   M = H₂
13 b R = CH(CH₃)₂ ,   M = Cu
13 c R = CH(CH₃)₂ ,   M = Co
13 d R = CH(CH₃)₂ ,   M = Zn
14 a R = CH₂CH(CH₃)₂ ,   M = H₂
14 b R = CH₂CH(CH₃)₂ ,   M = Cu
15 a R = CH₂C(CH₃)₃ ,   M = H₂
15 b R = CH₂C(CH₃)₃ ,   M = Cu
15 c R = CH₂C(CH₃)₃ ,   M = Co
15 d R = CH₂C(CH₃)₃ ,   M = Zn

SCHEME 1

doline 12 was converted to 2,9,16,23-tetraneopentoxyphthalocyanine (15a) (Method A) and subsequently to 2,9,16,23-tetraneopentoxyphthalocyaninato copper (15b) and 2,9,16,23-tetraneopentoxyphthalocyaninato cobalt(II) (15c) (Method D). Treatment of phthalonitrile 9 under the conditions of Method B using copper, cobalt, and zinc salts yielded 15b, 15c, and 2,9,16,23-tetraneopentoxyphthalocyaninato zinc (15d) in varying yields (Table 1; Scheme 1). The structures of 13a−d, 14a−b, and 15a−d were confirmed by spectroscopic and elemental analysis (see experimental section and Table 2).

A comparison of the yields of metallophthalocyanines by three different routes (Table 1) shows that a combination of Methods A and D, i.e. formation of metal-free phthalocyanines followed by metal insertion, or Method C, using DBN as a condensing agent, is superior to Method B. In fact, in our hands, organic soluble metallophthalocyanines are most conveniently prepared in the purest state, and in the highest yield, by metal insertion into metal-free phthalocyanines (Methods A and D). Direct preparation of metallophthalocyanines by Method C gives metallophthalocyanines contaminated by impurities difficult to remove by chromatographic methods.

The selection of the 4-isopropoxy group as a substituent of a phthalonitrile and hence of its isoindoline was predicated on the fact that a bulky isopropoxy group in 7 and 10 similar to the less accessible 4-tert-butylphthalonitrile (22) would inhibit aggregation processes and lead to organic solvent soluble phthalocyanines. Indeed, 13a proved to be exceedingly solu-

TABLE 1. Yields of monomeric metallophthalocyanines by different synthetic methods
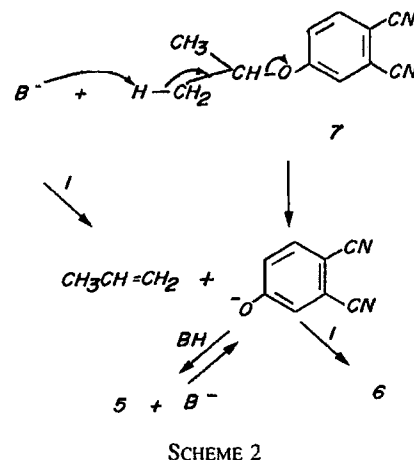
Starting material	Method[a]	Salt	Product	Yield (%)
7	A	[b]	13a	38
7	B	CuCN	13b	34
7	B	CoCl₂	13c	20
7	B	Co(CN)₂	[c]	—
7	B	Co(OAc)₂	13c	37
7	B	ZnCl₂	13d	35
7	C	CuCl₂	13b	49
7	C	CoCl₂	13c	46
7	C	Co(OAc)₂	13c	35
7	C	ZnCl₂	13d	31
9	A	[b]	15a	45
9	B	CuCN	15b	17
9	B	Co(OAc)₂	15c	29
9	B	ZnCl₂	15d	2
9	B	Zn(OAc)₂	15d	27
14a	D	Cu(OAc)₂	14b	74
15a	D	CuCl₂	15b	94[d]
15a	D	CoCl₂	15c	94[d]

[a]See text for reaction conditions and references for Methods A−D.
[b]Method A gives metal-free phthalocyanines and no salt is used.
[c]No reaction.
[d]The overall yield, which is a combination of Methods A and D, is 42%.

SCHEME 2

ble (Table 2) in organic solvents and hence was readily separable from polymer-supported phthalocyanines (11, 12) and, as shown below, separable from a binuclear phthalocyanine. Although 13a−d were prepared as pure compounds, it was noted that some deterioration occurred with age and, indeed, old samples had to be rechromatographed before their use in electrochemical studies. Since the phthalocyanine nucleus is reputed to be extremely stable to decomposition, we believed for two reasons that the isopropoxy group was responsible for this instability. Firstly, isopropyl ethers are known to readily form peroxides and, secondly, base catalyzed elimination of the isopropyl group may occur as shown in Scheme 2.

The formation of 6 in the preparation of 7 at temperatures higher than room temperature shows that the mechanistic scheme shown in Scheme 2 is at least partially operative. We have shown that pure 7 on reaction with K₂CO₃ or KNO₂ at 80°C does liberate, upon protonation, 5 without concomitant formation of 6, since no 1 is available. Some earlier studies (23) on the formation of tert-butyl aryl ethers have shown that

TABLE 2. Absorption spectra of mononuclear and binuclear phthalocyanines and their solubilities in CH_2Cl_2 at 24°C

Phthalocyanine	λ max (nm) (ε log)						Solubility (mol/L)
13a	342 (4.40)	388 (4.09)	608 (3.98)	640 (4.19)	670 (4.58)	706 (4.64)	0.78
13b	338 (4.74)	384 (4.37)	614 (4.47)	638 (4.48)	677 (4.93)		0.62
13c	328 (4.72)	386 (4.32)	608 (4.40)	,	674 (4.92)		0.84
13d	342 (4.67)	384 (4.26)	614 (4.32)		682 (4.96)		0.30
14a	343 (4.98)	390 (4.54)	610 (4.47)	642 (4.66)	670 (4.97)	706 (5.02)	0.013
14b	337 (4.76)	384 (4.40)	620 (4.59)		682 (4.89)		0.018
15a	341 (4.57)	390 (4.27)	608 (4.17)	642 (4.36)	670 (4.73)	705 (4.79)	1.10
15b	338 (4.82)	380 (4.42)	614 (4.57)		680 (5.09)		0.26
15c	335 (4.74)	390 (4.31)	620 (4.52)		680 (4.97)		0.15
15d	344 (4.91)	384 (4.57)	614 (4.60)		680 (5.18)		0.43
25		384 (4.10)	618 (4.57)		682 (4.99)		—
26a	336 (4.99)	384 (4.69)	612 (4.80)	636 (4.90)	668 (4.84)	700 (4.69)	0.0057
26b	336 (5.08)	384 (4.72)		628 (5.06)	676 (5.03)		0.00028
26c	320 (4.95)	386 (4.56)		626 (4.92)	670 (4.88)		0.00071
27a	332 (5.00)	384 (4.66)	610 (4.76)	638 (4.90)	670 (4.81)	700 (4.66)	0.35
27b	320 (4.95)	380 (4.37)		626 (4.77)	668 (4.76)		0.039

eliminative processes as described above do occur but also that elimination more likely occurs through an alternate pathway involving the initial nucleophilic addition adduct. In any case, it became apparent that the 4-isopropoxy group of 7 and 10 was not ideally suited to subsequent use as a "partner" in the synthesis of binuclear phthalocyanines. It was for these reasons that the isobutoxy derivatives 8 and 11 were prepared. The isobutoxy group is not a secondary ether and hence is less susceptible to peroxide formation, and in addition only contains one hindered β-hydrogen for participation in possible elimination reactions. It was subsequently shown, however, that the isobutoxyphthalocyanines, 14a and 14b, prepared from 11, were considerably less soluble than their isopropoxy analogs, 13a and 13b (Table 2). The 4-neopentoxy derivatives, 9 and 12, are primary hindered ethers and contain no β-hydrogens for possible elimination reactions. Most importantly, the neopentoxyphthalocyanine, 15a, derived from 12, proved to be exceedingly soluble in organic solvents (Table 2) and ultimately exhibited little decomposition with age. The formation of 9 at room temperature using the standard procedure (15) gave 9 in 86% yield in 84 h in a small scale reaction. On a large scale, the reaction was only completed after 144 h. Since 9 could not undergo β-elimination processes such as 7, an evaluation of the yield of 9 at different temperatures was undertaken and it was shown that 9 should be prepared in optimal yield in reasonable times at 60°C (Table 3). At higher temperatures, the formation of 5 by the displacement of the nitro group by carbonate or nitrite becomes important (18).

The syntheses of binuclear phthalocyanines

A straightforward route to binuclear phthalocyanines would involve a *mixed* condensation of a bisphthalonitrile or its isoindoline derivatives with a simple phthalonitrile or isoindoline in solution. Since phthalocyanines are so insoluble, the above simple approach would give insoluble, inseparable mixtures of mononuclear phthalocyanines, binuclear phthalocyanines, and by-products, as even good preparations of mononuclear phthalocyanines occur in less than 50% yield. The development (11, 12) of exceedingly soluble mononuclear phthalocyanines and particularly 15a described above indicated that even binuclear phthalocyanines may be soluble and separable

TABLE 3. Yields of 9 from 1 at different temperatures and reaction times

Temperature (°C)	Time (h)[a]	Yield (%)
22	84	86
60	18	82
70	10	76
80	5	66

[a]Starting material 1 was completely consumed after the given reaction times.
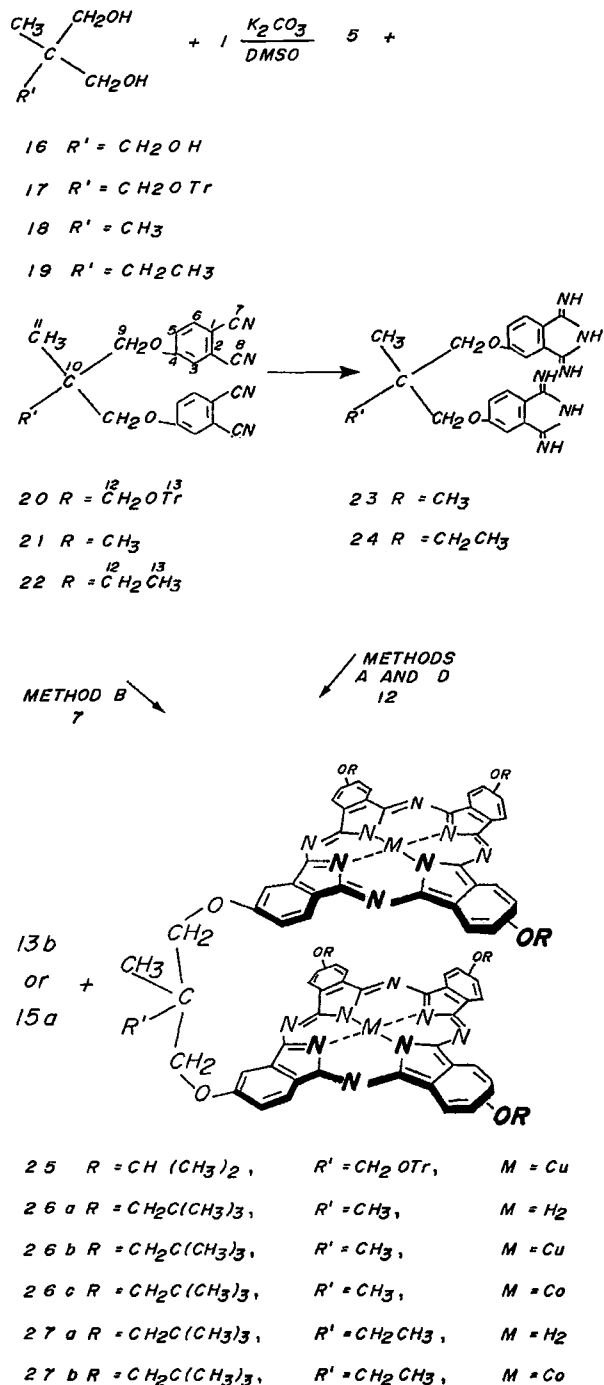
by chromatography (12).

Initially, we had been interested in preparing not only binuclear phthalocyanines but also one containing a "handle" suitable for attachment to electrodes (13), polymers (24), or micelles (25). In addition, we wished to prepare binuclear phthalocyanines, incorporating five-, four-, or three-atom covalent bridges, as these bridges seemed most likely to yield phthalocyanine dimers having electrocatalytic and photocatalytic activity. Bisphthalonitriles can be readily prepared (16) by treatment of symmetrical diols with 1. The goal of obtaining binuclear phthalocyanines incorporating a five-atom bridge thus requires a bisphthalonitrile incorporating a five-atom bridge. The symmetrical diol forming this bridge should not have hydrogen atoms available for β-elimination. Treatment of excess 2-hydroxymethyl-2-methyl-1,3-propanediol (16) with triphenylmethyl chloride (trityl chloride) in pyridine yielded upon column chromatography 68% (based on trityl chloride) of 2-methyl-2-trityloxymethyl-1,3-propanediol (17).

Symmetrical diols 17, 2,2-dimethyl-1,3-propanediol (18), and 2-ethyl-2-methyl-1,3-propanediol (19), reacted with more than two equivalents of 1 and K_2CO_3 in dimethylsulfoxide (DMSO) (16) to give 1,3-bis(3′,4′-dicyanophenoxy)-2-methyl-2-trityloxymethylpropane (20), 1,3-bis(3′,4′-dicyanophenoxy)-2,2-dimethylpropane (21), and 1,3-bis(3′,4′-dicyanophenoxy)-2-ethyl-2-methylpropane (22) respectively. Bisnitriles 21 and 22 were converted to their bisisoindolines 23 and 24 as before and used in subsequent condensations without further purification. For our first mixed condensation for the preparation of binuclear phthalocyanines we decided to try the direct route of reacting bisphthalonitrile 20 with 4-isopropoxyphthalonitrile

(7) using cuprous cyanide in DMF (Method B), as Method C was known to generate many by-products. Flash chromatography (26) using 2-methoxyethanol — toluene (5:200) as eluant removed the mononuclear copper phthalocyanine **13**b, formed by self-condensation of **7**. Further elution gave the binuclear phthalocyanine, 1,3-bis-2'-(9',16',23'-triisopropoxyphthalocyaninato copper)-2-methyl-2-trityloxymethylpropane (**25**), in 1% yield (Scheme 3). Characterization of **25** was based on elemental and spectroscopic analysis and its method of synthesis. Elemental analysis of **25**, which still contains the trityl blocking group, is more meaningful than elemental analysis of any detritylated dimer, as **25** exhibits a more considerable difference in its calculated analysis than the related monomer **13**b. Indeed, the close but not perfect analysis indicates the structure **25**, rather than a monomeric species. The mass spectrum of **25** was most informative and, after much effort using the FAB techniques (27) and using thioglycerol as solvent, a parent ion with m/z centered at 1859.5 amu was observed. A major fragment ion at 1816 ($M^+ - 43$) was indicative of loss of an isopropyl group, consistent with structure **25**. The much slower chromatographic mobility of **25** compared to **13**b further suggested **25** as the most likely structure. The infrared spectrum of **25** gives us an indication of the purity of our compounds, as by-product impurities exhibit absorptions in the nitrile or carbonyl regions of the spectra which are absent in both pure mononuclear and binuclear phthalocyanines. The ultraviolet spectrum of **25** and all mononuclear and binuclear phthalocyanines are given in Table 2 for comparison purposes, as small but significant differences are apparent between metal-free and metallophthalocyanines and between mononuclear and binuclear phthalocyanines.

Although the synthesis of the first binuclear phthalocyanine **25** was achieved using Method B and **7** as the "partner" in the condensation, the yield was very low. For this reason the formation of binuclear phthalocyanines using Method A (via diiminoisoindolines) and using 5-neopentoxy-1,3-diiminoisoindoline (**12**) as the "partner" was attempted. Heating the bis-isoindolines **23** or **24** at 150°C with a large excess of **12** in 2-N,N-dimethylaminoethanol for 24 h (Method A) under argon yielded a dark blue solution which was diluted with water giving blue coloured residues. Flash chromatography of solutions of these residues separated the mononuclear phthalocyanine **15**a from the desired binuclear phthalocyanines 1,3-bis-2'-(9',16',23'-trineopentoxyphthalocyaninoxy)-2,2-dimethylpropane (**26**a) and 1,3-bis-2'-(9',16',23'-trineopentoxyphthalocyaninoxy)-2-ethyl-2-methylpropane (**27**a) respectively. The relatively high yields of **26**a (17%) and **27**a (10%) achieved by Method A as compared to Method B for **25** (1%) more than compensated for the extra effort of making the isoindolines. Simple treatment of **26**a with anhydrous cupric acetate in toluene at 100°C for 17 h gave the binuclear phthalocyaninato dicopper derivative **26**b in 54% yield, while similar reactions of **26**a or **27**a with anhydrous cobaltous chloride gave the binuclear phthalocyaninato dicobalt(II) derivatives **26**c and **27**b in 60 and 74% yields respectively. Binuclear phthalocyanines, **26**a–c and **27**a–b, exhibited parent ions in their mass spectra using the FAB system and o-nitrophenyl octyl ether (ONPOE) as solvent. The infrared spectra of **26**a and **27**a exhibit characteristic N—H absorptions at 3300 and 1020 cm^{-1} (28), similar to metal-free mononuclear phthalocyanines **13**a, **14**a, and **15**a. The ^{1}H nmr spectra of **26**a and **27**a show a characteristic broad N—H absorption peak at approximately −6.0 ppm as do **13**a, **14**a, and **15**a at high concentrations.

Other peaks in the ^{1}H nmr spectra, however, are also very broad, which renders ^{1}H nmr spectroscopy less useful for characterization of phthalocyanines, both monomeric and dimeric. It is likely that the ^{1}H nmr signals are broad due to both aggregation effects and the fact that all the mononuclear and binuclear phthalocyanines described herein are a mixture of a large number of possible positional isomers. Even using a high field instrument and multiple scans, a dilute solution of **15**a yielded a spectrum showing broad absorptions, and hence the multiplicity of positional isomers is the likely primary cause of this effect. The ^{13}C nmr spectra (see Experimental), of **13**a,

16 R' = CH₂OH

17 R' = CH₂OTr

18 R' = CH₃

19 R' = CH₂CH₃

20 R = CH₂OTr

21 R = CH₃

22 R = CH₂CH₃

23 R = CH₃

24 R = CH₂CH₃

METHOD B
7

METHODS A AND D
12

13b or **15**a

25	R = CH(CH₃)₂,	R' = CH₂OTr,	M = Cu
26a	R = CH₂C(CH₃)₃,	R' = CH₃,	M = H₂
26b	R = CH₂C(CH₃)₃,	R' = CH₃,	M = Cu
26c	R = CH₂C(CH₃)₃,	R' = CH₃,	M = Co
27a	R = CH₂C(CH₃)₃,	R' = CH₂CH₃,	M = H₂
27b	R = CH₂C(CH₃)₃,	R' = CH₂CH₃,	M = Co

SCHEME 3

TABLE 4. ^{13}C Chemical shifts of 7−9 and 20−22

Carbon[a]	δ ppm					
	7	8	9	20	21	22
1	106.3	106.1	106.7	107.1	107.7	107.4
2	117.1	116.5	117.2	117.0	117.6	117.4
3	119.9[b]	119.2	119.5[b]	119.2[b]	119.8[b]	119.5[b]
4	161.1	161.9	162.6	161.5	162.4	162.0
5	120.3[b]	119.2	119.8[b]	119.5[b]	120.0[b]	119.7[b]
6	135.1	135.1	135.3	135.1	135.6	135.3
7	115.3[c]	115.1[c]	115.9	115.1[c]	115.7[c]	115.2[c]
8	115.7[c]	115.6[c]	115.9	115.5[c]	116.1[c]	115.7[c]
9	71.6	75.0	78.9	70.5	74.1	72.0
10	21.5[d]	27.6	31.9	40.4	36.1	38.3
11	—	18.5	26.4	17.3	21.8	18.3
12	—	—	—	63.5	—	26.6
13	—	—	—	86.4[e]	—	7.3

[a]The numbering of the carbon atoms in 7−9 and 20−22 follows that given for these structures in Schemes 1 and 2 and does not follow from the names of these compounds. All compounds were run in CDCl$_3$ except 21, which was run in CD$_2$Cl$_2$.

[b]These assignments may be interchanged.

[c]These assignments may be interchanged.

[d]This value is typical of methyl carbon atoms and correlates well with carbon 11 for other compounds in the table.

[e]This assignment is for the quaternary carbon of the trityl group. The phenyl groups absorb at 143.3, 128.4, 127.7, and 127.0, consistent with previous assignments (30).

13d, 14a, 15a, 15d, 26a, and 27a give sharp absorbancies, characteristic of the given structures. The reduced solubilities of 26a and 27a compared to 13a and 15a meant that even overnight scans of these samples on a Bruker 400-MHz nmr spectrometer could not show most of the quaternary carbon atoms. The ^{13}C nmr of 7−9 and 20−22 have been assigned using standard correlations (29) (Table 4). The absorption spectra of all mononuclear and binuclear phthalocyanines reported herein are reported in Table 2. Mononuclear metal-free and metallophthalocyanines give well-known characteristic absorption spectra (10) and the present availability of binuclear metal-free and metallophthalocyanines shows that these dimeric phthalocyanines are different from the monomeric phthalocyanines and from each other. Both mononuclear and binuclear metal-free phthalocyanines exhibit absorption maxima between 700 and 706 nm with the binuclear ones absorbing near 700 nm. Metallophthalocyanines do not give absorption maxima at this wavelength. Other differences, especially between monomers and dimers, are reflected in intensity changes which in tabular form appear minor, but in graphic form (Fig. 1) of one example of each class show that simple inspection can often identify the phthalocyanine as mononuclear or binuclear, and metal-free or containing metal.

The successful syntheses of the first characterized binuclear phthalocyanines rest largely on the preparation of monomeric phthalocyanines, which are exceedingly soluble in organic solvents, and their subsequent separation from binuclear phthalocyanines which still exhibit significant solubility in organic solvents. From Table 2 one can see that metallophthalocyanines are generally less soluble than metal-free phthalocyanines, and binuclear phthalocyanines are understandably less soluble than mononuclear phthalocyanines. Thus the difference in solubility of metal-free mononuclear phthalocyanine (15a) and a binuclear metallophthalocyanine (26c) is over three orders of magnitude, but 26c and other
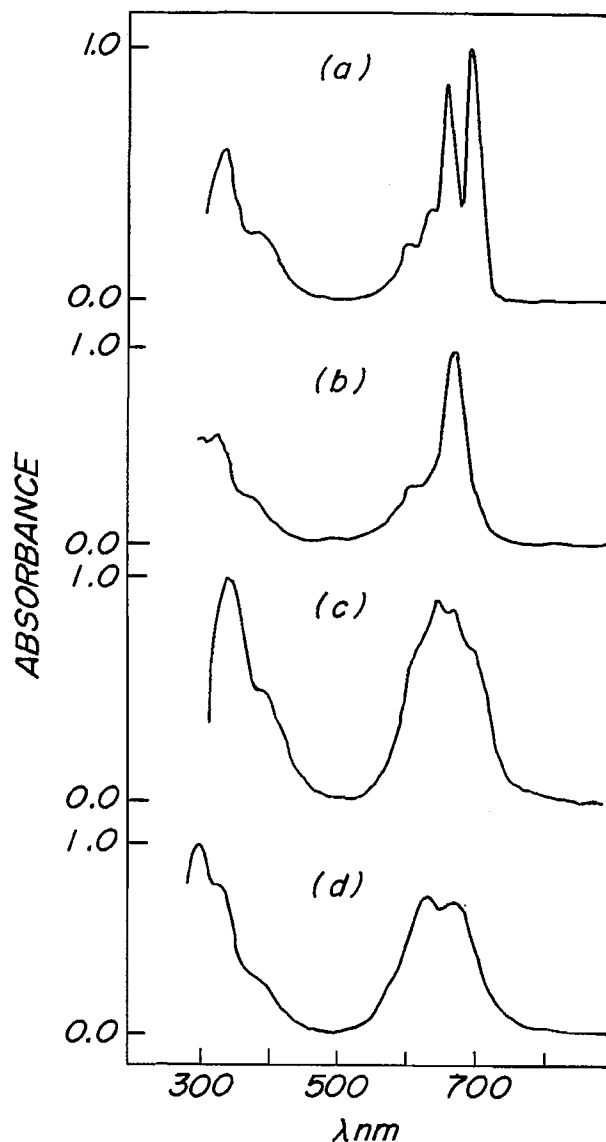

FIG. 1. The λ (nm) visible spectra in CH$_2$Cl$_2$ at room temperature of (a) a mononuclear metal-free phthalocyanine, 13a, (b) a mononuclear metallophthalocyanine, 13c, (c) a binuclear metal-free phthalocyanine, 27a, (d) a binuclear metallophthalocyanine, 27b.

phthalocyanine dimers are still sufficiently soluble to purify and characterize. A full analysis of 26a−c and 27a−b by visible spectroscopy and electrochemical methods under a variety of conditions has been undertaken and a preliminary report has appeared (31).

Experimental

Matheson high purity argon was used to maintain inert atmosphere conditions. Infrared (ir) spectra were recorded on a Pye Unicam SP1000 infrared spectrophotometer using KBr discs for solids or as neat films between NaCl discs. Nuclear magnetic resonance (nmr) spectra for protons were recorded on a Varian LM 360 spectrometer using deuterochloroform as solvent and tetramethylsilane as the internal standard. The positions of the signals are reported in δ units. (The splittings of the signals are described as singlets (s), doublets (d), triplets (t), quartets (q), or multiplets (m).) A Bruker WH250 or WH400 spectrometer was used for all ^{13}C nmr spectra and for ^{1}H nmr spectra of 13a, 13d, 14a, 15a, 15d, 26a, and 27a at 10^{-2} to 10^{-1} M.

The visible−ultraviolet spectra (uv) were recorded on a Perkin−Elmer−Hitachi 340 spectrometer. Mass spectra (ms) were recorded at 70 eV on a VG Micromass 16F mass spectrometer in the EI mode.

The FAB 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. The sample was dissolved in chloroform and a microliter of the resulting solution added to a microliter of o-nitrophenyloctylether on the probe tip. The spectra of the molecular ions of the binuclear phthalocyanines were obtained by signal averaging up to 256 scans over the appropriate mass range. The number in parentheses after the indicated ion shows the percentage of the base peak represented by that ion. Melting points (mp) were determined using a Kofler hot stage melting point apparatus and are uncorrected. Thin-layer chromatography (tlc) was performed using silica gel G as the adsorbent. All reactions were stirred with a magnetic stirrer. All solvents were freshly distilled before use. Microanalyses were performed by Guelph Chemical Laboratories Ltd., Guelph, Ont.

Bis-(3,4-dicyanophenyl)ether (6) and 4-isopropoxyphthalonitrile (7)

At room temperature

In a minor modification of Siegl's procedure (15) 4-nitrophthalonitrile (1.64 g, 9.49 mmol), isopropanol (2.0 mL, 26 mmol), and anhydrous potassium carbonate (2.94 g, 21.3 mmol) were stirred at room temperature under an argon atmosphere in 10 mL of dry DMF for 43 h. The potassium carbonate was added in three portions. The crude reaction mixture was poured into water (300 mL). The precipitate was collected by filtration, washed thoroughly with water, and dried. The crude product was purified by silica gel column chromatography using ether − petroleum ether (2:3) as the eluting solvent. It was then recrystallized from a mixture of ether−hexanes to give 1.21 g of slightly yellow crystals of 4-isopropoxyphthalonitrile (7), mp 58−59°C (lit. (11, 15) mp 56−57°C) in 69% yield.

At 50−60°C

In another experiment, 17.3 g of 4-nitrophthalonitrile (0.10 mol) reacted with 24 mL of isopropanol (0.31 mol) and 32 g of anhydrous potassium carbonate (0.23 mol) in 120 mL of dry DMF and the mixture *was heated at 50−60°C* under Ar for 93 h. Under these conditions and using an identical work-up as before, a mixture of bis(3,4-dicyanophenyl)ether (6) (15) and (7) was obtained. Compound 7 was separated from the insoluble 6 by extraction with ether. The 4-isopropoxyphthalonitrile (7) was further purified by column chromatography, followed by recrystallization as before to yield 6.10 g of (7) in 33% yield.

Further purification of 6 by recrystallization from acetonitrile gave in 44% yield 6.0 g of 6, mp 256−257°C (lit. (15) mp 254−256°C).

4-Isobutoxyphthalonitrile (8)

Treatment of 5.19 g (30 mmol) of 1 with 4.44 g (60 mmol) of isobutyl alcohol (3) in DMF for 240 h at room temperature as described above for the preparation of 7 yielded after distillation in a Kugelrohr apparatus 5.3 g of 4-isobutoxyphthalonitrile (8) in 87% yield. Thin-layer chromatography of the crude reaction mixture indicated the presence of a small amount of 4-hydroxyphthalonitrile (5) (18) but this product was not isolated. Crystallization of a small sample of 8 from ethyl acetate − petroleum ether gave colourless crystals of 8, mp 49−49.5°C; ir (cm⁻¹): 2240 (CN), 1600 (C=C), 1562 (C=C); ¹H nmr (CDCl₃) δ: 7.9−7.2 (m, 3H, aromatic), 3.9 (d, 2H, CH_2O, J = 6 Hz), 2.2 (m, 1H, CH), 1.1 (d, 6H, $(CH_3)_2C$, J = 6.0 Hz); ms, m/z: 200 (M⁺, 29), 142 (42), 144 (40), 127 (21), 57 (100), 56 (70), 55 (21), 43 (24), 41 (43), 39 (56). Anal. calcd. for $C_{12}H_{12}N_2O$: C 71.98, H 6.04, N 13.99; found: C 72.08, H 5.84, N 13.98.

4-Neopentoxyphthalonitrile (9)

A solution of 1.73 g (10 mmol) of 1, 2.30 g (26 mmol) of neopentyl alcohol, and 3.4 g (25 mmol) of potassium carbonate was stirred *at 60°C* (Table 3) as described for the preparation of 7 above. Column chromatography of the reaction product on silica using ethyl acetate − petroleum ether (1:19) gave in 82% yield 1.60 g of 4-neopentoxy-

phthalonitrile (9), mp 61.5−62°C; ir (cm⁻¹): 2230 (CN), 1590 (C=C), 1562 (C=C); ¹H nmr (CDCl₃) δ: 7.9−7.2 (m, 3H, aromatic), 3.75 (s, 2H, CH_2O), 1.05 (s, 9H, CH_3C); ms, m/z: 214 (M⁺, 9), 199 (16), 157 (2), 145 (3), 72 (7), 71 (91), 70 (14), 57 (31), 55 (22), 43 (100), 41 (11). Anal. calcd. for $C_{13}H_{14}N_2O$: C 72.87, H 6.58, N 13.07; found: C 72.89, H 6.66, N 12.89.

Thin-layer chromatography of the crude reaction product indicated the presence of a small amount of 5 (18) but this product was not isolated.

Preparation of 5-isopropoxy-1,3-diiminoisoindoline (10), 5-isobutoxy-1,3-diiminoisoindoline (11), and 5-neopentoxy-1,3-diiminoisoindoline (12)

All diiminoisoindolines were prepared as previously described (19). In a typical example 246 mg (1.15 mmol) of 9 was converted to 297 mg of 12 which was used directly in condensation reactions without further purification. Compounds 10−12 did not exhibit nitrile absorptions in their ir spectra.

Preparation of 2,9,16,23-tetraisopropoxyphthalocyanine (13a), 2,9,16,23-tetraisobutoxyphthalocyanine (14a), and 2,9,16,23-tetraneopentoxyphthalocyanine (15a) (Method A)

Compound 13a was previously prepared in our laboratory (11, 12) from 10 using the procedure of Beach et al. (19) and purified by column chromatography using ether − petroleum ether as eluant.

A solution of 11 derived from 600 mg of 8 in 2-N,N-dimethylaminoethanol underwent self-condensation as for the preparation of 13a to give 285 mg of a crude reaction product. Flash chromatography (26) of this product using 2-methoxyethanol − toluene (1:40) as eluant gave upon evaporation of the solvent a purer product, still containing a trace of fluorescent material on examination by tlc. Further purification by flash chromatography yielded upon evaporation of the solvent 163 mg of very pure 2,9,16,23-tetraisobutoxyphthalocyanine (14a) as a shiny blue solid in 27% yield; ir (cm⁻¹): 3300 (NH), 1630 (C=C), 1245, 1100, 1015 (NH), 750; ¹H nmr (CD₂Cl₂, 400 MHz) δ: 7.5−6.6 (m, 12H, aromatic), 3.7 (br s, 8H, CH_2O), 2.2 (m, 4H, CH), 1.2 (br s, 24H, CH_3), −5.8 (very br s, 2H); ¹³C nmr (CD₂Cl₂, 400 MHz) δ: 159.9 (aromatic C—O), 121.9, 121.7, 117.2, 103.6, 74.5 (CH_2—O), 28.6 ($CHCH_2$), 19.3 (CH_3); ms m/z: 804 (M⁺, 54), 803 (100), 802 (82), 746 (17). Anal. calcd. for $C_{48}H_{50}N_8O_4$: C 71.79, H 6.29, N 13.95; found: C 72.02, H 5.84, N 13.98.

Similarly, the isoindoline 12, derived from 246 mg of phthalonitrile 9, yielded on condensation a crude product. Flash chromatography using freshly distilled toluene as eluant gave upon evaporation of the solvent 112 mg of a dark blue, shining solid in 45% yield; ir (cm⁻¹): 3290 (NH), 1620 (C=C), 1240, 1100, 1060, 1015 (NH), 750; ¹H nmr (CD₂Cl₂, 250 MHz) δ: 7.6−6.0 (m, 12H, aromatic), 3.8 (s, 8H, CH_2O), 1.5 (s, 36H, CH_3), −6.5 (br, 2H, NH); ¹³C nmr (CD₂Cl₂, 250 MHz) δ: 160.6 (aromatic C—O), 122.1, 117.4, 117.2, 78.6 (CH_2—O), 78.4 (CH_2O), 32.5 (CH_3C), 27.3 (CH_3C); ms, m/z: 859 (M⁺, 100), 858 (62), 801 (2), 789 (23). Anal. calcd. for $C_{52}H_{58}N_8O_4$: C 72.70, H 6.80, N 13.04; found: C 72.78, H 6.86, N 13.00.

General procedures for the preparation of mononuclear metallophthalocyanines (Methods B and C)

Mononuclear metallophthalocyanines were prepared in varying yields (Table 1) according to the procedures of Pawlowski and Hanack (20) (Method B) and Tomoda et al. (21) (Method C) from the corresponding phthalonitriles. The metallophthalocyanines were isolated from the reaction mixture by dilution with water, filtration, and thorough washing with water, except for the case in which cuprous cyanide was used as the salt, in which the reaction mixture was treated with aqueous ammonia prior to washing with water. The metallophthalocyanines were purified by flash chromatography (26) using 2-methoxyethanol − toluene 1:40 as the eluting solvent.

2,9,16,23-Tetraisopropoxyphthalocyaninatocopper (13b)

In a typical procedure (Method B) (20), 0.21 g (1.15 mmol) of 4-isopropoxyphthalonitrile (7) reacted with 0.15 g (1.66 mmol) of cuprous cyanide in 2 mL of DMF at 145°C for 20 h to give, after the standard work-up described above, 0.080 g of 2,9,16,23-tetraiso-

propoxyphthalocyaninatocopper (**13***b*) in 34% yield as a dark blue solid; ir (cm⁻¹): 1610 (C=C), 1245, 1100, 1055, 750; ms, m/z: 809 (100), 808 (M⁺, 55), 807 (67), 765 (36), 724 (16). *Anal*. calcd. for $C_{44}H_{40}N_8O_4Cu$: C 65.37, H 4.99, N 13.86, Cu 7.86; found: C 65.00, H 5.24, N 13.53, Cu 7.47.

In a typical procedure using Method C (21), 0.38 g (2.0 mmol) of **7** reacted with 0.14 g (1.0 mmol) of cupric chloride and 0.62 g (5 mmol) of diazabicyclononane (DBN) in 10 mL of absolute alcohol at reflux temperatures for 24 h to give, after the standard work-up, 0.20 g of **13***b* in 49% yield. Although Method C gave **13***b* in higher yields than Method B, repetitive flash chromatography of the reaction product was necessary to remove some fluorescent impurities and hence, in general, Method B or Method D (see below) is preferred.

2,9,16,23-Tetraisopropoxyphthalocyaninatocobalt(II) (13c)

Using Methods B and C, **7** was readily converted (Table 1) into 2,9,16,23-tetraisopropoxyphthalocyaninatocobalt(II) (**13***c*), isolated as a shining dark blue solid; ir (cm⁻¹): 1615 (C=C), 1245, 1100, 1060, 755; ms, m/z: 804 (M⁺, 100), 803 (49), 762 (19). *Anal*. calcd. for $C_{44}H_{40}N_8O_4Co$: C 65.75, H 5.02, N 13.94, Co 7.33; found: C 65.73, H 4.99, N 13.63, Co 7.49.

2,9,16,23-Tetraisopropoxyphthalocyaninatozinc (13d)

Using methods B and C, **7** was converted (Table 1) into 2,9,16,23-tetraisopropoxyphthalocyaninatozinc (**13***d*), isolated as a shining, dark blue solid; ir (cm⁻¹): 1610 (C=C), 1240, 1100, 1050, 750; ¹³C nmr (CD₂Cl₂, 400 MHz) δ: 159.3 (aromatic C—O), 125.4, 121.7, 109.4, 71.5 (CH_2—O), 70.6 (CH_2—O), 22.7 (CH_3), 21.8 (CH_3); ms, m/z: 813 (64), 812 (79), 811 (96), 810 (M⁺, 95), 809 (100), 808 (70), 767 (31). *Anal*. calcd. for $C_{44}H_{40}N_8O_4Zn$: C 65.23, H 4.98, N 13.83, Zn 8.07; found: C 65.41, H 5.00, N 13.76, Zn 7.76.

Metal insertion reactions on metal-free phthalocyanines. 2,9,16,23-Tetraisobutoxyphthalocyaninatocopper (14b) (Method D in toluene)

To a solution of 100 mg (0.12 mmol) of 2,9,16,23-tetraisobutoxyphthalocyanine (**14***a*) in 10 mL of toluene was added 150 mg (0.83 mmol) of cupric acetate. The solution was stirred at 100°C under an argon atmosphere for 3 h. The crude reaction mixture was applied to 3 tlc preparative plates, and eluted 3 times with 2-methoxyethanol — toluene (1:100) to give a dark green band which was extracted with toluene in a Soxhlet extractor. Further purification by flash chromatography using 2-methoxyethanol — toluene (1:20) gave in 74% yield 80 mg of 2,9,16,23-tetraisobutoxyphthalocyaninatocopper (**14***b*) as a dark blue, shining solid; ir (cm⁻¹): 1620 (C=C), 1250, 1105, 1065, 755; ms, m/z: 867 (28), 866 (M⁺, 56), 865 (71), 864 (100), 863 (59), 808 (25). *Anal*. calcd. for $C_{48}H_{48}N_8O_4Cu$: C 66.53, H 5.60, N 12.77, Cu 7.02; found: C 66.68, H 5.61, N 12.96, Cu 7.35.

2,9,16,23-Tetraneopentoxyphthalocyaninatocopper (15b) and 2,9,16,23-tetraneopentoxyphthalocyaninatocobalt(II) (15c) (Method D, in DMF and 2-N,N-dimethylaminoethanol)

To a solution of 41 mg (0.048 mmol) of **15***a* in 3 mL of a 1:2 mixture of dry DMF and 2-N,N-dimethylaminoethanol was added 10 mg (0.074 mmol) of anhydrous cupric chloride. The mixture was heated for 1 h under an argon atmosphere using an oil bath heated to 110°C. The mixture was cooled to room temperature and directly subjected to flash chromatography using freshly distilled toluene as the eluting solvent to give in 94% yield (Table 1) 41 mg of 2,9,16,23-tetraneopentoxyphthalocyaninatocopper (**15***b*) as a dark blue, shining solid; ir (cm⁻¹): 1615 (C=C), 1240, 1100, 1060, 745; ms, m/z: 922 (78), 921 (M⁺, 81), 920 (100), 864 (4), 850 (9). *Anal*. calcd. for $C_{52}H_{56}N_8O_4Cu$: C 67.84, H 6.13, N 12.17, Cu 6.90; found: C 68.10, H 6.24, N 11.89, Cu 6.97.

Similarly, 33 mg of **15***a* gave in 94% yield (Table 1) 33 mg of 2,9,16,23-tetraneopentoxyphthalocyaninocobalt(II) (**15***c*) as a dark blue, shining solid; ir (cm⁻¹): 1615 (C=C), 1240, 1100, 1065, 750; ms, m/z: 916 (M⁺, 100), 915 (47), 859 (7), 846 (19). *Anal*. calcd. for $C_{52}H_{56}N_8O_4Co$: C 68.18, H 6.16, N 12.23, Co 6.43; found: C 68.22, H 6.14, N 12.07, Co 6.94.

Compounds **15***b* and **15***c* were also prepared directly from **9** by the methods of Pawlowski and Hanack (20) (Method B, Table 1).

2,9,16,23-tetraneopentoxypthalocyaninatozinc (15d)

Using a modification of the procedure of Pawloski and Hanack (20) (Method B), 394 mg (1.84 mmol) of 4-neopentoxyphthalonitrile (**9**) was suspended in 2 mL of dry DMF. Zinc acetate (1.04 g, 5.66 mmol) was added and the mixture heated using an oil bath at 155°C under argon. The clear reaction mixture turned yellow after 1 h and dark green after an additional 1 h. After heating for 20 h at 155°C, the mixture was cooled to room temperature, diluted with water, filtered, and washed thoroughly with water. The crude product was purified by flash chromatography using petroleum ether − ether (6:1) as the eluting solvent to give in 27% yield (Table 1) 114 mg of 2,9,16,23-tetraneopentoxyphthalocyaninatozinc (**15***d*) as a dark blue, shining solid; ir (cm⁻¹): 1610 (C=C), 1240, 1100, 1060, 750; ¹H nmr (CD₂Cl₂, 250 MHz) δ: 7.7−6.1 (m, 12H, aromatic), 3.5 (s, 8H, CH_2O), 1.3 (s, 36H, CH_3); ¹³C nmr (CD₂Cl₂, 250 MHz) δ: 160.1 (aromatic C—O), 149.5, 121.7, 121.3, 116.9, 116.6, 104.2, 103.9, 78.2 (CH_2O), 78.1 (CH_2O), 32.2 (CH_3C), 27.1 (CH_3C), 26.8 (CH_3C), 26.5 (CH_3C); ms, m/z: 925 (52), 924 (84), 923 (91), 922 (M⁺, 97), 921 (100), 868 (2), 853 (40). *Anal*. calcd. for $C_{52}H_{56}N_8O_4Zn$: C 67.71, H 6.12, N 12.15, Zn 7.07; found: C 67.80, H 6.39, N 11.85, Zn 6.94.

2-Methyl-2-trityloxymethyl-1,3-propanediol (17)

To a solution of 1,1,1-tris(hydroxymethyl)ethane (**16**) (6.48 g, 54.00 mmol) in 15 mL of dry pyridine, triphenylmethyl chloride (2.60 g, 9.32 mmol) was added and the mixture was stirred for 22 h at room temperature under exclusion of moisture (CaCl₂ drying tube). The mixture was then poured into 180 mL of ice-water and extracted 4 times with ether. The combined ether extracts were washed six times with water, dried over anhydrous MgSO₄, and evaporated to give a viscous oil which was dried under high vacuum for 4 h. The crude product was purified by column chromatography on silica gel using a mixture of chloroform−hexane (3:1) as the eluting solvent. Evaporation of the solvent yielded a product which was recrystallized from a mixture of ether−hexane to give in 68% yield 2.18 g of white crystals, mp 127−128°C; ir (cm⁻¹): 3360 (OH), 1600 (C=C), 1500, 1495, 1050, 770, 710, 705; ¹H nmr (CDCl₃, 60 MHz) δ: 7.6−7.2 (m, 15H, aromatic), 3.65 (d, 4H, CH_2O, J = 6 Hz), 3.2 (s, 2H, CH_2O), 2.4 (t, 2H, OH, J = 6 Hz), 0.8 (s, 3H, CH_3); ¹³C nmr (CDCl₃, 400 MHz) δ: 143.7 (aromatic C-1'), 128.6 and 127.9 (aromatic C-2', C-6', C-3', C-5'), 127.1 (aromatic C-4'), 86.7 (PhC), 67.8 (CH_2OC), 67.0 (CH_2OH), 41.1 (CCH₂), 17.3 (CH_3); ms, m/z: 362 (M⁺, 3), 285 (20), 259 (50), 239 (100), 183 (80), 105 (75), 77 (23). *Anal*. calcd. for $C_{24}H_{26}O_3$: C 79.53, H 7.23; found: C 79.58, H 7.19.

1,3-Bis(3',4'-dicyanophenoxy)-2-methyl-2-trityloxymethylpropane (20) 1,3-bis(3',4'-dicyanophenoxy)-2,2-dimethylpropane (21), and 1,3-bis(3',4'-dicyanophenyl)-2-ethyl-2-methylpropane (22)

A solution of 1.09 g (3.01 mmol) of **17**, 1.07 g (6.18 mmol) of **1**, and 1.75 g (12.68 mmol) of anhydrous potassium carbonate was heated at 65°C in 7 mL of dry DMSO by the method of Keller *et al*. (16). The reaction mixture was filtered and washed with methylene chloride (CH₂Cl₂). The filtrate was diluted with CH₂Cl₂ and washed thoroughly 6 times with water and finally with saturated sodium chloride. After drying over anhydrous magnesium sulfate (MgSO₄), the solvent was evaporated to give 1.77 g of a light brown solid. The crude product was purified by flash chromatography using chloroform−hexane (3:1) as the eluting solvent. Evaporation of the solvent yielded an oil which was dissolved in warm methanol and rapidly cooled to −35°C (but not lower) to give in 56% yield 1.02 g of 1,3-bis(3',4'-dicyanophenyl)-2-methyl-2-trityloxymethylpropane (**20**) as light yellow crystals, mp 89−92°C; ir (cm⁻¹): 2240 (CN), 1600 (C=C), 1495, 1255, 1090, 1030, 710, 700; ¹H nmr (CDCl₃, 60 MHz) δ: 7.80−7.05 (m, 21H, aromatic), 4.03 (s, 4H, CH_2O), 3.30 (s, 2H, CH_2O), 1.30 (s, 3H, CH_3); ms, m/z: 614 (M⁺, 18), 537 (20), 283 (10), 243 (65), 240 (100), 183 (48), 144 (19), 105 (58). *Anal*. calcd. for $C_{40}H_{30}N_4O_3$: C 78.16, H 4.92, N 9.11; found: C 78.18, H 4.72, N 8.92.

Similarly, a solution of 1.04 g (10.0 mmol) of 2,2-dimethyl-1,3-propanediol (18), 3.81 g (22 mmol) of 1, and 6.7 g (48.6 mmol) of anhydrous K_2CO_3 in 10 mL of dry DMSO gave a crude reaction product. The reaction mixture was filtered and washed with ethyl acetate. The filtrate was diluted with ethyl acetate, thoroughly washed with water until the aqueous layer was clear, and finally washed with a saturated sodium chloride solution. After drying over anhydrous $MgSO_4$, the solvent was evaporated to give a dark brown solid. The crude product was purified by column chromatography on silica gel using benzene—acetonitrile (9:1) as the eluting solvent. Evaporation of the solvent and recrystallization of the residue from acetonitrile—water gave 1.36 g (38%) of 1,3-bis(3',4'-dicyanophenoxy)-2,2-dimethylpropane (21) as creamy crystals, mp 168–169°C; ir (cm^{-1}): 2240 (CN), 1600 (C=C), 1260, 1100, 1040, 845; ^1H nmr (acetone-d_6, 60 MHz) δ: 8.10–7.42 (m, 6H, aromatic), 4.27 (s, 4H, CH_2OC), 1.27 (s, 6H, CH_3); ms, m/z: 356 (M^+, 11), 213 (30), 171 (88), 127 (43). Anal. calcd. for $C_{21}H_{16}N_4O_2$: C 70.78, H 4.52, N 15.72; found: C 70.74, H 4.37, N 15.43.

In a manner similar to that described above for the preparation of 21, 1.60 g of 2-ethyl-2-methyl-1,3-propanediol (19) yielded a crude reaction product. Thin-layer chromatography of this product using benzene—acetonitrile (9:1) as eluant exhibited the presence of a minor amount of 4-hydroxyphthalonitrile (5). Thus, the ethyl acetate filtrate was washed several times with water, followed by 0.5 M cold NaOH, water, and finally saturated NaCl solution. The ethyl acetate solution yielded upon the normal work-up a dark brown solid. The aqueous layer was acidified with dilute HCl and the organic material was extracted into ethyl acetate. The ethyl acetate was dried over anhydrous $MgSO_4$, filtered, and evaporated to give 560 mg of 5 (18) which was not further purified. Purification of the dark brown solid, obtained from the original ethyl acetate extract above, yielded, upon recrystallization from ethyl acetate — hexanes, 1.84 g (37%) of 1,3-bis-(3',4'-dicyanophenoxy)-2-ethyl-2-methylpropane (22) as creamy crystals, mp 157–158°C; ir (cm^{-1}): 2240 (CN), 1600 (C=C), 1260, 1095, 1025, 845; ^1H nmr (CDCl$_3$, 60 MHz) δ: 7.87–7.18 (m, 6H, aromatic), 4.03 (s, 4H, CH_2O), 1.62 (q, 2H, CH_2C, J = 7 Hz), 1.18 (s, 3H, CH_3C), 1.10 (t, 3H, CH_3CH_2, J = 7 Hz); ms, m/z: 370 (M^+, 23), 227 (46), 185 (60), 171 (65), 127 (52). Anal. calcd. for $C_{22}H_{18}N_4O_2$: C 71.34, H 4.90, N 15.12; found: C 71.30, H 5.03, N 15.09.

Preparation of the bis-1,3-diiminoisoindolines 23 and 24

Compounds 23 and 24 were prepared from 21 and 22 respectively as described above for 10–12 with one minor exception. As 21 and 22 were only slightly soluble in methanol at room temperature, these compounds were dissolved in a solution of sodium methoxide in methanol at 65°C and ammonia was bubbled into this solution for 1 h at 65°C and for 3 h under reflux conditions.

1,3-Bis-2'-(9',16',23'-triisopropoxyphthalocyaninoxycopper)-2-methyl-2-trityloxymethylpropane (25)

A mixture of 0.14 g (0.23 mmol) of 20, 1.0 g (5.4 mmol) of 7, and 1.54 g (17.23 mmol) of cuprous cyanide was heated at 130°C (oil bath) in 7.5 mL of dry DMF for 20 h under argon atmosphere (Method B) (20). After dilution with ammonia, the product was filtered and washed with water. The dark blue-green residue was dissolved in toluene and chromatographed under argon using the flash chromatography technique. Elution with 2-methoxyethanol — toluene (1:40) gave, upon solvent evaporation, 340 mg of 2,9,16,23-tetraisopropoxyphthalocyaninatocopper (13b) in 31% yield. Elution with 2-methoxyethanol — toluene (1:4) gave a slightly impure product. Thin-layer chromatography of this product exhibited a major blue spot and slightly faster moving green impurity (2-methoxyethanol — toluene, 1:4 as eluant). Further purification by flash chromatography using a small diameter column (1 cm) gave in 1% yield 6 mg of the pure dimer, 1,3-bis-2'-(9',16',23'-triisopropoxyphthalocyaninatocopper)-2-methyl-2-trityloxymethylpropane (25) as a dark blue, shining solid; ir $(cm^{-1}$: 1615 (C=C), 1250, 1120, 1105, 1060, 755; ms, m/z: 1859.5 (M^+), 1816 ($M^+ - 43$). Anal. calcd. for

$C_{106}H_{90}N_{16}O_9Cu_2$: C 68.48, H 4.88, N 12.05; found: C 67.85, H 5.34, N 12.53.

1,3-Bis-2'-(9',16',23'-trineopentoxyphthalocyaninoxy)-2,2-dimethyl-propane (26a) and 1,3-bis-2'-(9',16',23'-trineopentoxyphthalo-cyaninoxy)-2-ethyl-2-methylpropane (27a)

The two crude diiminoisoindolines 12 and 23 obtained from 4.2 g (19.6 mmol) of 4-neopentoxyphthalonitrile (9) and 249 mg (0.7 mmol) of 1,3-bis-(3',4'-dicyanophenoxy)-2,2-dimethylpropane (21), respectively, were heated at 150°C (oil bath) in 30 mL of 2-N,N-dimethylaminoethanol for 23 h under an argon atmosphere. The mixture gradually changed colour from yellow to dark blue. After cooling to room temperature, the mixture was diluted with water and the blue coloured residue was filtered and washed thoroughly with water until the filtrate was colourless. The crude product was purified in two separate batches by flash chromatography using a 5 cm wide column packed with silica gel 9 cm high. The dark blue-green product was preadsorbed on silica and eluted with 1500 mL of freshly distilled toluene to give 1.92 g of the monomeric 2,9,16,23-tetraneopentoxyphthalocyanine (15a) in 46% yield. Further elution with 2-methoxy-ethanol — toluene in ratios of 1:40 and 1:10 yielded, after solvent evaporation, 340 mg of a purified product, containing traces of monomer 15a and some green material (fluorescent under uv) which moved closely behind the desired product when examined by tlc (2-methoxyethanol — toluene, 1:40 as eluting solvent). Flash chromatography of this purified material on a smaller column 3 cm wide removed, on elution with toluene and 2-methoxyethanol — toluene (1:100), all traces of monomer 15a. Further elution with 2-methoxy-ethanol — toluene (1:20) yielded some fractions of a very pure, dark blue product. Other fractions were still contaminated with the green material. Purification of these fractions was achieved using preparative tlc and 2-methoxyethanol — toluene (1:20) as eluting solvent. Finally, the product was purified by flash chromatography as above to give in 17% yield 195 mg of 1,3-bis-2'-(9',16',23'-trineopentoxy-phthalocyaninoxy)-2,2-dimethylpropane (26a) as a very pure, dark blue, shining solid; ir (cm^{-1}): 3300 (NH), 1615 (C=C), 1240, 1100, 1055, 1020 (NH), 750; ^1H nmr (CD$_2$Cl$_2$, 400 MHz) δ: 8.21–7.12 (br), 4.05–3.65 (br), 1.42 (br), −6.12 (br); ^{13}C nmr (CD$_2$Cl$_2$, 400 MHz) δ: 32.35 (CH_3C), 27.20 (CH_3C); ms, m/z: 1645 (100), 1644 (M^+, 84). Anal. calcd. For $C_{99}H_{104}N_{16}O_8$: C 72.24, H 6.37, N 13.61; found: C 72.47, H 6.27, N 13.49.

Similarly, the two crude isoindolines 12 and 24 obtained from 5.6 g (26.2 mmol) of 9 and 0.4 g (1.08 mmol) of 22, respectively, yielded 1.72 g of 15a in 31% yield and 184 mg in 10% yield of 1,3-bis-2'-(9',16',23'-trineopentoxyphthalocyaninoxy)-2-ethyl-2-methyl-propane (27a) as a dark blue, shining solid; ir (cm^{-1}): 3310 (NH), 1618 (C=C), 1240, 1100, 1058, 1020 (NH), 750; ^1H nmr (CDCl$_3$, 400 MHz) δ: 9.4–6.8 (br), 4.2–3.6 (br), 1.8–0.8 (br), −5.8 − (−6.4) (br); ^{13}C nmr (CD$_2$Cl$_2$, 400 MHz) δ: 78.6 (CH_2O), 32.4 (CCH_3), 30.1 (CCH_2), 27.2 (CH_3C), 26.6 (CCH_2CH_3); ms, m/z: 1662 (100), 1660 (M^+, 41), 1658 (30). Anal. calcd. for $C_{100}H_{106}N_{16}O_8$: C 72.35, H 6.44, N 13.50; found: C 72.51, H 6.77, N 13.56.

1,3-Bis-2'-(9',16',23'-trineopentoxyphthalocyaninoxycopper)-2,2-dimethylpropane (26b), 1,3-bis-2'-(9',16',23'-trineopentoxy-phthalocyaninoxycobalt II)-2,2-dimethylpropane (26c), and 1,3-bis-2'-(9',16',23'-trineopentoxyphthalocyaninoxycobalt II)-2-ethyl-2-methylpropane (27b)

A mixture of 50 mg (0.03 mmol) of 26a, 23 mg (0.13 mmol) of anhydrous cupric acetate, and 10 mL of freshly distilled toluene was heated at 100°C for 17 h under an argon atmosphere. The solution was cooled and purified by flash chromatography (26) by direct application of the crude reaction product to the column. Elution with 2-methoxyethanol — toluene (7:200) gave, after solvent evaporation, 29 mg (54% yield) of a dark blue, shining product which was washed with anhydrous ether to remove very minor fluorescent impurities (detected by tlc) leaving 28 mg of very pure 1,3-bis-2'-(9,16,23-tri-neopentoxyphthalocyaninoxycopper)-2,2-dimethylpropane (26b); ir

(cm^{-1}): 1615 (C=C), 1240, 1100, 1060, 750; ms, m/z: 1772, 1771, 1770, 1769, 1768 (M$^+$), 1767. *Anal.* calcd. for C$_{99}$H$_{100}$N$_{16}$O$_8$Cu$_2$: C 67.22, H 5.70, N 12.67, Cu 7.18; found: C 67.41, H 5.52, N 12.40, Cu 6.83.

Similarly, 50 mg (0.03 mmol) of **26a** and 105 mg (0.81 mmol) of anhydrous cobaltic chloride in 15 mL of a 1:2 mixture of 2-methoxyethanol − toluene was heated at 100°C for 20 h to give, after purification as above, 32 mg (60% yield) of 1,3-bis-2′-(9′,16′,23′-trineopentoxyphthalocyaninoxycobaltII)-2,2-dimethylpropane (**26c**) as a dark blue, shining solid: ir (cm^{-1}): 1615 (C=C), 1240, 1100, 1068, 755; ms, m/z: 1761 (61), 1760 (M$^+$, 100), 1759. *Anal.* calcd. for C$_{99}$H$_{100}$N$_{16}$O$_8$Co$_2$: C 67.57, H 5.73, N 12.73, Co 6.70; found: C 67.92, H 5.88, N 12.84, Co 6.25.

Similarly, 70 mg (0.04 mmol) of **27a** and 57 mg (0.44 mmol) of anhydrous cobaltic chloride in 10 mL of a 3:7 mixture of 2-methoxyethanol − toluene were heated at 110°C for 24 h under an argon atmosphere. Purification as above gave 55 mg (74% yield) of pure 1,3-bis-2′-(9′,16′,23′-trineopentoxyphthalocyaninatocobaltII)-2-ethyl-2-methylpropane (**27b**) as a dark blue, shining solid; ir (cm^{-1}): 1620 (C=C), 1245, 1100, 1068, 758; ms, m/z: 1774 (M$^+$, 100). *Anal.* calcd. for C$_{100}$H$_{102}$N$_{16}$O$_8$Co$_2$: C 67.71, H 5.80, N 12.63, Co 6.64; found: C 68.14, H 6.21, N 12.61, Co 6.64.

Acknowledgements

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