

The use of bisphthalonitriles in the synthesis of side-strapped 1,11,15,25-tetrasubstituted phthalocyanines

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Abstract: Nucleophilic aromatic substitution reactions of 3-nitrophthalonitrile yield 3-hydroxyphthalonitrile and 3-neopentoxyphthalonitrile, the latter of which condensed to 1,8,15,22-tetraneopentoxyphthalocyanine as a mixture of isomers. Bisphthalonitriles such as 1,3-bis(2',3'-dicyanophenoxy)-2,2-dipentylpropane, 1,3-bis(2',3'-dicyanophenoxy)-2,2-diethylpropane, 1,3-bis(2',3'-dicyanophenoxy)-2,2-dioctylpropane, and 1,3-bis(2',3'-dicyanophenoxy)-2-methyl-2-trityloxymethylpropane all gave bis-crown-like 1,11,15,25-tetrasubstituted phthalocyanines as pure compounds when treated with lithium octoxide in 1-octanol at 196°C. A host of nine other bisphthalonitriles including 1,5-bis(2',3'-dicyanophenoxy)-3-oxapentane, 1,1-bis(2',3'-dicyanophenoxy)methylcyclohexane, 1,2-bis(2',3'-dicyanophenoxy)methylbenzene, and 2,5-bis(2',3'-dicyanophenoxy)methylfuran did not dimerize to mononuclear phthalocyanines. The "gem dimethyl" effect was suggested as a reason for the successful macrocyclizations.

Key words: nucleophilic aromatic substitution, phthalonitriles, bisphthalonitriles, 1,11,15,25-tetrasubstituted phthalocyanines.

Résumé : Les réactions de substitutions aromatiques nucléophiles du 3-nitrophthalonitrile conduisent au 3-hydroxyphthalonitrile et au 3-néopentoxyphthalonitrile; ce dernier se condense pour conduire à la 1,8,15,22-tétranéopentoxyphthalocyanine sous la forme d'un mélange d'isomères. Lorsqu'on soumet les bisphthalonitriles, tels que les 1,3-bis(2',3'-dicyanophénoxy)-2,2-dipentylpropane, 1,3-bis(2',3'-dicyanophénoxy)-2,2-diéthylpropane, 1,3-bis(2',3'-dicyanophénoxy)-2,2-dioctylpropane et 1,3-bis(2',3'-dicyanophénoxy)-2-méthyl-2-trityloxyméthylpropane, à un traitement par de l'octylate de lithium en présence d'octan-1-ol à 196°C on obtient toujours des phthalocyanines 1,11,15,25-tétrasubstituées à l'état pur qui ressemblent à des couronnes doubles. Neuf autres bisnaphthonitriles, y compris les 1,5-bis(2',3'-dicyanophénoxy)-3-oxapentane, 1,1-bis(2',3'-dicyanophénoxy)méthylcyclohexane, 1,2-bis(2',3'-dicyanophénoxy)méthylbenzène et 2,5-bis(2',3'-dicyanophénoxy)méthylfuran, ne se dimérisent pas en phthalocyanines mononucléaires. L'effet «gem-diméthyle» a été suggéré pour expliquer le succès des macrocyclisations qui ont réussi.

Mots clés : substitution aromatique nucléophile, phthalonitriles, bisphthalonitriles, phthalocyanines 1,11,15,15-tétrasubstituées.

[Traduit par la rédaction]

Introduction

The synthesis of pure isomers of tetrasubstituted phthalocyanines (Pc) having one substituent in each of the benzene rings remains a difficult problem (1). Single isomers of 2,9,16,23-(2), 2,9,17,24-(3), and 1,8,15,22-tetrasubstituted phthalocyanines (4), and a 1,2-naphthalocyanine (5) have been prepared capitalizing on reactive substrates (2) or electronic (3) or steric constraints (4, 5) but methods towards the synthesis of pure 1,11,15,25-tetrasubstituted phthalocyanines have been only briefly reported by us in a preliminary communication (6). Recently, some specific pure Pc isomers have been separated by chromatography (7). We decided upon a "constrained" approach towards the synthesis of phthalocyanines having substituents in the 1,11,15,25 positions. If we could dimerize bisphthalonitriles with appropriate bridging groups, then 1,11,15,25-tetrasubstituted phthalocyanines containing bridg-

ing substituents (side straps) in the 1,25 and 11,15 positions would be obtained. The difficulty in this approach is the fact that polymerization would compete with dimerization. After exploring many different conditions we found that that condensation of bisphthalonitriles under high dilution at high temperatures for short reaction times led in some cases to the desired phthalocyanines as shown below.

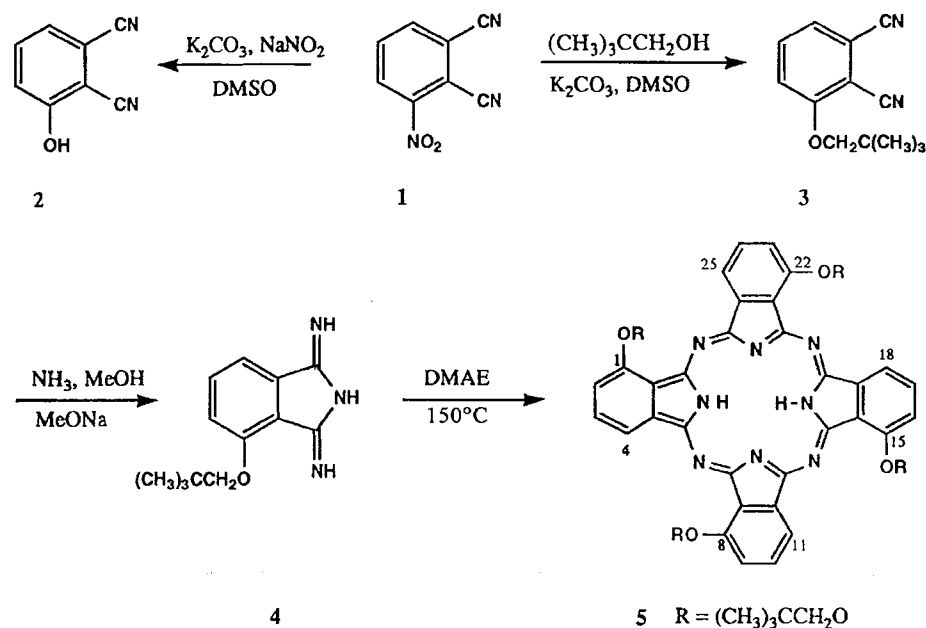
Results and discussion

Nucleophilic aromatic substitution reactions on 3-nitrophthalonitrile (1) (9) are not all that common (4, 8, 9) and hence we decided to examine some simple reactions of 1. Thus treatment of 1 with K_2CO_3 and $NaNO_2$ in DMSO at reflux for 0.5 h, as for the preparation of 4-hydroxyphthalonitrile (10), led to 3-hydroxyphthalonitrile (2) in 43% yield. Similarly, treatment of 1 with neopentanol (2,2-dimethyl-1-propanol) and K_2CO_3 in DMSO at room temperature for 6 days gave 3-neopentoxyphthalonitrile in 63% yield. The long reaction times were necessary to drive the reaction to completion probably due to steric hindrance of the substitution at the 3-position (4, 8) and the bulky alcohol used. Conversion of 3 to its diiminoisoindoline 4 proceeded normally (11, 12). Condensation of 4 at 150°C in 2-N,N-dimethylaminoethanol (DMAE) (11, 12)

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Scheme 1.



gave 1,8,15,22-tetraneopentoxyphthalocyanine (5) in 16% yield as a mixture with its 1,8,15,25, 1,8,18,25, and 1,11,15,25 isomers (Scheme 1).

Having established that phthalocyanines containing bulky substituents at positions adjacent to the macrocyclic core are readily prepared, we directed our attention towards the preparation of bisphthalonitriles bridged at the 3-position, for eventual dimerization to 1,11,15,25-tetrasubstituted phthalocyanines. Earlier, we had suggested (12) that β -hydrogens on substituents could lead to β -elimination reactions under the basic conditions of Pc formation and hence we concentrated our attention on bridging groups containing no hydrogens at the β -position, particularly β,β -dialkyl groups. Thus, treatment of **1** with a series of β,β -disubstituted-1,3-propanediols, such as the known 2-methyl-2-trityloxymethyl-1,3-propanediol (6) (12), the commercially available 2,2-diethyl-1,3-propanediol (7), 2,2-dipentyl-1,3-propanediol (8), and 2,2-dioctyl-1,3-propanediol (9), and K₂CO₃ in dimethyl sulfoxide (DMSO) at 20°C² while evacuated (4, 6) gave the bisphthalonitriles **10–13** in 43–94% yields. Diols **8** and **9** were prepared by lithium aluminum hydride reduction of diethyl 2,2-dipentylmalonate (13) and diethyl 2,2-dioctylmalonate (14), respectively. Dimerization of **10–13** under high-dilution conditions with lithium octoxide in 1-octanol at 196°C for 10 min gave the 1,25:11,15-bis(side-strapped) phthalocyanines **14–17** in 7–21% yields. Pcs **14**, **16**, and **17** were readily metallated to their phthalocyaninato zinc(II) compounds **18–20** in 90% yield by heating with zinc acetate in a 1:1 mixture of pyridine and *N,N*-

dimethylformamide for 20 h at reflux conditions (Scheme 2). Attempts at cleavage of the side-strapped Pcs **14**³ and **19** as examples, using BBr₃ (15, 16) as previously described for 2,9,16,23-tetraneopentoxyphthalocyanine (17), simply gave recovered starting materials, while cleavage with AlI₃ (18) gave decomposition of the phthalocyanine macrocycle.

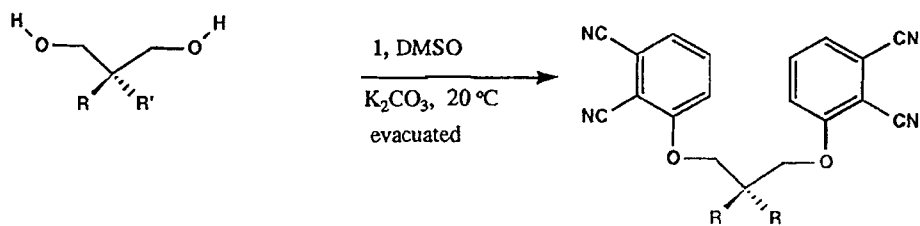
Phthalocyanines **14** and **18** existed as an unequal mixture of *cis* and *trans* isomers as shown by NMR spectroscopy while Pc **15** was too insoluble for useful studies. Indeed, the insolubility of **15** and the attendant difficulties of purification meant that satisfactory analysis could not be obtained for this compound, although we feel that confirmation of structure is on firm ground with a good HRMS (see Experimental). The problems of working with **15** in fact led to the design of Pcs **16** and **17** having larger alkyl chains generating soluble, more readily characterized Pcs. Pcs **16**, **17**, **18**, and **19** were all sufficiently soluble for easy separation and study. In an attempt to obtain symmetrical hydroxymethyl substituents at the β -position and also to tie back the β -substituents into a ring system so that subsequent cleavage might proceed more readily, 5,5-dihydroxymethyl-2-phenyl-1,3-dioxane (**21**) (19) and 1,1-dihydroxymethylcyclohexane (**22**) (20) were treated as above, but over a 12–16 day period, to give 5,5-bis(2',3'-dicyanophenoxy)methyl-2-phenyl-1,3-dioxane (**23**) and 1,1-bis(2',3'-(dicyanophenoxy)methyl)cyclohexane (**24**) in 73 and 65% yields, respectively (Scheme 3). Neither **23** nor **24** could be induced to undergo formation of mononuclear phthalocyanines and it appeared that only polymeric pigments were formed.

In attempts to make a larger variety of side-strapped phthalocyanines, including those of crown ethers and benzylic ethers that could be more readily cleaved (4), we treated a host

² Side-products at higher temperatures and shorter reaction times included **2**, etherols such as 3-(2',3'-dicyanophenoxy)-2,2-diethylpropan-1-ol, and bis(2,3-dicyanophenyl)ether (BDPE), mp 223–226°C; FT-IR(cm⁻¹): 3087, 3035, 2238 (C≡N), 1565, 1461, 1270, 813; ¹H NMR (acetone-*d*₆) δ : 7.02 (m, 4H), 6.78 (d, 2H, *J* = 8 Hz); ¹³C NMR (acetone-*d*₆) δ : 158.29, 136.95, 131.18, 124.76, 118.24, 115.81, 113.02, 108.87; EI-MS for C₁₆H₆N₄O, *m/z* (relative intensity): 270 (M⁺, 100) 242 (13) 127 (10).

³ The trityl groups in **14** were removed by BBr₃ to give a mixture in 31% yield of the appropriate *cis* and *trans* diols, as a light blue solid; EI-MS for C₄₂H₃₄N₈O₆, *m/z* (relative intensity): 746 (M⁺, 100), 716 (20), 355 (18), 281 (22), 207 (37), 119 (39), 73 (42).

Scheme 2.



6 R = CH₃, R' = CH₂OTr

7 R = R' = C₂H₅

8 R = R' = C₅H₁₁

9 R = R' = C₈H₁₇

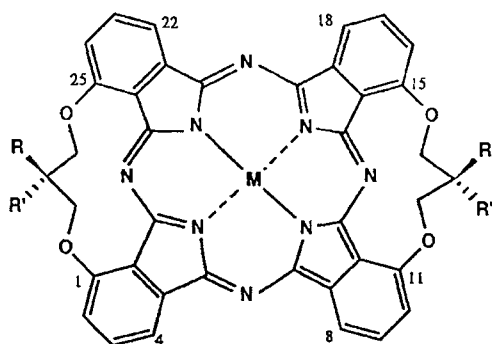
10 R = CH₃, R' = CH₂OTr

11 R = R' = C₂H₅

12 R = R' = C₅H₁₁

13 R = R' = C₈H₁₇

(1) Li octoxide/
1-octanol
(2) Zn(OAc)₂



14 R = CH₃, R' = CH₂OTr, M = H₂, + *trans*

15 R = R' = C₂H₅, M = H₂

16 R = R' = C₅H₁₁, M = H₂

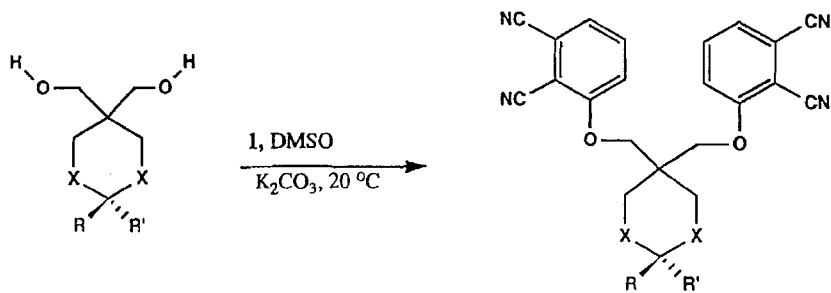
17 R = R' = C₈H₁₇, M = H₂

18 R = CH₃, R' = CH₂OTr, M = Zn, + *trans*

19 R = R' = C₅H₁₁, M = Zn

20 R = R' = C₈H₁₇, M = Zn

Scheme 3.



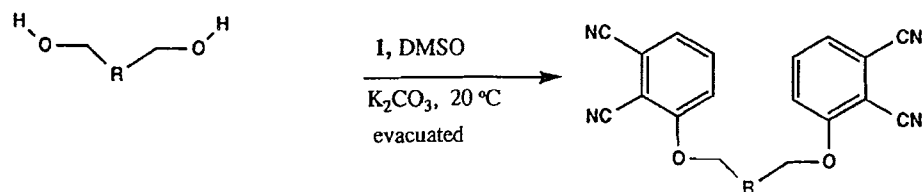
21 R = R' = H, X = O

22 R = R' = H, X = CH₂

23 R = R' = H, X = O

24 R = Ph, R' = H, X = CH₂

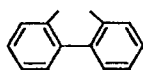
Scheme 4.

25 R = -CH₂OCH₂-

26 R =



27 R =



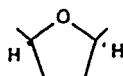
28 R =



29 R =



30 R =

31 R = -CH₂OCH₂-

32 R = R in 26

33 R = R in 27

34 R = R in 28

35 R = R in 29

36 R = R in 30

of known symmetrical diols such as diethylene glycol (**25**), 1,2-dihydroxymethylbenzene (**26**), 2,2'-bis(hydroxymethyl)biphenyl (**27**) (21), 5-*tert*-butyl-1,3-dihydroxymethylbenzene (**28**) (22), 2,5-dihydroxymethylfuran (**29**), and *cis*-2,5-bis(hydroxymethyl)tetrahydrofuran (**30**) (23) as before to give the new bisphthalonitriles **31–37** in 19–56% yields. Unfortunately, none of **31–37** cyclized to bis side-strapped phthalocyanines under our standard conditions described above.

It is curious that among the 13 symmetrical bisphthalonitriles prepared for this study, only **10–13** underwent dimerization to mononuclear phthalocyanines. With hindsight it is possible to see that perhaps the “*gem* dimethyl (Thorpe–Ingold) effect” (24–26) is operating here as only **10–13** have noncyclic β,β -dialkyl substituents. The *gem* dimethyl effect was originally promulgated to explain favoured cyclization reactions in five- to seven-membered rings containing β,β -dimethyl substituents, but was later expanded to macrocyclic ring systems (27).

Spectroscopic and physical properties

It is well known that electron-donating substituents at the 1, 4, 8, 11, 15, 18, 22, and 25 positions of the phthalocyanine nucleus (cf. **5**) result in an enhanced bathochromic shift of the Q-band in their UV–VIS spectra (1, 7, 28, 29), when compared to similar substitution at the 2, 3, 9, 10, 16, 17, 23, and 24 positions of the Pc nucleus. Thus, **5** shows a typical λ_{\max} at 726 nm. Surprisingly, **14–17** exhibit λ_{\max} values at 708–711 nm (Fig. 1) rather than the values at ~ 730 nm exhibited in related pure 1,8,15,22-alkoxy-substituted Pcs (4, 7) and another pure 1,11,15,25-alkoxy-substituted Pc (7). We believe that the

nature of the alkoxy substituent constrained in a ring system may cause the lone pair of electrons to lie partially out of conjugation with the benzo groups. Cook et al. (29) noticed that in one of their octaalkoxyphthalocyanines containing additional chloro substituents at the 2, 3, 9, 10, 16, 17, 23, and 24 positions, the λ_{\max} is shifted hypsochromically by about 20 nm relative to other octaalkoxyphthalocyanines, and this latter example could be regarded as a partially constrained phthalocyanine. As usual, the Pc zinc(II) derivatives **18–20** (Table 2, Fig. 2) exhibit λ_{\max} values of the Q-band having a hypsochromic shift of 20–25 nm compared to their metal-free counterparts.

The UV–VIS spectrum of **19** (Fig. 2) showed a spectral profile consistent with a PcM of D_{4h} symmetry in which a single intense Q-band absorption is found. The single Q-band absorption in the UV–VIS spectrum (suggesting a PcM with D_{4h} symmetry) conflicts somewhat with the actual geometry of **19** in which the 1,25:11,15-bis(side-strapped) PcZn **18** is, on a macromolecular scale, of D_{2h} symmetry. This observation strongly suggests that the peripheral side-strap substituents do not affect, or only very weakly affect, the Pc macrocycle molecular orbitals involved in the Q-band HOMO–LUMO electron transition. These results are markedly different from other D_{2h} “opposite” Pcs in which Q-band splitting for metallophthalocyanines is observed (30, 31).

The ¹H NMR of ZnPc **18** taken in THF-*d*₈ clearly showed the ABX splitting pattern generated by the aromatic hydrogens of the Pc macrocycle (doublet–triplet–doublet at 9.02, 7.99, and 7.68 ppm, respectively). As for metal-free **14**, the presence of two possible side strap isomers generated two multiplets at 5.38 and 5.17 ppm for the methylene CH₂ hydro-

Fig. 1. The electronic spectrum for metal-free bis side-strapped Pc (**16**).

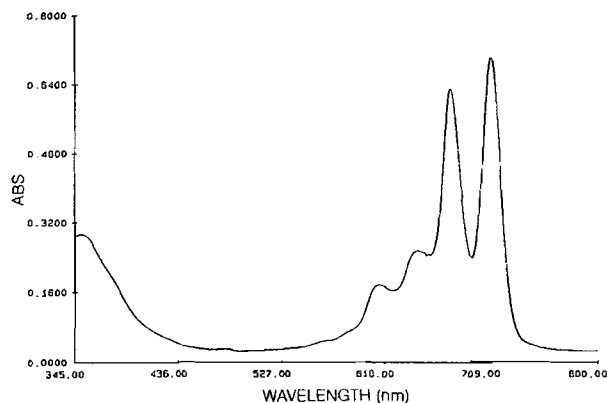
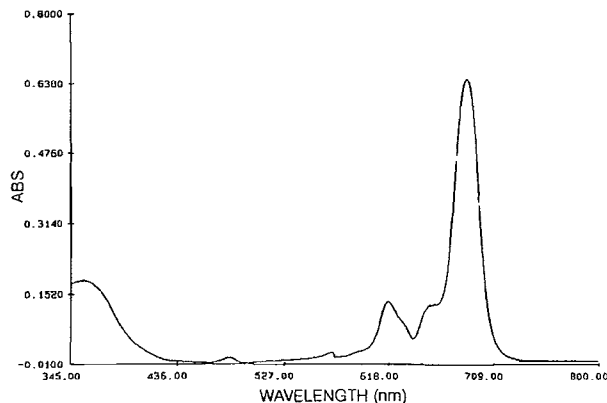


Fig. 2. The electronic spectrum of bis side-strapped zinc (II) Pc (**19**).



gens of the side-straps in addition to two pairs of singlets that arise from the 2'-methylene $\text{CH}_2\text{-OTr}$ and 2'-methyl CH_3 hydrogens at 3.66, 3.64 and 1.65, 1.62 ppm, respectively.

The NMR spectrum of **17** was examined in the most detail as it was the most soluble of the bis side-strapped Pcs. The ^1H NMR spectrum of **17** in benzene- d_6 clearly showed the doublet-triplet-doublet signals arising from the ABX-spin-type aromatic hydrogens, and a singlet signal corresponding to the CH_2 hydrogens of the side straps. The internal N-H protons were evident as a broad proton signal shifted upfield to -6 ppm (6). Such a large upfield ^1H NMR chemical shift of the N-H hydrogens is typical for Pcs at high concentration or for cofacial binuclear Pcs (12, 32). This upfield chemical shift is a reflection of the strong cone of aromaticity generated by the ring current of the Pc macrocycle (32). At high Pc concentrations, or for Pcs that have a tendency toward cofacial π - π interaction (i.e., Pc aggregates, cofacial binuclear Pcs), the shielding imparted by the Pc macrocycle has profound effects upon the chemical shifts of hydrogens of proximal Pc neighbours.

These shielding effects experienced by the aromatic, side-strap, and internal hydrogens were explored by the acquisition of ^1H NMR spectra at varying concentrations of **17** in $\text{THF-}d_8$ (Table 1, Fig. 3 and 4). These data indicate that as the Pc solution concentration increases, Pc aggregation (or π - π stacking)

Table 1. ^1H NMR dilution shifts (ppm) of aromatic, side-strap, and internal hydrogens for Pc **17**.

17 (mol/L)	$-\log$ 17	Aryl H-a	Aryl H-b	Aryl H-c	Strap CH_2	N-H
0.0050	2.301	7.75	7.27	6.83	4.32	-5.79
0.0025	2.602	7.91	7.39	6.96	4.45	-5.44
0.0005	3.301	8.32	7.67	7.25	4.74	-4.34

occurs, and results in shifts of Pc macrocycle (and side-strap) hydrogen signals to higher field. The shielding effects imparted by the Pc macrocycle affect the internal N-H hydrogens, the aromatic hydrogens, and the side-strap methylene (CH_2) hydrogens to varying degrees. For instance, the internal N-H hydrogens show the largest changes in chemical shift ($\Delta\delta = 1.45$ ppm), whereas the change in chemical shift of the side-strap hydrogens is smaller ($\Delta\delta = 0.41$ ppm). It appears that, in general, the hydrogen atoms closest to the core of the phthalocyanine macrocycle are most strongly influenced by the cone of aromaticity and π - π stacking shielding effects. This information can be used in assigning the signals observed in the ^1H NMR spectrum to the three types of Pc ring hydrogens. It would seem plausible that the aromatic hydrogen experiencing the greatest change in chemical shift as a result of changing the Pc concentration would be the aromatic hydrogen closest to the Pc core. In Pc isomers such as **17**, these would be the hydrogens at the 4, 8, 18, and 22 positions of the macrocycle and would be represented by one of the two doublet signals observed in the aromatic region of the ^1H NMR spectrum. The furthest downfield doublet signal (i.e., that closest to 8 ppm) exhibited the largest change of chemical shift ($\Delta\delta = 0.56$ ppm) relative to the doublet found near 7 ppm ($\Delta\delta = 0.42$ ppm). Even though there was only a one order of magnitude change in the concentration of Pc **17**, the data obtained from this experiment suggest that the 4-, 8-, 18-, and 22-position hydrogens can be assigned to this most downfield doublet signal (H-a in Fig. 3). This allowed an assignment of the highest field aromatic doublet signal (ca. 7 ppm) to the hydrogens at the 2, 10, 16, and 24 positions (H-c, i.e., adjacent to the side strap) and, intuitively, the triplet signal (ca. 7.5 ppm) to the hydrogens at the 2, 9, 16, and 23 positions of the Pc macrocycle. These hydrogen assignments were confirmed upon acquisition of a NOESY-NMR spectrum of **17**. Through-space NOE effects were observed between the side-strap CH_2 and macrocycle H-c hydrogens (i.e., the hydrogens in the position *ortho* to the side-strap), further validating the Pc ring hydrogen assignments determined from the ^1H NMR dilution shift experiment.

All new phthalocyanines and phthalonitriles exhibited parent ions in their FAB or EI mass spectra. IR data and good elemental analysis were consistent with the assigned structures. The directed syntheses of phthalocyanines having the unique substitution pattern at the 1,11,15,25 positions have been demonstrated by constraining the substitution pattern with bridges at the 1,25 and 1,11 positions.

Experimental

All organic solvents were dried by appropriate methods and distilled before use. All reagents were freshly distilled, or

Fig. 3. ^1H NMR dilution shifts of aromatic, side-strap, and internal hydrogens for Pc 17 taken in $\text{THF-}d_8$.

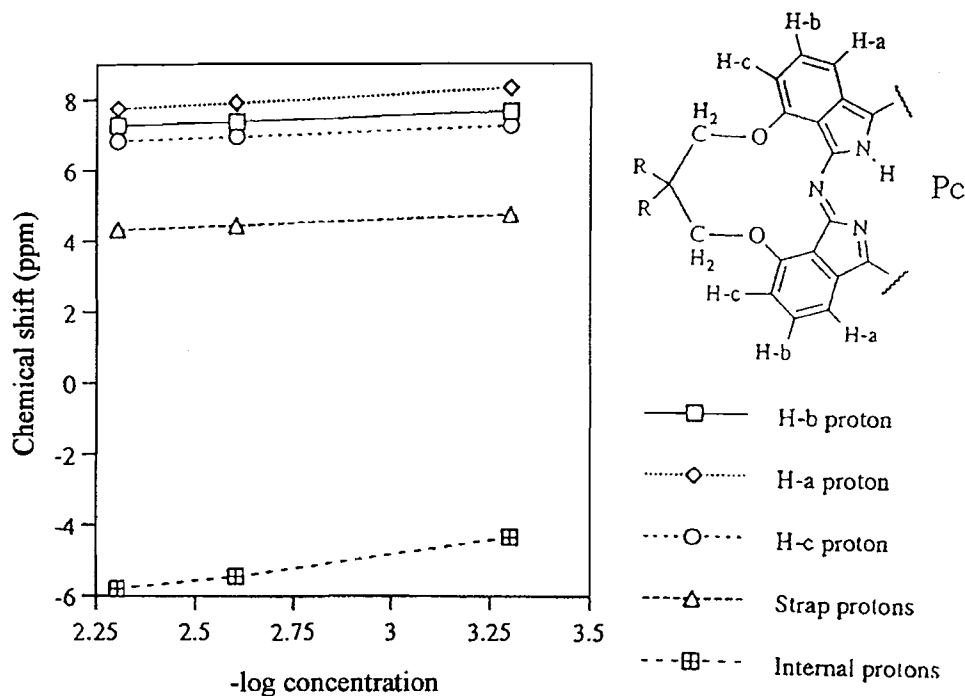
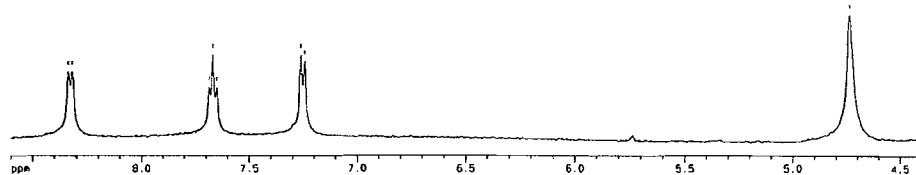


Fig. 4. The ^1H NMR spectrum of the downfield region of Pc 17 at 2.5×10^{-4} M in THF.



were recrystallized and then dried under reduced pressure, before use. Anhydrous potassium carbonate (K_2CO_3) was finely ground, oven dried at 250°C for 36 h, and then stored in sealed vials. Unless otherwise noted, magnetic stirring methods under an inert atmosphere (Matheson High Purity argon) were utilized during distillation or reaction processes, and round-bottom glass vessels chosen such that the quantity of reagents and solvent did not exceed half of the available volume. Water-cooled condensers were used if reaction processes were held near, or at, reflux conditions. Melting points were determined using a Kofler hot-stage melting point apparatus and are reported uncorrected. Infrared spectroscopy was performed on either a Pye Unicam SP3-200 or a Perkin Elmer 1310 infrared spectrophotometer and FTIR spectroscopy was performed on a Unicam Mattson 3000 FTIR spectrometer using samples prepared as KBr discs unless otherwise noted. Mass spectral analyses were performed by Dr. B. Khow (York University, North York, Ontario, Canada), Dr. R. Smith (McMaster University, Hamilton, Ontario, Canada), and Dr. R. N. Cerny (Midwest Center for Mass Spectrometry, University of Nebraska-Lincoln, Lincoln, Nebraska, U.S.A.). HRMS were performed by Dr. R. Smith (McMaster University,

Hamilton, Ontario, Canada). Nuclear magnetic resonance (NMR) spectroscopy was performed at 295–300 K unless otherwise noted, using either a Bruker Aspect AM3000 or a Bruker ARX 400 high-field Fourier Transform instrument. Chemical shifts are reported in parts per million relative to a tetramethylsilane (TMS) internal standard. Splitting patterns of proton resonances are described as singlets (s), doublets (d), triplets (t), quartets (q), doublets of doublets (dd), multiplets (m), or as broad signals (br). Coupling constants for signals other than singlets and multiplets are reported in hertz. ^{13}C NMR resonances are reported as the proton-decoupled chemical shifts. In addition to one-dimensional (1D) ^1H NMR and ^{13}C NMR, compounds requiring absolute structure determination were elucidated using combinations of 2D ^1H NMR (COSY and NOESY) and 2D carbon-proton (XH) correlations.

3-Hydroxyphthalonitrile (2)

In a manner similar to that previously described in the preparation of 4-hydroxyphthalonitrile (10), 865 mg (5.00 mmol) of 3-nitrophthalonitrile (1) (8, 9) was dissolved in 5 mL of DMSO. K_2CO_3 (760 mg, 5.51 mmol) and NaNO_2 (345 mg,

5.00 mmol) were added and the mixture heated at reflux for 30 min. After cooling, the reaction mixture was diluted with 20 mL of H₂O, and the mixture acidified to pH 3 with HCl and then centrifuged. The pellet was collected, resuspended in distilled water, homogenized by sonication, and again centrifuged. The supernatant liquid was discarded and the residue washed with methanol. The highly insoluble orange crude product was purified by column chromatography, using silica gel as the adsorbent and acetone as the eluting solvent. Evaporation of the solvent under reduced pressure gave a yellow solid that was recrystallized from glacial acetic acid to give 312 mg (43%) of **2** as an amorphous pale yellow solid (TLC: 10% CH₃CN–Bz, *R_f* = 0.03), mp 233–235°C; FT-IR (cm⁻¹): 3228br (O–H), 3072, 2255 (C≡N), 2230 (C≡N), 1584, 1467, 1316, 975, 807; ¹H NMR (DMSO-*d*₆) δ: 7.62 (t, 1H, *J* = 8 Hz), 7.39 (d, 1H, *J* = 8 Hz), 7.29 (d, 1H, *J* = 8 Hz); ¹³C NMR (DMSO-*d*₆) δ: 162.42, 135.09, 123.75, 122.08, 116.16, 114.75, 114.50, 100.68; EI-MS *m/z* (%): 144 (M⁺, 100), 116 (85), 89 (12). Anal. Calcd. for C₈H₄N₂O: C 66.67, H 2.78, N 19.44; found: C 66.77, H 2.95, N 18.76.

3-Neopentoxyphtalonitrile (3)

Compound **3** was prepared in similar fashion to 4-neopentoxyphtalonitrile (**12**) from 2.60 g (15 mmol) of 3-nitrophthalonitrile (**1**), 2.65 g (30 mmol) of neopentanol (3,3-dimethyl-1-propanol), and 5.0 g (36 mmol) of K₂CO₃ in 14 mL of DMF. A drying tube was used to maintain anhydrous conditions over the course of the 6 day reaction period required for complete consumption of **1**. The reaction mixture was poured into 100 mL of ice-cooled water and the organic products extracted with 3 x 30 mL of EtOAc. The EtOAc extracts were combined, washed once with 70 mL of cold water, once with 10 mL of brine, and then dried over MgSO₄. The drying agent was removed by filtration and the filtrate evaporated under reduced pressure to give 2.88 g of a crude product. The crude product was purified by column chromatography using 20% EtOAc – petroleum ether as the eluting solvent and then by recrystallization from EtOAc–hexane to give 1.77 g of white crystalline **3** (mp 120–121.5°C). A second crop of **3** was obtained from the mother liquor by addition of hexane followed by cooling to 5°C (0.24 g, mp 119–120.5°C). The combined yield of **3** was 2.01 g (62.6%) (TLC: 20% EtOAc – petroleum ether, *R_f* = 0.30); IR (cm⁻¹): 3080, 2950, 2220 (C≡N), 1580, 1470, 1300, 1055 (C–O), 790; ¹H NMR (CDCl₃) δ: 7.61 (t, 1H, *J* = 8 Hz), 7.33 (d, 1H, *J* = 8 Hz), 7.20 (d, 1H, *J* = 8 Hz), 3.74 (s, 2H), 1.10 (s, 9H); ¹³C NMR (CDCl₃) δ: 161.72, 134.49, 124.84, 116.87, 116.81, 115.34, 112.87, 104.94, 79.51, 32.05, 26.33; EI-MS *m/z* (%): 214 (M⁺, 5.6), 199 (12.5), 116 (5.3), 71 (100), 43 (84). Anal. calcd. for C₁₃H₁₄N₂O: C 72.87, H 6.59, N 13.07; found: C 73.20, H 6.60, N 13.23.

4-Neopentoxy-1,3-diiminoisoindoline (4)

Sodium methoxide was prepared from methanol (25 mL) and cleaned sodium metal (35 mg, 1.5 mmol). When methoxide formation was complete, 374.5 mg (1.750 mmol) of **3** was added, the mixture heated to reflux, and gaseous NH₃ bubbled through the solution. After 4.5 h of NH₃ addition the solution colour changed from colourless to light yellow. A small aliquot of the solution was removed and the solvent evaporated under reduced pressure. The absence of a C≡N stretch in the IR spectrum of this sample indicated that the reaction was

complete. The reaction mixture was cooled to room temperature (RT) and concentrated to dryness under reduced pressure to give 467.1 mg of crude **4** (TLC: 20% EtOAc – petroleum ether, *R_f* = 0.01). The yellowish crude product was not further purified and was used immediately in the preparation of PcH₂ **5**; IR (cm⁻¹): 3460–3150br, 3320, 2980, 1605, 1480, 1260, 1055.

1,8,15,22-Tetraneopentoxyphtalocyanine (5)

A solution of 467 mg (1.75 mmol) of diiminoisoindoline **4** in 3 mL of 2-*N,N*-dimethylaminoethanol (DMAE) was heated at 150°C (silicon oil bath) for 36 h. The mixture was cooled to RT and the dark green-black slurry poured into 15 mL of cold water. Cold methanol (30 mL) was added, the mixture homogenized, and the fine precipitate centrifuged and collected in six fractions. The supernatant liquid from each fraction was discarded, and the pellets were resuspended in 5 mL of methanol and centrifuged. This centrifugation procedure was repeated until the supernatant liquid was almost colourless (four cycles). The pellets were combined to give 148 mg of crude material that was purified by flash chromatography using toluene as the eluting solvent. The first product eluted was concentrated under reduced pressure to give 58.6 mg (16%) of PcH₂ **5** as a dark blue, shining solid (TLC: 2% 2-methoxyethanol–toluene, *R_f* = 0.70), mp > 325°C; UV–VIS (THF) λ_{max} (nm): 318, 354, 630, 664, 696, 726; IR (cm⁻¹): 3280 (N–H), 2950, 1580, 1490, 1330, 1250 (Ar–O–C), 1055, 1035, 1000, 740s; ¹H NMR (THF-*d*₈) δ: 9.30–7.54 (m, 12H), 4.74–4.23 (m, 8H), 1.64–1.19 (m, 36H), –0.18 (m, 2H); EI-MS *m/z* (%): 858 (M⁺, 100), 578 (17), 205 (30), 71 (18), 28 (29). Anal. calcd. for C₅₂H₅₈N₈O₄: C 72.73, H 6.76, N 13.05; found: C 72.56, H 6.60, N 12.87.

General methods of bisphthalonitrile syntheses

Method I (refs. 4, 33)

The distilled or recrystallized diol was placed in a 50 mL round-bottom flask equipped with a magnetic stirrer and distilled DMSO or DMF was added (5 mL/mmol diol) and heated to 50°C. Anhydrous K₂CO₃ (3–4 molar equiv.) and 2.2–2.5 equivalents of 3-nitrophthalonitrile (**1**) (8, 9) were added, the joint was well greased, fitted with a MgSO₄ drying tube, and the slurry stirred at rt, producing a pink-red coloured heterogeneous mixture. Two additional 0.25 equivalents of K₂CO₃ were then added at 24 h intervals and the mixture stirred for an additional 3 days or until all of **1** had been consumed. At each 24 h interval, the reaction slurry was briefly homogenized by sonication and the component profile monitored by TLC (10% CH₃CN–Bz).

At the end of the reaction period the mixture was poured into ice-water, the flask rinsed with water, and the rinsings were added to the ice-water. The orange-brown precipitate was collected by centrifugation, washed with 40 mL of 10% NaHCO₃ (aq.) (removing red-coloured products and yellow-coloured 3-hydroxyphtalonitrile (**2**)), and then with water. The residue was then washed with methanol, removing yellow coloured materials (mono-reacted diol and any excess **1**). The crude off-white coloured product was analyzed by TLC and recrystallized from either hot ethyl acetate, methanol, acetone, benzene, or acetonitrile. If TLC analysis indicated the presence of impurities (in particular, BDPE²) in excess of approx-

imately 15%, the crude product was first purified by column chromatography using silica gel adsorbant and 10% CH₃CN–Bz as the eluting solvent and then recrystallized. The white bisphthalonitrile was dried overnight at 70°C at 10⁻³ Torr (1 Torr = 133.3 Pa).

Method II

The distilled or recrystallized diol was placed in a 50 mL round-bottom flask equipped with a magnetic stirrer and distilled DMSO was added (5 mL/mmol diol). Anhydrous K₂CO₃ (0.54 equiv.) and 0.50 equivalent of **1** were added; the joint was well greased and then fitted with a Quick-Fit stopcock valve. The flask was evacuated to an internal pressure of approximately 20 Torr, the valve closed, and the mixture stirred rapidly at rt, immediately producing a pale pink heterogeneous mixture.

At 24 h intervals, the reaction slurry was briefly homogenized by brief sonication (with swirling) and the component profile monitored by TLC (10% CH₃CN–Bz). The flask was reevacuated and the slurry stirred. If all of **1** had been consumed, additional aliquots of carbonate (0.54 equiv.) and of **1** (0.50 equiv.) were added prior to evacuation and stirring. After the addition of 2.20–2.50 equivalents of **1**, the mixture was stirred for an additional 24 h and then monitored by TLC. Additional K₂CO₃ (0.5–1.5 equiv.) was added if unreacted **1** was present and the mixture then stirred for a further 24–96 h. The reaction mixture was then worked up as for Method I.

2,2-Dipentylpropan-1,3-diol (**8**)

In a manner similar to that previously described (19), a solution of 3.00 g (10.0 mmol) of diethyl 2,2-dipentylmalonate (**13**) in 4 mL of Et₂O was added dropwise to a stirred 5–10°C suspension of 1.15 g (30.3 mmol) of lithium aluminum hydride (LiAlH₄) in 25 mL of Et₂O. After addition of the diester, the mixture was heated at reflux for 2 h and then stirred at RT overnight. Active LiAlH₄ was quenched by addition of 2 mL of EtOAc and then 2 mL of 95% EtOH. The inorganic salts were removed by filtration through Celite, washed with Et₂O, and the filtrate was concentrated to dryness under reduced pressure. The oily residue was dissolved in 30 mL of Et₂O and extracted successively with 20 mL portions of 6 M NaOH, 4 M HCl, twice with 40 mL of H₂O, and finally with one 10 mL portion of brine. The organic phase was dried over MgSO₄ and then filtered. The filtrate was evaporated under reduced pressure to give 903 mg of a pale yellow oil. Distillation of this oil under reduced pressure gave 800 mg (37%) of diol **8** as a clear, colourless oil, bp 114–117°C/5 × 10⁻³ Torr; ¹H NMR (CDCl₃): 3.92 (s, 2H, OH), 3.52 (s, 4H, CH₂OH), 1.37–1.24 (m, 16H, 4 × CH₂), 0.90 (t, 6H, J = 7 Hz, CH₃); ¹³C NMR (CDCl₃) δ: 69.45, 41.03, 32.77, 30.80, 22.58, 22.52, 14.04; CI-MS (NH₃) *m/z* (%): 234 (M⁺ + 1 + NH₃, 100). Hygroscopic **8** was analyzed as its product **12**.

2,2-Dioctylpropan-1,3-diol (**9**)

In a manner similar to the preparation of diol **8**, a solution of 7.75 g (20.0 mmol) of diethyl 2,2-dioctylmalonate (**14**) in 30 mL of Et₂O was added dropwise to a stirred 5–10°C suspension of 3.00 g (80.0 mmol) of LiAlH₄ in 50 mL of Et₂O. After addition of the diester, the mixture was heated to reflux for 2 h and then stirred at RT overnight. Active LiAlH₄ was quenched by addition of 5 mL of EtOAc and then 5 mL of 95% EtOH

(aq.). The inorganic salts were removed by filtration through Celite, washed with Et₂O, and the filtrate was concentrated to dryness under reduced pressure. The sticky white residue was dissolved in 60 mL of Et₂O and extracted successively with 40 mL portions of 6 M NaOH, 4 M HCl, twice with 40 mL of H₂O, and finally with one 10 mL portion of brine. The organic phase was dried over MgSO₄ and evaporated under reduced pressure to give a yellowish oil. Distillation of the residue under reduced pressure gave 4.13 g (69%) of diol **9** as a colourless viscous oil that slowly solidified to a white wax at RT (23°C), bp 159–162°C/5 × 10⁻³ Torr; IR (cm⁻¹): 3500–3200br (OH), 2950, 2860, 1470, 1380w, 1030, 720; ¹H NMR (CDCl₃) δ: 3.56 (s, 4H), 1.27–1.22 (br m, 30H), 0.88 (t, 6H, J = 7 Hz); ¹³C NMR (CDCl₃) δ: 69.47 (CH₂OH), 41.00 (4°C), 31.88, 30.79, 30.58, 29.55, 29.32, 22.85, 22.66, 14.08 (CH₂CH₃); EI-MS *m/z* (%): 282 (2), 269 (22), 252 (19), 154 (22), 139 (27), 111 (33), 97 (60), 83 (79), 69 (100). Anal. calcd. for C₁₉H₄₀O₂: C 76.00, H 13.42; found: C 76.43, H 13.96.

1,3-Bis(2',3'-dicyanophenoxy)-2-methyl-2-trityloxymethylpropane (**10**)

Bisphthalonitrile **10** was prepared by Method II from 0.900 g (2.49 mmol) of diol **6** (**12**), 1.159 g (6.70 mmol) of 3-nitrophthalonitrile (**1**), and 1.460 g (10.6 mmol) of K₂CO₃ in 20 mL of DMSO at RT over a 6 day period. Aqueous work-up and EtOH washing of the crude product gave a pink coloured crude product. Recrystallization of this crude product from EtOAc–hexanes gave 1.44 g (94%) of white crystalline **10** (TLC: 10% CH₃CN–Bz, R_f = 0.85), mp 233–235°C; IR (cm⁻¹): 3090, 2920, 2220 (C≡N), 1580, 1450, 1290, 1060, 790, 700; ¹H NMR (CD₃CN) δ: 7.72 (t, 2H, J = 8 Hz), 7.5–7.2 (m, 19H), 4.22 (s, 4H), 3.30 (s, 2H), 1.27 (s, 3H); ¹³C NMR (acetone-*d*₆) δ: 162.02, 144.71, 136.30, 129.42, 128.63, 127.84, 126.46, 118.73, 117.00, 116.25, 113.76, 105.07, 87.43, 72.02, 64.50, 41.83, 17.58; EI-MS *m/z* (%): 614 (M⁺, 6), 537 (9), 243 (100), 165 (35), 105 (29). Anal. calcd. for C₄₀H₃₀N₄O₃: C 78.19, H 4.88, N 9.12; found: C 77.66, H 4.75, N 9.30.

1,3-Bis(2',3'-dicyanophenoxy)-2,2-diethylpropane (**11**)

Bisphthalonitrile **11** was prepared by Method II from 692 mg (5.23 mmol) of commercially available 2,2-diethylpropan-1,3-diol (**7**), 2.00 g (11.56 mmol) of **1**, and 3.05 g (22.1 mmol) of K₂CO₃ in 10 mL of DMSO over a 7 day period. The yield of off-white solid **11**, after purification by column chromatography using 10% acetonitrile–benzene as eluting solvent and recrystallization from acetonitrile, was 870 mg (43%) (TLC: 10% CH₃CN–Bz, R_f = 0.79), mp 216–218°C; IR (cm⁻¹): 3080, 2960, 2220 (C≡N), 1580s, 1470, 1450, 1290, 1050 (C–O), 795s; ¹H NMR (CD₃CN) δ: 7.67 (t, 2H, J = 8 Hz), 7.35 (d, 2H, J = 8 Hz), 7.34 (d, 2H, J = 8 Hz), 4.11 (s, 4H), 1.63 (q, 4H, J = 15, 7.5 Hz), 0.94 (t, 6H, J = 7.5 Hz); ¹³C NMR (acetone-*d*₆) δ: 162.25, 136.34, 126.46, 119.03, 116.96, 116.23, 113.94, 104.99, 71.98, 42.14, 23.69, 7.42; EI-MS *m/z* (%): 384 (M⁺, 3), 259 (4), 241 (50), 145 (38), 97 (80), 55 (100). Anal. calcd. for C₂₃H₂₀O₂N₄: C 71.88, H 5.21, N 14.58; found: C 72.24, H 4.78, N 14.99.

1,3-Bis(2',3'-dicyanophenoxy)-2,2-dipentylpropane (**12**)

Bisphthalonitrile **12** was prepared by Method II from 0.72 g

(3.3 mmol) of 2,2-dipentylpropan-1,3-diol (**8**), 1.40 g (8.1 mmol) of **1**, and 2.1 g (15.2 mmol) of K_2CO_3 in 7 mL of DMSO at RT over a 9 day period. Aqueous work-up and methanol washing of the solid reaction products gave a yellowish crude solid. Recrystallization of the crude product from acetonitrile gave 0.81 g (52%) of white crystalline **12** (TLC: 10% CH_3CN -Bz, $R_f = 0.78$), mp 173–174°C; IR (cm^{-1}): 3080, 2960, 2210 ($C\equiv N$), 1585, 1475, 1285, 1055, 795. 1H NMR (CD_3CN) δ : 7.71 (t, 2H, $J = 8$ Hz), 7.45 (m, 4H), 4.13 (s, 4H), 1.54 (m, 4H), 1.3 (m, 12H), 0.86 (t, 6H, $J = 7$ Hz); ^{13}C NMR (acetone- d_6) δ : 162.27, 136.34, 126.48, 119.08, 116.94, 116.23, 113.95, 104.97, 72.56, 42.05, 33.25, 31.80, 23.05, 22.92, 14.22; EI-MS m/z (%): 469 ($M^+ + 1$, 50), 453 (10), 439 (18), 397 (21), 368 (30), 325 (72), 144 (100). Anal. calcd. for $C_{29}H_{32}N_4O_2$: C 74.36, H 6.84, N 11.97; found: C 74.20, H 6.93, N 12.00.

1,3-Bis(2',3'-dicyanophenoxy)-2,2-dioctylpropane (**13**)

Bisphthalonitrile **13** was prepared by Method II from 3.05 g (10.2 mmol) of 2,2-dioctylpropan-1,3-diol (**9**), 3.9 g (22.5 mmol) of **1**, and 7.4 g (54 mmol) of K_2CO_3 in 25 mL of DMSO at RT over an 8 day period. Aqueous work-up and methanol washing of the solid reaction products gave a crude yellowish solid that was recrystallized from acetonitrile. A second recrystallization from ethyl acetate gave 3.17 g (57%) of white crystalline **13** (TLC: 10% CH_3CN -Bz, $R_f = 0.80$), mp 163–165°C; FT-IR (cm^{-1}): 3083, 2927, 2862, 2225 ($C\equiv N$), 1518s, 1463, 1294, 1045, 798. 1H NMR (acetone- d_6) δ : 7.86 (t, 2H, $J = 8$ Hz), 7.71 (d, 2H, $J = 8$ Hz), 7.55 (d, 2H, $J = 8$ Hz), 4.31 (s, 4H), 1.64 (m, 4H), 1.32 (m, 24H), 0.84 (t, 6H, $J = 7$ Hz); ^{13}C NMR (acetone- d_6) δ : 162.26, 136.35, 126.46, 119.06, 116.95, 116.22, 113.94, 104.99, 72.48, 42.06, 32.54, 31.66, 30.94, 29.88, 23.26, 23.11, 14.30; EI-MS m/z (%): 552 (M^+ , 4.7), 523 (4.6), 509 (2.8), 495 (2.4), 469 (3.4), 409 (55), 145 (22), 43 (100). Anal. calcd. for $C_{35}H_{44}N_4O_2$: C 76.09, H 7.97, N 10.14; found: C 75.92, H 8.52, N 10.27.

General method of bis side-strapped phthalocyanine synthesis

A solution of the bisphthalonitrile was made using 1-octanol, tetrahydrofuran (THF), or mixtures of 1-octanol and THF. A syringe pump was used to add the bisphthalonitrile dropwise (ca. 0.02 mmol/min) to lithium octoxide in 1-octanol heated at reflux (ca. 196°C) in a modified air-cooled distillation apparatus that allowed rapid removal of cosolvent. In general, 10 mL of 1-octanol containing excess lithium metal was used for every 100 mg of bisphthalonitrile added. Pc formation was usually evident after 20 s of bisphthalonitrile addition. Upon addition of the bisphthalonitrile, the mixture was heated at reflux for an additional 2–10 min and then allowed to cool to RT. Water was then added and the mixture neutralized by addition of HCl (aq.) (ca. pH 7), giving a suspension that was homogenized by ultrasound. The mixture was then concentrated to near dryness under reduced pressure and the crude Pc product purified by centrifugation and chromatographic and recrystallization techniques.

1,25:11,15-Bis(2'-methyl-2'-trityloxymethylpropan-1',3'-dioxy)phthalocyanine (**14**)

PcH₂ **14** was prepared, using the general method, by an 18 min dropwise addition of a solution of 300 mg (0.49 mmol) bis-

phthalonitrile **6** in 7 mL of THF to 30 mL of 1-octanol containing 50 mg (2.2 mmol) of cleaned lithium metal at 200°C. After addition of **6**, the mixture was heated at reflux for an additional 5 min and then cooled to RT. A general method work-up (similar to that of **17**) gave 200 mg of a blue-green crude solid. The solid was dissolved in THF, adsorbed on normal grade silica gel, then purified by flash chromatography (benzene as eluant) to yield a first fraction of almost pure **14** (determined by TLC). PcH₂ **14** was rechromatographed under the same conditions to yield 48 mg (16%) of **14** as a dark blue solid, mp >350°C; IR (cm^{-1}): 3280 (N-H), 3050, 2910, 2860, 1580, 1480, 1250 (Ar-O-C), 1030, 745, 700; UV-VIS (THF) λ_{max} nm log ϵ : 330 (4.75), 618 (4.45), 656 (4.64), 680 (5.11), 712 (5.13); 1H NMR (380 K)(pyridine- d_5) δ : 9.07 (m, 4H), 8.06 (m, 16H), 7.84 (d, 4H, $J = 6$ Hz), 7.57 (m, 14H), 7.40 (t, 4H, $J = 7$ Hz), 5.41 (m, 4H), 5.21 (m, 4H), 4.00 and 3.99 (2s, 4H), 1.93 and 1.92 (2s, 6H), -1.70 (br s, 2H); +FAB-MS m/z : 1231 ($M^+ + 1$). Anal. calcd. for $C_{80}H_{62}N_8O_6$: C 78.05, H 5.04, N 9.11; found: C 77.93, H 5.21, N 8.88.

1,25:11,15-Bis(2',2'-diethylpropan-1',3'-dioxy)phthalocyanine (**15**)

Cleaned lithium metal (50 mg, 7.1 mmol) and 1-octanol (50 mL) were placed in a 100 mL three-neck flask and the mixture heated to 195–200°C until lithium 1-octoxide formation was complete. The flask was fitted for the modified distillation and a solution of 500 mg (1.3 mmol) of bisphthalonitrile **11** in 30 mL of THF was prepared. A syringe pump was used to add the solution of **11** to the well-stirred alkoxide at 195–200°C over a 20 min period and the evaporated THF was collected. The mixture was then heated for an additional 5 min and then cooled to RT. Water (5 mL) was added and the mixture was concentrated to near dryness under reduced pressure and then neutralized by the addition of dilute HCl (aq.). The solid material was suspended in 15 mL of MeOH and homogenized by ultrasound. The grey-green solid was collected and washed by repeated centrifugation and resuspension in MeOH. Finally, the pellet was dissolved in 5 mL of 50% THF-Bz and purified by silica-gel flash chromatography using benzene as the eluting solvent. A first fraction consisting of a diffuse band of blue pigment was collected. Immobile green and brown materials were not eluted from the column. The solvent of the collected fraction (ca. 300 mL) was removed under reduced pressure to yield 35 mg (7%) of PcH₂ **15** as a blue solid, mp >350°C; IR (cm^{-1}): 3280 (N-H), 2930, 2840, 1590, 1450, 1250 (Ar-O-C), 1040, 810, 750s. UV-VIS (benzene) λ_{max} nm (log ϵ): 352 (4.75), 614 (4.52), 646 (4.70), 672 (5.11), 708 (5.14). 1H NMR (CF_3COOD) δ : 9.05 (d, 4H, $J = 8$ Hz), 8.49 (t, 4H, $J = 8$ Hz), 8.03 (d, 4H, $J = 8$ Hz), 5.10 (s, 8H), 2.13 (q, 8H, $J = 7$ Hz), 1.25 (t, 12H, $J = 7$ Hz); EI-MS m/z (%): 770 (M^+ , 35), 211 (10), 145 (31), 55 (100); HRMS required for $C_{46}H_{42}N_8O_4$: 770.33290; found: 770.33220.

1,25:11,15-Bis(2',2'-dipentylpropan-1',3'-dioxy)phthalocyanine (**16**)

PcH₂ **16** was prepared as above from a 3 mL THF/1-octanol (2:1) solution of 150 mg (3.21×10^{-2} mmol) of bisphthalonitrile **12** added over a 5 min period to 15 mL of 1-octanol containing 15 mg (2.2 mmol) of lithium metal at 195–200°C. The mixture was heated for an additional 2 min, cooled to RT and worked up as previously described. PcH₂ **16** was separated

from dimeric and oligomeric Pc products by flash column chromatography (3% Bz-toluene as eluting solvent) as a fast moving blue pigment F1. A slower moving blue-green component was eluted after changing the eluting solvent to 1% THF-toluene. The desired fast moving mononuclear Pc pigment **16** was then treated twice by flash column chromatography (3% Bz-toluene as eluting solvent). This pigment was recrystallized from pyridine to yield 31.5 mg (21%) of PcH₂ **16** as a bright blue solid, mp >350°C; IR (cm⁻¹): 3300 (N-H), 2940, 2850, 1585w, 1460, 1250 (Ar-O-C), 1035, 800w, 745s; UV-VIS (THF) λ_{max} nm (log ε): 352.5 (4.76), 614 (4.53), 645 (4.70), 674 (5.10), 709 (5.14); ¹H NMR (benzene-d₆) δ: 8.87 (d, 4H, *J* = 8 Hz), 8.28 (t, 4H, *J* = 8 Hz), 7.75 (d, 4H, *J* = 8 Hz), 4.83 (s, 8H), 1.90 (m, 8H), 1.54 (m, 8h), 1.32 (m, 16H), 0.80 (m, 12H), -4.5 (s, 2H); +FAB-MS *m/z* (%): 940 (M⁺, 2), 869 (1.2), 772 (1), 759 (1), 687 (0.5), 614 (1.5), 460 (5), 307 (34), 154 (100). Anal. calcd. for C₅₈H₆₆N₈O₄: C 76.05, H 8.02, N 10.14; found: C 75.92, H 8.52, N 10.27.

1,25:11,15-Bis(2',2'-dioctylpropan-1',3'-dioxy)phthalocyanine (17)

PcH₂ **17** was prepared as for **15** from a 20 mL THF/1-octanol (2:1) solution of 1.11 g (2.02 mmol) of bisphthalonitrile **13** added over a 7 min period to 75 mL of 1-octanol containing 85 mg (12.1 mmol) of lithium metal at 195–200°C. The mixture was heated for an additional 5 min, cooled to RT and worked up as previously described. The desired PcH₂ **17** was separated from oligomeric Pc pigments by flash chromatography (benzene as eluting solvent). Flash chromatography of this nearly pure pigment (benzene as eluting solvent) gave 207 mg (19%) of **17** as a dark blue, shining solid, mp >350°C; IR (cm⁻¹): 3290 (N-H), 2930, 2850, 1590w, 1460w, 1255 (Ar-O-C), 1030, 805w, 740s; UV-VIS (THF) λ_{max} nm (log ε): 352.5 (4.79), 613 (4.58), 646 (4.73), 675 (5.12), 709 (5.17); ¹H NMR (benzene-d₆) δ: 7.92 (d, 4H, *J* = 7 Hz), 7.25 (t, 4H, *J* = 7 Hz), 6.88 (d, 4H, *J* = 7 Hz), 4.44 (s, 8H), 1.58–1.88 (m, 56H), 1.15 (t, 12H, *J* = 6.8 Hz), -5.99 (s, 2H) (see Table 3); EI-MS *m/z* (%): 1107 (M⁺ + 1, 32), 1077 (5), 806 (8), 660 (18), 556 (100). Anal. calcd. for C₇₀H₉₀N₈O₄: C 75.91, H 8.19, N 10.12; found: C 75.58, H 8.52, N 9.88.

1,25:11,15-Bis(2'-methyl-2'-trityloxymethylpropan-1',3'-dioxy)phthalocyaninatozinc(II) (18)

PcZn **18** was prepared from 23 mg (1.87 × 10⁻² mmol) of PcH₂ **14** and 50 mg (0.27 mmol) of Zn(OAc)₂ in a mixture of 2.5 mL of Py and 2.5 mL of DMF heated at reflux for 20 h. After cooling to RT, the solvents were removed under reduced pressure and the crude product purified by column chromatography using 20% THF-Bz as the eluting solvent. The solvents were removed under reduced pressure to give 22 mg (91%) of PcZn **18**, mp >330°C; UV-VIS (THF) λ_{max} nm (log ε): 336 (4.71), 617 (3.92), 654 (4.40), 686 (5.33); ¹H NMR (THF-d₈) δ: 9.02 (d, 4H, *J* = 7.5 Hz), 7.99 (t, 4H, *J* = 7.5 Hz), 7.77 (m, 12H), 7.68 (d, 4H, *J* = 7.5 Hz), 7.38 (m, 12H), 7.26 (m, 6H), 5.38 (m, 4H), 5.17 (m, 4H), 3.66 and 3.64 (2s, 4H), 1.65 and 1.62 (2s, 6H); +FAB-MS *m/z*: cluster at 1295 (M+2). Anal. calcd. for C₈₀H₆₀N₈O₆Zn: C 74.24, H 4.64, N 8.66; found: C 74.39, H 4.46, N 8.23.

1,25:11,15-Bis(2',2'-dipentylpropan-1',3'-dioxy)phthalocyaninato zinc(II) (19)

PcH₂ **16** (50 mg, 5.3 × 10⁻² mmol) was dissolved in a mixture

of 10 mL of pyridine and 8 mL of DMF. Zinc acetate (0.5 mg, 2.72 mmol) was added and the mixture heated to reflux for 14 h. The mixture was allowed to cool, the solvents were removed under reduced pressure, and the crude product was purified by flash chromatography using THF as eluting solvent. The THF was removed under reduced pressure and the product recrystallized from pyridine to give 47 mg (89%) of PcZn **19** as fine light-blue needles, mp >350°C; UV-VIS (THF) λ_{max} nm (log ε): 356 (4.74), 617 (4.62), 655 (4.56), 686 (5.42); ¹H NMR (benzene-d₆) δ: 8.87 (d, 4H, *J* = 8 Hz), 8.28 (t, 4H, *J* = 8 Hz), 7.74 (d, 4H, *J* = 8 Hz), 4.83 (s, 8H), 1.91 (m, 8H), 1.54 (m, 8H), 1.27 (m, 16H), 0.80 (t, 12H, *J* = 6.7); +FAB-MS *m/z* (%): 1002 (M⁺+1, 100), 932 (10), 821 (18), 640 (29), 634 (27), 610 (23). Anal. calcd. for C₅₈H₆₄N₈O₄Zn: C 69.48, H 6.43, N 11.18; found: C 69.51, H 6.50, N 10.92.

1,25:11,15-Bis(2',2'-dioctylpropan-1',3'-dioxy)phthalocyaninato zinc(II) (20)

PcH₂ **17** (67.7 mg, 6.12 × 10⁻² mmol) was added to a mixture of 20 mL of pyridine and 20 mL of DMF containing 112 mg (0.61 mmol) of Zn(OAc)₂. The mixture was heated at reflux overnight and then cooled to RT. The solvents were removed under reduced pressure and the pigment purified by column chromatography (Et₂O as the eluting solvent). After evaporation of the solvent under reduced pressure, 62 mg (87%) of PcZn **20** was obtained, mp >330°C; UV-VIS (THF) λ_{max} nm (log ε): 356 (4.63), 480 (3.11), 617 (4.49), 655 (4.46), 685.5 (5.17); ¹H NMR (THF-d₈) δ: 8.94 (d, 4H, *J* = 7 Hz), 7.96 (t, 4H, *J* = 7 Hz), 7.56 (d, 4H, *J* = 7 Hz), 5.16 (br s, 8H), 1.96 (m, 8H), 1.89 (m, 8H), 1.60 (m, 40H), 1.00 (t, 12H, *J* = 7 Hz); +FAB-MS *m/z* (%): 1171 (M⁺ + 1, 100), 905 (34), 791 (36), 641 (85), 626 (23), 612 (66). Anal. calcd. for C₇₀H₈₈N₈O₄Zn: C 71.81, H 7.58, N 9.57; found: C 71.53, H 7.11, N 9.93.

5,5-Bis(2',3'-dicyanophenoxymethyl)-2-phenyl-1,3-dioxane (23)

Bisphthalonitrile **23** was prepared by Method II from 1.11 g (5 mmol) of 5,5-dihydroxymethyl-2-phenyl-1,3-dioxane (**21**) (19), 1.75 g (10.1 mmol) of **1**, and 3.1 g (22.5 mmol) of K₂CO₃ in 25 mL of DMSO at RT over a 16 day period. Aqueous work-up and methanol washing of the reaction products gave a pink-coloured solid. Double recrystallization of the pink solid from EtOAc gave 1.83 g (77%) of white crystalline **23** (TLC: 5% CH₃CN-Bz, R_f = 0.43), mp 180–182.5°C; IR (cm⁻¹): 3180, 3100s, 2990, 2880, 2245 (C≡N), 1585s, 1470br, 1395, 1300br, 1115, 1060br, 800s, 740, 700s; ¹H NMR (CD₃CN) δ: 7.74 (t, 2H, *J* = 8 Hz), 7.60 (d, 2H, *J* = 8 Hz), 7.50–7.36 (m, 7H), 5.59 (s, 1H), 4.70 (s, 2H), 4.55 (d, 2H, *J* = 12 Hz), 4.19 (s, 2H), 4.12 (d, 2H, *J* = 12 Hz); ¹³C NMR (DMSO-d₆) δ: 160.74 and 160.53, 137.95, 136.09 and 136.02, 129.07, 128.19, 126.31, 126.20, 118.94 and 118.69, 115.73 and 115.70, 115.29 and 115.27, 113.48 and 113.39, 103.45 and 113.38, 101.40, 68.85, 68.42, 67.82, 38.36; EI-MS *m/z* (%): 476 (M⁺, 63), 475 (23), 399 (5), 197 (60), 157 (25), 105 (100), 77 (22). Anal. calcd. for C₂₈H₂₀N₄O₄: C 70.58, H 4.23, N 11.76; found: C 70.25, H 4.66, N 12.00.

1,1-Bis(2',3'-dicyanophenoxymethyl)cyclohexane (24)

Bisphthalonitrile **24** was prepared by Method II from 0.72 g (5 mmol) of 1,1-dihydroxymethylcyclohexane (**22**) (20), 2.25 g (13 mmol) of **1**, and 2.65 g (19 mmol) of K₂CO₃ in 20 mL of

DMSO over a 12 day period at RT. Aqueous work-up and methanol washing gave a pink coloured crude product. Double recrystallization of the crude product from acetone gave 1.28 g (65%) of bisphthalonitrile **24** as colourless crystals (TLC: 10% CH₃CN–Bz, $R_f = 0.63$), mp 246–247°C; IR (cm⁻¹): 3080s, 2910, 2850, 2220 (C≡N), 1775s, 1450br, 1290br, 1050, 930, 790s, 730; ¹H NMR (CD₃CN) δ: 7.72 (t, 2H, $J = 8$ Hz), 7.48 (d, 2H, $J = 8$ Hz), 7.42 (d, 2H, $J = 8$ Hz), 4.22 (s, 4H), 1.69–1.53 (m, 10H); ¹³C NMR (DMSO-*d*₆) (330 K) δ: 160.84, 135.40, 125.21, 118.60, 115.17, 114.94, 112.90, 103.06, 72.24, 38.02, 28.87, 25.16, 20.32; EI-MS m/z (%): 396 (M⁺, 32), 252 (100), 157 (77), 144 (87), 127 (93). Anal. calcd. for C₂₄H₂₀N₄O₂: C 72.73, H 5.05, N 14.14; found: C 73.03, H 4.77, N 13.78.

1,5-Bis(2',3'-dicyanophenoxy)-3-oxapentane (31)

Bisphthalonitrile **31** was prepared by Method II from 0.795 g (7.50 mmol) of diethylene glycol (**25**), 2.17 g (18.3 mmol) of **1**, and 3.04 g (22.1 mmol) of K₂CO₃ in 10 mL of DMSO at 50°C over a 6 day period. After work-up by Method I, bisphthalonitrile **31** was obtained from the crude product by column chromatography (15% CH₃CN–Bz as the eluting solvent) as the first fraction collected. After recrystallization from acetonitrile, 509 mg (19%) of **31** was obtained as white needles (TLC: 15% CH₃CN–Bz, $R_f = 0.50$), mp 223–224°C; IR (cm⁻¹): 3090, 2925, 2220 (C≡N), 1580, 1470, 1300, 1140, 1065, 795; ¹H NMR (CD₃CN) δ: 7.70 (t, 2H, $J = 8$ Hz), 7.45 (d, 2H, $J = 8$ Hz), 7.44 (d, 2H, $J = 8$ Hz), 4.34 (t, 4H, $J = 4$ Hz), 3.94 (t, 4H, $J = 4$ Hz); ¹³C NMR (DMSO-*d*₆) (330 K) δ: 160.73, 135.21, 125.49, 118.64, 115.25, 115.14, 113.03, 69.35, 68.57; EI-MS m/z (%): 358 (M⁺, 4.5), 215 (17), 171 (100), 145 (25), 116 (14). Anal. calcd. for C₂₀H₁₄N₄O₃: C 67.04, H 3.91, N 15.64; found: C 66.73, H 3.87, N 15.42.

A second fraction eluted from the column consisted of a mixture (by TLC) of BDPE² and a monosubstitution product (etherol).

1,2-Bis(2',3'-dicyanophenoxy)methylbenzene (32)

Bisphthalonitrile **32** was prepared by Method II from 1.068 g (7.5 mmol) of 1,2-dihydroxymethylbenzene (**26**) (Aldrich), 3.0 g (17.3 mmol) of **1**, and 3.0 g (21.7 mmol) of K₂CO₃ in 10 mL of DMSO at RT over a 6 day period. After aqueous work-up and washing with MeOH an off-white crude product was recovered. Recrystallization of the crude product from acetonitrile gave 760 mg (26%) of white **32** as an amorphous solid (TLC: 5% CH₃CN–Bz, $R_f = 0.24$), mp 254–256°C; FT-IR (cm⁻¹): 3167, 3085, 2924, 2235 (C≡N), 1583s, 1469, 1453, 1272, 1037, 802, 767, 734; ¹H NMR (CDCl₃) δ: 7.83 (t, 2H, $J = 8$ Hz), 7.73 (d, 2H, $J = 8$ Hz), 7.61 (m, 4H), 7.46 (m, 2H), 5.54 (s, 4H); ¹³C NMR (CDCl₃) δ: 169.24, 135.28, 133.34, 128.66, 128.52, 125.69, 118.64, 115.24, 115.20, 113.09, 103.24, 68.88; EI-MS m/z (%): ion signals not observed. Anal. calcd. for C₂₄H₁₄N₄O₂: C 73.85, H 3.59, N 14.36; found: C 73.64, H 3.57, N 14.45.

2,2'-Bis(2'',3''-dicyanophenoxy)methylbiphenyl (33)

Bisphthalonitrile **33** was prepared by Method II from 400 mg (1.9 mmol) of 2,2'-dihydroxymethylbiphenyl (**27**) (21), 750 mg (4.34 mmol) of **1**, and 900 mg (6.52 mmol) of K₂CO₃ in 10 mL of DMSO over 4 days at RT. After aqueous work-up and methanol washing, the yellowish crude product was recrystallized twice from benzene to give 370 mg (42%) of bisphthalonitrile **33** as an off-white solid (TLC: 15% CH₃CN–Bz, $R_f = 0.80$), mp 193–194°C; FT-IR (cm⁻¹): 3085, 3030, 2892, 2229 (C≡N), 1581s, 1470s, 1301, 1286, 1034, 801, 789, 692; ¹H NMR (CDCl₃) δ: 7.57 (m, 4H), 7.42 (m, 4H), 7.36 (m, 2H), 7.31 (d, 2H, $J = 8$ Hz), 7.17 (d, 2H, $J = 8$ Hz), 4.92 (m, 4H); ¹³C NMR (CDCl₃) δ: 160.77, 139.94, 134.83, 132.19, 130.21, 130.04, 129.06, 128.54, 125.22, 116.98, 116.88, 115.19, 113.14, 104.44, 70.04; EI-MS m/z (%): 466 (M⁺, 8), 463 (10), 437 (9), 324 (42), 283 (38), 179 (100). Anal. calcd. for C₃₀H₁₈N₄O₂: C 77.25, H 3.86, N 12.02; found: C 76.85, H 3.78, N 11.88.

lonitrile **33** as an off-white solid (TLC: 15% CH₃CN–Bz, $R_f = 0.80$), mp 193–194°C; FT-IR (cm⁻¹): 3085, 3030, 2892, 2229 (C≡N), 1581s, 1470s, 1301, 1286, 1034, 801, 789, 692; ¹H NMR (CDCl₃) δ: 7.57 (m, 4H), 7.42 (m, 4H), 7.36 (m, 2H), 7.31 (d, 2H, $J = 8$ Hz), 7.17 (d, 2H, $J = 8$ Hz), 4.92 (m, 4H); ¹³C NMR (CDCl₃) δ: 160.77, 139.94, 134.83, 132.19, 130.21, 130.04, 129.06, 128.54, 125.22, 116.98, 116.88, 115.19, 113.14, 104.44, 70.04; EI-MS m/z (%): 466 (M⁺, 8), 463 (10), 437 (9), 324 (42), 283 (38), 179 (100). Anal. calcd. for C₃₀H₁₈N₄O₂: C 77.25, H 3.86, N 12.02; found: C 76.85, H 3.78, N 11.88.

1,3-Bis(2',3'-dicyanophenoxy)methyl-5-tert-butylbenzene (34)

Bisphthalonitrile **34** was prepared by Method II from 388 mg (2.00 mmol) of 3,5-dihydroxymethyl-tert-butylbenzene (**28**) (**22**), 850 mg (4.91 mmol) of **1**, and 1.06 g (7.68 mmol) of K₂CO₃ in 10 mL of DMSO at RT over a 5 day period. Aqueous work-up and methanol washing gave a greyish crude product. Recrystallization of this solid from acetonitrile gave 413 mg (46%) of white crystalline **34** (TLC: 15% CH₃CN–Bz, $R_f = 0.76$), mp 180–181°C; FT-IR (cm⁻¹): 3089, 2954, 2869, 2234 (C≡N), 1583s, 1471, 1295s, 1083, 795; ¹H NMR (acetone-*d*₆) δ: 7.86 (t, 2H, $J = 8$ Hz), 7.73 (d, 2H, $J = 8$ Hz), 7.67 (s, 2H), 7.59 (d, 2H, $J = 8$ Hz), 7.48 (s, 1H), 5.47 (s, 4H), 1.36 (s, 9H); ¹³C NMR (acetone-*d*₆) δ: 162.03, 153.12, 136.72, 136.16, 126.61, 125.63, 124.77, 119.42, 117.30, 116.32, 114.05, 105.43, 72.23, 35.46, 31.54; EI-MS m/z (%): 446 (M⁺, 15), 304 (46), 288 (38), 273 (12), 247 (100). Anal. calcd. for C₂₈H₂₂N₄O₂: C 75.34, H 4.93, N 12.56; found: C 75.39, H 4.96, N 12.55.

2,5-Bis(2',3'-dicyanophenoxy)methylfuran (35)

Bisphthalonitrile **35** was prepared by a modification of Method II (using less than 2 equiv. of **1**) from 1.28 g (10.0 mmol) of 2,5-dihydroxymethylfuran (**29** (Aldrich)), 3.15 g (18.2 mmol) of **1** and 3.4 g (24.6 mmol) of K₂CO₃ in 25 mL of DMSO over a 6 day reaction period at RT. Aqueous work-up and MeOH washing of the reaction product gave a brown solid. Recrystallization of the highly insoluble crude product from 140 mL of acetone gave 1.94 g (56%, **1**) of white crystalline **35** (TLC: 15% CH₃CN–Bz, $R_f = 0.57$), mp >330°C; FT-IR (cm⁻¹): 3370, 3090, 2920, 2232 (C≡N), 1585s, 1474s, 1275s, 1030s, 809; ¹H NMR (CD₃CN) δ: 7.78 (t, 2H, $J = 8$ Hz), 7.60 (d, 2H, $J = 8$ Hz), 7.52 (d, 2H, $J = 8$ Hz), 6.66 (s, 2H), 5.29 (s, 4H); ¹³C NMR (DMSO-*d*₆) (330 K) δ: 159.92, 149.45, 135.17, 125.94, 118.96, 115.35, 115.20, 112.94, 112.11, 103.44, 63.33; EI-MS m/z (%): 382 (M⁺ + 2, 1.1), 237 (85), 144 (75), 116 (100), 94 (97). Anal. calcd. for C₂₂H₁₂N₄O₃: C 69.47, H 3.16, N 14.74; found: C 69.21, H 3.03, N 14.53.

cis-2,5-Bis(2',3'-dicyanophenoxy)methyltetrahydrofuran (36)

Bisphthalonitrile **36** was prepared by Method II from 0.66 g (5 mmol) of *cis*-2,5-bis(hydroxymethyl)tetrahydrofuran (**30**) (**23**), 2.10 g (12.1 mmol) of **1**, and 2.40 g (17.4 mmol) of K₂CO₃ in 10 mL of DMSO at RT over a 10 day period. Work-up and recrystallization from methanol gave 820 mg (43%) of greyish-yellow crystalline **36** (TLC: 15% CH₃CN–Bz, $R_f = 0.55$), mp 186–188°C; FT-IR (cm⁻¹): 3085, 2977, 2879, 2226 (C≡N), 1563s, 1465s, 1260, 1100, 789; ¹H NMR (acetone-*d*₆)

δ : 7.81 (t, 2H, $J = 8$ Hz), 7.62 (d, 2H, $J = 8$ Hz), 7.53 (d, 2H, $J = 8$ Hz), 4.39 (m, 2H), 4.34 (m, 2H, $J = 4.2$ Hz), 4.29 (m, 2H, $J = 4.2$ Hz), 2.15 (m, 4H); ^{13}C NMR (acetone- d_6) δ : 162.44, 135.12, 126.36, 119.09, 117.11, 116.31, 114.20, 104.90, 78.69, 72.72, 28.30; +FAB-MS m/z (%): 385 ($M^+ + 1$, 100). Anal. calcd. for $\text{C}_{22}\text{H}_{16}\text{N}_4\text{O}_3$: C 68.75, H 4.17, N 14.58; found: C 68.65, H 4.16, N 14.24.

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