3.6 mmol) in CH_2Cl_2 (2 mL) at 0 °C. The mixture was warmed to room temperature and stirred overnight. The mixture was washed with dilute HCL, aqueous Na_2CO_3, and water, in this order. The solution was dried and evaporated, and the residue was subjected to dry column chromatography (silica gel, CH_2Cl_2–CCl_4, 3:1) to give 0.121 g (55%) of DTA: colorless crystals; mp 137–138 °C (EtOH); ^1H NMR δ 7.23 (t, J = 4.4 Hz, 2 H), 7.83 (dd, J = 4.8, 0.9 Hz, 2 H), 8.04 (dd, J = 3.8, 0.9 Hz, 2 H); ^{13}C NMR δ 83.4 (s), 128.8 (d), 136.7 (d), 136.9 (d), 143.7 (s), 168.0 (s); IR (KBr) 1640 cm^{-1} (C═O); MS m/z (relative intensity) 246 (M^+, 45), 190 (29), 135 (28), 111 (100), 83 (18). Anal. Calcd for $C_{12}H_6O_2S_2$: C, 58.52; H, 2.46. Found: C, 58.37; H, 2.62.

Reaction of 1f with Di-2-thenoylacetylene (DTA). A mixture of **1f** (0.296g, 0.632 mmol) and DTA (0.187 g, 0.76 mmol) in xylene (50 mL) was refluxed for 6 h under N_2. The mixture was cooled to room temperature and evaporated. The dark-purple residue was subjected to dry column chromatography (silica gel, CH_2Cl_2–CCl_4, 1:1 and then 2:1) to give 41 mg of unreacted **1f** and 265 mg (62%) of 5,6-di-2-thenoyl-1,3,4,7-tetra-2-thienylbenzo[*c*]thiophene (**16**). **16**: yellow crystals; mp 310–311 °C (CH_2Cl_2–hexane); ^1H NMR δ 6.54 (br s, 2 682 (dd, J = 3.7, 0.9 Hz, 2 H), 6.71 (dd, J = 5.2, 3.7 Hz, 2 H), 6.85 (br s, 4 H), 6.95 (d, J = 4.2 Hz, 2 H), 7.15 (dd, J = 5.2, 0.9 Hz, 2 H), 7.34 (d, J = 3.2 Hz, 2 H), 7.45 (d, J = 4.6 Hz, 2 H); IR (KBr) 1660 cm^{-1} (C═O); UV–vis (CH_2Cl_2) λ_{max} (nm) (log ϵ) 423 (4.18), 295 (4.70), 250 (sh, 4.75); MS m/z (relative intensity) 682 (M^+, 100); HRMS calcd for $C_{34}H_{18}O_2S_7$ m/z 681.9352, found 681.9360. Anal. Calcd for $C_{34}H_{18}O_2S_7$: C, 59.80; H, 2.66. Found: C, 59.08; H, 2.80.

Reaction of 1f and 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). To a degassed solution of DDQ (19.4 mg, 0.085 mmol) in CH_2Cl_2 (10 mL) was added degassed solution of **1f** (40.0 mg, 0.085 mmol) in CH_2Cl_2 (15 mL). The mixture was stirred at room temperature overnight. By filtration of the mixture, 8.3 mg of black precipitates were collected. Adding hexane to the filtrate yielded an additional amount (0.9 mg) of the brown powder: mp >360 °C. Anal. Found: C, 45.06; H, 1.64; N, 7.12.

Syntheses of Monometalated and Unsymmetrically Substituted Binuclear Phthalocyanines and a Pentanuclear Phthalocyanine by Solution and Polymer Support Methods

Clifford C. Leznoff,*[†] Polina I. Svirskaya,[†] Ben Khouw,[†] Ronald L. Cerny,[‡] Penny Seymour,[†] and A. B. P. Lever[†]

Department of Chemistry, York University, North York (Toronto), Ontario, Canada M3J 1P3, and Midwest Center for Mass Spectrometry, University of Nebraska—Lincoln, Lincoln, Nebraska 68558

Received February 5, 1990

Binuclear phthalocyanines in which two different phthalocyanine nuclei are covalently linked through five-atom bridges, derived from 2-ethyl-2-methylpropane-1,3-diol, are prepared. In the examples, one phthalocyanine ring is always substituted with neopentoxy substituents, while the other phthalocyanine ring is unsubstituted or contains *tert*-butyl substituents or a neopentoxy-substituted copper phthalocyanine, constituting a binuclear phthalocyanine in which only one ring is metalated. The precursor, 2-(2-(hydroxymethyl)-2-methylbutoxy)-9,16,23-trineopentoxyphthalocyanine was prepared in solution and also by solid-phase methods, using polymer-bound trityl chloride derived from a 1% divinylbenzene-co-styrene copolymer. A metal-free pentanuclear phthalocyanine, in which four phthalocyaninyl groups are covalently bound to the four benzo groups of a central phthalocyanine nucleus, is described and characterized by FAB mass spectroscopy. In some experiments some rare examples of demetalation of some zinc phthalocyanines are noted during phthalocyanine formation. A modified flash chromatography procedure proved to be useful for separating similarly substituted mononuclear phthalocyanines.

Using face-to-face porphyrin dimers, held together by a pair of covalent amide bridges[1,2] or by a single rigid aromatic bridge,[3,4] the four-electron reduction of dioxygen to water, without forming free hydrogen peroxide, has been achieved. In most examples, it was the dicobalt porphyrin dimers that were the active catalysts. Collman et al.[5] have shown that a mixed metal cobalt–silver cofacial porphyrin dimer may also be an interesting catalyst.

As the porphyrin dimer catalysts tend to decompose after several cycles, we have been attempting to find similar catalysts that would be more stable under similar conditions. To this end we have prepared, for the first time, a whole series of binuclear phthalocyanines[6-8] (Pcs), covalently linked by 5, 4, 3, 2, 1, 0 and "–1" bridges and a unique tetranuclear phthalocyanine.[9] To date, however, none of the multinuclear Pcs have achieved the desired four-electron of O_2, although the two-electron reduction of many of the multinuclear Pcs have been more efficient[9,10] relative to simple mononuclear Pcs. Perhaps, this fact is not too surprising as only a very few of the porphyrin dimers prepared by Collman's group[1,2] were good catalysts and it is difficult to predict the exact cofacial

---

[†] York University.

[‡] Midwest Center for Mass Spectrometry.

(1) Collman, J. P.; Denisevich, P.; Konai, Y.; Marrocco, M.; Koval, C.; Anson, F. C. *J. Am. Chem. Soc.* **1980**, *102*, 6027.

(2) Collman, J. P.; Anson, F. C.; Bencosme, S.; Chong, A.; Collins, T.; Denisevich, P.; Evitt, E.; Geiger, T.; Ibers, J. A.; Jameson, G.; Konai, Y.; Koval, C.; Meier, K.; Oakley, P.; Pettman, R. B.; Schmittou, E.; Sessler, J. In *Organic Synthesis Today and Tomorrow*; Trost, B. M., Hutchinson, C. R., Eds.; Pergamon: Oxford, 1981. Bencosme, C. S.; Collman, J. P.; Anson, F. C. *J. Am. Chem. Soc.* **1983**, *105*, 2710.

(3) Chang, C. K.; Abdalmuhdi, I. *J. Org. Chem.* **1983**, *48*, 5388. Chang, C. K.; Liu, H. Y.; Abdalmuhdi, I. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 164.

(4) Fillers, J. P.; Ravichandran, K. G.; Abdalmuhdi, I.; Tulinsky, A.; Chang, C. K. *J. Am. Chem. Soc.* **1986**, *108*, 417.

(5) Collman, J. P.; Bencosme, C. S.; Durand, R. R., Jr.; Kreh, R. P.; Anson, F. C. *J. Am. Chem. Soc.* **1983**, *105*, 2699.

(6) Leznoff, C. C. In *Phthalocyanines-Properties and Applications*; Leznoff, C. C., Lever, A. B. P., Eds.; Verlag Chemie: New York, 1989; Chapter 1.

(7) Leznoff, C. C.; Marcuccio, S. M.; Greenberg, S.; Lever, A. B. P.; Tomer, K. B. *Can. J. Chem.* **1985**, *63*, 623.

(8) (a) Marcuccio, S. M.; Svirskaya, P. I.; Greenberg, S.; Lever, A. B. P.; Leznoff, C. C.; Tomer, K. B. *Can. J. Chem.* **1985**, *63*, 3057. (b) Leznoff, C. C.; Lam, H.; Marcuccio, S. M.; Nevin, W. A.; Janda, P.; Kobayashi, N.; Lever, A. B. P. *J. Chem. Soc., Chem. Commun.* **1987**, 699. (c) Lam, H.; Marcuccio, S. M.; Svirskaya, P. I.; Greenberg, S.; Lever, A. B. P.; Leznoff, C. C.; Cerny, R. L. *Can. J. Chem.* **1989**, *67*, 1087.

0022-3263/91/1956-0082$02.50/0

geometry, necessary for a four-electron reduction, beyond saying that the metal centers of the two macrocycles should be between 3.5 and 5.0 Å. As mixed metal and other unsymmetrically substituted binuclear Pcs had not previously been prepared, we wished to examine their synthesis toward the goal of suggesting to us a suitable geometry for achieving a four-electron reduction of O_2 by stable Pcs. In addition, all previous binuclear Pcs had bulky neopentoxy substituents, and we believed that the bulky groups were preventing the two Pc rings from achieving complete cofaciality. We felt that it might be possible to prepare a binuclear Pc containing only one ring having bulky neopentoxy[11] groups, while the other ring was unsubstituted except for the bridge, and that the one ring containing bulky groups would be sufficient to enable the binuclear Pc to be soluble enough for isolation and purification. Although most porphyrin mixed metal dimers are most easily made by cyclization of two separate porphyrin monomers containing different metals,[1,12a] other methods include a cyclization procedure yielding a mixture of separable porphyrin dimers[12b] and an interesting example in which a silver porphyrin is used as a protecting group in the synthesis of mixed metal porphyrin dimers.[5] Like porphyrin dimers can be separated by chromatography,[12b] but the more highly aggregating[9,13] Pcs would be difficult to separate by this method. Binuclear Pcs are prepared by the simultaneous formation of the two Pc rings from a bridged bisphthalonitrile,[8] and hence methods similar to those used in porphyrin chemistry[14] are not yet applicable, and, lastly, the formation of Pcs[15] occurs at higher temperatures (150 °C) than porphyrins so that the likelihood of transmetalation is high and, as shown below, this complication did arise.

Results and Discussion

Our strategy for the synthesis of binuclear Pcs, containing differently substituted Pc rings, was based on some of our earlier work[16] in which very rare unsymmetrical mononuclear Pcs, containing one unique "handle" or functionally active substituent, was prepared using polymer-bound trityl chloride as a supporting blocking group.[17] In this way, first one Pc ring containing one group of substituents or metal can be prepared followed by the stepwise elaboration of the second Pc nucleus containing no metal or different substituents.

Preparation of Mononuclear Phthalocyanines. Treatment of 4-nitrophthalonitrile (1)[16] with excess 2-ethyl-2-methylpropane-1,3-diol (2) and base gave the desired hydroxy ether 3 and some bis ether 4.[7] Hydroxy ether 3 was protected using trityl chloride (TrCl) (5) in pyridine[19] or polymer-supported TrCl (6)[17] and 4-(dimethylamino)pyridine (DMAP) as catalyst[20] to give 7 and 8, respectively (Scheme I). Phthalonitriles 7 and 8 and the unprotected phthalonitrile 3 were converted[20,22] to their respective diiminoisoindolines 9–11. Self-condensation of 9 or 11 in 2-(dimethylamino)ethanol (DME) under standard conditions[6,21] gave the tetrakis(trityloxy)phthalocyanine 12 and the tetrahydroxyphthalocyanine 13, respectively. Furthermore, the trityl groups of 12 could be removed under very mild conditions with iodotrimethylsilane $[(CH_3)_3SiI]$,[23] giving the free tetrahydroxyphthalocyanine 13. This cleavage procedure does not cleave neopentoxy[11] groups and is thus compatible with the planned synthesis of unsymmetrical binuclear Pcs described below (Scheme I). Treatment of 13 with zinc acetate $Zn(OAc)_2$ in toluene gave the tetrahydroxy Zn derivative 14. Compound 14 was recently tested[24] for its efficiency as a possible candidate for use in photodynamic therapy, but its synthesis is described herein for the first time.

Condensation of the insoluble polymer-bound diiminoisoindoline 10 with a large excess of 5-neopentoxy-1,3-diiminoisoindoline (15)[6] (derived from 4-neopentoxyphthalonitrile[6,25]) as previously described[16] gave the unsymmetrically substituted polymer-bound Pc 16 and the symmetrical 2,9,16,23-tetraneopentoxyphthalocyanine[11] (17), formed by self-condensation of 15 (Scheme II). Filtration and Soxhlet extraction of polymer 16 removed all of 17 from 16. Cleavage of 16 with trimethylsilyl iodide as for 8 and 12 yielded the desired monohydroxytrineopentoxyphthalocyanine[11] 18 in 18% yield, from which the Zn(II) 19 was formed. In addition, the cleavage of 16 gave, after very extensive chromatographic separations (see the Experimental Section) 18, and dihydroxydineopentoxyphthalocyanines 20 and 21 as a mixture of inseparable isomers which can be designated as the "adjacent" isomers 20 and the "opposite" isomers 21 using a terminology recently proposed for similar isomers in the porphyrin series.[26] As a comparison, condensation of 11 and excess 15 as before in a homogeneous solution gave a more complex mixture of substituted Pcs. In another experiment 10 condensed with a small excess of 15 to see if the polymer-bound isoindoline would self-condense. In fact, substantial self-condensation did occur. Extensive chromatographic separation procedures not only gave pure samples of 17, 18, 20, and 21, isolated from the polymer-supported experiment using a large excess of 15 above, but also small samples of a trihydroxyneopentoxyphthalocyanine 22 and even the symmetrical tetrahydroxyphthalocyanine 13, prepared from the polymer supported experiment using a small excess of 15 (Scheme II). As envisioned the polymer-bound reaction was cleaner, giving fewer condensation products than a similar solution condensation, but the formation of 20 and 21 still shows that even on a polymer support conformational mobility is sufficiently high that two, and even more polymer-bound

---

(9) Nevin, W. A.; Liu, W.; Greenberg, S.; Hempstead, M. R.; Marcuccio, S. M.; Melnik, M.; Leznoff, C. C.; Lever, A. B. P. *Inorg. Chem.* **1987**, *26*, 891.

(10) Janda, P.; Kobayashi, N.; Auburn, P. R.; Lam, H.; Leznoff, C. C.; Lever, A. B. P. *Can. J. Chem.* **1989**, *67*, 1109.

(11) Neopentoxy is 2,2-dimethylpropoxy.

(12) (a) Ward, B.; Wang, C.-B.; Chang, C. K. *J. Am. Chem. Soc.* **1981**, *103*, 5236. (b) Landrum, J. T.; Grimmett, D.; Haller, K. J.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1981**, *103*, 2640.

(13) Giraudeau, A.; Lovati, A.; Gross, M.; Andre, J. J.; Simon, J.; Su, C. H.; Kadish, K. M. *J. Am. Chem. Soc.* **1983**, *105*, 2917. Abkowitz, M.; Monahan, A. R. *J. Phys. Chem.* **1973**, *58*, 2281.

(14) *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. 1.

(15) Moser, F. H.; Thomas, A. L. *Phthalocyanine Compounds*; Reinhold: New York; Chapman and Hall: London, 1963. Moser, F. H.; Thomas, A. L. *The Phthalocyanines*; CRC: Boca Raton, 1983; Vol. 1, p 2. Lever, A. B. P. *Adv. Inorg. Chem. Radiochem.* **1965**, *7*, 27.

(16) Hall, T. W.; Greenberg, S.; McArthur, C. R.; Khouw, B.; Leznoff, C. C. *Nouv. J. Chim.* **1982**, *6*, 653.

(17) Fyles, T. M.; Leznoff, C. C. *Can. J. Chem.* **1976**, *54*, 935.

(18) Siegl, W. O. *J. Heterocycl. Chem.* **1981**, *18*, 1613.

(19) Michelson, A. M.; Todd, A. R. *J. Chem. Soc.* **1953**, 951. Weimann, G.; Khorana, H. G. *J. Am. Chem. Soc.* **1962**, *84*, 419.

(20) Chaudhary, S. K.; Hernandez, O. *Tetrahedron Lett.* **1979**, 95. Hernandez, O.; Chaudhary, S. K.; Cox, R. H.; Porter, J. *Tetrahedron Lett.* **1981**, *22*, 1491.

(21) Brach, P. J.; Grammatica, S. J.; Ossanna, O. A.; Weinberger, L. *J. Heterocycl. Chem.* **1979**, *7*, 1403.

(22) Pawlowski, G.; Hanack, M. *Synthesis* **1980**, 287.

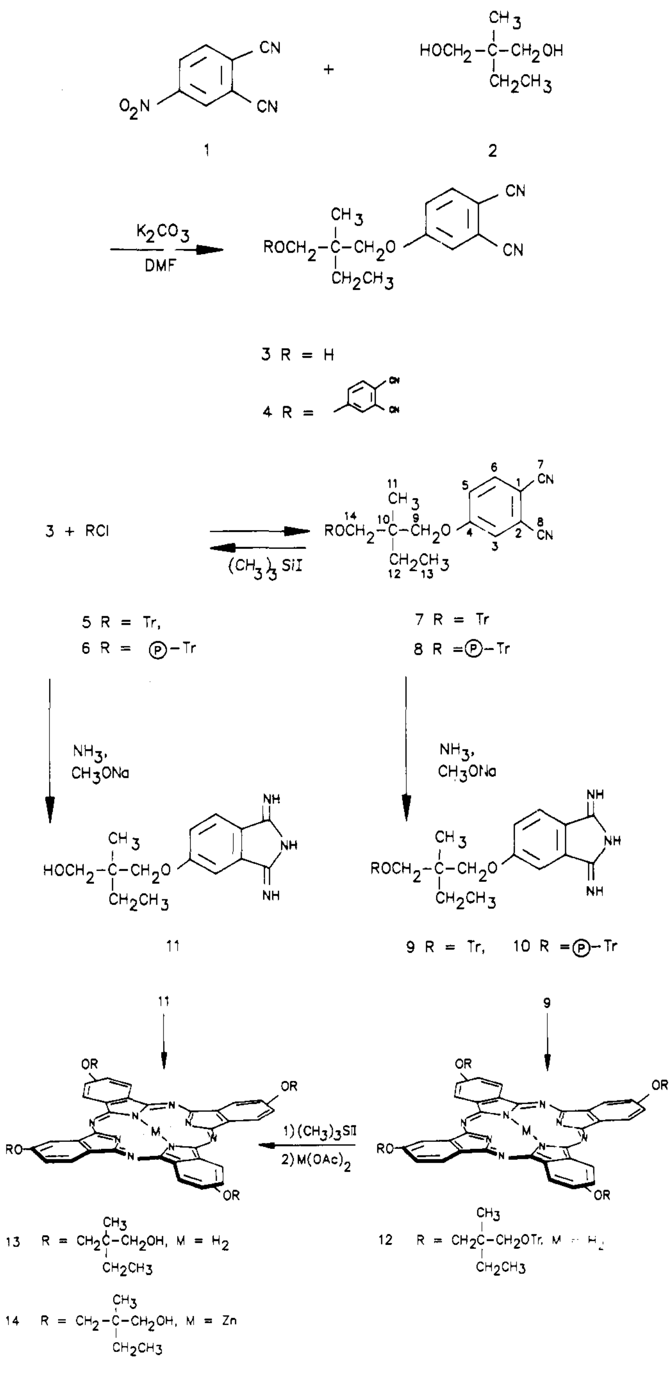
(23) Jung, M. E.; Lyster, M. A. *J. Org. Chem.* **1977**, *42*, 3761.

(24) Leznoff, C. C.; Vigh, S.; Svirskaya, P. I.; Greenberg, S.; Drew, D. M.; Ben-Hur, E.; Rosenthal, I. *Photochem. Photobiol.* **1989**, *49*, 279.

(25) Barger, W. R.; Snow, A. W.; Wohltjen, H.; Jarvis, N. L. *Thin Solid Films* **1985**, *133*, 197.

(26) Milgrom, L. R.; Mofidi, N.; Jones, C. C.; Harriman, A. *J. Chem. Soc. Perkim Trans. 2* **1989**, 301.

Scheme I



groups can participate in the condensation, depending on the reaction conditions.

Chromatographic Separation of Different Mononuclear Phthalocyanines. In general, the separation of different substituted mononuclear Pcs from each other by any method including extensive chromatography is difficult,[27] although a few successful examples have been reported.[27-30] It is believed that aggregation phenomena inhibit clean separations and even single spots on thin-layer chromatography (TLC) can actually be mixtures of compounds. Examination of these fractions by mass spectroscopy (MS) has in some cases delineated possible contamination by other Pc compounds.[27] Since mononuclear Pcs **13**, **17**, **18**, **20**, and **21**, and **22**, all contain different numbers of hydroxy groups it was felt that chromatographic separation of *this* mixture produced in the mixed condensation of **11** and **15** might be possible. We have previously found[16] that vacuum liquid chromatography[31] was a powerful tool for the chromatographic separation of very similar compounds including Pcs, but the procedure was tedious and elution times slow. We slightly changed the flash chromatography procedure of Still et al.[32] in a manner similar to, but not identical with, Taber's modification[33] in packing the columns used for flash chromatography. Mainly, the columns are packed with flash chromatography grade silica (20–45 μm) *under vacuum* for several minutes (see the Experimental Section). Under these conditions, separations of organic compounds approached the resolution of vacuum liquid chromatography but at elution rates of flash chromatography. Each fraction isolated was analyzed by MS so that pure samples of **13**, **17**, **18**, **20** and **21**, and **22** could be obtained and mixed fractions could be rechromatographed. It should be noted that the possible "adjacent" and "opposite" isomers **20** and **21** could not be separated, and characterization rests solely on MS and elemental analysis. Each one of **13**, **17**, **18**, and **20–22** itself exists as a mixture of very closely related regioisomers[34] which in all cases show up as one spot on TLC. For compound **18**, however, we noted that silica TLC of pure **18** on most TLC plates exhibited one spot, but on some brands (Eastman Kodak) three very closely distinct bands developed and were separated by preparative TLC. MS of all three bands gave identical spectra consistent with structure **18**. Compound **18** could exist as a mixture of eight closely related regiomers, and it is possible that these distributed themselves into three fractions. Examination of each of these bands and also of the **20** and **21** mixture by NMR spectroscopy did not aid us in identifying specific isomers of **20** and **21** or of any regiomers of **13**, **17**, **18**, and **22**.

Preparation of Unsymmetrical Binuclear Phthalocyanines. Treatment of a mixture of **1** and **18** with K_2CO_3 in dimethylformamide (DMF) for 5 days at room temperature led to a metal-free monophthalonitrilo-substituted Pc **23** (Scheme III). Metal insertion of Zn and Cu into metal-free **23** was readily achieved by heating **23** with Zn and Cu acetate **24** and **25**, respectively. Conversion of the monophthalonitrilo-substituted Pcs **23–25** into their diiminoisoindolino Pcs **26–28**, respectively, was accomplished as for **9–11** above except that dioxane or tetrahydrofuran (THF) was required as a cosolvent to effect solubilization of the poorly soluble **23–25** in methanol. The key mixed condensation reactions of **26** with a large excess of the simple diiminoisoindolines **29** and **30**, derived from 4-*tert*-butylphthalonitrile and phthalonitrile, respectively, under standard conditions for binuclear Pc formation gave the unsymmetrical binuclear Pcs **31** and **32**, respectively, along with the simple mononuclear Pcs **33** and **34**, derived from self-condensation of **29** and **30**. The preparation of binuclear Pc **31** proceeded smoothly as expected as both neopentoxy and *tert*-butyl groups are bulky and facilitate solubilization of Pcs. Binuclear Pc **32** was predictably less soluble due to the lack of substituents on one ring, and this fact led to losses in the purification steps so that the ul-

---

(27) Leznoff, C. C.; Greenberg, S.; Khouw, B.; Lever, A. B. P. *Can. J. Chem.* **1987**, *65*, 1705.

(28) Piechocki, C.; Simon, J. *J. Chem. Soc., Chem. Commun.* **1985**, 259.

(29) Allcock, H. R.; Neenan, T. X. *Macromolecules* **1986**, *19*, 1496.

(30) Duggan, P. J.; Gordon, P. F. Eur. Pat. Appl. 1985, EP 155780; *Chem. Abstr.* **1987**, *105*, 70242r.

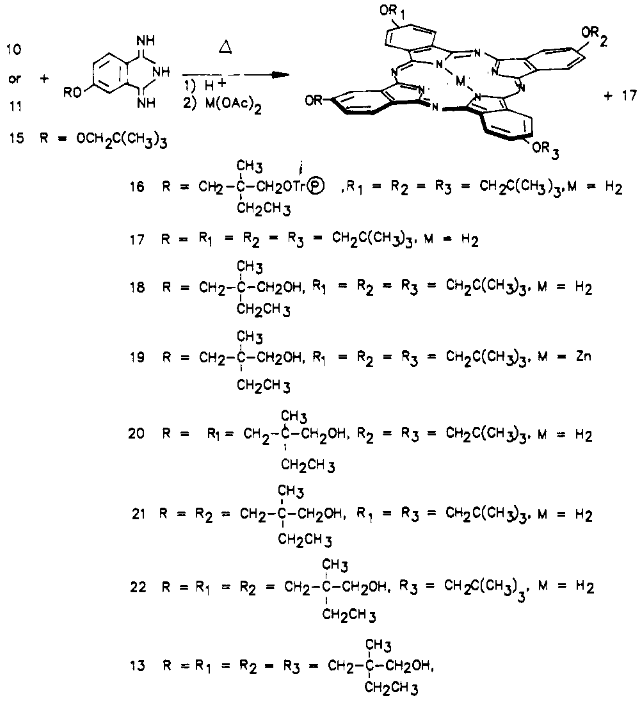
(31) Targett, N. M.; Kilcoyne, J. P.; Green, B. *J. Org. Chem.* **1979**, *44*, 4692.

(32) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(33) Taber, D. T. *J. Org. Chem.* **1982**, *47*, 1351.

(34) Greenberg, S.; Lever, A. B. P.; Leznoff, C. C. *Can. J. Chem.* **1988**, *66*, 1059; Gaspard, S.; Maillard, Ph. *Tetrahedron* **1987**, *43*, 1083.

Scheme II



timate isolated yield of pure **32** was only 1.8%. The ultraviolet–visible (UV–vis) spectrum of binuclear **32** was surprising and appeared similar to metal-free *mononuclear* Pcs. These data indicate to us that **32** does not have a cofacial conformation at all and exhibits the characteristics of two Pc rings separated by an infinitely long chain. It thus appears that the bulky neopentoxy, *tert*-butyl, and other groups actually *promote* cofacial conformations. Our recent synthesis of a binuclear Pc, containing two Pc rings having no substituents, except for a very bulky group in the *bridge* affording solubility, shows a similar lack of cofacial behavior.[35]

The reactions of the Zn Pc **27** or the Cu Pc **28** with an excess of the diiminoisoindoline **15** in mixed condensations led in the former case to a, as previously described,[6] *symmetrical* binuclear Pc **35** *devoid* of Zn as determined by fast-atom bombardment (FAB) MS but gave the desired monocopper binuclear Pc **37** in the latter example. Careful examination of the mononuclear Pc fractions produced in these reactions, exhibited the expected formation of metal-free **17**, from self-condensation of **15**, but some 2,9,16,23-tetraneopentoxyphthalocyaninatozinc(II) (**36**) was also detected by FAB MS for the reaction with **27**. Transmetalation from **27** to **36** through unknown pathways had obviously occurred.[36]

Preparation of a Pentanuclear Phthalocyanine. When the tetrahydroxyphthalocyanine **13** was mixed with excess **1** and K_2CO_3 in DMF for 7 days, all four hydroxy groups of **13** displaced the nitro group of **1** to afford the metal-free tetraphthalonitrilophthalocyanine **38** in 87% yield. Treatment of **38** with Zn or Cu salts led to the Zn and Cu Pcs **39** and **40**, respectively. Compounds **38–40** were readily converted to their respective tetrakis(diiminoisoindolines) **41–43**. Condensation of **41** with an excess of **15** led to the first known pentanuclear Pc **44** (Scheme IV) in 12% yield, although pentanuclear porphyrins[37] and a mixed tetraporphyrinylphthalocyanine[38] have been recently described.

An attempt to make the pentanuclear Pc in which the core Pc ring contained Zn and the peripheral Pc rings were metal-free gave metal-free **44**. Again Zn demetalation occurred under the condensation reaction conditions.[36]

Spectroscopic Properties of the Phthalocyanines. The infrared (IR), nuclear magnetic resonance (NMR), and FAB mass spectra were consistent with the structures of the binuclear and multinuclear Pcs previously described.[7,8] The UV–vis spectrum of **37** shows two prominent peaks in the Q-band region (see the Experimental Section) typical of an aggregated (cofacial and intramolecular),[39] dimetalated binuclear Pc, and indicative of close contact between the Cu and metal-free halves of the molecule. The only evidence of the presumed lower symmetry of this species is a weak shoulder near 704 nm.

Metal-free Pcs fluoresce strongly from the Q band.[15] Relative to mononuclear species **17**, under the same concentration conditions (ca. 2×10^{-6} M in toluene/ethanol (3:2 v/v), and corrected for inner filter effects, the binuclear metal-free species **35** emits at essentially the same wavelength (709 nm) but with some 10% of the intensity of the mononuclear species. Evidently there is significant intramolecular quenching. Copper Pcs are not expected to emit due to the presence of low-lying d states. The monocopper species **37** does in fact emit (at 703 nm) with a corrected intensity approximately half that of the binuclear metal-free species **35**. One might conclude that the emission from the metal-free half of the molecule is largely but not totally quenched by the Cu half. However, it is possible that total quenching is occurring in cofacial conformers and that the emission comes from a very small concentration of open, nonaggregated conformers, which do not show up in the absorption spectrum.

Conclusion

The synthesis of the monohydroxymethyl-substituted Pcs **18** and **19** by solution and solid-phase methods and their separation from byproducts **20–22** by a modified flash chromatographic procedure has allowed us to prepare, via **18**, binuclear Pcs in which each Pc ring has different substituents and in one example one metal and no metal. Fluorescence spectroscopy showed this latter compound (**37**) was largely but not completely quenched by the lone Cu atom. The first known pentanuclear Pc **44** was prepared and characterized.

Experimental Section

General Methods. General experimental conditions and spectroscopic instrumentation used have been described.[8c] All solvents used were freshly distilled, salts were anhydrous, and reactions were conducted under argon.

4-(2-(Hydroxymethyl)-2-methylbutoxy)benzene-1,2-dicarbonitrile (3) [4-(2-(Hydroxymethyl)-2-methylbutoxy)phthalonitrile]. To a solution of 5.19 g (30 mmol) of 4-nitrophthalonitrile[16,40] (**1**) in 20 mL of DMF was added 5.30 g (45 mmol) of 2-ethyl-2-methyl-1,3-propanediol (**2**) and 10.5 g (75 mmol) of finely ground K_2CO_3. The K_2CO_3 was added in four equal portions

---

[35] Leznoff, C. C.; Greenberg, S. *Tetrahedron Lett.* **1989**, *30*, 5555.

[36] Preliminary control experiments indicated that the solubility of the Pc macrocycle, the nature of the encapsulated metal, and the presence of the bisdiiminoisoindolines under the conditions of Pc formation all play important roles in transmetalation, but an extensive detailed study of transmetalation in Pcs must await further studies.

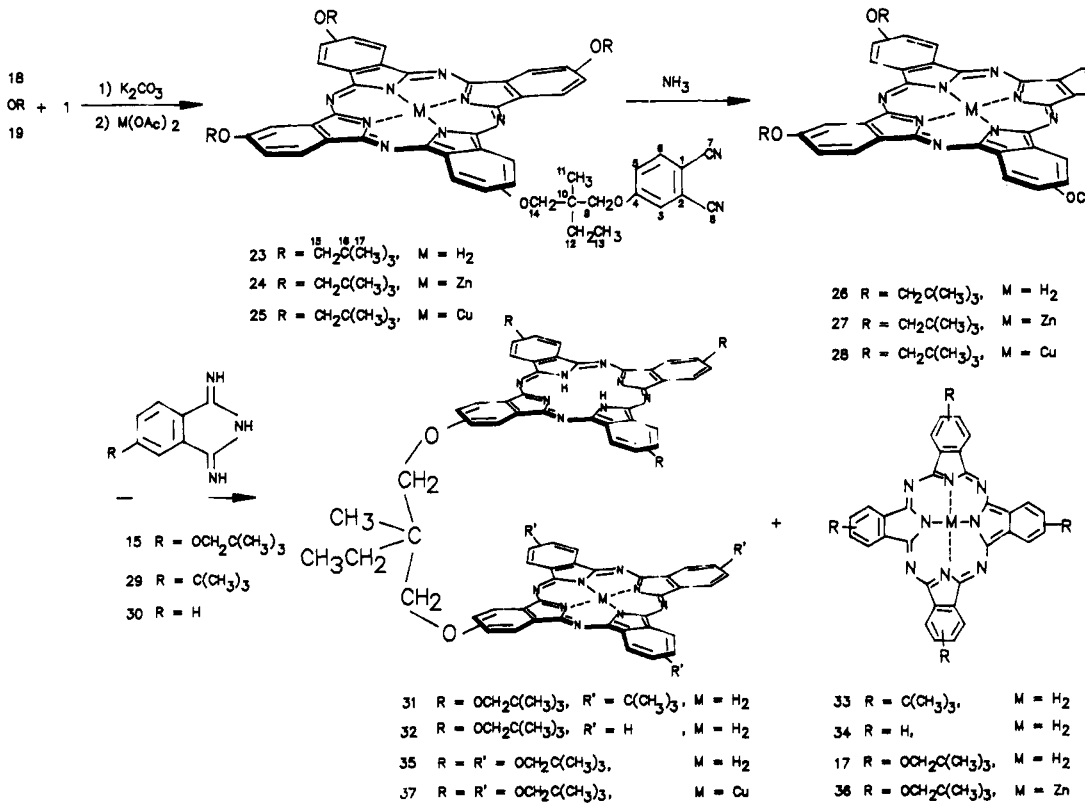
[37] Wennerström, O.; Ericsson, H.; Raston, I.; Svensson, S.; Pumlott, W. *Tetrahedron Lett.* **1989**, *30*, 1129. Milgrom, L. R. *J. Chem. Soc., Perkin Trans. 1* **1983**, 2535.

[38] Kobayashi, N.; Nishiyama, Y.; Ohya, T.; Sato, M. *J. Chem. Soc., Chem. Commun.* **1987**, 390.

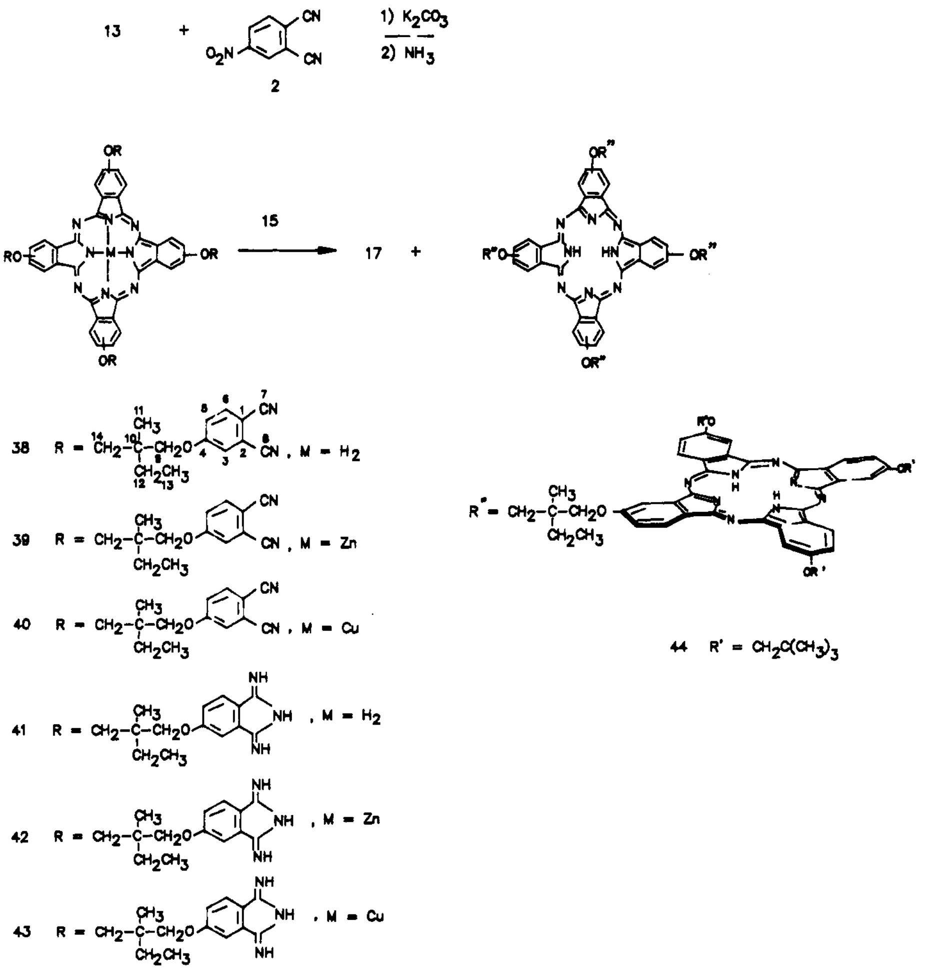
[39] Dodsworth, E. S.; Lever, A. B. P.; Seymour, P.; Leznoff, C. C. *J. Phys. Chem.* **1985**, *89*, 5698.

[40] Drew, H. D. K.; Kelly, D. B. *J. Chem. Soc.* **1941**, 639.

Scheme III



Scheme IV



at 12-h intervals, and the mixture was stirred at room temperature for a total of 48 h. The reaction mixture was filtered and washed four times with ethyl acetate. The filtrate was washed with 300 mL of cold water and brine and dried over magnesium sulfate. The crude product was purified by silica gel column chromatography (5 × 25 cm) using acetonitrile–benzene ($CH_3CN–C_6H_6$) (1:19) as eluant which gave 0.7 g of 1,3-bis(3,4-dicyanophenyl)-2-ethyl-2-methylpropane (**4**), mp 157–159 °C (lit.[7] mp 157–158 °C), and 1.5 g of a mixture of **3** and **4** (fraction 2).

Further elution with $CH_3CN–C_6H_6$ (1:9) gave 5.5 g of compound **3**. An additional 1.0 g of **3** was isolated by rechromatography of the above fraction 2. The combined fractions of **3** (6.5 g) were distilled as a clear, viscous oil to give 6.3 g (86%) of pure **3**, bp 195–205 °C (0.01 Torr, Kugelrohr apparatus): IR (neat, NaCl) ν_{max} 3450, 3060, 2900, 2240, 1600, 1500, 1250, 840 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.87–7.68 (m, 1 H, Ar H-5), 7.31–7.21 (m, 2 H, Ar H-3,6), 3.89 (q, 2 H, CH_2OAr), 3.55 (q, 2 H, CH_2OH, $J = 7$ Hz), 1.91 (s, 1 H, OH), 1.44 (q, 2 H, CH_2C, $J = 7$ Hz), 0.97 (s, 3 H, CH_3), 0.89 (t, 3 H, CH_3CH_2, $J = 7$ Hz); ^{13}C NMR ($CDCl_3$) ppm 162.0 (C_4), 134.7 (C_6), 119.4 (C_5), 119.1 (C_3), 116.3 (C_2), 115.3 + 114.8 (C_8, C_7), 105.8 (C_1), 72.9 (C_{14}), 65.3 (C_9), 38.5 (C_{10}), 25.8 (C_{12}), 17.5 (C_{11}), 6.3 (C_{13}); MS for $C_{14}H_{16}N_2O_2$ m/z (relative intensity) 244 (M^+, 41), 227 (64), 226 (47), 213 (4), 171 (88), 157 (100), 127 (94). Anal. Calcd for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 11.47. Found: C, 68.94; H, 6.77; N, 11.49.

4-(2-Methyl-2-((triphenylmethoxy)methyl)butoxy)benzene-1,2-dicarbonitrile (7) [4-(2-Methyl-2-((trityloxy)methyl)butoxy)phthalonitrile]. To a solution of 2.44 g (10 mmol) of **3** in 40 mL of dry pyridine (py) was added 4.0 g (14 mmol) of freshly prepared TrCl (**5**), and the mixture was stirred at room temperature for 48 h. The pyridine hydrochloride was filtered and washed with dry ethyl acetate, and the filtrate was evaporated under vacuum at 30–40 °C. The oily product was purified on silica gel using $CH_3CN–C_6H_6$, 1:19, as eluant to give 2 g (83%) of pure **7**, mp 105–106 °C: IR (KBr) ν_{max} 2220, 1600, 1490, 1450, 1300, 1250, 1000, 840 cm^{-1}; ^{1}H NMR δ 7.68–7.06 (m, 18 H, Ar), 3.89 (dd, 2 H, CH_2OAr), 3.05 (q, 2 H, CH_2OTr, $J = 7$ Hz), 1.52–1.38 (q, 2 H, CH_2CH_3), 0.97 (s, 3 H, CH_3), 0.77 (t, 3 H, CH_2CH_3, $J = 6$ Hz); ^{13}C NMR ($CDCl_3$) ppm 162.2 (C_4), 135.1 (C_6), 128.7 (Tr), 127.6 (Tr), 127.0 (Tr), 119.8 (C_5), 119.1 (C_3), 117.3 (C_2), 115.7 + 115.2 (C_8, C_7), 106.9 (C_1), 86.2 (Tr), 72.9 (C_{14}), 65.2 (C_9), 38.8 (C_{10}), 27.0 (C_{12}), 18.7 (C_{11}), 7.4 (C_{13}); MS for $C_{33}H_{30}N_2O_2$, m/z (relative intensity) 486 (M^+, 100), 409, 332, 255, 243. Anal. Calcd for $C_{33}H_{30}N_2O_2$: C, 81.45; H, 6.21; N, 5.75. Found: C, 81.47; H, 6.88; N, 5.80.

Polymer-Bound 4-(2-Methyl-4-((triphenylmethoxy)methyl)butoxy)benzene-1,2-dicarbonitrile (8). To 12 g (15.6 mmol of Cl/g) of freshly prepared polymer-bound TrCl (**6**)[17] in 100 mL of py–CH_2Cl_2 (1:1) was added 10 g (40.9 mmol) of **3** and 0.2 g of DMAP.[20] The suspension was stirred at room temperature for 48 h. The polymer was filtered and washed with py, CH_2Cl_2, and ethyl acetate to give filtrate A. The polymer was further washed with water, methanol, CH_3CN, and ether. The air-dried polymer was extracted in a Soxhlet apparatus with CH_2Cl_2, ethyl acetate, and THF for 5–6 h for each solvent. The polymer was washed with dry ether and air-dried to give 13.5 g of polymer **8**: IR (KBr) ν_{max} 2230 cm^{-1}; ^{13}C NMR δ 162.2 (C_4), 134.9 (C_6), 146.0 + 134.0 + 133.0 + 128.0 + 127.0 + 125.0 ($C_{polymer}$), 120.2 (C_5), 119.6 (C_3), 117.2 (C_2), 115.2 + 115.0 + (C_8, C_7), 107.0 (C_1), 73.0 (C_{14}), 66.9 (C_9), 38.7 (C_{10}), 26.9 (C_{12}), 18.7 (C_{11}), 8.3 (C_{13}).

From filtrate A, 8.0 g of **3** was recovered. The loading capacity of polymer **8** was determined by cleavage with $(CH_3)_3SiI$.[23] Thus 0.5 g of **8** in 5 mL of CH_2Cl_2 and 0.2 mL of $(CH_3)_3SiI$ was stirred at room temperature for 24 h to yield 65 mg of pure **3**, showing polymer **8** to have a loading capacity of 0.53 mmol/g for **3**.

1,3-Diiminoisoindolines 9, 10, and 11. Ammonia was bubbled into a stirred solution of 50 mg of Na in 50 mL of dry methanol and 0.97 g (2 mmol) of **7** for 1 h at room temperature and for 4 h under reflux conditions. Evaporation (with foaming) of the solvent gave 1.04 g of crude **9**.

To a solution of 250 mg of Na in 40 mL of methanol and 55 mL of THF was added 6.0 g of **8**. Ammonia was bubbled into the suspension as above, and the polymer was filtered, washed with THF, and vacuum-dried to give 6.0 g of green polymer **10**.

In a similar manner 2.0 g (82 mmol) of **3** reacted with NH_3 in a 1:2 mixture of methanol and THF (33 mL), containing 200 mg of sodium methoxide. The solvent was evaporated to give 2.0 g of the slightly green crude **11**.

In all examples reactions were continued until the crude 1,3-diiminoisoindolines did not exhibit nitrile absorptions in their IR spectra. Compounds **9**–**11** were used in condensation reactions without further purification.

2,9,16,23-Tetrakis(2-methyl-2-((triphenylmethoxy)methyl)butoxy)phthalocyanine (12). A solution of 1.04 g of crude **9** in 8 mL of 2-(dimethylamino)ethanol (DME) was heated for 48 h at 160 °C (oil bath). The dark blue reaction mixture was diluted with water, filtered, washed with water and CH_3CN (until the filtrate was colorless), dried, and purified by flash chromatography[32] using toluene as eluant to afford 0.47 g (40%) of a blue shining solid of pure **12**: UV–vis λ_{max} (CH_2Cl_2) 706 (log ϵ 5.14), 672 (5.16), 648 (4.85), 608 (4.66), 394 (4.78), 346 nm (5.01); IR (KBr) ν_{max} 3280 (NH), 3040, 2920, 1605, 1490, 1450, 1250, 1010 (NH), 840 cm^{-1}; ^{1}H NMR δ 9.4–8.4 (m), 7.74–7.24 (m), 3.89–3.84 (m), 3.55–3.51 (m), 1.46–1.44 (m), 0.99–0.97 (m), 0.92–0.87 (m), –1.34 (br); MS for $C_{132}H_{122}N_8O_8$ m/z (relative intensity) 1949 (M + 1, 13), 1706 (M – Tr, 16), 1464 (M – 2Tr + 1, 19), 1222 (M – 3Tr + 2, 28), 980 (M – 4Tr + 3, 100), 879. Anal. Calcd for $C_{132}H_{122}N_8O_8$: C, 81.36; H, 6.31; N, 5.75. Found: C, 81.16; H, 6.49; N, 5.85.

2,9,16,23-Tetrakis(2-(hydroxymethyl)-2-methylbutoxy)phthalocyanine (13). Condensation of 2.0 g of crude 1,3-diiminoisoindoline **11** in 6 mL of DME as for **9** gave after partial purification by flash chromatography using THF as eluant, a crude product. Further purification on a second column, using hexane–THF, 1:3, as eluant, gave 0.78 g (42%) of a dark solid, soluble in dimethyl sulfoxide (DMSO) and py, slightly soluble in methanol and ethanol, and insoluble in toluene, C_6H_6, ether, and CH_3CN, as pure **13**: UV–vis λ_{max} (EtOH) 702 (log ϵ 4.57), 664 (4.64), 638 (4.60), 384 (4.32), 336 nm (4.70); IR (KBr) ν_{max} 3290 (NH), 1610, 1240, 1100, 1010 (NH), 825 cm^{-1}; ^{1}H NMR (pyridine-d_5) δ 8.71–7.02 (br), 6.40 (s), 4.44–4.35 (m), 4.17–4.14 (m), 2.01–1.96 (m), 1.58–1.44 (m), 1.29–1.23 (m), –3.47 (s); ^{13}C NMR (pyridine-d_5) ppm 161.3 (C_4), 147.4 + 137.5 + 127.5 + 125.9 + 118.0 + 105.8 + 105.4 (aromatic C), 72.7 (C_{14}), 66.3 (C_9), 30.8 (C_{10}), 27.4 (C_{12}), 19.3 (C_{11}), 8.5 (C_{13}); MS for $C_{56}H_{66}N_8O_8$ m/z (relative intensity) 980 (M + 1, 69), 950 (100), 878 (40), 848 (53), 778 (17). Anal. Calcd for $C_{56}H_{66}N_8O_8$: C, 68.68; H, 6.79; N, 11.44. Found: C, 68.96; H, 7.19; N, 11.56.

In a different preparation of **13**, 30 mg of pure **12** in 5 mL of CH_2Cl_2 was stirred with 0.2 mL of $(CH_3)_3SiI$ to afford 30 mg of a crude product. Flash chromatography using THF as eluant yielded 20 mg of pure **13**, identical in all respects with **13** prepared above.

2,9,16,23-Tetrakis(2-(hydroxymethyl)-2-methylbutoxy)phthalocyaninatozinc(II) (14). To 98 mg (0.1 mmol) of **13** in 5 mL of a 1:2 mixture of 2-methoxyethanol–toluene was added 55 mg (0.2 mmol) of $Zn(OAc)_2$. The mixture was stirred at 110–115 °C for 30 h. The total cooled reaction mixture was applied to a 1-cm diameter flash chromatography column and eluted with ether, which removes reactant solvent and impurities. Further elution with freshly distilled THF–hexane, 3:2, gave 92 mg (88%) of a dark blue solid (more soluble in organic solvents than **13**) as pure **14**:[24] UV–vis λ_{max} (EtOH) 682 (log ϵ 5.14), 672 (5.10), 616 (4.45), 352 (4.82), 288 nm (4.38); IR (KBr) ν_{max} 1600, 1250, 1100, 1060, 750 cm^{-1}; MS for $C_{56}H_{64}N_8O_8Zn$ m/z (relative intensity) 1040, 1041, 1042 (48), 940 (100), 840 (100), 740. Anal. Calcd for $C_{56}H_{64}N_8O_8Zn$: C, 64.51; H, 6.19; N, 10.75; Zn, 6.27. Found: C, 64.30; H, 6.40; N, 11.00; Zn, 5.79.

Polymer-Bound 4-(2-Methyl-2-((triphenylmethoxy)methyl)butoxy)phthalocyanine (16). Using a method previously described for mixed condensations of polymer-bound 1,3-diiminoisoindolines,[16] a slurry of 2.0 g (1.06 mmol) of **10** and 4.1 g (19 mmol, 6 times excess) of 5-neopentoxy-1,3-diiminoisoindoline[11] (**15**)[7] in 26 mL of a 1:1 mixture of DME and DMF was stirred under reflux conditions (bath temperature 160 °C) for 48 h. After the suspension was cooled to room temperature, polymer **16** was filtered and washed twice with DMF, at least 10 times with water, methanol, and CH_3CN to afford filtrate A. Further washing with ether, THF, and ether again gave filtrate B. Filtrate B was evaporated to give a dark blue solid. Filtrate A was diluted with a large volume of water and the dark blue precipitate was filtered, washed with water and CH_3CN, and combined with the product for filtrate B. This crude dark blue material was extracted in a Soxhlet extractor with methanol and then with CH_3CN until the filtrates were clear. Purification of the residue by flash chromatography using toluene–hexane, 3:1, as eluant gave 2.1 g (52%) of pure 2,9,16,23-tetraneopentoxyphthalocyanine (**17**)[7,25] as a dark, blue solid.

The black polymer **16** was extracted in a Soxhlet extractor successively with ether, CH_2Cl_2, toluene, and THF until the extract was colorless (ca. 3–5 h for each solvent). The black residue was finally washed with ether and dried to give 2.2 g of black polymer **16**.

2,9,16-Tris(2,2-dimethylpropoxy)-23-(2-(hydroxymethyl)-2-methylbutoxy)phthalocyanine[11] (18), 2,9-Bis(2,2-dimethylpropoxy)-16,23-bis(2-(hydroxymethyl)-2-methylbutoxy)phthalocyanine[11] (20) + 2,16-Bis(2,2-dimethylpropoxy)-9,23-bis(2-(hydroxymethyl)-2-methylbutoxy)phthalocyanine[11] (21). A suspension of 1.9 g of polymer **16** in 20 mL of CH_2Cl_2 and 0.5 mL of $(CH_3)_3SiI$ was stirred for 24 h. The polymer was filtered, washed with CH_2Cl_2 and ether, and extracted in a Soxhlet extractor first with toluene and finally with THF until the extracts were clear. A green polymer (1.5 g) was recovered and air-dried. The combined extracts were evaporated to dryness to yield 0.4 g of a green-blue residue, which was washed with water and CH_3CN until colorless. The resulting residue (0.27 g) was dissolved in toluene, preabsorbed on silica gel, and purified by flash chromatography using a 1.5 × 25 cm column. Elution with toluene afforded a trace (3–4 mg) of **17**. Further elution with 2-methoxyethanol–toluene (1:199 to 1:49) gave 170 mg of a middle fraction (B) while continued elution with 2-methoxyethanol–toluene (3:97 to 1:19) yielded 70 mg of a final fraction (C). Each fraction was analyzed by TLC, UV–vis, and MS. The mass spectrum of the middle fraction (B) exhibited peaks at an amu of 888 consistent with **18** and a minor peak at 918 consistent with **20** and **21**. Further purification of fraction B by flash chromatography as above gave 162 mg (18% based on **8**) of a dark blue solid of pure **18** (with no contamination with **20** or **21** when analyzed by MS): UV–vis (CH_2Cl_2) λ_{max} 704 (log ϵ 4.20), 670 (4.67), 656 (4.52), 614 (4.32), 390 (4.47), 342 nm (4.61); IR (KBr) ν_{max} 3200 (NH), 1620, 1250, 1100, 1020 (NH), 750 cm^{-1}; ^1H NMR (C_6D_6) δ 8.05–6.98 (m), 4.17–4.01 (m), 3.98–3.57 (m), 3.17–2.97 (m), 1.61 (s), 1.40–1.28 (m), 1.05–0.85 (m), −3.5 to −5.3 (br); MS for $C_{53}H_{60}N_8O_5$ m/z (relative intensity) 889 (M + 1, 100), 818 (27), 788 (25). Anal. Calcd for $C_{53}H_{60}N_8O_5$: C, 71.59; H, 6.80; N, 12.60. Found: C, 71.74; H, 6.99; N, 13.01.

In some instances TLC examination of **18** exhibited three closely spaced bands when eluted as follows. To three preparative TLC plates 50 mg of pure **18** was applied and developed 12 times with increasing amounts of 2-methoxyethanol–toluene (1:199 to 3:97). Three narrow dark blue bands (R_f = 0.43, 0.37 and 0.25) were observed along with interband streaking. Elution of each band and analysis by MS revealed only **18** for each band. As **18** *does* exist as a mixture of eight closely related regioisomers, it is likely that they could group themselves into partially separable groups of isomers.

Elution of fraction C by flash chromatography using 2-methoxyethanol–toluene (3:97) as eluant gave 60 mg (6.5% based on **8**) of a dark blue solid of pure **20** and **21**: UV–vis λ_{max} (CH_2Cl_2) 704 (log ϵ 4.84), 662 (4.84), 656 (4.76), 644 (4.68), 388 (4.61), 342 nm (4.80); IR (KBr) ν_{max} 3400 (br), 3280 (NH), 1610, 1240, 1090, 1015 (NH), 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.05–7.00 (m), 4.01–3.75 (v br), 1.58–1.43 (m), 1.31–1.25 (m), 1.17–1.04 (m), −5.57 (br); MS for $C_{54}H_{62}N_8O_6$ m/z (relative intensity) 919 (M + 1, 100), 848 (25), 818 (34), 603 (39), 577 (45), 549 (51). Anal. Calcd for $C_{54}H_{62}N_8O_6$: C, 70.56; H, 6.80; N, 12.19. Found: C, 70.47; H, 6.78; N, 12.45.

2-(2,2-Dimethylpropoxy)-9,16,23-tris(2-(hydroxymethyl)-2-methylbutoxy)phthalocyanine[11] 22, 18, 20 and 21, and 13. From 6.0 g (3.2 mmol) of polymer-bound 1,3-diiminoisoindoline **10** and 4.8 g (20 mmol, 2 times excess) of **15** in 50 mL of a 1:1 mixture of DME and DMF was isolated 2.0 g (41%) of pure **17** and 6.5 g of polymer-bound Pcs (**16**) as described above. A suspension of 5 g of this batch of polymer **16** in 50 mL of 0.3 M HCl in dioxane was stirred at room temperature for 48 h. The polymer was washed as described above to give 4.1 g of cleaved polymer and 0.8 g of a crude Pc-containing product, showing that the polymer had a loading capacity of 0.35 mmol/g. This crude product was purified by the repetitive use of our *modified* silica gel flash chromatography described herein as for **18** and (**20** and **21**) described above. As many as 10 columns were required to separate mixed fractions at every stage. Finally, elution with increasing amounts of 2-methoxyethanol–toluene (1:199–1:19) gave in all combined fractions 182 mg (7.7% based on **8**) of a pure blue shining phthalocyanine **18**, 120 mg (4.9% based on **8**) of a mixture of **20** and **21**, 10 mg (0.4% based on **8**) of pure dark blue **22**: UV–vis λ_{max} (CH_2Cl_2) 702 (log ϵ 4.61), 672 (464), 648 (4.54), 390 (sh), 340 nm (4.64); MS for $C_{55}H_{64}N_8O_7$ m/z (relative intensity) 948 (M^+, 68), 860 (100), 758 (13). Anal. Calcd for $C_{55}H_{64}N_8O_7$: C, 69.59; H. 6.79; N, 11.80. Found: C, 69.57; H, 6.74; N, 11.59.

From the last fractions 10 mg (0.4% based on **8**) of pure **13** was also isolated.

In a solution-phase experiment, a mixture of the two crude 1,3-diiminoisoindolines **11** and **15** prepared from 0.78 g (3 mmol) of **3** and 8.3 g (39 mmol) of 4-neopentoxyphthalonitrile,[7,25] respectively, was condensed in 25 mL of DME as described above for **16** to give 6.5 g of crude product. Extensive chromatography as above eventually afforded 3.1 g (37%) of pure **17**, 1.0 g (38% based on **3**) of pure **18**, 0.12 g (8.2% based on **3**) of **20** and **21**, and mixtures containing **22** and **13**.

2-(2-((3′,4′-Dicyanophenoxy)methyl)-2-methylbutoxy)-9,16,23-tris(2,2-dimethylpropoxy)phthalocyanine[11] (23). As described for **3**, 0.40 g (0.45 mmol) of **9**, 0.60 g (3.46 mmol) of **1** in 16 mL of dry DMF and 0.69 g (5 mmol) of K_2CO_3 (added in six equal portions over 5 days) was stirred at room temperature for 5 days. The crude product was purified by flash chromatography. Elution with 400 mL of C_6H_6 removed all of the excess **1**. Further elution with $CH_3CN–C_6H_6$ (3:97) gave 0.41 g of a mixture of **23** and starting **18**. Rechromatography of this mixture on a 1.5 × 25 cm column using the same eluant yielded 0.20 g of pure **23** and 0.20 g of a mixture of **23** and **18**. To this latter mixture was added 0.30 g (1.73 mmol) of **1**, and K_2CO_3 (10–15 mg) was added every day with stirring during a 3-week period. Flash chromatography of this product yielded crude **23**, which was washed with methanol to remove minor fluorescent impurities. A final flash chromatography yielded 0.17 g of the dark blue shiny **23**, soluble in organic solvents, slightly soluble in CH_3CN, and not soluble in alcohols. The reaction yielded in total 0.36 g (79%) of pure **23**: UV–vis λ_{max} (CH_2Cl_2) 702 (log ϵ 5.04), 666 (5.00), 648 (4.80), 606 (4.53), 390 (sh), 350 (4.83); IR (KBr) ν_{max} 3295 (NH), 2240 (CN), 1610, 1240, 1095, 1015 (NH), 750 cm^{-1}; ^1H NMR δ 7.75–7.25 (m), 4.21–4.12 (m), 4.01–3.40 (m), 1.98–1.83 (m), 1.33–0.95 (m), −7.72 (br); ^{13}C NMR ppm 162.2 (C_4), 159.31 + 149.4 + 128.9 + 128.2 + 125.3 ($C_{aromatic}$), 135.3 (C_6), 121.0 (C_5), 119.6 (C_3), 117.4 (C_2), 115.6 + 115.2 (C_8, C_7), 107.2 (C_1), 74.4 (C_9), 73.0 (C_{15}), 71.4 (C_{14}), 38.6 (C_{10}), 31.9 (C_{16}), 26.9 (C_{17}), 21.4 (C_{12}), 18.8 (C_{11}), 7.8 (C_{13}); MS for $C_{61}H_{62}N_{10}O_5$ m/z 1013 (M − 1). Anal. Calcd for $C_{61}H_{62}N_{10}O_5$: C, 72.16; H, 6.15; N, 13.80. Found: C, 72.18; H, 6.40; N, 13.43.

2-(2-((3′,4′-Dicyanophenoxy)methyl)-2-methylbutoxy)-9,16,23-tris(2,2-dimethylpropoxy)phthalocyaninatozinc(II)[11] (24). A mixture of 0.14 g (0.14 mmol) of **23** and 0.10 g (0.55 mmol) of $Zn(OAc)_2$ in 7 mL of a 2:5 mixture of 2-methoxyethanol–toluene was heated (bath temperature 115 °C) for 2 h. The cooled mixture was applied directly to a normal grade silica gel column and eluted with $CH_3CN–C_6H_6$ (3:97 to 1:99) to give 0.14 g of a crude product. Washing with methanol removed some impurities and flash chromatography on a 1.2 × 15 cm column using $CH_3CN–C_6H_6$ (3:97 to 5:95) gave 0.13 g (90%) of pure **24**: UV–vis λ_{max} (CH_2Cl_2) 684 (log ϵ 5.36), 674 (5.27), 616 (4.72), 346 nm (5.15), λ_{max} (toluene) 686 (log ϵ 5.06), 672 (5.00), 614 (4.56), 362 nm (4.85); IR (KBr) ν_{max} 2230 (CN), 1605, 1240, 1100, 1050, 750 cm^{-1}; ^1H NMR δ 7.70–6.78 (m), 4.85–3.42 (m), 1.61–1.42 (m), 1.22–0.83 (m); ^{13}C NMR ppm 162.2 (C_4), 159.5 + 149.3 + 148.4 + 129.0 + 128.2 + 125.3 ($C_{aromatic}$), 135.2 (C_6), 121.4 (C_5), 119.6 (C_3), 117.4 (C_2), 115.6 + 115.1 (C_8, C_7), 107.2 (C_1), 74.0 (C_9), 73.0 (C_{14}), 71.4 (C_{15}), 38.4 (C_1), 31.9 (C_{16}), 26.9 (C_{17}), 26.4 (C_{12}), 18.8 (C_{11}), 7.8 (C_{13}); MS for $C_{61}H_{60}N_{10}O_5Zn$ m/z 1079, 1078, 1077, 1076 (M^+ cluster). Anal. Calcd for $C_{61}H_{60}N_{10}O_5Zn$: C, 67.92; H, 5.60; N, 12.98; Zn, 6.06. Found: C, 67.99; H, 5.56; N, 12.25; Zn, 6.53.

In a different experiment, to 0.086 g (0.09 mmol) of **19** and 0.10 g (0.57 mmol) of **1** in 5 mL of DMF was added 0.40 g (2.9 mmol) of K_2CO_3 in seven portions over 7 days. Flash chromatography as for the isolation of **24** above gave an impure product. Preparative TLC of this crude product and successive elutions with

CH_3CN–C_6H_6 mixtures (3:97 to 1:9) gave a fast-moving spot which after isolation yielded 0.04 g (43%) of very pure **24**, identical with that produced above.

2-(2-((3′,4′-Dicyanophenoxy)methyl)-2-methylbutoxy)-9,16,23-tris(2,2-dimethylpropoxy)phthalocyaninatocopper(II)[11] (25). A mixture of 0.12 g (0.12 mmol) of **23** and 0.10 g (0.55 mmol) of $Cu(OAc)_2$ was treated as above for **24** to give 0.12 g (94%) of a pure blue solid of **25**: UV–vis λ_{max} (CH_2Cl_2) 684 (log ε 5.18), 672 (5.01), 614 (4.85), 340 nm (4.94), λ_{max} (toluene) 684 (log ε 5.19), 672 (5.10), 612 (4.66), 348 nm (4.82); IR (KBr) ν_{max} 2240 (CN), 1610, 1235, 1090, 750 cm^{-1}; MS for $C_{61}H_{66}N_{10}O_5Cu$ m/z 1077, 1076, 1075 (M^+ cluster). Anal. Calcd for $C_{61}H_{66}N_{10}O_5Cu$: C, 68.04; H, 5.61; N, 13.00; Cu, 5.90. Found: C, 67.81; H, 5.68; N, 12.80; Cu, 5.48.

1,3-Diiminoisoindolines 26–30. In a manner similar to that described above for **9–11**, 0.08 g of Na reacted with 5 mL of methanol to which was added 0.40 g (0.4 mmol) of **23** in 40 mL of dioxane and 10 mL of THF to afford 0.4 g of **26**.

Similarly 0.07 g of **24** gave 0.07 g (0.07 mmol) of **27** and 0.47 g (0.43 mmol) of **25** gave 0.47 g of **28**.

Treatment of 1.47 g (8.0 mmol) of commercially available 4-*tert*-butylphthalonitrile[41] as above for **9** gave 1.47 g of **29**, while treatment of 3.1 g (2.4 mmol) of phthalonitrile in 120 mL of methanol–THF (1:5) gave 3.1 g of **30**. The crude products **26–30** did not exhibit any nitrile absorption in their IR spectra and were directly used in subsequent condensations.

1-(2′-(9′,16′,23′-Tris(1,1-dimethylethyl)phthalocyaninoxy))-3-(2′-(9′,16′,23′-tris(2,2-dimethylpropoxy)phthalocyaninoxy))-2-ethyl-2-methylpropane[11,41] (31). The two crude 1,3-diiminoisoindolines **26**, prepared from 2.0 g (0.2 mmol) of **23**, and **29**, prepared from 1.47 g (8 mmol) of 4-*tert*-butylphthalonitrile, in 6 mL of DME were heated at 160 °C (oil bath) for 48 h. The dark blue reaction mixture was cooled, poured into water, filtered, and washed thoroughly with water and CH_3CN until the filtrate was colorless. The crude product (2.5 g) was dissolved in toluene and preabsorbed onto normal silica gel for flash chromatography on a 5 × 30 cm column. Elution with hexane–toluene (1:1 to 1:4) yielded 0.65 g (44%) of dark blue 2,9,16,23-tetrakis(1,1-dimethylethyl)phthalocyanine[42] (**33**). Further elution with toluene and 2-methoxymethanol–toluene (1:199 to 1:49) gave 0.065 g of crude binuclear **31** contaminated with some **33**. This fraction was rechromatographed using a 3:197 mixture of 2-methoxyethanol–toluene as eluant to provide upon evaporation 0.03 g (9%) of a blue, shiny solid, very soluble in organic solvents, of pure **31**: UV–vis λ_{max} (CH_2Cl_2) 638 (log ε 5.01) 338 nm (5.07), λ_{max} (toluene) 638 (log ε 5.01), 340 nm (5.04); IR (KBr) ν_{max} 3300 (NH), 1615, 1240, 1100, 1015 (NH), 750 cm^{-1}; ^1H NMR δ 9.57–9.50 (m), 8.90–7.99 (br), 7.82–7.38 (m), 4.28–3.53 (m), 1.82–1.46 (m), 1.45 (s), 1.44 (s), 1.43–1.23 (m), 0.95–0.91 (m), −4.44 to −6.5 (br); MS for $C_{97}H_{100}N_{16}O_5$ m/z 1571.8, 1570.8, 1569.8, 1568.8 (M^+ cluster). Anal. Calcd for $C_{97}H_{100}N_{16}O_5$: C, 74.20; H, 6.42; N, 14.27. Found: C, 74.34; H, 6.52; N, 13.54.

1-(2′-(9′,16′,23′-Tris(1,1-dimethylethyl)phthalocyaninoxy))-2-ethyl-2-methyl-3-(2-phthalocyaninoxy)propane[41] (32). The two crude 1,3-diiminoisoindolines **26**, prepared from 2.0 g (0.2 mmol) of **23**, and **30**, prepared from 3.1 g (2.4 mmol) of phthalonitrile, in 12 mL of DME were heated at 160 °C for 60 h. The reaction mixture was diluted with water, filtered, washed thoroughly with water, and dried. Exhaustive extraction of the blue solid in a Soxhlet extractor, first with methanol and then CH_3CN, removed many impurities but left the insoluble Pc **34** and the binuclear Pc **32** in the residue. Further extraction using CH_2Cl_2 and then THF dissolved binuclear **32** in the filtrate leaving the insoluble **34** in the thimble. Evaporation of the filtrate gave 20 mg of crude binuclear **32**. Flash chromatography of this product on a short 1 × 3 cm column using CH_2Cl_2 and finally THF as eluants gave 5 mg (2%) of pure dark blue **32**: UV–vis λ_{max} (CH_2Cl_2) 692 (log ε 4.71), 656 (4.68), 638 (4.34), 600 (4.12), 338 nm (4.52), λ_{max} (THF) 692 (log ε 4.92), 656 (4.94), 636 (4.57), 596 (4.35), 338 nm (4.75); exact mass calcd for $C_{85}H_{76}N_{16}O_5$ m/z 1400.6183, obsd m/z 1400.62.

1,3-Bis(2′-(9′,16′,23′-tris(2,2-dimethylpropoxy)phthalocyaninoxy))-2-ethyl-2-methylpropane[11] (35) via 27. Two crude 1,3-diiminoisoindolines **15** and **27**, prepared from 0.5 g (2.3 mmol) of 4-neopentoxyphthalonitrile[7] and 0.07 g (0.07 mmol) of **24**, were heated in 5 mL of DME at 160 °C (oil bath) for 48 h. The resulting mixture was worked up as described below for **32**. The crude product (0.28 g) was separated by flash chromatography to give 0.08 g (17%) of pure **17** using hexane–toluene (1:1) as eluant, followed by 0.0058 g (1%) of **36**, and 10 mg (9%) of **32** (MS of **32** identical with MS of **32** previously described).

1,3-Bis(2′-(9′,16′,23′-tris(2,2-dimethylpropoxy)phthalocyaninoxy))-2-ethyl-2-methylpropanemonocopper(II)[11] (37). Two crude 1,3-diiminoisoindolines **15** and **28**, prepared from 2.8 g (13 mmol) of 4-neopentoxyphthalonitrile[7] and 0.47 g (0.43 mmol) of **25**, respectively, were treated as for **35**. The dark blue reaction mixture was cooled, poured into water, filtered, and washed thoroughly with water and CH_3CN until the filtrate was colorless. The crude, dried product (1.5 g) was dissolved in toluene and preabsorbed onto silica gel for flash chromatography on a 5 × 30 cm column. Elution with hexane–toluene (1:2) gave 1.04 g (37%) of pure **17**. Further elution with hexane–toluene (1:3, 1:4), toluene, and a 1:199 mixture of 2-methoxyethanol–toluene gave 0.12 g of a mixture of **17** and **31**. Finally, elution with 2-methoxyethanol–toluene (1:99, 1:4) gave 0.25 g of a dark blue fraction of higher molecular weight Pcs and impurities which were not further investigated. The mixed monomer–dimer fraction were rechromatographed using hexane–toluene (1:4) and toluene as eluants to provide 0.03 g (12%) of a dark blue shining solid of pure **37**: UV–vis λ_{max} (CH_2Cl_2) 672 (log ε 4.87), 638 (4.91), 336 nm (4.98), λ_{max} (toluene) 704 sh, 674 (log ε 4.99), 638 (5.01), 400 sh, 340 nm (5.05); IR (KBr) ν_{max} 3310 (w, NH), 1620, 1245, 1100, 1070, 1020 (s, NH) cm^{-1}; MS for $C_{100}H_{104}N_{16}O_8Cu$ m/z (relative intensity) 1723.75 + 1722.75 + 1721.75 (100) + 1720.75 + 1719.75 (M^+ cluster). Anal. Calcd for $C_{100}H_{104}N_{16}O_8Cu$: C, 69.72; H, 6.08; N, 13.01; Cu, 3.69. Found: C, 70.02; H, 6.21; N, 12.87; Cu, 3.50.

2,9,16,23-Tetrakis(2-((3′,4′-dicyanophenoxy)methyl)-2-methylbutoxy)phthalocyanine (38). To a mixture of 0.52 g (0.5 mmol) of **13** and 1.8 g (10.5 mmol) of **2** in 15 mL of DMF was added 3.0 g (21 mmol) of finely ground K_2CO_3 in 0.2-g portions every 12 h over 7 days with vigorous stirring. The reaction mixture was filtered and washed four times with 50 mL of ethyl acetate. The filtrate was washed with 300 mL of water, dried over $MgSO_4$, filtered, and evaporated to dryness. Extraction of the residue with ether in a Soxhlet apparatus for 6 h removed the excess **2**. Flash chromatography of the remaining blue residue using ethyl acetate–THF (4:1) or hexane–THF (2:3) as eluant gave a blue product **38**, which was very soluble in CH_3CN, THF, and ethyl acetate; moderately soluble in CH_2Cl_2; and insoluble in ether, C_6H_6, toluene, and methanol. Chromatography yielded 0.68 g (87%) of pure **38**: UV–vis λ_{max} (CH_2Cl_2) 720 (log ε 4.64), 668 (4.57), 644 (4.22), 608 (4.13), 486 sh (3.75), 344 nm (4.45); IR (KBr) ν_{max} 3300 (NH), 2240 (CN), 1600, 1260, 1105, 1020 (NH), 840 cm^{-1}; ^1H NMR δ 9.42–8.79 (br), 7.57–7.04 (br), 4.14–3.91 (m), 1.65–1.49 (m), 1.27–0.87 (m), −1.04 (br); ^{13}C NMR ppm 162.4 (C_4), 135.3 (C_6), 119.6 (C_3, C_5), 117.6 (C_2), 115.6 + 115.2 (C_8, C_7), 105.5 (C_1), 65.3 (C_9), 38.7 (C_{10}), 27.1 (C_{12}), 19.0 (C_{11}), 8.0 (C_{13}); MS for $C_{88}H_{74}N_{16}O_8$ m/z (relative intensity) 1484 (54), 1483 (M + 1, 100), 1482 (93), 1256 (62), 1128 (4), 1029 (15). Anal. Calcd for $C_{88}H_{74}N_{16}O_8$: C, 71.23; H, 5.02; N, 15.10. Found: C, 71.22; H, 5.28; N, 15.37.

2,9,16,23-Tetrakis(2-((3′,4′-dicyanophenoxy)methyl)-2-methylbutoxy)phthalocyaninatozinc(II) (39). A mixture of 0.20 g (0.13 mmol) of **38** and 0.10 g (0.5 mmol) of $Zn(OAc)_2$ in 70 mL of a 2:5 mixture of 2-methoxyethanol–toluene was heated at 115 °C for 2 h. Flash chromatography of the crude reaction mixture using CH_3CN–C_6H_6 (1:19) as eluant gave 0.16 g (78%) of pure **39**: UV–vis λ_{max} (CH_2Cl_2) 686 (log ε 5.13), 672 (5.00), 614 (4.63), 346 nm (4.91); IR (KBr) ν_{max} 2245 (CN), 1600, 1480, 1255, 1100, 1060, 840 cm^{-1}; MS for $C_{88}H_{72}N_{16}O_8Zn$ m/z 1549, 1548, 1547 (M^+, 100), 1546.5, 1545.5, 1544.6, 1421, 1321, 1194, 1094. Anal. Calcd for $C_{88}H_{72}N_{16}O_8Zn$: C, 68.32; H, 4.69; N, 14.49; Zn, 4.22. Found: C, 67.85; H, 4.98; N, 14.02; Zn, 4.80.

2,9,16,23-Tetrakis(2-((3′,4′-dicyanophenoxy)methyl)-2-methylbutoxy)phthalocyaninatocopper(II) (40). Similarly, 0.15 g (0.10 mmol) of **38** and 0.18 g (1 mmol) of $Cu(OAc)_2$ gave a crude product which was chromatographed on silica gel using THF. Further purification on a silica gel column by elution with

---

[41] *tert*-Butyl is 1,1-dimethylethyl.

[42] Mikhalenko, S. A.; Barkanova, S. V.; Lebebev, O. L.; Lukyanets, E. A. *Zh. Obshch. Khim.* **1971**, *41*, 2735; *J. Gen. Chem. USSR* **1971**, *41*, 2770. Hanack, M.; Metz, J.; Pawlowski, G. *Chem. Ber.* **1982**, *11*, 351.

CH_3CN–C_6H_6 (1:9) gave 0.1 g (65%) of a THF and CH_3CN-soluble blue product **40**: UV–vis λ_{max} (CH_2Cl_2) 682 (log ϵ 5.01), 674 (4.93), 614 (4.41), 364 (4.25), 340 nm (4.62); IR (KBr) ν_{max} 2240 (CN), 1600, 1250, 1100, 1080, 750 cm^{-1}; MS for $C_{88}H_{72}N_{16}O_8Cu$ *m/z* (relative intensity) 1546.5 (65), 1545.5 (100), 1544.5 (100), 1543.5 (64), 1402, 1320, 1091. Anal. Calcd for $C_{88}H_{72}N_{16}O_8Cu$: C, 68.39; H, 4.69; N, 14.90; Cu, 4.11. Found: C, 68.17; H, 5.50; N, 14.57; Cu, 3.74.

Tetrakis(1,3-diiminoisoindolines) 41, 42, and 43. As previously described for **26–28**, **38–40** yielded **41–43**.

2,9,16,23-Tetrakis(2-((2′-(9′,16′,23′-tris(2,2-dimethylpropoxy)phthalocyaninoxy))methyl)-2-methylbutoxy)phthalocyanine[11] **(44).** The two crude 1,3-diiminoisoindolines **41** and **15**, prepared from 0.11 g (0.08 mmol) of **38** and 0.65 g (3 mmol) of 4-neopentoxyphthalonitrile,[7,25] were dissolved in 10 mL of DME and heated at 160 °C for 48 h. The dark blue residue was diluted with water, filtered, and washed with water, CH_3CN, and methanol. Flash chromatography of 0.5 g of dry crude material using hexane–toluene (1:1 to 1:4) and toluene as eluants gave 0.29 g (45%) of pure **17**. Further elution with 2-methoxyethanol–toluene (1:199 to 1:9) yielded 0.07 g of a mixture of **17** and **44**. Continued elution with THF gave 0.06 g of more **44** containing fluorescent and green impurities. Some of these impurities were removed by extraction with CH_3CN. Rechromatography of these last two fractions on a 5 × 50 cm gel permeation chromatography column,[9,43] packed with Bio-Beads SX1, 200–450 mesh, yielded a front running pentanuclear Pc fraction. Further flash chromatography of this band on a short column using freshly distilled THF as solvent gave 0.04 g (12%) of pure **44**: UV–vis λ_{max} (CH_2Cl_2) 698 sh (log ϵ 4.64), 662 sh (4.73), 636 (4.78), 336 nm (4.81); IR (KBr) ν_{max} 3280 (NH), 1600, 1250, 1080, 1010 (NH), 790, 750 cm^{-1}; MS for $C_{244}H_{250}N_{40}O_{20}$ *m/z* 4062. Anal. Calcd for $C_{244}H_{250}N_{40}O_{20}$: C, 72.13; H, 6.20; N, 13.79. Found: C, 72.04; H, 6.23; N, 13.72.

Modifications to the Flash Chromatography[32,33] **Procedure.** The column was prepared with a small plug of glass wool in the bottom of the column overlaid by a short layer of sand and flash chromatography grade silica gel as previously described. The bottom stopcock was opened and connected to a vacuum pump and evacuated for at least 5 min before solvent was added to the column. Solvent was added under vacuum until the solvent reached the bottom of the silica gel, at which time the stopcock was closed. The column was allowed to equilibrate for a minimum of 7 min, at which time the solvent fully wetted all the silica gel. The compounds or mixture to be separated was dissolved in an appropriate solvent and preabsorbed on normal-grade silica gel and applied to the top of the column. Forced elution with nitrogen on argon as before[32,33] effected excellent separations.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for financial support of this research. This work was also partially funded by the Office of Naval Research (Washington) and by the Midwest Center for Mass Spectrometry, a National Science Foundation Regional Instrumentation Facility (Grant No. CHE8211164).

Registry No. **1**, 31643-49-9; **2**, 77-84-9; **3**, 130326-30-6; **4**, 93673-02-0; **5**, 76-83-5; **7**, 130326-31-7; **9**, 130326-32-8; **11**, 130326-33-9; **12**, 130326-34-0; **13**, 130326-35-1; **14**, 121309-84-0; **15**, 93672-99-2; **17**, 93673-00-8; **18**, 130326-37-3; **19**, 130326-47-5; **20**, 130326-38-4; **21**, 130326-39-5; **22**, 130326-40-8; **23**, 130326-41-9; **24**, 130326-48-6; **25**, 130326-49-7; **26**, 130326-42-0; **27**, 130326-50-0; **28**, 130326-51-1; **29**, 52319-97-8; **30**, 3468-11-9; **31**, 130326-43-1; **32**, 130326-44-2; **33**, 35984-93-1; **34**, 574-93-6; **35**, 93673-06-4; **36**, 93581-78-3; **37**, 130350-28-6; **38**, 130326-45-3; **39**, 130326-52-2; **40**, 130326-53-3; **41**, 130326-46-4; **42**, 130326-54-4; **43**, 130326-55-5; **44**, 130433-48-6; DMAP, 1122-58-3; NH_3, 7664-41-7; 4-*tert*-butylphthalonitrile, 32703-80-3; phthalonitrile, 91-15-6.

---

(43) Anton, J. A.; Kwong, J.; Loach, P. A. *J. Heterocycl. Chem.* **1976**, *13*, 717.