

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231565839>

Syntheses of monometalated and unsymmetrically substituted binuclear phthalocyanines and a pentanuclear phthalocyanine by solution and polymer support methods

ARTICLE *in* THE JOURNAL OF ORGANIC CHEMISTRY · JANUARY 1991

Impact Factor: 4.72 · DOI: 10.1021/jo00001a019

CITATIONS

60

READS

14

6 AUTHORS, INCLUDING:



Ron Cerny

University of Nebraska at Lincoln

148 PUBLICATIONS 5,365 CITATIONS

SEE PROFILE



A.B.P. Lever

York University

324 PUBLICATIONS 13,159 CITATIONS

SEE PROFILE

AD-A225 363

DTIC
ELECTE
AUG 15 1990
S D

OFFICE OF NAVAL RESEARCH

Contract N00014-84-G-0201

Task No. 0051-865

Technical Report #34

The Synthesis of Monometallated and Unsymmetrically Substituted Binuclear
Phthalocyanines and a Pentanuclear Phthalocyanine
by Solution and Polymer Support Methods

By

C.C. Leznoff*, P.I. Svirskaya, B. Khouw, R.L. Cerny, P. Seymour and A.B.P. Lever

in

Journal of Organic Chemistry

York University
Department of Chemistry, 4700 Keele St., North York
Ontario, Canada M3J 1P3

Reproduction in whole, or in part, is permitted for any purpose of the United States Government

*This document has been approved for public release and sale; its distribution is unlimited

*This statement should also appear in Item 10 of the Document Control Data-DD form 1473. Copies of the form available from cognizant contract administrator

90 019

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY Unclassified		3. DISTRIBUTION/AVAILABILITY OF REPORT As it appears on the report	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE			
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Report # 34		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
6a. NAME OF PERFORMING ORGANIZATION A.B.P. Lever, York University Chemistry Department	6b. OFFICE SYMBOL (if applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research	
6c. ADDRESS (City, State, and ZIP Code) 4700 Keele St., North York, Ontario M3J 1P3 Canada		7b. ADDRESS (City, State, and ZIP Code) Chemistry Division 800 N. Quincy Street Arlington, VA 22217 U.S.A.	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (if applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-84-G-0201	
8c. ADDRESS (City, State, and ZIP Code)		10. SOURCE OF FUNDING NUMBERS	
		PROGRAM ELEMENT NO.	PROJECT NO.
		TASK NO.	WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) The Synthesis of Monometallated and Unsymmetrically Substituted Binuclear Phthalocyanines and a Pentanuclear Phthalocyanine by Solution and Polymer Support Methods			
12. PERSONAL AUTHOR(S) C.C. Leznoff*, P.I. Svirskaya, B. Khouw, R.L. Cerny, P. Seymour and A.B.P. Lever			
13a. TYPE OF REPORT Technical	13b. TIME COVERED FROM Aug. '89 TO Aug. '90	14. DATE OF REPORT (Year, Month, Day) August 3, 1990	15. PAGE COUNT 43
16. SUPPLEMENTARY NOTATION			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	
		Phthalocyanine, Binuclear, Pentanuclear, Polymer Support	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) Binuclear phthalocyanines in which two different phthalocyanine nuclei are covalently linked through five-atom bridges. derived from 2-ethyl-2-methylpropan-1,3-diol are prepared. In the examples, one phthalocyanine ring is always substituted with neopentoxv substituents, while the other phthalocyanine ring is unsubstituted or contains a tert-butyl substituents or a neopentoxysubstituted copper phthalocyanine, constituting a bicuclear phthalocyanine in which only one ring is metallated. The precursor, 2-(2-hydroxymethyl-2-methylbutoxy)-9,16,23-trineopentoxyphtalocyanine ⁴¹ was prepared in solution and also by solid phase methods, using polymer-bound trityl chloride derived from a 1% divinylbenzene-co-styrene co-polymer. 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 demetallation of some zinc phthalocyanines are noted during phthalocyanine formation. A modified flash chromatography procedure proved to be useful for separating similarly substituted mononuclear phthalocyanines.			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION Unclassified/unlimited	
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. Ronald A. De Marco		22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL

TECHNICAL REPORT DISTRIBUTION LIST - GENERAL

Office of Naval Research (2)
Chemistry Division, Code 1113
800 North Quincy Street
Arlington, Virginia 22217-5000

Commanding Officer (1)
Naval Weapons Support Center
Dr. Bernard E. Douda
Crane, Indiana 47522-5050

Dr. Richard W. Drisko (1)
Naval Civil Engineering
Laboratory
Code L52
Port Hueneme, CA 93043

David Taylor Research Center (1)
Dr. Eugene C. Fischer
Annapolis, MD 21402-5067

Dr. James S. Murday (1)
Chemistry Division, Code 6100
Naval Research Laboratory
Washington, D.C. 20375-5000

Dr. Robert Green, Director (1)
Chemistry Division, Code 385
Naval Weapons Center
China Lake, CA 93555-6001

Chief of Naval Research (1)
Special Assistant for Marine
Corps Matters
Code 00MC
800 North Quincy Street
Arlington, VA 22217-5000

Dr. Bernadette Eichinger (1)
Naval Ship Systems Engineering
Station
Code 053
Philadelphia Naval Base
Philadelphia, PA 19112

Dr. Sachio Yamamoto (1)
Naval Ocean Systems Center
Code 52
San Diego, CA 92152-5000

Dr. Harold H. Singerman (1)
David Taylor Research Center
Code 283
Annapolis, MD 21402-5067

Defense Technical Information Center (2)
Building 5, Cameron Station
Alexandria, VA 22314

ENCLOSURE(2)

ONR Electrochemical Sciences Program
Robert J. Nowak, Program Manager

Professor Hector Abruña
 Department of Chemistry
 Cornell University
 Ithaca, NY 14853
 413d018

Professor Allen Bard
 Department of Chemistry
 The University of Texas at Austin
 Austin, TX 78712-1167
 413a002

Professor James Brophy
 Department of Physics
 University of Utah
 Salt Lake City, UT 84112
 413d015

Professor Bruce Dunn
 Department of Materials Science and
 Engineering
 University of California, Los Angeles
 Los Angeles, CA 90024
 413d011

Professor Gregory Farrington
 Laboratory for Research on the
 Structure of Matter
 3231 Walnut Street
 Philadelphia, PA 19104-6202
 413d003

Professor Martha Greenblatt
 Department of Chemistry
 Rutgers University
 Piscataway, NJ 08854
 413d008

Professor Adam Heller
 Department of Chemical Engineering
 University of Texas at Austin
 Austin, TX 78712-1062
 413h007

Professor C. A. Angell
 Arizona State University
 Department of Chemistry
 Tempe, AZ 85287
 413d007

Professor Lesser Blum
 Department of Physics
 University of Puerto Rico
 Rio Piedras, PUERTO RICO 00931
 4133002

Professor Daniel Buttry
 Department of Chemistry
 University of Wyoming
 Laramie, WY 82071
 4133019

Professor Andrew Ewing
 Department of Chemistry
 152 Davey Laboratory
 Pennsylvania State University
 University Park, PA 16802
 4133030

Professor W. R. Fawcett
 Department of Chemistry
 University of California, Davis
 Davis, CA 95616
 4133020

Professor Joel Harris
 Department of Chemistry
 University of Utah
 Salt Lake City, UT 84112
 413a005

Professor Pat Hendra
 The University
 Southampton SO9 5NH
 ENGLAND
 4134001

ONR Electrochemical Sciences Program
Robert J. Nowak, Program Manager

Professor Joseph Hupp
Department of Chemistry
Northwestern University
Evanston, IL 60208
4133025

Professor A. B. P. Lever
Department of Chemistry
York University
4700 Keele Street
North York, Ontario M3J 1P3
4131025

Professor Rudolph Marcus
Division of Chemistry and Chemical
Engineering
California Institute of Technology
Pasadena, CA 91125
4133004

Professor Royce W. Murray
Department of Chemistry
University of North Carolina
Chapel Hill, NC 27514
4133015

Professor Richard Pollard
Department of Chemical Engineering
University of Houston, University Park
4800 Calhoun, Houston, TX 77004
413d016

Dr. Donald Sandstrom
Boeing Aerospace Company
P.O. Box 3999, M/S 87-08
Seattle, WA 98124-2499
4133007

Professor D. E. Irish
Department of Chemistry
University of Waterloo
Waterloo, Ontario, CANADA N2L 3G1
4133017

Professor Nathan S. Lewis
Division of Chemistry and Chemical
Engineering
California Institute of Technology
Pasadena, CA 91125
413d017

Professor Charles Martin
Department of Chemistry
Texas A&M University
College Station, TX 77843
413d005

Dr. Michael R. Philpott
IBM Research Division
Almaden Research Center
650 Harry Road
San Jose, CA 95120-6099
4133011

Professor B. S. Pons
Department of Chemistry
University of Utah
Salt Lake City, UT 84112
4133010

Professor Jack Simons
Department of Chemistry
University of Utah
Salt Lake City, UT 84112
4131050

ONR Electrochemical Sciences Program
Robert J. Nowak, Program Manager

Dr. H. Gilbert Smith
EG&G Mason Research Institute
57 Union Street
Worcester, MA 01608
413k003

Dr. Stanislaw Szpak
Code 634
Naval Ocean Systems Center
San Diego, CA 92152-5000
4131006

Professor Michael Weaver
Department of Chemistry
Purdue University
West Lafayette, IN 49707
4133001

Professor Geroge Wilson
Department of Chemistry
University of Kansas
Lawrence, KS 66045
413k002

Professor Ernest Yeager
Case Center for Electrochemical
Sciences
Case Western Reserve University
Cleveland, OH 44106
4133008

Professor Ulrich Stimming
Department of Chemical Engineering
and Applied Chemistry
Columbia University
New York, NY 10027
4133014

Professor Petr Vanýsek
Department of Chemistry
Northern Illinois University
DeKalb, IL 60115
413k001

Professor Henry White
Department of Chemical Engineering
and Materials Science
421 Washington Ave., SE
Minneapolis, MN 55455
400o027yip

Professor Mark S. Wrighton
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, MA 02139
4131027

THE SYNTHESSES OF MONOMETALLATED 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

*York University

*Midwest Center for Mass Spectrometry

Abstract

Binuclear phthalocyanines in which two different phthalocyanine nuclei are covalently linked through five-atom bridges, derived from 2-ethyl-2-methylpropan-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 a tert-butyl substituents or a neopentoxysubstituted copper phthalocyanine, constituting a binuclear phthalocyanine in which only one ring is metallated. The precursor, 2-(2-hydroxymethyl-2-methylbutoxy)-9,16,23-trineopentoxypthalocyanine⁴¹ was prepared in solution and also by solid phase methods, using polymer-bound trityl chloride derived from a 1% divinylbenzene-co-styrene co-polymer. 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 demetallation of some zinc phthalocyanines are noted during phthalocyanine formation. A modified flash chromatography procedure proved to be useful for separating similarly substituted mono-nuclear 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 but Collman et al⁵ have shown that a mixed metal cobalt-silver cofacial porphyrin dimer could also promote a four-electron reduction of O₂.

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^{6,7,8}, covalently linked by 5, 4, 3, 2, 1, 0 and "-1" bridges and a unique tetranuclear phthalocyanine⁹. To date, however, none of the multinuclear phthalocyanines have achieved the desired four-electron of O₂, although the two-electron reduction of many of the multinuclear phthalocyanines have been more efficient^{9,10} relative to simple mononuclear phthalocyanines. 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 co-facial 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 phthalocyanines had not previously been prepared, we wished to examine their synthesis towards the goal of suggesting to us a suitable geometry for achieving a four-electron reduction of O₂ by stable phthalocyanines. In addition, all previous binuclear phthalocyanines had bulky neopentoxy substituents and we believed that the bulky groups were prevent-

ing the two phthalocyanine rings from achieving complete cofaciality. We felt that it might be possible to prepare a binuclear phthalocyanine containing only one ring having bulky neopentoxy⁴¹ 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 phthalocyanine 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,^{1,11} other methods include a cyclization procedure yielding a mixture of separable porphyrin dimers¹² and an interesting example in which a silver porphyrin is used as a protecting group in the synthesis of mixed metal porphyrin dimers⁵. Like porphyrin dimers can be separated by chromatography¹², but the more highly aggregating^{9,13} phthalocyanines would be difficult to separate by this method. Binuclear phthalocyanines are prepared by the simultaneous formation of the two phthalocyanine rings from a bridged bisphthalonitrile⁸ and hence methods similar to those used in porphyrin chemistry¹⁴ are not yet applicable and, lastly, the formation of phthalocyanines¹⁵ 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 phthalocyanines, containing differently substituted phthalocyanine rings, was based on some of our earlier work¹⁶ in which very rare unsymmetrical mononuclear phthalocyanines, containing one unique "handle" or functionally active substituent was prepared using polymer-bound trityl chloride as a supporting blocking group¹⁷. In this way, first one phthalocyanine ring containing one group of

substituents or metal can be prepared followed by the stepwise elaboration of the second phthalocyanine nucleus containing no metal or different substituents.

Preparation of Mononuclear Phthalocyanines.

Thus, treatment of 4-nitrophthalonitrile (1)¹⁶ with excess 2-ethyl-2-methylpropan-1,3-diol (2) and base gave the desired hydroxy ether 3 and some bis ether 4⁷. The alcohol of hydroxy ether 3 was protected using trityl chloride (5) in pyridine¹⁹ or polymer-supported trityl chloride(6)¹⁷ and 4-dimethylaminopyridine as catalyst²⁰ to give 7 and 8 respectively (Scheme I). The protected 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-N,N-dimethylaminoethanol under standard conditions^{6,21} gave the tetratrityloxyphthalocyanine 12 and the tetrahydroxyphthalocyanine 13 respectively. Furthermore, the protecting trityl groups of 12 could be removed under very mild conditions with trimethylsilyl iodide²³ giving the free phthalonitrile 3 and the tetrahydroxyphthalocyanine 13 respectively. This cleavage procedure does not cleave neopentoxy groups and is thus compatible with the planned synthesis of unsymmetrical binuclear phthalocyanines described below (Scheme 1). Treatment of 13 with zinc acetate in toluene gave the tetrahydroxy zinc derivative 14. Compound 14 was recently tested²⁴ 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 bisdiiminoisoindoline 10 with a large excess of 5-neopentoxy-1,3-bisdiiminoisoindoline (15)⁶ (derived from 4-neopentoxyphthalonitrile^{6,25}) as previously described¹⁶ gave the

unsymmetrically substituted polymer-bound phthalocyanine **16** and the symmetrical 2,9,16,23-tetraneopentoxypthalocyanine⁴¹ (**17**), formed by self-condensation of **15**. 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 monohydroxytrineopentoxypthalocyanine⁴¹ **18** in 18% yield. Metal free **18** was readily converted into its zinc (II) derivative **19** with zinc acetate in toluene. In addition, the cleavage of **16** gave, after very extensive chromatographic separations (see Experimental) **18**, and dihydroxydineopentoxypthalocyanines **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 series²⁶. As a comparison, condensation of **11** and excess **15** as before in a homogeneous solution gave a more complex mixture of substituted phthalocyanines. 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 trihydroxyneopentoxypthalocyanine **22** and even the symmetrical tetrahydroxyphthalocyanine **13**, prepared from the polymer supported experiment using a small excess of **15**. 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 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 phthalocyanines from each other by any method including extensive chromatography is difficult²⁷, although a few successful examples have been reported²⁷⁻³⁰. 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 has in some cases delineated possible contamination by other phthalocyanine compounds²⁷. Since mononuclear phthalocyanines **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 found¹⁶ that vacuum liquid chromatography³¹ was a powerful tool for the chromatographic separation of very similar compounds including phthalocyanines but the procedure was tedious and elution times slow. We slightly changed the flash chromatography procedure of Still et al³² in a manner similar to, but not identical with, Taber's modification³³ in packing the columns used for flash chromatography. Mainly, the columns are packed with flash chromatography grade silica (20-45 μ m) under vacuum for several minutes (see Experimental). 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 mass spectroscopy 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 mass spectroscopy and elemental analy-

sis. Each one of **13**, **17**, **18** and **20-22** itself exists as a mixture of very closely related regioisomers³⁴ 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. Mass spectroscopy 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.

The synthesis of the monohydroxy substituted phthalocyanines **18** and **19** allowed us to proceed with the syntheses of the unsymmetrically substituted binuclear phthalocyanines by the following route (Scheme II). Treatment of a mixture of **1** and **18** with potassium carbonate in dimethylformamide (DMF) for five days at room temperature led to a metal-free monophthalonitrilo substituted phthalocyanine **23**. Metal insertion of zinc and copper into metal-free **23** was readily achieved by heating **23** with zinc and copper acetate to give zinc and copper phthalocyanines **24** and **25** respectively. Conversion of the monophthalonitrilo substituted phthalocyanines **23-25** into their diiminoisoindolino phthalocyanines **26-28** respectively was accomplished as for **9-11** above except that dioxane or tetrahydrofuran was required as a co-solvent 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 phthalocyanine formation gave the unsymmetrical binuclear phthalocyanines **31** and **32**, respectively, along with the simple mononuclear phthalocyanines **33** and **34**, derived from self-condensation of **29** and **30**. The preparation of binuclear phthalocyanine **31** proceeded smoothly as expected as both neopentoxy and tert-butyl groups are bulky and facilitate solubilization of phthalocyanines. Binuclear phthalocyanine **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 ultimate isolated yield of pure **32** was only 1.8%. The uv-vis spectrum of binuclear **32** was surprising and appeared similar to metal-free mononuclear phthalocyanines. These data indicate to us that **32** does not have a cofacial conformation at all and exhibits the characteristics of two phthalocyanine 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 phthalocyanine, containing two phthalocyanine rings having no substituents, except for a very bulky group in the bridge affording solubility, shows a similar lack of cofacial behaviour³⁵.

The reactions of the zinc phthalocyanine **27** or the copper phthalocyanine **28** with an excess of the diiminoisoindoline **15** in mixed condensations led in the former case to a as previously described⁶ symmetrical binuclear phthalocyanine **35** devoid of zinc as determined by FAB mass spectroscopy, but gave the desired monocopper binuclear phthalocyanine **37**, in the latter example. Careful examination of the mononuclear phthalocyanine fractions produced in these reactions, exhibited the expected formation of metal-free **17**, from self-condensation of **15**, but some 2,9,16,23-

tetraneopentoxo phthalocyaninatozinc(II) (**36**) was also detected by FAB mass spectroscopy for the reaction with **27**. Transmetallation from **27** to **36** through unknown pathways had obviously occurred³⁶.

Preparation of a Pentanuclear Phthalocyanine.

When the tetrahydroxyphthalocyanine **13** was mixed with excess 4-nitrophthalonitrile **1** and K_2CO_3 in DMF for seven days, all four hydroxy groups displaced the nitro group of **1** to afford the metal-free tetraphthalonitrilophthalocyanine **41** in 87% yield. Treatment of **41** with zinc or copper salts led to the zinc and copper phthalocyanines **42** and **43** respectively. Compounds **41-43** were readily converted to their respective tetradiiminoisoindolines **44-46**. Condensation of **41** with an excess of **15** led to the first known pentanuclear phthalocyanine **47** in 12% yield, although pentanuclear porphyrins³⁷ and a mixed tetraporphyrinylphthalocyanine³⁸ have been recently described.

Scheme IV

An attempt to make the pentanuclear phthalocyanine in which the core phthalocyanine ring contained zinc and the peripheral phthalocyanine rings were metal-free gave metal-free **47**. Again zinc demetallation occurred under the condensation reaction conditions³⁶.

Spectroscopic Properties of the Phthalocyanines.

The infrared, NMR and FAB mass spectra were consistent with the structures of the binuclear and multinuclear phthalocyanines previously described^{7,8}. The ultraviolet-visible (uv-vis) spectrum of **37** shows two prominent peaks in the Q-band region (see expt.) typical of an aggregated (cofacial and intramolecular),³⁹ dimetallated binuclear phthalocyanine, and indicative of close contact between the copper 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 phthalocyanines 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 phthalocyanines 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 one 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 copper 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, non-aggregated conformers, which do not show up in the absorption spectrum.

Conclusion

The synthesis of the monohydroxymethyl substituted phthalocyanines **18** and **19** by solution and solid phase methods and their separation from by-products **20-22** by a modified flash chromatographic procedure has allowed us to prepare, via **18** binuclear phthalocyanines in which each phthalocyanine 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 copper atom. The first known pentanuclear phthalocyanine **47** was prepared and characterized.

Experimental Section

General Methods.

Matheson high purity argon was used to maintain inert atmosphere conditions. Infrared (IR) spectra were recorded on a Pye Unicam SP1000 infrared spectrophotometer using KBr discs for solids or as neat films between NaCl discs. Nuclear magnetic resonance (NMR) spectra for carbons and protons were recorded on a Bruker AM300 NMR spectrometer using deuteriochloroform as a solvent and tetramethylsilane as the internal standard unless otherwise stated. The ^1H NMR spectra of the phthalocyanines were obtained by averaging 500-3000 scans over the absorption range while ^{13}C NMR spectra on saturated solutions of phthalocyanines were obtained by averaging 5000-15,000 scans over the absorption range. The positions of the signals are reported in δ units. (The splittings of the signals are described as singlets (s), doublets (d), triplets (t), quartets (q), or multiplets (m).) The visible-ultraviolet spectra (UV) were recorded on a Hewlett Packard HP8451A Diode Array spectrophotometer. Fluorescence spectra were recorded using a Varian SF 330 spectrofluorimeter. Mass spectra (MS) were recorded at 70 eV on a VG Micromass 16F mass spectrometer in the EI mode. The FAB spectra were obtained with a Kratos MS-50 triple analyzer mass spectrometer equipped with a FAB ion source of standard Kratos design and Ion Tech atom gun. The sample was dissolved in chloroform and a microlitre of the resulting solution added to a microlitre of *m*-nitrobenzyl alcohol on the probe tip. The spectra of the molecular ions of the binuclear phthalocyanines were obtained by signal averaging up to 256 scans over the appropriate mass range. The number in parentheses after the indicated ion shows the percentage of the base peak represented by that ion. Melting

points (mp) were determined using a Kofler hot stage melting point apparatus and are uncorrected. Thin-layer chromatography (TLC) was performed using silica gel G as the absorbent. Flash chromatography was performed using silica gel of particule size 20-45 μ m. All reactions were stirred with a magnetic stirrer. All solvents were freshly distilled before use. Microanalyses were performed by Guelph Chemical Laboratories Ltd., Guelph, Ont.

4-(2-Hydroxymethyl-2-methylbutoxy)benzene-1,2-bicarbonitrile (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 dry dimethylformamide (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 anhydrous potassium carbonate. The K_2CO_3 was added in four equal portions 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, brine and dried over magnesium sulfate. The crude product was purified by silica gel column chromatography (5 x 25 cm) using acetonitrile-benzene (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 acetonitrile-benzene (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 (0.01 Torr, Kugelrohr apparatus): IR (neat, NaCl) ν_{max} 3450, 3060, 2900, 2240, 1600, 1500, 1250, 840 cm^{-1} ; 1H NMR ($CDCl_3$) δ 7.87-7.68 (m, 1H, Ar H-5), 7.31-7.21 (m, 2H, Ar

H-3,6), 3.89 (q, 2H, CH₂OAr), 3.55 (q, 2H, CH₂OH, J=7 Hz), 1.91 (s, 1H, O-H), 1.44 (q, 2H, CH₂C, J=7 Hz), 0.97 (s, 3H, CH₃), 0.89 (t, 3H, CH₃CH₂, J=7 Hz); ¹³C NMR (CDCl₃) ppm 162.0 (C₄), 134.7 (C₆), 119.4 (C₅), 119.1 (C₃), 116.3 (C₂), 115.3 + 114.8 (C₈, C₇), 105.8 (C₁), 72.9 (C₁₄), 65.3 (C₉), 38.5 (C₁₀), 25.8 (C₁₂), 17.5 (C₁₁), 6.3 (C₁₃); MS for C₁₄H₁₆N₂O₂, m/z (relative intensity) 244 (M⁺, 41), 227 (64), 226 (47), 213 (4), 171 (88), 157 (100), 127 (94). Anal. Calcd. for C₁₄H₁₆N₂O₂: C, 68.83; H, 6.60; N, 11.47. Found: C, 68.94; H, 6.77; N, 11.49.

4-(2-Methyl-2-triphenylmethoxybutoxy)benzene-1,2 dicarbonitrile (7) [4-(2-methyl-2-trityloxybutoxy)phthalonitrile].

To a solution of 2.44 g (10 mmol) of **3** in 40 mL of dry pyridine was added 4.0 g (14 mmol) of freshly prepared trityl chloride (**5**) and the mixture was stirred at room temperature for 48 h. The pyridine hydrochloride was filtered, washed with dry ethyl acetate and the filtrate evaporated under vacuum at 30-40 °C. The oily product was purified on silica gel using acetonitrile-benzene 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; ¹H NMR δ 7.68-7.06 (m, 18H, Ar), 3.89 (dd, 2H, CH₂OAr), 3.05 (q, 2H, CH₂OTr, J=7 Hz), 1.52-1.38 (q, 2H, CH₂CH₃), 0.97 (s, 3H, CH₃), 0.77 (t, 3H, CH₂CH₃, J=6 Hz); ¹³C NMR (CDCl₃) ppm 162.2 (C₄), 135.1 (C₆), 128.7 (Tr), 127.6 (Tr), 127.0 (Tr), 119.8 (C₅), 119.1 (C₃), 117.3 (C₂), 115.7 + 115.2 (C₈, C₇), 106.9 (C₁), 86.2 (Tr), 72.9 (C₁₄), 65.2 (C₉), 38.8 (C₁₀), 27.0 (C₁₂), 18.7 (C₁₁), 7.4 (C₁₃); MS for C₃₃H₃₀N₂O₂, m/z (relative intensity) 486 (M⁺, 100), 409, 332, 255, 243. Anal. Calcd. for C₃₃H₃₀N₂O₂: 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-triphenylmethoxymethylbutoxy)benzene-1,2-dicarbonitrile (8).

To 12 g (15.6 mmol Cl/g) of freshly prepared polymer-bound trityl chloride (**6**)¹⁷ in 100 mL of dry pyridine-dichloromethane (1:1) was added 10 g (40.9 mmol) of **3** and 0.2 g of 4,4-dimethylaminopyridine²⁰. The suspension was stirred at room temperature for 48 h under argon. The polymer was filtered and washed with pyridine, dichloromethane and ethyl acetate to give filtrate A. The polymer was further washed with water, methanol, acetonitrile and ether. The air-dried polymer was extracted in a Soxhlet apparatus with dichloromethane, ethyl acetate and tetrahydrofuran 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 ($\text{C}_{\text{polymer}}$), 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 iodotrimethylsilane²³. Thus 0.5 g of **8** in 5 mL of dry dichloromethane and 0.2 mL of iodotrimethylsilane 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 sodium in 50 mL of dry methanol and 0.97 g (2 mmol) of **7** for 1 h at room temperature and 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 sodium in 40 mL of dry methanol and 55 mL of freshly distilled dry tetrahydrofuran (THF) was added 6.0 g of **8**. Ammonia was bubbled into the suspension as above and the polymer was filtered, washed with dry 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 ammonia in a 1:2 mixture of dry methanol and dry 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 bis-1,3-diiminoisoindolines did not exhibit nitrile absorptions in the IR spectra. Compounds **9-11** were used in condensation reactions without further purification.

2,9,16-23-Tetra-(2-methyl-2-triphenylmethoxymethylbutoxy)phthalocyanine (12).

A solution of 1.04 g of crude **9** in 8 mL of 2-N,N-dimethylaminoethanol (DME) was heated for 48 h at 160 °C (oil bath) under an argon atmosphere. The dark blue reaction mixture was diluted with water, filtered, washed with water and acetonitrile (until the filtrate was colorless), dried and purified by flash chromatography³² using toluene as eluant to afford 0.47 g (40%) of a blue shining solid of pure **12**: UV-vis λ_{max} (CH₂Cl₂) 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; ¹H 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 C₁₃₂H₁₂₂N₈O₈, $\underline{m/z}$ (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-Tetra-(2-hydroxymethyl-2-methylbutoxy)phthalocyanine (13).

Condensation of 2.0 g of crude 1,3-bisdiiminoisoindoline 11 in 6 mL of DME under conditions similar to that described 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 pyridine, slightly soluble in methanol and ethanol, and insoluble in toluene, benzene, ether and acetonitrile, 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} ; 1H 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 dry dichloromethane was stirred with 0.2 mL of iodotrimethylsilane to afford 30 mg of a crude product. Flash chromatography using THF as eluant yielded 20 mg of pure 13, identical in all respect to 13 prepared above.

**2,9,16,23-Tetra-(2-hydroxymethyl-2-methylbutoxy)phthalocyaninatozinc(II)
(14).**

To 98 mg (0.1 mmol) of **13** in 5 mL of a 1:2 mixture of dry 2-methoxy-ethanol-toluene was added 55 mg (0.2 mmol) of anhydrous zinc acetate. The mixture was stirred at 110-115 °C for 30 h under an argon atmosphere. 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 $\text{C}_{56}\text{H}_{64}\text{N}_8\text{O}_8\text{Zn}$, m/z (relative intensity) 1040, 1041, 1042 (48), 940 (100), 840 (100), 740. Anal. Calcd. for $\text{C}_{56}\text{H}_{64}\text{N}_8\text{O}_8\text{Zn}$: 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-triphenylmethoxymethylbutoxy)phthalocyanine
(16).**

Using a method previously described for mixed condensations of polymer-bound bis-1,3-diiminoisoindolines¹⁶, a slurry of 2.0 g (1.06 mmol) of **10** and 4.1 g (19 mmol, 6 times excess) of 5-neopentoxo-1,3-diiminoisoindoline⁴¹ (**15**)⁷ in 26 mL of a 1:1 mixture of dry DME and DMF was stirred under reflux conditions (bath temperature 160 °C) for 48 h under an argon atmosphere. After the suspension was cooled to room temperature, polymer **16** was filtered, washed twice with DMF, at least ten times with water, methanol, and acetonitrile 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 acetonitrile and combined with the product for filtrate B. This crude dark blue material was extracted in a Soxhlet extractor with methanol and then with acetonitrile 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-tetraneopentoxithalocyanine (17)^{7,25} as a dark, blue solid.

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

2,9,16-Tri-(2,2-dimethylpropoxy)-23-(2-hydroxymethyl-2-methylbutoxy)phthalocyanine⁴¹ (18); 2,9-Di-(2,2-dimethylpropoxy)-16,23-(2-hydroxymethyl-2-methylbutoxy)phthalocyanine⁴¹ (20) + 2,16-Di-(2,2-dimethylpropoxy)-9,23, -(2-hydroxymethyl-2-methylbutoxy)phthalocyanine⁴¹ (21).

A suspension of 1.9 g of polymer 16 in 20 mL of dry, freshly distilled dichloromethane and 0.5 mL of iodotrimethylsilane was stirred for 24 h under argon. The polymer was filtered, washed with dichloromethane 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 acetonitrile until colorless. The resulting residue (0.27 g) was dissolved in toluene, pre-absorbed on silica gel and purified by flash chromatography using a 1.5 x 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 mass spectrometry. 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 mass spectroscopy): 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 $\text{C}_{53}\text{H}_{60}\text{N}_8\text{O}_5$, m/z (relative intensity) 889 ($M + 1$, 100) 818 (27), 788 (25). Anal. Calcd. for $\text{C}_{53}\text{H}_{60}\text{N}_8\text{O}_5$: 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 3 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 mass spectroscopy 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 $\text{C}_{54}\text{H}_{62}\text{N}_8\text{O}_6$, m/z (relative intensity) 919 ($M + 1$, 100), 848 (25), 818 (34), 603 (39), 577 (45), 549 (51). Anal. Calcd. for $\text{C}_{54}\text{H}_{62}\text{N}_8\text{O}_6$: 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-tri-(2-hydroxymethyl-2-methyl-butoxy)phthalocyanine⁴¹ (22), (18), (20 and 21), and 13.

From 6.0 g (3.2 mmol) of polymer-bound bis-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 phthalocyanines (**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 phthalocyanine 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 $\text{C}_{55}\text{H}_{64}\text{N}_8\text{O}_7$, m/z (relative intensity) 948 (M^+ , 68), 860 (100), 758 (13). Anal. Calcd. for $\text{C}_{55}\text{H}_{64}\text{N}_8\text{O}_7$: 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-bis-diiminoisoindolines **11** and **15** prepared from 0.78 g (3 mmol) of **3** and 8.3 g (39 mmol) of 4-neopentoxypthalonitrile^{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 **8**) of **20** and **21**, and mixtures containing **22** and **13**.

2-[2-(3',4'-Dicyanophenoxymethyl)-2-methylbutoxy]-9,16,23-tri(2,2-dimethylpropoxy)phthalocyanine⁴¹ (23**).**

As described above for the formation of **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 anhydrous potassium carbonate (added in six equal portions over five days) was stirred at room temperature for five days. The crude product was purified by flash chromatography. Elution with 400 mL of benzene removed all of the excess **1**. Further elution with acetonitrile-benzene (3:97) gave 0.41 g of a mixture of **23** and starting **18**. Rechromatography of this mixture on a 1.5 x 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 anhydrous K₂CO₃ (10-15 mg) was added every day with stirring during a three 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 acetonitrile 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 ($\log \epsilon$ 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 ($\text{C}_{\text{aromatic}}$), 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 $\text{C}_{61}\text{H}_{62}\text{N}_{10}\text{O}_5$, m/z 1013 ($\text{M}-1$). Anal. Calcd. for $\text{C}_{61}\text{H}_{62}\text{N}_{10}\text{O}_5$: C, 72.16; H, 6.15; N, 13.80. Found: C, 72.18; H, 6.40; N, 13.43.

2-[2-(3',4'-Dicyanophenoxymethyl)-2-methylbutoxy]-9,16,23-tri-(2,2-dimethylpropoxy)-phthalocyaninatozinc(II)⁴¹ (24).

A mixture of 0.14 g (0.14 mmol) of **23** and 0.10 g (0.55 mmol) of anhydrous zinc acetate 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 acetonitrile-benzene (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 x 15 cm column using acetonitrile-benzene (3:97 to 5:95) gave 0.13 g (90%) of pure **24**: UV-vis λ_{\max} (CH_2Cl_2) 684 ($\log \epsilon$ 5.36), 674 (5.27), 616 (4.72), 346 nm (5.15), λ_{\max} (toluene) 686 ($\log \epsilon$ 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 ($\text{C}_{\text{aromatic}}$), 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

(C₁₆), 26.9 (C₁₇), 26.4 (C₁₂), 18.8 (C₁₁), 7.8 (C₁₃); MS for C₆₁H₆₀N₁₀O₅Zn, m/z 1079, 1078, 1077, 1076 (M⁺ cluster). Anal. Calcd. for C₆₁H₆₀N₁₀O₅Zn: 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 dry DMF was added 0.40 g (2.9 mmol) of K₂CO₃ in seven portions over seven days under argon. Flash chromatography as for the isolation of **24** above gave an impure product. Preparative TLC of this crude product and successive elutions with acetonitrile-benzene mixtures (3:97 to 1:9) gave a fast moving spot which after isolation yielded 0.04 g (43%) of very pure **24**, identical to that produced above.

2-[2-(3',4'-Dicyanophenoxymethyl)-2-methylbutoxy]-9,16,23-tri-(2,2-dimethylpropoxy)phthalocyaninatocopper(II)⁴¹ (25).

A mixture of 0.12 g (0.12 mmol) of **23** and 0.10 g (0.55 mmol) of anhydrous copper acetate was treated as above for **24** to give 0.12 g (94%) of a pure blue solid of **25**: UV-vis λ_{\max} (CH₂Cl₂) 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 C₆₁H₆₆N₁₀O₅Cu, m/z 1077, 1076, 1075 (M⁺ cluster). Anal. Calcd. for C₆₁H₆₆N₁₀O₅Cu: 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 sodium 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-butylphthalonitrile⁴² 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 CH₃OH: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',-Tri-(1,1-dimethylethyl)phthalocyaninoxy)]-3-[2'-(9',16',12'-tri-(2,2-dimethylpropoxy)phthalocyaninoxy)]-2-ethyl-2-methylpropane^{41,42} (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 under argon. The dark blue reaction mixture was cooled, poured into water, filtered and washed thoroughly with water and acetonitrile until the filtrate was colorless. The crude product (2.5 g) was dissolved in toluene and pre-absorbed onto normal silica gel for flash chromatography on a 5 x 30 cm column. Elution with hexane-toluene (1:1 to 1:4) yielded 0.65 g (44%) of dark blue 2,9,16,23-tetra-(1,1-dimethylethyl)phthalocyanine^{42,43} (**33**). Further elution with toluene and 2-methoxyethanol-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} (CH₂Cl₂) 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'-Tri-(1,1-dimethylethyl)phthalocyaninoxy)]-2-ethyl-2-methyl-3-(2-phthalocyaninoxy)propane⁴² (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 under an argon atmosphere. 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 acetonitrile, removed many impurities but left the insoluble phthalocyanine **34** and the binuclear phthalocyanine **32** in the residue. Further extraction using dichloromethane 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 x 3 cm column using dichloromethane 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); MS, 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'-tri-(2,2-dimethylpropoxy)phthalocyaninoxy)]-2-ethyl-2-methylpropane⁴¹ (35) via (27).

Two crude 1,3-diiminoisoindolines **15** and **27**, prepared from 0.5 g (2.3 mmol) of 4-neopentoxypthalonitrile⁷ and 0.07 g (0.07 mmol) of **24** were heated in 5 mL of DME at 160 °C (oil bath) for 48 h under argon. 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'-tri-(2,2-dimethylpropoxy)phthalocyaninoxy)]-2-ethyl-2-methylpropane Monocopper(II)⁴¹ (37).

Two crude 1,3-diiminoisoindolines **15** and **28**, prepared from 2.8 g (13 mmol) of 4-neopentoxypthalonitrile⁷ and 0.47 g (0.43 mmol) of **25** respectively, were treated as for the preparation of **35** above. The dark blue reaction mixture was cooled, poured into water, filtered and washed thoroughly with water and acetonitrile 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 x 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 phthalocyanines and impurities which were not further investigated. The mixed monomer-dimer fraction were rechromatography 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 $\text{C}_{100}\text{H}_{104}\text{N}_{16}\text{O}_8\text{Cu}$, m/z (relative intensity) 1723.75 + 1722.75 + 1721.75 (100) + 1720.75 + 1719.75 (M^+ cluster). Anal. Calcd. for $\text{C}_{100}\text{H}_{104}\text{N}_{16}\text{O}_8\text{Cu}$: 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-Tetra-[2-(3',4'-dicyanophenoxy)methyl]-2-methyl-butoxy]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 dry DMF was added 3.0 g (21 mmol) of finely ground anhydrous potassium carbonate 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 acetonitrile, THF and ethyl acetate; moderately soluble in dichloromethane and insoluble in ether, benzene, toluene, and methanol. Thus, 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 $C_{88}H_{74}N_{16}O$: C, 71.23; H, 5.02; N, 15.10. Found: C, 71.22; H, 5.28; N, 15.37.

2,9,16,23-Tetra-[2-(3',4'-dicyanophenoxyethyl)-2-methyl-butoxy]phthalocyaninatozinc(II) (39).

A mixture of 0.20 g (0.13 mmol) of **38** and 0.10 g (0.5 mmol) of anhydrous zinc acetate in 70 mL of a 2:5 mixture of 2-methoxyethanol-toluene was heated at 115 °C for 2 h under an argon atmosphere. Flash chromatography of the crude reaction mixture using acetonitrile-benzene (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-Tetra-[2-(3',4'-dicyanophenoxyethyl)-2-methyl-butoxy]phthalocyaninatocopper(II) (40).

Similarly, 0.15 g (0.10 mmol) of **38** and 0.18 g (1 mmol) of anhydrous copper acetate gave a crude product which was chromatographed on silica gel using freshly distilled THF. Further purification on a silica gel column by elution with acetonitrile-benzene (1:9) gave 0.1 g (65%) of a THF and acetonitrile 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 $C_{88}H_{72}N_{16}O_8 Cu$, m/z (relative intensity) 1546.5 (65), 1545.5 (100), 1544.5 (100), 1543.5 (64), 1402, 1320,

1091. Anal. Calcd. for $C_{88}H_{72}N_{16}O_8$ Cu: 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**, 0.15 g (1 mmol) of **38** was added to 10 mL of a 1:2 mixture of methanol-THF to which 0.1 g of sodium had been added. Ammonia was bubbled into the solution for 1 h at room temperature and for 4 h under reflux conditions. Evaporation of the solvent gave 0.15 g of crude **41** which was used directly in the next step. Similarly, 0.07 g (0.04 mmol) of **39** gave crude **42**. Both **41** and **42** were slightly soluble in methanol and hot DME. A similar reaction on 0.15 g (0.1 mmol) of **40** gave a precipitate of **43** which was insoluble in the above solvents. Infrared spectra of **41-43** did not show the presence unreacted **38-40**.

2,9,16,23-Tetra-[2-(23'-(2',9',16'-tri-(2,2-dimethylpropoxy)phthalocyaninoxymethyl)-2-methylbutoxy)]phthalocyanine⁴¹ (44).

The two crude 1,3-bisdiiminoisoindolines **41** and **15**, prepared from 0.11 g (0.08 mmol) of **38** and 0.65 g (3 mmol) of 4-neopentoxypthalonitrile^{7,25} were dissolved in 10 mL of DME and heated at 160 °C for 48 h under argon. The dark blue residue was diluted with water, filtered and washed with water, acetonitrile 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 acetonitrile. Rechromatography of these last two fractions on a 5 x 50 cm gel permeation chromatography column^{9,44}, packed with Bio-Beads SX1, 200-450 mesh, yielded

a front running pentanuclear phthalocyanine 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 ($\log \epsilon$ 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 $\text{C}_{244}\text{H}_{250}\text{N}_{40}\text{O}_{20}$, m/z 4062. Anal. Calcd. for $\text{C}_{244}\text{H}_{250}\text{N}_{40}\text{O}_{20}$: 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 five minutes before solvent is added to the column. Solvent is added under vacuum until the solvent reaches the bottom of the silica gel at which time the stopcock was closed. The column was allowed to equilibrate for a minimum of seven minutes at which time the solvent fully wetted all the silica gel. The compounds or mixture to be separated were dissolved in an appropriate solvent and preabsorbed on normal grade silica gel and applied to the top of the column. Forced elution with nitrogen or argon as before^{32,33} effected excellent separations.

Acknowledgement.

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).

References and Notes

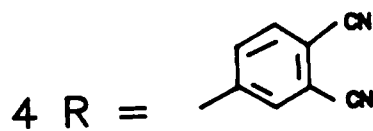
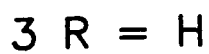
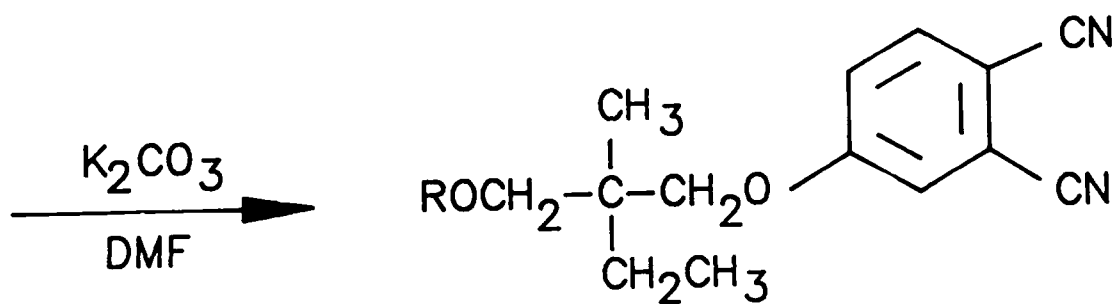
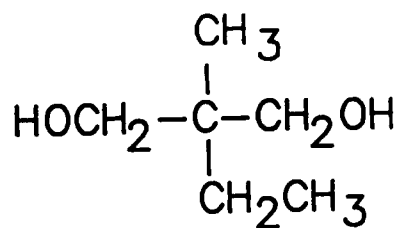
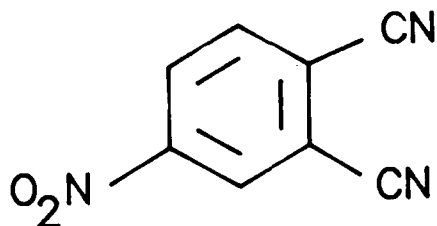
- (1) Collman, J. P.; Denisevich, P.; Konai, Y.; Marrocco, M.; Koval, C.; Anson, F. C. J. Am. Chem. Soc. **1980**, 102, 6027.
- (2) Collman, J. P.; Anson, F. C.; Bencosme, S.; Chong, A.; Collins, T.; Denisevich, P.; Evitt, E.; Geiger, T.; Ibers, J. A.; Jameson, G.; Konai, Y.; Koval, C.; Meier, K.; Oakley, P.; Pettman, R. B.; Schmittou, E.; Sessler, J. In Organic Synthesis Today and Tomorrow; Trost, B.M., Hutchinson, C. R.; Bencosme, C. S.; Collman, J. P.; Anson, F. C. J. Am. Chem. Soc. **1983**, 105, 2710; Collman, J. P.; Anson, F. C.; Barnes, C. E.; Bencosme, C. S.; Geiger, T.; Evitt, E. R.; Kreh, R. P.; Meier, K.; Pettman, R. B. J. Am. Chem. Soc. **1983**, 105, 2694.
- (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) Liu, H. Y.; Abdalmuhdi, I.; Chang, C. K.; Anson, F. C. J. Phys. Chem. **1985**, 89, 665; 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 Jr., R. R.; 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.

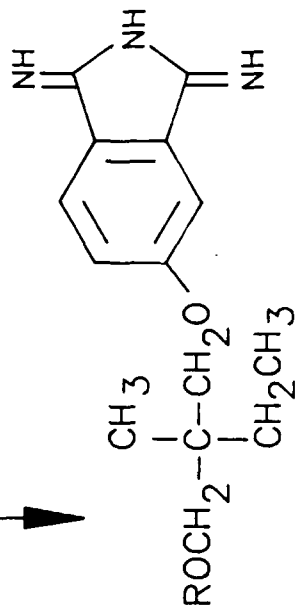
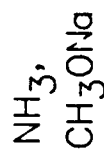
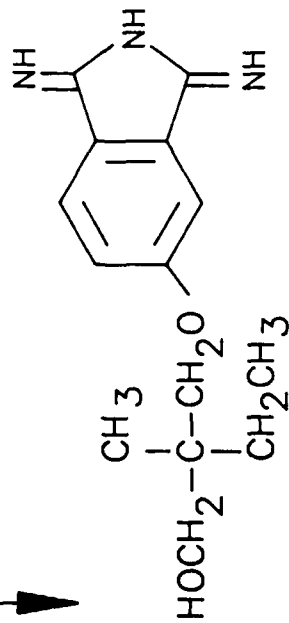
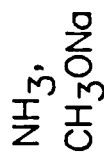
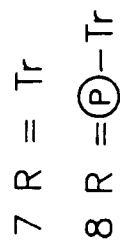
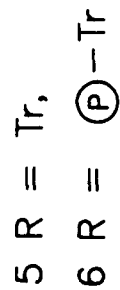
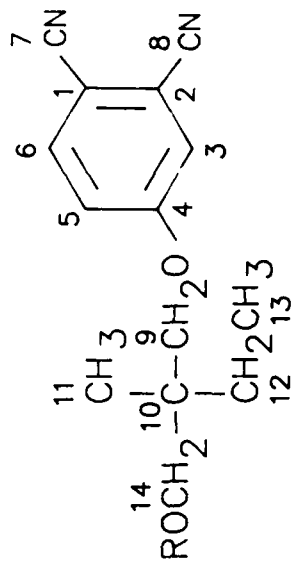
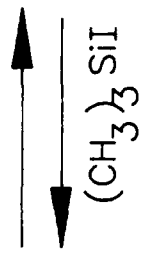
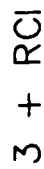
- (8) Marcuccio, S. M.; Svirskaya, P. I.; Greenberg, S.; Lever, A. B. P.; Leznoff, C. C.; Tomer, K. B. Can. J. Chem. **1985**, 63, 3057; Greenberg, S.; Marcuccio, S. M.; Leznoff, C. C.; Lam, H.; Marcuccio, S. M.; Nevin, W. A.; Janda, P.; Kobayashi, N.; Lever, A. B. P. J. Chem. Soc. Chem. Commun. **1987**, 699; 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.
- (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) Lever, A. B. P.; Hempstead, M. R.; Leznoff, C. C.; Liu, W.; Melnik, M.; Nevin, W. A.; Seymour, P. Pure and Appl. Chem. **1986**, 58, 1467; Janda, P.; Kobayashi, N.; Auburn, P. R.; Lam, H.; Leznoff, C. C.; Lever, A. B. P. Can. J. Chem. **1989**, 67, 1109.
- (11) Ward, B.; Wang, C-B.; Chang, C. K. J. Am. Chem. Soc. **1981**, 103, 5236.
- (12) 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, 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. Heterocyc. 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**, 20, 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. Heterocyc. 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.
Perkin Trans. II **1989**, 301 (1989).
- (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.

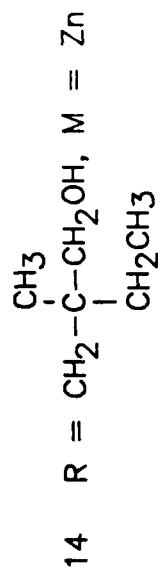
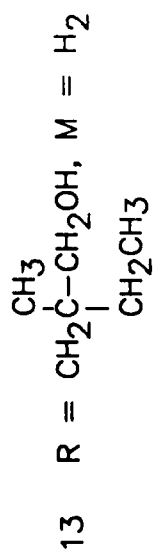
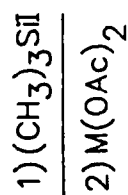
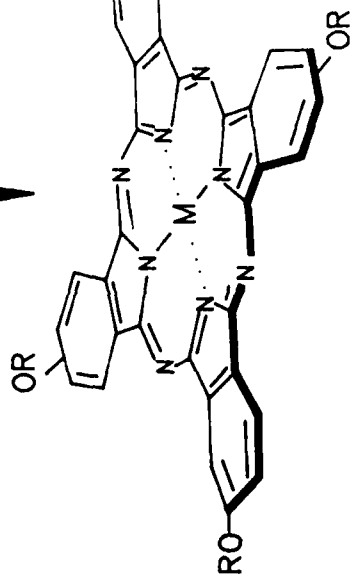
- (31) Targett, N. M.; Kilcoyne, J. P.; Green, B. J. Org. Chem. **1979**, 44, 4692.
- (32) Still, W. C.; Kahn, M.; Mitra, A. J. Org. Chem. **1978**, 43, 2923.
- (33) Taber, D. T. J. Org. Chem. **1982**, 47, 1351.
- (34) Greenberg, S.; Lever, A. B. P.; Leznoff, C. C. Can. J. Chem. **1988**, 66, 1059; Gaspard, S.; Maillard, Ph. Tetrahedron **1987**, 43, 1083.
- (35) Leznoff, C. C.; Greenberg, S. Tetrahedron Lett. **1989**, 30, 5555.
- (36) Preliminary control experiments indicated that the solubility of the phthalocyanine macrocycle, the nature of the encapsulated metal, and the presence of the bisdiminoisoindolines under the conditions of phthalocyanine formation all play important roles in transmetallation, but an extensive detailed study of transmetallation in phthalocyanines 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. I **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.
- (41) Neopentoxy is 2,2-dimethylpropoxy
- (42) tert-Butyl is 1,1-dimethylethyl

- (43) Mikhalenko, S. A.; Barkanova, S. V. Lebebev, O. I.; 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.
- (44) Anton, J. A.; Kwong, J.; Loach, P. A. J. Heterocycl. Chem. **1976**, 13,
717.

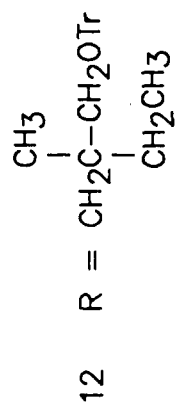
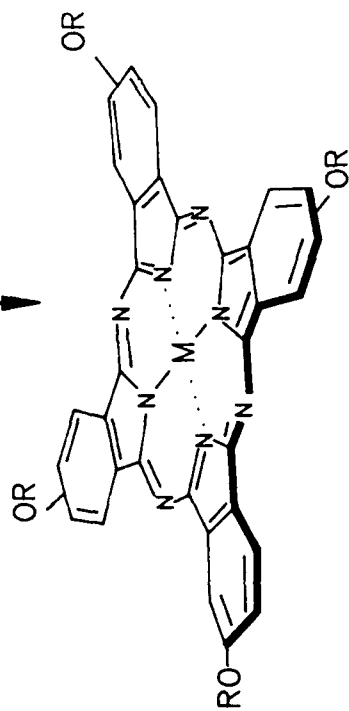


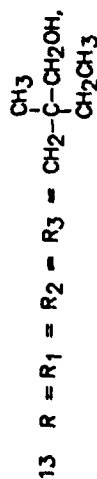
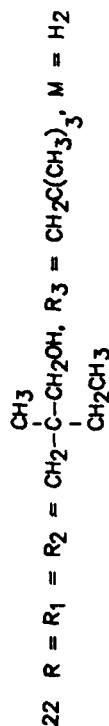
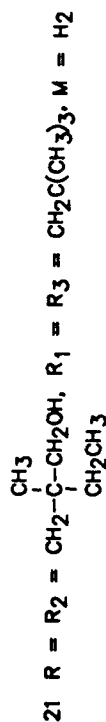
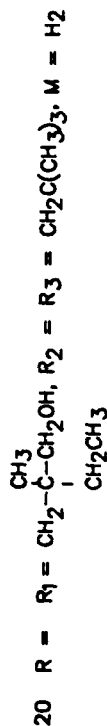
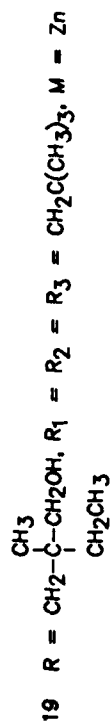
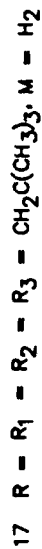
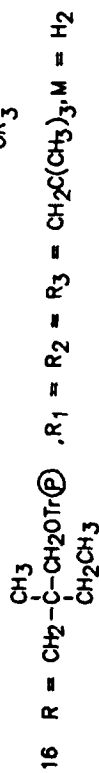
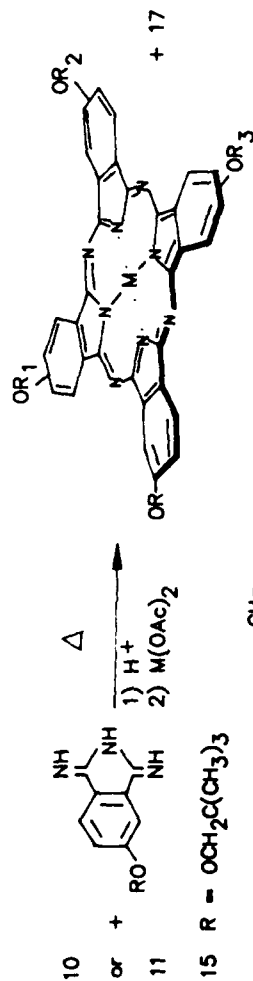


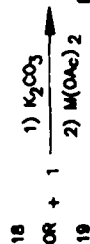
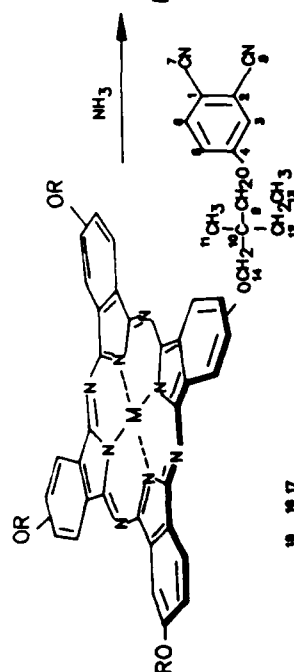
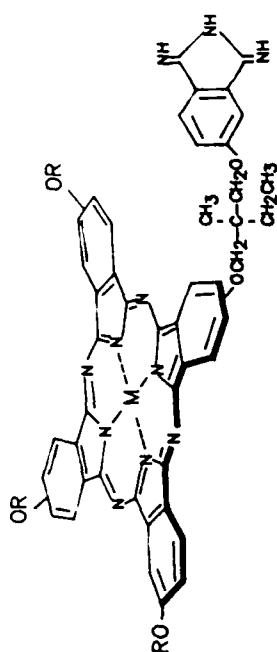
11



9

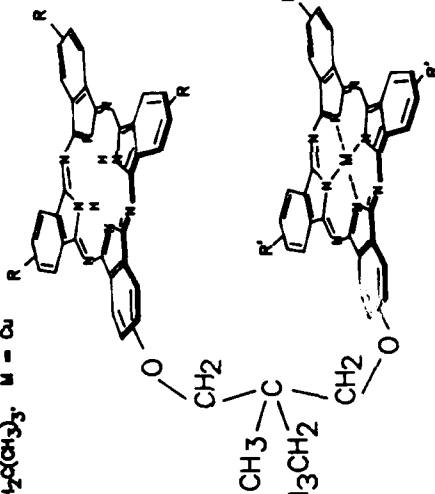
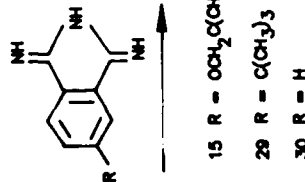




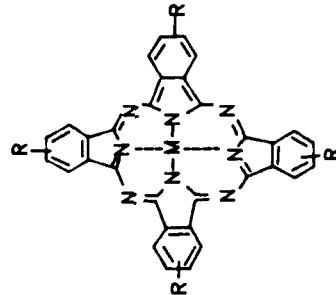


- 23 R = CH₂C(CH₃)₃, M = H₂
24 R = CH₂C(CH₃)₃, M = Zn
25 R = CH₂C(CH₃)₃, M = Cu

- 26 R = CH₂C(CH₃)₃, M = H₂
27 R = CH₂C(CH₃)₃, M = Zn
28 R = CH₂C(CH₃)₃, M = Cu



- 31 R = OCH₂C(CH₃)₃, R' = C(CH₃)₃, M = H₂
32 R = OCH₂C(CH₃)₃, R' = H, M = H₂
35 R = R' = OCH₂C(CH₃)₃, M = H₂
37 R = R' = OCH₂C(CH₃)₃, M = Cu



- 33 R = C(CH₃)₃, M = H₂
34 R = H, M = H₂
17 R = OCH₂C(CH₃)₃, M = H₂
36 R = OCH₂C(CH₃)₃, M = Zn

