

Synthesis and electrochemistry of linear and cofacial conjugated binuclear phthalocyanines covalently linked by alkyne and alkene bridges

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Semihydrogenation of 1,2-bis(3,4-dicyanophenyl)ethyne gave *cis*-1,2-bis(3,4-dicyanophenyl)ethene. From these precursors, binuclear phthalocyanines were produced containing linear binuclear phthalocyanines having an ethyne bridge and a mixture of *cis* and *trans* isomers of binuclear phthalocyanines linked by an ethene bridge. The *cis* and *trans* isomers could be separated and differentiated by gel permeation chromatography as the very extended *trans* isomer elutes faster than the cofacial globular *cis* isomer. Strong coupling between the conjugated binuclear phthalocyanine was not observed when examined by cyclic voltammetry.

Key words: phthalocyanines, cofacial, binuclear, cyclic voltammetry.

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La semi-hydrogénation du 1,2-bis(3,4-dicyanophényl)éthyne conduit au *cis*-1,2-bis(3,4-dicyanophényl)éthène. À l'aide de ces précurseurs, on a préparé des phthalocyanines binucléaires contenant des phthalocyanines binucléaires linéaires possédant un pont éthyne et un mélange des isomères *cis* et *trans* des phthalocyanines binucléaires liées par un pont éthène. On a pu séparer et différencier les isomères *cis* et *trans* grâce à la chromatographie à perméation de gel; en effet l'isomère *trans*, plus étendu, s'élue plus rapidement que l'isomère *cis* globulaire cofacial. Lorsqu'on les a soumis à de la voltampérométrie cyclique, on n'a pas observé de couplage important entre la phthalocyanine binucléaire conjuguée.

Mots clés: phthalocyanines, cofacial, binucléaire, voltampérométrie cyclique.

[Traduit par la rédaction]

Introduction

It has been shown (1-4) that binuclear porphyrins, constrained to lie in cofacial configurations, are effective in catalyzing the 4e reduction of O₂ to H₂O. The long-term instability of these porphyrin catalysts, however, has led us to prepare the more stable cofacial binuclear and multinuclear (5-7) phthalocyanines (8-10), having bridges of five (5, 8), four (6), three (7), two (6), one (9), zero (7), and even "(-1)" bridges (10). The electrochemistry of some of these cofacial (7, 11) and conjugated planar (10) metallophthalocyanines exhibited interesting mixed valence species, but only the 2e reduction of O₂ was observed, albeit with greater efficiency than mononuclear species. We had never attempted to prepare a binuclear phthalocyanine that is both conjugated and cofacial but we have now succeeded in this quest and report its synthesis, and its spectroscopic and electrochemical properties.

Results and discussion

Synthetic aspects

Semihydrogenation of 1,2-bis(3,4-dicyanophenyl)ethyne (1) (6) in acetonitrile with Lindar's catalyst (12) gave *cis*-1,2-bis(3,4-dicyanophenyl)ethene (2) in 94% yield. Treatment of 1 and 2 with gaseous ammonia in a solution of sodium methoxide in methanol (5, 13) gave their respective diiminoisoindolines 3 and 4. Mixed condensation (5, 13) of 3 with the diiminoisoindoline (5) (5) derived from 4-neopentoxypthalonitrile (5, 14) gave, upon chromatographic purification using flash (15) and gel permeation chromatography (8, 16), 2,9,16,23-

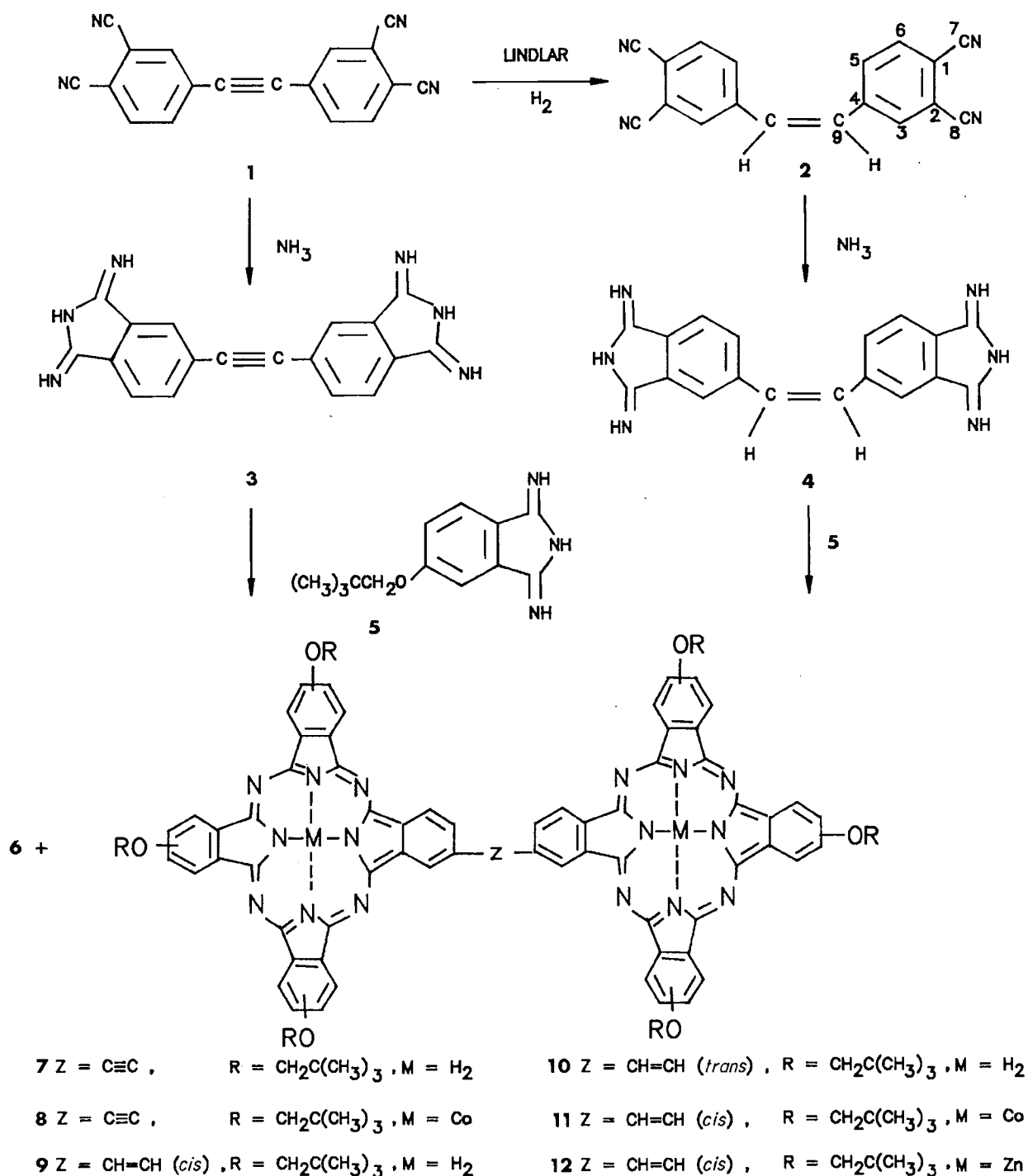
tetraneopentoxypthalocyanine (6) in 49% yield and the desired binuclear phthalocyanine (7), linked by an ethyne group in 7.4% yield (Scheme 1). Binuclear phthalocyanine 7 was readily converted into its diCo(II) derivative (8) by treatment with anhydrous CoCl₂ in 77% yield. Similarly, condensation of 4 and 5 gave mononuclear 6 in 53% yield and a mixture of the *cis* and *trans* binuclear phthalocyanines 9 and 10, linked by ethene groups (Scheme 1). Gel permeation chromatography, using tetrahydrofuran as eluant, succeeded in separating the linear fast-moving *trans*-binuclear bisphthalocyaninylethene (10) from the slower cofacial *cis*-binuclear bisphthalocyaninylethene (9). The infrared spectra of 9 and 10 were not characteristically different for these *cis* and *trans* isomers and their mass spectral data were identical. Unfortunately, the NMR spectra of 8-10 were uninformative due to their insolubility in appropriate solvents and the fact that these compounds consist of a mixture of 36 regioisomers, with the result that most NMR signals are broad and featureless. Both isomers gave good elemental analysis. These isomers exhibited similar spectral and analytical data but did show mobility differences on gel permeation chromatography. In addition, the major product is the *cis*-9, the predicted product, while the formation of *trans*-10 by known facile *cis*-*trans* isomerization is understandable. Metallation of 9 with CoCl₂ or Zn(OAc)₂ gave the diCo(II) and diZn(II) derivatives 11 and 12 respectively.

Electronic spectra

The *trans* metal-free species 10 has an electronic spectrum typical of a largely uncoupled mononuclear metal-free phthalocyanine (5, 18) while the *cis* isomer 9 has a blue-shifted Q-band spectrum consistent with extensive intramolecular coupling

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SCHEME 1

(18–20). Similar extensive intramolecular coupling is observed in the spectra of the *cis* dimetallated species **11** and **12**, which exhibit typical broad, blue-shifted *Q*-band absorption (8, 11, 18, 19, 21, 22) (Fig. 1). They likely therefore adopt a basically cofacial conformation required by the *cis*-ethene linkage.

Electrochemistry

Differential pulse voltammetry (DPV) data for the cobalt complexes **8** and **11** are reported in Table 1. These complexes are not nearly so well behaved electrochemically as most

previously described cobalt phthalocyanine derivatives (8, 11, 18). Although DPV peaks were obtained as listed, the cyclic voltammograms were generally broad and ill-defined, showing a series of overlapping and apparently irreversible waves.

Comparison with the control, CoTNPc (**18**) species leads to fairly obvious assignments. The ethyne derivative, **8**, has redox processes, as assigned, at potentials almost identical with those of the corresponding mononuclear CoTNPc. No splitting of these waves is noted. The first oxidation is then assigned to the simultaneous oxidation of both rings to the *bis*-Co^{II}Pc(-1)

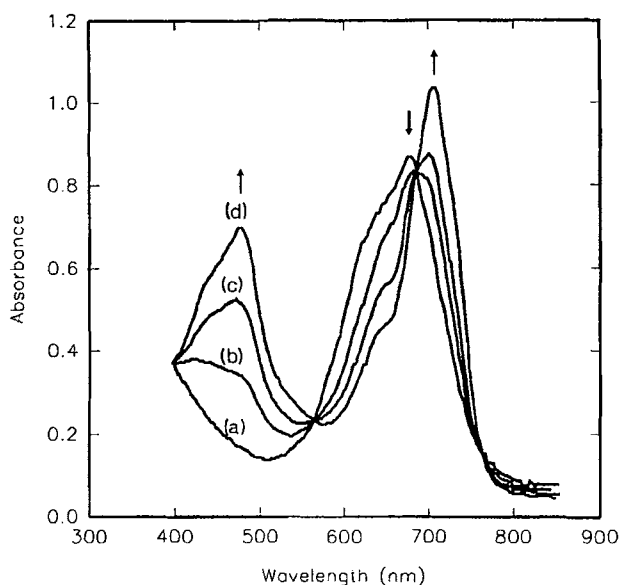


FIG. 1. Spectroelectrochemistry of CoPc=PcCo in DCB solution with 0.1 M TBAP, deoxygenated by Ar. Bulk electrolysis at -1 V vs. SCE reference electrode. Spectra taken using the Guided Wave fiber optic probe: (a) starting oxidized form $\text{Co}^{\text{II}}\text{Pc} = \text{PcCo}^{\text{II}}$; (d) final reduced form $\text{Co}^{\text{I}}\text{Pc} = \text{PcCo}^{\text{I}}$. Spectra changed during the bulk electrolysis from (a) to (d) according to arrows.

TABLE I. Electrochemical data^a

Complex	Process			
	I	II	?	III
CoTNPc ^b	0.03	-0.91	-2.07	
Ethyne 8	0.14	-0.87	-2.09	
<i>cis</i> -Ethene 11	0.13	-0.91	-1.52	-1.80

^aDifferential pulse voltammetry data, E_1 values approximated as the means of the forward and reverse peak positions, in DCB, in volts vs. ferricenium/ferrocene. This couple is observed in these studies at 0.495 V vs. AgCl/Ag on a platinum electrode surface.

^bData from ref. 18.

radical phthalocyanine species, and reduction involves the simultaneous reduction to the *bis*-Co^IPc(-2) species, and then subsequently, at -2.09 V (vs. ferrocene), reduction to the *bis*-Co^IPc(-3) species.

The *cis* cobalt ethene complex **11** also shows potentials at roughly those exhibited by CoTNPc but the apparent $[\text{Co}^{\text{I}}\text{Pc}(-2)]_2^{2-}/[\text{Co}^{\text{I}}\text{Pc}(-3)]_2^{4-}$ process is about 0.2 V more positive than expected. This last observation is reminiscent of the behaviour of recently described naphthalene (**11**, **21**) and anthracene (**11**) bridged cobalt phthalocyanines, which show splitting of their $\text{Co}^{\text{II}}/\text{Co}^{\text{I}}$ couples and the formation of mixed valence $\text{Co}^{\text{II}}\text{Pc} \cdot \text{Co}^{\text{I}}\text{Pc}$ species. Spectroelectrochemical studies (Fig. 1) polarized just negative of this wave (at -1.0 V vs. ferrocene) give a spectrum λ_{max} 475 nm (MLCT), 708 nm (Q band) typical of a fully reduced cobalt(I) phthalocyanine species (**5**, **8**, **10**, **11**, **18**, **21**, **22**), and unlike a mixed valence $\text{Co}^{\text{II}}\text{Pc} \cdot \text{Co}^{\text{I}}\text{Pc}$ binuclear species. The reduction is fully reversible (Fig. 2) since spectroelectrochemical reoxidation regenerated the original spectrum. There is no spectroscopic evidence for a mixed valence intermediate.

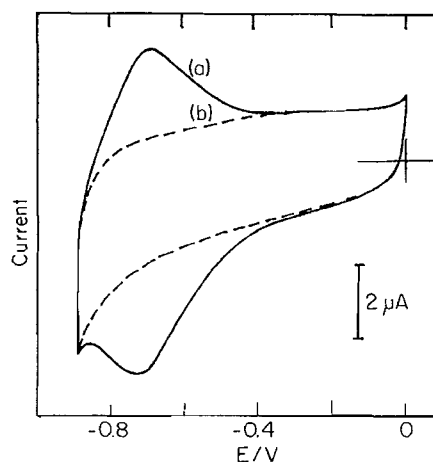


FIG. 2. Cyclic voltammetry of HOPG/CoPc=PcCo electrode in aqueous solution of 0.1 M phosphate buffer, pH = 7, Ar, scan rate $\nu = 100$ V/s, potential vs. SCE. (a) HOPG/CoPc=PcCo; (b) HOPG (residual current).

We conclude therefore that the interaction between the rings in the ethene derivative **11** is too small to stabilize the mixed valence $\text{Co}^{\text{II}}\text{Pc} \cdot \text{Co}^{\text{I}}\text{Pc}$ species. Moreover, there appears to be an additional redox process at -1.52 V (vs. ferrocene). The origin of the -1.52 V couple is obscure; it may indeed be due to an impurity process.

Oxygen reduction

Complexes **8** and **11** were also deposited as monolayer films on highly pyrolytic graphite rotating disk electrodes following methods described earlier (23). These modified electrodes electrocatalyze the reduction of molecular oxygen in a two-electron process to hydrogen peroxide. No four-electron reduction to oxygen was observed. Since we have extensively discussed the two-electron reduction of oxygen by cobalt phthalocyanines in the past (11, 23) no further discussion is presented here.

Experimental

Matheson high purity argon was used to maintain inert atmosphere conditions. Infrared (ir) spectra were recorded on a Pye Unicam SP1000 infrared spectrophotometer using KBr discs. Nuclear magnetic resonance (nmr) spectra for protons and carbons were recorded on a Bruker AM300 nmr spectrometer. The position of signals is reported in δ units. (The splitting of the signals is described as singlets (s), doublets (d), triplets (t), quartets (q), doublets of doublets (dd), or multiplets (m)). The ¹H nmr spectra of 10^{-4} M solutions of the phthalocyanines were obtained by averaging 500–3000 scans over the absorption range. The ultraviolet-visible spectra (uv) were recorded on a Hewlett Packard HP8451A diode array spectrophotometer. 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 approximate 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. Flash chromatography was performed using silica gel of particle size 20–45 μm . All reactions were stirred with a magnetic stirrer. All solvents were freshly distilled before use. Thin-layer

chromatography (tlc) was performed using silica gel G as the absorbant. Microanalyses were performed by Guelph Chemical Laboratories Ltd., Guelph, Ontario.

Electrochemical data were obtained with a Princeton Applied Research (PARC) model 173 potentiostat, or a PARC model 174A polarographic analyzer coupled to a PARC model 175 universal programmer. Cyclic voltammetry and differential pulse voltammetry (DPV) were carried out under an atmosphere of argon, or nitrogen, using a conventional three-electrode cell. The working electrode was described by the cross-sectional area of a 27-gauge platinum wire (area 10^{-3} cm²), and sealed in glass. A platinum wire also served as the counter electrode. The reference electrode was a silver wire quasireference electrode, referenced internally to the ferricenium/ferrocene (Fc⁺/Fc) couple.

Spectroelectrochemical measurements were made with a 0.45-mm path-length optically transparent thin-layer electrode (OTTLE) cell, utilizing a gold minigrad (500 lines/in., 60% transmittance) (17), in conjunction with the Hitachi Perkin-Elmer model 340 spectrometer.

Preparation of 1,2-bis(3,4-dicyanophenyl)ethylene (1)

Compound 1 was prepared as reported by Marcuccio *et al.* (6); yield 85%, mp 285–287°C (lit. (6) mp 286–288°C); ¹H nmr (DMSO-*d*₆, 300 MHz) δ: 8.42 (d, *J* = 1.6 Hz, 2H, ArH-3), 8.22 (d, *J* = 8 Hz, 2H, ArH-6), 8.11 (d, *J* = 8 Hz, 2H, ArH-5).

Preparation of 1,2-bis(3,4-dicyanophenyl)ethene (2)

A solution of 1.0 g (3.6 mmol) of pure 1 in 300 mL of acetonitrile was stirred under hydrogen (1 atm (101.3 kPa), 25°C) in the presence of Lindlar's catalyst (12) (250 mg) until absorption of hydrogen (88 mL) had ceased. The catalyst was filtered and the filtrate was evaporated to give 0.950 g (94% yield) of a yellow powder 2. Recrystallization in methanol yielded white, needle-like crystals, mp 196–197°C; ir (cm⁻¹): 3090–2920, 2210 (CN), 1590, 1550, 1490, 1380, 1230, 920, 870, 850, 810, 770, 720; uv (CH₃CN) λ_{max} (log ε): 308 (4.09), 276 (4.07), 224 (4.38); ¹H nmr (DMSO-*d*₆, 300 MHz) δ: 8.00 (s, 2H, ArH-3), 7.98 (d, *J* = 8 Hz, 4H, ArH-6), 7.61 (d, *J* = 8 Hz, 2H, ArH-5), 6.95 (s, 2H, CH=CH); ¹³C nmr δ: 141.2 (C-4), 134.1 + 134.0 (C-5 + C-9), 133.6 (C-3), 131.0 (C-6), 115.8 + 115.6 (C-7 + C-8), 115.1 (C-2), 113.3 (C-1); ms *m/z*: 280(M⁺), 254. Anal. calcd. for C₁₈H₈N₄: C 77.13, H 2.87, N 19.98; found: C 77.10, H 3.21, N 20.17.

Preparation of the bis-1,3-diiminoisoindoline of 1,2-bis(3,4-dicyanophenyl)ethyne (3)

The bisphthalonitrile 1, 0.30 g (1.08 mmol), was added to a solution of 30 mg of sodium in 30 mL of dry methanol. Since the bisphthalonitrile 1 did not dissolve, the mixture was heated to 60°C. The mixture was stirred at 60°C for 0.75 h under reflux conditions, while ammonia gas was bubbled into the solution. The reaction mixture gradually turned green during which time a green precipitate was observed. The reaction was cooled to room temperature and the addition of ammonia gas was discontinued. Evaporation of the solvent gave crude 3, which was used directly in condensation reactions without further purification. Compound 3 did not exhibit a nitrile absorption in its ir spectrum.

Preparation of the bis-1,3-diiminoisoindole of 1,2-bis(3,4-dicyanophenyl)ethene (4)

The bisphthalonitrile 2, 0.300 g (1.07 mmol), was added to a solution of 30 mg of sodium in 30 mL of dry methanol. The mixture was stirred at room temperature for 0.75 h while ammonia gas was bubbled into the solution. The reaction mixture gradually became green, during which time a green precipitate was observed. The addition of ammonia gas was discontinued. Evaporation of the solvent gave crude 4, which was used directly in condensation reactions without further purification. Compound 4 did not exhibit a nitrile absorption in its ir spectrum.

Preparation of the 1,2-bis-2'-(9',16',23'-trineopentoxypthalocyaninyl)ethyne (7)

The two crude diiminoisoindolines 5 and 3, obtained from 6.0 g (28 mmol) of 4-neopentoxypthalonitrile (5) (5), and 300 mg (1.08 mmol) of 1, were heated to 150°C (oil bath) in 30 mL of

2-*N,N*-dimethylaminoethanol for 72 h under an argon atmosphere. The mixture was cooled to room temperature, diluted with water, filtered, and washed thoroughly with water followed by methanol until the filtrate was almost clear. The crude product was extracted with methanol in a Soxhlet apparatus until the extract was clear of brown and yellow impurities. The crude product was purified by flash chromatography using a 5 cm diameter column packed with flash silica gel 12 cm high. The crude product was preabsorbed on a small amount of flash silica gel and eluted with toluene to give 300 g of the monomeric 2,9,16,23-tetraneopentoxypthalocyanine (6) in 49% yield. Further elution with 2-methoxyethanol/toluene (2:98) gave a fraction consisting largely of dimer 7, containing traces of monomer and some green material. Finally, elution with 2-methoxyethanol/toluene (1:4) gave a green fraction consisting largely of trimer and impurities. The dimer fraction was further purified by gel permeation chromatography (8, 16). Elution with tetrahydrofuran removed all traces of monomer and green material from the major dimer band. Evaporation of the solvent gave a dark blue product. This product was washed with acetonitrile/acetone to remove traces of fluorescent impurities, detectable by tlc using toluene/2-methoxyethanol (98:2) as eluant to give, in 7.4% yield, 125 mg of 7 as a dark blue, shiny solid; ir (cm⁻¹): 3300 (N-H), 1610, 1480, 1400, 1240, 1100, 1020 (N-H), 750; uv (*o*-dichlorobenzene (DCB)) λ_{max} (log ε): 678 (4.36), 660 (4.39), 648 (4.45); ms *m/z*: 1569.8 (23), 1568.8 (58), 1567.8 (M⁺ + 1, 100), 1566.8 (M⁺, 86). Anal. calcd. for C₉₆H₉₄N₁₆O₆: C 73.54, H 6.04, N 14.29; found: C 73.30, H 5.95, N 13.94.

Preparation of 1,2-bis-2'-(9',16',23'-trineopentoxypthalocyaninyl)ethyne dicobalt(II) (8)

A mixture of 50 mg (0.032 mmol) of metal-free dimer 7 and 100 mg (0.77 mmol) of anhydrous cobalt(II) dichloride in 10 mL of a 1:1 mixture of 2-methoxyethanol/dichlorobenzene was heated at 16°C for 20 h under an argon atmosphere. The crude reaction mixture, after cooling, was evaporated under high vacuum to remove the 2-methoxyethanol/dichlorobenzene. The remaining residue was precipitated with a water/methanol (1:1) mixture. After filtering, the dark blue, shiny solid obtained was extracted with methanol in a Soxhlet apparatus until the extract was clear. The dark blue solid was dried to give 41 mg (76% yield) of 8; ir (cm⁻¹): 1620, 1530, 1480, 1410, 1380, 1240, 1100, 760; uv (DCB) λ_{max} (log ε): 686 (4.21), 658 (4.23), 650 (4.19), 638 (4.18), 630 (4.19), 302 (4.33), 262 (4.04); ms *m/z*: 1683.6 (23), 1682.6 (58), 1681.6 (M⁺ + 1, 100), 1680.6 (M⁺, 86). Anal. calcd. for C₉₆H₉₀N₁₆O₆Co₂: C 68.56, H 5.39, N 13.39, Co 7.01; found: C 67.82, H 5.68, N 12.99, Co 6.80.

Preparation of cis and trans 1,2-bis-2'-(9',16',23'-trineopentoxypthalocyaninyl)ethene (9 and 10)

The two crude diiminoisoindolines, 5 and 4, obtained from 6.0 g (28 mmol) of 4-neopentoxypthalonitrile (5) and 300 mg (1.07 mmol) of 2, were heated to 150°C (oil bath) in 30 mL of 2-*N,N*-dimethylaminoethanol for 72 h under an argon atmosphere. The mixture was cooled to room temperature, diluted with water, filtered, and washed thoroughly with water followed by methanol until the filtrate was almost clear. The crude product was extracted with methanol in a Soxhlet apparatus until the extract was clear of brown and yellow impurities. The crude product was purified by flash chromatography using a 5 cm diameter column packed with flash silica gel 12 cm high. The crude product was preabsorbed on a small amount of flash silica gel and eluted with toluene/hexane (1:1) to give 3.2 g of the monomeric 6 in 53% yield. Further elution with toluene gave a fraction consisting largely of dimer and monomer. Finally, elution with 2-methoxyethanol/toluene (2:98) gave a green fraction consisting largely of trimer and impurities. The dimer fraction was further purified by flash chromatography (3 cm diameter column). Elution with toluene/hexane (25:75) up to 100% toluene gave an even purer fraction of dimer with a small trace of monomer. This dimer fraction was further purified by gel permeation chromatography (8, 16) applying no more than 50 mg of dimer per chromatographic run. Elution with tetrahydrofuran removed all traces of monomer. The main dimer band of 9 was observed but a front-running blue band consisting of 10 was also noticed. These two

fractions were collected separately. Evaporation of the solvent gave 470.3 mg of **9** and **10** (28% yield, 378 mg of **9** and 92.3 mg of **10**) as dark blue solids, having identical ir and ms spectroscopic properties; ir (cm^{-1}): 3300 (N-H), 1620, 1480, 1400, 1240, 1100, 10.20 (N-H), 750; uv for **9** (DCB) λ_{max} (log ϵ): 704 (5.06), 650 (5.00), 344 (5.08); uv for **10** λ_{max} (log ϵ): 704 (4.76), 678 (4.77), 658 (4.78), 650 (4.77), 340 (4.86); ms m/z : 1571.7 (23), 1570.7 (58), 1569.7 ($M^+ + 1$, 100), 1568.7 (M^+ , 86). Anal. calcd. for $\text{C}_{96}\text{H}_{90}\text{N}_{16}\text{O}_6\text{Co}_6$ for **9**: C 73.44, H 6.16, N 14.27; found: C 73.51, H 6.52, N 14.24. Anal. calcd. $\text{C}_{96}\text{H}_{96}\text{N}_{16}\text{O}_6$ for **10**: C 73.44, H 6.16, N 14.27; found: C 73.85, H 6.39, N 14.55.

Preparation of the 1,2-bis-2'-(9',16',23'-trineopentoxyphtalocyaninyl)ethyne dicobalt(II) (11)

A mixture of 50 mg (0.032 mmol) of metal-free dimer (**9**) and 100 mg (0.77 mmol) of anhydrous cobalt(II) dichloride in 13 mL of a 5:3:5 mixture of 2-methoxyethanol/dichlorobenzene/toluene was heated at 160°C for 20 h under an argon atmosphere. Flash chromatography of the crude reaction mixture on a 3 cm diameter column of flash silica gel and elution with dimethylformamide (DMF) gave, in 78.5% yield, 42.2 mg of **11** as a dark blue solid; ir (cm^{-1}): 1615, 1480, 1400, 1240, 1100, 1015, 755; uv (DCB) λ_{max} (log ϵ): 682 (4.82), 650 (4.76), 300 (4.91); ms m/z : 1685.6 (23), 1684.6 (58), 1683.6 ($M^+ + 1$, 100), 1682.6 (M^+ , 86). Anal. calcd. for $\text{C}_{96}\text{H}_{92}\text{N}_{16}\text{O}_6\text{Co}_2$: C 68.48, H 5.50, N 13.31, Co 7.00; found: C 68.71, H 5.85, N 13.54, Co 6.50.

Preparation of 1,2-bis-2'-(9',16',23'-trineopentoxyphtalocyaninyl)ethene dizinc(II) (12)

A mixture of 60 mg (0.038 mmol) of metal-free dimer **9** and 100 mg (0.54 mmol) of anhydrous zinc acetate in 13 mL of a 5:3:5 mixture of 2-methoxyethanol/dichlorobenzene/toluene was heated at 160°C for 20 h under an argon atmosphere. Flash chromatography of the crude reaction mixture on a 3 cm diameter column of flash silica gel and elution with 2-methoxyethanol/toluene (1:3) gave, in 89% yield, 57.7 mg of **12** as a dark blue solid; ir (cm^{-1}): 1610, 1490, 1395, 1340, 1235, 1100, 1060, 1015, 750; uv (DCB) λ_{max} (log ϵ): 688 (4.99), 658 (4.91), 650 (4.88), 342 (4.99), 300 (4.85); ms m/z : 1701.6 (18), 1700.6 (31), 1699.6 (46), 1698.6 (68), 1697.6 (84), 1696.6 (100), 1695.6 (82), 1694.6 (85), 1693.6 ($M^+ + 1$, 54), 1692.6 (M^+ , 47). Anal. calcd. for $\text{C}_{96}\text{H}_{92}\text{N}_{16}\text{O}_6\text{Zn}_2$: C 67.96, H 5.46, N 13.20, Zn 7.70; found: C 67.53, H 5.40, N 13.03, Zn 7.22.

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