J. Org. Chem. **2000,** *65,* 2733−2739

Synthesis of Novel Push−Pull Unsymmetrically Substituted Alkynyl Phthalocyanines

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Received November 30, 1999

Two families of “push−pull” phthalocyanines **1**−**3** having an unusually strong dipole moment have been prepared. The syntheses of unsymmetrically substituted phthalocyanines **1a**,**b** and **2** bearing one or two electron-withdrawing 4-nitrophenylethynyl moieties, respectively, and six alkoxy substituents were performed by combination of a zinc or nickel templated cyclotetramerization and cross-coupling palladium mediated methodologies. In a similar way, the “push−pull” compounds **3a**,**b** having a reversal substitution pattern, characterized by the presence of one electron-donor 4-(dimethylamino)phenylethynyl unit and six strong acceptor alkylsulfonyl substituents were prepared. The compounds show very large second-order nonlinear optical responses.

Introduction

Metallophthalocyanines (MPcs)[1,2] are two-dimensional 18 π-electron conjugated systems, which have been intensively investigated for many technological applications. Modifications of Pcs are usually made by incorporating a wide variety of central metal ions, by peripheral substitution of the macrocycle,[1,2] or by preparation of analogues.[3] Their chemical flexibility facilitates the tailoring of their electrophysical parameters in a very broad range.

It has been suggested that unsymmetrically substituted Pcs with suitable donor and acceptor groups should exhibit second-order nonlinear optical (NLO) responses.[4,5] Some research effort has been carried out in order to study noncentrosymmetric peripherally substituted Pcs for this particular purpose,[6−8] but the synthetic challenge of developing new Pc-based targets capable of displaying efficient intramolecular charge-transfer remains open.[9]

In the present paper, and as a continuation of our interest in the preparation of Pc systems with extended conjugation using double and triple bonds as linkers,[8a,10] we describe the preparation of new “push−pull” phthalocyanines **1**−**3** and preliminary studies of their second-order NLO properties. Taking into account that the exploitation of phthalocyanines in nonlinear optics demands good solubility, for example for the organization of the molecules in thin films, the butoxy- and propylsulfonyl groups provide these compounds with enough solubility in organic solvents for this purpose. The new phthalocyanines reported in this paper show the highest dipolar moments and second-order nonlinear responses described until now in the literature for unsymmetrically substituted phthalocyanines.

Results and Discussion

The preparation of the unsymmetrically substituted Pcs **1a**,**b** bearing an electron-acceptor nitrophenylethynyl moiety was attempted in two different ways.

Statistical templated condensation[11] (Scheme 1) of 4,5-

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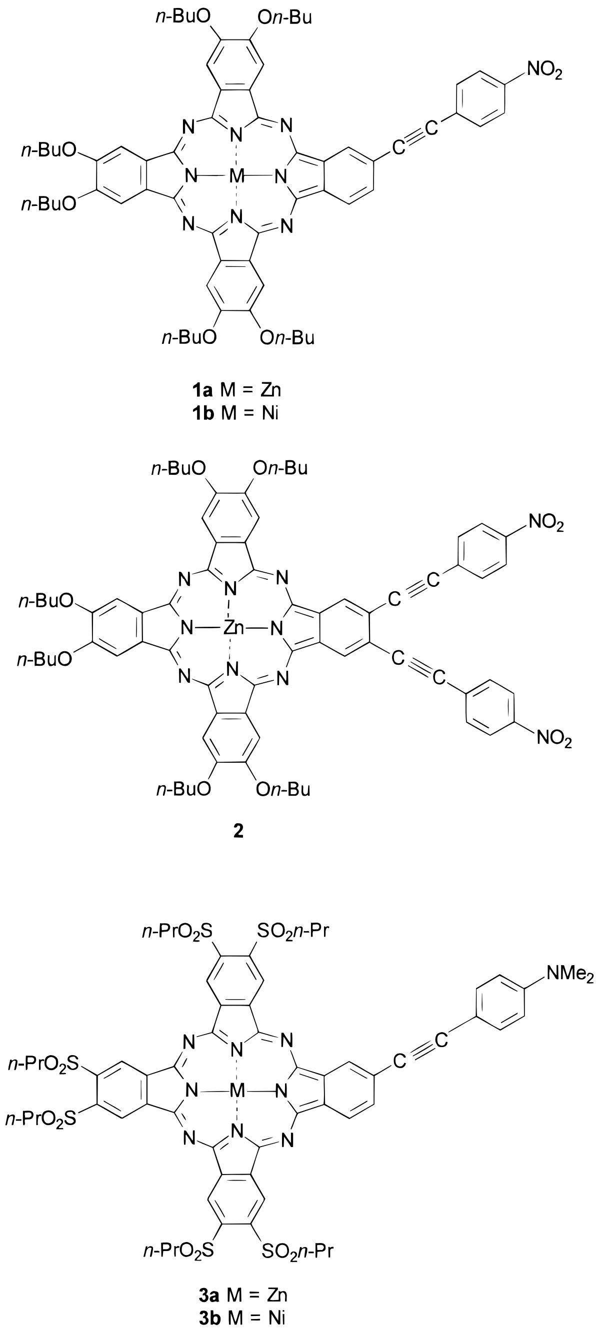
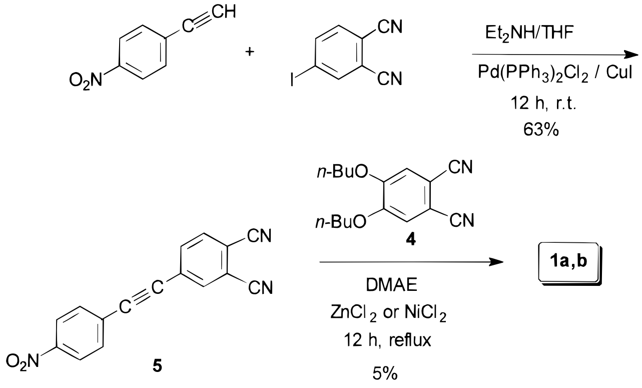
Chart 1



dibutoxyphthalonitrile[12] (**4**) and phthalonitrile **5**, the latter being prepared by palladium-mediated cross-coupling of 4-iodophthalonitrile[13] and 4-nitrophenylethyne,[14] afforded a mixture of the corresponding octabutoxyphthalocyaninate metal(II) and the unsymmetrical compound **1a** or **1b**. The zinc compound **1a** could be isolated with much difficulty by chromatography in low yield (5%), whereas the separation of **1b** from the corresponding reaction mixture was not possible, due to the strong tendency to aggregation of the corresponding polyalkoxyphthalocyaninatos.

Scheme 1. Synthesis of Nitrophenylethynylphthalocyanine Metal(II) Complexes 1a,b by Statistical Condensation



To overcome these problems a second strategy was followed for the preparation of **1a**,**b** (Scheme 2). Statistical condensation of **4** and phthalonitrile **6**[15] in the presence of the appropriate metal salt yielded compounds **7a**,**b** in moderate yield (13−19%). The protecting group was then removed[16] to afford alkynyl compounds **8a**,**b**. Further reaction of **8a**,**b** with *p*-iodonitrobenzene in the presence of a catalyst formed in situ by adding triphenylarsine to tris(dibenzylidenacetone)dipalladium(0) $[Pd_2(dba)_3]$,[17] in order to prevent the homocoupling reaction of the dialkynyl compound, yielded **1a**,**b** in good yield.

Figure 1 shows the UV−visible spectra of the hexabutoxy(nitrophenylethynyl)phthalocyaninato **1a** and its precursor **8a**. The optical characteristics of the new conjugated system differs from that of unsymmetrical parent terminal alkyne **8a**. The Soret band is centered at 357 nm for both compounds. However, while **8a** shows a single broad Q-band at 681 nm, the push−pull phthalocyanine **1a** exhibits a remarkable split Q-band at 677 and 696 nm. The observed shifting to the red of the Q-band can be attributed to the extended π-conjugation of the system, as found previously by us in other conjugated systems prepared.[10a,18] Similar results were obtained for compounds **1b** and **8b**.

The synthesis of compound **2** bearing two electron-withdrawing (4-nitrophenyl)ethynyl substituents was carried out starting from the diiodophthalocyanine **9**[19] by cross-coupling with 4-ethynylnitrobenzene using bis[triphenylphosphine]palladium(II) dichloride $[Pd(PPh_3)_2Cl_2]$ as catalyst and an excess of potassium iodide[20] (Scheme 3). LSIMS spectrum of **2** shows an isotopic pattern at *m*/*z* 1299−1301 corresponding to the protonated molecular ion. A singlet centered at 6.9 ppm in the ^1H NMR spectrum identifies the aromatic protons of the Pc-ring. The moderate solubility of compound **2** in organic solvents, like in the case of Pcs **1** and **3**, precludes the registration of useful ^{13}C NMR spectra.

The UV/vis spectrum of compound **2** is depicted in Figure 1. The optical features of this highly conjugated

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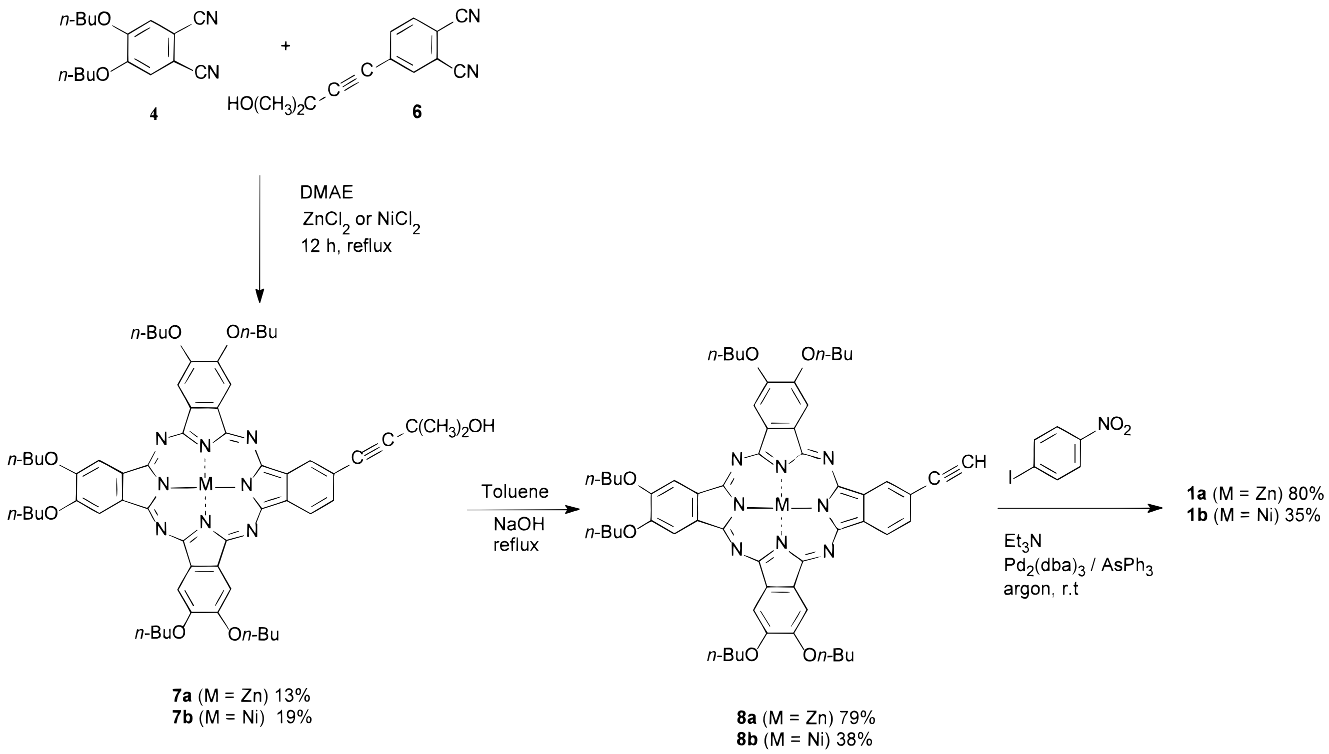
Scheme 2. Synthesis of Phthalocyanine Metal(II) Complexes 1a,b by a Cross-coupling Method



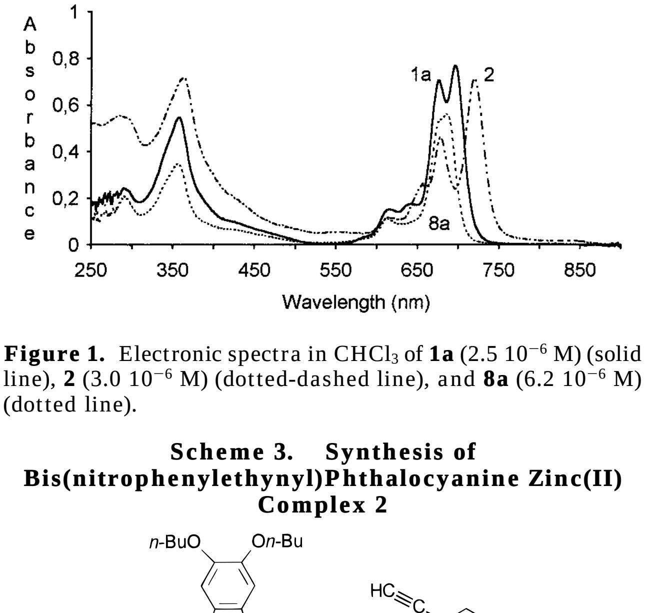
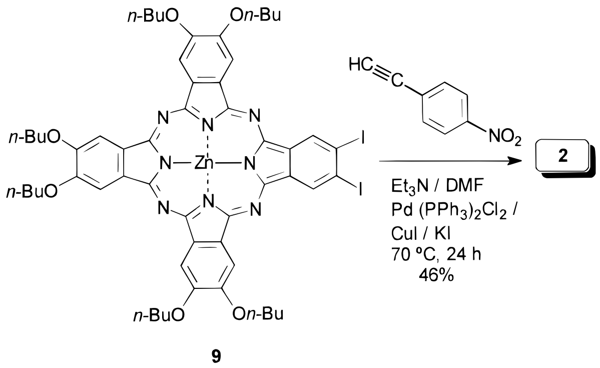


Figure 1. Electronic spectra in CHCl$_3$ of **1a** (2.5 10^{-6} M) (solid line), **2** (3.0 10^{-6} M) (dotted-dashed line), and **8a** (6.2 10^{-6} M) (dotted line).

Scheme 3. Synthesis of Bis(nitrophenylethynyl)Phthalocyanine Zinc(II) Complex 2



system differ remarkably from those of the related monoalkynyl-substituted species **1a** (Figure 1). The Soret (B) transition of **2** in the near UV-region of the spectrum spans a wavelength range of 300−440 nm, similar to that of compound **1a**. However, while the monoalkynyl compound **1a** shows a split Q-band (677 and 696 nm), the diethynyl derivative **2** exhibits a strongly split Q-band (672 and 713 nm), as well as a remarkable broadening and red-shift of this absorption. The same effect has been observed in alkynyl-linked Pc-dyads previously reported by us[10a] in which an electronic connection between the two Pc subunits has been clearly established.[21] The red-shifting has to be attributed to the enlargement of the π-conjugated system being the splitting of the Q-band, a consequence of the strong asymmetry of the molecule.

The preparation of "push−pull" compounds **3a**,**b** having a reversal substitution pattern was also achieved following two different pathways. The first one is depicted in Scheme 4 and it consists of the statistical reaction of appropriately substituted phthalonitriles **11** and **12** in a 2:1 ratio in the presence of the corresponding zinc and nickel acetates. In the present case, a mixture of *o*-dichlorobenzene−DMF was used as solvent in order to prevent the side reactions on the sulfonyl group which take place under the presence of more nucleophilic solvents.[22] In these conditions, the corresponding octapropylsulfonylphthalocyaninatos of zinc(II) and nickel(II) **13a**,**b** (not represented) were obtained accompanying **3a** and **3b**, respectively. The compounds were separated by column chromatography. The starting material **11** was synthesized in two steps, in good yield, starting from 4,5-dichlorophthalonitrile[23] by nucleophilic substitution with propylthiol in the presence of K$_2$CO$_3$ to give **10**, followed by oxidation with H$_2$O$_2$ in acetic acid as indicated in Scheme 4. The second precursor **12** was prepared from 4-(*N*,*N*-dimethylamino)phenylethyne[24] by reaction with 4-iodophthalonitrile in the presence of bis[triphenylphos-

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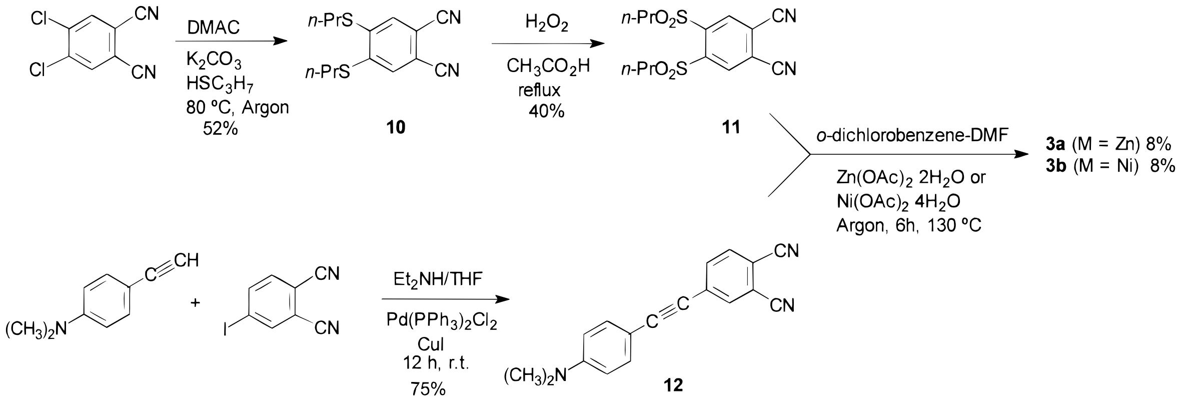
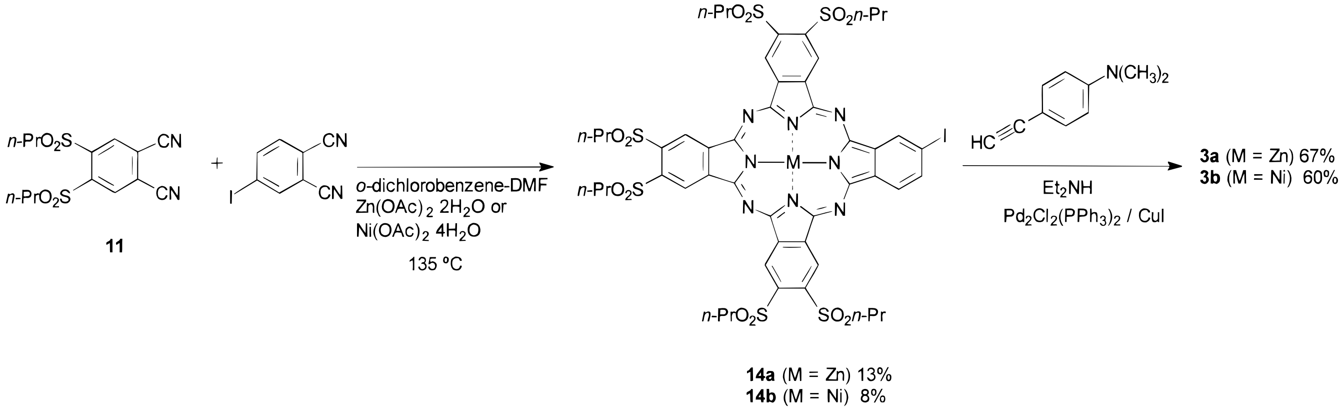
Scheme 4. Synthesis of (dimethylaminophenyl)Ethynylphthalocyanine Metal(II) Complexes 3a,b by Statistical Condensation



Scheme 5. Synthesis of (dimethylaminophenyl)Ethynylphthalocyanine Metal(II) Complexes 3a,b by a Cross-coupling Method



phine]palladium(II) dichloride [$Pd(PPh_3)_2Cl_2$] and catalytic amounts of copper(I) iodide in good yield.

Compounds **3a**,**b** can also be obtained following the pathway depicted in Scheme 5. Compound **11** and 4-iodophthalonitrile were reacted in a templated condensation reaction to afford a statistical mixture of compounds from which the monoiodo derivatives **14a**,**b** could be isolated by column chromatography. In this reaction variable amounts of the corresponding octa(propylsulfonyl)phthalocyaninato metal(II) **13a**,**b** (not represented), formed by cyclotetramerization of the major starting material **11**, were obtained. The amount of these and other statistical distribution compounds accompanying **14a**,**b** depends obviously on the ratio of the starting materials. Compounds **14a**,**b** were then reacted with 4-(*N*,*N*-dimethylamino)phenylethyne as described above in the preparation of **12** to afford phthalocyanines **3a**,**b** in good yield.

Figure 2 shows the UV/vis spectra of compound **3a** and its precursor **14a**. The "push−pull" phthalocyanine **3a** shows a broad and not well-resolved split Q-band (686 and 711 nm). In this case the precursor **14a** already shows splitting of the Q-band. The enlargement of the π-conjugated system is again responsible for the red-shifting of the Q-band in **3a**.

Similar results were obtained when comparing **3b** and **14b**. It is remarkable that the spectrum of the nickel precursor **14b** shows only one Q-band centered at 686 nm. The different behavior of **14a** and **14b** should be attributable to the different kind of central metal.

Preliminary second-order NLO studies on phthalocyanines **1**−**3** have been carried out. The permanent dipole moments in the ground state were experimentally obtained from capacitance measurements in chloroform solutions by a classical Guggenheim method.[25] HRS experiments[26,27] were performed by measuring the intensity of the second-order scattered light on focusing an intense laser beam on a chloroform solution. The measurements were carried out at 1.064 μm which is directly emitted by a nanosecond Q-switched Nd: YAG laser. Both the permanent dipole moments μ and the β_{HRS} susceptibilities of the compounds are the highest reported in the literature for unsymmetrical "push−pull" phthalocyanines.[5,8a] Zinc derivatives **1a** and **3a** show higher μ

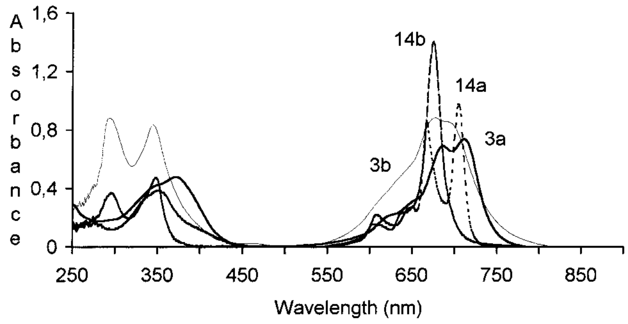


Figure 2. Electronic spectra in $CHCl_3$ of: **3a** (3.6×10^{-6} M) (solid line), **3b** (3.5×10^{-6} M) (thin line), **14a** (6.7×10^{-6} M) (dotted line), and **14b** (7.0×10^{-6} M) (dashed line).

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and β values than the corresponding nickel compounds **1b** and **3b**. Thus for example, compound **1a** shows a dipole moment of 39 D and a β value of 220×10^{-30} esu, while the nickel compound **1b** shows μ and β values of 28 D and 73×10^{-30} esu, respectively. Similar results were obtained for compounds **3**. The different β values of compounds **1a** and **1b** seem to indicate that the central metal could play an important role. Compound **2** containing two electron-withdrawing groups is less soluble in chloroform than the structurally related compound **1a**. For these reason, the experimental dipole moment μ could not be obtained with accuracy. The β_{HRS} value for **1a** can be estimated in ca. 500×10^{-30} esu, thus indicating the importance of the substitution pattern. The NLO properties of this new family of phthalocyanines and other related compounds is being studied in detail.[27]

Experimental Section

2,3,9,10,16,17-Hexabutoxy-23-[2-(4-nitrophenyl)ethynyl]-phthalocyaninato Zinc(II) or Nickel(II) (1a,b). Method A (cross-coupling method): A mixture of 0.048 mmol of **8a** or **8b** and 4-iodonitrobenzene (14 mg, 0.058 mmol) was stirred at room temperature in freshly distilled and deaerated triethylamine in the presence of $[Pd_2(dba)_3]$ (6 mg, 0.006 mmol) and $AsPh_3$ (10 mg, 0.032 mmol) under argon atmosphere. The reaction was monitored by TLC until all the starting material had reacted. After the solvent was evaporated under reduced pressure, the product was extracted with CH_2Cl_2 and washed with water. After removing the organic solvent, the blue-green solid obtained was purified by chromatography on silica gel, using a mixture of CH_2Cl_2−MeOH (100:1).

1a: Reaction time: 20 h. Yield: 44 mg (80%). Mp > 200 °C; ^{1}H NMR (300 MHz, TFA-*d*) δ: 8.7−8.1 (m, 13H), 4.45 (m, 12H), 2.0 (m, 12H), 1.65 (m, 12H), 1.0 (m, 18H); FT-IR (KBr) ν: 3502, 2880, 1550, 1281, 1092 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ϵ): 696 (5.4), 677 (5.4), 615 (4.8), 357 nm (5.2); MS-FAB (m-NBA) *m/z* (%): 1157−1155 (isotopic pattern) (100) $[(M + H)^+]$, 1100−1098 (isotopic pattern) (22) $[(M - C_4H_9)^+]$. Anal. Calcd for $C_{64}H_{67}N_9O_8Zn{\cdot}4H_2O$: C, 62.61; H, 6.16; N, 10.27. Found: C, 62.95; H, 6.32; N, 9.91.

1b: Reaction time: 24 h. Yield: 10 mg (35%). Mp > 200 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.5 (broad signal, 13H), 4.4 (m, 12H), 2.12 (m, 12H), 1.45 (m, 12H), 0.8 (m, 18H); FT-IR (KBr) ν: 3450, 2870, 1555, 1300, 1091 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ϵ): 687 (4.9), 668 (4.9), 313 nm (4.8); MS-FAB (m-NBA) *m/z* (%): 1150−1148 (isotopic pattern) (21) $[(M + H)^+]$, 881 (100). Anal. Calcd for $C_{64}H_{67}N_9O_8Ni{\cdot}3H_2O$: C, 63.90; H, 6.12; N, 10.48. Found: C, 63.95; H, 6.02; N, 10.75.

Method B (statistical method): A mixture of 4,5-dibutoxyphthalonitrile[12] (**4**) (300 mg, 1.09 mmol) and phthalonitrile **5** (99 mg, 0.36 mmol) was heated at reflux in (dimethylamino)ethanol (DMAE) (2 mL) under argon for 12 h in the presence of zinc(II) chloride (48 mg, 0.36 mmol). After the solvent was concentrated under reduced pressure, the solid residue was extracted with CH_2Cl_2 and washed with water. Compound **1a** was isolated from the octabutoxyphthalocyaninato zinc(II) by 3-fold column chromatography on silica gel using a mixture of hexane−THF (5:1) as eluent, to yield 14 mg (5%).

2,3,9,10,16,17-Hexabutoxy-23,24-bis[2-(4-nitrophenyl)-ethynyl]phthalocyaninato Zinc(II) (2). A mixture of bis-[triphenylphosphine]palladium(II) dichloride $[Pd(PPh_3)_2Cl_2]$ (4.2 mg, 2.94 mmol) and CuI (12.5 mg, 2.38 mmol) was added to a solution of diiodophthalocyanine **9**[19] (71.5 mg, 0.057 mmol) and 4-nitroethynylbenzene (33 mg, 4.85 mmol) in freshly distilled and deaerated DMF and triethylamine (1:5) (2 mL). The reaction mixture was heated with stirring at 70 °C under argon atmosphere for 10 min, and then potassium iodide (44 mg, 7.30 mmol) was added slowly.[20] The mixture was left at that temperature overnight. The solvent was removed under reduced pressure, and the crude product was purified by chromatography on silica gel using a mixture of hexane−dioxane (2:1) as eluent, to yield 34 mg (46%) of **2**. Mp > 200 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.0−7.2 (m, 12H), 4.0−3.8 (m, 12H), 1.8 (m, 12H), 1.57 (m, 12H), 1.04 (m, 18H); FT-IR (KBr) ν: 3104, 2207, 1637, 1600, 1385, 1342 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ϵ): 713 (4.9), 672 (4.8), 610 (4.3), 361 nm (4.9); MS-FAB (m-NBA) *m/z* (%): 1304−1298 (isotopic pattern) (100) $[(M + H)^+]$, 1242−1245 (isotopic pattern) (16). Anal. Calcd for $C_{72}H_{70}N_{10}O_{10}Zn{\cdot}H_2O$: C, 65.57; H, 5.50; N, 10.62. Found: C, 65.73; H, 5.67; N, 10.38.

23-[2-(4-(*N,N*-Dimethylamino)phenyl)ethynyl]-2,3,9,-10,16,17-hexakis(propylsulfonyl)phthalocyaninato Zinc-(II) or Nickel(II) (3a,b). Method A (cross-coupling method): A mixture of 0.048 mmol of phthalocyaninatos **14a**,**b** and 8 mg (0.057 mmol) of 4-(*N,N*-dimethylamino)phenylethyne[24] was dissolved in freshly distilled and deaerated diethylamine (for **14a**) or piperidine (for **14b**) in the presence of $[PdCl_2(PPh_3)_2]$ (6 mg, 0.008 mmol) and CuI (2 mg, 0.01 mmol). The mixture was stirred at room temperature under argon atmosphere. The reaction was monitored by TLC until the starting phthalocyanine had reacted. Then, the solvent was removed under reduced pressure, and the residue was extracted with CH_2Cl_2 and washed with water. The phthalocyaninatos **3a**,**b** were purified by chromatography using a mixture of CH_2Cl_2−MeOH (50:1) as eluent.

3a: Green solid. Reaction time: 4 h. Yield: 43 mg (67%). Mp > 200 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.78 (s, 3H), 8.68 (s, 3H), 8.38 (s, 2H), 7.85 (broad signal, 2H), 5.95 (broad signal, 2H), 4.45 (m, 6H), 3.6 (m, 12H), 1.8 (m, 12H), 1.05 (2xt, 18H); FT-IR (KBr) ν: 3440, 2960, 2510, 1290, 1085 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ϵ): 711(5.3), 686 (5.3), 372 nm (5.1); MS-FAB (m-NBA) *m/z* (%): 1359−1356 (isotopic pattern) (100) $[(M + H)^+]$, 1146−1142 (isotopic pattern) (18) $[(M - 2 \times SO_2C_3H_7)^+]$. Anal. Calcd for $C_{60}H_{61}N_9O_{12}S_6Zn{\cdot}3H_2O$: C, 51.10; H, 4.79; N, 8.94. Found: C, 51.50; H, 4.82; N, 8.60.

3b: Green solid. Reaction time: 12 h. Yield: 38 mg (60%). Mp > 200 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.6 (s, 3H), 6.9 (s, 6H), 4.05 (m, 12H), 3.1 (m, 6H), 1.25 (m, 12H), 0.87 (m, 18H); FT-IR (KBr) ν: 3445, 2950, 2500, 1291, 1070 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ϵ): 701(4.3), 677 (4.4), 345 nm (4.4); MS-FAB (m-NBA) *m/z* (%): 1350 (25) $[(M + H)^+]$, 936 (100) $[(M - 4 \times SO_2C_3H_7)^+]$. Anal. Calcd for $C_{60}H_{61}N_9O_{12}S_6Ni{\cdot}3H_2O$: C, 51.31; H, 4.34; N, 8.98. Found: C, 51.10; H, 4.63; N, 9.14.

Method B (statistical method): A mixture of 4,5-bis-(propylsulfonyl)phthalonitrile (**11**) (400 mg, 1.17 mmol) and 4-[2-(4-(*N,N*-dimethylamino)phenyl)ethynyl]pthalonitrile (**12**) (159 mg, 0.58 mmol) was heated at 130 °C in a mixture of *o*-dichlorobenzene−DMF (5:1) under argon for 6 h in the presence of the corresponding metallic salt, zinc(II) acetate dihydrate $[Zn(OAc)_22H_2O]$, or nickel(II) acetate tetrahydrate $[Ni(OAc)_24H_2O]$, (0.58 mmol). After the solvent was concentrated under reduced pressure, the blue green solid was extracted with CH_2Cl_2 and washed with water. Compound **3a** was isolated from the octapropylsulfonylphthalocyaninato zinc-(II) by chromatography on silica gel using a mixture of $CHCl_3$ and ethanol (400:1) as eluent, whereas for **3b** a mixture of CH_2Cl_2−ethanol (40:1) was employed.

3a: Yield: (60 mg, 8%).

3b: Yield: (47 mg, 8%).

4-[2-(4-Nitrophenyl)ethynyl]phthalonitrile (5). A mixture of 4-nitrophenylethyne[14] (0.68 g, 4.6 mmol) and 4-iodophthalonitrile[13] (1 g, 3.9 mmol) was dissolved in freshly distilled diethylamine (20 mL) and dry THF (10 mL) in the presence of $[Pd(PPh_3)_2Cl_2]$ (28 mg, 0.039 mmol) and CuI (3.7 mg, 0.019 mmol). The reaction mixture was stirred for 12 h under argon atmosphere. Then, the solvent was removed under reduced pressure and the crude reaction mixture diluted with CH_2Cl_2 and washed with water. The brown solid obtained was purified by chromatography on silica gel using a mixture of toluene and hexane (3:1) as eluent, to yield 0.67 g (63%) of **5** as orange solid. Mp 214−215 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 8.3 (d, $J = 6.4$ Hz, 2H), 7.98 (s, 1H), 7.85 (s, 2H), 7.7 (d, $J = 6.4$ Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 147.5, 136.5, 136.4, 134.3, 133.1, 127.6, 126.9, 123.9, 115.6, 115.5, 115.1, 114.6, 92.9, 90.5; MS (EI, 70 eV) *m/z* (%): 273 (100) $[M^+]$, 226

(22) [(M − NO2)$^+$]. Anal. Calcd for $C_{16}H_7N_3O_2$: C, 70.33; H, 2.58; N, 15.38. Found: C, 69.97; H, 2.80; N, 14.98.

2,3,9,10,16,17-Hexabutoxy-23-(3-hydroxy-3-methyl-1-butynyl)phthalocyaninato Zinc(II) or Nickel(II) (7a,b). A mixture of 4,5-dibutoxyphthalonitrile (**4**)[12] (500 mg, 1.83 mmol) and 4-(3-hydroxy-3-methyl-1-butynyl)phthalonitrile (**6**)[15] (128 mg, 0.61 mmol) was heated at reflux in (dimethylamino)ethanol (DMAE) (2 mL) under argon for 12 h in the presence of the corresponding metallic salt (MCl_2) (0.61 mmol). After the solvent was concentrated under reduced pressure, the blue green solid was extracted with CH_2Cl_2 and washed with water. Compound **7a** was isolated from the octabutoxyphthalocyaninato zinc(II) by chromatography on silica gel using a mixture of CH_2Cl_2 and ethanol (30:1) as eluent, whereas for **7b** a mixture of CH_2Cl_2−2-propanol (400:1) was employed.

7a: Green solid. Yield: 86 mg (13%). Mp > 200 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.78 (s, 6H), 7.58 and 7.4 (2 × s, 3H), 4.67 and 4.43 (2 × m, 13H), 2.89 (m, 12H), 1.91 (m, 12H), 1.3 (m, 24H); ^{13}C NMR (75 MHz, TFA-*d*) δ: 153.7, 150.5, 125.0, 118.7, 115.7, 115.0, 114.3, 111.2, 110.5, 107.5, 106.8, 97.5, 69.8, 29.7, 17.7, 11.05, 10.6; UV/vis ($CHCl_3$) λ_{max} (log ϵ): 685 (5.1), 613 (4.4), 356 nm (5.0); MS-FAB (m-NBA) *m*/*z* (%): 1093−1091 (isotopic pattern) (100) [(M + H)$^+$], 1034 (32) [(M − C_4H_9)$^+$]. Anal. Calcd for $C_{61}H_{70}N_8O_7Zn\cdot 3H_2O$: C, 63.89; H, 6.68; N, 9.77. Found: C, 63.58; H, 6.54; N, 9.61.

7b: Green solid. Yield: 130 mg (19%). Mp > 200 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.6 and 6.06 (2 × s, 9H), 4.1 (m, 12H), 3.49 (m, 1H), 1.85 (m, 12H), 1.61 (m, 12H), 1.25 (m, 24H); UV/vis ($CHCl_3$) λ_{max} (log ϵ): 676 (5.2), 610 (4.7), 291 nm (5.4); MS-FAB (m-NBA) *m*/*z* (%): 1087−1085 (isotopic pattern) (100) [(M + H)$^+$]. Anal. Calcd for $C_{61}H_{70}N_8O_7Ni\cdot 4H_2O$: C, 63.27; H, 6.79; N, 9.68. Found: C, 63.62; H, 6.93; N, 9.65.

2,3,9,10,16,17-Hexabutoxy-23-ethynylphthalocyaninato Zinc(II) or Nickel(II) (8a,b). A mixture of phthalocyaninatos (**7a** or **7b**) (0.091 mmol) and powdered sodium hydroxide (4 mg, 0.091 mmol) in dry toluene was heated at reflux until the starting phthalocyaninate had reacted. After the solvent was removed under reduced pressure, the residue was extracted with CH_2Cl_2 and washed with water. The crude reaction was purified by column chromatography on silica gel using a mixture of CH_2Cl_2−MeOH (100:1) as eluent.

8a: Reaction time: 4 h. Yield: 74 mg (79%). Mp > 200 °C; ^{1}H NMR (300 MHz, TFA-*d*) δ: 9.13, 8.69, 8.29 (3 × m, 9H), 4.65 (m, 12H), 3.7 (m, 1H), 2.28 (m, 12H), 1.89 (m, 12H), 1.29 (m, 18H); FT-IR (KBr) ν: 3500, 2885, 1280, 1092 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ϵ): 681 (4.9), 613 (4.3), 357 nm (4.7); MS-FAB (m-NBA) *m*/*z* (%): 1035−1033 (isotopic pattern) (100) [(M + H)$^+$], 977 (25) [(M − C_4H_9)$^+$]. Anal. Calcd for $C_{58}H_{64}N_8O_6Zn\cdot H_2O$: C, 66.13; H, 6.32; N, 10.64. Found: C, 65.87; H, 6.72; N, 10.33.

8b: Reaction time: 2 h. Yield: 37 mg (38%). Mp > 200 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.55, 7.13, 7.11 (3 × m, 9H), 4.12 (m, 12H), 3.37 (m, 1H), 2.17 and 1.81 (m, 12H), 1.58 (m, 12H), 0.87 (m, 18H); FT-IR (KBr) ν: 3500, 2880, 1282, 1091 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ϵ): 672 (5.4), 620 (5.0), 291 nm (5.4); MS-FAB (m-NBA) *m*/*z* (%): 1027 (100) [(M + H)$^+$]. Anal. Calcd for $C_{58}H_{64}N_8O_6Ni\cdot 3H_2O$: C, 64.38; H, 6.00; N, 10.36. Found: C, 64.65; H, 6.12; N, 10.38.

4,5-Bis(propylthio)phthalonitrile (10). A mixture of 4,5-dichlorophthalonitrile[23] (5 g, 25 mmol) and K_2CO_3 (10.31 g, 75 mmol) was stirred in dimethylacetamide (DMAC) (132 mL) at room temperature and under argon atmosphere for 10 min. Then, 5 mL (55 mmol) of propanothiol was added, and the mixture was stirred at 80 °C for 12 h. The crude reaction was diluted with CH_2Cl_2, and the organic phase was washed several times with H_2O. Removal of the solvent at reduced pressure yielded 10.76 g (52%) as white solid. Mp 141−142 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.44 (s, 2H), 3.01 (t, $J = 6.8$ Hz, 4H), 1.79 (m, 4H), 1.09 (t, $J = 6.8$ Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 114.1, 128.1, 115.6, 110.9, 34.5, 21.5, 13.5; MS (EI 70 eV) *m*/*z* (%): 276 (100) [M$^+$]. Anal. Calcd for $C_{14}H_{16}N_2S_2$: C, 60.83; H, 5.83; N, 10.13. Found: C, 60.67; H, 5.85; N, 9.94.

4,5-Bis(propylsulfonyl)phthalonitrile (11). Five grams (18 mmol) of 10 was stirred with acetic acid (100 mL) under reflux. Then, 83 mL of H_2O_2 was added slowly, and the mixture reaction was stirred at this temperature for 3 h. The yellow solution was poured into water, and the white solid obtained was filtered and washed with water. The solid was dried under vacuum with P_2O_5. Yield: 2.44 g (40%). Mp 189−190 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 8.68 (s, 2H), 3.65 (m, 4H), 1.8 (m, 4H), 1.07 (t, $J = 7.3$ Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 144.4, 137.5, 121.1, 113.0, 58.7, 16.3, 12.9; MS (EI 70 eV) *m*/*z* (%): 339 (10) [M$^+$], 325 (100) [(M − CH_3)$^+$]. Anal. Calcd for $C_{14}H_{16}N_2O_4S_2$: C, 49.40; H, 4.74; N, 8.24. Found: C, 49.09; H, 4.72; N, 7.93.

4-[2-(4-(*N*,*N*-Dimethylamino)phenyl)ethynyl]pthalonitrile (12). A mixture of 4-(*N*,*N*-dimethylamino)phenylethyne[24] (0.66 g, 4.6 mmol) and 4-iodophthalonitrile[13] (1 g, 3.9 mmol) was dissolved in freshly distilled diethylamine (16 mL) and THF (20 mL) in the presence of $[Pd(PPh_3)_2Cl_2]$ (28 mg, 0.039 mmol) and CuI (3.7 mg, 0.019 mmol). The reaction mixture was stirred for 12 h under argon atmosphere. Then, the solvent was removed under reduced pressure, and the crude reaction mixture was diluted with CH_2Cl_2 and washed with water. The orange solid obtained was purified by chromatography on silica gel using a mixture of hexane−CH_2Cl_2 (3:2) as eluent, to yield 0.79 g (75%) of **12**. Mp 165−168 °C (decomposition); ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.84 and 7.73 (2 × s, 3H), 7.42 (dd, $J = 2.09$ Hz, $J' = 6.89$ Hz, 2H), 6.66 (dd, $J = 2.09$ Hz, $J' = 6.89$ Hz, 2H), 3.03 (s, 6H); ^{13}C NMR (50 MHz, DMSO-d_6) δ: 150.8, 135.4, 135.2, 134.1, 133.1, 129.1, 115.9, 115.2, 111.7, 106.4, 98.4; MS (EI 70 eV) *m*/*z* (%): 271 (100) [M$^+$]. Anal. Calcd for $C_{18}H_{13}N_3\cdot H_2O$: C, 75.00; H, 5.20; N, 14.58. Found: C, 75.15; H, 5.05; N, 14.24.

23-Iodo-2,3,9,10,16,17-hexakis(propylsulfonyl)phthalocyaninato Zinc(II) (14a). A mixture of 4,5-bis(propylsulfonyl)phthalonitrile (**11**) (500 mg, 1.47 mmol) and 4-iodophthalonitrile[13] (116 mg, 0.49 mmol) was heated at reflux in (2 mL) of a mixture of *o*-dichlorobenzene−DMF (3:1) under argon for 12 h in the presence of zinc acetate dihydrate $[Zn(OAc)_2\cdot 2H_2O]$ (0.49 mmol). After the solvent was concentrated under reduced pressure, the residue was extracted with CH_2Cl_2 and washed with water. The phthalocyaninato **14a** was isolated from a mixture of Pcs by chromatography on silica gel using a mixture of CH_2Cl_2−MeOH (30:1). The triiodobis(propylsulfonyl)phthalocyaninato zinc(II) (**15a**) was obtained as the first eluted compound, the phthalocyaninato **14a** was the second one, and finally 2,3,9,10,16,17,23,24-octakis(propylsulfonyl)phthalocyaninato zinc(II) (**13a**) was eluted.

14a: Yield: 86 mg (13%). Mp > 200 °C; ^{1}H NMR (300 MHz, TFA-*d*) δ: 10.5, 10.25, 9.65, 9.25 (4 × m, 6H), 8.85 (d, 2H), 8.6 (s, 1H), 4.15 (m, 8H), 3.8 (m, 4H), 2.2 and 1.95 (2xm, 12H), 1.35 (m, 12H), 1.05, (m, 6H); FT-IR (KBr) ν: 3450, 2966, 2927, 1291, 1142, 1083 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ϵ): 703 (5.2), 669 (5.1), 643 (sh) (4.6), 609 (sh) (4.4), 368 nm (4.8); MS-FAB (m-NBA) *m*/*z* (%): 1340−1338 (isotopic pattern) (100) [(M + H)$^+$], 1129−1125 (isotopic pattern) (18) [(M − 2 × $SO_2C_3H_7$)$^+$]. Anal. Calcd for $C_{50}H_{51}N_8IO_{12}S_6Zn\cdot 4H_2O$: C, 42.56; H, 4.21; N, 7.94. Found: C, 42.22; H, 4.26; N, 7.67.

15a: Yield: 60 mg (10%). Mp > 200 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.81 (s, 2H), 7.7−7.4 (m, 9H), 3.89 (t, 4H), 1.73 (broad signal, 4H), 1.24 (s, 6H); UV/vis ($CHCl_3$) λ_{max} (log ϵ): 689 (5.2), 678 (5.1), 643 (4.7), 361 nm (4.9); MS (FAB, m-NBA) *m*/*z* (%): 1169−1165 (isotopic pattern) (100) [(M + H)$^+$], 956−952 (isotopic pattern) (29) [(M − 2 × $SO_2C_3H_7$)$^+$]. Anal. Calcd for $C_{38}H_{25}N_8I_3O_4S_2Zn\cdot 3H_2O$: C, 37.35; H, 2.56; N, 9.17. Found: C, 37.11; H, 2.70; N, 9.28.

13a: Yield: 50 mg (7%). Mp > 200 °C; ^{1}H NMR (300 MHz, TFA-*d*) δ: 10.4 (s, 8H), 3.88 (broad signal, 16H), 1.9 (m, 16H), 1.25 (s, 24H); FT-IR (KBr) ν: 3329, 2971, 1292, 1144, 1102 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ϵ): 686 (5.6), 617 (sh) (4.7), 376 nm (4.9); MS-FAB (m-NBA) *m*/*z* (%): 1427−1425 (isotopic pattern) (100) [(M + H)$^+$], 1213−1211 (isotopic pattern) (15) [(M − 2 × $SO_2C_3H_7$)$^+$]. Anal. Calcd for $C_{56}H_{64}N_8O_{16}S_8Zn\cdot H_2O$: C, 46.55; H, 4.76; N, 7.75. Found: C, 46.88; H, 4.60; N, 7.38.

23-Iodo-2,3,9,10,16,17-hexakis(propylsulfonyl)phthalocyaninato Nickel(II) (14b). A mixture of 4,5-bis(propylsulfonyl)phthalonitrile (**11**) (500 mg, 1.47 mmol) and 4-iodophthalonitrile (116 mg, 0.49 mmol) was heated at reflux in (2 mL) of a mixture of *o*-dichlorobenzene−DMF (3:1) in the presence of nickel(II) acetate tetrahydrate [$Ni(OAc)_2 \cdot 4H_2O$] (98 mg, 0.49 mmol) under argon for 12 h. After the solvent was concentrated under reduced pressure, the blue residue was extracted with CH_2Cl_2 and washed with water. The phthalocyaninato **14b** was isolated from 2,3,9,10,16,17,23,24-octakis-(propylsulfonyl)phthalocyaninato nickel(II) (**13b**) by a double column chromatography on silica gel using a mixture of CH_2Cl_2−2-propanol (100:1), and CH_2Cl_2−hexane−dioxane (2:1:1), as eluents.

14b: Blue solid. Yield: 54 mg (8%). Mp > 200 °C; ^1H NMR (300 MHz, $CDCl_3$) δ: 8.8 (broad signal, 4H), 7.0−6.5 (broad signal, 5H), 3.67 (m, 12H), 1.44 (m, 12H), 1.19 (m, 18H); FT-IR (KBr) ν: 3441, 2969, 2935, 1295, 1108, 1085 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ϵ): 686 (5.6), 617 (sh) (4.7), 376 nm (4.9); MS-FAB (m-NBA) m/z (%): 1335−1333 (isotopic pattern) (100) [$(M + H)^+$]. Anal. Calcd for $C_{50}H_{51}N_8IO_{12}S_6Ni \cdot 4H_2O$: C, 42.71; H, 4.23; N, 7.97. Found: C, 42.89; H, 4.36; N, 7.76.

13b: Yield: 84 mg (15%). Mp > 200 °C; ^1H NMR (300 MHz, $CDCl_3$) δ: 10.5 (broad signal, 8H), 4.0 (m, 16H), 2.14 (m, 16H), 1.2 (m, 24H); UV/vis ($CHCl_3$) λ_{max} (log ϵ): 674 (5.2), 607 (sh) (4.4), 348 nm (4.7); MS-FAB (m-NBA) m/z (%): 1421−1419 (isotopic pattern) (100) [$(M + H)^+$].

Acknowledgment. This work was supported by CICYT and Comunidad de Madrid (Spain) through grants MAT-99-0180 and 07N/0020/98, respectively. A Graduated Research Fellowship of the Comunidad de Madrid to Eva María Maya is gratefully acknowledged.

Supporting Information Available: ^1H and ^{13}C NMR data. This material is available free of charge via the Internet at http://pubs.acs.org.

JO991843F