Synthesis of New Push-Pull Unsymmetrically Substituted Styryl Metallophthalocyanines: Targets for Nonlinear Optics

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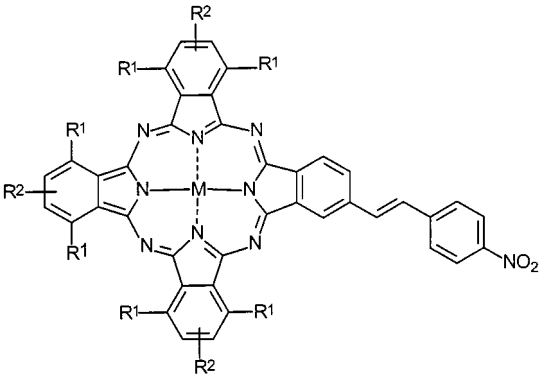
Keywords: Phthalocyanines / Conjugation / UV/Vis spectroscopy / Nonlinear optics

Following our studies on styryl phthalocyanines with extended conjugation, we report here the synthesis and characterization of new push-pull unsymmetrically substituted styryl phthalocyanines **2**–**6**. They have been prepared for studying the influence of the position and electronic character of the substituents and the role of the central metal atom on their optical properties.

Introduction

In the field of nonlinear optics, organic materials based on delocalized π-electron systems have attracted a great deal of research interest.[1] In particular, phthalocyanines[2−4] and related compounds such as porphyrins,[5] hemiporphyrazines[6] and subphthalocyanines[7] have been extensively studied because these molecules offer the advantage of large nonlinear optical susceptibilities and enormous architectural flexibility.

Although it has been suggested that noncentrosymmetric donor-acceptor substituted phthalocyanines should display second-order nonlinear optical responses,[8] there have been few reports on this subject,[9] probably due to the difficulty



1 R^1 = H, R^2 = $C(CH_3)_3$, M = 2H
2 R^1 = H, R^2 = $C(CH_3)_3$, M = Co
3 R^1 = H, R^2 = $C(CH_3)_3$, M = Ni
4 R^1 = H, R^2 = $C(CH_3)_3$, M = Cu
5 R^1 = C_8H_{17}, R^2 = H, M = Ni
6 R^1 = OC_8H_{17}, R^2 = H, M = Ni

in the synthesis and purification of this kind of compounds.

It has been theoretically and experimentally demonstrated that the second-order optical nonlinearities can be significantly enhanced by increasing the number of polarizable electrons between the donor and acceptor end groups.[8] Considering these facts, we have now designed and synthesized noncentrosymmetric push-pull phthalocyanines **1**−**6** with extended conjugation. The main goal of this work is to make available a set of compounds for studying the influence of the position and electronic character of the substituents, as well as the role of the central metal atom, on the optical properties of phthalocyanines. Thus, we have prepared two series of compounds, varying either the number, position and electronic character of the donor substituents (**3**, **5** and **6**) or the central metal ion (**1**−**4**).

Results and Discussion

The preparation of the previously described metal-free phthalocyanine **1**[10] was attempted following a modified procedure. The mixed condensation of 4-*tert*-butyl-1,2-dicyanobenzene (**8a**)[11] and 4-*p*-nitrostyryl-1,2-dicyanobenzene (**7**),[10] in a 3:1 ratio in the presence of a lithium alkoxide (Scheme 1) yielded a statistical mixture of lithium phthalocyanines which were converted into the metal-free derivatives by treatment with acetic acid. The unsymmetrically substituted compound **1** was isolated by column chromatography as a mixture of regioisomers in a 14% yield.

The synthesis of metallic complexes **2**−**4** was carried out by statistical condensation of a mixture of 4-*tert*-butyl-1,2-dicyanobenzene (**8a**)[11] and 4-*p*-nitrostyryl-1,2-dicyanobenzene (**7**),[10] in a 3:1 molar ratio, in the presence of the corresponding metal salt [$CoCl_2 \cdot 6H_2O$, $Ni(OAc)_2 \cdot 4H_2O$ or $Cu(OAc)_2 \cdot H_2O$] (Scheme 1). The statistical mixture of compounds was chromatographed on silica gel using toluene as eluent. The first eluted component was, in all the cases, the corresponding symmetrically substituted tetra-*tert*-butylphthalocyanine complex followed by the corresponding phthalocyanine bearing one conjugated attractor moiety (11−18% yield).

The procedure followed for preparing phthalocyanine **5** was the lithium alkoxide catalyzed condensation of 1,2-dicyano-3,6-dioctylbenzene (**8b**)[12] and phthalonitrile **7**, and subsequent treatment with acetic acid to convert the in-

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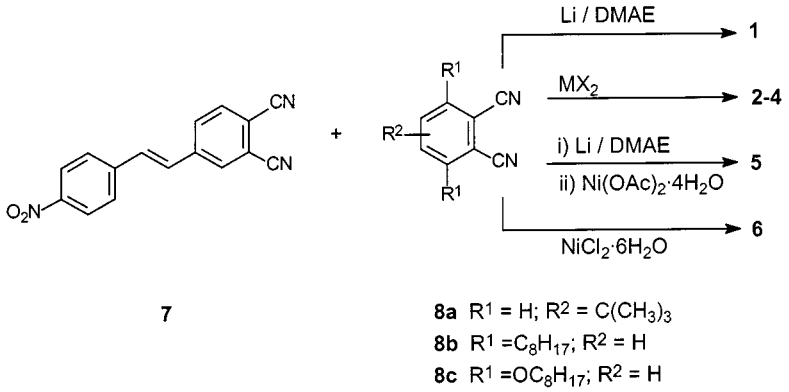

Scheme 1. Synthesis of phthalocyanines **1**−**6**

itially formed statistical mixture of lithium phthalocyanines into the corresponding metal-free phthalocyanines, which were finally treated with nickel acetate tetrahydrate in standard conditions (Scheme 1). Column chromatography (hexane/dichloromethane, 2:1) allows to isolate the symmetrically substituted phthalocyanine and the desired compound **5**. A 9:1 molar ratio of **8b** and **7** in the statistical condensation was found to be the most appropriate to improve the yield, probably due to the lower reactivity of the sterically hindered phthalonitrile **8b** than that of **7**. Nevertheless, the yield of **5** is much lower (8%) than those of **2**−**4**.

Finally, compound **6** was prepared by statistical condensation of the appropriate phthalonitriles **8c**[13] and **7** in a 9:1 ratio, with nickel chloride in (dimethylamino)ethanol (Scheme 1). The mixture of products obtained was chromatographed on silica gel using hexane/dioxane mixtures of increasing polarity. The elution of the octakis(octyloxy)phthalocyanine was followed by the elution of the unsymmetrically susbtituted macrocycle **6**, which was isolated in a 8% yield. This compound decomposes in chloroform solution when exposed to light.

Compounds **2**−**6** were characterized by elemental analysis, IR and UV/Vis spectroscopies, fast-atom bombardment mass spectrometry (FAB MS) and ^{1}H NMR in the case of diamagnetic complexes. Phthalocyanine **3** shows in the ^{1}H-NMR spectrum ($CDCl_3$) a large number of signals for the *tert*-butyl groups since it is a mixture of regioisomers. Several signals appear also at $\delta = 8.5-5.1$, assignable to the aromatic and olefinic protons. In the spectra of **5** and **6**, the signals for the aromatic protons in nonequivalent environments are well resolved. The non-equivalence of the alkyl chains is also observed, especially for the signals corresponding to the first methylene group linked to the phthalocyanine ring in the case of **5** and to the oxygen atom in the case of **6**.

The position of the Q-band of phthalocyanines **1**−**6** changes according to the kind of central metal atom and the type, number and positions of the peripheral substituents. Thus, the UV/Vis spectrum of metal-free phthalocyanine **1** shows the two typical Q-bands of a non-metallated Pc system, centered at 681 and 699 nm, and an additional band at a higher wavelength (717 nm) indicative of a splitting of the excited electronic levels (Figure 1).[10] When some metal ions are included into the cavity of **1**, the average position of the Q-bands of the resulting metal complexes (**2**−**4**) is sligthly shifted to the blue with respect to the parent metal-free compound (Figure 1), especially in the case of cobalt (**2**) and nickel (**3**) complexes which show split Q-bands centered at around 680 nm. The most noticeable change in the UV/Vis spectra occurs in the second series of compounds (**3**, **5**, **6**), when varying the number of the donor substituents, their position and electron affinity. In Figure 1 it is possible to appreciate a red-shift of the Q-band for compound **5** and especially for compound **6**, corresponding to the presence of substituents on the inner benzenoid positions.[14]

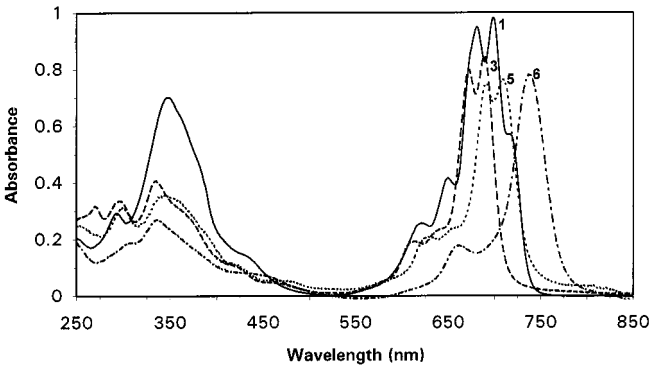

Figure 1. UV/Vis spectra of phthalocyanines **1** (continuous line), **3** (dashed), **5** (dotted) and **6** (dashed-dotted) in chloroform solution (ca. $1\cdot10^{-5}$ M)

Preliminary second-order NLO studies of phthalocyanines **1**−**6** have been carried out. The permanent dipole moments of these compounds are quite high and range from 4.6 D (compound **1**) to 22.7 D (compound **6**); γ_{EFISH} susceptibilities for these molecules have been measured at 1.907 μm in $CHCl_3$ solution. From these data, a quantitative estimate of the dipolar off-resonant $\beta_v(0)$ coefficients has been obtained. These β values, ranging from $14\cdot10^{-30}$ to $45\cdot10^{-30}$ esu, are the highest reported in the literature for unsymmetrically substituted phthalocyanines. Thus for example, compound **5** shows a $\mu\cdot\beta_v(0)$ value of $511\cdot10^{-48}$ esu, having a dipole moment of 12.6 D. A more detailed study on the NLO properties of this new family of compounds has been now undertaken.

Experimental Section

General: Phthalonitriles **7**[10] and **8a**−**c**[11−13] were prepared according to previously described procedures. (Dimethylamino)ethanol was freshly distilled and collected in the presence of 4 Å molecular sieves before using it. Silica gel used for chromatography was Merck Silica Gel 60 (particle size 0.040−0.063 mm). − Melting points: Büchi 504392 type S apparatus (open capillaries, uncorrected values). − ^{1}H-NMR spectra: Bruker AC-200 (200 MHz) spectrometer (TMS at δ = 0, $CHCl_3$ at δ = 7.26 as internal standard). − UV/Vis spectra: Perkin−Elmer Model Lambda 6 spectrophotometer. − IR spectra: PU 9716 Philips spectrophotometer. − MS: MAT 900 (Finnigan MAT, GmbH, Bremen) spectrometer. − Elemental analyses: CHN elemental analyser Perkin−Elmer 2400.

9,16,23-Tri-*tert*-butyl-2-(*p*-nitrostyryl)phthalocyanine (1) (only one regioisomer is named):[10] A small piece of clean lithium metal (1.2 mmol) was placed in a round-bottom flask with 3 mL of (dimethylamino)ethanol and the mixture stirred under argon until complete reaction of the lithium metal. 4-*tert*-Butyl-1,2-dicyanobenzene (**8a**) (0.60 g, 3.26 mmol) and phthalonitrile **7** (0.30 g, 1.09 mmol) were then added and the mixture was refluxed for 14 h. The mixture was allowed to cool down, poured onto glacial acetic acid and stirred for 30 min. The precipitate was isolated by centrifugation and washed several times with MeOH/H_2O (10:1). The mixture of phthalocyanines was chromatographed with CH_2Cl_2/hexane (2:1). The first eluted component was identified as tetra-*tert*-butylphthalocyanine. Phthalocyanine **1** was eluted in the second fraction. Yield: 14%, dark-green powder; m.p. > 250°C. − ^{1}H NMR ($CDCl_3$): δ = 9.2−8.7 (2 × m, arom. H), 8.3−7.9 (2 × m, arom. H) 7.7−7.4 (2 × m, arom. H), 7.0−6.3 (2 × m, olef. H), 1.9−1.75 [8 × s, C(CH_3)$_3$]. −UV/Vis ($CHCl_3$): λ_{max} (log ε/$dm^3mol^{-1}cm^{-1}$) = 347 nm (4.99), 430 sh, 621 (4.55), 650 (4.76), 681 (5.12), 699 (5.13), 717 (4.90). − IR (KBr): $\tilde{\nu}$ = 2955 cm^{-1}, 1610 (C=N), 1590 (C=C), 1520 (NO_2), 1340 (NO_2), 1110, 1090, 1010, 830, 750. − MS (FAB$^+$, *m*-NBA); *m/z* (%): 830 (100) [(M + H)$^+$]. − $C_{52}H_{47}N_9O_2{\cdot}2H_2O$ (866.0): calcd. C 72.11, H 5.93, N 14.55; found C 71.75, H 5.54, N 14.36.

General Procedure for the Preparation of Phthalocyanines 2−4: A mixture of 4-*tert*-butyl-1,2-dicyanobenzene (**8a**) (0.60 g, 3.26 mmol), phthalonitrile **7** (0.30 g, 1.09 mmol) and the corresponding metal salt (1.3 mmol) in (dimethylamino)ethanol (3 mL) was refluxed under argon for 14 h. After cooling, MeOH/H_2O (10:1) (30 mL) was added and the precipitate isolated by centrifugation and washed several times with the same mixture of solvents. The mixture of phthalocyanines was chromatographed on silica gel, using toluene as eluent. The first eluted component was identified in all the cases as the corresponding (tetra-*tert*-butylphthalocyaninato)metal(II) complex. Phthalocyanines **2**−**4** were eluted as regioisomeric mixtures in the second fractions.

[9,16,23-Tri-*tert*-butyl-2-(*p*-nitrostyryl)phthalocyaninato]cobalt(II) (2) (only one regioisomer is named): After purification by column chromatography, as indicated above, the isolated solid was triturated with hot acetonitrile. Yield: 11%, dark-green powder; m.p. > 250°C. − ^{1}H-NMR spectrum is uninformative for the cobalt complex since only broad signals for *tert*-butyl groups can be observed due to the paramagnetic character of this compound. − UV/Vis ($CHCl_3$): λ_{max} (log ε/$dm^3mol^{-1}cm^{-1}$) = 293 nm (4.68), 333 (4.84), 614 (4.50), 637 sh, 672 (5.02), 688 (5.06). − IR (KBr): $\tilde{\nu}$ = 2955 cm^{-1}, 1610 (C=N), 1590 (C=C), 1520 (NO_2), 1340 (NO_2), 1110, 1090, 1010, 830, 750. − MS (FAB$^+$, *m*-NBA); *m/z* (%): 887 (100) [(M + H)$^+$]. − $C_{52}H_{45}CoN_9O_2{\cdot}H_2O$ (904.9): calcd. C 69.02, H 5.23, N 13.93; found C 68.49, H 5.09, N 13.67.

[9,16,23-Tri-*tert*-butyl-2-(*p*-nitrostyryl)phthalocyaninato]nickel(II) (3) (only one regioisomer is named): The pure product was obtained after chromatography followed by trituration with hot methanol. Yield: 18%, dark-green powder; m.p. > 250°C. − ^{1}H NMR ($CDCl_3$): δ = 8.5−5.1 (various signals, arom. and olef. H), 1.70−1.55 [12 × s, C(CH_3)$_3$]. − UV/Vis ($CHCl_3$): λ_{max} (log ε/$dm^3mol^{-1}cm^{-1}$) = 296 nm (4.87), 335 (4.95), 613 (4.66), 639 sh, 672 (5.20), 689 (5.23). − IR (KBr): $\tilde{\nu}$ = 2955 cm^{-1}, 1615 (C=N), 1590 (C=C), 1515 (N−O), 1410, 1340 (N−O), 1280, 1255, 1095, 945, 830, 750. − MS (FAB$^+$, *m*-NBA); *m/z* (%): 888, 886 (100) [(M + H)$^+$]. − $C_{52}H_{45}N_9NiO_2{\cdot}H_2O$ (904.7): calcd. C 69.04, H 5.24, N 13.93; found C 69.26, H 5.37, N 14.46.

[9,16,23-Tri-*tert*-butyl-2-(*p*-nitrostyryl)phthalocyaninato]copper(II) (4) (only one regioisomer is named): Trituration with hot methanol afforded the pure product. Yield: 16%, dark-green powder; m.p. > 250°C. − ^{1}H NMR spectrum is uninformative for the copper complex since only broad signals for *tert*-butyl groups can be observed due to the paramagnetic character of this compound. − UV/Vis ($CHCl_3$): λ_{max} (log ε/$dm^3mol^{-1}cm^{-1}$) = 342 nm (5.11), 619 (4.75), 643 sh, 681 (5.26), 697 (5.33). − IR (KBr): $\tilde{\nu}$ = 2955 cm^{-1}, 1615 (C=N), 1590 (C=C), 1510 (N−O), 1395, 1340 (N−O), 1280, 1255, 1090, 1050, 830, 750. − MS (FAB$^+$, *m*-NBA); *m/z* (%): 894, 892 (100) [(M + H)$^+$]. − $C_{52}H_{45}CuN_9O_2{\cdot}H_2O$ (909.6): calcd. C 68.67, H 5.21, N 13.86; found C 68.54, H 4.96, N 13.70.

[23-*p*-(Nitrostyryl)-1,4,8,11,15,18-hexaoctylphthalocyaninato]-nickel(II) (5): A small piece of clean lithium metal (0.5 mmol) was placed in a round-bottom flask with 4 mL of (dimethylamino)ethanol and the mixture stirred under argon until complete reaction of the lithium metal. Phthalonitriles **8b** (1.38 g, 3.92 mmol) and **7** (0.12 g, 0.43 mmol) were then added to the mixture. After heating at reflux temperature for 10 h, the mixture was allowed to cool and poured onto glacial acetic acid and stirred for 30 min. The solid was collected by centrifugation and washed several times with methanol. After drying, the statistical mixture of metal-free phthalocyanines was allowed to react with Ni(OAc)$_2{\cdot}4H_2O$ (0.35 g, 1.41 mmol) in refluxing (dimethylamino)ethanol (2 mL) for 12 h. After cooling, methanol was added and the solid obtained was isolated by centrifugation and chromatographed on silica gel (hexane/CH_2Cl_2, 2:1). The desired product was eluted in the second fraction. Trituration with hot methanol afforded the pure product. Yield: 8%, green powder; m.p. > 250°C. − ^{1}H NMR ($CDCl_3$): δ = 8.26 (m, 2 H, AA′XX′ system), 7.61, 7.45 (2 × m, 5 H, arom. 22-H, 24-H, 25-H; AA′XX′ system), 7.33 (s, 2 H, arom. H_9, H_{10}), 7.19 (m, 2 H, arom. 3-H, 16-H), 6.95 (m, 2 H, arom. 2-H, 17-H), 6.68 (AB system, $J_{A\text{-}B}$ = 16.5 Hz, 2 H, olef. H), 4.1, 4.0, 3.9, 3.25, 3.0 (5 × m, 12 H, CH_2O), 2.05, 1.9, 1.5−1.0 (3 × m, 72 H, CH_2), 0.85, 0.71 (2 × m, 18 H, CH_3). − UV/Vis ($CHCl_3$): λ_{max} (log ε/$dm^3mol^{-1}cm^{-1}$) = 340 nm (4.54), 630 (4.26), 660 sh, 692 (4.89) 709 (4.91). IR (KBr): $\tilde{\nu}$ = 2918 cm^{-1}, 2849, 1591 (C=C), 1516 (N−O), 1463, 1341 (N−O), 1094, 803. − MS (FAB$^+$, *m*-NBA); *m/z* (%): 1393, 1391 (100) [(M + H)$^+$]. − $C_{88}H_{117}N_9NiO_2{\cdot}5H_2O$ (1481.7): calcd. C 71.33, H 8.64, N 8.51; found C 70.98, H 8.29, N 8.13.

[23-(*p*-Nitrostyryl)-1,4,8,11,15,18-hexakis(octyloxy)phthalocyaninato]nickel(II) (6): A mixture of **8c** (1.51 g, 3.92 mmol), **5** (0.12 g, 0.43 mmol) and $NiCl_2{\cdot}6H_2O$ (0.34 g, 1.43 mmol) in (dimethylamino)ethanol (4 mL) was refluxed under argon for 14 h. After cooling, methanol was added and the solid isolated by centrifugation and chromatographed on silica gel (hexane/dioxane, 15:1). The first eluted compound was the symmetric octakis(octyloxy)phthalocyaninatonickel(II). The amount of dioxane was then gradually changed to hexane/dioxane (5:1) in order to separate **6**. Complete purification was achieved by further column chromatography

on silica gel (toluene/2-propanol, 50:1). Yield: 8%, dark-green powder; m.p. > 250°C. – ^{1}H NMR ($CDCl_3$): δ = 9.1 (m, 3 H, arom. 22-H ***((AUTHOR: H***$_{22}$ etc. means 22 H etc.!)), 24-H, 25-H), 8.31 (m, 2 H, AA′XX′ system), 8.12 (d, *J* = 7.5 Hz, 2 H, arom. 2-H, 17-H), 7.71 (m, 2 H, AA′XX′ system), 7.5 (m, 6 H, arom. 3-H, 9-H, 10-H, 16-H, olef. H), 4.77 (m, 8 H, CH_2O), 4.58 (m, 4 H, CH_2O), 2.4, 2.2, 1.9, 1.6−1.2 (4 × m, 72 H, CH_2), 0.85, 0.75 (2 × m, 18 H, CH_3). – UV/Vis ($CHCl_3$): λ_{max} (log ε/dm^{3}mol^{-1}cm^{-1}) = 332 nm (4.66), 660 (4.47), 737 (5.11). – IR (KBr): $\tilde{\nu}$ = 2956 cm^{-1}, 2922, 2852, 1611 (C=N), 1590 (C=C), 1506 (N−O), 1340 (N−O), 1318, 1263, 1082−1034 (C−O−C), 804, 794. – MS (FAB$^+$, *m*-NBA); *m/z* (%): 1489, 1487 (100) [(M + H)$^+$]. – $C_{88}H_{117}N_9NiO_8{\cdot}5H_2O$ (1577.7): calcd. C 66.99, H 8.11, N 7.99; found C 66.34, H 7.84, N 8.47.

Acknowledgments

This work was supported by CICYT and Comunidad de Madrid (Spain) through grants MAT−96−0654 and 07N/0020/1998, respectively. We thank Prof. F. Agulló-López and G. Rojo for nonlinear optical measurements.

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Received March 11, 1999
[O99143]