Synthesis of Novel Unsymmetrically Substituted Push-Pull Phthalocyanines

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The synthesis and characterization of novel non-centrosymmetrically push-pull substituted metal-free phthalocyanines **3**−**9** are described. The compounds have different donor (dialkoxy, *tert*-butyl, methyl, *p*-tolylthio) and/or attractor (*p*-tolylsulfinyl, *p*-tolylsulfonyl, nitro) functional groups, are soluble in organic solvents, and are especially designed to study their second- and third-order nonlinear optical properties. Compounds **7**−**9** are mixtures of the four corresponding regioisomers. For preparing the unsymmetrical phthalocyanines **7**−**9**, the effectiveness of the *subphthalocyanine route*, using different substituted diiminoisoindolines as reagents, has been tested. Furthermore, a comparison between this method *versus* the statistical one has been done. The results obtained show that the ring enlargement reaction of subphthalocyanines to obtain unsymmetrically substituted phthalocyanines is not a selective reaction but a multistep process, which depends dramatically on the nature of the substituents on the subphthalocyanines, the reactivity of the iminoisoindoline, the solvent, and other factors that limit its general synthetic utility. Preliminary data of the experimental second-order hyperpolarizabilities of compounds **3**−**9** are also given.

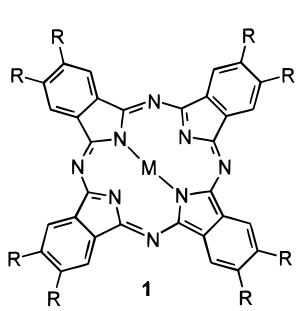
Introduction

Molecules with nonlinear optical (NLO) properties have been extensively studied because of their potential applications in optical communications, data storage, and electrooptical signal processing.[1] Increasingly, organic molecules are becoming targets for these applications mainly due to their processability and the possibility of tailoring the molecules with the desired physicochemical parameters.[2,3] Whereas an electron-delocalized organic system is the single prerequisite for achieving a third-order nonlinear response, second-order nonlinear effects are present only in non-centrosymmetric molecules, and their enhancement has relied on push-pull systems.

Symmetrically substituted phthalocyanines (Pcs, **1**) have emerged as novel targets toward materials with third-order nonlinear optical applications due to their extensively delocalized 18 π-electron system and the possibility of very easily modifying their electronic distribution by incorporation of different metal atoms in the center or through peripheral or axial substitution.[4] Unsymmetrically substituted phthalocyanines carrying donor and/or acceptor groups have been suggested as interesting candidates for second harmonic generation.[5] However, up to date very few studies have been carried out in this area.[6] The main reason could be the difficulty in the preparation and purification of this kind of phthalocyanine systems.

Different strategies to synthesize non-centrosymmetric phthalocyanines have been reported,[7] the most common one being the statistical condensation reaction between two different substituted phthalonitriles[8] or diiminoisoindolines.[9] The disadvantage of this method is that a mixture of products is always formed, making their separation difficult by chromatographic techniques.

Within this context, it is worth noting that the preparation of unsymmetrical Pcs can be effected through ring enlargement of subphthalocyanines[10] (subPcs, **2**) by reaction with substituted diiminoisoindolines. This strategy was claimed to have three advantages over the mixed condensation methods: normally relatively good yields (8−20%), easy purification by column chromatography of the unsymmetric Pcs, and, most importantly, selectivity, since only one Pc compound was obtained in the reaction.[10a]



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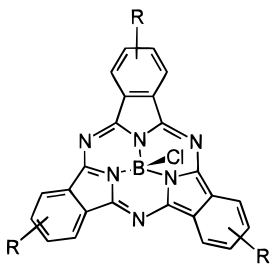

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However, some authors[11,12] have reported recently that the ring enlargement reaction of subPcs for obtaining

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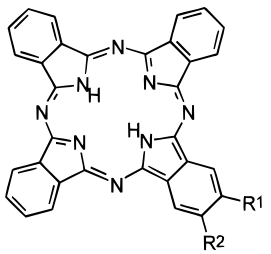
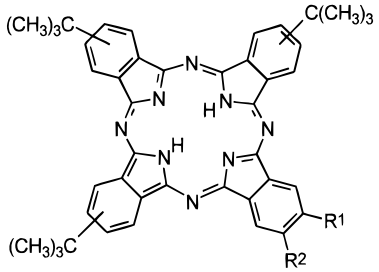
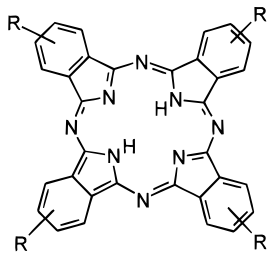
Chart 1



3 $R^1 = R^2 = OC_8H_{17}$
4 R^1 = H, R^2 = *tert*-butyl
5 R^1 = H, R^2 = *p*-thiotolyl
6 R^1 = H, R^2 = *p*-tolylsulfinyl



7 R^1 = H, R^2 = *p*-tolylsulfonyl
8 R^1 = H, $R^2 = NO_2$
9 $R^1 = R^2 = CH_3$



10 R = *p*-tolylsulfinyl
11 R = *p*-tolylsulfonyl
12 R = *tert*-butyl

substituted phthalocyanines is actually, in a general way, a nonselective multistep reaction. Opening and breaking of the subPc often takes place leading to mixtures of all possible statistical products.

During the last few years we have focused on the preparation[13] and study of NLO properties[14] of phthalocyanines and related compounds. This paper reports the synthesis and characterization of novel non-centrosymmetrically substituted metal-free phthalocyanines **3**−**9**. These species are soluble in organic solvents and have been especially designed to study their second and third-order nonlinear optical properties. They consist in one series of mono- and disubstituted Pcs having different donor [dialcoxy (**3**), *tert*-butyl (**4**), *p*-tolylthio (**5**)] or attractor [*p*-tolylsulfinyl (**6**)] functional groups, and another series of tetra- and pentasubstituted push-pull Pcs containing three *tert*-butyl groups each and also *p*-tolylsulfonyl (**7**), nitro (**8**), methyl (**9**) moieties as substituents. Moreover, we have prepared three identically tetrasubstituted Pcs **10**−**12**, bearing *p*-tolylsulfinyl, *p*-tolylsulfonyl, and *tert*-butyl substituents, in order to compare their nonlinear optical responses with those of the noncentrosymmetric ones. Compounds **7**−**12** are mixtures of the four corresponding regioisomers.

For preparing the unsymmetrical Pcs we have tested the effectiveness of the subphthalocyanine method using different substituted diiminoisoindolines and subphthalocyanines as reagents. Furthermore, a comparison between this method versus the statistical one has been done.

Results and Discussion

The 5,6-bis(octyloxy)-1,3-diiminoisoindoline[15] (**13**), 5-*tert*-butyl-1,3-diiminoisoindoline[16] (**14**), 5,6-dimethyl-1,3-diiminoisoindoline[17] (**15**), and 5-nitro-1,3-diiminoisoindoline[18] (**16**) employed in the synthesis of the unsymmetrical phthalocyanines were prepared following methods described in the literature.

The preparation of the (*p*-tolylthio)phthalonitrile (**17**) was accomplished by *ipso* substitution on 4-nitrophthalonitrile with *p*-methylthiophenol in presence of a base in 90% yield. The oxidation of **17** to the corresponding sulfinyl and sulfonyl derivatives **18** and **19** was performed using *m*-chloroperbenzoic acid (*m*-CPBA) as oxidizing agent in 94 and 96% yield, respectively. The diiminoisoindolines **20**−**22** were obtained in excellent yields by reacting the corresponding phthalonitriles **17**−**19** with NH_3(g) in MeOH as solvent and NaOMe as catalyst (Scheme 1).

Chlorosubphthalocyanine **23** and tri-*tert*-butylchlorosubphthalocyanine **24** were prepared following the Meller and Ossko method,[19] as reported previously by us,[14c] from the corresponding phthalonitriles in the presence of BCl_3.

The synthesis of the mono- and disubstituted unsymmetrical phthalocyanines **3**−**6** was carried out by reaction of the subphthalocyanine **23** with the appropriate diiminoisoindoline (Scheme 2) in *N*,*N*-dimethylaminoethanol (DMAE) at 80 °C. The ratio diiminoisoindoline/subphthalocyanine employed in the reactions was variable according to the reactivity of each diiminoisoindoline.

Thus, from ratios of 3:1 for **13**/**23** and 9:1 for **14**/**23**, 2,3-bis(octyloxy)phthalocyanine **3** and 2-*tert*-butylphthalocyanine **4** were obtained in 90% and 57% yields, respectively. In both cases, a small amount of unsubstituted phthalocyanine (**1**, R = H, M = H_2) coming from **23** was detected by FAB-MS and separated by flash column chromatography. The lower reactivity of the *tert*-butyldiiminoisoindoline **14** in comparison to that of the bis(octyloxy)diiminoisoindoline **13** makes necessary the use of a higher excess of **14** to avoid the formation of significant amounts of **1** (R = H, M = H_2).

Reaction of bis(octyloxy)diiminoisoindoline **13** with subPc **23** in pentanol/DBU as solvent at 80 °C affords a mixture of H_2Pc, di-, tetra-, hexa-, and octaalkoxyphthalocyanines. Moreover, the lowest yields of **3** were obtained either when DMAE was replaced by a mixture of dimethyl sulfoxide/dichlorobenzene (DMSO/DCB), solvent normally used in this type of reaction,[10,11,20] or when

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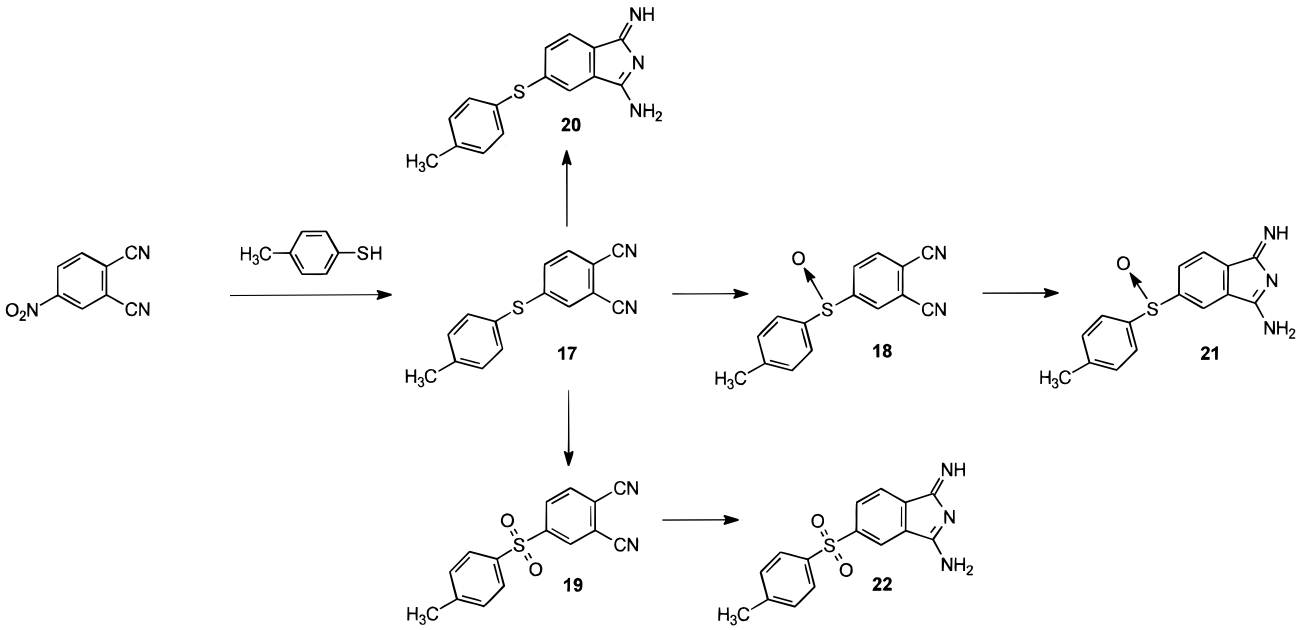
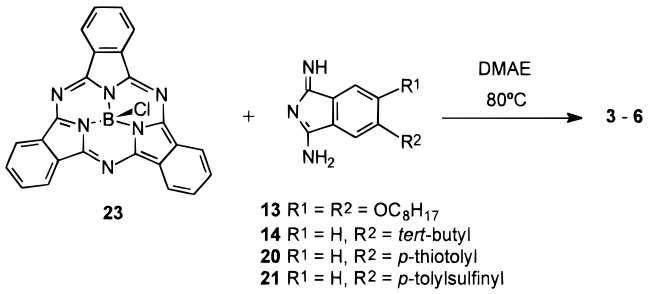
Scheme 1



Scheme 2



the molar ratio of diiminoisoindoline/subphthalocyanine was lower than 9:1.

These facts indicate that the solvent plays an essential role in the mechanism of formation of unsymmetrical Pcs from subPcs. It has been demonstrated that certain solvents catalyze the opening of the subPc **23**. Thus for example, when compound **23** was heated overnight in pentanol or ethoxyethanol at 80 °C, unsubstituted Pc (**1**, R = H, M = H_2) was obtained in moderate yield. However, when treated under the same reaction conditions in less nucleophilic solvents, such as DMSO/DCB or DCB/chloronaphthalene or even in DMAE, only traces of the unsubstituted Pc were observed.

Bis(octyloxy)diiminoisoindoline **13** was also reacted with subPc **23** in the presence of a metallic salt ($FeSO_4$, $NiCl_2$) for facilitating a template condensation in order to obtain only the corresponding metal bis(octyloxy)-phthalocyaninate, using different molar ratios of the reactants (from 7:1 to 1:3) in DMAE or DCB/DMSO as solvents. In agreement with previously reported results,[11,12] the presence of a metal ion increases the yield of the expected unsymmetrical Pc but also leads to a higher amount of statistical distribution compounds. The cleavage of subPc **23** by means of a transition metal ion has been demonstrated because reaction of **23** with $FeSO_4$ or $NiCl_2$ in the solvents mentioned above in the absence of diiminoisoindoline affords the corresponding unsubstituted metallophthalocyanine (**1**, R = H, M = Fe, Ni).

On the other hand, in the preparation of (tolylthio)-phthalocyanine **5** and (tolylsulfinyl)phthalocyanine **6**, besides free unsubstituted phthalocyanine (H_2Pc, **1**, R = H), di- and trisubstituted phthalocyanines were detected by FAB-MS. The expected phthalocyanines **5** and **6** were purified from the reaction mixture by column chromatography. These results could be explained by taking into account the high reactivity of diiminoisoindolines **20** and **21**, which facilitates their self-condensation.

Mono- and disubstituted phthalocyanines **3**−**6** are scarcely soluble in organic solvents. At room temperature these compounds are slightly soluble in chloroform but increasingly so upon heating.

With the aim of increasing the solubility in organic solvents, different push-pull tetra- and pentasubstituted unsymmetrical phthalocyanines **7**−**9** also have been synthesized, and a comparative study of the yield obtained employing the subPc route and the diiminoisoindoline-statistical method was accomplished (Scheme 3).

Compounds **7**−**9** were prepared from diiminoisoindolines **22**, **16**, or **15**, respectively, by reaction with tri-*tert*-butylsubphthalocyanine (**24**) in a 4:1 molar ratio using a mixture of DCB/DMSO (7:3) as solvent. The same compounds were prepared by the statistical method by reacting *tert*-butyldiiminoisoindoline **14** and the corresponding diiminoisoindoline **22**, **16**, or **15** in a 3:1 molar ratio using DMAE as solvent (Scheme 3).

Selective formation of the expected substituted phthalocyanines **7**−**9** was not achieved by either method. In both pathways, besides compounds **7**−**9** mixtures of all the statistical condensation products were obtained as observed by FAB-MS. Thus, for example, in the reaction of subPc **24** with (*p*-tolylsulfonyl)-1,3-diiminoisoindoline (**22**) it was possible to separate by flash column chromatography tetra-*tert*-butylPc **12**, the expected tri-*tert*-butyl(tolylsulfonyl)Pc **7**, and di-*tert*-butylbis(tolylsulfonyl)Pc as pure compounds. In the cases of **8** and **9**, due, respectively, to the limited solubility of the nitro-substituted Pcs in organic solvents and the similar retention time of all the alkyl-substituted Pcs, it was only possible to isolate by chromatographic techniques the

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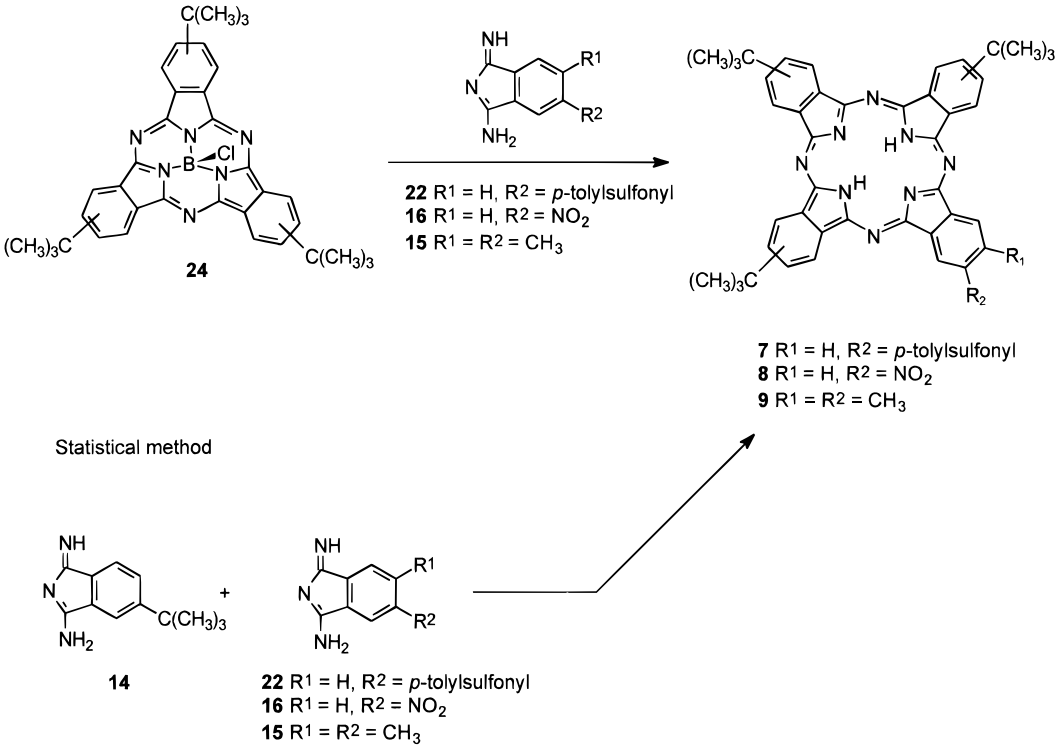
Scheme 3. Subphthalocyanine Method



tetra-*tert*-butylPc **12** and the corresponding phthalocyanine **8** or **9**.

The overall yields for the preparation of phthalocyanines **7**−**9** are fairly low (3−15%) by either method tried, mainly due to the numerous purification steps. Therefore, from the experiments carried out it is not possible to favor one of the two methods. However, although both pathways contain the same number of steps, in our opinion the statistical method is preferable to the subphthalocyanine one because of the higher yields and easier purification processes in the preparation of the starting diiminoisoindolines from the corresponding phthalonitriles in the first case, in comparison with the preparation of subPcs from the same phthalonitriles by the second pathway.

Tetrasubstituted phthalocyanines **10** and **11** were prepared as structural isomer mixtures in 33% and 37% yield, respectively, from the corresponding diiminoisoindolines **21** and **22**, after purification by flash chromatography.

All the compounds were characterized by NMR, IR, MS-FAB, UV-visible, and elemental analysis (see Experimental Section).

All these results and the suggested mechanisms for the synthesis of related Pcs[21] and hemiporphyrazines[22] would allow the pathway depicted in Scheme 4 for the ring enlargement of subPcs to be proposed. According to this mechanism, reaction between a diiminoisoindoline **I** with a subphthalocyanine **II** would go through an open four-unit compound **III**. This tetramer could evolve in three different ways depending on the reactants and on the reaction conditions.

Route a: By cyclization to give the expected Pc **IV**.

Route b: By cleavage in two fragments, either thermal or promoted by attack of a solvent molecule (for example ROH), to afford one or two diiminoisoindoline dimers such as **V**, **VI**, **VII** and/or **VIII**, among other possible products. Self-condensation of two units of **VI** or **VIII** would yield the symmetrically substituted Pc **X**, whereas condensation of **V** and **VI**, for example, would lead to **IV**. On the other hand self-condensation of **V** or **VII** could originate **IX**.

Route c: Cleavage of tetramer **III** by attack of diiminoisoindoline **I** to yield different two- or three-unit compounds that would evolve in a similar way as shown in route b.

In another route, self-condensation of the diiminoisoindoline **I** would lead to the dimer **XI** which could react either with **VII**, with **VIII** or self-condense to afford respectively **XII**, **XIII**, or **XIV** (Scheme 5).

The experimental results found in the present work are in agreement with the schemes outlined above and with previous findings reported by us.[12] This behavior should be general for the reactions of subphthalocyanines and diiminoisoindolines, and the relative importance of the pathways represented in Schemes 4 and 5 would depend on the nature of the reactants (substituents, reactivity) and on the reaction conditions (solvent, temperature).

In conclusion, the generally low yields obtained in the synthesis of Pcs following the subphthalocyanine method and the results presented here show that the ring enlargement reaction of subphthalocyanines is not a selective reaction but a multistep process which depends dramatically on several factors.

Experimental second order hyperpolarizabilities $\gamma(-3\omega;\omega,\omega,\omega)$ and $\gamma(-2\omega;\omega,\omega,0)+\mu\beta(-2\omega;\omega,\omega)/5kT$ have been determined from THG and EFISH techniques at 1340 and 1060 nm, respectively. The values of γ THG and γ EFISH found for compounds **3**−**12** are in the range of 1 to 5 × 10^{-33} esu. To the best of our knowledge, no

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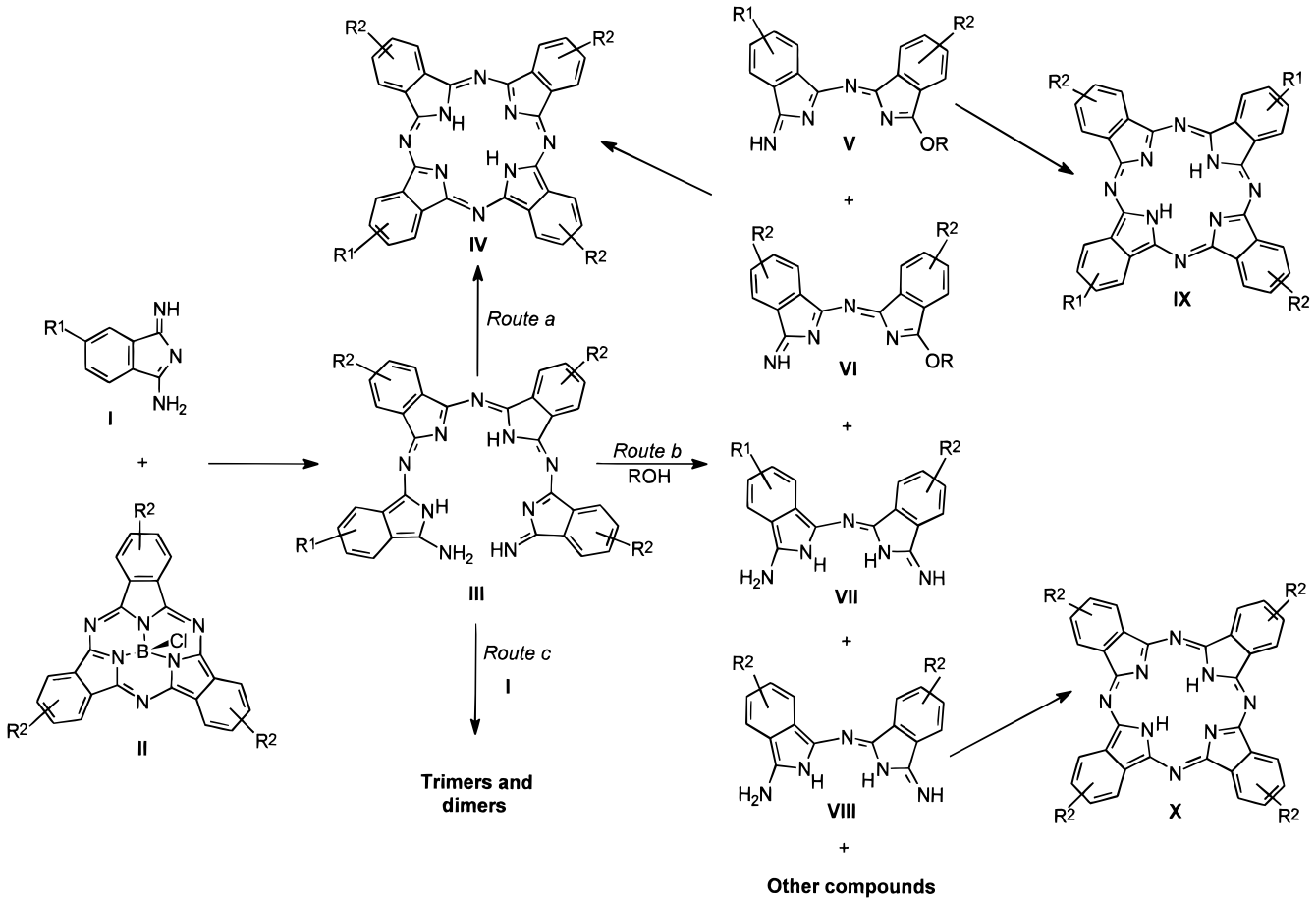
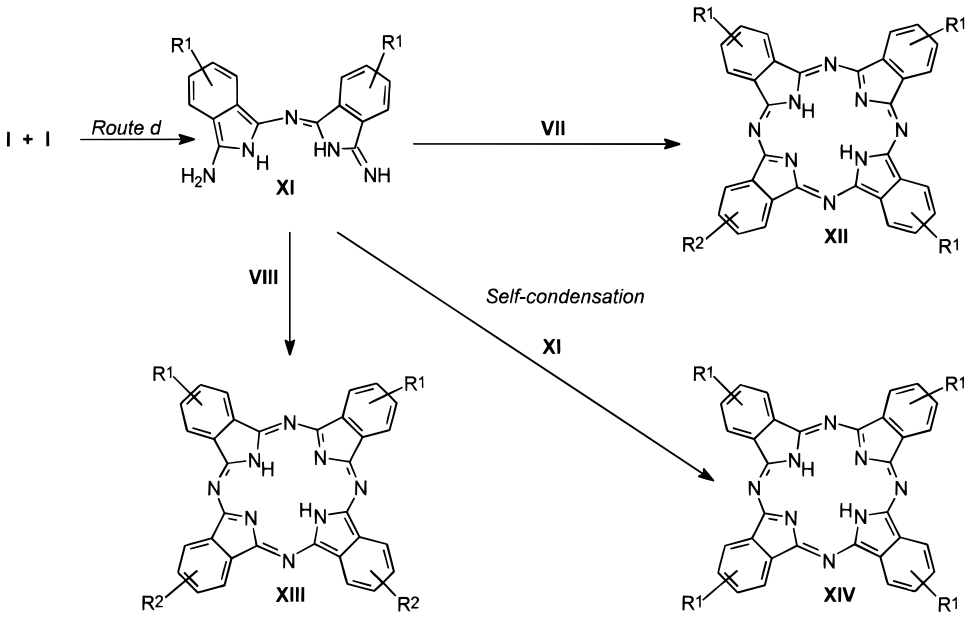
Scheme 4



Scheme 5



previous molecular NLO data in solution of non-centrosymmetric Pcs have been reported. More details about these measurements will be reported elsewhere.

Experimental Section

1,2-Dicyano-4-(tolylthio)benzene (17). A mixture of 520 mg (3 mmol) of 3-nitrophthalonitrile,[18a] 372 mg (3 mmol) of *p*-methylthiophenol, and 455 mg (4.5 mmol) of K_2CO_3 in 10 mL of DMSO was stirred for 12 h under argon atmosphere at room temperature. After removal of the solvent, water was added and the product was extracted with CH_2Cl_2 (3 × 50 mL) and dried over Na_2SO_4. Yield 90%; white solid; mp 142−143 °C; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 2.44 (s, 3H), 7.2−7.4 (m, 3H), 7.42 and 7.60 (AA′BB′ system, 4H) ppm;^{13}C-NMR (50 MHz, $CDCl_3$) δ 21.3, 110.7, 115.1, 115.5, 116.0, 124.3, 129.5, 129.6, 131.2, 133.1, 135.3, 141.1, 149.0 ppm; EI-MS *m*/*z* 250 [M^+, 100], 235 (24); IR (KBr) ν 2200 cm^{-1}. Anal. Calcd for $C_{15}H_{10}N_2S$: C, 71.97; H, 4.03; N, 11.24; S, 12.80. Found: C, 71.97; H, 4.09; N, 10.96; S, 12.49.

1,2-Dicyano-4-(tolylsulfinyl)benzene (18). To a solution of 848 mg (2.5 mmol) of *m*-chloroperbenzoic acid in 30 mL of CH_2Cl_2 at −78 °C were slowly added 500 mg (2 mmol) of (tolylthio)phthalonitrile **17** in 40 mL of CH_2Cl_2. After the addition was finished, the temperature was kept at −78 °C during 30 min. Then, a saturated sodium sulfite solution was added and the mixture was warmed to room temperature, extracted with CH_2Cl_2 (3 × 50 mL), and dried over Na_2SO_4. The white solid obtained was purified by column chromatography (silica gel, CH_2Cl_2). Yield 94%; white solid; mp 125 °C; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 2.41 (s, 3H), 7.33 and 7.40 (AA′BB′ system, 4H), 7.8−8.0 (m, 3H) ppm; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 21.6, 114.1, 114.2, 117.2, 119.5, 128.2, 130.6, 131.6, 132.1, 134.5, 135.8, 146.2, 147.3 ppm; EI-MS *m*/*z* 266 [M^+, 100], 250 (60); IR (KBr) ν 2215, 1060, 810, 680 cm^{-1}. Anal. Calcd for $C_{15}H_{10}N_2OS$: C, 67.65; H, 3.78; N, 10.52; S, 12.70. Found: C, 67.68; H, 3.83; N, 10.23; S, 12.44.

1,2-Dicyano-4-(tolylsulfonyl)benzene (19). To a solution of 848 mg (2.5 mmol) of *m*-chloroperbenzoic acid in 30 mL of CH_2Cl_2 cooled at 0 °C was slowly added 250 mg (1 mmol) of (tolylthio)phthalonitrile **17** in 25 mL of CH_2Cl_2. After the addition was finished, the mixture was warmed to room temperature and kept for 30 min. Then, a saturated sodium sulfite solution was added, and the organic phase was extracted with CH_2Cl_2 (3 × 50 mL) and dried over Na_2SO_4. Yield 96%; white solid; mp 170 °C; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 2.45 (s, 3H), 7.39 and 7.84 (AA′BB′ system, 4H), 7.97 (d, 1H, J = 8.3 Hz), 8.30 (dd, 1H, J = 8.3 Hz, J = 2.5 Hz), 8.52 (d, 1H, J = 2.5 Hz) ppm; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 21.6, 114.0, 114.1, 117.1, 119.7, 128.2, 130.6, 131.6, 132.1, 134.5, 135.7, 146.2,147.2; EI-MS *m*/*z* 282 [M^+, 100]; IR (KBr) ν 2210, 1320, 1150, 675 cm^{-1}. Anal. Calcd for: $C_{15}H_{10}N_2OS$: C, 63.82; H, 3.57; N, 9.92; S, 11.35. Found: C, 63.85; H, 3.50; N, 10.12; S, 11.27.

5-(Tolylthio)-1,3-diiminoisoindoline (20). Through a mixture of 750 mg (3 mmol) of dicyano derivative **17** and a catalytic amount of NaOMe in 40 mL of MeOH was bubbled NH_3 at room temperature for 1 h. Then, the stirred mixture was refluxed for 4 h maintaining the ammonia flow. After cooling, the solvent was evaporated and the residue was washed with an aqueous saturated solution of NH_4Cl and isolated by filtration. Yield 99%; mp 185−186 °C dec; ^{1}H-NMR (200 MHz, CD_3OD) δ 2.41 (s, 3H), 7.29 (d, 1H, J = 8.3 Hz), 7.37 (dd, 1H, J = 2.5 Hz, J = 8.3 Hz), 7.67 (d, 1H, J = 2.5 Hz), 7.43 and 7.73 (AA′BB′ system, 4H) ppm; ^{13}C-NMR (50 MHz, CD_3OD): 21.3, 121.8, 122.9, 129.9, 131.2, 131.7, 134.7, 135.2, 138.8, 140.6, 145.4, 172.0 ppm; EI-MS *m*/*z* 267 [M^+, 100], 145 (27); IR (KBr) ν 3300, 1700, 1680, 1540 cm^{-1}. Anal. Calcd for $C_{15}H_{13}N_3S\cdot H_2O$: C, 63.13; H, 4.59; N, 14.72; S, 11.23. Found: C, 63.35; H, 4.77; N, 14.50; S, 10.93.

5-(Tolylsulfinyl)-1,3-diiminoisoindoline (21). Following the same procedure described above for the synthesis of **20**, from 300 mg (1 mmol) of dicyano derivative **18** and a catalytic amount of NaMeO in 30 mL of MeOH was obtained 280 mg (98%) of **21** as a white solid. Mp 145−146 °C dec. ^{1}H-NMR (200 MHz, CD_3OD) δ 2.41 (s, 3H), 7.66 and 7.98 (AA′BB′ system, 4H), 8.0−8.6 (m, 3H) ppm;^{13}C- NMR (50 MHz, CD_3-OD) 21.4, 118.6, 123.5, 126.5, 128.7, 131.5, 138.8, 140.2, 142.4, 144.2, 150.5, 171.7, 171.5 ppm; EI-MS *m*/*z* 283 [M^+, 100], 267 (25); IR (KBr) ν 3300, 1710, 1680, 1550, 1060, 810, 650 cm^{-1}. Anal. Calcd for $C_{15}H_{13}N_3OS\cdot H_2O$: C, 59.78; H, 5.01; N, 13.94; S, 10.64. Found: C, 59.94; H, 4.99; N, 13.84; S, 10.52.

5-(Tolylsulfonyl)-1,3-diiminoisoindoline (22). Following the same procedure described above for the synthesis of **20** from 570 mg (2 mmol) of dicyano derivative **19** and a catalytic amount of NaMeO in 40 mL of MeOH was obtained 550 mg (92%) of **22** as a white solid. Mp 220−222 °C dec; ^{1}H- NMR (200 MHz, CD_3OD) δ 2.43 (s, 3H), 7.4 and 7.9 (AA′BB′ system, 4H), 8.04 (d, 1H, J = 8.3), 8.14 (dd, 1H, J = 8.3 Hz, J = 2.5 Hz), 8.50 (d, 1H, J = 2.5 Hz) ppm; ^{13}C- NMR (50 MHz, CD_3OD) δ 21.5, 121.8, 123.5, 126.5, 131.3, 131.8, 138.8), 139.2, 141.7, 146.5, 170.4, 171.7, 171.5 ppm; EI-MS *m*/*z* 299 [M^+, 100]; IR (KBr) ν 3300, 1710, 1680, 1550, 1320, 1150, 675 cm^{-1}. Anal. Calcd for $C_{15}H_{13}N_3O_2S\cdot H_2O$: C, 56.77; H, 5.08; N, 13.24; S, 10.10. Found: C, 56.80; H, 4.88; N, 13.13; S, 9.99.

Synthesis of Phthalocyanines. 2,3-Bis(octyloxy)-phthalocyanine (3). A mixture of 130 mg (0.3 mmol) of subphthalocyanine[14c] **23** and 360 mg (0.9 mmol) of 5,6-bis-(octyloxy)-1,3-diiminoisoindoline[15] (**13**) in 20 mL of dimethylaminoethanol was heated at 80 °C for 12 h under an argon atmosphere. After cooling, the mixture was diluted with 50 mL of MeOH and the precipitate was centrifuged. The solid was extracted in a Soxhlet apparatus with MeOH for 24 h. The residue was purified by flash chromatography (SiO_2, eluent CH_2Cl_2) to afford 208 mg (90%) of a dark green solid. Mp 240−245 °C; ^{1}H-NMR (200 MHz, $CDCl_3$) δ −2.0 (broad signal, 2H), 1.04 (t, 6H), 1.9−0.9 (m, 20H), 2.2, (m, 4H), 4.32 (t, 4H), 7.7 (m, 6H), 8.1 (m, 2H), 8.4 (m, 2H), 8.6 (m, 2H), 8.9 (m, 2H) ppm; FAB-MS (3-NOBA) *m*/*z* 771 [M + H^+], 770 [M^+]; UV/vis ($CHCl_3$) λ_{max} (log ϵ/dm^3 mol^{-1} cm^{-1}) 695 (5.21), 659 (5.13), 640 (4.74), 599 (4.51), 431 (4.30), 339 (4.91) nm; IR (KBr) ν 1630, 1615, 1500, 1480, 1450,1290, 1110, 1010, 890, 750 cm^{-1}. Anal. Calcd for $C_{48}H_{50}N_8O_2\cdot 2H_2O$: C, 71.44; H, 6.73; N, 13.88. Found: C, 71.21; H, 6.83; N, 13.76.

2-*tert*-Butylphthalocyanine (4). This compound was synthesized from subphthalocyanine **23** (215 mg, 0.5 mmol) and 5-*tert*-butyl-1,3-diiminoisoindoline[16] **14** (905 mg, 4.5 mmol) in DMAE (20 mL) as solvent, at 80 °C as described for the preparation of **3**. After cooling, the mixture was diluted with 50 mL of MeOH, and the precipitate was centrifuged and washed with MeOH in a Soxhlet extractor. The product was finally purified by flash chromatography (SiO_2, CH_2Cl_2/MeOH 20:1). Yield 57%; blue solid; mp > 300 °C; ^{1}H- NMR (200 MHz, $CDCl_3$) δ 1.9 (s, 9H), 7.7−9.0 (m, 15H) ppm. MS-FAB (3-NOBA) *m*/*z* 571 [M + H^+], 570 [M^+]; UV/vis ($CHCl_3$) λ_{max} (log ϵ/dm^3 mol^{-1} cm^{-1}): 695 (5.17), 658 (5.13), 639 (4.71), 597 (4.47), 358 (sh), 339 (4.87) nm; IR (KBr) ν 1620, 1350, 1330, 1320, 1020, 890, 760, 750, 730 cm^{-1}. Anal. Calcd for $C_{36}H_{26}N_8\cdot H_2O$: C, 73.44; H, 4.79; N, 19.03. Found: C; 73.30; H, 4.82; N, 18.94.

2-(Tolylthio)phthalocyanine (5). Following the same procedure described in the preparation of **3**, starting from a mixture of subphthalocyanine **23** (130 mg, 0.3 mmol) and 5-(tolylthio)-1,3-diiminoisoindoline (**20**) (240 mg, 0.9 mmol) in 20 mL of DMAE and after purification of the compound by flash column chromatography (SiO_2, CH_2Cl_2) was obtained 20 mg (11%) of **5** as a dark blue solid. Mp > 300 °C; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 2.49 (s, 3H), 7.7−9.0 (m, 19H) ppm; FAB-MS (3-NOBA) *m*/*z* 637 [M + H^+], 636 [M^+]; UV/vis ($CHCl_3$) λ_{max} (log ϵ/dm^3 mol^{-1} cm^{-1}) 700 (5.00), 663 (5.00), 641 (4.70), 610 (4.49), 424 (sh), 340 (4.87) nm; IR (KBr) ν 1610, 1020, 820, 750 cm^{-1}. Anal. Calcd for $C_{39}H_{24}N_8S\cdot H_2O$: C, 71.54; H, 4.00; N, 17.11; S, 4.90. Found: C, 71.17; H, 3.89; N, 16.81; S, 5.01.

2-(Tolylsulfinyl)phthalocyanine (6). Compound **6** was synthesized following the previous described methodology for the preparation of **3** from 130 mg (0.3 mmol) of subphthalocyanine **23** and 255 mg (0.9 mmol) of 5-(tolylsulfinyl)-1,3-diiminoisoindoline (**21**) in 20 mL of DMAE after final purification by column chromatography (SiO_2, CH_2Cl_2/MeOH, 15:1). Yield 10%; dark blue solid; mp > 300 °C. ^{1}H-NMR (200 MHz, $CDCl_3$) δ 2.5 (s, 3H), 7.7−9.0 (m, 19H) ppm; FAB-MS (3-NOBA) *m*/*z* 653 [M + H^+], 652 [M^+]; UV/vis ($CHCl_3$) λ_{max} (log ϵ/dm^3 mol^{-1} cm^{-1}) 687 (5.11), 661 (5.13), 637 (4.84), 608 (4.64), 341 (4.75) nm; IR (KBr) ν 1620, 1020, 750 cm^{-1}. Anal. Calcd for $C_{39}H_{24}N_8OS\cdot H_2O$: C, 69.83; H, 3.90; N, 16.70; S, 4.78. Found: C, 69.65; H, 3.87; N, 16.64; S, 4.82.

9,16,23-Tri-*tert*-butyl-2-(tolylsulfonyl)phthalocyanine[23] (7). (a) Subphthalocyanine Method. A mixture of tri-*tert*-butylsubphthalocyanine (**24**) (240 mg, 0.4 mmol) and 5-(tolylsulfonyl)-1,3-diiminoisoindoline (**22**) (480 mg, 1.6 mmol) in 7 mL of DCB and 3 mL of DMSO was heated at 80 °C for 24 h. After cooling at room temperature the reaction mixture was treated with methanol and the precipitate filtered off obtaining a blue solid. From the complex mixture (TLC) of phthalocyanines was separated 9 mg (3%) of **7** by flash column chromatography (SiO_2, CH_2Cl_2). Mp > 300 °C; ^{1}H- NMR (200 MHz, $CDCl_3$) δ −2.92 (s, 1H), −2.71 (s, 1H), 1.8−2.1 (m, 27H), 2.50, 2.51 (2xs, 3H), 7.4−9.6 (m, 16H) ppm; FAB-MS (3-NOBA)

(23) For simplicity reasons, only one of the four structural isomers will be named as example.

m/*z* 837 [M + H$^+$], 836 [M$^+$]; UV/vis ($CHCl_3$) λ_{max} (log ϵ/dm^3 mol^{-1} cm^{-1}) 711 (sh), 687 (5.00), 618 (4.33), 341 (4.59) nm; IR (KBr) ν 1620, 1330, 1170, 1020, 750, 690 cm^{-1}. Anal. Calcd for $C_{51}H_{48}N_8O_2S\cdot 2H_2O$: C, 70.16; H, 6.00; N, 12.83; S, 3.65. Found: C, 70.10; H, 5.90; N, 12.71; S, 3.74.

From the above mentioned column chromatography was isolated 4 mg (0.7%) of **di-*tert*-butylbis(tolylsulfonyl)-phthalocyanine**. Mp > 300 °C; ^{1}H- NMR (200 MHz, $CDCl_3$) δ −4.5 to 4.9 ppm (2 broad signals, 2H), 1.7−1.9 (broad signal, 18H), 2.5−2.6 (m, 6H), 7.5−9.3 (m, 20H) ppm; FAB-MS (3-NOBA) *m*/*z* 935 [M + H$^+$], 934 [M$^+$];UV/vis ($CHCl_3$) λ_{max} (log ϵ/dm^3 mol^{-1} cm^{-1}) 698 (5.09), 669 (5.01), 642 (4.60), 614 (4.50), 347 (4.86) nm; IR (KBr) ν 1630, 1620, 1330, 1170, 1020, 750 690 cm^{-1}. Anal. Calcd for $C_{54}H_{46}N_8O_4S_2\cdot H_2O$: C, 68.05; H, 5.07; N, 11.75; S, 6.73. Found: C, 68.17; H, 4.98; N, 11.70; S, 6.81.

(b) Statistical Method. A mixture of 1.8 g (9 mmol) of 5-*tert*-butyl-1,3-diiminoisoindoline[16] (**14**) and 897 mg (3 mmol) of 5-(tolylsulfonyl)-1,3-diiminoisoindoline (**22**) in 10 mL of DMAE was heated at 150 °C for 7 h under an argon atmosphere. The reaction mixture was treated with MeOH and the precipitate filtered. After flash column chromatography (SiO_2, CH_2Cl_2), 240 mg (9%) of **7** and 181 mg (13%) of di-*tert*-butylbis(tolylsulfonyl)phthalocyanine were obtained.

9,16,23-Tri-*tert*-butyl-2-nitrophthalocyanine[23,24] (8). (a) Subphthalocyanine Method. Compound **8** was synthesized in a similar way to **7** starting from 310 mg (0.55 mmol) of tri-*tert*-butylsubphthalocyanine[10a] (**24**) and 410 mg (2.2 mmol) of 5-nitro-1,3-diiminoisoindoline[18b] (**16**) in 7 mL of DCB and 3 mL of DMSO. After cooling, the reaction mixture was treated with diethyl ether and centrifuged. The residue was washed with hot MeOH and then extracted with toluene in a Soxhlet apparatus, yielding 60 mg (15%) of **8**. Mp > 300 °C; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.6−1.7 (m, 27H), 7.4−8.5 (m, 12H) ppm; FAB-MS (3-NOBA) *m*/*z* 728 [M + H$^+$], 727 [M$^+$]; UV/vis ($CHCl_3$) λ_{max} (log ϵ/dm^3 mol^{-1} cm^{-1}) 692 (5.00), 679 (5.01), 644 (4.70), 624 (4.64), 337 (4.80) nm; IR (KBr) ν 1680, 1550, 1360 cm^{-1}. Anal. Calcd for: $C_{44}H_{41}N_9O_2\cdot H_2O$: C, 70.85; H, 5.80; N, 16.90. Found: C, 70.73; H, 5.64; N, 16.90.

(b) Statistical Method. A mixture of 542 mg (3 mmol) of 5-*tert*-butyl-1,3-diiminoisoindoline (**14**) and 180 mg (1 mmol) of 5-nitro-1,3-diiminoisoindoline (**16**) in 5 mL of DMAE was stirred at reflux temperature under an argon atmosphere for 7 h. After cooling, MeOH was added and a dark green powder precipitated. Purification by flash column chromatography (SiO_2, hexane/$CHCl_3$, 1:2) afforded 14 mg (2%) of **8**.

9,16,23-Tri-*tert*-butyl-2,3-dimethylphthalocyanine[23] (9). (a) Subphthalocyanine Method. A mixture of 270 mg (0.48 mmol) of tri-*tert*-butylsubphthalocyanine (**24**) and 330 mg (1.92 mmol) of 5,6-dimethyl-1,3-diiminoisoindoline[17] (**15**) in a mixture of 7 mL of DCB and 3 mL of DMSO was heated at 80 °C for 20 h under an argon atmosphere. After cooling, the solvent was removed under reduced pressure and the residue was washed with hot methanol. Compound **9** was purified by flash column chromatography (SiO_2, toluene/hexane 5:2) to afford 13 mg (4%) of **9.** Mp > 300 °C; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.9 ppm (broad signal, 27H), 2.4 (s, 6H), 7.4−9.5 (m, 11H) ppm; FAB-MS (3-NOBA) *m*/*z* 711 [M + H$^+$], 710 [M$^+$]; UV/vis ($CHCl_3$) λ_{max} (log ϵ/dm^3 mol^{-1} cm^{-1}) 701 (5.10), 664 (5.04), 644 (4.57), 603 (4.28), 342 (4.80) nm; IR (KBr) ν 2960, 2800, 2780, 1615, 1480, 1100, 755 cm^{-1}. Anal. Calcd for: $C_{46}H_{46}N_8\cdot 2H_2O$: C, 73.96; H, 6.74; N, 15.00. Found: C, 73.94; H, 6.82; N, 15.34.

(b) Statistical Method. A mixture of 540 mg (2.7 mmol) of 5-*tert*-butyl-1,3-diiminoisoindoline (**14**) and 156 mg (0.9 mmol) of 5,6-dimethyl-1,3-diiminoisoindoline (**15**) in 5 mL of DMAE was heated at 150 °C for 24 h. The reaction mixture was treated as described above to yield 40 mg (12%) of **9**.

2,9,16,23-Tetrakis(tolylsulfinyl)phthalocyanine[23] (10). 5-(Tolylsulfinyl)-1,3-diiminoisoindoline **(18)** (425 mg, 1.5 mmol) in 10 mL of DMAE was heated at 150 °C for 7 h. After cooling, 20 mL of methanol was added and a blue solid precipitated. Purification by flash column chromatography (SiO_2, CH_2Cl_2/MeOH 15:1) afforded 142 mg (36%) of **10**. Mp > 300 °C; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 2.0−2.6 (broad signal, 12H), 7.4−9.5 (m, 28H) ppm; FAB-MS (3-NOBA) *m*/*z* 1067 [M + H$^+$], 1066 [M$^+$]; UV/vis ($CHCl_3$) λ_{max} (log ϵ/dm^3 mol^{-1} cm^{-1}): 701 (5.09), 665 (5.03), 645 (4.67), 638 (4.66), 605 (4.47), 346 (4.85) nm; IR (KBr) ν 1590, 1060, 800, 740 cm^{-1}. Anal. Calcd for $C_{60}H_{42}N_8O_4S_4\cdot H_2O$: C, 66.40; H, 4.06; N, 10.32; S, 11.82. Found: C, 66.33; H, 3.90; N, 10.40; S, 11.89.

2,9,16,23-Tetrakis(tolylsulfonyl)phthalocyanine[23] (11). 5-(Tolylsulfonyl)-1,3-diiminoisoindoline (**22**) (450 mg, 1.5 mmol) in 10 mL of DMAE was heated at 150 °C for 7 h. After cooling, 20 mL of methanol was added and a blue solid precipitated. Purification by flash column chromatography (SiO_2, CH_2Cl_2/MeOH, 40:1) led to 138 mg (33%) of **11**. Mp > 300 °C. ^{1}H-NMR (200 MHz, $CDCl_3$) δ 2.4−2.6 (4xs, 12H), 7.4−10.0 (m, 28H) ppm; FAB-MS (3-NOBA) *m*/*z* 1131 [M + H$^+$], 1130 [M$^+$]; UV/vis ($CHCl_3$) λ_{max} (log ϵ/dm^3 mol^{-1} cm^{-1}): 701 (5.09), 664 (5.00), 647 (4.55), 636 (4.54), 602 (4.35), 349 (4.76) nm; IR (KBr) ν 1590, 1300, 1150, 690 cm^{-1}. Anal. Calcd for: $C_{60}H_{42}N_8O_8S_4\cdot 2H_2O$: C, 61.43; H, 3.97; N, 9.60; S, 10.99. Found: C, 61.74; H, 3.92; N, 9.55; S, 10.52.

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Supporting Information Available: Assignment of the ^{13}C NMR signals of the compounds **17**−**22** (1 page). This material is contained in libraries on microfiche, inmediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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