A New Substitution Pattern in Subphthalocyanines: Regioselective Synthesis and Separation of “*ortho*” Derivatives

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The regioselective preparation of *ortho*-substituted subphthalocyanides was achieved employing 3-substituted phthalonitrile derivatives as starting materials. A mechanistic proposal has been outlined.

Introduction

Subphthalocyanines[1] (SubPcs, **a** and **b** in Figure 1) are cone-shaped[2] macrocycles comprising three N-fused diiminoisoindoline units around a boron core. Their particular structure and their 14 π-electron extended aromatic[3] ring make them ideal candidates for a study of their second order nonlinear optical (NLO) properties, [4] their potential use in PhotoDynamic Therapy,[4e] and for the preparation of Langmuir–Blodgett films.[5] SubPcs have also been employed as precursors in the synthesis of unsymmetrically substituted phthalocyanines through a ring expansion reaction with appropriate diiminoisoindoline derivatives.[6] Until now, only peripheral “*meta*”-tri- (**a** in Figure 1) and -hexasubstituted (**b** in Figure 1) derivatives have been described.[1–4]

Trisubstituted SubPcs (one group in each isoindole subunit) have been isolated as 3:1 mixtures of constitutional isomers with C_1 and C_3 symmetries, that could be resolved only in one case by HPLC.[2b] So far, the NLO properties of trisubstituted SubPcs have been exclusively studied with such mixtures of isomers.[4b–4f] Therefore, the preparation of regioisomerically pure subphthalocyanines should open the way towards regioisomerically pure unsymmetrically substituted phthalocyanines[7] and would provide a set of dipolar and octupolar compounds for studying their second harmonic generation (SHG) properties.[4b–4f]

In this paper, we describe the synthesis of a series of 3-substituted phthalonitrile derivatives and their subsequent cyclotrimerization in the presence of boron(III)trichloride to yield “*ortho*”-substituted chlorosubphthalocyanines (Scheme 1). This substitution pattern renders the C_1 and C_3 constitutional isomers of the axially substituted chlorosubphthalocyanines structurally different enough from each other to make possible, for the first time, their easy separation by column chromatography.[1] For the sake of consistency with former work in our laboratory, and also for chemical compatibility reasons with BCl_3, we chose as substituents for this study the groups NO_2, I, SC_3H_7, and $SO_2C_3H_7$. By studying the regioselectivity of the processes leading to the formation of the SubPcs we have been able to outline a mechanistic proposal based on steric factors.[8]

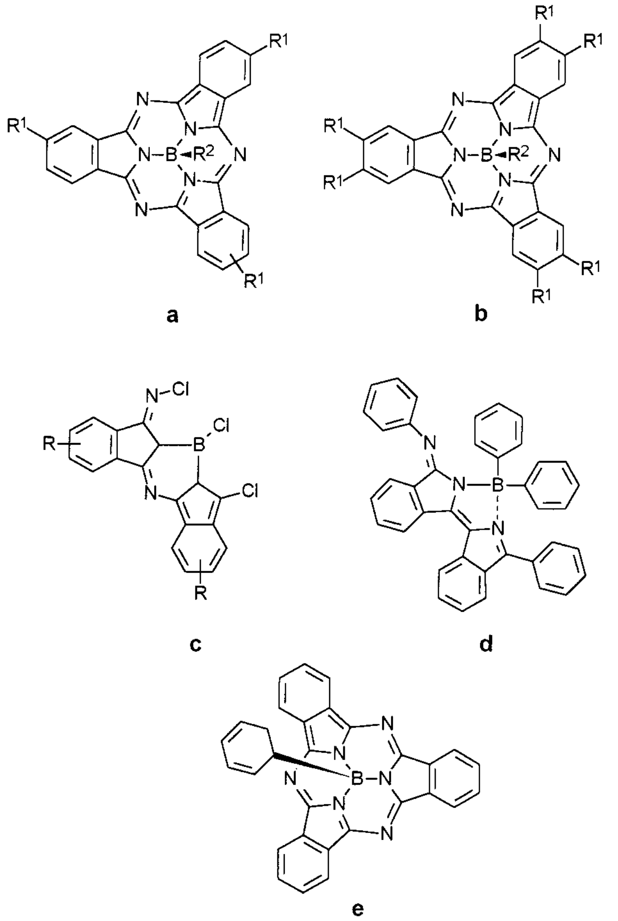

Figure 1. (**a**) “*meta*”-tri- and (**b**) “*meta*”-hexa-substituted SubPcs, (**c**) proposed intermediate, (**d**) boron beta-isoindigo complex,[2d] and (**e**) phenyl-boronsubphthalocyanine

Results and Discussion

The synthesis of 1,2-dicyano-3-nitrobenzene[9a] (**1**) and 1,2-dicyano-3-iodobenzene[9b–9c] (**2**) was achieved according to literature procedures. 1,2-Dicyano-3-propylthiobenzene

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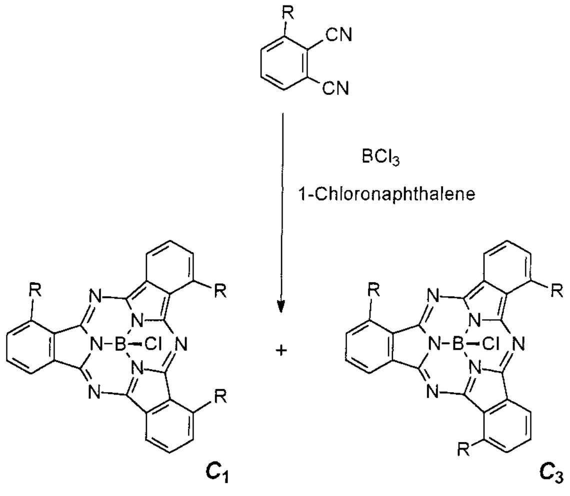


R	Dicyano precursor	Regioisomer C_1	Regioisomer C_3
NO_2	**1**	**5a**	**5b**
I	**2**	**6a**	**6b**
SC_3H_7	**3**	**7a**	**7b**
$SO_2C_3H_7$	**4**	**8a**	**8b**

Scheme 1. Synthesis of SubPcs **5**–**8**

(**3**) was obtained in 95% yield by reacting compound **1** with propanethiol in the presence of K_2CO_3 in dimethylacetamide. Oxidation of compound **3** with *m*CPBA in CH_2Cl_2 afforded 1,2-dicyano-3-propylsulfonylbenzene (**4**) in 83% yield. The subphthalocyanines **5**–**8** were prepared (Scheme 1) by slowly introducing previously condensed BCl_3 into a solution of the corresponding dicyano derivatives **1**–**4** in 1-chloronaphthalene under heating (60–120 °C). The regioisomers **5a** and **5b** were separated in 10% overall yield (4 and 6%, respectively) by column chromatography on silica gel with CH_2Cl_2 as eluent [R_f(**5a**) = 0.5, R_f(**5b**) = 0.7]. Similar results were obtained with regioisomers **6a** and **6b** which were also isolated by column chromatography with CH_2Cl_2/hexane (1:1) as eluent [R_f(**6a**) = 0.5, R_f(**6b**) = 0.75] in 4 and 7% yields, respectively. Any attempts at purifying subphthalocyanine **7** were unsuccessful since it decomposed slowly in the presence of air and quickly on silica gel, alumina, or in solution. ^1H NMR spectroscopic data from the partially decomposed compound do not allow the determination of the ratio **7a**:**7b**. However, compound **7** was identified by FAB-MS. Subphthalocyanine **8** was purified by column chromatography [SiO_2, CH_2Cl_2/hexane (1:1)], but the two regioisomers **8a** and **8b** could not be resolved. The overall yield for the formation of **8a** + **8b** was 15%.[10]

The ^1H NMR spectra of subphthalocyanines **5**–**8** show characteristic low field signals at 8–9.5 ppm attributable to the aromatic protons. The spectra of the constitutional isomers **5b** and **6b** reveal the expected dd, dd, triplet pattern in accordance with the C_3 symmetry of the macrocycles. On the other hand, the spectra of the C_1 constitutional isomers **5a** and **6a** show the loss of the local symmetry environments experienced by each aromatic proton, giving rise to three complex systems. In the case of subphthalocyanine **8**, ^1H NMR spectroscopy reveals (Figure 2) the presence of two sets of resonances for the isomers **8a** and **8b** in a 92:8 ratio.

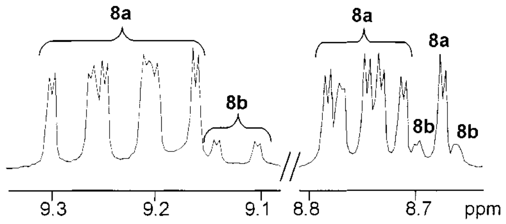
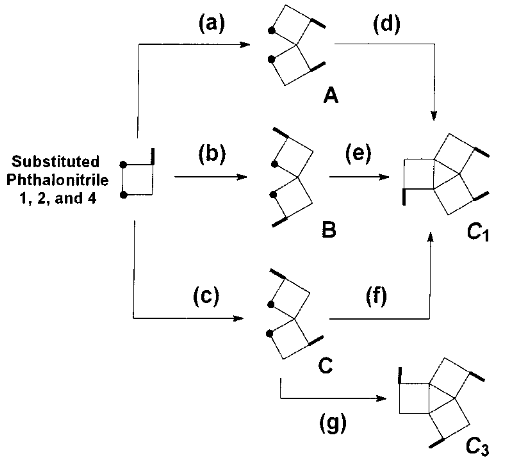


Figure 2. Portions of the ^1H NMR (200 MHz, $CDCl_3$) spectrum of SubPc **8**

The overall shapes of the UV/visible spectra are quantitatively and qualitatively similar to that previously found in "*meta*" substituted compounds, thus indicating that the presence of substituents in the *ortho* positions does not modify the geometrical features of the cone-shaped structure.

In the light of these and previous results, we propose a mechanistic pathway (Scheme 2) in which a dimeric intermediate (**c** in Figure 1), formed by reaction of two phthalonitrile molecules with BCl_3, would be involved. This hypothetical species is closely related to the boron beta-isoindigo complex (**d** in Figure 1) which was isolated and characterized by X-ray analysis by Engel et al. in the preparation of phenylsubphthalocyanine (**e** in Figure 1) from phthalonitrile and triphenylborane.[2d] The proposed intermediate (**c** in Figure 1) would react with a new molecule of substituted phthalonitrile to yield the corresponding SubPc. Regarding the regioselectivity of the process, the synthesis of "*meta*"-trisubstituted SubPcs[1,4b,4e] has always yielded a mixture of constitutional isomers C_1 and C_3 in a statistical 3:1 ratio. This fact shows the negligible steric and electronic influence of the substituents on the final ratio of compounds. On the contrary, the effect of substitution on the



Scheme 2. Proposed reaction pathway leading to the formation of SubPcs **5**–**8**

regioselectivity in the "*ortho*" series is remarkable. Thus, the constitutional isomers **5a** and **5b** have been isolated in ca. 1:1.5 ratio starting from compound **1**, which is far from the statistical ratio (3:1) observed for the "*meta*" derivatives. Similar results have been obtained for the triiodo-substituted compounds **6a** and **6b**. This situation changes dramatically in the case of compounds **8a** and **8b**. Here a mixture of both components with symmetries C_1 and C_3 was isolated in ca. 9:1 ratio, also far from the statistical value.

These experimental results can be explained on the basis of steric effects. Following the schematic pathway depicted in Scheme 2, the *ortho*-substituted phthalonitriles **1**,**2** and **4** could follow three different routes (**a**), (**b**), or (**c**) to afford the corresponding intermediates **A**, **B**, and **C** of the type **c** in Figure 1. The phthalonitriles **1** and **2**, bearing nitro and iodo substituents, respectively, may react preferentially via the most sterically favorable routes (**b**) and (**c**) leading to intermediates **B** and **C**. Further evolutions of intermediate **B** via route (**e**) and of intermediate **C** via route (**f**) are sterically disfavored when compared with the evolution of intermediate **C** via route (**g**). This may explain the high C_3/C_1 ratio observed experimentally in the formation of subphthalocyanines **5** and **6**. In the case of phthalonitrile **4**, which bears a bulkier propylsulfonyl substituent in position 3, route (**c**) may become sterically unfavorable along with route (**a**). Thus, route (**b**), which is now highly favored, would yield intermediate **B** which would have to evolve via the sterically unfavorable route (**e**) and yield a high C_1/C_3 ratio as observed experimentally in the formation of subphthalocyanine **8**.

Unfortunately, the choice of substituents on the starting phthalonitriles, that could provide a deeper understanding of the electronic effects in the SubPc formation, is not free since the high reactivity of boron derivatives precludes the introduction of many functional groups, like alkoxy,[11] in the "*ortho*" positions of the SubPc core. These results are in good agreement with those obtained by Hanack and coworkers in the phthalocyanine series,[8] in which a strong influence of the substituents on the isomer distributions was observed in the formation of the corresponding 1(4)- or "*ortho*"-tetrasubstituted phthalocyanines from substituted phthalonitriles.

Other mechanisms might be operating in the formation of subphthalocyanines from phthalonitriles as a function of the reaction conditions employed. Efforts are being made to establish what these might be.

Conclusion

In summary, we have described for the first time the preparation of *ortho*-substituted SubPcs pointing out that this is a regioselective process that can be rationalized in terms of steric effects affecting the arrangements of the three isoindole building blocks. A mechanistic proposal has also been outlined.

Experimental Section

Melting points are uncorrected. Column chromatography was performed on silica gel Merck-60 (230–400 mesh, 60 Å) and TLC on aluminum sheets precoated with silica gel 60 F_{254} (E. Merck) with the indicated solvents. All dry solvents were freshly distilled under argon over an appropriate drying agent before use. Compounds **1**[9a] and **2**[9b,9c] have been previously described.

1,2-Dicyano-3-propylthiobenzene (3): 1,2-Dicyano-3-nitrobenzene (**1**) (1.00 g, 5.6 mmol), dry K_2CO_3 (1.20 g, 8.7 mmol) and 20 mL of dimethylacetamide (DMAC) were placed in a 50 mL round bottom flask equipped with a magnetic stirrer, rubber seal and globe. After a stream of argon had been passed through the slurry in order to remove oxygen, 1-propanethiol (0.58 mL, 0.48 g, 6.3 mmol) was added through a syringe and the resulting mixture stirred at room temperature during 24 h. The reaction mixture was poured into 50 mL of cold water, the precipitate collected and crystallized from cold ethanol to yield 1.07 g (95%) of 1,2-dicyano-3-propylthiobenzene (**3**) as a white solid: m.p. 71–72°C. – ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.65–7.51 (m, 3 H), 3.02 (t, ^3J = 7 Hz, 2 H), 1.83–1.63 (m, 2 H), 1.06 (t, ^3J = 7 Hz, 3 H). – ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 133.0, 131.5, 129.9, 117.7, 115.7, 114.2, 35.5, 22.4, 13.8. – MS (EI); *m*/*z* (%): 202 (33) [M$^+$]. – $C_{11}H_{10}N_2S$ (202.27): calcd. C 65.32, H 4.98, N 13.85, S 15.85; found C 65.37, H 4.68, N 13.70, S 15.99.

1,2-Dicyano-3-propylsulfonylbenzene (4): To a solution of 1,2-dicyano-3-propythiobenzene (**3**) (0.50 g, 2.5 mmol) in dry CH_2Cl_2 (25 mL) cooled to 0°C was slowly added *m*-chloroperbenzoic acid (2.14 g, 12.4 mmol) in dry CH_2Cl_2 (120 mL). The mixture was warmed to room temperature and vigorously stirred at this temperature for 48 h. A saturated sodium sulfite solution was then added, the aqueous phase was extracted three times with CH_2Cl_2 (50 mL) and the combined organic phases were dried over sodium sulfate. The solvent was removed under reduced pressure and the solid was recrystallized from toluene/heptane (1:3) to give 0.48 g (83%) of 1,2-dicyano-3-propylsulfonylbenzene (**4**) as a white solid: m.p. 167–168°C. – ^{1}H NMR (CD_3COCD_3, 200 MHz): δ = 8.49–8.42 (m, 2 H), 8.25 (t, ^3J = 8 Hz, 1 H), 3.54–3.46 (m, 2 H), 2.09–2.03 (m, 2 H), 1.045 (t, ^3J = 7 Hz, 3 H). – ^{13}C NMR (CD_3COCD_3, 50 MHz): δ = 138.0, 134.5, 134.4, 119.3, 115.0, 113.1, 56.5, 16.3, 12.1. – MS (EI); *m*/*z* (%): 234 (20) [M$^+$]. – $C_{11}H_{10}N_2O_2S$ (234.27): calcd. C 56.40, H 4.30, N 11.96, S 13.68; found C 56.46, H 4.07, N 11.94, S 13.75.

Chloro(1,8,18-trinitro)- and Chloro(1,8,15-trinitrosubphthalocyaninato)boron(III) (5a and 5b): BCl_3 (0.2 mL), previously condensed at –78°C, was added through a cannula to a magnetically stirred solution of 1,2-dicyano-3-nitrobenzene (**1**) (500 mg, 2.9 mmol) in dry 1-chloronaphthalene (1.0 mL) under Ar. The mixture was stirred at room temperature for 15 min, warmed up to 75°C and kept at that temperature for 7 h. The resulting purple mixture was cooled down to room temperature. The solid residue was washed with 50 mL hexane and was purified by column chromatography on silica gel using CH_2Cl_2 as eluent. The first eluted component, was further purified by column chromatography on silica gel using Et_2O/Hexane (5:1) as eluent, giving 33 mg (6%) of compound **5b** as a deep purple solid: m.p. > 200 °C. – IR (KBr) 1538, 1347, 1119, 732 cm^{-1}. – ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.22 (dd, 3 H, ^3J = 8 Hz, ^4J = 1 Hz), 8.65 (dd, 3 H, ^3J = 8 Hz, ^4J = 1 Hz), 8.11 (t, 3 H, ^3J = 8 Hz). – MS (FAB, *m*NBA); *m*/*z* (%): 566 (5) [M + H]$^+$. – UV/Vis ($CHCl_3$) λ_{max} (log ε/dm^3 mol^{-1} cm^{-1}): 566 (4.5), 519 (sh), 304 (4.3), 246 (4.3). – HRMS calcd. for $C_{24}H_{10}BClN_9O_6$: 566.0536; found 566.0527. The second eluted component was compound **5a** (22 mg, 4%) as a deep purple solid: m.p. > 200 °C. – IR (KBr)

1539, 1347, 795, 736 cm^{-1}. – ^{1}H NMR (300 MHz, CDCl$_3$): δ = 9.17 (dd, ^{3}J = 8 Hz, ^{4}J = 1 Hz, 1 H), 9.13 (dd, ^{3}J = 8 Hz, ^{4}J = 1 Hz, 1 H), 9.10 (dd, ^{3}J = 8 Hz, ^{4}J = 1 Hz, 1 H), 8.59 (dd, ^{3}J = 8 Hz, ^{4}J = 1 Hz, 1 H), 8.58 (dd, ^{3}J = 8 Hz, ^{4}J = 1 Hz, 1 H), 8.55 (dd, ^{3}J = 8 Hz, ^{4}J = 1 Hz, 1 H), 8.08 (t, ^{3}J = 8 Hz, 1 H), 8.05 (t, ^{3}J = 8 Hz, 1 H), 8.01 (t, ^{3}J = 8 Hz, 1 H). – MS (FAB, *m*NBA): *m*/*z* (%): 566 (10) [M + H]$^{+}$. – UV/Vis (CHCl$_3$) λ_{max} (log ε/dm^3 mol^{-1} cm^{-1}): 569 (4.5), 561 (sh), 534 (sh), 515 (sh), 295 (4.5), 242 (4.5). – HRMS calcd. for $C_{24}H_{10}BClN_9O_6$: 566.0536; found 566.0533.

Chloro(1,8,18-triiodo)- and Chloro(1,8,15-triiodosubphthalocyaninato)boron(III) (6a and 6b): BCl$_3$ (0.05 mL), previously condensed at –78°C, was added through a cannula to a magnetically stirred solution of 1,2-dicyano-3-iodobenzene (**2**) (98 mg, 0.38 mmol) in dry 1-chloronaphthalene (0.1 mL) under argon. The mixture was stirred at room temperature for 15 min, warmed to 120°C and kept at that temperature for 4 h. The resulting purple mixture was then cooled to room temperature. The solid residue was washed with 25 mL hexane and was purified by column chromatography on silica gel with hexane/CH$_2$Cl$_2$ (1:1) as eluent. The fractions containing the first component, after further purification on silica gel with CH$_2$Cl$_2$ as eluent, gave 7 mg (7%) of compound **6b** as a deep purple solid: m.p. > 200°C. – IR (KBr) 1251, 1136, 1099, 788 cm^{-1}. – ^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.98 (dd, ^{3}J = 8 Hz, ^{4}J = 1 Hz, 3 H), 8.42 (dd, ^{3}J = 8 Hz, ^{4}J = 1 Hz, 3 H), 7.66 (t, ^{3}J = 8 Hz, 3 H). – MS (FAB, *m*NBA): *m*/*z* (%): 808 (28) [M + H]$^{+}$. – UV/Vis (CHCl$_3$) λ_{max} (log ε/dm^3 mol^{-1} cm^{-1}): 577 (4.4), 560 (sh), 534 (3.8), 502 (sh), 295 (4.0), 285 (4.0), 241 (4.1). – HRMS calcd. for $C_{24}H_9BClI_3N_6$: 807.7805; found 807.7820. The last fractions, containing the second component, after further purification on silica gel with CH$_2$Cl$_2$ as eluent, gave 4 mg (4%) of compound **6a** as a deep purple solid: m.p. > 200°C. – IR (KBr) 1235, 1095, 788, 754 cm^{-1}. – ^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.95 (dd, ^{3}J = 8 Hz, ^{4}J = 1 Hz 1 H), 8.93 (dd, ^{3}J = 8 Hz, ^{4}J = 1 Hz, 1 H), 8.91 (dd, ^{3}J = 8 Hz, ^{4}J = 1 Hz, 1 H), 8.44 (dd, ^{3}J = 8 Hz, ^{4}J = 1 Hz, 1 H), 8.43 (dd, ^{3}J = 8 Hz, ^{4}J = 1 Hz, 1 H), 8.42 (dd, ^{3}J = 8 Hz, ^{4}J = 1 Hz, 1 H), 7.65 (t, ^{3}J = 8 Hz, 1 H), 7.63 (t, ^{3}J = 8 Hz, 1 H), 7.62 (t, ^{3}J = 8 Hz, 1 H). – MS (FAB, *m*NBA): *m*/*z* (%): 808 (18) [M + H]$^{+}$. – UV/Vis (CHCl$_3$) λ_{max} (log ε/dm^3 mol^{-1} cm^{-1}): 579 (4.4), 560 (sh), 540 (3.9), 501 (sh), 308 (sh), 288 (4.2), 244 (4.2). – HRMS calcd. for $C_{24}H_{10}BClN_9O_6$: 807.7805; found 807.7835.

Chloro(1,8,18-tripropylthio)- and Chloro(1,8,15-tripropylthiosubphthalocyaninato)boron(III) (7): BCl$_3$ (0.2 mL), previously condensed at –78°C, was added through a cannula to a magnetically stirred solution of 1,2-dicyano-3-propylthiobenzene (**3**) (1.00 g, 4.95 mmol) in dry 1-chloronaphthalene (1.0 mL) under argon. The mixture was stirred at room temperature for 15 min, then warmed to 130°C and kept at that temperature for 30 min. The resulting purple mixture was then cooled to room temperature. The solid residue was washed immediately with 25 mL of dry hexane. Flash chromatography on silica gel with CH$_2$Cl$_2$ as eluent gave a purple black compound (10 mg, 1%): m.p. > 200°C. – ^{1}H NMR (200 MHz, CDCl$_3$): δ = 8.85–7.74 (m, 9 H), 3.45–0.85 (m, 21 H). – UV/Vis (CHCl$_3$) λ_{max} (nm): 605, 563 (sh), 368 (sh), 250. – MS (FAB, *m*NBA): *m*/*z* (%): 653 (2) [M + H]$^{+}$.

Chloro(1,8,18-tripropylsulfonyl)- and Chloro(1,8,15-tripropylsulfonylsubphthalocyaninato)boron(III) (8a and 8b): BCl$_3$ (0.1 mL), previously condensed at –78°C, was added through a cannula to a magnetically stirred solution of 1,2-dicyano-3-propylsulfonylbenzene (**4**) (500 mg, 2.14 mmol) in dry 1-chloronaphthalene (0.5 mL) under argon. The mixture was stirred at room temperature for 15 min, warmed to 120°C and kept at that temperature for 4 h. The resulting purple mixture was cooled to room temperature. The solid residue was washed with 25 mL hexane and purified by column chromatography on silica gel with first hexane, then Et$_2$O, and finally CH$_2$Cl$_2$ to yield 80 mg (15%) of subphthalocyanine **8** purple solid. A ratio **8a**:**8b** of 92:8 was estimated by integration of the relevant signals of the ^{1}H NMR spectrum (Figure 2). M.p. > 200°C. – IR (KBr) 1320, 1147, 1107, 806 cm^{-1}. – ^{1}H NMR (300 MHz, CDCl$_3$): δ = 9.29 (dd, ^{3}J = 8 Hz, ^{4}J = 1 Hz, 1 H, **8a**), 9.23 (dd, ^{3}J = 8 Hz, ^{4}J = 1 Hz, 1 H, **8a**), 9.18 (dd, ^{3}J = 8 Hz, ^{4}J = 1 Hz, 1 H, **8a**), 9.12 (dd, ^{3}J = 8 Hz, ^{4}J = 1 Hz, 1 H, **8b**), 8.76 (dd, ^{3}J = 8 Hz, ^{4}J = 1 Hz, 1 H, **8a**), 8.75 (dd, ^{3}J = 8 Hz, ^{4}J = 1 Hz, 1 H, **8a**),), 8.69 (dd, ^{3}J = 8 Hz, ^{4}J = 1 Hz, 1 H, **8a**), 8.68 (dd, ^{3}J = 8 Hz, ^{4}J = 1 Hz, 1 H, **8b**), 8.21 (t, ^{3}J = 8 Hz, 1 H, **8a**), 8.20 (t, ^{3}J = 8 Hz, 1 H, **8a**), 8.18 (t, ^{3}J = 8 Hz, 1 H, **8a**), 8.16 (t, ^{3}J = 8 Hz, 1 H, **8b**), 4.56–4.43 (m, 4 H, **8a** + **8b**), 4.32–4.07 (m, 2 H, **8a** + **8b**), 2.18–1.47 (m, 6 H, **8a** + **8b**), 1.09–0.91 (m, 9 H, **8a** + **8b**). – MS (FAB, *m*NBA): *m*/*z* (%): 749 (15) [M + H]$^{+}$. – UV/Vis (CHCl$_3$) λ_{max} (log ε/dm^3 mol^{-1} cm^{-1}): 558 (4.6), 543 (sh), 514 (sh), 307 (4.5). – HRMS calcd. for $C_{33}H_{31}BClN_6O_6S_3$: 749.1249; found 749.1264.

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