Synthesis of Unsymmetrically Substituted Subphthalocyanines

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Abstract: A series of new unsymmetrically substituted subphthalocyanines containing iodo or octylthioether substituents on the outer aromatic rings have been synthesized. The statistical reaction of one equivalent of 1,2-dicyano-3-iodobenzene whether with two equivalents of 1,2-dicyano-4-octylthiobenzene or with two equivalents of 1,2-dicyano-4,5-dioctylthiobenzene in the presence of boron trichloride in 1-chloronaphthalene yielded in both cases all the possible expected unsymmetrically substituted subphthalocyanines, which were separated by column chromatography on silica gel. All compounds were identified by FAB mass spectrometry and then characterized by HR-LSIMS spectrometry. The unambiguous characterization of each constitutional isomer was made possible by careful examination of the symmetry environment experienced by each proton on their ^{1}H-NMR spectra.

Keywords: boron · cyclotrimerizations · nitrogen heterocycles · subphthalocyanines · topochemistry

Introduction

Subphthalocyanines (SubPcs),[1] comprising three *N*-fused diiminoisoindoline units around a boron core, have a cone-shaped trigonal structure[2] (Figure 1) which does not prevent them from possessing an aromatic nature.[3] Their curved molecular surface make them attractive candidates for the construction of three-dimensional cage compounds in the same way as CTVs,[4] fullerene segments,[5] or related topological systems.[6] Furthermore, their C_3 symmetry axis gives rise, upon appropriate substitution, to chirality.

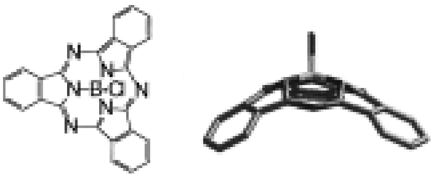

Figure 1. Representations of chloro(subphthalocyaninato) boron(III).

On the other hand, SubPcs are also precursors of unsymmetrical substituted phthalocyanines (Pcs) through ring expansion reactions.[7] For these reasons the synthesis of adequately functionalized regioisomerically pure SubPcs is an important goal to be pursued. The design and preparation of appropiately substituted SubPcs is also extremely important in the field of nonlinear optics in which this class of compounds have shown very interesting second-order properties of octupolar character.[8]

Until now, only two reports on pure trisubstituted regioisomers have been published[9] and only SubPcs bearing identical peripheral substituents have been described.[1, 3, 7–10]

In this article, we report (Schemes 1 and 2) on the synthesis of the first unsymmetrically substituted SubPcs **1**–**4**, and the separation of their regioisomers **1a**–**d**, **2a**–**d**, **3**, and **4a**–**c** by preparative column chromatography. The choice of starting materials **5**, **6**, and **7** bearing iodo and octylthio substituents, with similar reactivities towards BCl_3, was made taking into account our previous experience in SubPc synthesis and also their ability to undergo further functionalization once incorporated within the SubPc framework.[10]

Results and Discussion

Synthesis: The synthesis of 1,2-dicyano-3-iodobenzene[11] (**5**), 1,2-dicyano-4-octylthiobenzene[8b] (**6**), and 1,2-dicyano-4,5-dioctylthiobenzene[8b] (**7**) was achieved according to literature procedures. SubPcs **1**–**2**, **8**–**9** were prepared as a mixture (Scheme 1) by slowly introducing previously condensed BCl_3 into a solution of compounds **5** and **6**, in a 1:2 ratio, in 1-chloronaphthalene at 150 °C. The overall yield for SubPc **1**–**2**, **8**–**9** formation was 17 %. Similarly, SubPcs **3**–**4**, **9**–**10** were obtained (Scheme 2), starting from a 1:2 ratio of dicyano compounds **5** and **7**, in a 21 % overall yield.

SubPcs **1**–**4**, **8**–**10** were separated and purified by successive column chromatographies on silica gel using different

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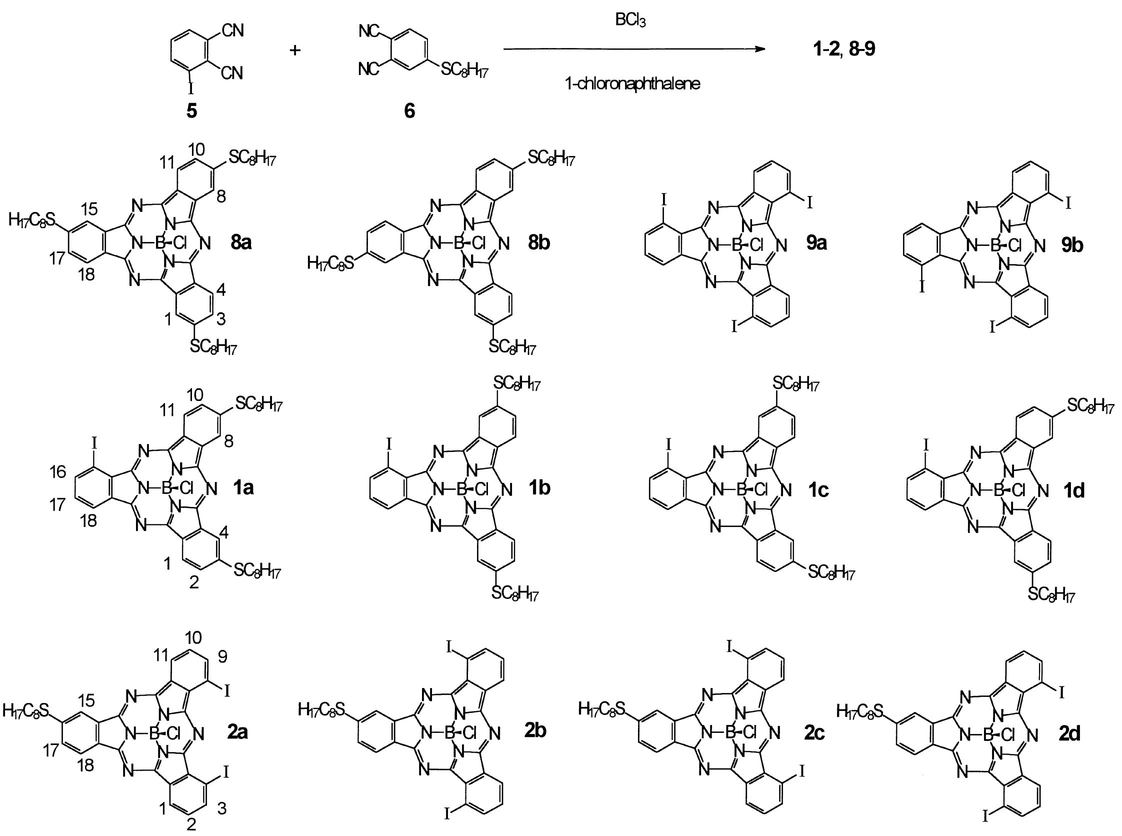
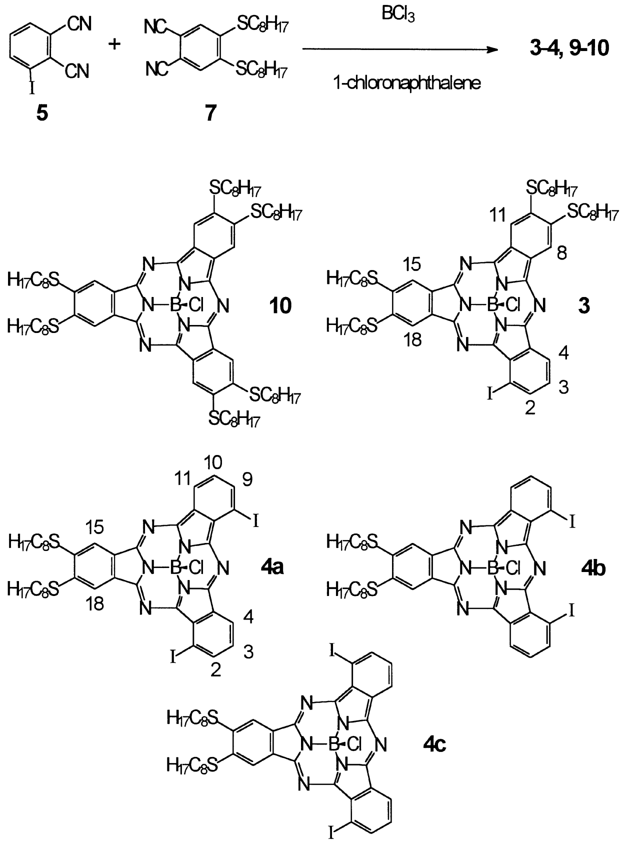


Scheme 1. Synthesis of subphthalocyanines **1**–**2**, **8**–**9**.



Scheme 2. Synthesis of subphthalocyanines **3**–**4**, **9**–**10**.

solvent systems when necessary as described in the experimental section.

The constitutional isomers **8a** and **8b**, previously described as their statistical mixture[1, 3, 7–10] (in a 1:3 ratio), were isolated and characterized in yields of 0.3 and 0.7%, respectively. The SubPcs **1** comprising two thioether- and one iodo-containing isoindole units were also isolated as **1a** (2.3%), **1b** (0.8%), and a 1:1 mixture of **1c** and **1d** (combined yield 4.5%). SubPcs **2** comprising one thioether- and two iodo-containing isoindole units were also isolated as **2a** (0.1%), **2b** (0.2%), and a 1:1 mixture of **2c** and **2d** (0.3%). SubPc **9** was isolated only as its asymmetric isomer **9b** in 1% yield.[9b]

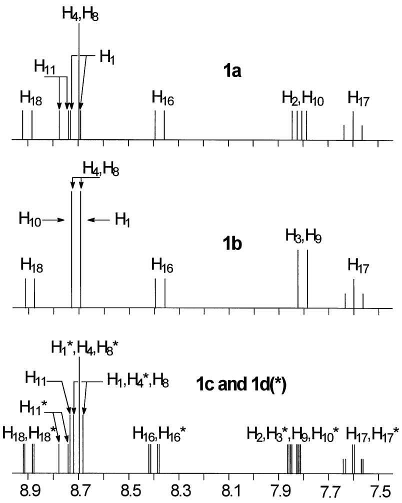
SubPc **3** was obtained in a 0.7% yield and SubPcs **4a**–**c** were obtained in 1.1, 0.4, and 0.9% yield, respectively. When starting from a 1:2 ratio of **5** and **6**, the theoretical statistical ratio of SubPc formation in the case all starting materials and the intermediate compounds possess the same reactivity, is 30, 44, 22, and 4% for SubPcs **1**, **2**, **8**, and **9**, respectively. These theoretical results are to be compared with the experimental ones, calculated from the data described before, which are 7, 78, 11, and 4%, respectively. In the case of the reaction between dicyano compounds **5** and **7**, the theoretical values for SubPcs **3**, **4**, **9**, and **10** formation are 44, 22, 4, and 30%, respectively, to be compared with 31, 17, 23, and 29% obtained experimentally.

Characterization: All compounds were identified by FAB-MS and further characterized by HR-LSIMS. ^{1}H-NMR spectra of

SubPcs **1**–**4**, **8**–**10** show characteristic low field signals at $\delta = 7.8-9.0$, attributables to the aromatic protons resonances, which are in agreement with the expected patterns corresponding to their respective symmetries. Schemes 3–5 give[12] a schematic representation of the ^{1}H-NMR spectra obtained experimentally.

The spectra of isomers **8a** and **8b** (Scheme 1) are very similar, they differ only in the signals corresponding to protons $\mathbf{H_3}$, $\mathbf{H_{10}}$, and $\mathbf{H_{17}}$ which appear as a doublet in the case of C_3 symmetric SubPc **8a** and as a more complex multiplet in the case of asymmetric SubPc **8b**.

The ^{1}H-NMR spectrum of SubPc **1a** reveals (Scheme 3) the presence of expected resonances at $\delta = 7.6$, 8.4, and 8.9 corresponding to the protons $\mathbf{H_{17}}$, $\mathbf{H_{16}}$, and $\mathbf{H_{18}}$, respectively. Two sets of two doublets at $\delta = 7.81$ and 7.82 for $\mathbf{H_2}$ and $\mathbf{H_{10}}$, and at 8.71 and 8.76 for $\mathbf{H_1}$ and $\mathbf{H_{11}}$ characterize the asymmetric environment experienced by the protons close to the iodo-containing isoindole unit of the SubPc.

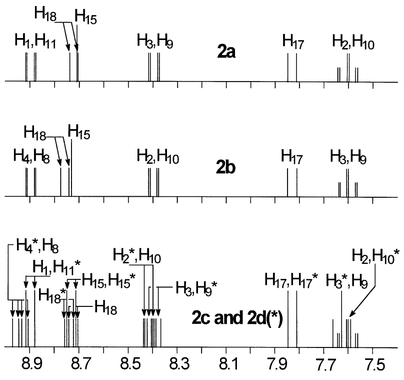


Scheme 3. Schematic representation of a portion of the ^{1}H-NMR spectra (300 MHz, CDCl$_3$) of subphtalocyanines **1a**–**d**.

The spectrum of SubPc **1b** shows (Scheme 3) virtually the same pattern as observed for SubPc **1a** for the resonances corresponding to the protons $\mathbf{H_{16}}$, $\mathbf{H_{17}}$, and $\mathbf{H_{18}}$ belonging to the iodo-containing isoindole unit. As expected in this case, the effect of the asymmetry brought by the iodine-containing unit resides only in the splitting of the singlet corresponding to the protons $\mathbf{H_1}$ and $\mathbf{H_{11}}$ into two singlets at $\delta = 8.70$ and 8.73, respectively.

The ^{1}H-NMR spectrum of the 1:1 mixture of SubPcs **1c** and **1d** shows (Scheme 3) the expected splitting of the protons corresponding to the iodo-containing isoindole unit. In this case, the characteristic region at about $\delta = 8.7$ reveals the presence of a singlet at $\delta = 8.70$ corresponding to protons $\mathbf{H_1}$*, $\mathbf{H_4}$, and $\mathbf{H_8}$*, another singlet at 8.73 corresponding to proton $\mathbf{H_{11}}$, a doublet at $\delta = 8.71$ associated with protons $\mathbf{H_1}$, $\mathbf{H_4}$*, and $\mathbf{H_8}$, and finally a doublet at $\delta = 8.76$ corresponding to proton $\mathbf{H_{11}}$*.

The spectrum of SubPc **2a** reveals (Scheme 4) the expected symmetrical pattern in which there is a slight splitting of the signals corresponding to the protons of the iodo-containing isoindole unit.



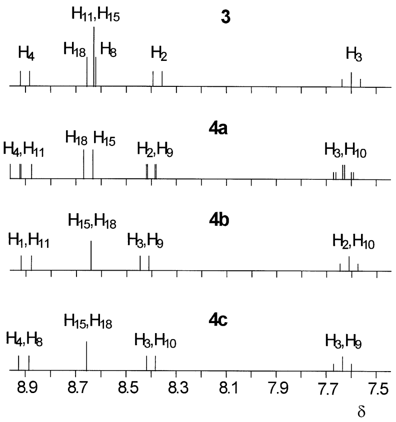
Scheme 4. Schematic representation of a portion of the ^{1}H-NMR spectra (300 MHz, CDCl$_3$) of subphtalocyanines **2a**–**d**.

The ^{1}H-NMR spectrum of SubPc **2b** is (Scheme 4) very similar to that of SubPc **2a**. It differs only in the deshielding of the protons $\mathbf{H_{15}}$ and $\mathbf{H_{18}}$ from $\delta = 8.71$ to 8.73 and from 8.73 to 8.77, respectively, as a consequence of the proximity of the iodine atom.

The spectrum of the 1:1 mixture of SubPcs **2c** and **2d** reveals (Scheme 4) a very strong asymmetrization of the signals brought by the relative positions of the iodine atoms. Therefore, protons $\mathbf{H_3}$* and $\mathbf{H_9}$ appear as one triplet slightly deshielded at $\delta = 7.63$, whereas protons $\mathbf{H_2}$ and $\mathbf{H_{10}}$* give rise to two triplets at $\delta = 7.60$ and 7.61, respectively. The same phenomenon is observed in the case of protons $\mathbf{H_3}$, $\mathbf{H_9}$*, $\mathbf{H_{10}}$, and $\mathbf{H_2}$*.

The ^{1}H-NMR spectrum of SubPc **3** shows (Scheme 5) the asymmetrization brought by the iodo-containing isoindole unit on the signals corresponding to protons $\mathbf{H_8}$ and $\mathbf{H_{18}}$ that appear as two singlets at $\delta = 8.62$ and 8.66, respectively.

The spectrum of SubPc **4a** reveals (Scheme 5) a slight splitting (0.01 ppm) of the signals corresponding to the iodo-containing isoindole unit protons $\mathbf{H_{2-4}}$ and $\mathbf{H_{9-11}}$. Protons $\mathbf{H_{15}}$ and $\mathbf{H_{18}}$, as in the case of SubPc **3**, gave rise to two singlets at $\delta = 8.63$ and 8.67, respectively.



Scheme 5. Schematic representation of a portion of the ^{1}H-NMR spectra (300 MHz, CDCl$_3$) of subphtalocyanines **3**, **4a**–**c**.

The ^{1}H-NMR spectra of SubPcs **4b** and **4c** reveals (Scheme 5) very simple patterns in accordance with the C_s symmetry of the molecules.

UV/Vis spectrophotometry shows that the position of the Q-band is blueshifted as the number of iodine atoms increase within the SubPc molecule: λ_{max}(**8**) = 588 nm > λ_{max}(**1**) = 584 nm > λ_{max}(**2**) = 581 nm > λ_{max}(**9**)[9] = 577 nm for **9a** and 579 nm for **9b**. Similarly, λ_{max}(**10**) = 602 nm > λ_{max}(**3**) = 594 nm > λ_{max}(**4**) = 586–587 nm > λ_{max}(**9**)[9] = 577 nm for **9a** and 579 nm for **9b**. It is very important to be able to fine-tune the Q-band position as far as the nonlinear optical properties of the SubPcs are concerned.[8]

Conclusion

In summary, we have described for the first time the preparation of unsymmetrically substituted SubPcs that are relevant for both their potential synthetic applications and physical properties. Furthermore, the presence of one or two iodine atom within the framework of compounds **1a–d**, **2a–d**, **3**, and **4a–c** together with their curved-like structures render them very attractive for their potential use as building blocks for the construction of higher order molecular assemblies using for example cross coupling metal mediated methodologies with appropriate alkyne derivatives.[10]

Experimental Section

UV/Visible and infrared measurements were carried out on Perkin–Elmer Model Lambda 6 and Philips PU-9716, respectively. FAB-MS and HRMS spectra were determined on a VG AutoSpec instrument. NMR spectra were recorded with a Bruker AC-300 (300 MHz) spectrometer. Column chromatographies were 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) using the indicated solvents. All dry solvents were freshly distilled under argon over an appropriate drying agent before use.

Compounds 1a, 1b, 1c, 1d, 2a, 2b, 2c, 2d, 8a, 8b, and 9b: 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-iodobenzene (**5**) (160 mg, 0.62 mmol) and 1,2-dicyano-4-octylthiobenzene (**6**) (344 mg, 1.26 mmol) in dry 1-chloronaphthalene (1.0 mL) under Ar. The mixture was stirred at room temperature for 15 min, warmed up to 150 °C and kept at that temperature for 5 h. The resulting purple mixture was cooled down to room temperature. The solid residue was washed with hexane (50 mL) and was purified by successive column chromatographies on silica gel using solvent systems indicated below. After the first column, subphthalocyanine compounds (54 mg) were collected, that corresponds to 17% yield of subphthalocyanine formation (based on a statistical distribution of compounds). All compounds are dark purple in the solid state and intense violet in chloroform solutions.

Chloro(3,9-dioctylthio-15-iodosubphthalocyaninato)boron(III) (1a): 12.2 mg (2.3%); m.p. > 200 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.81-0.91$ (m, 6H), 1.20–1.40 (m, 20H), 1.75–1.86 (m, 4H), 3.14–3.30 (m, 4H), 7.61 (t, $^3J = 8$ Hz, 1H), 7.81 (dd, $^3J = 8$ Hz, $^4J = 1$ Hz, 1H), 7.82 (dd, $^3J = 8$ Hz, $^4J = 1$ Hz , 1H), 8.38 (dd, $^3J = 8$ Hz, $^4J = 1$ Hz, 1H), 8.70 (s, 2H), 8.71 (dd, $^3J = 8$ Hz, $^4J = 1$ Hz, 1H), 8.76 (dd, $^3J = 8$ Hz, $^4J = 1$ Hz, 1H), 8.90 (dd, $^3J = 8$ Hz, $^4J = 1$ Hz, 1H); FAB-MS: m/z: 844 $[M]^+$, 845 $[M+H]^+$; UV/Vis ($CHCl_3$): λ_{max} (log ε/dm^3 mol^{-1} cm^{-1}) = 260 (4.6), 287 (4.5), 367 (sh), 397 (sh), 537 (sh), 584 nm (4.6); IR (KBr, cm^{-1}): $\tilde{\nu} = 2924$, 2852, 1652, 1636, 1605, 1385, 1261, 1133, 1096, 1072, 1045, 806, 786; HR-LSIMS calcd for $C_{40}H_{43}N_6IS_2BCl$: $[M]^+$: m/z: 844.1817, found: 844.1857; TLC: R_f: 0.81 (ethyl acetate/hexane 1:4), R_f: 0.33 (toluene/hexane 2:3).

Chloro(2,10-dioctylthio-15-iodosubphthalocyaninato)boron(III) (1b): 4.4 mg (0.8%); m.p. > 200 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.81-0.93$ (m, 6H), 1.20–1.41 (m, 20H), 1.75–1.86 (m, 4H), 3.14–3.30 (m, 4H), 7.60 (t, $^3J = 8$ Hz, 1H), 7.81 (dd, $^3J = 8$ Hz, $^4J = 1$ Hz, 1H), 8.38 (dd, $^3J = 8$ Hz, $^4J = 1$ Hz, 1H), 8.70 (s, 1H), 8.71 (d, $^3J = 8$ Hz, 2H), 8.73 (s, 1H), 8.90 (dd, $^3J = 8$ Hz, $^4J = 1$ Hz, 1H); FAB-MS: m/z: 844 $[M]^+$, 845 $[M+H]^+$; UV/Vis ($CHCl_3$): λ_{max} (log ε/dm^3 mol^{-1} cm^{-1}) = 289 (4.6), 365 (3.9), 409 (sh), 540 (sh), 584 nm (4.6); IR (KBr, cm^{-1}): $\tilde{\nu} = 2957$, 2924, 2853, 1636, 1604, 1457, 1437, 1187, 1099, 969, 787, 750, 705; HR-LSIMS calcd for $C_{40}H_{43}N_6IS_2BCl$: $[M]^+$: m/z: 844.1817, found: 844.1837; TLC: R_f: 0.73 (ethyl acetate/hexane 1:4).

Chloro(3,10-dioctylthio-15-iodosubphthalocyaninato)boron(III) (1c) and chloro(2,9-dioctylthio-15-iodosubphthalocyaninato)boron(III) (1d): combined 23.6 mg (4.5%); m.p. > 200 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.81-0.91$ (m, 12H), 1.20–1.40 (m, 40H), 1.75–1.86 (m, 8H), 3.14–3.30 (m, 8H), 7.60 (t, $^3J = 8$ Hz, 1H), 7.61 (t, $^3J = 8$ Hz, 1H), 7.69–7.83 (m, 4H), 8.36–8.40 (m, 2H), 8.70 (s, 3H), 8.71 (d, $^3J = 8$ Hz, 3H), 8.73 (s, 1H), 8.76 (d, $^3J = 8$ Hz, 1H), 8.88–8.91 (m, 2H); FAB-MS: m/z: 844 $[M]^+$, 845 $[M+H]^+$; UV/Vis ($CHCl_3$): λ_{max} (log ε/dm^3 mol^{-1} cm^{-1}) = 291 (4.5), 366 (3.9), 401 (sh), 539 (sh), 584 nm (4.6); IR (KBr, cm^{-1}): $\tilde{\nu} = 2924$, 2852, 1604, 1458, 1437, 1385, 1259, 1187, 1134, 1097, 1073, 1047, 967, 805, 783, 752, 703; HR-LSIMS calcd for $C_{40}H_{43}N_6IS_2BCl$: $[M]^+$: m/z: 844.1817, found: 844.1833; TLC: R_f: 0.64 (ethyl acetate/hexane 1:4).

Chloro(4,8-diiodo-16-octylthiosubphthalocyaninato)boron(III) (2a): 1.0 mg (0.1%); m.p. > 200 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.80-0.93$ (m, 3H), 1.20–1.43 (m, 10H), 1.75–1.85 (m, 2H), 3.18–3.28 (m, 2H), 7.61 (2t, $^3J = 8$ Hz, 2H), 7.83 (dd, $^3J = 8$ Hz, $^4J = 1$ Hz, 1H), 8.42 (dd, $^3J = 8$ Hz, $^4J = 1$ Hz, 2H), 8.71 (s, 1H), 8.73 (dd, $^3J = 8$ Hz, $^4J = 1$ Hz, 1H), 8.90 (dd, $^3J = 8$ Hz, $^4J = 1$ Hz, 2H); FAB-MS: m/z: 826 $[M]^+$, 827 $[M+H]^+$; UV/Vis ($CHCl_3$): λ_{max} (log ε/dm^3 mol^{-1} cm^{-1}) = 578 (4.8), 562 (sh), 538 (sh), 283 nm (4.8); IR (KBr, cm^{-1}): $\tilde{\nu} = 2964$, 2924, 2853, 1636, 1262, 1095, 1032, 803; HR-LSIMS calcd for $C_{32}H_{26}N_6I_2SBCl$: $[M]^+$: m/z: 825.9811, found: 825.9817; TLC: R_f: 0.43 (ethyl acetate/hexane 1:4), R_f: 0.38 (acetone/hexane 2:3).

Chloro(1,11-diiodo-16-octylthiosubphthalocyaninato)boron(III) (2b): 1.7 mg (0.2%); m.p. > 200 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.81-0.92$ (m, 3H), 1.19–1.42 (m, 10H), 1.75–1.86 (m, 2H), 3.17–3.24 (m, 2H), 7.62 (t, $^3J = 8$ Hz, 1H), 7.63 (t, $^3J = 8$ Hz, 1H), 7.83 (dd, $^3J = 8$ Hz, $^4J = 1$ Hz, 1H), 8.40 (dd, $^3J = 8$ Hz, $^4J = 1$ Hz, 2H), 8.73 (s, 1H), 8.77 (dd, $^3J = 8$ Hz, $^4J = 1$ Hz, 1H), 8.91 (dd, $^3J = 8$ Hz, $^4J = 1$ Hz, 2H); FAB-MS: m/z: 826 $[M]^+$, 827 $[M+H]^+$; UV/Vis ($CHCl_3$): λ_{max}(log ε/dm^3 mol^{-1} cm^{-1}) = 288 (4.7), 405 (sh), 536 (sh), 563 (sh), 581 nm (4.8); IR (KBr, cm^{-1}): $\tilde{\nu} = 2923$, 2852, 1718, 1637, 1604, 1458, 1432, 1389, 1271, 1241, 1182, 1132, 1095, 1037, 966, 787, 751, 702; HR-LSIMS calcd for $C_{32}H_{26}N_6I_2SBCl$: $[M]^+$: m/z: 825.9811, found: 825.9813; TLC: R_f: 0.52 (ethyl acetate/hexane 1:4).

Chloro(4,11-diiodo-16-octylthiosubphthalocyaninato)boron(III) (2c) and chloro(1,8-diiodo-16-octylthiosubphthalocyaninato)boron(III) (2d): 2.7 mg (0.3%); m.p. > 200 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.81-0.92$ (m, 6H), 1.19–1.41 (m, 20H), 1.76–1.87 (m, 4H), 3.17–3.27 (m, 4H), 7.60 (t, $^3J = 8$ Hz, 1H), 7.61 (t, $^3J = 8$ Hz, 1H), 7.63 (2t, $^3J = 8$ Hz, 2H), 7.82 (dd, $^3J = 8$ Hz, $^4J = 1$ Hz, 2H), 8.40 (dd, $^3J = 8$ Hz, $^4J = 1$ Hz, 1H), 8.41 (dd, $^3J = 8$ Hz, $^4J = 1$ Hz, 1H), 8.42 (2dd, $^3J = 8$ Hz, $^4J = 1$ Hz, 2H), 8.70–8.75 (m, 4H), 8.89 (dd, $^3J = 8$ Hz, $^4J = 1$ Hz, 2H), 8.92 (dd, $^3J = 8$ Hz, $^4J = 1$ Hz, 1H), 8.95 (dd, $^3J = 8$ Hz, $^4J = 1$ Hz, 1H); FAB-MS: m/z: 826 $[M]^+$, 827 $[M+H]^+$; UV/Vis ($CHCl_3$): λ_{max} (log ε/dm^3 mol^{-1} cm^{-1}) = 287 (4.7), 400 (sh), 539 (sh), 563 (sh), 581 nm (4.8); IR (KBr, cm^{-1}): $\tilde{\nu} = 2959$, 2924, 2853, 1458, 1258, 1190, 1098, 1069, 966, 804, 784, 752, 703; HR-LSIMS calcd for $C_{32}H_{26}N_6I_2SBCl$: $[M]^+$: m/z: 825.9811, found: 825.9832; TLC: R_f: 0.52 (ethyl acetate/hexane 1:4), R_f: 0.44 (acetone/hexane 2:3).

Chloro(2,9,16-trioctylthiosubphthalocyaninato)boron(III) (8a): 1.0 mg (0.3%); m.p. > 200 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.81-0.92$ (m, 9H), 1.19–1.41 (m, 30H), 1.75–1.86 (m, 6H), 3.14–3.30 (m, 6H), 7.80 (dd, $^3J = 8$ Hz, $^4J = 1$ Hz, 3H), 8.70 (s, 3H), 8.71 (d, $^3J = 7$ Hz, 3H); FAB-MS: m/z: 862 $[M]^+$, 863 $[M+H]^+$; UV/Vis ($CHCl_3$): λ_{max} (log ε/dm^3 mol^{-1} cm^{-1}) = 588 (4.6), 540 (sh), 366 (4.2), 292 nm (4.6); IR (KBr, cm^{-1}): $\tilde{\nu} = 2958$, 2925, 2853, 1447, 1262, 1099, 1070, 1034, 797; HR-LSIMS calcd for $C_{48}H_{60}N_6S_3BCl$: $[M]^+$: m/z: 862.3823, found: 862.3839; TLC: R_f: 0.88 (ethyl acetate/hexane 1:4).

Chloro(2,9,17-trioctylthiosubphthalocyaninato)boron(III) (8b): 2.5 mg (0.7%); m.p.: > 200 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.82-0.92$ (m, 9 H), 1.20 – 1.41 (m, 30 H), 1.75 – 1.85 (m, 6 H), 3.16 – 3.30 (m, 6 H), 7.78 – 7.82 (m, 3 H), 8.70 (s, 3 H), 8.71 (d, $^3J = 7$ Hz, 3 H); FAB-MS: *m*/*z*: 862 $[M]^+$, 863 $[M+H]^+$; UV/Vis ($CHCl_3$): λ_{max} (log ε/dm^3 mol^{-1} cm^{-1}) = 585 (4.6), 540 (sh), 366 (4.2), 349 (4.2), 291 nm (4.6); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2963, 2925, 2854, 1734, 1636, 1464, 1262, 1034, 802; HR-LSIMS calcd for $C_{48}H_{60}N_6S_3BCl$: $[M]^+$: *m*/*z*: 862.3823, found: 862.3798; TLC: R_f: 0.81 (ethyl acetate/hexane 1:4), R_f: 0.25 (toluene/hexane 2:3).

Chloro(1,8,18-triiodosubphthalocyaninato)boron(III) (9b): 2.0 mg (1 %); compound possessing identical physical data as described previously.[9b]

Compounds 3, 4a, 4b, 4c, 9b, and 10: 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-iodobenzene (**5**, 101 mg, 0.40 mmol) and 1,2-dicyano-4,5-dioctylthiobenzene (**7**, 331 mg, 0.80 mmol) in dry 1-chloronaphthalene (1.0 mL) under Ar. The mixture was stirred at room temperature for 15 min, warmed up to 150 °C and kept at that temperature for 5 h. The resulting purple mixture was cooled down to room temperature. The solid residue was washed with hexane (50 mL) and was purified by successive column chromatographies on silica gel using solvent systems indicated below. After the first column, the subphthalocyanine compounds (91 mg) were collected, which corresponds to a 21 % yield of subphthalocyanine (based on a statistical distribution of compounds). Compounds **3**, **4a – c** and **9b** were obtained as dark purple solids, and compound **10** was obtained as a green solid.

Chloro(1-iodo-9,10,16,17-tetraoctylthiosubphthalocyaninato)boron(III) (3): 3.1 mg (0.7 %); m.p. > 200 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.79 - 0.95$ (m, 12 H), 1.21 – 1.48 (m, 40 H), 1.69 – 1.95 (m, 8 H), 3.19 – 3.34 (m, 8 H), 7.60 (t, $^3J = 8$ Hz, 1 H), 8.38 (d, $^3J = 8$ Hz, 1 H), 8.62 (s, 1 H), 8.63 (s, 2 H), 8.66 (s, 1 H), 8.90 (d, $^3J = 8$ Hz, 1 H); FAB-MS: *m*/*z*: 1132 $[M]^+$, 1133 $[M+H]^+$; UV/Vis ($CHCl_3$): λ_{max}(log ε/dm^3 mol^{-1} cm^{-1}) = 594 (4.6), 577(sh), 555(sh), 420 (4.2), 357 (4.2), 304 (4.6), 242 (4.5); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2925, 2389, 1637, 1619, 1044; HR-LSIMS calcd for $C_{56}H_{75}N_6IS_4BCl$: $[M]^+$: *m*/*z*: 1132.3762, found: 1132.3769; TLC: R_f: 0.86 (ethyl acetate/hexane 1:4).

Chloro(1,8-diiodo-16,17-dioctylthiosubphthalocyaninato)boron(III) (4a): 2.2 mg (1.1 %); m.p. > 200 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.80 - 0.96$ (m, 6 H), 1.20 – 1.46 (m, 20 H), 1.66 – 1.92 (m, 4 H), 3.18 – 3.34 (m, 4 H), 7.62 (t, $^3J = 8$ Hz, 1 H), 7.63 (t, $^3J = 8$ Hz, 1 H), 8.36 – 8.44 (m, 2 H), 8.63 (s, 1 H), 8.67 (s, 1 H), 8.91 (d, $^3J = 8$ Hz, 1 H), 8.96 (d, $^3J = 8$ Hz, 1 H); FAB-MS: *m*/*z*: 970 $[M]^+$, 971 $[M+H]^+$; UV/Vis ($CHCl_3$): λ_{max}(log ε/dm^3 mol^{-1} cm^{-1}) = 586 (4.7), 569(sh), 544(sh), 430 (4.2), 299 (4.6), 242 (4.6); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2924, 1638, 1618, 1100; HR-LSIMS calcd for $C_{40}H_{42}N_6I_2S_2BCl$: $[M]^+$: *m*/*z*: 978.0783, found: 970.0785; TLC: R_f: 0.76 (ethyl acetate/hexane 1:4).

Chloro(4,8-diiodo-16,17-dioctylthiosubphthalocyaninato)boron(III) (4b): 0.9 mg (0.4 %); m.p. > 200 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.79 - 0.92$ (m, 6 H), 1.21 – 1.42 (m, 20 H), 1.65 – 1.92 (m, 4 H), 3.19 – 3.35 (m, 4 H), 7.61 (t, $^3J = 8$ Hz, 2 H), 8.43 (d, 2 H), 8.64 (s, 2 H), 8.90 (d, $^3J = 8$ Hz, 2 H); FAB-MS: *m*/*z*: 970 $[M]^+$, 971 $[M+H]^+$; UV/Vis ($CHCl_3$): λ_{max}(log ε/dm^3 mol^{-1} cm^{-1}) = 587 (4.7), 570(sh), 545(sh), 420(sh), 288 (4.7), 242 (4.7); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2925, 1638, 1618, 1385, 1096; HR-LSIMS calcd for $C_{40}H_{42}N_6I_2S_2BCl$: $[M]^+$: *m*/*z*: 970.0783, found: 970.0780; TLC: R_f: 0.70 (ethyl acetate/hexane 1:4).

Chloro(1,11-iodo-16,17-dioctylthiosubphthalocyaninato)boron(III) (4c): 1.7 mg (0.9 %); m.p. > 200 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.80 - 0.92$ (m, 6 H), 1.23 – 1.42 (m, 20 H), 1.65 – 1.93 (m, 4 H), 3.19 – 3.34 (m, 4 H), 7.63 (t, $^3J = 8$ Hz, 2 H), 8.40 (d, 2 H), 8.66 (s, 2 H), 8.91 (d, $^3J = 8$ Hz, 2 H); FAB-MS: *m*/*z*: 970 $[M]^+$, 971 $[M+H]^+$; UV/Vis ($CHCl_3$): λ_{max}(log ε/dm^3 mol^{-1} cm^{-1}) = 586 (4.7), 570(sh), 548(sh), 434 (4.2), 297 (4.6), 243 (4.6); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2924, 1637, 1402, 1096; HR-LSIMS calcd for $C_{40}H_{42}N_6I_2S_2BCl$: $[M]^+$: *m*/*z*: 970.0783, found: 970.0788; TLC: R_f: 0.58 (ethyl acetate/hexane 1:4).

Chloro(1,8,18-triiodosubphthalocyaninato)boron(III) (9b): 2.9 mg (2.7 %); compound possessing identical physical data as described previously.[9b]

Chloro(2,3,9,10,16,17-hexaoctylthiosubphthalocyaninato)boron(III) (10): 6.0 mg (1.7 %); compound possessing identical physical data as described previously.[8b]

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[12] For the sake of simplification, the *meta* couplings (1 Hz) are not represented in the schematic spectra in Schemes 2 and 3. See Supporting Information for the experimental ^{1}H-NMR spectra.

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