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Peripheral Functionalization of Subphthalocyanines

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The optimization of synthetic methodologies that lead to novel synthetically and electronically valuable SubPc molecules is of great interest for the use of these molecules in applied fields. In this work, we describe some useful procedures for the incorporation of diverse functional groups in the periphery of the SubPc macrocycle. Different metal-catalyzed cross-coupling reactions, including Stille or Suzuki couplings and palladium-catalyzed borylation or amination reactions, have been optimized in order to obtain high yields and avoid SubPc decomposition. In addition, we report on the scope of the use of ether functionalities in the condensation reaction with BCl_3 and on the synthesis of a trihydroxy-SubPc, a very valuable compound that could be obtained by deprotection of a silyloxy-SubPc precursor.

Introduction

Organic molecular materials enjoy a number of characteristics that make them very attractive for application in nanoscale optoelectronic devices.[1] Their functional versatility and the possibility of influencing their properties by modification of the molecular structure have prompted synthetic chemists to investigate novel, reliable and efficient methods for their functionalization. Key issues for optimal performance, such as the molecular electronic characteristics, the supramolecular organization, the interaction with other molecules, or the processability of the bulk material, can now be controlled to some extent by rational synthetic design.

Among these organic materials, subphthalocyanines (SubPcs, Figure 1)[2] are emerging as promising chromophores with potential applications in optical data storage,[3] nonlinear optics,[4] energy and electron transfer systems,[5] light-emitting diodes,[6] anion sensing,[7] and supramolecular chemistry.[8] These aromatic macrocycles possess a singular conical structure[9] imposed by steric factors and stabilized by the tetrahedral nature of a central boron atom that, to date, is the only element that has been fitted within the central cavity. SubPcs are prepared by a condensation reaction of phthalonitriles in the presence of a boron halide (usually BCl_3),[2,10] which leads to the templated formation of a three-membered ring, as opposed to other metals that lead to the more widely known four-membered phthalocyanines (Pcs).[11]

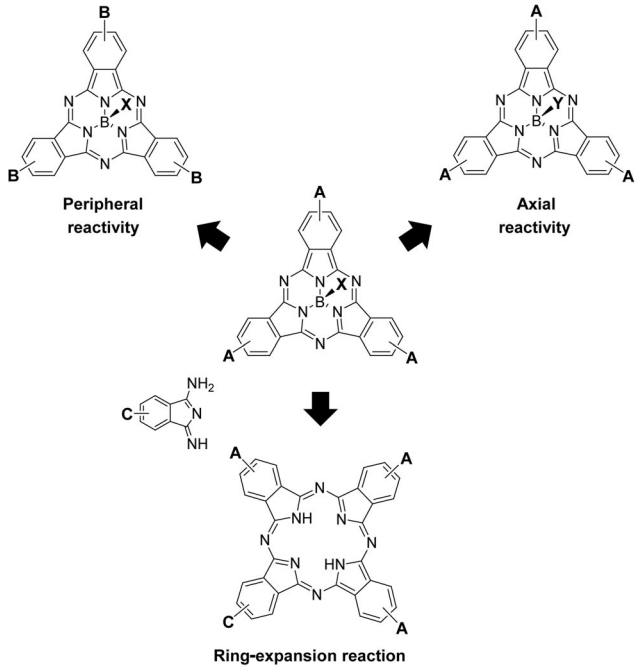

Figure 1. Different modes of subphthalocyanine reactivity.

Regarding their functionalization, SubPcs are versatile molecules whose reactivity can be divided in three different groups (Figure 1):[2] a) axial reactivity, b) peripheral reactivity and c) ring expansion reactions. The three of them differ in the reactive center: a) the axial B–X bond, b) the peripheral functional groups on the aromatic carbon atoms, or c) the imine-type core, respectively. Both axial and peripheral reactions produce modified SubPcs while ring expansion results in the loss of the SubPc constrained skeleton and the formation of low-symmetry Pcs.[12]

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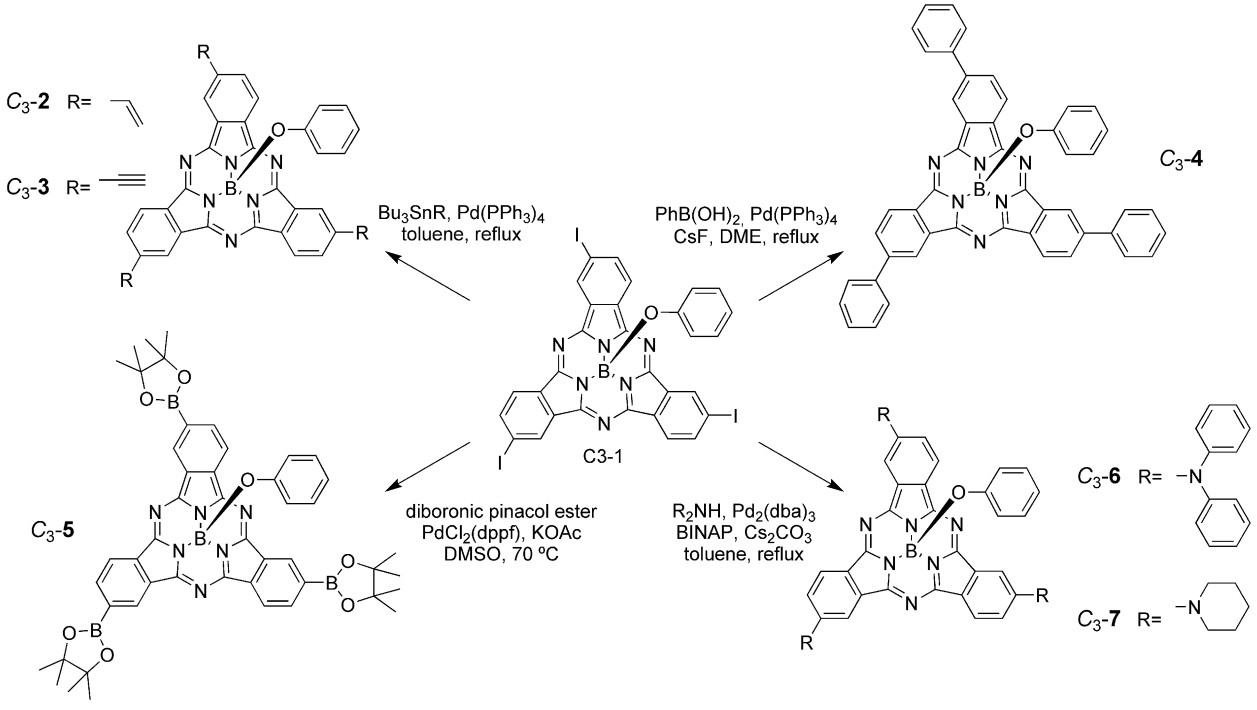
Despite the numerous examples in the literature concerning the axial functionalization of SubPcs,[13] the functionalization of the peripheral benzene rings have not been yet developed to the same scope.[14] Quite often, the main problem encountered in the functionalization of these singular molecules is their chemical instability, which usually leads to decomposition via ring-opening. Indeed, the constrained SubPc ring is frequently destroyed in the presence of nucleophiles at high temperatures or in acidic or basic media. In addition, the harsh conditions required for their synthesis limit to a great extent the kind of functional groups that can be introduced in the precursor phthalonitriles, the most typical being: halogen atoms, nitro groups, *tert*-butyl groups, thioethers, or sulphones. A good number of functional groups, like amines, ethers, sulfoxides,[15] carbonyl derivatives, or unsaturated bonds react rapidly with the boron reagents employed in SubPc synthesis so their use is most frequently restricted. The development of novel functionalization approaches of the SubPc core is therefore of utmost importance, since it will grant a wider functional versatility to these chromophores that could be exploited in several applied fields.

In this work, we describe some useful procedures for the incorporation of diverse functional groups in the periphery of the SubPc macrocycle. Different metal-catalyzed cross-coupling reactions were tested as a reasonable continuation of the work developed in our group on the coupling of iodoSubPcs with terminal alkynes.[14,5c] These include the well-known Stille or Suzuki couplings and palladium-catalyzed borylation or amination reactions. In many cases, the typical synthetic procedures for these transformations had to be modified so that SubPc decomposition was avoided. In addition, we report on the scope of the use of ether functionalities in the condensation reaction with BCl_3 and on the synthesis of a trihydroxySubPc, a very valuable compound that could be obtained by cleavage of the silyloxy-SubPc precursor.

Results and Discussion

The C_3-symmetrical regioisomer of a triiodoSubPc (C_3-**1**)[5b] was made to react using diverse cross-coupling methodologies (Scheme 1), such as Stille[16] or Suzuki[17] reactions and palladium-catalyzed borylation[18] or amination[19] procedures. Compound C_3-**1** was chosen as the common starting material in these reactions due to three main reasons: *i)* iodoarenes are usually the best-suited precursors in Pd-catalyzed cross-couplings, *ii)* the C_3-symmetry of the SubPc helped in the monitoring of the reaction and in the characterization of the products, and *iii)* the axial position is protected with a phenoxy group, since chloro-SubPcs were found to be less stable in most of the reaction conditions described hereafter and led quite often to decomposition products.

Tributylstannane derivatives were found to be appropriate sources for the introduction of synthetically valuable vinyl and ethynyl moieties via Stille cross-coupling reaction in the presence of (tetrakistriphenylphosphane)palladium(II) [$Pd(PPh_3)_4$].[20] The reactions were carried out using an excess of the stannane reagent in order to achieve total substitution on each of the three reactive positions. The 72% and 64% yields obtained for C_3-**2** and C_3-**3**, respectively, can be considered quite high, taking into account



Scheme 1. Palladium-catalyzed cross-coupling reactions carried out on triiodoSubPc C_3-**1**.

that three C–C bonds are being formed. The extension of the conjugation in the final products is clearly manifested in their absorption spectra. Concretely, the *Q*-band of the macrocycle experiences a red shift of 13 nm for C_3-**2** and 11 nm for C_3-**3** with respect to C_3-**1**.

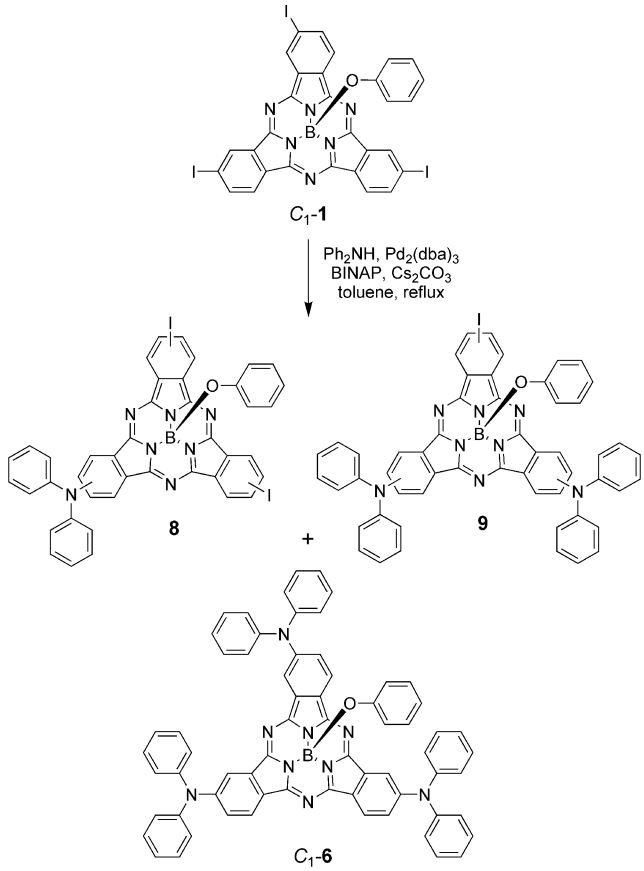
For the synthesis of triphenylSubPc C_3-**4**, the use of typical Suzuki reaction conditions, namely aqueous carbonate or hydroxide bases in organic solvents such as acetone or dimethoxyethane,[17] resulted in the immediate decomposition of the macrocycle. Nonetheless, we found that the weaker basicity and poorer nucleophilicity of fluoride ions[21] respected the structure of the macrocycle, while effecting a high-yielding phenyl-phenyl coupling (87%). In view of the high diversity of commercial aryl boronic acids/esters and their synthetic ease, this mild procedure may be very practical for the incorporation of a wide range of functionalities to the SubPc chromophore.

Due to our interest in the preparation of synthetic intermediates which may be employed for the direct carbon–carbon coupling of different active units, the synthesis of SubPc C_3-**5**, bearing pinacol boronate groups in the peripheral benzene rings, was as well projected. The most common method for the introduction of boronic acids/esters on aromatic rings involves the quenching of previously formed aryllithium or magnesium reagents with boronic esters.[17] SubPcs are destroyed immediately in these conditions and, for the synthesis of C_3-**5**, a milder procedure was considered, making use of a reported palladium-catalyzed reaction between diboronic esters and aryl iodides.[18a] We want to remark that compound C_3-**5**, together with SubPcs C_3-**2** and C_3-**3**, represent very interesting scaffolds for subsequent coupling of other units (via Suzuki, Heck or Sonogashira couplings, respectively) or as monomers in reactions leading to branched functional polymers.

Finally, since we are interested in modulating the electronic properties of SubPcs by way of their peripheral functionalization, a suitable method for the introduction of amine groups into the macrocycle was searched. Direct condensation reaction of amino-substituted phthalonitriles in the presence of BCl_3 does not lead, as expected, to any SubPc product, not even in the case of the poorly basic 4-diphenylaminophthalonitrile. During the last years, however, the development of catalytic procedures for carbon–nitrogen bond formation has been the subject of an intense research in organometallic chemistry, mainly represented by the work performed in the groups of Hartwig and Buchwald.[19] These kind of amination reactions are commonly carried out in the presence of palladium complexes with chelating (BINAP or DPPF, among others)[22] or sterically encumbered phosphanes (tri-*o*-tolyl, tri-*tert*-butyl, biarylphosphanes).[23] For the completion of the catalytic cycle, a base, usually sodium *tert*-butoxide, is required.[24] More recently, the use of copper complexes has represented an alternative to palladium catalysts in specific cases.[25]

In the first attempts at synthesizing SubPc **6**, we observed that the use of this kind of alkoxide bases in refluxing toluene produced the decomposition of the macrocycle. Several alternatives to this general method, compatible with base-sensitive functional groups have been reported.[26] These essentially comprise the addition of crown-ethers[26a] or certain electron-rich chelating phosphanes,[26c] which allow the reaction to take place at room temperature, and the use of milder bases, such as cesium carbonate.[26b] Indeed, it was found that carrying out the reaction in the presence of the Cs_2CO_3 base resulted in excellent yields of C_3-**6** (87%)[5b] and C_3-**7** (74%). However, this result was, specially for C_3-**7**, rather difficult to reproduce and in some instances the reaction proceeded very slowly, ultimately leading to the decomposition of the macrocycle. It was noted that the relative loading ratio of palladium with respect to the chelating phosphane and SubPc C_3-**1** was determinant for the successful formation of C_3-**6** and C_3-**7**, yielding the best results upon addition of 3% $Pd_2(dba)_3$ and 3% BINAP ligand per aryl iodide moiety.

Interestingly, the sequential introduction of the three amino groups into the SubPc aromatic ring gives rise to a spectacular change of the color of the reaction from intense pink (C_3-**1**) to blue and, finally, green (C_3-**6**). Intermediate compounds **8** and **9**, substituted with one or two diphenylamino groups, were isolated as a mixture of regioisomers in the reaction of the C_1 regioisomer **1** (C_1-**1**) and 2 equiv. (per SubPc) of the amine (Scheme 2).



Scheme 2. Products of the amination reaction of SubPc C_1-**1** with 2 equiv. of diphenylamine.

UV/Vis experiments showed that the introduction of each amino group into the macrocycle gave rise to a broadening and a red shift of the SubPc *Q*-band of about 15 nm, as well as to the manifestation of new features around 450 nm, which are probably due to n-π* transitions (Figure 2). These significant changes in the electronic absorption of these molecules produced a variety of different colors. Thus, SubPcs C_1-**1**, **8**, **9** and C_1-**6** are, respectively, pink, blue, green-blue and green solids. In diluted solutions, however, compounds **8** and **9** present dark red colors, similar to those of thioether-substituted SubPcs.

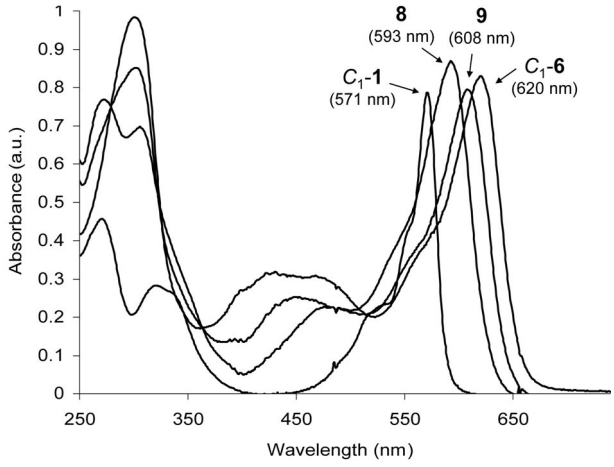
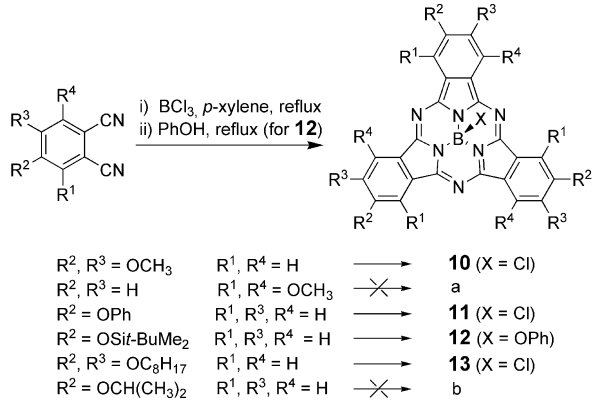


Figure 2. Electronic absorption spectra of $CHCl_3$ solutions of SubPcs C_1-**1**, **8**, **9** and C_1-**6**. The *Q*-band is red-shifted by ca. 15 nm for each diphenylamino group in the periphery of the SubPc macrocycle.

As stated in the introduction, the drastic conditions required for the synthesis of SubPcs prevents the incorporation of a good number of functional groups. Among these, ether groups, which have been widely employed in Pc chemistry, are one of the most important. So far, the high tendency of boron Lewis acids to cleave ether groups[27] precluded the synthesis of oxygen-substituted macrocycles from alkyloxyphthalonitriles.[28] The magnitude of this oxygen–carbon cleavage is closely related to the tendency of this carbon atom to stabilize an eventual positive charge [$(Alkyl)_3C > (Alkyl)_2HC > (Alkyl)H_2C > CH_3 > Ph$].[27a] In order to investigate the applicability of ether functionalized benzodinitriles in the BCl_3-templated formation of SubPcs we made to react different precursors (Scheme 3).

We found that methoxy-, phenoxy-[5b] and silyloxyphthalonitriles were robust enough to survive the cyclotrimerization reaction conditions and SubPcs **10**, **11**, **12** could be obtained in moderate to low yields (usually below 40%). However, the position of these substituents on the starting phthalonitrile was found to be determinant for cyclotrimerization. For instance, whereas SubPc **10** could be obtained in 21% yield from 4,5-dimethoxyphthalonitrile, its 3,6-substituted isomer did not lead to any SubPc product. On the other hand, the condensation of 4,5-dioctyloxyphthalonitrile did lead to a magenta-coloured material but TLC analysis of the reaction revealed the presence of a large number of different SubPc products, probably resulting from all the possible cleavages of the ether groups and their axially hydroxy-substituted analogues produced in the presence of the silica gel (see below). Only traces of the corresponding hexaoctyloxySubPc **13** (as identified by FAB-MS), being the less polar compound in this mixture, could be isolated.

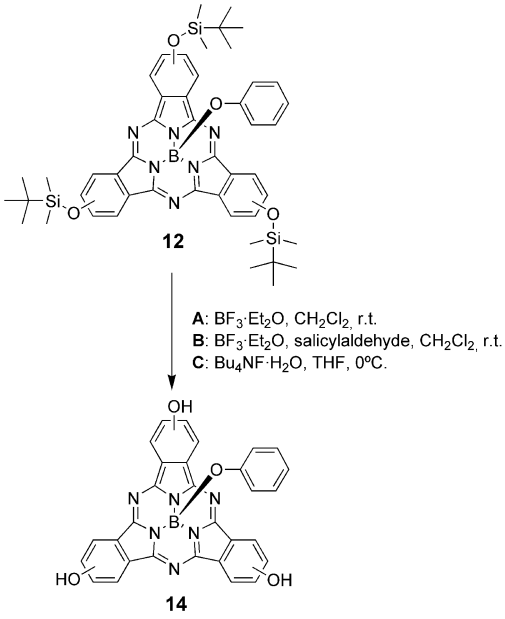


Scheme 3. Condensation reaction of different ether-substituted phthalonitriles, leading to SubPcs **10**, **13**, and **11**, **12** (as a statistical mixture of C_3 and C_1 regioisomers). a: The condensation reaction with 3,6-dimethoxyphthalonitrile did not lead to any SubPc material. b: Isopropyl ether groups were cleaved during the condensation reaction, resulting in traces of trihydroxySubPc.

However, we thought that the idea of employing the boron halide to perform the condensation reaction and, at the same time, to completely cleave the ether substituents could be an entry to trihydroxySubPcs. Therefore, 4-isopropoxyphthalonitrile was made to react with an excess of BCl_3 forming a product that was not soluble in CH_2Cl_2 but very soluble in methanol. This compound was identified by ^1H NMR and FAB-MS as the mixture of regioisomers of trihydroxysubphthalocyanine bearing a hydroxyl group in its axial position (due to axial substitution during chromatography on silica gel, see below). Nonetheless, the yield was very low (<1%) and the complete purification of this compound could not be achieved.

The sought trihydroxySubPc coud be finally obtained, however, via deprotection reaction of the silyloxy groups in compound **12**. Substitution of the original axial chlorine atom by a phenoxy group was again essential for the success of this synthetic route. On one hand, the purification of the chloroSubPc derivative formed in the condensation reaction of 4-(*tert*-butyldimethylsilyloxy)-phthalonitrile with BCl_3 by column chromatography resulted in poor yields, due to the fast substitution of the axial chlorine atom by an hydroxy group within the silica gel phase. On the other hand, the axial phenoxy ligand acted again as a protecting group during the subsequent cleavage of the silyl ether substituents, where the corresponding chloroSubPc decomposed rapidly. Therefore, the phenoxy ligand was introduced just after the cyclotrimerization reaction, without isolating the corresponding chloroSubPc intermediate, leading to compound **12**.

Several fluoride-mediated deprotection procedures[29] were applied to SubPc **12**, all of them leading to trihydroxy-SubPc **14** as a mixture of C_3 and C_1 regioisomers (Scheme 4).



Scheme 4. Synthesis of trihydroxySubPc **14** (micture of C_3 and C_1 regioisomers) by deprotection of SubPc **12** using three different methods (**A**, **B** and **C**).

The reaction between boron trifluoride etherate and **12** in CH_2Cl_2 (method A, Scheme 4) proceeded very slowly and only traces of deprotected material were detected after 2 d at room temperature. However, the addition of *o*-hydroxybenzaldehyde (method B) greatly accelerates the process[30] and SubPc **14** could be obtained in 26% yield after 12 h. In fact, it has been reported that the reaction between boron trifluoride and salicylaldehide derivatives rapidly generates a complex that releases hydrofluoric acid, the actual species that effects the O–Si bond cleavage.[31] The use of THF solutions of the typical tetrabutylammonium fluoride reagent (method C) resulted in the deprotection of the silylether groups in similar yields (30%) as method B, though the reaction rate was higher (3 h at 0 °C). It is important that the reaction temperature and time do not exceed these values or otherwise the decomposition of the SubPc macrocycle starts to compete.

Conclusions

In this work we have developed different methodologies to functionalize the peripheral positions of SubPcs that preserve the structure of the macrocycle. These and other synthetic approaches will certainly be very useful for the employment of these singular chromophores in applied fields.

Experimental Section

General Methods: Melting points (m.p.) were determined in a Büchi 504392-S apparatus and are uncorrected. UV/Vis spectra were recorded with a Hewlett–Packard 8453 instrument. IR spectra were recorded on a Bruker Vector 22 spectrophotometer. LSI-MS and HR-MS spectra were determined on a VG AutoSpec apparatus. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AC-300 instrument. Elemental analyses were performed with a Perkin–Elmer 2400 CHN equipment. Elemental analyses were not always possible to obtain reliably, so the identification of the compound was made by HR-MS analysis. Column chromatography was carried out on Merck silica gel 60 (230–400 mesh, 60 Å), and TLC on aluminum sheets precoated with Merck silica gel 60 F_{254}). Chemicals were purchased from commercial suppliers and used without further purification. 4-Isopropoxyphthalonitrile,[32] 4-phenoxyphthalonitrile,[33] 4,5-dimethoxyphthalonitrile,[34] 3,6-dimethoxyphthalonitrile,[35] and 4,5-dioctyloxyphthalonitrile[36] were prepared according to the reported procedures. The synthesis and characterization of the C_3 and C_1 regioisomers of SubPcs **1**[5b] and **6**,[5b] as well as SubPc **11**,[37] has been described in the literature.

4-(*tert*-Butyldimethylsilyloxy)phthalonitrile: A mixture of 4-hydroxyphthalonitrile (1.44 g, 10 mmol) and *tert*-butyldimethylsilyl chloride (1.66 g, 11 mmol) was dissolved in THF. To the stirred solution, triethylamine (5 mL) was slowly added at room temperature and the mixture was further stirred at that temperature for 16 h.[38] The solvent was then eliminated and the resulting yellowish oil was subjected to purification by flash column chromatography on silica gel using a 20:1 mixture of hexane/ethyl acetate as eluent. It is important to perform this last step as quickly as possible, since the Si–O bond in the product were found to cleave slowly on silica gel. 4-(*tert*-Butyldimethylsilyloxy)phthalonitrile was obtained as a white solid (2.12 g; 82%); m.p. 45–47 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.67 (d, J_o = 8.8 Hz, 1 H), 7.19 (d, J_m = 1.2 Hz, 1 H), 7.12 (dd, J_o = 8.8 Hz, J_m = 1.2 Hz, 1 H), 0.98 (s, 9 H), 0.27 (s, 6 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 159.7, 135.3, 125.0, 124.8, 117.5, 115.6, 106.7, 25.6, 25.4, 18.2 ppm. LSI-MS (*m*-NBA): *m*/*z* = 258 $[M]^+$ (15%), 201 $[M - C(CH_3)_3]^+$ (100%). HRLSI-MS ($C_{14}H_{18}N_2OSi$) $[M]^+$: calcd. 258.1188; found 258.1191. FT-IR (KBr): $\tilde{\nu}$ = 2989, 2934, 2888, 2850 (C–H), 2230 (C≡N), 1599, 1486, 1257, 1225 (C–O), 853, 796, 741, 689 cm^{-1}. Elemental analysis ($C_{14}H_{18}N_2OSi$): calcd. C 65.08, H 7.02, N 10.84; found C 64.27, H 7.65, N 10.34.

4-(Diphenylamino)phthalonitrile: To a stirred suspension of 4-nitrophthalonitrile (2.1 g, 12.1 mmol) and dry K_2CO_3 (2.5 g, 18.1 mmol) in dry dimethylacetamide (DMAC) (20 mL) was added diphenylamine (2.04 g, 12.1 mmol). The resulting mixture was stirred under argon at room temperature for 12 h. Subsequently, the mixture was poured onto 100 mL of cold water and the precipitate was collected by filtration and subjected to column chromatography on silica gel using a 1:2 mixture of CH_2Cl_2/hexane as the eluent. 4-(Diphenylamino)phthalonitrile was obtained as a light yellow solid (3.10 g; 86%). Alternatively, this product can also be prepared via a Pd-catalyzed amination reaction between 4-iodophthalonitrile and diphenylamine, following a similar procedure to the one described below for the amination of SubPcs; m.p. 136–138 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.47 (d, J_o = 8.2 Hz, 1 H), 7.45–7.35 (m, 5 H), 7.26 (t, $J_{o'}$ = 8.0 Hz, 2 H), 7.17 (d, J_o = 8.0 Hz, 4 H), 7.15 (m, 1 H), 7.09 (dd, J_o = 8.2 Hz, J_m = 1.8 Hz, 1 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 151.6, 144.4, 134.3, 130.3, 126.6, 126.5, 121.9, 121.1, 116.7, 116.3, 115.6, 104.1 ppm. LSI-MS (*m*-NBA): *m*/*z* = 295 $[M]^+$ (100%). HRLSI-MS ($C_{20}H_{13}N_3$) $[M]^+$: calcd. 295.1109; found 295.1111. FT-IR (KBr): $\tilde{\nu}$ = 3077, 2221 (C≡N), 1595, 1498 (C=C), 1326 (C–N), 1197, 1132, 817, 751, 716 cm^{-1}.

Trivinyl-Subphthalocyanine C_3-2: A mixture of triiodoSubPc C_3-**2** (43 mg, 0.05 mmol) and $Pd(PPh_3)_4$ (8.6 mg, 0.0075 mmol) was

placed in a 25-mL oven-dried round-bottomed flask. The flask was purged with argon and dry and deoxygenated toluene (2 mL) was added. Then, a solution of tributyl(vinyl)tin (0.25 mmol) in dry and deoxygenated toluene (1 mL) was added through a syringe. The mixture was then stirred to reflux for 6 h. The solvent was evaporated and the solid residue was thoroughly washed with cold hexane and subjected to column chromatography on silica gel in a 4:1 mixture of hexane/THF. Compound C_3-**2** was further purified washing with hexane and methanol, obtaining a dark purple solid (20 mg, 72% yield); m.p. > 250 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.74 (d, J_m = 1.8 Hz, 3 H), 8.63 (d, J_o = 8.0 Hz, 3 H), 7.87 (dd, J_o = 8.0 Hz, J_m = 1.8 Hz, 3 H), 6.91 (dd, ^3J_E = 17.4, ^3J_Z = 10.9 Hz, 3 H), 6.68 (dd, $J_o = J_{o'}$ = 7.6 Hz, 2 H), 6.53 (t, $J_{o'}$ = 7.6 Hz, 1 H), 5.98 (d, ^3J_E = 17.4, 3 H), 5.38 (d, ^3J_Z = 10.9, 3 H), 5.34 (d, J_o = 7.6 Hz, 2 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 152.5, 151.3, 151.1, 139.5, 136.5, 131.6, 130.0, 128.9, 127.8, 122.2, 121.5, 119.9, 119.1, 116.3 ppm. LSI-MS (*m*-NBA): *m*/*z* = 566 $[M]^+$ (15%). HRLSI-MS ($C_{36}H_{23}N_6OB$) $[M]^+$: calcd. 566.2026; found 566.2042. UV/Vis ($CHCl_3$): λ_{max} [log ε ($dm^3 mol^{-1} cm^{-1}$)] = 584 (4.6), 538 (sh), 336 (4.3), 267 (4.3) nm. FT-IR (KBr): $\tilde{\nu}$ = 3065, 3038, 1643 (C=C), 1599, 1540, 1466, 1407, 1355, 1235, 1126, 1039 (B–O), 860, 714 cm^{-1}.

Triethynyl-Subphthalocyanine C_3-3: A mixture of triiodoSubPc C_3-**3** (43 mg, 0.05 mmol) and $Pd(PPh_3)_4$ (8.6 mg, 0.0075 mmol) was placed in a 25-mL oven-dried round-bottomed flask. The flask was purged with argon and dry and deoxygenated toluene (2 mL) was added. Then, a solution of tributyl(ethynyl)tin (0.22 mmol) in dry and deoxygenated toluene (1 mL) was added through a syringe. The mixture was stirred to reflux for 6 h. The solvent was then evaporated and the solid residue was thoroughly washed with cold hexane and subjected to column chromatography on silica gel in a 4:1 mixture of hexane/THF. Compound C_3-**3** was further purified washing with hexane and methanol, obtaining a dark purple solid (18 mg, 64% yield); m.p. > 250 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.96 (d, J_m = 1.8 Hz, 3 H), 8.76 (d, J_o = 8.2 Hz, 3 H), 7.99 (dd, J_o = 8.2 Hz, J_m = 1.8 Hz, 3 H), 6.76 (dd, $J_o = J_{o'}$ = 7.6 Hz, 2 H), 6.64 (t, $J_{o'}$ = 7.6 Hz, 1 H), 5.37 (d, J_o = 7.6 Hz, 2 H), 3.35 (s, 3 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 152.0, 151.0, 150.8, 137.1, 132.1, 131.6, 129.1, 128.7, 123.2, 122.7, 121.3, 118.8, 89.1, 78.2 ppm. LSI-MS (*m*-NBA): *m*/*z* = 560 $[M]^+$ (10%). HRLSI-MS ($C_{36}H_{17}BN_6O$) $[M]^+$: calcd. 560.1557; found 560.1587. UV/Vis ($CHCl_3$): λ_{max} [log ε ($dm^3 mol^{-1} cm^{-1}$)] = 582 (4.5), 531 (sh), 341 (4.2), 277 (4.2) nm. FT-IR (KBr): $\tilde{\nu}$ = 3316, 3022 (C–H), 2132 (C≡C), 1613, 1443, 1359, 1232, 1126, 1042 (B–O), 863, 722, 677 cm^{-1}.

Triphenyl-Subphthalocyanine C_3-4: A magnetically stirred mixture of triiodoSubPc C_3-**1** (43 mg, 0.05 mmol), phenylboric acid (22 mg, 0.18 mmol), $Pd(PPh_3)_4$ (8.6 mg, 0.0075 mmol) and powdered CsF (68 mg, 0.45 mmol) in 4 mL of DME was heated to reflux for 5 h. After cooling to room temperature, CH_2Cl_2 (30 mL) was added and the resulting solution was washed twice with water (10 mL) and dried with Na_2SO_4. The drying agent was filtered and the solvent was removed, yielding a dark purple solid that was subjected to column chromatography on silica gel using a 4:1 mixture of hexane/ethyl acetate. Compound C_3-**4** was then washed with methanol, obtaining a dark purple solid (31 mg, 87% yield); m.p. > 250 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 9.07 (d, J_m = 1.6 Hz, 3 H), 8.87 (d, J_o = 8.2 Hz, 3 H), 7.13 (dd, J_o = 8.2 Hz, J_m = 1.6 Hz, 3 H), 7.77 (d, J_o = 7.6 Hz, 6 H), 7.43 (dd, $J_o = J_{o'}$ = 7.6 Hz, 6 H), 7.31 (t, $J_{o'}$ = 7.6 Hz, 3 H), 6.81 (dd, $J_o = J_{o'}$ = 7.6 Hz, 2 H), 6.66 (t, $J_{o'}$ = 7.6 Hz, 1 H), 5.50 (d, J_o = 7.6 Hz, 2 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 152.5, 151.6, 151.2, 143.1, 140.4, 131.7, 129.7, 129.0, 128.9, 128.0, 127.7, 122.5, 121.5, 120.6, 119.1 ppm. LSI-MS (*m*-NBA): *m*/*z* = 716 $[M]^+$ (30%). HRLSI-MS ($C_{48}H_{29}N_6OB$) $[M]^+$: calcd. 716.2496; found 716.2512. UV/Vis ($CHCl_3$): λ_{max} [log ε ($dm^3 mol^{-1} cm^{-1}$)] = 578 (4.5), 527 (sh), 332 (4.4), 288 (4.4) nm. FT-IR (KBr): $\tilde{\nu}$ = 3039, 3021 (C–H), 1593, 1469 (C=C), 1300, 1246, 1117, 1047 (B–O), 943, 863, 803, 752, 713, 684 cm^{-1}. Elemental analysis ($C_{24}H_{13}BN_6O$): calcd. C 69.93, H 3.18, N 20.39; found C 69.77, H 3.27, N 20.34.

Tripinacolborate-Subphthalocyanine C_3-5: A 10 mL flask, charged with the palladium catalyst $PdCl_2$(dppf) (2.7 mg, 0.0045 mmol), KOAc (44 mg, 0.45 mmol), diboronic pinacol ester (46 mg, 0.18 mmol) and subphthalocyanine C_3-**1** (43 mg, 0.05 mmol), was flushed with argon. Then, freshly distilled DMSO (3 mL) was added and the mixture was stirred at 70 °C for 16 h. The product was extracted with toluene (20 mL), washed with water (2 × 10 mL) and dried with anhydrous magnesium sulfate. After filtration and evaporation, the solid residue was dissolved in cold hexane and filtered. The solvent was then eliminated at low pressure, obtaining compound C_3-**5** as a pink viscous solid (27 mg, 62% yield); m.p. > 250 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 9.26 (d, J_m = 1.8 Hz, 3 H), 8.60 (d, J_o = 8.2 Hz, 3 H), 8.26 (dd, J_o = 8.2 Hz, J_m = 1.8 Hz, 3 H), 7.08 (dd, $J_o = J_{o'}$ = 7.6 Hz, 2 H), 6.80 (t, $J_{o'}$ = 7.6 Hz, 1 H), 5.19 (d, J_o = 7.6 Hz, 2 H), 1.18 (s, 36 H) ppm. LSI-MS (*m*-NBA): *m*/*z* = 866 $[M]^+$ (5%). HRLSI-MS ($C_{48}H_{50}B_4N_6O_7$) $[M]^+$: calcd. 866.4113; found 866.4100. UV/Vis ($CHCl_3$): λ_{max} [log ε ($dm^3 mol^{-1} cm^{-1}$)] = 575 (4.6), 523 (sh), 322 (4.2), 282 (4.2) nm. Elemental analysis ($C_{48}H_{50}B_4N_6O_7$): calcd. C 66.56, H 5.82, N 9.70; found C 66.22, H 5.73, N 9.85.

Tricyclohexamine-Subphthalocyanine C_3-7: An oven-dried 25 mL flask was charged with finely ground Cs_2CO_3 (147 mg, 0.45 mmol), $Pd_2(dba)_3$ (4 mg, 0.0045 mmol), BINAP (2.8 mg, 0.0045 mmol), freshly distilled piperidine (51 mg, 0.6 mmol) and SubPc C_3-**1** (43 mg, 0.05 mmol). The flask was then purged with argon and dry toluene (5 mL) was added through a syringe. The mixture was heated to reflux under argon atmosphere with continuous stirring for 8 h. The solution was cooled to room temperature, diluted with toluene (20 mL), filtered and concentrated to ca. 2–3 mL. The crude product was then purified by flash chromatography on silica gel using a 4:1 mixture of hexane/THF as eluent. SubPc C_3-**7** could be further purified washing with cold hexane and cold methanol, obtaining a deep green solid (27 mg, 74% yield); m.p. > 250 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.57 (d, J_o = 8.8 Hz, 3 H), 8.18 (d, J_m = 2.0 Hz, 3 H), 7.43 (dd, J_o = 8.8 Hz, J_m = 2.0 Hz, 3 H), 6.74 (dd, $J_o = J_{o'}$ = 7.6 Hz, 2 H), 6.59 (t, $J_{o'}$ = 7.6 Hz, 1 H), 5.43 (d, J_o = 7.6 Hz, 2 H), 3.49 (m, 12 H), 1.85–1.40 (m, 18 H) ppm. LSI-MS (*m*-NBA): *m*/*z* = 737 $[M]^+$ (10%), 644 [M – axial phenoxy group]$^+$ (20%). HRLSI-MS ($C_{45}H_{44}BN_9O$) $[M]^+$: calcd. 737.3762; found 737.3760. UV/Vis ($CHCl_3$): λ_{max} [log ε ($dm^3 mol^{-1} cm^{-1}$)] = 621 (4.4), 449 (4.0), 304 (4.2) nm. FT-IR (KBr): $\tilde{\nu}$ = 3035, 2967 (C–H), 1601, 1534, 1487, 1466, 1306 (C–N), 1243, 1221, 1107, 1066 (B–O), 903, 751, 697 cm^{-1}.

Procedure for the Synthesis of SubPcs 8 and 9: An oven-dried 25 mL flask was charged with finely ground Cs_2CO_3 (147 mg, 0.45 mmol), $Pd_2(dba)_3$ (4 mg, 0.0045 mmol), BINAP (2.8 mg, 0.0045 mmol), diphenylamine (39 mg, 0.1 mmol) and SubPc C_1-**1** (43 mg, 0.05 mmol). The flask was then purged with argon and dry toluene (5 mL) was added through a syringe. The mixture was heated to reflux under argon atmosphere with continuous stirring for 8 h in both cases. The solution was cooled to room temperature, diluted with toluene (20 mL), filtered and concentrated to ca. 2–3 mL. The crude product was then purified by flash chromatography on silica gel using a 4:1 mixture of hexane/THF as eluent. Subphthalocyanines **8**, **9** and C_1-**6**,[5b] eluting in that order, could be further purified

washing with cold hexane and cold methanol. 10 mg (24%) of precursor SubPc C_1-**1** was recovered from this reaction.

Subphthalocyanine 8 (Mixture of 3 Regioisomers): (9 mg, 20% yield); m.p. > 250 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 9.18–9.05 (m), 8.6–8.3 (m), 8.3–8.0 (m), 7.67–7.58 (m), 7.40–7.28 (m), 7.26–7.08 (m), 6.78–6.68 (m), 6.65–6.57 (m), 5.40–5.30 (m) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 153.3, 153.1, 152.9, 152.3, 152.1, 151.5, 151.0, 150.7, 150.2, 149.3, 149.2, 148.7, 147.0, 138.0, 137.7, 137.4, 133.6, 132.1, 131.5, 131.0, 130.9, 130.5, 128.8, 128.6, 128.3, 131.3, 131.2, 129.8, 128.9, 125.63, 125.58, 125.5, 124.3, 124.2, 123.5, 123.4, 123.32, 123.27, 123.2, 123.1, 121.7, 119.0, 114.1, 114.0, 113.9, 96.0, 95.6, 95.5, 95.3. LSI-MS (*m*-NBA): *m*/*z* = 907 $[M]^+$ (10%), 814 [M – axial phenoxy group]$^+$ (10%). HRLSI-MS ($C_{42}H_{24}BI_2N_7O$) $[M]^+$: calcd. 907.0225; found 907.0225. UV/Vis ($CHCl_3$): λ_{max} [log ε ($dm^3 mol^{-1} cm^{-1}$)] = 593 (4.6), 487 (4.0), 309 (4.4), 276 (4.5) nm. FT-IR (KBr): $\tilde{\nu}$ = 3045 (C–H), 1603, 1547, 1477, 1445, 1322 (C–N), 1269, 1183, 1065 (B–O), 826, 747, 703 cm^{-1}.

Subphthalocyanine 9 (Mixture of 3 Regioisomers): (13 mg, 27% yield); m.p. > 250 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 9.18–9.02 (m), 8.60–8.25 (m), 8.15–7.95 (m), 7.58–7.45 (m), 7.4–7.0 (m), 6.79–6.69 (m), 6.64–6.55 (m), 5.45–5.31 (m) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 153.6, 152.8, 152.7, 152.1, 152.0, 151.5, 151.2, 150.7, 150.5, 150.3, 150.2, 149.6, 149.4, 148.7, 147.22, 147.17, 147.1, 138.0, 137.7, 137.4, 133.6, 133.4, 132.1, 131.5, 131.2, 131.0, 130.94, 130.88, 130.5, 129.0, 128.4, 128.2, 129.73, 129.67, 128.9, 125.6, 125.5, 125.4, 125.3, 124.4, 124.3, 124.2, 123.4, 123.3, 123.1, 123.0, 122.9, 121.3, 118.9, 114.5, 114.4, 114.0, 113.9, 95.0, 94.7 ppm. LSI-MS (*m*-NBA): *m*/*z* = 949 $[M]^+$ (10%), 856 [M – axial phenoxy group]$^+$ (10%). HRLSI-MS ($C_{54}H_{34}BIN_8O$) $[M]^+$: calcd. 948.1993; found 948.2015. UV/Vis ($CHCl_3$): λ_{max} [log ε ($dm^3 mol^{-1} cm^{-1}$)] = 608 (4.5), 453 (4.0), 305 (4.5) nm. FT-IR (KBr): $\tilde{\nu}$ = 3061, 3022 (C–H), 1607, 1480, 1445, 1320 (C–N), 1277, 1183, 1059 (B–O), 825, 756, 699 cm^{-1}.

Hexamethoxy-Subphthalocyanine (10): In a 25-mL two-necked round-bottomed flask, equipped with a condenser, magnetic stirrer and rubber seal, BCl_3 (5 mL, 1 M solution in *p*-xylene) was added to 4,5-dimethoxyphthalonitrile (0.94 g, 5 mmol) under argon atmosphere. The reaction mixture was stirred under vigorous reflux for 10 min. The solvent was removed by vacuum distillation and the resulting red-brown solid was subjected to column chromatography on silica gel using a 3:1 mixture of hexane/ethyl acetate. SubPc **10** was further purified by precipitation from methanol/water (20:1), obtaining a red solid (0.21 g, 21% yield); m.p. > 250 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.24 (s, 6 H), 4.21 (s, 18 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 149.0, 144.2, 128.7, 115.3, 54.3 ppm. LSI-MS (*m*-NBA): *m*/*z* = 610 $[M]^+$ (5%), 575 [M – Cl]$^+$ (20%). HRLSI-MS ($C_{30}H_{24}BClN_6O_6$) $[M]^+$: calcd. 610.1539; found 610.1535. UV/Vis ($CHCl_3$): λ_{max} [log ε ($dm^3 mol^{-1} cm^{-1}$)] = 572 (4.4), 530 (sh), 406 (3.9), 286 (4.1) nm. FT-IR (KBr): $\tilde{\nu}$ = 2849 (C–H), 1515, 1306, 1257, 1171, 953 (B–Cl), 784, 696 cm^{-1}.

Tri(*tert*-butyldimethylsilyloxy)-Subphthalocyanine 12 (1:3 mixture of C_3 and C_1 regioisomers): In a 25-mL two-necked round-bottomed flask, equipped with a condenser, magnetic stirrer and rubber seal, BCl_3 (5 mL, 1 M solution in *p*-xylene) was added to 4-(*tert*-butyldimethylsilyloxy)phthalonitrile (1.29 g, 5 mmol) under argon atmosphere. The reaction mixture was stirred under vigorous reflux for 10 min. Phenol (470 mg, 5 mmol) was directly added to the reaction slurry in *p*-xylene and the mixture was stirred at 100 °C for 3 h. The solid obtained was washed with a 2:1 mixture of methanol/water and subjected to flash column chromatography on silica gel using a 5:1 mixture of hexane/ethyl acetate as eluent. Compound **12** was obtained as a reddish viscous solid (0.16 g, 11% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.70–8.62 (m), 8.25–8.15 (m), 7.42–7.33 (m), 6.76 (dd, J_o = $J_{o'}$ = 7.6 Hz), 6.60 (t, $J_{o'}$ = 7.6 Hz), 5.39 (d, J_o = 7.6 Hz), 1.07 (m), 0.35 (m) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 159.6, 151.4, 150.8, 150.6, 150.5, 150.4, 149.2, 148.9, 130.9, 130.6, 128.8, 125.2, 125.1, 123.3, 121.4, 119.4, 118.9, 112.7, 112.6, 29.7, 25.7, 18.5 ppm. LSI-MS (*m*-NBA): *m*/*z* = 878 $[M]^+$ (100%), 785 [M – axial phenoxy group]$^+$ (95%). HRLSI-MS ($C_{48}H_{29}BN_6O_4$) $[M]^+$: calcd. 878.3999; found 878.4015. UV/Vis ($CHCl_3$): λ_{max} [log ε ($dm^3 mol^{-1} cm^{-1}$)] = 573 (4.5), 526 (sh), 330 (4.1), 271 (4.3) nm. FT-IR (KBr): $\tilde{\nu}$ = 2936, 2884, 2850, 1525, 1471, 1430, 1318, 1266, 1055 (B–O), 817, 752, 710 cm^{-1}.

Trihydroxy-Subphthalocyanine 14 (1:3 Mixture of C_3 and C_1 Regioisomers)

Method A: This method is essentially the same as Method B, but without salicylaldehyde; it proceeded very slowly, and only traces of deprotected material were detected after 2 d at room temperature.

Method B: To a mixture of SubPc **12** (35 mg, 0.04 mmol), and salicylaldehyde (29 mg, 0.24 mmol) in CH_2Cl_2 (3 mL) was added, at room temperature, $BF_3{\cdot}Et_2O$ (0.1 mL, 1 mmol). The solution color immediately changed from intense pink to blue. The mixture was stirred for 24 h at room temperature and the solvent was evaporated. The solid residue was dissolved in ethyl acetate, the solution recovering its original pink color, and 0.1 M HCl was added (2 mL). The organic layer was washed with brine (10 mL) and dried with $MgSO_4$. Compound **14** was purified by column chromatography on silica gel using a 10:1 mixture of CH_2Cl_2/THF as eluent. Precipitation from a hexane/CH_2Cl_2 mixture yielded a pink solid (6 mg, 26% yield).

Method C: A solution of SubPc **12** (35 mg, 0.04 mmol) in 3 mL of THF was cooled down to 0 °C and tetrabutylammonium fluoride monohydrate (420 mg, 1.5 mmol), dissolved in 1 mL of cold THF was added. The solution color immediately changed from intense pink to blue. The mixture was stirred for 3 h at 0 °C and then ethyl acetate was added, the solution recovering its original pink color. Immediately after, a 0.1 M HCl solution was added (2 mL) and the organic layer was washed with brine (10 mL) and dried with $MgSO_4$. Compound **14** was then purified by column chromatography on silica gel using a 10:1 mixture of CH_2Cl_2/THF as eluent. Precipitation from a hexane/CH_2Cl_2 mixture yielded a pink solid (7 mg, 30% yield); m.p. > 250 °C. ^{1}H NMR (300 MHz, MeOD, 25 °C): δ = 8.73–8.67 (m), 8.21–8.15 (m), 7.50–7.40 (m), 6.82–6.70 (m), 6.65–6.55 (m), 5.43–5.37 (m) ppm. ^{13}C NMR (75.5 MHz, MeOD, 25 °C): δ = 160.6, 160.3, 152.0, 150.9, 150.8, 150.6, 149.8, 149.7, 133.2, 133.0, 128.7, 124.8, 122.2, 121.7, 121.6, 119.1, 119.0, 118.7, 107.9, 107.8, 107.7 ppm. LSI-MS (*m*-NBA): *m*/*z* = 536 $[M]^+$ (5%), 443 [(M-axial group)$^+$] (20%). HRLSI-MS ($C_{30}H_{17}BN_6O_4$) $[M]^+$: calcd. 536.1404; found 536.1386. UV/Vis ($CHCl_3$): λ_{max} [log ε ($dm^3 mol^{-1} cm^{-1}$)] = 575 (4.5), 527 (sh), 307 (4.1), 279 (4.3) nm. FT-IR (KBr): $\tilde{\nu}$ = 3378 (O–H), 3045 (C–H), 1595, 1490, 1432, 1377, 1238, 1206, 1105, 1039 (B–O), 983, 810, 756, 708 cm^{-1}.

Supporting Information (see also the footnote on the first page of this article): Figure S1, ^{1}H NMR spectra of all new compounds, including 4-(*tert*-butyldimethylsilyloxy)phthalonitrile, 4-diphenylamino-phthalonitrile, and SubPcs C_3-**2**, C_3-**3**, C_3-**4**, C_3-**5**, C_3-**7**, **8**, **9**, **10**, **12** and **14**, as well as complete assignment of ^{1}H and ^{13}C NMR signals.

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