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Synthesis, Characterization, and Properties of Subporphyrazines: A New Class of Nonplanar, Aromatic Macrocycles with Absorption in the Green Region

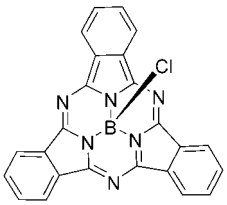
M. Salomé Rodríguez-Morgade,[a] Sagrario Esperanza,[a] Tomás Torres,*[a] and Joaquín Barberá[b]

Abstract: Novel subphthalocyanine analogues that display strong absorption in the green region have been synthesized by using a boron template cyclotrimerization of maleonitrile derivatives. The spectroscopic properties of these macrocycles indicate that, like subphthalocyanines, they have 14 π electrons and are aromatic compounds with a conical shape. The removal of the three fused benzene rings from the subphthalocyanine skeleton produces a 75–80 nm blue shift of the Q-band and a slight lowering of the absorption coefficients for this band. In addition, the reduction of the π system from 18 to 14 electrons that accompanies progression from porphyrazines to subporphyrazines causes a hypsochromic shift of the Q-band of around 100 nm. Subporphyrazines that are peripherally functionalized with six thioether chains, and in which the sulfur atoms are attached directly to the pyrrole moieties, exhibit optical features that may be explained in terms of the extension of π conjugation over the six thiolene groups, as well as strong π donation from the sulfur lone pairs to the macrocycle. These two effects are quantitatively and qualitatively very similar to those observed for porphyrazines that possess the same type of substitution. In addition, the mesomorphic behavior at low temperatures of a macrocycle that is substituted with six thiododecyl chains was demonstrated by using differential scanning calorimetry and optical polarising microscopy.

Keywords: absorption · macrocycles · subphthalocyanines · subporphyrazines · UV/Vis spectroscopy

Introduction

In 1972, the first subphthalocyanine (the lowest homologues of the various, structurally modified tetraazaporphyrins), was synthesized; namely chlorosubphthalocyanine[1] (**1**). However, detailed studies of the chemical structure, general synthesis, and physical features of the subphthalocyanines (SubPcs), were not reported until twenty years later.[2–4]



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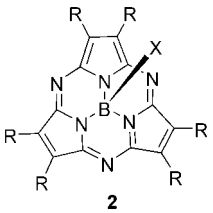

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These tribenzotriazaporphyrin analogues, bearing boron within their central cavity, are of great interest due to their specific structure and physicochemical characteristics. On the one hand, their 14 π-electron aromatic core confers optical properties related to those of phthalocyanines (Pcs), but with some notable differences. For example, the reduced π conjugation with respect to Pcs results in Soret and Q-bands at shorter wavelengths (300 and 560 nm, respectively).[4a] This quality makes SubPcs potentially useful as optical recording media.[5] On the other hand, the absorption coefficients of the Soret and Q-bands also decrease with respect to those of Pcs, and the smaller Q-band is attributed to the

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nonplanar, concave shape of the SubPcs.[6] The aromatic, conical shape of SubPcs accounts for other physical features, such as octupolar character, and hence, for extraordinary nonlinear optical properties.[4a] In addition, SubPcs are potentially useful as precursors of interesting three-dimensional architectures. For example, the subphthalocyanine fused dimer[7] exists as two topological *syn* and *anti* extended conjugated isomers. On the other hand, SubPcs have been employed as building blocks for the construction of molecular cages,[8] and have been proposed as subunits for potential nanometer-sized "heterofullerenoids".[4a]

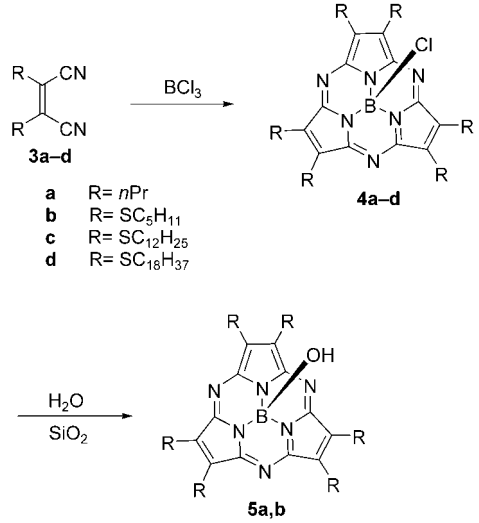
Contrary to what might be expected, the nonplanar structure of SubPcs has not prevented their organization in condensed phases. Indeed, spin-coated[9] and Langmuir–Blodgett films[10] based on these macrocycles have been prepared. Furthermore, chlorosubphthalocyanines containing thioether functions have displayed mesogenic behavior at room temperature, exhibiting head-to-tail, polar, columnar stacking, which forms a hexagonal array with random polarity.[11] Further studies on the mesogenic properties of SubPcs suggest that, unlike some porphyrazines,[12] their liquid crystalline behavior is strongly dependent on axial substitution, with the result that hydroxy and silyloxy axially substituted macrocycles are isotropes over a wide temperature range.[13]

The physical properties of SubPcs can also be modulated by introducing different substituents at the periphery of the macrocycle. Despite their laborious synthesis, the number of new SubPcs bearing a wide range of functional groups has been increasing in recent years.[4,14] For this study, we developed a different approach to peripherally modified SubPcs by replacing the isoindole moieties of these macrocycles by pyrrole rings, thus producing the corresponding subporphyrazine (subtriazaporphyrin) analogues (**2**). This strategy would provide a new family of tripyrrole macrocycles, in which some subphthalocyanine properties (e.g., conical shape and aromatic nature) could be preserved and others (e.g., absorption profiles, reactivity, or supramolecular organization) could be tailored. Furthermore, the efficient modulation of subporphyrazine properties through their peripheral substitution with selected specific functions is possible, because the substituents are attached directly at the β-positions of the pyrrole moieties. Consequently, a more efficient coupling between the peripheral groups and the aromatic azaporphyrinic core is expected.[15] We report the synthesis and characterization of subporphyrazines that possess alkyl and thioether chains at their periphery.[16] In addition, we have explored their liquid crystalline properties, since, in principle, their molecular shape defines a discotic mesomorphism, and long alkyl and thioalkyl chains usually give rise to porphyrazines exhibiting mesogenic properties.[12,17] In this respect, we studied the effect of the length of the peripheral thioether chains.

Abstract in Spanish: *Mediante ciclotrimerización asistida por boro de derivados de maleonitrilo, se han sintetizado nuevos análogos de subftalocianina que absorben en el verde. Las propiedades espectroscópicas de estos macrociclos indican que, al igual que las subftalocianinas, estos derivados poseen 14 electrones π y son compuestos aromáticos con forma cónica. La eliminación de los tres anillos de benceno fusionados del esqueleto de la subftalocianina produce un desplazamiento hacia el azul de 75–80 nm en la banda Q, además de una ligera reducción del coeficiente de absorción de dicha banda. Desde otro punto de vista, la reducción del sistema π de 18 a 14 electrones al pasar de una porfirazina a una subporfirazina, causa un desplazamiento hipsocrómico de aproximadamente 100 nm en la banda Q. Cuando se funcionalizan las subporfirazinas en su periferia con seis cadenas tioalquilo, los átomos de azufre están unidos directamente a los anillos de pirrol, y debido a esto, los macrociclos tienen propiedades ópticas especiales, que pueden justificarse considerando una extensión de la conjugación a través de los grupos tioleno, además de una fuerte donación π desde los pares solitarios de los átomos de azufre hacia el macrociclo. Estos dos efectos son muy similares, tanto cuantitativa como cualitativamente, a los observados en porfirazinas con el mismo tipo de sustitución. Adicionalmente, se ha puesto de manifiesto el comportamiento mesomórfico a baja temperatura del macrociclo sustituido con seis cadenas tiododecilo, mediante técnicas de DSC y microscopía óptica de luz polarizada.*

Results and Discussion

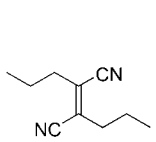
Synthesis of subporphyrazines: The backbone of SubPcs is usually assembled through a boron template cyclotrimerization of phthalonitrile derivatives.[4] Similarly, subporphyrazines (SubPzs) **4a–d** were prepared by treating dipropylmaleonitrile **3a**,[18] or the corresponding dithioalkyl-substituted maleonitrile **3b–d**,[12] with boron trichloride at 140 °C (Scheme 1).



Scheme 1. Synthesis of subporphyrazines.

The isolation of these chlorosubporphyrazines is complicated by their high solubility in most aromatic and aliphatic solvents and, especially, by their lability in silica gel when nonpolar eluents are used. Under the latter conditions, substitution of the chlorine atom by water occurs, resulting in the corresponding axially substituted hydroxysubporphyrazine. Thus, compounds **5a**,**b** were synthesized by treating the crude reactions obtained for **4a**,**b** with silica gel in a nonpolar solvent, such as hexanes. On the other hand, we had observed that compounds **4a–d** were not hydrolyzed during flash chromatography of the crude reactions on silica gel by using either an 8:1 mixture of hexane/ethyl acetate or more polar blends. However, to completely separate chlorosubporphyrazines from the corresponding succinimides[19] and other byproducts, and to obtain pure samples, it was necessary to repeat the flash column chromatography, this time using cyanopropyldichlorosilyl-modified silica gel as a solid support,[20] and hexane as the eluent. Compounds **4a**, **4b**, and **4d** were obtained at high purity and no substantial hydrolysis was observed during the process. For the isolation of compound **4c**, further gel permeation chromatography on BioBeads, with toluene as the eluent, was necessary. The yields for the macrocyclization step ranged from 8 to 22%. In addition, the hydroxy-substituted compounds **5a**,**b** were obtained in 8 and 5% yields, respectively, presumably due to partial decomposition of the SubPz substrates during hydrolysis.

To increase the overall yield for the synthesis of some of these compounds, cyclotrimetrization of fumaronitriles **6**[18] and **7**[21] was attempted under the same reaction conditions as those described above. By using this strategy, we intended



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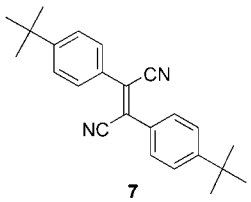

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to elucidate the photochemical isomerization step, which is necessary for the synthesis of dialkyl-substituted maleonitrile derivatives.[18] In addition, this alternative would provide a route for the synthesis of other SubPzs, such as aryl-substituted macrocycles, the maleonitrile precursors of which have not yet been reported. Disappointingly, no SubPz was detected by UV/Vis spectrophotometric analysis on the reaction crudes.

Characterization of subporphyrazines: The structures of subporphyrazines **4** and **5** were established from ^{1}H and ^{13}C NMR, UV/Vis, and IR spectroscopy, as well as mass spectrometry. For the chlorosubporphyrazines **4a–d**, MALDI-TOF MS revealed molecular ions as low intensity peaks at $m/z = 532$, 892, 1481, and 1986, respectively, together with more intense signals at $m/z = 497$, 857, 1446, and 1951, respectively, that may be assigned to a loss of the chlorine ion under the mass spectrometric conditions.

The ^{1}H NMR spectra (see Supporting Information) show the expected multiplets that correspond to the aliphatic moieties, with deshielded chemical shifts. This is particularly noticeable for the methylene groups located closer to the aromatic cores, due to the diamagnetic ring current of the macrocycles. Thus, SubPz **4a** reveals a multiplet centered at $\delta =$ 3.09 ppm, assignable to twelve CH_2 protons, which is shifted 0.74 ppm downfield with respect to the corresponding triplet exhibited by its maleonitrile precursor **3a**.[18] The ^{1}H NMR spectra of the thioalkyl-substituted series **4b–d** are identical, except for the integration of the multiplets centered at $\delta =$ 1.26 ppm, which are assigned to the fourth and further methylene groups of the aliphatic chains (see Supporting Information). Perhaps the most remarkable feature for this series is the presence of two groups of multiplets at $\delta =$ 3.70–3.93 and 3.99–4.16 ppm, each integrating for six protons that correspond to the first methylene moieties of the thioalkyl functions. Notably, maleonitriles **3b–d** display the corresponding methylene signal as a triplet at $\delta = 3.11$ ppm. The conversion of this triplet into several multiplets reveals a nonequivalence between the first methylenic protons of SubPzs **4b–d**, which can be attributed to the restricted rotation of the S–CH_2 bonds due to sterical constraints. Moreover, polarizable sulfur atoms from the thioether functions could effect charge transfer to the neighboring subporphyrazinic core, giving rise to an extended π system that involves the thiolene moieties. Similar π donation has been observed for porphyrazines substituted by electron-rich heteroatoms,[15,22] such as sulfur,[23] oxygen,[24] or nitrogen.[25] Under this assumption, free rotation of the large sulfur atoms, which possess two bulky lone pairs, would also be restricted to allow conjugation with the SubPz nucleus. The conical shape of the macrocycle, together with the anisotropy produced by the presence of an electronegative chlorine ion on the axial position, cause differences of around 0.2 ppm between some of the methylenic protons attached directly to the sulfur atom. The nonequivalence between the methylene moieties, and even between macrocyclic pyrrole rings, is also apparent from ^{13}C NMR spectroscopic analysis. This differs from the NMR spectra of thioalkyl-substituted subphthalocyanines, in which no such differences are found for the analogous signals, due to the separation of the thioalkyl moieties from the macrocycle's core by fused benzene rings.[11,13] The NMR spectra of hydroxysubporphyrazines **5a**,**b** revealed no differences with respect to the corresponding chlorinated compounds, except for the presence of broad, well-shielded signals at $\delta = -0.94$ for **5a** and -1.47 ppm for **5b**, which have been assigned to the axial hydroxy groups, confirming the aromaticity of these compounds.

Electronic absorption spectroscopy: It was anticipated that the formal removal of the three benzene rings from the subphthalocyanine skeleton would produce compounds with altered optical properties. The UV/Vis spectra of SubPzs **4**

and **5** confirm the proposed structures and also the structural considerations inferred from their ^{1}H NMR spectra. Thus, hexapropyl-substituted compounds **4a** and **5a** displayed very similar UV/Vis spectra, composed of two equally intense absorption bands at $\lambda = 295$ and 501 nm for **4a**, corresponding to the Soret and Q-transitions, respectively (Figure 1). Progression from a phthalocyanine to the similarly substituted subphthalocyanine reduces the π-conjugated system from 18 to 14 π electrons and induces changes in the UV/Vis spectra that are best exemplified by an approximately 100 nm hypsochromic shift of the Q-band.[4a] Taking into account that the Q-band of octaethylporphyrazinato magnesium(II) is seen at $\lambda = 597$ nm,[26] the corresponding absorption exhibited by **4a** and **5a** at $\lambda \sim 500$ nm fulfils the expected blue-shift magnitude.

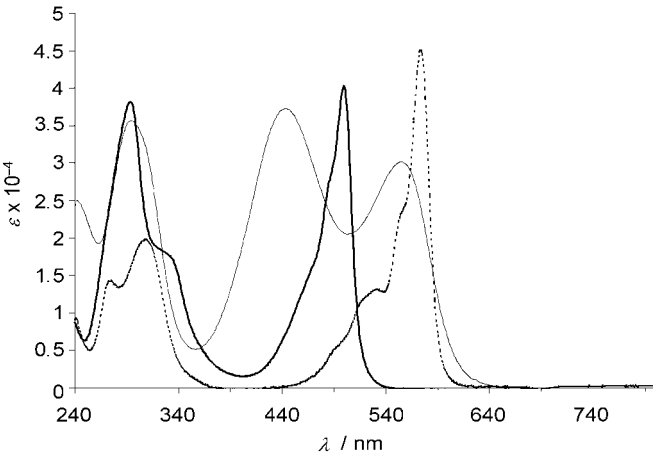

Figure 1. UV/Vis spectra of SubPc **1** (dashed line), SubPz **4a** (thick line), and SubPz **4d** (thin line) in chloroform.

The UV/Vis spectra of the thioalkyl-substituted series **4b–d** are qualitatively identical, exhibiting a Soret peak at $\lambda = 298$ nm in addition to two broad bands at 444 and 559 nm (Figure 1). The band at 444 nm is assigned to n→π* transitions from the peripheral sulfur lone-pair electrons into a π* macrocyclic orbital, and its high intensity is diagnostic of the strong π donation. Similar effects have been described for octakis(dimethylamino)porphyrazines.[25b] Moreover, the absorption at 559 nm is assigned to the Q-band of the SubPz, and corresponds to a blue-shift of 110 nm with respect to the comparable Q-band of the octakis(octylthio)porphyrazinato nickel(II).[26] Compound **5b** exhibits a very similar electronic pattern. The bathochromic shift of 59 nm exhibited by the Q-band of the hexakis(thioalkyl)subporphyrazines, with respect to the hexapropyl-substituted derivatives, may be rationalized in terms of the extended π conjugation over the six thiolene groups. Judging by the electronic spectra, this delocalization seems to be more important than for thioether-substituted subphthalocyanines. In the latter case, when compared to alkyl-substituted SubPcs, only half of this low-energy shift is observed for the same band. Notably, the Q-bands described for the two previously reported SubPzs appear at $\lambda = 411$ nm for the tricyanotri(*o*-trifluoromethylphenyl)subporphyrazine[16b,c] and 378 nm for hexakis(*tert*-butylphenyl)subporphyrazine.[16a] According to our results, we would expect these bands to appear at around 500 and 530 nm, respectively.[26]

Calorimetric analysis and optical textures: The phase behavior of SubPz **4** and **5** is summarized in Table 1. Solid crystalline subporphyrazines **4a**, **4d**, and **5a** show unequivocal phase transitions to isotropic liquids when observed by using microscopy. Moreover, heating and cooling curves for compounds **4a** and **4d** (see Supporting Information) are well resolved and unaffected by thermal treatment, with peak temperatures corresponding to melting endotherms of 168 and 38 °C, respectively, associated with enthalpy values of 37.3 and 109.0 kJ mol^{-1}, respectively. The differential scanning calorimetry (DSC) heating curve of macrocycle **5a**, however, shows discontinuous changes, indicative of solid polymorphism. Thus, the melting endotherm of a solution-crystallized sample is characteristic of a multiphase system, with a melting temperature of 141 °C and a total enthalpic change of 16.6 kJ mol^{-1}. No crystallization is observed upon cooling, but rather a glass transition, characterized by $T_g = 19$ °C, occurs. The second DSC heating scan for **5a** exhibits an enthalpic value of 13.7 kJ mol^{-1}, which corresponds to crystallization at 88 °C. Furthermore, melting takes place at 133 °C, with an associated enthalpy of 13.4 kJ mol^{-1}, apparently being the corresponding endotherm, which is a single one, although still quite wide. The crystallization of **5a** upon heating is also observed under polarized light as a birefringent texture that appears at 88 °C.

Table 1. Phase transition temperatures and enthalpies for SubPzs determined by using differential scanning calorimetry. All values correspond to the second thermal treatment, except for compound **5a**.

	T [°C] (ΔH [kJ mol^{-1}])	
SubPz	Heating	Cooling
4a	K 168(37.3) I	I 124(34.8) K
4b	–	–
4c	LC 6(8.4) I	I 10(4.9) LC
4d	K 38(109.0) I	I 34(111.7) K
5a	[a]K 141(16.6) I [b]G 19(0.1) I 88(13.7) K′ [b]K′ 133(13.4) I	I 34(3.0×10^{-2}) G
5b	–	–

[a] First heating. [b] Second heating. T = temperature onset; K, K′ = solid crystalline phase; I = isotropic phase; LC = liquid crystalline phase; G = glass phase.

Subporphyrazines bearing thiopentyl chains **4b** and **5b** are isotropic liquids at room temperature and demonstrate no transition phase upon heating or cooling. In contrast, SubPz **4c**, endowed with six peripheral thiododecyl chains, exhibits mesomorphic behavior under polarized light, characterized by a birefringent texture at 10 °C that is difficult to identify. Calorimetric analysis confirms that compound **4c** is

an isotropic liquid at room temperature, which exhibits a transition to a mesophase at 6 °C upon heating, involving an enthalpy change of 8.4 kJ mol^{-1}. This small molar enthalpy value appears within the typical range expected for the transition to a liquid crystalline phase. No further crystallization peaks for **4c** are detected upon cooling to −20 °C.

X-ray diffraction: X-ray diffraction patterns for SubPzs were registered at room temperature for both virgin and annealed samples. Annealing was performed by heating the compound for 1 min at a temperature at which it is a fluid liquid, followed by cooling of the sample to room temperature. The low-temperature value (6 °C) of the isotropic liquid→liquid crystal transition for **4c** prevented us from obtaining a clear X-ray diffraction pattern, with which the nature of the mesogenic phase detected by DSC and optical polarising microscopy could be determined. In all other cases, the X-ray patterns confirmed the phase transitions observed by optical and calorimetric techniques. Thus, compound **4a** exhibits identical sharp rings on both the virgin and annealed samples that are characteristic of its crystalline nature, and the same occurs for **4d**. In addition, SubPz **4d** exhibits, in the small-angle region, three Bragg equidistant reflections indicative of a lamellar crystalline phase with 29 Å of separation between layers, and a distance of 4.08 Å between macrocycles. Compound **5a** is clearly crystalline prior to thermal treatment, as indicated by its sharp rings. However, the X-ray pattern of an annealed sample lacks Bragg reflections, denoting the presence of an amorphous structure, which is in agreement with the glass phase observed by DSC analysis. Further heating at 90 °C provides evidence for its polymorphism; a crystalline pattern, which is different to that exhibited by the virgin sample, is obtained.

Conclusion

In this study we have synthesized and unequivocally characterized new SubPzs. As expected, the changes to the optical properties of these macrocycles, induced by the formal replacement of all isoindole rings in the SubPc framework by pyrrole moieties, are qualitatively comparable to those achieved on progression from phthalocyanines to porphyrazines. Consequently, SubPzs absorb at shorter wavelengths than SubPcs, and this characteristic makes them potentially applicable as optical recording media.[27] In addition, the SubPz cores of **4** and **5** were strongly coupled to their peripheral substitutents, which is of great interest for further applications of these types of systems to areas like, for example, nonlinear optics.

Chlorosubphthalocyanines bearing thioalkyl chains of 10–18 carbon atoms in length exhibit liquid crystalline behavior,[11] as do octakis(alkylthio)metalloporphyrazines possessing alkyl chains with 4–12 carbon atoms.[12,17] Conversely, the ability of SubPzs to form liquid crystalline phases is highly dependent on the number of atoms in the peripheral thioalkyl chains. Thus, we have observed mesogenic behavior for only the SC_{12}-hexasubstituted system (**4c**), but not for their lower SC_5 and higher SC_{18} homologues. This is not surprising, considering that the aromatic "disc" of SubPzs is markedly smaller than that of the subphthalocyanines and porphyrazines. Therefore, the range of peripheral aliphatic chains that can promote organization as liquid crystals should be more restricted for the former compounds.

Experimental Section

Materials: UV/Vis spectra were recorded by using a Hewlett–Packard 8453 instrument. IR spectra were recorded by using a Bruker Vector 22 spectrophotometer. FAB-MS (fast atom bombardment mass spectrometry) spectra were determined by using a VG AutoSpec instrument. MALDI-TOF MS and HRMS (high-resolution mass spectrometry) spectra were recorded by using a Bruker Reflex III spectrometer. NMR spectra were recorded by using a Bruker WM-200-SY and Bruker AC-300 instruments. Silica gel Merck-60 (230–400 mesh, 60 Å) was used for the preparation of the hydroxysubporphyrazines **5**. Column chromatography was performed by using silica gel Merck-60 (230–400 mesh, 60 Å) and cyanopropyldichlorosilyl-modified silica gel, which was prepared without endcapping, according to a reported procedure.[20] The loading of the cyano-bonded silica gel was determined by elemental analysis with a Perkin–Elmer 2400 apparatus, and was 6.94 % C. TLC was performed on aluminum sheets precoated with silica gel 60 F_{254} (E. Merck). Gel permeation chromatography was carried out by using Biobeads SX-3. Chemicals were purchased from Aldrich and used as received without further purification. Dicyano precursors **3a–d**,[12] **6**,[18] and **7**[21] were prepared according to reported procedures. Thermal behavior was investigated by using a Nikon polarizing microscope equipped with a Linkam THMS600 hot stage, and by DSC with a TA-Instruments DSC-2910 operated at a scanning rate of 10 °C min^{-1} in a nitrogen atmosphere. The apparatus was calibrated with indium (156.6 °C, 28.4 J g^{-1}). X-ray patterns were obtained by using a pinhole camera (Anton–Paar), operating with a point-focused Ni-filtered $Cu_{K\alpha}$ beam. The sample was held in Lindemann glass capillaries (1 mm in diameter) and heated when necessary, by means of a variable-temperature attachment. The patterns were collected on flat photographic film.

General procedure for the synthesis of chlorosubporphyrazines 4a–d A solution of BCl_3 in xylene (1 M, 1.0 mL = 1.0 mmol) was added under argon to the corresponding maleonitrile **3a–d** (1.0 mmol), and the mixture was stirred at 140 °C for 45 min. The solvent was evaporated under reduced pressure and the residues were treated as follows:

*Chloro[1,2,6,7,11,12-hexapropylsubporphyrazinate]boron(III) (**4a**)*: The crude was extracted with hexanes, the solution was removed by using a rotary evaporator, and the residue was subjected to chromatography on silica gel (eluent: hexanes/ethyl acetate, 8:1). Further chromatography on cyanopropyldichlorosilyl-modified silica gel (eluent: hexanes) afforded **4a** as an orange, crystalline solid (yield = 22 %). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.2–3.0 (m, 12H; pyrr-CH_2), 2.1–2.0 (m, 12H; pyrr-CH_2CH_2), 1.18 ppm (t, 18H; CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 155.8 (C^3, C^5, C^8, C^{10}, C^{13}, C^{15}), 136.7 (C^1, C^2, C^6, C^7, C^{11}, C^{12}), 26.9 ($C^{1'}$), 24.8 ($C^{2'}$), 14.6 ppm ($C^{3'}$); IR (KBr): $\tilde{\nu}$ = 2957, 2930, 2866 (C−H) 1742, 1718, 1684, 1649 (C=N), 1460, 1410, 1380, 1375, 1236, 1167, 1084, 933 (B−Cl), 781, 719, 692 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (log ε) = 295 (4.58), 335 (sh), 501 nm (4.60); MS (MALDI-TOF, 7,7,8,8-tetracyano-*p*-quinodimethane, (TCNQ)): *m/z*: 532 $[M]^+$, 514 $[M-Cl+OH]^+$, 497 $[M-Cl]^+$; HRMS (MALDI-TOF): calcd for $C_{30}H_{42}BClN_6$: 532.325; found: 532.327.

*Chloro[1,2,6,7,11,12-hexakis(pentylthio)subporphyrazinate]boron(III) (**4b**)*: The crude reaction was subjected to chromatography on silica gel (eluent: hexanes/ethyl acetate, 8:1). Further chromatography on cyanopropyldichlorosilyl-modified silica gel (eluent: hexanes) afforded **4b** as a dark red syrup (yield = 8 %). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.2–4.0, 4.0–3.7 (2 m, 12H; SCH_2), 2.0–1.9 (m, 12H; SCH_2CH_2), 1.7–1.4 (2 m,

24H; CH_2), 0.94 ppm (t, 18H; CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 154.3, 153.8, 153.6, 152.7, 152.2, 150.8, 149.4, 134.4, 134.1, 133.4, 132.4, 132.0 (C-macrocycle), 35.0, 34.7, 34.2 (SCH_2), 31.1, 30.9, 30.2, 30.0, 22.3 (CH_2), 14.0 ppm (CH_3); IR (NaCl): $\tilde{\nu}$ = 2924, 2856 (C–H) 1726, 1645, 1587 (C=N), 1477, 1450, 1423, 1383, 1356, 1302, 1275, 1169, 1128, 999, 862, 727, 673 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} ($\log\varepsilon$) = 299 (4.38), 444 (4.40), 559 nm (4.32); MS (MALDI-TOF, TCNQ): *m/z*: 892–895 $[M]^+$, $[M+H]^+$, 857–860 $[M-Cl]^+$, $[M-Cl+2H+H]^+$; HRMS (MALDI-TOF): calcd for $C_{42}H_{66}BClN_6S_6$: 892.345; found: 892.343.

*Chloro[1,2,6,7,11,12-hexakis(dodecylthio)subporphyrazinate]boron(*III*)* (***4c***): The crude reaction was subjected to chromatography on silica gel (eluent: hexanes/ethyl acetate, 8:1), and then on cyanopropyldichlorosilyl-modified silica gel (eluent: hexanes). Finally, gel permeation chromatography on Biobeads SX-3 (eluent: toluene) yielded **4c** as a dark red syrup (yield = 8%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.2–4.0, 4.0–3.7 (2 m, 12H; SCH_2), 2.0–1.9 (m, 12H; SCH_2CH_2), 1.7–1.5 (m, 12H; CH_2), 1.26 (brs, 96H; CH_2), 0.88 ppm (t, 18H; CH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 154.4, 153.8, 153.6, 152.7, 150.8, 149.4, 134.4, 134.1, 133.3, 132.3, 132.0 (C-macrocycle), 35.1, 34.8, 34.3 (SCH_2), 31.9, 30.5, 30.4, 29.7, 29.4, 29.3, 29.0, 28.8, 22.7 (CH_2), 14.1 ppm (CH_3); IR (NaCl): $\tilde{\nu}$ = 2924, 2856 (C–H) 1726, 1657, 1587 (C=N), 1466, 1398, 1358, 1290, 1265, 1124, 1003, 854, 729, 675 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} ($\log\varepsilon$) = 297 (4.18), 442 (4.18), 559 nm (4.12); MS (MALDI-TOF, TCNQ): *m/z*: 1481–1486 $[M]^+$, $[M+2H+H]^+$, 1446–1449 $[M-Cl]^+$, $[M-Cl+2H+H]^+$; HRMS (MALDI-TOF): calcd for $C_{84}H_{150}BClN_6S_6$: 1481.002; found: 1481.002.

*Chloro[1,2,6,7,11,12-hexakis(octadecylthio)subporphyrazinate]boron(*III*)* (***4d***): The crude reaction was subjected to chromatography on silica gel (eluent: hexanes/ethyl acetate, 8:1), and then on cyanopropyldichlorosilyl-modified silica gel (eluent: hexanes), affording **4d** as a dark red, crystalline solid (yield = 8%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.1–4.0, 4.0–3.7 (2 m, 12H; SCH_2), 2.0–1.9 (m, 12H; SCH_2CH_2), 1.6–1.5 (m, 12H; CH_2), 1.26 (brs, 168H; CH_2), 0.88 ppm (t, 18H; CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 154.4, 153.8, 153.6, 152.7, 152.2, 150.8, 149.4, 134.4, 134.1, 133.3, 132.3, 132.0 (C-macrocycle), 35.1, 34.8, 34.3 (SCH_2), 31.9, 30.5, 30.4, 29.7, 29.4, 29.3, 29.2, 29.0, 28.9, 22.7 (CH_2), 14.1 ppm (CH_3); IR (NaCl): $\tilde{\nu}$ = 2916, 2849 (C–H) 1722, 1630 (C=N), 1466, 1360, 1288, 1173, 1115, 999, 860, 721, 675 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} ($\log\varepsilon$) = 298 (4.55), 446 (4.57), 558 nm (4.48); MS (MALDI-TOF, TCNQ): *m/z*: 1986–1991 $[M]^+$, $[M+2H+H]^+$, 1951–1454 $[M-Cl]^+$, $[M-Cl+2H+H]^+$; HRMS (MALDI-TOF): calcd for $C_{120}H_{222}BClN_6S_6$: 1985.566; found: 1985.568.

General procedure for the synthesis of hydroxysubporphyrazines 5a,b A solution of BCl_3 in xylene (1 M, 1.0 mL = 1.0 mmol) was added under argon to the corresponding maleonitrile **3a**,**b** (1.0 mmol), and the mixture was stirred at 140 °C for 45 min. The solvent was evaporated under reduced pressure and the residues were extracted with hexanes. Silica gel (50 g) was added to the resulting solution in hexanes, and the suspension was stirred at room temperature for 15 min. After filtration the silica gel was washed with ethyl acetate and the combined extracts were obtained by using a rotary evaporator. The residue was subjected by chromatography on silica gel (eluent: hexanes-hexanes/ethyl acetate, 8:1 gradient), affording the corresponding hydroxysubporphyrazine.

*Hydroxy[1,2,6,7,11,12-hexapropylsubporphyrazinate]boron(*III*)* (***5a***): Compound **5a** was obtained as an orange crystalline solid (yield = 8%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.1–2.9 (m, 12H; pyrr-CH_2), 2.0–1.9 (m, 12H; pyrr-CH_2CH_2), 1.16 (t, 18H; CH_3), −0.94 ppm (brs, 1H; O*H*); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 157.0 (C^3, C^5, C^8, C^{10}, C^{13}, C^{15}), 135.5 (C^1, C^2, C^6, C^7, C^{11}, C^{12}), 26.7 ($C^{1'}$), 24.9 ($C^{2'}$), 14.6 ($C^{3'}$); IR (KBr): $\tilde{\nu}$ = 3584–3271 (br, O–H), 2955, 2928, 2874 (C–H) 1713, 1655 (C=N), 1479, 1452, 1412, 1387, 1244, 1194, 1167, 1115, 1088, 1047, 777, 731 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} ($\log\varepsilon$) = 289 (4.45), 327 (sh), 500 nm (4.38); MS (FAB, NBA): *m/z*: 515 $[M+H]^+$, 514 $[M]^+$, 497 $[M-OH]^+$; HRMS (MALDI-TOF): calcd for $C_{30}H_{43}BN_6O$: 514.358; found: 514.359.

*Hydroxy[1,2,6,7,11,12-hexakis(pentylthio)subporphyrazinate]boron(*III*)* (***5b***): Compound **5b** was obtained as a dark red syrup (yield = 5%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.1–3.9, 3.8–3.6 (2 m, 12H; SCH_2), 2.0–1.9 (m, 12H; SCH_2CH_2), 1.6–1.3 (2 m, 24H; CH_2), 0.93 (t, 18H; CH_3), −1.47 ppm (brs, 1H; O*H*); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 155.8, 155.2, 155.1, 154.2, 153.7, 150.7, 132.6, 132.4, 131.5, 131.4, 130.7 (C-macrocycle), 35.0, 34.8, 34.3 (SCH_2), 31.1, 30.1, 22.3 (CH_2), 14.0 ppm (CH_3); IR (NaCl): $\tilde{\nu}$ = 3665–3074 (br, O–H), 2953, 2926, 2858 (C–H) 1717, 1666, 1585 (C=N), 1452, 1344, 1263, 1177, 1109, 1041, 795, 733 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} ($\log\varepsilon$) = 288 (4.27), 430 (4.09), 550 nm (4.03); MS (MALDI-TOF, dithranol): *m/z*: 874–878 $[M]^+$, $[M+2H+H]^+$, 857–859 $[M-OH]^+$, $[M-OH+2H]^+$; HRMS (MALDI-TOF): calcd for $C_{42}H_{67}BN_6OS_6$-OH: 857.376; found: 857.376.

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