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ARTICLE *in* CHEMISTRY · FEBRUARY 2008

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Synthesis, Characterization, Molecular Structure and Theoretical Studies of Axially Fluoro-Substituted Subazaporphyrins

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Abstract: A new and general synthetic method for the preparation of fluoro-substituted subazaporphyrins is reported that involves the treatment of the corresponding chloro- or aryloxy-substituted subazaporphyrins (SubAPs) with $BF_3{\cdot}OEt_2$. The strategy has been applied to both subphthalocyanines (SubPcs) and subporphyrazines (SubPzs). The yields were high for the latter, although low yields were obtained for the benzo derivatives. In contrast to the corresponding chloro derivatives, fluorosubazaporphyrins are quite robust towards hydrolysis. All of the new compounds were characterized by several spectroscopic techniques, which included ^{1}H, ^{13}C, ^{19}F, ^{15}N, and ^{11}B NMR spectroscopy, IR spectroscopy, UV/Vis spectrophotometry, and mass spectrometry (both high and low resolution). In addition, DFT calculations provided theoretical NMR spectroscopy values that are in good agreement with the experimental ones. The high dipole moments exhibited by the fluorosubazaporphyrins as a result of the presence of a fluorine atom in an axial position are responsible for the spontaneous and singular supramolecular aggregation of the macrocycles in the crystalline state. The molecular and crystal structures of two one-dimensional fluorine SubAPs, namely, a SubPc and a SubPz, are discussed. Molecules of the same class stack in alternating configurations along the *c* axis, which gives rise to columns that contain large numbers of monomers. SubPz **3c** forms aggregates with the macrocycles arranged in a parallel fashion with the B–F bonds perfectly aligned within a column, whereas with SubPc **3b** the neighboring columns cause a commensurate sinusoidal distortion along the columns in the *c* direction, which prevents the alignment of the B–F bonds. However, the most remarkable feature, common to both crystalline architectures, is the extremely short and unusual intermolecular F···N distances of the contiguous molecules, which are shorter than the sum of the corresponding van der Waals radii. Theoretical calculations have shown that these short distances can be explained by the existence of a cooperativity effect as the number of monomers included in the cluster increases.

Keywords: crystal structures · density functional calculations · fluorine · phthalocyanines · porphyrinoids

Introduction

Aromatic or π-conjugated curved compounds have been the object of many theoretical and experimental studies in recent years as a consequence of their intriguing chemical and physical properties.[1,2] Among them, subazaporphyrins[3–7] (SubAPs) are heteroaromatic chromophores that constitute the lower homologues of tetraazaporphyrins (phtha-

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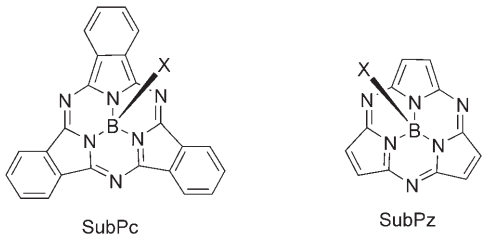
Supporting information for this article is available on the WWW under http://www.chemeurj.org/or from the author. It contains characterization data for new compounds **1**–**3** (^{1}H, ^{13}C, ^{11}B and ^{19}F NMR, IR, MS and UV/Vis spectra, and ^{15}N NMR spectra for compounds **1c** and **2c**). X-ray crystallographic data (CIF file) and tables for **3b** and **3c.** Calculated chemical shifts for the subazaporphyrins.

locyanines (Pcs) and porphyrazines (Pzs)) because they consist of three instead of four *N*-fused 1,3-diiminoisoindole or 2,5-diiminopyrrole units, respectively (Scheme 1). Although



Scheme 1. Subazaporphyrins (SubAPs): Structures of a subphthalocyanine (SubPc) and a subporphyrazine (SubPz).

these kinds of macrocycles have been known since the seventies, the major developments in this field have only taken place since the nineties, and only very recently have the corresponding subporphyrinic systems been reported.[8] SubAPs display a 14π-electron aromatic core arranged in a bowl-shaped structure that turns out to be fascinating both theoretically and practically. In addition, substitution at the periphery of the macrocycles allows their physical and/or chemical properties to be fine-tuned. Hence, a wide range of functional groups have recently been introduced with the aim of constructing SubAP-based π-extended oligomers,[9] metallosupramolecular cages,[10] nonlinear optical chromophores,[11–13] liquid crystals,[14] and multicomponent assemblies for use, for example, in electron- and energy-transfer processes.[15]

With respect to axial substitution (X in Scheme 1), the nature of the functional groups bound to the boron atom also has a substantial influence on the properties of the macrocycle.[3a] Thus, for example, SubPcs endowed with six peripheral thioalkyl chains display mesomorphic behavior at room temperature, exhibiting head-to-tail polar columnar stacking that forms a hexagonal array with random polarity.[14] However, although this liquid crystalline behavior is observed when the axial substituent is a chlorine atom,[6,14] hydroxy- and silyloxy-axially substituted macrocycles are isotropic over a wide range of temperatures.[16] In principle, most SubAPs are synthesized as the chloro derivatives because these compounds exhibit a perfect balance between synthetic accessibility and ease of purification.[3a,17] To obtain a specific macrocycle, a phthalonitrile or a maleonitrile precursor is cyclotrimerized in the presence of boron trichloride in a high-boiling point solvent, such as *p*-xylene. Subsequently, the halogen atom can be easily replaced by reaction with nucleophiles, particularly aromatic alcohols,[3a,17] to increase the solubility of the compound, to modulate its physicochemical properties, or even to introduce new functions for specific applications.[18]

The preparation of fluorosubphthalocyanine by the reaction of phthalonitrile with $PhBF_2$[19] or $Et_2O{\cdot}BF_3$[20] has also been described. However, yields have either not been reported[20] or are very low[19] for either method and the application of these procedures to the cyclotrimerization of other dinitriles failed to afford other peripherally substituted SubAP derivatives.[21] However, there are several reasons to be interested in the preparation of fluorosubazaporphyrins. On one hand, the B–F bond is more robust than the B–Cl or B–Br bonds, and consequently, SubAPs that contain a fluorine atom at the axial position should be more stable towards hydrolysis. This is especially important for the efficient isolation and purification of SubAPs peripherally functionalized with donor functions such as alkyl or thioether groups.[6,16] On the other hand, control over the organization of molecular building blocks into desired functional structures is essential for the construction of molecule-based miniature devices with advanced functions. As mentioned above, the supramolecular organization of macrocycles in the solid state,[3a,9a,18a] in thin films,[13] and in liquid crystals[6,14,16] depends, to a certain extent, on the nature and size of the axial substituents.[9,16,22] In this respect, the smaller size and the specific electronic characteristics of the fluorine atom should significantly influence the interactions between macrocycles and affect their organization in condensed phases. In addition, structures with defined geometry may form spontaneously through supramolecular aggregation if selective and directional noncovalent interactions are exploited. In this context, fluorine substituents are supposed to play a role in stabilizing aromatic stacks.[23]

The nature of the axial substituent produces differences in the SubAP molecular polarity that should have a significant influence on the cooperative effects between molecules, and consequently, on the crystalline architecture. It was expected that high dipole moments in these compounds[24] would contribute to the development of a strong one-dimensional (1D) molecular association, which could be useful in the assembly of molecular wires and cables.[25] In contrast, interactions between molecules with low dipole moments give rise to crystals without specific directions. This is an attractive challenge because it is known that properties such as electrical conductivity are related to strong one-dimensional molecular interactions that are dramatically different in different directions in crystals. Thus, for example, coordination complexes with planar macrocyclic π-conjugated ligands, like phthalocyanine, crystallize in one-dimensional columns that show high electrical conductivity when they are partially oxidized.[26]

In addition, some organized columnar structures have been shown to have applications in photovoltaics.[27] In this regard, it is known that the performance of solar cells depends critically on the self-organizing properties of both donor and acceptor components.[28] SubAPs that may have either donor or acceptor characteristics depending on the nature of their substituents[18a,b] are very promising candidates to be used as components in solar cells.[29] Therefore, and because of our interest in this field,[11c] we have investigated the organization of SubAPs in the solid state.

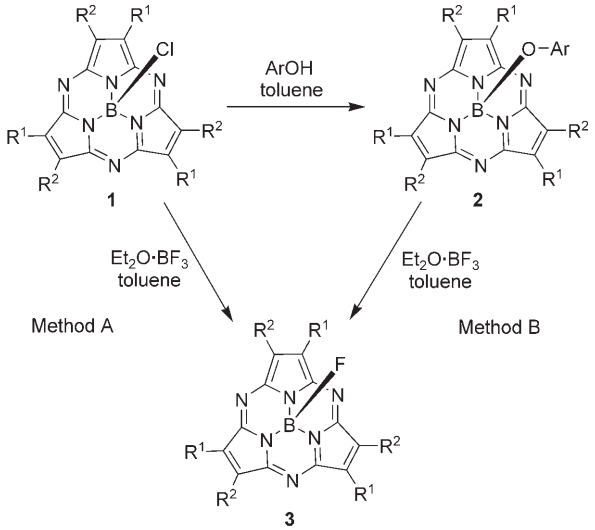
Herein, we wish to report a straightforward and general route to SubAPs that contain fluorine in the axial position. The molecular and crystal structures of two one-dimensional

fluorine SubAPs are also described as well as the spectroscopic characterization of all of the compounds and DFT calculations on the monomers, dimers, trimers, and tetramers.

Results and Discussion

Synthesis and spectroscopic characterization: Our approach to the synthesis of fluorosubazaporphyrin derivatives takes advantage of the easy access to chlorosubazaporphyrins. Thus, the method reported herein relies on the effective cyclotrimerization of dinitriles assisted by BCl_3[6,17] for the assembly of the SubAP backbone. Subsequently, we established that treatment of these chloro derivatives with a large excess of $Et_2O{\cdot}BF_3$ affords the corresponding macrocycles axially functionalized with fluorine (Scheme 2, Method A). This method is applicable to both types of macrocycles although the conversion takes place in low yields for benzo derivatives **3a** and **3b** (see Table 1).

Subporphyrazine **1c** turned out to be more reactive and the corresponding fluoro derivative **3c** was easily obtained (see Table 1). This result could be predicted taking into account the higher reactivity of the axial position in the tripyrrolic series compared with the corresponding benzo derivatives.[6,3b] Moreover, the resulting SubAPs (**3a–c**) were easily isolated by chromatography on silica gel and no hydrolysis was observed either during the reaction or in the purification process even when the macrocycles had peripheral donor substituents, for example, **3c**.[6]



Scheme 2. Synthesis of fluorosubazaporphyrins **3a–c**.

Table 1. Reaction times and yields for the synthesis of SubAPs **3a–c**.

Compound	Method	Reaction time [h]	Yield [%]
3a	A	3	17
3a	B	3	14
3b	A	1.25	15
3b	B	3	12
3c	A	0.25	68
3c	B	1	63

In an alternative procedure, fluorosubazaporphyrins **3a–c** were prepared by treating the corresponding aryloxy-substituted macrocycles **2a–c**[30,31] with excess $Et_2O{\cdot}BF_3$ in toluene (Scheme 2, Method B). This method is particularly useful for the synthesis of macrocycles with donor substituents at the periphery because in these cases isolation of the chloro derivatives has proven to be very tedious on account of the lability of the axial position.[6,12b,13,15,17] Therefore, the crude material (**1a–c**) formed from the cyclotrimerization reaction between the starting dinitrile and BCl_3[6,17] was treated in situ with a phenol derivative to give the corresponding less-labile aryloxy-functionalized macrocycles **2a–c**,[30,31] which were isolated by column chromatography on silica gel. Further treatment of these compounds with $Et_2O{\cdot}BF_3$ afforded macrocycles **3a–c** in yields comparable to those of Method A (see Table 1).

As expected, fluoro derivatives **3a–c** proved to be much more robust towards hydrolysis than their corresponding chloro-substituted analogues (**1a–c**) and this was evident when following the reaction by TLC because no spot corresponding to the related hydroxysubazaporphyrin was detected once the reaction was complete.[32] The greater strength of the B–F bond compared with the B–Cl and even the B–OH bond was also evidenced by mass spectrometry; the mass spectra of all of the fluorosubazaporphyrins prepared in this work exhibited the molecular ion $[M]^+$ as the unique peak or was accompanied by negligible signals assignable to $[M-F]^+$. This differs from the data recorded for compounds **1a–c** and **2a–c**; in these cases peaks associated with the loss of the axial substituents were the most intense peaks observed in the spectra.[6,30,31] The new compounds were also characterized by ^1H, ^{13}C, ^{19}F, ^{15}N, and ^{11}B NMR spectroscopy, IR spectroscopy, UV/Vis spectrophotometry, and HRMS. In addition, crystal structures for fluorosubazaporphyrins **3b** and **3c**, ^{15}N NMR spectra for macrocycles **1c** and **2c**, and ^{19}F and ^{11}B NMR spectra for the **1** and **2** series are provided for comparative purposes.

Compounds **3a–c** are indistinguishable by ^1H NMR spectroscopy from the corresponding chloro derivatives **1a–c** (see Table 2 and the Supporting Information). Moreover, the aryloxy substituents of **2a–c** appear to be shifted to higher fields as a consequence of the diatropicity of the macrocycles. These signals prove the structures of these compounds. The ^{11}B NMR spectra exhibit typical upfield signals for tetragonal boron derivatives at $\delta = -13.8$ to -15.8 ppm, which are coupled to the fluorine nuclei in compounds **3a–c** with coupling constants in the order of 30 Hz (see Table 2). Only very small differences between the two halogenated series **1a–c** and **3a–c** are observed in the ^{13}C NMR spectra and peripheral substitution has no effect on the fluorine, nitrogen, and boron chemical shifts either

Table 2. Spectroscopic data for SubAPs **1**–**3**.

	NMR data					
	^{1}H	^{13}C	^{19}F	^{11}B	^{15}N	λ_{max} [nm] (log (ε [M^{-1}cm^{-1}]))
1a[a]	8.7–8.6 (AA′BB′ system, 6H), 7.9–7. 8 (AA′BB′ system, 6H)	–	–	−13.8	–	565 (4.4), 529 (sh), 308 (4.1), 273 (4.1)
2a[a]	8.9–8.8 (m, 6H), 7.8–7.9 (m, 6H), 6.73 (d, J = 8.7 Hz, 2H), 5.28 (d, J = 8.7 Hz, 2H), 1.06 (s, 9H)	151.7, 150.3, 143.8, 131.2, 130.0, 125.9, 122.4, 117.9, 34.0, 31.5	–	−15.1	–	563 (5.0), 548 (sh), 529 (sh), 304 (4.7), 271 (4.7)
3a[a]	8.9–8.8 (AA′BB′ system, 6H), 7.9–7.8 (AA′BB′ system, 6H)	151.3, 131.3, 130.1, 122.5	−156.0 to −155.8 (m, J = 30.6, 1F)	−14.3 (d, J = 30.6)	–	563 (4.8), 520 (sh), 307 (4.5), 268 (4.5), 255 (4.5)
1b[b]	–	146.9, 144.8–144.1 (m, 6C), 141.3–140.6 (m, 6C), 115.2–114.7 (m, 6C)	−147.7 (AA′BB′ system, 6F) −137.0 (AA′BB′ system, 6F),	−14.2	–	574 (4.5), 556 (sh), 530 (sh), 311 (4.1), 277 (4.0)
2b[b]	6.80 (d, J = 8.9 Hz, 2H), 5.27 (d, J = 8.9 Hz, 2H), 1.10 (s, 9H)	147.6, 147.3, 143.8, 142.7–143.5 (m, 6C), (m, 6C), 139.3–140.0 125.1, 116.5, 113.7–113.9 (m, 6C), 32.7, 30.2	−147.4 (AA′BB′ system,6F) −136.5 (AA′BB′ system, 6F),	−15.1	–	570 (4.7), 555 (sh), 530 (4.2), 307 (4.4)
3b[b]	–	148.3, 143.9–143.4 (m, 6C), 141.9–141.4, (m, 6C), 115.2–114.9 (m, 6C)	−155.3 to 155.5 (m, J = 28.9, 1F) −136.95 (AA′BB′ system, 6F), −147.5 (AA′BB′ system,6F),	−14.5 (d, J = 28.9)	–	571 (4.9), 553 (sh), 529 (4.4), 490 (sh), 308 (4.6), 278 (sh), 267 (4.5)
1c[b]	3.2–3.0 (m, 12H; pyrr-CH_2), 2.1–2.0 (m, 12H; pyrr-CH$_2$CH_2), 1.18 (t, 18H; CH$_3$)	155.8 (C3, C5, C8, C10, C13, C15), 136.7 (C1, C2, C6, C7, C11, C12), 26.9 (C1′), 24.8 (C2′), 14.6 (C3′)	–	−14.3	−221.3 (m, N16, N17, N18) −127.7 (N4, N9, N14),	501 (4.6), 335 (sh), 295 (4.6)
2c[b]	6.8–6.7 (m, 2H; 3″-H), 6.7–6.6 (m, 1H; 4″-H), 5.22 (d, J = 8 Hz, 2H; 2″-H), 3.2–3.0 (m, 12H; pyrr-CH_2), 2.1–2.0 (m, 12H; pyrr-CH$_2$CH_2), 1.16 (t, 18H; CH$_3$)	157.1 (PhO), 153.3 (C3, C5, C8, C10, C13, C15), 135.9 (C1, C2, C6, C7, C11, C12), 128.4 (PhO), 120.6 (PhO), 119.0 (PhO), 26.7 (C1′), 24.8 (C2′), 14.6 (C3′)	–	−15.8	−217.2 (m, N16, N17, N18) −129.0 (N4, N9, N14),	499 (4.6), 316 (4.4), 285 (4.6)
3c[b]	3.2–3.0 (m, 12H; pyrr-CH_2), 2.1–2.0 (m, 12H; pyrr-CH$_2$CH_2), 1.20 (t, 18H; CH$_3$)	157.1 (C3, C5, C8, C10, C13, C15), 136.3 (C1, C2, C6, C7, C11, C12), 26.8 (C1′), 24.9 (C2′), 14.6 (C3′)	−157.6 to −157.3 (m, J = 29.6)	−15.0 (d, J = 29.6)	–	499 (4.6), 324 (4.4), 282 (4.6)

[a] NMR spectra recorded in 70:30 CS_2/$CDCl_3$. [b] NMR spectra recorded in $CDCl_3$.

(see Table 2 and the Supporting Information). Calculated chemical shifts (see Figure S40 in the Supporting Information) are in good agreement with experimental values.

The introduction of a fluorine atom into the axial position of SubAPs does not have a significant effect on the electronic spectra of **3a–c** even though small differences are observed in the high-energy region, namely, Soret Bands and bands at around 330 nm (see Table 2). This result is in contradiction with the sensing mechanism attributed to a recently reported fluoride subphthalocyanine-based chemodosimeter.[33]

Crystal structure: Appropriate single crystals for X-ray diffraction were obtained by slowly cooling a saturated solution of **3c** in hexanes and by slow evaporation of a chloroform solution of **3b**.

The crystal structure of fluoro[1,2,6,7,11,12-hexapropylsubporphyrazinato]boron(III) (**3c**) exhibits the cone shape common in this kind of molecule[7b] with the boron atom coordinated to three nitrogen atoms and the fluorine atom situated at the vertex of an almost regular tetrahedron, the fluorine atom is directed outside of the molecule in the axial position (Figure 1A). The asymmetric unit consists of three independent thirds of a molecule that, by applying the ternary axis, generate three independent molecules with the B–F bonds directed along the ternary symmetry axis (Figure 1B). In two of these molecules the fluorine atom is directed downwards and in one of them it is directed upwards; all of them are stacked along the *c* axis. Molecules of the same class stack in an alternating configuration along the *c* direction to give rise to columns. The number of columns formed by "down" molecules is twice that of those formed by "up" molecules such that each down column is surrounded by six up and each up column is surrounded by three down and three up (Figure 1C). In spite of this, no significant geometrical differences have been found among them, at least at the data collection temperature (100 K). Some selected distances are shown in Table 3.

Table 3. Selected bond lengths [Å] and interatomic distances (<3 Å) for compounds **3b** and **3c** determined by X-ray analysis.

3b		**3c**	
B1–F1	1.395(5)	B1–F1	1.400(8)
B1–N1	1.491(6)	B1–N1	1.491(4)
B1–N3	1.500(6)	B12–F12	1.374(8)
B1–N5	1.478(6)	B12–N12	1.493(4)
B2–F14	1.389(5)	B13–F13	1.387(8)
B2–N7	1.493(6)	B13–N13	1.495(4)
B2–N9	1.471(6)	B1···B1	4.414(8)
B2–N11	1.502(6)	B12···B13′	4.402(8)
B3–F27	1.385(6)	B12···B13″	4.426(8)
B3–N13	1.486(6)	F1···N13	2.980(4)
B3–N15	1.495(6)	F1···N15	2.887(4)
B3–N17	1.492(6)	F14···N5	2.802(4)
B1···B2	4.517(6)	F27···N7	2.969(4)
B1···B3	4.566(6)	F17···N9	2.820(4)
B3···B2	4.487(6)		
F1···N1	2.806(6)		

Surprisingly, the intermolecular F···N distances of the contiguous molecules (see Table 3) are considerably shorter than the sum of the corresponding van der Waals radii (1.47 (F)+1.50 (N) = 3.02 Å). To the best of our knowledge there is only one other compound that displays a comparable F···N distance and that is for an anion–cation interaction (2.778 Å, DILNER, CSD Refcode) between the fluorine atoms of a BF_4^- anion and a nitrogen atom of a pyridinium quaternary salt.

The crystal structure of **3b**[35] shows features quite similar to those of compound **3c** (Figures 1D and Table 3). The asymmetric unit consists of three independent molecules that are also stacked in columns, as in **3c**, but in **3b** the effects of the neighboring columns provoke a commensurate sinusoidal distortion along the columns in the *c* direction. These effects prevent the alignment of the B–F bonds (Figures 1E). Furthermore, in **3b** the same number of up and down columns exist and the structure can be thought of as being formed of alternating planes of same-sense columns perpendicular to the *a* direction, which is reminiscent of the close packing of spheres in an ABAB (down-up-down-up) se-

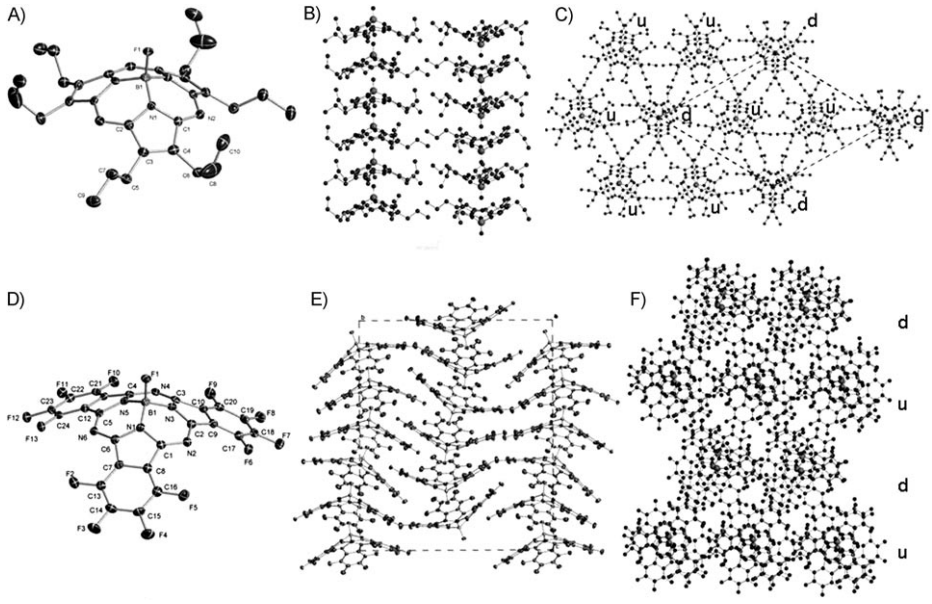


Figure 1. Molecular structures showing thermal ellipsoids at the 50% probability level of **3b** (A) and **3c** (D). Views showing the columns along the *c* axis for **3b** (B) and **3c** (E) and the columns packing along the *ab* plane of **3b** (C) and **3c** (E) (u = up, d = down). Hydrogen atoms have been omitted for clarity.

quence (Figures 1F).[36] This close packing explains the relatively high calculated value of the density (1.872 $g\,cm^{-3}$) for an organic compound. Again, some intermolecular F···N distances in **3b** are shorter than the sum of the van der Waals radii (Table 3). This achiral molecule packs in a chiral space group, that is, $P2_12_12_1$, a fact that may be relevant in the context of its second-order nonlinear optical properties in the solid state, which requires such a noncentrosymmetric organization.[37]

Theoretical calculations: To check the characteristics of the molecular interactions within the crystal structures, the geometries of the monomer, dimer, trimer, and tetramer of the unsubstituted fluorosubazaporphyrin (**3d**, $R^1=R^2=H$) were calculated by using B3LYP/6-31G* computational methods. C_{3v} symmetry was adopted in the calculation to simulate the crystal environment. The interaction energies and dipole moments of these systems are reported in Table 4. The interaction energies, dipole moments, and intermolecular distances all indicate the existence of a cooperativity effect as the number of monomers included in the cluster increases.

Figure 2. Molecular structure of the fluorosubazaporphyrin dimer $(\mathbf{3d})_2$ showing the bond critical points and bond paths.

Table 4. Energetic, electronic (dipole moments in D), and geometric characteristics of the fluorosubazaporphyrin clusters considered.

	E_{rel} [kcal mol^{-1}]	μ [D]	$\Delta\mu$ [D]	F···F distances [Å]
3d	0.00	3.14	0.00	–
$(\mathbf{3d})_2$	−4.00	6.95	0.66	4.771
$(\mathbf{3d})_3$	−8.34	10.98	1.55	4.754, 4.765
$(\mathbf{3d})_4$	−12.81	15.12	2.55	4.750, 4.755, 4.765

The values reported in Table 4 are related to the number of **3d** units ($n=1$–4). The best relationships ($r^2>0.999$) are the following: $d_{F\cdots F}$ (Å) $=4.75+0.188n^{-3}$, $\Delta\mu$ (D) $=-0.52+0.43n+0.08n^2$, and E_{rel} (kcal mol^{-1}) $=3.82-3.69n-0.12n^2$. These equations can be used to predict the properties of larger ($n>4$) aggregates. In the case of the intermolecular F···F distance, the equation predicts that this distance rapidly tends towards 4.75 Å as n becomes large (the experimental value is 4.42 Å). For the corresponding F···N distance ($d_{F\cdots N}$ (Å) $=3.07+0.125n^{-3}$), the extrapolated distance for a long column is 3.07 Å (experimental value, Table 3, 2.81 Å). Thus, both calculated distances are slightly longer than the experimental ones as a result of the crystal field produced by the surrounding columns.

Analysis of the electron density of the dimer sheds some light on the nature of the intermolecular interactions that produce such a drastic shortening of the distances between macrocycles within a column. Thus, the arrangement of **3c** into columnar crystalline structures implies more than simple π stacking along the c direction. It also implies the presence of three bond critical points (bcps) between the fluorine atoms of one of the molecules and the fluorosubazaporphyrin above. In addition, three bcps are found that can be associated with π–π interactions between the two molecules (Figure 2).

From these studies we can conclude that subporphyrazine **3c** in the solid state forms one-dimensional aggregates made up of a large, unprecedented number of subunits for this kind of macrocycle. The driving force for this organization in the crystal state presumably arises from the high dipole moment exhibited by the monomers as a result of the presence of an extremely electronegative fluorine atom attached to the axial position of the macrocycle. In turn, the assembly of the molecules produces a stabilizing effect that increases with the number of monomers. Therefore, each column of **3c** can be regarded as a single-strand molecular cable that contains a central electronic molecular wire surrounded by an insulating hydrocarbon cover.[38] Whether sinusoidal conformations like that of subphthalocyanine **3b** and parallel stacking like that in **3c** can interconvert by increasing or decreasing the temperature is under investigation.

Conclusion

We have described a way to construct supramolecular architectures in the crystalline state by using SubAPs as monomers. The method exploits the high dipole moments exhibited by axially substituted fluorosubazaporphyrins, which favor their spontaneous aggregation into one-dimensional columnar assemblies. Quite unexpectedly, the packing is extremely tight with unusually short intermolecular distances and a cooperative stabilizing effect that could allow access to electronic molecular wires. The scope of the method is rather wide owing to the development of a general synthetic procedure for the preparation of the fluorosubazaporphyrin monomers. Theoretical calculations afford spectroscopic data for the monomers that match very well the experimen-

tal values obtained and provide some insight into the nature of the molecular interactions within the crystal structures. The electron-conducting properties of the crystalline aggregates will be the subject of future studies.

Experimental Section

General methods: UV/Vis spectra were recorded with a Hewlett-Packard 8453 instrument. IR spectra were recorded with a Bruker Vector 22 spectrometer. FAB-MS spectra were determined with a VG AutoSpec instrument. MALDI-TOF MS and HRMS spectra were recorded with a Bruker Reflex III spectrometer. NMR spectra were recorded with Bruker AC-300, AMX-300, and DRX-500 instruments. Column chromatography was carried out on silica gel (Merck-60, 230–400 mesh, 60 Å) and TLC was performed on aluminum sheets precoated with silica gel 60 F_{254} (E. Merck). Chlorosubazaporphyrins **1a–c**,[6,30,31] aryloxysubazaporphyrins **2a,b**,[30,31] and dipropylmaleonitrile[39] were prepared as previously reported. All of the other chemicals were purchased from Aldrich and used as received without further purification.

Phenoxy[1,2,6,7,11,12-hexapropylsubporphyrazinate]boron(III) (2c): A 1 M solution of BCl_3 in xylene (1.0 mL, 1.00 mmol) was added under an argon atmosphere to dipropylmaleonitrile (200 mg, 1.23 mmol) and the mixture was heated at 140 °C for 45 min. The solvent was evaporated under reduced pressure, the residue was dissolved in toluene (2 mL), and phenol (579 mg, 6.11 mmol) was added. The resulting solution was stirred at reflux for 2 h and afterwards the solvent was removed by rotary evaporation. Column chromatography of the residue on silica gel using a 20:1 mixture of hexanes and ethyl acetate gave **2c** (56 mg, 23 %) as an orange solid (see Table 2). M.p. > 250 °C; IR (KBr):ν = 2955, 2874 (C−H) 1589 (C=N), 1464, 1250, 1169, 1088, 1020, 899, 806, 760, 725 cm^{-1}; MS (MALDI-TOF, dithranol): m/z = 590 $[M]^+$, 591 $[M+H]^+$, 497 $[M-PhO]^+$; HRMS (MALDI-TOF): m/z calcd for $C_{36}H_{48}BN_6O$ $[M+H]^+$: 591.398; found: 591.396; elemental analysis calcd (%) for $C_{36}H_{48}BN_6O$: C 73.09, H 8.18, N 14.21; found: C 73.31, H 7.98, N 14.35.

General procedure for synthesis of subphthalocyanines 3a,b (Methods A and B): SubPc **1a,b** or **2a,b** (0.155 mmol) was dissolved in toluene (1 mL). EtO·BF_3 (0.5 mL, 25 equiv) was added, the solution was stirred at 110 °C under argon and the reaction was monitored by TLC until completion. The reaction times ranged from 1–3 h and are specified in Table 1 together with the yields in each case. At the end of the reaction, the solution was cooled to room temperature, and the solvent was evaporated to give a rosy solid. The crude product was flushed with argon before being subjected to column chromatography on silica gel.

(Fluorosubphthalocyaninato)boron(III), 3a: Chromatography using a 4:1 mixture of toluene and ethyl acetate afforded **3a** as a magenta solid (see Table 2). M.p. > 250 °C; IR (KBr) ν = 1450, 1385(C−N), 1277, 1188, 1124, 1057, 733 cm^{-1}; MS (MALDI-TOF, dithranol): m/z: 415 $[M+H]^+$; HRMS (MALDI-TOF): m/z calcd for $C_{24}H_{13}BN_6F$ $[M+H]^+$: 415.127; found 415.128; elemental analysis calcd (%) for $C_{24}H_{12}BFN_6$: C 69.59, H 2.92, B 2.61, F 4.59, N 20.29; found: C 69.57, H 2.95, B 2.58, F 4.63, N 20.27.

Fluoro(1,2,3,4,8,9,10,11,15,16,17,18-dodecafluorosubphthalocyaninato)boron(III) (3b): Chromatography using a 15:1 mixture of hexanes and ethyl acetate afforded **3b** as a pink solid (see Table 2). M.p. > 250 °C; IR (KBr): ν = 1533, 1481 (C−N), 1259, 1121 ,1113 (C−F), 1072 (B−F), 964 cm^{-1}; MS (MALDI-TOF, TCNQ): m/z: 630 $[M]^+$; HRMS (LSI): calcd for $C_{24}BF_{13}N_6$ $[M]^+$: 630.007; found: 630.009; elemental analysis calcd (%) for $C_{24}BF_{13}N_6$: C 45.75, B 1.72, F 39.20, N 13.34; found: C 45.77, B 1.69, F 39.19, N 13.35.

Fluoro(1,2,6,7,11,12-hexapropylsubporphyrazinato)boron(III) (3c): **Method A**: A solution of **1c** (50 mg, 0.095 mmol) in BF_3·OEt_2 (0.5 mL) was stirred at room temperature for 15 min. BF_3·OEt_2 was evaporated at reduced pressure and the residue was purified by chromatography on silica gel using a 20:1 mixture of hexanes and ethyl acetate as eluent to afford **3c** (35 mg, 68 %) as an orange crystalline solid (see Table 2). M.p. > 250 °C; IR (KBr):ν = 2959, 2868 (C−H) 1628 (C=N), 1460, 1252, 1169, 1095, 1014 (B−F), 804, 770, 723 cm^{-1}; MS (MALDI-TOF, TCNQ): m/z: 516 $[M]^+$; HRMS (MALDI-TOF): m/z calcd for $C_{30}H_{42}BFN_6$: 516.355; found: 516.355.

Method B: BF_3·OEt_2 (126µl, 1.00 mmol) was added to a solution of the phenoxy derivative **2c** (47 mg, 0.08 mmol) in toluene (3 mL) and the solution was stirred at room temperature for 1 h. The solvent and excess reagent were evaporated under reduced pressure and the crude was purified by column chromatography on silica gel using a 20:1 mixture of hexanes and ethyl acetate as eluent to afford **3c** (26 mg, 63 %).

X-ray crystal structures analysis: A single crystal of **3b** was mounted on a glass fiber by using an epoxy adhesive, whereas a single crystal of **3c** was fished with a loop from a drop of a suspension of the crystal in perfluoropolyether oil (FOMBLIN 140/13, Aldrich). Intensity data for **3b** were collected at room temperature on a Bruker Kappa Apex II diffractometer by using $Mo_{K\alpha}$ radiation (λ = 0.71069 Å), whereas data for **3c** was collected at 100 K with an Oxford NOVA diffractometer equipped with a µ source and CCD area detector by using Cu_K radiation (λ = 1.54178 Å). In both instances ϕ and ω scans with narrow frames were used for data collection.

Theoretical methods of calculation: The geometries of the systems were optimized with the hybrid HF/DFT, B3LYP, and the 6-31G* basis set (6-311++G** for the GIAO calculations of the monomers) as implemented in the Gaussian 03 package.[40–44] The electron densities were analyzed within the atoms-in-molecules (AIM)[45] framework by using the AIM2000 program.[46]

Acknowledgement

This work was carried out with financial support from the Ministerio de Ciencia y Tecnología (Project Nos. CTQ2006-14487-C02-01/BQU, CTQ2005-08933/BQU, and Consolider-Ingenio 2010 CSD2006–0015), the Comunidad Autónoma de Madrid (Project MADRISOLAR, ref. S-0505/PPQ/0225) and the EU (MRTN-CT-2006-035533, Solar-N-type and COST Action D35). Thanks are given to the CTI (CSIC) for allocation of computer time. M.S.R.-M. thanks the Spanish MEC for an R&C contract.

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Received: September 30, 2007
Published online: December 28, 2007

