

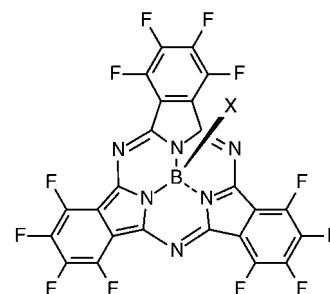
concentration, because a complete penetration of the incident light through the sample was not required. The distribution function analysis (DFA) data were used to investigate multi-modal particle size distributions in the liquid samples. HRTEM images were recorded by using a Philips CM 200 FEG TEM operated at 200 kV. The ^{29}Si MAS experiments were carried out with 4 mm ZrO_2 rotors in a commercial double resonance probe using a DSX advance impulse spectrometer (Bruker DSX Avance 500) working at a resonance frequency of 99.369 MHz. The samples were examined by using a single-pulse acquisition. The 90° pulse length and the recycle delay were set to 3.0 μs and 40 s. The XRD measurements were performed on a Scintag XDS 2000 diffractometer using $\text{CuK}\alpha$ radiation. IR spectra were recorded from KBr pellets on a Bruker Equinox 55 spectrometer. Prior to the XRD and IR measurements, nanosized crystals were separated from the mother liquor by one-step centrifugation at 20000 rpm for 1 h, and redispersed in an ultrasonic bath in doubly distilled water for 2 h prior to further investigations. Solid products were obtained by freeze-drying of the centrifuged samples.

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Synthesis, Separation, and Characterization of the Topoisomers of Fused Bicyclic Subphthalocyanine Dimers**

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Subphthalocyanines (SubPcs, **1**)—lower homologues of phthalocyanines—are nonplanar cone-shaped aromatic macrocycles comprising three N-fused diiminoisindoline units around a boron atom core.^[1] The 14 π -electron system



1a X = Cl
1b X = OPh

characteristic of these compounds confers interesting optical properties that have been exploited in the fields of dyes, nonlinear optics, and photonic devices.^[1] Moreover, these properties may be fine-tuned since the axial (X) and peripheral positions in SubPcs (see **1**) can be easily functionalized or derivatized.^[1] On the other hand, the intrinsic chirality of subphthalocyanines with C_3 or C_1 symmetries represents^[2] also a promising feature that enhances their potential as building blocks for the construction of complex molecules.^[1]

One focus of our current efforts is the stepwise synthesis of extended π surfaces.^[3] Thus, we have recently described the preparation of heterobinuclear azaporphyrinic systems^[4a] as well as multinuclear annulene–phthalocyanines.^[4b] In this regard, although fused binuclear phthalocyanine dimers are well-known,^[5] only one example of a fused subphthalocyanine dimer analogue, whose characterization data (^1H NMR and UV/Vis spectroscopy) do not agree with any of the characteristic features described herein, has been claimed.^[6]

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Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

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Herein we report on the synthesis of fused subphthalocyanine dimers (Scheme 1), and show for the first time that this kind of binuclear system is actually formed as a mixture of two topoisomers that have been separated and characterized.

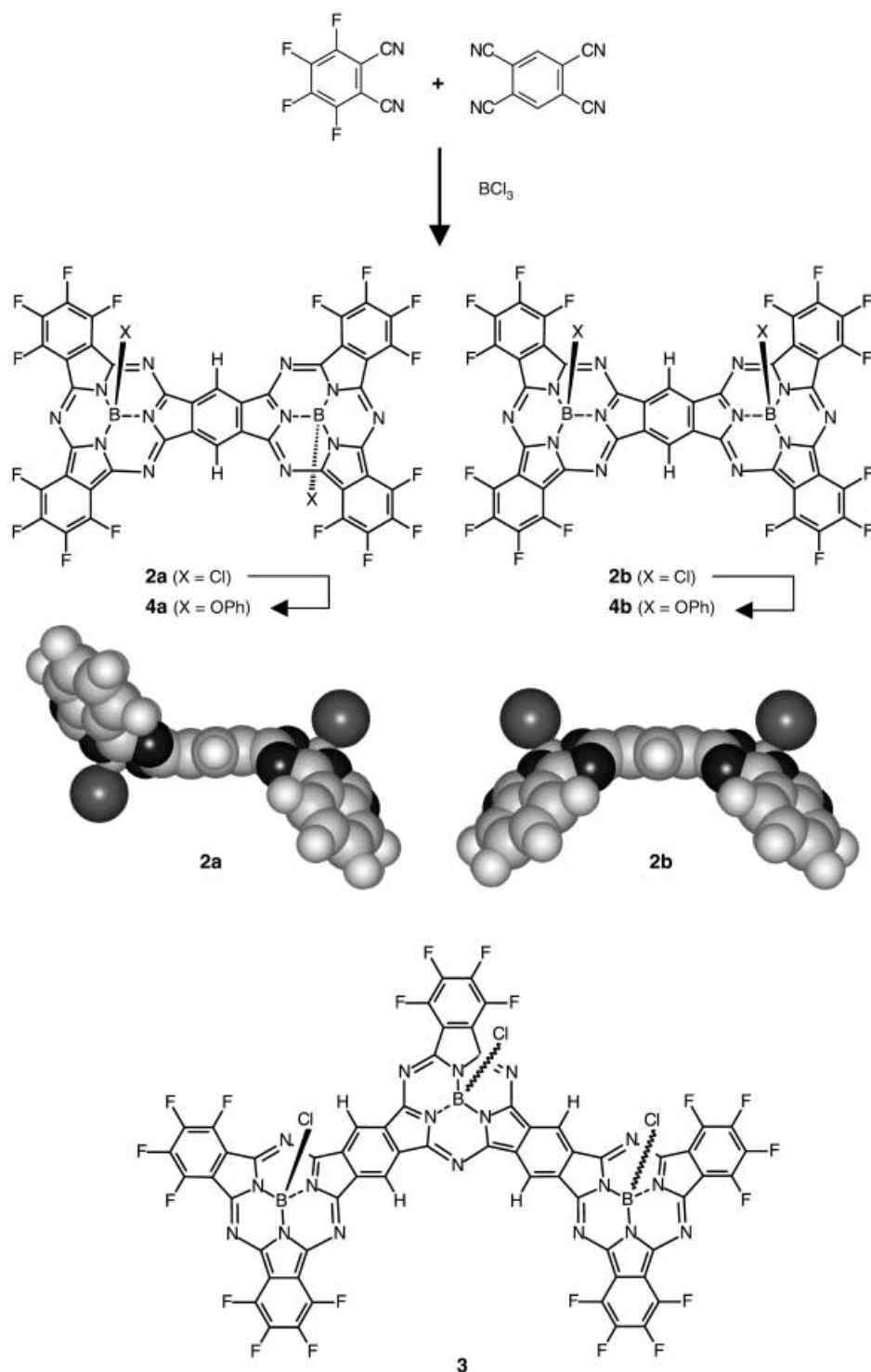
The dichloro-SubPc dimers **2a** and **2b** (Scheme 1) were synthesized by statistical condensation of ten equivalents of tetrafluorophthalonitrile and one equivalent of 1,2,4,5-benzenetetracarbonitrile in the presence of three equivalents of boron trichloride according to a procedure similar to the one

described in reference [7]. After purification by column chromatography on silica gel, bright blue dimers **2a** and **2b** (Scheme 1) and purple SubPc **1a** were obtained in 9, 11, and 43 % yield, respectively. Very small quantities of a mixture of the dark blue trimer **3**, which theoretically consists of three topoisomers (*syn,syn*, *syn,trans*, and *trans,trans*), were also isolated.

^1H NMR spectra of topoisomers **2a** and **2b** showed a singlet at $\delta = 10.48$ and 10.46 ppm, respectively, corresponding to the

protons attached to the central benzene ring.^[8] These very high chemical shifts indicate unambiguously the aromatic character of the junction between the two subphthalocyanine halves of the molecules. The small difference between the chemical shifts corresponding to each topoisomer shows that the geometry of the molecule does not influence very much the ring currents. The UV/Vis spectra (Figure 1) of dimers **2a** and **2b** revealed the presence of the expected B and Q bands characteristic of porphyrazines. Both spectra showed a Q-band region composed of 1) a sharp band at 693 and 692 nm, respectively, whose intensity ($\lg(\epsilon) = 4.9$) is comparable to that of Pcs, and 2) three less intense bands at about 660, 630, and 600 nm, whose intensity ($\lg(\epsilon) = 4.4\text{--}4.5$) is comparable to that of SubPcs. The UV/Vis spectrum of trimer **3** shows a very intense ($\lg(\epsilon) = 4.9$) Q band at 755 nm along with smaller bands at shorter wavelength (Figure 1). The huge shifts for the Q band (118–119 nm for **2a** and **2b**, and 181 nm for **3a–c**, with respect to the position of the Q band in SubPc **1a**) along with their higher intensity clearly indicate that the SubPc subunits within the dimers and trimers are fully conjugated.^[9]

The substitution of the chlorine atom in the axial position of dimers **2a** and **2b** by a bulkier group, such as a phenoxy group, allowed the assignment of the resulting topoisomers **4a** and **4b** (Scheme 1). Thus, the previous reaction between 1,2,4,5-benzenetetracarbonitrile and tetrafluorophthalonitrile was performed and the crude reaction product was treated with phenol at 120 °C overnight (Scheme 1). Dimers **4a** and **4b**



Scheme 1. Synthesis of compounds **2a,b**, **3a–c**, and **4a,b**.

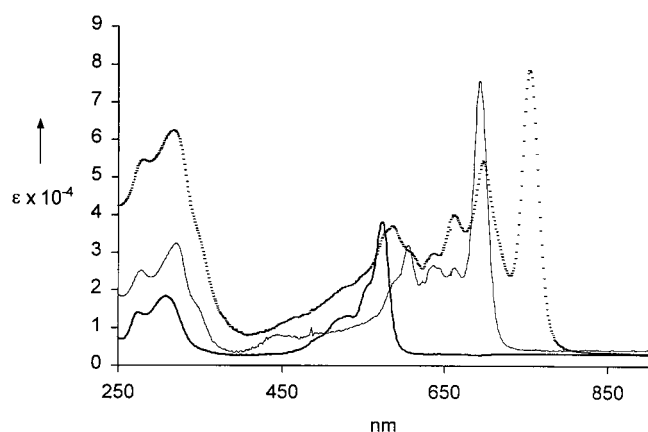


Figure 1. UV/Vis spectra of compounds **2b**, **1b**, and **3a–c** in chloroform.

were obtained, after purification by column chromatography, in 6 and 7% yields, respectively. Symmetrical SubPc **1b** was isolated in 34% yield and single crystals suitable for X-ray crystallography were obtained by slow evaporation from a solution of **1b** in acetone.^[10] The X-ray crystal structure of SubPc **1b** (Figure 2) is very similar to those of other SubPcs in the few examples reported,^[11] thus demonstrating the rigid character of the cone-shaped macrocyclic core that remains virtually unchanged.^[1]

However, remarkably, the packing in the solid state is (Figure 3) very different from the ones already observed and shows infinite one-dimensional hydrogen-bonded arrays of SubPcs. Two subPcs are intermolecularly connected by two C–H⋯F hydrogen bonds between protons H2 and H3 and fluorine atoms F3 and F4, respectively (See Figure 2 and 3).^[12]

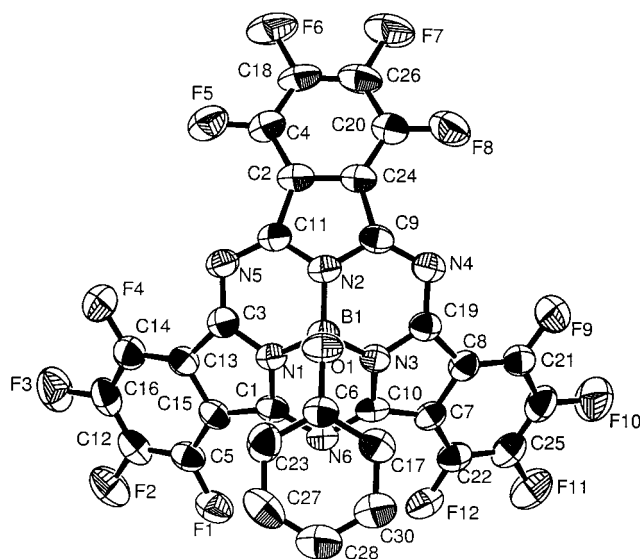


Figure 2. Structure of the subphthalocyanine **1b** (ORTEP representation).

¹H NMR spectra of compounds **4a** and **4b** both exhibit a singlet at $\delta = 10.40$ and 10.36 ppm, respectively, in a similar way as **2a** and **2b**. Moreover, all three spectra corresponding to **4a**, **4b**, and **1b** showed signals at $\delta = 6.8$ – 5.3 ppm corresponding to the protons on the phenyl group. In particular, the *ortho* aromatic protons close to the SubPc ring give rise to very shielded doublets at $\delta_1 = 5.36$, $\delta_2 = 5.49$, and $\delta_3 = 5.31$ ppm in **4a**, **4b**, and **1b**, respectively, as a consequence of the strong ring currents produced by the aromatic SubPc moieties. The chemical shift difference $\Delta\delta = \delta_2 - \delta_1 =$

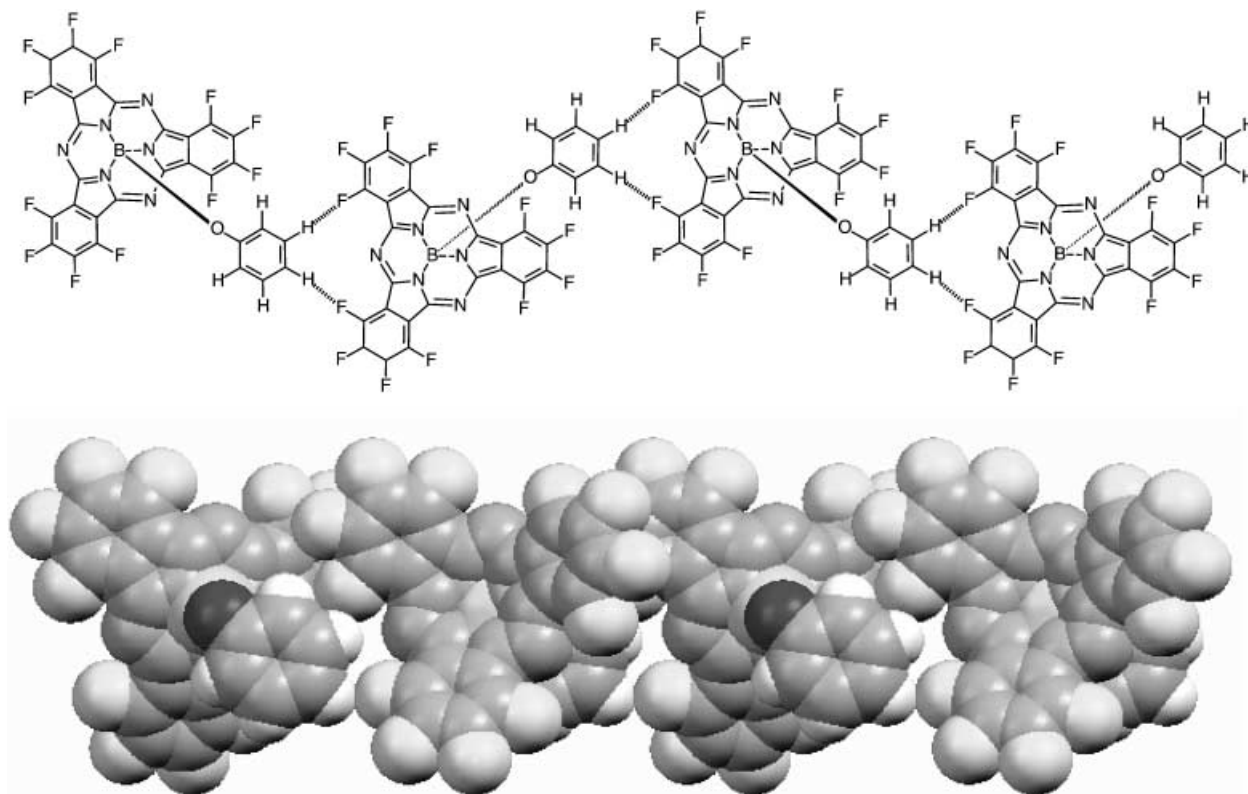


Figure 3. Schematic and CPK structure of the one-dimensional H-bonded array of subphthalocyanines in the X-ray crystal structure of **1b**.

0.13 ppm may be interpreted on the basis of computer-generated CPK models of topoisomers **4a** and **4b** (Figure 4).^[13]

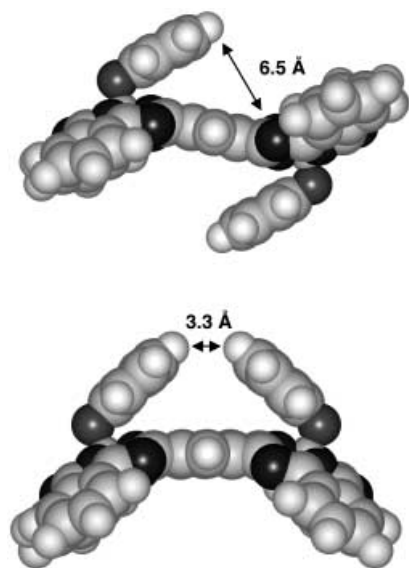


Figure 4. Computer-generated CPK models of the *syn* and *anti* topoisomers of dimer **2**, showing the shortest possible distances between the axial phenyl ring and the closest atom in the other half of the dimer.

In the *anti* topoisomer, the protons of the axial phenyl ring of one SubPc half are located^[14] at a distance ≥ 6.5 Å from the closest atoms of the other SubPc half, showing that these protons should give rise to ^1H NMR signals very similar to the ones of SubPc **1b**. On the other hand, the protons of the axial phenyl ring in the *syn* topoisomer are located^[14] at a distance ≥ 3.3 Å from the closest atoms of the other phenyl ring, thus showing a possible magnetic dipolar interaction between the two phenyl rings. In this way we propose the following model in which the *anti* isomer is **4a** ($\delta_1 \approx \delta_3$) and the *syn* isomer is **4b** ($\delta_2 \neq \delta_3$).^[15] Subsequently, it was shown that dimers **2a** and **2b**, when treated individually with phenol, gave rise to **4a** and **4b**, respectively. It was then possible to ascertain that **2a** and **2b** were *anti* and *syn* topoisomers, respectively.

In conclusion, we have synthesized and fully characterized the fused subphthalocyanine dimers **2a,b** and **4a,b**. The careful examination of NMR and X-ray data allowed the assignment of the structure of the topoisomers *anti* **4a** and *syn* **4b**. Chemical derivatization of **2a** and **2b** into **4a** and **4b** allowed the assignment of the topoisomers *anti* **2a** and *syn* **2b**. This represents, we believe, a first step towards the stepwise synthesis of larger fully conjugated SubPc structures.

Experimental Section

Compounds **1a**, **2a**, **2b**, and **3a–c**: BCl_3 (10.1 mL of a 1 M solution in *p*-xylene) was added dropwise to a solid mixture of tetrafluorophthalonitrile (561 mg, 2.81 mmol) and 1,2,4,5-benzenetetracarboxitrile (50 mg, 0.28 mmol). The reaction mixture was refluxed for three hours and after cooling down to room temperature, was flushed with argon. The resulting dark purple slurry was then evaporated under vacuo and subjected to various column chromatographies on silica gel using acetone/hexane (1:0 to 1:4, v/v). Four main fractions were collected; order of elution: **1a**, **2a**, **2b**, **3**;

note that the elution order of **2a** and **2b** is swapped when toluene/hexane mixtures are employed.

SubPc **1a**: Purple powder, 260 mg (43 %); see Supporting Information.

Dimer **2a**: Blue reddish powder, 27 mg (9 %); m.p. $>250^\circ\text{C}$; ^1H NMR (300 MHz, CDCl_3 , 25°C): δ = 10.48 ppm (s); IR (KBr): $\tilde{\nu}$ = 1539, 1487, 1400, 1285, 1225, 1165, 1115, 1067, 1020, 962, 858, 789, 638, 592, 557 cm^{-1} ; UV/Vis (CHCl_3): $\lambda_{\text{max}}(\text{lg}(\epsilon))$ = 693 (4.9), 661 (4.4), 635 (4.4), 604 (4.5), 592 (sh), 441 (3.7), 319 (4.5), 278 nm (4.4); MALDI-TOF: m/z : 1070.7 [M^+] and [$M^+ + \text{H}$]; HR-LSIMS calcd for $\text{C}_{42}\text{H}_{20}\text{N}_{12}\text{F}_{16}\text{B}_2\text{Cl}_2$: [M^+]: m/z : 1069.9833, found 1069.9845; elemental analysis calcd (%) for $\text{C}_{42}\text{H}_{20}\text{N}_{12}\text{F}_{16}\text{B}_2\text{Cl}_2$: C 47.10, H 0.19, N 15.69; found: C 47.56, H 0.26, N 15.25.

Dimer **2b**: Blue reddish powder, 33 mg (11 %); m.p. $>250^\circ\text{C}$; ^1H NMR (300 MHz, CDCl_3 , 25°C): δ = 10.46 ppm (s); IR (KBr): $\tilde{\nu}$ = 1535, 1481, 1400, 1273, 1219, 1165, 1111, 1070, 1016, 966, 856, 795, 708, 658, 586 cm^{-1} ; UV/Vis (CHCl_3): $\lambda_{\text{max}}(\text{lg}(\epsilon))$ = 692 (4.9), 662 (4.4), 636 (4.4), 605 (4.5), 592 (sh), 441 (3.9), 320 (4.5), 278 nm (4.4); MALDI-TOF: m/z : 1071.7 [M^+] and [$M^+ + \text{H}$]; HR-LSIMS calcd for $\text{C}_{42}\text{H}_{20}\text{N}_{12}\text{F}_{16}\text{B}_2\text{Cl}_2$: [M^+]: m/z : 1069.9833, found 1069.9825; elemental analysis calcd (%) for $\text{C}_{42}\text{H}_{20}\text{N}_{12}\text{F}_{16}\text{B}_2\text{Cl}_2$: C 47.10, H 0.19, N 15.69; found: C 47.61, H 0.31, N 15.51.

Trimer **3**: Dark blue powder, 6 mg (3 %); m.p. $>250^\circ\text{C}$; ^1H NMR (300 MHz, CDCl_3 , 25°C): δ = 10.58 (s), 10.53 (s), 10.51 (s), 10.48 (s), 10.44 ppm (s); IR (KBr): $\tilde{\nu}$ = 1733, 1625, 1537, 1517, 1483, 1402, 1281, 1220, 1166, 1112, 1058, 1017, 858, 794, 706, 653, 578 cm^{-1} ; UV/Vis (CHCl_3): $\lambda_{\text{max}}(\text{lg}(\epsilon))$ = 755 (4.9), 697 (4.6), 661 (4.5), 637 (4.4), 585 (4.5), 317 (4.6), 280 nm (4.6); MALDI-TOF: m/z : 1495.6 [M^+]; HR-LSIMS calcd for $\text{C}_{60}\text{H}_{18}\text{N}_{18}\text{F}_{20}\text{B}_3\text{Cl}_3$: [M^+]: m/z : 1493.9892, found 1493.9936; elemental analysis calcd (%) for $\text{C}_{60}\text{H}_{18}\text{N}_{18}\text{F}_{20}\text{B}_3\text{Cl}_3$: C 48.19, H 0.27, N 16.86; found: C 48.54, H 0.41, N 16.33.

Compounds **1b**, **4a**, and **4b**: A mixture of phenol (500 mg, 5.3 mmol) and the crude product from the previous reaction was warmed up to 120°C overnight. The resulting solid was then subjected to various column chromatographies on silica gel using dichloromethane, ethyl acetate/hexane (1/4), and acetone/hexane (1:0 to 1:4, v/v).

Subphthalocyanine **1b**: Purple powder, 224 mg (34 %); see Supporting Information.

Dimer **4a**: Dark blue powder, 20 mg (6 %); m.p. $>250^\circ\text{C}$; ^1H NMR (300 MHz, CDCl_3 , 25°C): δ = 10.40 (s, 2H), 6.75–6.60 (m, 6H), 5.36 ppm (d, J = 7.6 Hz, 4H); IR (KBr): $\tilde{\nu}$ = 1529, 1477, 1393, 1275, 1213, 1161, 1107, 1080, 968, 899, 702, 644, 598 cm^{-1} ; UV/Vis (CHCl_3): $\lambda_{\text{max}}(\text{lg}(\epsilon))$ = 688 (4.9), 657 (4.4), 631 (4.4), 600 (4.5), 587 (sh), 441 (3.7), 319 (4.4), 274 nm (4.3); MALDI-TOF: m/z : 1186.9 [M^+] and [$M^+ + \text{H}$]; HR-LSIMS calcd for $\text{C}_{54}\text{H}_{12}\text{N}_{12}\text{F}_{16}\text{B}_2\text{O}_2$: [M^+]: m/z : 1187.1137, found 1187.1146; elemental analysis calcd (%) for $\text{C}_{54}\text{H}_{12}\text{N}_{12}\text{F}_{16}\text{B}_2\text{O}_2$: C 54.67, H 1.02, N 14.17; found: C 55.11, H 1.32, N 13.77.

Dimer **4b**: Dark blue powder, 23 mg (7 %); m.p. $>250^\circ\text{C}$; ^1H NMR (300 MHz, CDCl_3 , 25°C): δ = 10.36 (s, 2H), 6.905–6.72 (m, 6H), 5.49 ppm (d, J = 8.2 Hz, 4H); IR (KBr): $\tilde{\nu}$ = 1531, 1477, 1396, 1265, 1225, 1103, 995, 903, 760, 708, 644, 594 cm^{-1} ; UV/Vis (CHCl_3): $\lambda_{\text{max}}(\text{lg}(\epsilon))$ = 689 (4.9), 657 (4.4), 631 (4.4), 601 (4.5), 586 (sh), 441 (3.9), 319 (4.5), 273 nm (4.5); MALDI-TOF: m/z : 1186.8 [M^+] and [$M^+ + \text{H}$]; HR-LSIMS calcd for $\text{C}_{54}\text{H}_{12}\text{N}_{12}\text{F}_{16}\text{B}_2\text{O}_2$: [M^+]: m/z : 1186.1137, found 1186.1190; elemental analysis calcd (%) for $\text{C}_{54}\text{H}_{12}\text{N}_{12}\text{F}_{16}\text{B}_2\text{O}_2$: C 54.67, H 1.02, N 14.17; found: C 54.95, H 1.27, N 13.64.

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- [8] These low-field proton signals at $\delta \approx 10.5$ ppm were not reported in reference [6].
- [9] Few examples have been described of intramolecular interactions between phthalocyanine subunits in related binuclear phthalocyanine systems in which the two Pc moieties are connected through benzene rings.^[5] In these cases, the Q band undergoes a shift to the red, which has been attributed to the enlargement of the π -conjugated system, with concomitant splitting of the Q band as a consequence of intramolecular electronic coupling between the Pc subunits. However, in these cases, both red-shifting and splitting were much smaller than observed in the present study for SubPc dimers **2** and trimers **3**.
- [10] CCDC-179556 (**1b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).
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- [12] Two types of intermolecular hydrogen bonds were found in the X-ray crystal structure of SubPc **1b**: 1) C27–H2–F3a defined by $d(\text{C}\cdots\text{F}) = 3.265 \text{ \AA}$, $d(\text{H}\cdots\text{F}) = 2.667 \text{ \AA}$, $(\text{C}–\text{H}\cdots\text{F}) = 167^\circ$ and 2) C28–H3–F4b defined by $d(\text{C}\cdots\text{F}) = 3.432 \text{ \AA}$, $d(\text{H}\cdots\text{F}) = 2.533 \text{ \AA}$, $(\text{C}–\text{H}\cdots\text{F}) = 143^\circ$.
- [13] The CPK models were generated on the basis of the X-ray crystal structure of compound **1b**. They do not correspond to any energy minimum.
- [14] For both the *anti* and *syn* isomers, the distances were calculated after tilting the phenyl ring towards the other half of the dimer (see Figure 4).
- [15] We discarded any possible intermolecular interactions or aggregation since the ¹H NMR chemical shifts as well as the UV bands are not sensitive to changes of concentration.

cis and *trans* Forms of a Binuclear Subphthalocyanine**

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In 1972 Mellor and Ossko^[1] reported the synthesis and spectroscopic characterization of the boron-containing subphthalocyanine (SubPc) macrocycle; the cone shape of SubPcs was confirmed by X-ray crystallography shortly thereafter.^[2] After a nearly 20 year hiatus, interest in these unusual systems was renewed when one of us (N.K.) published the synthesis and spectroscopic study of a binuclear SubPc in which two SubPc units shared a central benzene ring.^[3] As was subsequently pointed out, the bowl shape of the SubPc should result in *cis* and *trans* forms of the binuclear species, having C_{2v} and C_{2h} molecular symmetry, respectively.^[4]

We report here on the synthesis of a variation of the original binuclear SubPc, the separation of the *cis* and *trans* binuclear forms, and their spectroscopic and structural characterization (Scheme 1). In the original procedure 4-*tert*-butylphthalonitrile and 1,2,4,5-tetracyanobenzene were allowed to react in a 20:1 ratio with BBr_3 . We have replaced the 4-*tert*-butylphthalonitrile with tetrafluorophthalonitrile to prevent the formation of positional isomers that the 4-*tert*-butyl substituent engenders, and to reduce the number of benzo units that can undergo halogenation, an unavoidable side reaction when BBr_3 or BCl_3 is used in SubPc syntheses.^[5] We also report the X-ray crystal structure analysis of the perfluorinated monomer,^[6] derived from the cyclotrimerization of tetrafluorophthalonitrile, which is unavoidably the major product of the reaction.^[7]

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