Supporting Information

One-pot Synthesis of π-Extended Fluorenone-fused Subphthalocyanines

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1. **Experimental section**

1.1 **General methods**

Chemical reagents were purchased from Merck, Alfa Aesar, Acros Organics or TCI Europe and were used without further purification. *Synthetic grade* solvents were used for chemical reactions and column chromatography purifications and *anhydrous grade* for reactions under dry conditions.

The monitoring of the reactions has been carried out by thin layer chromatography (TLC), employing aluminium sheets coated with silica gel type 60 F254 (0.2 mm thick, Merck). The analysis of the TLCs was carried out with an UV lamp of 254 and 365 nm. Purification and separation of the synthesized products was performed by normal-phase column chromatography, using silica gel (230-400 mesh, 0.040-0.063 mm, Merck). Eluents along with the relative ratio in the case of solvent mixtures are indicated for each particular case.

Melting points were measured in open-end capillary tubes by using a Büchi B-540 apparatus, and are uncorrected.

Nuclear magnetic resonance spectra (\(^{1}\)H-, \(^{13}\)C-, \(^{19}\)F- and \(^{11}\)B-NMR) were recorded on a Bruker AV-300 or a Bruker DRX-500 spectrometers either in the Organic Chemistry Department or in the Interdepartmental Investigation Service of UAM. Deuterated solvent employed in each case is indicated in brackets, and its residual peak was used to calibrate the spectra using literature reference δ ppm values.¹

Mass spectra (MS) and high resolution mass spectra (HRMS) were recorded in the Interdepartmental Investigation Service of UAM, employing Electronic Impact (EI), or Matrix-Assisted Laser Desorption/Ionization Time-Of-Flight (MALDI-TOF), using a VG-AutoSpec spectrometer for EI, and a Bruker-Ultratrace-III spectrometer, with a Nd:YAG laser operating at 355 nm, for MALDI-TOF. The matrices and internal references employed are indicated for each spectrum.

Ultraviolet and visible (UV-Vis) spectra were recorded using solvents in the *spectroscopic grade* in the Organic Chemistry Department of UAM employing a JASCO-V660 spectrophotometer. The logarithm of the molar extinction coefficient (ε) is indicated in brackets for each maximum. Likewise, fluorescence measurements were carried out with a JASCO-V8600 spectrofluorometer. Fluorescence quantum yields (φ\(_F\)) of SubFcs were determined in toluene and calculated by using the following equation:²

\[
\phi^S = \phi^R \left( \frac{\text{Grad}^S}{\text{Grad}^R} \right) \left( \frac{\eta^R}{\eta^S} \right)^2
\]

Scripts R and S indicate reference and sample, respectively. Grad is the gradient from the plot of the integrated fluorescence intensity (at exc. λ = 520 nm) versus the absorption (at the same wavelength), and η is the refractive index of the solvent. Chloro-dodecafluoroSubPc (Cl-F\(_{12}\)SubPc) in benzonitrile (φ\(_F\) = 0.58) was used as reference.³

Infrared spectra were recorded in the Interdepartmental Investigation Service of UAM on a Bruker IFS 66v vacuum FT-IR spectrometer.

Electrochemical measurements were performed in the Organic Chemistry Department of UAM on an Autolab PGStat 30 equipment using a three electrode configuration system. The measurements were carried out in argon saturated THF solutions containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF\(_6\)). A platinum electrode (3 mm diameter) was used as the working electrode, and a platinum wire and a Ag/AgNO\(_3\) (0.01 M in acetonitrile) electrode were employed as the auxiliary and the reference electrode, respectively. Fc was used as an external reference and all the potentials were given relative to the Fc/Fc\(^+\) couple.

Single-crystal X-ray diffraction data collection for structure determinations were collected in the Interdepartmental Investigation Service of UAM at Bruker KAPPA APEX II CCD area-detector X-ray diffractometer operating with graphite-monochromated and Mo Kα alpha radiation (λ = 0.71073 Å). The data are absorption corrected with the program SADABS. Intensities are calculated with the SAINT software, which also incorporates polarization and Lorentz effect corrections. The structures were solved and refined using the Bruker SHELXTL Software Package.

HPLC experiments were conducted using an Agilent 1200 equipment with a Daicel Chiralpak IC column (10 mm Ø x 250 mm L).
1.2 Experimental procedures

3-(2′-Ethoxycarbonylphenyl)phthalonitrile 2

![Chemical structure of 3-(2′-Ethoxycarbonylphenyl)phthalonitrile 2]

Ethyl 2-(4,4',5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (0.88 g, 3.2 mmol), phthalonitrile 1 (0.88 g, 3.2 mmol), K₂PO₄ (2.04 g, 9.6 mmol), and PdCl₂(dppf)·CH₂Cl₂ (0.13 g, 5 mol%) were stirred under argon atmosphere in a mixture of toluene and water (1:1, 65 ml) at 90 °C for 20 h. The reaction mixture was cooled down to room temperature and diluted with water and toluene. The organic phase was separated, washed with water, and dried on anhydrous MgSO₄. After filtration of the drying agent, the solvent was eliminated under reduced pressure and the solid recrystallized from ethanol to yield 2 as a white solid (0.81 g, 92%). Mp = 107 °C.

**1H-NMR** (500 MHz, CDCl₃, 298 K): δ (ppm) = 8.16 (dd, J₀,m = 7.5, 1.5 Hz, 1H, H₃), 7.83 (dd, J₀,m = 8, 1.5 Hz, 1H, H₄), 7.75 (t, J₉ = 8 Hz, 1H, H₅), 7.69 (td, J₀,m = 7.5, 1.5 Hz, 1H, H₆), 7.62 (m, 2H, H₆,₅), 7.31 (dd, J₀,m = 7.5, 1.5 Hz, 1H, H₇), 4.14 (q, J₂ = 7.5 Hz, 2H, CH₂CH₂), 1.12 (t, J₂ = 7.5 Hz, 3H, CH₃CH₂).

**13C-NMR** (75 MHz, CDCl₃, 298 K): δ (ppm) = 166.0 (CO₂Et), 148.2, 138.0, 133.7, 132.6, 132.4, 132.0, 131.4, 130.8, 129.8, 129.7, 116.1, 115.9, 115.8 (CN), 114.7 (CN), 61.4 (CH₂CH₂), 14.0 (CH₃CH₂).

**FT-IR** (KBr): ν (cm⁻¹) = 3074, 2988, 2962, 2940, 2901, 2234 (δ C=O), 151.8, 151.3, 147.29, 146.0, 146.0, 144.0, 143.4, 141.9, 142.8, 138.0, 136.9, 136.0, 135.8, 134.7, 131.1, 129.2, 128.4, 127.7, 126.0, 125.4, 125.0, 124.6, 123.9.

**HRMS (EI):** m/z [M]+ calcd for C₉H₆ClFNO₂: 276.0899; found: 276.0895; Er (ppm) = 1.4.

**Boron (III) subfluorenocyanine 4a**

![Chemical structure of Boron (III) subfluorenocyanine 4a]

A mixture of tetrafluorophthalonitrile (300 mg, 1.50 mmol) and phthalonitrile 2 (207 mg, 0.75 mmol) was dissolved in o-DCB (1.1 ml) under argon atmosphere. A 1.0 M solution of BCl₃ in p-xylene (2.25 ml, 2.25 mmol) was then added through a syringe and the mixture was heated at 160 °C for 2 h. The reaction mixture was flushed with an argon stream to remove volatiles and then filtered through a celite plug. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography on silica gel (eluent: toluene/heptane 4:1) to yield SubFc 4a as a purple solid (207 mg, 41% yield). Mp > 250 °C.

**1H-NMR** (300 MHz, CDCl₃, 298 K): δ (ppm) = 9.87 (d, J₉ = 7.5 Hz, 1H, H₃), 8.89 (d, J₉ = 7.8 Hz, 1H, H₄), 8.24 (d, J₉ = 7.8 Hz, 1H, H₅), 7.93 (t, J₉ = 7.5 Hz, 1H, H₆), 7.76 (d, J₉ = 7.5 Hz, 1H, H₇), 7.54 (t, J₉ = 7.5 Hz, 1H, H₈).

**13C-NMR** (75 MHz, CDCl₃, 298 K): δ (ppm) = 192.7 (C=O), 151.8, 151.3, 147.29, 146.6, 146.0, 144.0, 143.4, 141.9, 142.8, 138.0, 136.9, 136.0, 135.8, 134.7, 131.1, 129.2, 128.4, 127.7, 126.0, 125.4, 125.0, 124.6, 123.9.

**19F-NMR** (470 MHz, CDCl₃, 298 K): δ (ppm) = -136.51 (m), -136.72 (m), -136.98 (m), -138.50 (m), -147.29 (m), -147.41 (m), -147.77 (m), -147.98 (m).

**UV-Vis (THF):** λmax (nm) (log ε) = 589 (4.88), 561 (sh), 540 (sh), 306 (4.71).

**FT-IR** (KBr): ν (cm⁻¹) = 2925, 2854, 1712 (ν C=O), 1649, 1615, 1581, 1532, 1483, 1431, 1401, 1273, 1233, 1173, 1118, 1080, 1063, 1031, 979, 943, 886, 844, 751, 717, 684, 648, 588, 571.

**MS (MALDI-TOF, DCTB):** m/z = 676.0 [M]+.

**HRMS (MALDI-TOF, DCTB+PPG450+790):** m/z [M]+ calcd. for C₃₁H₂₈BCIF₃N₉O: 676.0257; found: 676.0246. Er (ppm) = 1.6.

**XRD:** Monocrystals were obtained by slow vapor diffusion of hexane into toluene solution of 4a. Crystallographic data and some refining details are summarized in the following table:

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**Table:**

| Crystallographic Data | Details |
|-----------------------|---------|
| Space Group           | P1      |
| Cell Parameters       |         |
| a, b, c (Å)           |         |
| α, β, γ (°)           |         |
| Volume (Å³)           |         |
| Density (g/cm³)       |         |
| Z                     |         |
| Formula               | C₃₁H₂₈BCIF₃N₉O |
| Calculated Mass (g/mol) | 676.0257 |
| Found Mass (g/mol)    | 676.0246 |
| Er (ppm)              | 1.6     |
Boron (III) subfluorenocyanine 4b (mixture of three regioisomers)

The previous reaction also gave rise to SubFc 4b as a blue solid (26 mg, 10% yield). Mp > 250 °C.

$^1$H-NMR (300 MHz, CDCl$_3$, 298 K): $\delta$ (ppm) = 9.91 (d, $J_0 = 7.5$ Hz, 1.5H, H$_4$), 9.72 (d, $J_0 = 7.5$ Hz, 0.5H, H$_4$), 8.88 (m, 2H, H$_7$), 8.26 (m, 2H, H$_8$), 7.94 (m, 2H, H$_3$), 7.82 (m, 2H, H$_1$), 7.55 (m, 2H, H$_2$).

$^{19}$F-NMR (470 MHz, CDCl$_3$, 298 K): $\delta$ (ppm) = -137.39 (m), -138.91 (m), -139.07 (m), -148.18 (m), -148.60 (m), -148.85 (m).

UV-Vis (THF): $\lambda_{max}$ (nm) (log $\varepsilon$) = 605 (4.75), 571 (sh), 553 (sh), 310 (4.70).

FT-IR (KBr): $\nu$ (cm$^{-1}$) = 3072, 2922, 1712 ($\nu$ C=O), 1615, 1580, 1533, 1475, 1429, 1269, 1247, 1179, 1117, 1088, 1025, 956, 880, 840, 799, 755, 718, 706, 684, 636.

MS (MALDI-TOF, DCTB): $m/z$ = 706.1 [M$^+$].

HRMS (MALDI-TOF, DCTB+PPG450+790): $m/z$ [M$^+$] calcd. for C$_{31}$H$_{26}$BCIF$_8$N$_6$O$_{1.50}$: 706.0740; found: 706.0723. Er (ppm) = 2.4.

Boron (III) subphthalocyanine 3

The previous reaction also gave rise to SubPc 3 as a pink solid (11 mg, 2% yield). Mp > 250 °C.

$^1$H-NMR (500 MHz, C$_6$D$_{14}$Cl, 393 K): $\delta$ (ppm) = 8.93 (d, $J_0 = 7.5$ Hz, 1H, H$_1$), 8.38 (m, 1H, H$_3$), 8.06 (t, $J_0 = 7.5$ Hz, 1H, H$_2$), 7.90 (d, $J_0 = 7.5$ Hz, 1H, H$_4$), 7.77 (m, 2H, H$_{1,2}$), 7.61 (br, 1H, H$_6$), 3.75 (br, 2H, CH$_2$CH$_3$), 0.77 (br, 3H, CH$_2$CH$_3$).

UV-Vis (THF): $\lambda_{max}$ (nm) (log $\varepsilon$) = 579 (4.72), 562 (4.60), 538 (sh), 517 (4.32), 302 (4.52).

MS (MALDI-TOF, DCTB): $m/z$ = 722.1 [M$^+$].

HRMS (MALDI-TOF, DCTB+PPG790): $m/z$ [M$^+$] calcd. for C$_{33}$H$_{12}$BCIF$_8$N$_6$O$_2$: 722.0676; found: 722.0673. Er (ppm) = 1.0.
Boron (III) subfluorenocyanine 6a

A mixture of 4,5-dichlorophthalonitrile (295 mg, 1.50 mmol) and phthalonitrile 2 (207 mg, 0.75 mmol) was dissolved in o-DCB (1.1 ml) under an argon atmosphere. A 1.0 M solution of BCl$_3$ in p-xylene (2.25 ml, 2.25 mmol) was then added through a syringe and the mixture was heated at 160 °C for 2 h. The reaction mixture was flushed with an argon stream to remove volatiles and then filtered through a celite plug. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography on silica gel (eluent: toluene/ethyl acetate 60:1) to yield SubFc 6a as a purple solid (90 mg, 18% yield). Mp > 250 °C.

$^1$H-NMR (300 MHz, tol-d$_8$, 298 K): $\delta$ (ppm) = 9.76 (d, $J_o = 7.5$ Hz, 1H, $H_6$), 8.64 (s, 1H, $H_8$), 8.63 (s, 1H, $H_8$), 8.60 (s, 1H, $H_8$), 8.59 (s, 1H, $H_8$), 8.46 (d, $J_\alpha = 7.8$ Hz, 1H, $H_8$), 7.93 (d, $J_\alpha = 7.8$ Hz, 1H, $H_8$), 7.70 (d, $J_\alpha = 7.5$ Hz, 1H, $H_9$), 7.51 (t, $J_\alpha = 7.5$ Hz, 1H, $H_9$).

UV-Vis (THF): $\lambda_{max}$ (nm) (log $\epsilon$) = 599 (4.74), 584 (4.76), 556 (sh), 537 (4.51), 312 (4.66), 285 (4.64).

FT-IR (KBr): $\nu$ (cm$^{-1}$) = 3069, 1712 ($\nu$ C=O), 1610, 1581, 1544, 1466, 1435, 1419, 1381, 1358, 1320, 1288, 1255, 1230, 1195, 1161, 1096, 993, 962, 886, 853, 819, 792, 757, 717, 684, 659.

MS (MALDI-TOF, DCTB): $m/z$ = 670.0 [M]$^+$.

HRMS (MALDI-TOF, DCTB+PPG450+790): $m/z$ [M]$^+$ calcd. for C$_{18}$H$_{16}$BCl$_3$N$_4$O: 669.9425; found: 669.9410. Er (ppm) = 2.2.

Boron (III) subfluorenocyanine 6b (mixture of three regioisomers)

The previous reaction also gave rise to SubFc 6b as a blue solid (13 mg, 5% yield). Mp > 250 °C.

$^1$H-NMR (300 MHz, CDCl$_3$, 298 K): $\delta$ (ppm) = 9.89 = 9.81 (m, 2H, $H_8$), 8.99 (s, 1H, $H_8$), 8.91 (s, 1H, $H_8$), 8.83 (d, $J_\alpha = 7.8$ Hz, 2H, $H_8$), 8.21 (d, $J_\alpha = 7.8$ Hz, 2H, $H_8$), 7.95 (m, 2H, $H_8$), 7.79 (br, 2H, $H_8$), 7.54 (t, $J_\alpha = 7.2$ Hz, 2H, $H_8$).

UV-Vis (THF): $\lambda_{max}$ (nm) (log $\epsilon$) = 620 (4.75), 606 (4.77), 581 (4.52), 556 (sh), 311 (4.66), 291 (4.66).

FT-IR (KBr): $\nu$ (cm$^{-1}$) = 3070, 2924, 2852, 1716 ($\nu$ C=O), 1600, 1580, 1472, 1429, 1374, 1305, 1269, 1250, 1200, 1116, 1098, 1001, 972, 949, 908, 886, 845, 808, 789, 775, 755, 715.

MS (MALDI-TOF, DCTB): $m/z$ = 702.1 [M]$^+$.

HRMS (MALDI-TOF, DCTB+PPG450+790): $m/z$ [M]$^+$ calcd. for C$_{38}$H$_{38}$BCl$_3$N$_4$O$_2$: 702.0338; found: 702.0327. Er (ppm) = 1.5.

Boron (III) subfluorenocyanine 9a

A mixture of phthalonitrile (192 mg, 1.50 mmol) and phthalonitrile 2 (207 mg, 0.75 mmol) was dissolved in o-DCB (1.1 ml) under an argon atmosphere. A 1.0 M solution of BCl$_3$ in p-xylene (2.25 ml, 2.25 mmol) was then added through a syringe and the mixture was heated at 160 °C for 2 h. The reaction mixture was flushed with an argon stream to remove volatiles and then filtered through a celite plug. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography on silica gel (eluent: heptane/ethyl acetate 3:1) to yield SubFc 9a as a purple solid (40 mg, 10% yield). Mp > 250 °C.

$^1$H-NMR (300 MHz, CDCl$_3$, 298 K): $\delta$ (ppm) = 9.93 (d, $J_o = 7.5$ Hz, 1H, $H_6$), 9.91 = 8.85 (m, 4H, $H_8$), 8.84 (d, $J_\alpha = 7.8$ Hz, 1H, $H_9$), 8.16 (d, $J_\alpha = 7.8$ Hz, 1H, $H_9$), 8.00 = 7.97 (m, 4H, $H_8$), 7.88 (t, $J_\alpha = 7.8$ Hz, 1H, $H_8$), 7.76 (d, $J_\alpha = 7.8$ Hz, 1H, $H_8$), 7.47 (t, $J_\alpha = 7.8$ Hz, 1H, $H_9$).

UV-Vis (THF): $\lambda_{max}$ (nm) (log $\epsilon$) = 602 (4.84), 574 (4.83), 556 (sh), 532 (sh), 310 (4.82).

FT-IR (KBr): $\nu$ (cm$^{-1}$) = 3063, 2925, 2852, 1704 ($\nu$ C=O), 1612, 1576, 1462, 1441, 1392, 1283, 1234, 1202, 1189, 1161, 1141,
1118, 1089, 1048, 1013, 980, 947, 910, 847, 791, 759, 736, 713, 702, 632.

**MS (MALDI-TOF, DCTB):** \( m/z = 532.2 \ [\text{M}]^+ \).

**HRMS (MALDI-TOF, DCTB+PEGMeNa550):** \( m/z \ [\text{M}]^+ \) calcd. for C\(_{34}\)H\(_{14}\)BClN\(_6\)O: 532.1011; found: 532.0992. Er (ppm) = 3.6.

**Boron (III) subfluorenocyanine 9b (mixture of three regioisomers)**

The previous reaction also gave rise to SubFc 71 as a blue solid (5 mg, 2% yield). Mp > 250 °C.

\[ \text{\( ^1H \)-NMR (300 MHz, CDCl}_3, 298 K): \delta (ppm) = 9.97 – 9.91 (m, 2H, H\(_4\)), 8.95 – 8.83 (m, 4H, H\(_{\alpha,7}\)), 8.22 (d, \( J_\beta = 7.8 \text{ Hz}, 2H, H\_1 \)), 7.54 (t, \( J_\beta = 7.8 \text{ Hz}, 2H, H\_2 \)). \]

\[ \text{UV-Vis (THF): } \lambda_{\text{max}} (\text{nm} ) (\log e) = 626 (4.85), 600 (4.83), 574 (4.73), 552 (\text{sh}), 312 (4.84). \]

**MS (MALDI-TOF, DCTB):** \( m/z = 634.2 \ [\text{M}]^+ \).

**HRMS (MALDI-TOF, DCTB+PEGMeNa550):** \( m/z \ [\text{M}]^+ \) calcd. for C\(_{38}\)H\(_{16}\)BClN\(_6\)O\(_2\): 634.1117; found: 634.1114. Er (ppm) = 0.5.

**Boron (III) subfluorenocyanine 7a (mixture of four regioisomers)**

A mixture of 4,5-diiodophthalonitrile (570 mg, 1.50 mmol) and phthalonitrile 2 (207 mg, 0.75 mmol) was dissolved in o-DCB (1.1 ml) under an argon atmosphere. A 1.0 M solution of BCl\(_3\) in p-xylene (2.25 ml, 2.25 mmol) was then added through a syringe and the mixture was heated at 160 °C for 2 h. The reaction mixture was flushed with an argon stream to remove volatiles and then filtered through a celite plug. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography on silica gel (eluent: toluene/ethyl acetate 50:1) to yield SubFc 7a as a purple solid (116 mg, 15% yield). Mp > 250 °C.

\[ \text{\( ^1H \)-NMR (300 MHz, CDCl}_3, 298 K): \delta (ppm) = 9.81 (d, \( J_\beta = 7.8 \text{ Hz}, 1H, H\_4 \)), 9.40 (s, 1H, H\_\alpha ), 9.39 (s, 1H, H\_\alpha ), 9.38 (s, 1H, H\_\alpha ), 8.82 (d, \( J_\beta = 7.8 \text{ Hz}, 1H, H\_7 \)), 7.58 (t, \( J_\beta = 7.8 \text{ Hz}, 1H, H\_2 \)). \]

\[ \text{UV-Vis (THF): } \lambda_{\text{max}} (\text{nm} ) (\log e) = 607 (4.72), 593 (4.83), 564 (\text{sh}), 544 (4.49), 336 (\text{sh}), 287 (4.71). \]

**MS (MALDI-TOF, DCTB):** \( m/z = 1035.7 \ [\text{M}]^+ \).

**HRMS (MALDI-TOF, DCTB+PPG1000):** \( m/z \ [\text{M}]^+ \) calcd. for C\(_{31}\)H\(_{10}\)BClI\(_4\)N\(_6\)O: 1035.6876; found: 1035.6854. Er (ppm) = 2.1.

**Boron (III) subfluorenocyanine 8a (mixture of four regioisomers)**

A mixture of 4-iodophthalonitrile (381 mg, 1.50 mmol) and phthalonitrile 58 (207 mg, 0.75 mmol) was dissolved in o-DCB (1.1 ml) under an argon atmosphere. A 1.0 M solution of BCl\(_3\) in p-xylene (2.25 ml, 2.25 mmol) was then added through a syringe and the mixture was heated at 160 °C for 2 h. The reaction mixture was flushed with an argon stream to remove volatiles and then filtered through a celite plug. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography on silica gel (eluent: toluene/ethyl acetate 50:1) to yield SubFc 8a as a purple solid (71 mg, 12% yield). Three fractions corresponding to different groups of regioisomers were isolated. Mp > 250 °C.

\[ \text{\( ^1H \)-NMR (300 MHz, CDCl}_3, 298 K): \delta (ppm) = 9.94 – 9.84 (m, 1H, H\_4), 9.26 – 9.18 (m, 2H, H\_\alpha), 8.88 – 8.82 (m, 1H, H\_7). \]
8.56 (m, 2H, H\textsubscript{α}), 8.29 – 8.17 (m, 3H, H\textsubscript{β,8}), 7.95 – 7.50 (m, 3H, H\textsubscript{3,1,2}).

**MS (MALDI-TOF, DCTB):** m/z = 784.0 [M]\textsuperscript{+}.

**Boron (III) subfluorenocyanine 10a (mixture of four regioisomers)**

A mixture of 4-tert-butylphthalonitrile (276 mg, 1.50 mmol) and phthalonitrile 2 (207 mg, 0.75 mmol) was dissolved in o-DCB (1.1 ml) under an argon atmosphere. A 1.0 M solution of BCl\textsubscript{3} in p-xylene (2.25 ml, 2.25 mmol) was then added through a syringe and the mixture was heated at 160 °C for 2 h. The final purple mixture was flushed with an argon stream to remove volatiles and then filtered through a celite plug. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography on silica gel (eluent: toluene/heptane 4:1) to yield SubFc 10a as a purple solid (14 mg, 3% yield). Mp > 250 °C.

\textsuperscript{1}H-NMR (300 MHz, CDCl\textsubscript{3}, 298 K): \(\delta\) (ppm) = 10.04 – 9.92 (m, 1H, H\textsubscript{4}), 8.95 – 8.77 (m, 5H, H\textsubscript{α,7}), 8.23 – 8.16 (m, 1H, H\textsubscript{8}), 8.05 (d, \(J_o\) = 7.8 Hz, 2H, H\textsubscript{β}), 7.90 (t, \(J_o\) = 7.8 Hz, 1H, H\textsubscript{3}), 7.83 – 7.79 (m, 1H, H\textsubscript{1}), 7.56 – 7.49 (m, 1H, H\textsubscript{2}).

**UV-Vis (THF):** \(\lambda_{max}\) (nm) (\(\log\ v\)) = 607 (4.76), 578 (4.75), 559 (sh), 536 (sh), 310 (4.80).

**FT-IR (KBr):** \(\nu\) (cm\textsuperscript{-1}) = 2960, 2925, 2858, 1716 (\(\nu_{C=O}\)), 1613, 1578, 1468, 1441, 1396, 1364, 1310, 1264, 1230, 1187, 1161, 1109, 1090, 992, 955, 890, 843, 790, 759, 717, 685.

**MS (MALDI-TOF, DCTB):** m/z = 644.3 [M]\textsuperscript{+}.

**HRMS (MALDI-TOF, DCTB+PPG450+790):** m/z [M]\textsuperscript{+} calcd. for C\textsubscript{39}H\textsubscript{30}BClN\textsubscript{6}O: 644.2264; found: 644.2262. Er (ppm) = 0.3.
2. Additional information

![Three possible regioisomers for SubFc 4b.](image)

**Figure S1** Three possible regioisomers for SubFc 4b.

| Equivalents | Yield/% |
|-------------|---------|
| SubFc 4a    | SubFc 4b |
| 2 BC3       | 41 10   |
| 1 BC3       | 28 10   |
| 1 BC3 6     | 20 11   |
| 1 BC3 8     | 8 15    |

**Table S1** Reagent equivalents and yields of SubFcs 4a and 4b.

![Mass spectrum (MALDI-TOF, DCTB) of the crude reaction mixture upon cross-cyclotrimerization, in the presence of BC3 between phthalonitrile 2 and tetrafluorophthalonitrile.](image)

**Figure S2** Mass spectrum (MALDI-TOF, DCTB) of the crude reaction mixture upon cross-cyclotrimerization, in the presence of BC3 between phthalonitrile 2 and tetrafluorophthalonitrile.
Scheme S1 Cross-cycotrimerization between phthalonitrile 5 and tetrafluorophthalonitrile under the optimal reaction conditions.

Scheme S2 Proposed mechanism for the acyl chloride formation from SubPc 3.
Figure S3 IR spectra (KBr) of SubFcs 4a (left) and 4b (right) exhibiting carbonyl stretching bands at 1712 cm$^{-1}$.

Figure S4 Cyclic Voltammogram (scan rate: 100 mV s$^{-1}$) and Square-Wave voltammogram (SW frequency: 30 Hz) of SubFcs 4a (left) and 4b (right) in THF.
**Figure S5** ORTEP representation (50% probability level) of the molecular structure showing the bowl depth and the B—Cl distances (top), the upward spiral geometry of the fluorenone moiety (middle), and the unit cell (bottom). Distances are in Å.
**Figure S6** X-ray structure of SubFc 4a showing the two enantiomers (M and P) stacked alternatively. HPLC chromatogram exhibiting the separation of the two enantiomers of SubFc 4a (conditions: toluene/hexane 70:30, 0.8 ml min$^{-1}$, 20 °C).
Figure S7 UV-Vis (solid line) and fluorescence (dashed line) spectra of SubFs 4a, 4b, 6a, 6b, 7a, 9a, 9b and 10a in THF (exc. λ = 520 nm). Fluorescence quantum yields (Φ_F) are indicated.
3. **NMR spectra**

**Figure S8** $^1$H-NMR spectrum (CDCl$_3$, 300 MHz, 298 K) of phthalonitrile 2.

**Figure S9** $^{13}$C-NMR spectrum (CDCl$_3$, 75 MHz, 298 K) of phthalonitrile 2.
Figure S10 $^1$H-NMR spectrum (CDCl$_3$, 300 MHz, 298 K) of SubFc 4a.

Figure S11 $^{13}$C-NMR spectrum (CDCl$_3$, 300 MHz, 298 K) of SubFc 4a.
Figure S12 $^{19}$F-NMR spectrum (CDCl$_3$, 470 MHz, 298 K) of SubFc 4a.

Figure S13 $^{11}$B-NMR spectrum (CDCl$_3$, 160 MHz, 298 K) of SubFc 4a.
Figure S44 $^1$H-NMR spectrum (CDCl$_3$, 300 MHz, 298 K) of SubFc 4b.

Figure S15 $^{19}$F-NMR spectrum (CDCl$_3$, 470 MHz, 298 K) of SubFc 4b.
Figure S16 $^1$H-NMR spectrum (CD$_2$Cl$_2$, 500 MHz, 298 and 393 K) of SubPc 3.

Figure S57 $^1$H-NMR spectrum (tol-d$_8$, 300 MHz, 298 K) of SubFc 6a.
Figure S68 $^1$H-NMR spectrum (CDCl$_3$, 300 MHz, 298 K) of SubFc 6b.

Figure S19 $^1$H-NMR spectrum (CDCl$_3$, 300 MHz, 298 K) of SubFc 7a.
Figure S20 \(^1\)H-NMR spectrum (CDCl\(_3\), 300 MHz, 298 K) of SubFc 8a (fractions of different regioisomers).

Figure S21 \(^1\)H-NMR spectrum (CDCl\(_3\), 300 MHz, 298 K) of SubFc 9a.
Figure S22 $^1$H-NMR spectrum (CDCl$_3$, 300 MHz, 298 K) of SubFc 9b.

Figure S23 $^1$H-NMR spectrum (CDCl$_3$, 300 MHz, 298 K) of SubFc 10a.
4. References

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