

## Electronpoor *N*-substituted Imide-fused corannulenes

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### Supporting Information

#### Chemical Syntheses and Compound Characterization

##### General

All experiments were carried out under standard Schlenk conditions and argon atmosphere. 1,2-Dichloroethane (DCE) and Dimethylformamide were distilled from phosphorus pentoxide, and stored over molecular sieve (3 Å). Nickel powder (99,5 %, 150 micron) was obtained from ABCR GmbH & Co. KG. *N*-pentafluorophenyl maleimide was synthesized from maleic anhydride and pentafluoroaniline,<sup>[S1]</sup> *N*-heptafluorobutylmaleimide was synthesized by the same procedure using 2,2,3,3,4,4,4-Heptafluorobutylamine instead of pentafluoroaniline.

Melting points were determined on a Gallenkamp Melting Point Apparatus and are not corrected. IR spectra were recorded on a Nicolet iS10 MFR FT-IR Sp spectrometer (signals are denoted as following, s (strong), m (middle) and w (weak)). <sup>1</sup>H, <sup>19</sup>F and <sup>13</sup>C-NMR spectra were measured on a JEOL ECS 400 spectrometer or on a Bruker Instruments AVIII 700 at 23 °C. CDCl<sub>3</sub> and CD<sub>2</sub>Cl<sub>2</sub> were used as solvents and the residual solvent peak was taken as an internal standard (<sup>1</sup>H-NMR: CDCl<sub>3</sub> 7.26, CD<sub>2</sub>Cl<sub>2</sub> 5.30 ppm; <sup>13</sup>C-NMR: CDCl<sub>3</sub> 77.0 ppm, CD<sub>2</sub>Cl<sub>2</sub> 54.0 ppm; always proton-decoupled), <sup>19</sup>F-NMR spectra were referenced against external CFCl<sub>3</sub>. Mass spectra were measured on a MAT CH7A (EI, 80 eV, 3 kV). High resolution masses were determined by peak match method against perfluorokerosene. TLC analysis was performed using Merck Silica gel 60 F<sub>254</sub>.

### 1,6,7,10-tetramethylfluoranthene-9-fused pentafluorophenylmaleimide (1a)

In a 100 mL Schlenk flask 3,8-dimethylacenaphthylene-1,2-dione (500 mg, 2.38 mmol, 1.0 eq.), pentan-3-one (1.22 mL, 11.48 mmol, 4.8 eq.) were suspended in methanol (12 mL). A solution of potassium hydroxide (1 g, 17.82 mmol, 7.49 eq.) in methanol (5 mL) was added by syringe and the mixture was stirred for one hour at room temperature. The yellow solution was diluted with 50 mL dichloromethane and extracted three times with 10 % hydrochloric acid (50 mL). After drying with anhydrous sodium sulfate and quick removal of the solvent the crude product was transferred to a 50 mL Schlenk tube and vacuum dried. The vessel was purged with argon and nitrobenzene (11 mL) and 1-(perfluorophenyl)-1H-pyrrole-2,5-dione (691 mg 2.38 mmol, 1.0 eq.) were added in one portion. The dark red solution was stirred at 180 °C for 42 hours. The cooled reaction mixture was transferred to a small flask and the nitrobenzene was distilled off under reduced pressure, leaving a solid residue that was purified by column chromatography on silica gel (pentane/dichloromethane 3:1). The product was obtained as a yellow solid 494 mg (43 %).

**Mp:** 259 °C; **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): δ = 7.85 (½ AB, <sup>3</sup>J = 8.2 Hz, 2H), 7.48 (½ AB, <sup>3</sup>J = 8.2 Hz, 2H), 3.06 (s, 6H), 2.88 ppm (s, 6H); **<sup>19</sup>F-NMR** (376 MHz, CDCl<sub>3</sub>): AA'BB'C-type δ = -140.83-143.91 (m, *ortho*-2F), -150.87-153.18 (m, *para*-1F), -160.51-162.19 ppm (m, *meta*-2F); **<sup>13</sup>C{<sup>1</sup>H}-NMR (101 MHz, CDCl<sub>3</sub>):** δ = 166.01 (2C, CO), 146.61 (2C), 135.41 (2C), 134.15 (1C), 132.73 (2C), 132.21 (2C), 131.16 (2C), 128.48 (2C), 128.23 (2C), 126.53

(1C), 25.16 (2C), 19.60 ppm (2C); **MS** (EI, 130 °C):  $m/z$  493.1108 (found), 493.1101 (calc'd), 493 (100 %, [M]<sup>+</sup>), 445 (23 %), 293 (20 %), 119 (17 %). **IR**:  $\nu$  = 3476 (w), 2928 (w), 1775 (m), 1723 (s), 1606 (m) 1503 (s), 1465 (m), 1372 (s), 1348 (s), 1283 (s), 1193 (m), 1124 (s), 1093 (s), 976 (s), 842 (m), 794 (m) 708 (m), 625 (s) cm<sup>-1</sup>.

### Double cycloadduct with 1-(perfluorophenyl)-1H-pyrrole-2,5-dione (**2**)

If the reaction is run with acetic anhydride or toluene instead of nitrobenzene for the second transformation, **2** is obtained as major product in 68 % yield.

**Mp**: 316 °C; **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.62 (½ AB, <sup>3</sup>*J* = 8.1 Hz, 2H), 7.23 (½ AB, <sup>3</sup>*J* = 8.1 Hz, 2H), 3.27 (s, 4H), 2.80 (s, 6H), 2.66 ppm (s, 6H); **<sup>19</sup>F-NMR** (376 MHz, CDCl<sub>3</sub>): ABCDE-type  $\delta$  = -142.55 (dtd, *J* = 22.2, 6.7, 2.5 Hz, 1F), -142.68 (dtd, *J* = 22.2, 6.7, 2.2 Hz, 1F), -150.86 (tt, *J* = 21.5, 2.2, *para*-1F), -160.14 (tdd, *J* = 22.6, 6.3, 2.2, 1F), -160.98 ppm (tdd, *J* = 22.6, 6.3, 1.6, 1F); **<sup>13</sup>C{<sup>1</sup>H,<sup>19</sup>F}-NMR** (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 172.31 (4C), 143.15 (4C), 139.65 (2C), 137.69 (4C), 136.37 (4C), 132.75 (1C), 132.24 (2C), 129.77 (1C), 128.88 (2C), 125.66 (2C), 106.53 (2C), 52.01 (4C), 42.75 (2C), 26.34 (2C), 25.18 ppm (2C); **MS** (EI, 100 °C):  $m/z$  760.17702 (found), 760.14199 (calc'd), 495 (100 %, [M-C<sub>10</sub>H<sub>4</sub>F<sub>5</sub>NO<sub>2</sub>]<sup>+</sup>), 480 (15 %), 258 (34 %, [M-C<sub>18</sub>H<sub>4</sub>F<sub>10</sub>N<sub>2</sub>O<sub>4</sub>]<sup>+</sup>), 243 (26 %). **IR**:  $\nu$  = 2902 (m), 1720 (s), 1610 (w), 1517 (s), 1358 (m), 1296 (m), 1190 (m), 1183 (m), 987 (m), 832 (w), 790 (m), 741 (m), 628 cm<sup>-1</sup> (m).

### 1,6,7,10-tetramethylfluoranthene-9-fused heptafluorobutylmaleimide (1b)

In a 100 mL Schlenk flask 3,8-dimethylacenaphthylene-1,2-dione (800 mg, 3.80 mmol, 1.0 eq.), pentan-3-one (2.2 mL, 20.7 mmol, 5.5 eq.) were suspended with in dry methanol (44 mL). A solution of potassium hydroxide (1.76 g, 31.4 mmol, 8.3 eq.) in methanol (9 mL) was added by syringe and the mixture was stirred for one hour at room temperature. The yellow solution was diluted with 50 mL dichloromethane and extracted three times with 10 % hydrochloric acid (50 mL). After drying with anhydrous sodium sulfate and quick removal of the solvent, the crude product was transferred to a 50 mL Schlenk tube and vacuum dried. The vessel was purged with argon and nitrobenzene (13 mL) and 1-(2,2,3,3,4,4,4-heptafluorobutyl)-1H-pyrrole-2,5-dione (1.06 g, 3.8 mmol, 1.0 eq.) were added in one portion. The dark red solution was stirred at 180 °C for 72 hours. The cooled reaction mixture was transferred to a small flask and the nitrobenzene was removed under reduced pressure, leaving a solid residue that was purified by column chromatography on silica gel (pentane/dichloromethane 3:1). The product was obtained as a yellow solid 862 mg (45 %).

**Mp:** 231 °C; **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): δ = 7.81 (½ AB, <sup>3</sup>J = 8.2 Hz, 2H), 7.44 (½ AB, <sup>3</sup>J = 8.2 Hz, 2H), 4.33 (t, <sup>3</sup>J = 15.6 Hz, 2H), 3.01 (s, 6H), 2.84 ppm (s, 6H); **<sup>19</sup>F-NMR** (376 MHz, CDCl<sub>3</sub>): δ = -80.40 (t, <sup>3</sup>J = 9.4 Hz, 3F), -116.72 (dt, J = 15.0, 9.5 Hz, 2F), -127.50 (d, <sup>3</sup>J = 4.1 Hz, 2F); **<sup>13</sup>C{<sup>1</sup>H}-NMR (101 MHz, CDCl<sub>3</sub>):** δ = 167.94 (2C, CO), 146.35 (2C), 135.23 (2C), 134.15 (1C), 132.89 (2C), 132.22 (2C), 130.65 (2C), 128.33 (2C), 128.24 (2C), 126.58

(1C), 25.22 (2C), 19.47 ppm (2C); **MS** (EI, 140 °C):  $m/z$  509.12051 (found), 509.1226 (calc'd), 509 (100 %,  $[M]^+$ ), 340 (50 %,  $[M-C_3F_7]^+$ ), 239 (12 %). **IR**:  $\nu$  = 2922 (w), 1760 (m), 1708 (m), 1462 (w), 1403 (m), 1348 (s), 1220 (s), 1177 (s), 979 (s), 948 (s), 931 (s), 912 (s), 859 (s), 794 (s), 737 (m), 692 (m).

### Corannulene-fused pentafluorophenylmaleimide (3a)

In a 100 mL round bottom flask, **1a** (260 mg, 0.51 mmol, 1.0 eq.) was dissolved in tetrachloromethane (25 mL). *N*-bromosuccinimide (1.10 g, 6.13 mmol, 12.0 eq.) and 3% DBPO were added and the suspension was refluxed for 30 hours while irradiating with a 150W sunlight lamp. The reaction mixture was cooled and all volatiles were removed under reduced pressure. The solid residue was (partially) redissolved in dichloromethane (75 mL) and extracted four times with water (100 mL). After drying with anhydrous sodium sulfate and removal of the solvent the crude product was transferred to a 50 mL Schlenk tube and vacuum dried. A brown suspension formed upon addition of nickel powder (264 mg, 4.5 mmol, 8.8 eq.) and anhydrous DMF (20 mL) in an argon atmosphere, which was heated to 80 °C in the closed vessel for 8 hours and stirred overnight. The reaction was stopped by addition of water and the crude product was transferred to a separation funnel. Dichloromethane (75 mL) was added and the organic layer was washed with water (5 x 200 mL). After drying with anhydrous sodium sulphate, the product was finally purified by column chromatography on silica gel (pentane/dichloromethane 1:1). The product was obtained from the first yellow fraction, a yellow solid 65.7 mg (45 %). Crystals suitable for X-ray analysis were obtained by slow evaporation of a  $CDCl_3$  solution at room temperature.

**Mp:** 285 °C; **<sup>1</sup>H-NMR** (700 MHz, CDCl<sub>3</sub>): δ = 8.44 (d, <sup>3</sup>J = 8.8 Hz, 2H), 7.98 (d, <sup>3</sup>J = 8.8 Hz, 2H), 7.89 (d, <sup>3</sup>J = 8.7 Hz, 2H), 7.84 ppm (d, <sup>3</sup>J = 8.7 Hz, 2H); **<sup>19</sup>F-NMR** (376 MHz, CDCl<sub>3</sub>): AA'BB'C-type δ = -142.17-142.35 (m, *ortho*-2F), -151.04-151.26 (m, *para*-1F), -160.64-160.82 ppm (m, *meta*-2F); **<sup>13</sup>C{<sup>1</sup>H}-NMR** (175 MHz, CDCl<sub>3</sub>): δ = 165.88 (C=O, 2C), 138.98 (C<sub>Hub</sub>, 2C), 135.93 (C<sub>Hub</sub>, 1C), 135.07 (C<sub>Hub</sub>, 2C), 132.31 (C<sub>flank</sub>, 2C), 131.84 (C<sub>flank</sub>, 2C), 131.10 (C<sub>flank</sub>, 1C), 129.86 (C<sub>rim</sub>, 2C), 139.19 (C<sub>rim</sub>, 2C), 127.65 (C<sub>rim</sub>, 2C), 125.48 (C<sub>rim</sub>, 2C), 125.04 ppm (C<sub>ipso</sub>, 2C); **MS** (EI, 150 °C): *m/z* 485.0464 (found), 485.0475 (calc'd), 485 (100 %, [M]<sup>+</sup>), 441 (29 %), 423 (15 %), 248.1 (41 %, [M-C<sub>8</sub>F<sub>5</sub>NO<sub>2</sub>]<sup>+</sup>), 124.1 (17 %, [M-C<sub>8</sub>F<sub>5</sub>NO<sub>2</sub>]<sup>2+</sup>). **IR:** ν = 2919 (m), 292849 (m), 1775 (m), 1724 (s), 1507 (s), 1355 (s), 1293 (s), 1131 (m), 1086 (m), 987 (s), 1386 (w), 900 (m), 842 (m), 797 (s), 732 (s), 701 (s), 642 (s).

### Corannulene-fused heptafluorobutylmaleimide (**3b**)

In a 100 mL round bottom flask, **1b** (143 mg, 0.28 mmol, 1.0 eq.) was dissolved in tetrachloromethane (20 mL). *N*-bromosuccinimide (603 mg, 3.39 mmol, 12.0 eq.) and 3% DBPO were added and the suspension was refluxed for 32 hours while irradiating with a 150W sunlight lamp. The reaction mixture was cooled and all volatiles were removed under reduced pressure. The solid residue was (partially) redissolved in dichloromethane (75 mL) and extracted five times with water (150 mL). After drying with anhydrous sodium sulfate and removal of the solvent the crude product was transferred to a 50 mL Schlenk tube and vacuum dried. A brown suspension formed upon addition of nickel powder (146 mg, 2.46 mmol, 8.8 eq.) and anhydrous DMF (20 mL) in an argon atmosphere, which was heated to 80

°C in the closed vessel for 8 hours and stirred overnight. The reaction was stopped by addition of water and the crude product was transferred to a separation funnel. Dichloromethane (75 mL) was added and the organic layer was washed with water (5 x 200 mL). After drying with anhydrous sodium sulphate, the product was finally purified by column chromatography on silica gel (pentane/dichloromethane 3:1). The product was obtained from the first yellow fraction, a yellow solid 43.4 mg (31 %).

**Mp:** 264 °C; **<sup>1</sup>H-NMR** (700 MHz, CDCl<sub>3</sub>): δ = 8.45 (d, <sup>3</sup>J = 8.8 Hz, 2H), 7.99 (d, <sup>3</sup>J = 8.8 Hz, 2H), 7.90 (d, <sup>3</sup>J = 8.6 Hz, 2H), 7.85 (d, <sup>3</sup>J = 8.6 Hz, 2H), 4.47 (t, <sup>3</sup>J = 15.7 Hz, 2H); **<sup>19</sup>F-NMR** (376 MHz, CDCl<sub>3</sub>): δ = -80.39 (t, <sup>3</sup>J = 9.4 Hz, 3F), -116.85 (dt, J = 15.5, 9.5 Hz, 2F), -127.43 (d, <sup>3</sup>J = 5.1 Hz, 2F); **<sup>13</sup>C{<sup>1</sup>H}-NMR** (175 MHz, CDCl<sub>3</sub>): δ = 166.82 (C=O, 2C), 137.93 (C<sub>Hub</sub>, 2C), 134.93 (C<sub>Hub</sub>, 1C), 135.14 (C<sub>Hub</sub>, 2C), 131.22 (C<sub>flank</sub>, 2C), 130.17 (C<sub>flank</sub>, 2C), 131.11 (C<sub>flank</sub>, 1C), 128.69 (CH<sub>rim</sub>, 2C), 128.03 (CH<sub>rim</sub>, 2C), 126.62 (CH<sub>rim</sub>, 2C), 124.49 (CH<sub>rim</sub>, 2C), 123.96 ppm (C<sub>ipso</sub>, 2C); **MS** (EI, 130 °C): *m/z* 501.0584 (found), 501.0600 (calc'd), 501 (86 %, [M]<sup>+</sup>), 332 (100 %, [M-C<sub>3</sub>F<sub>4</sub>]<sup>+</sup>), 248 (23 %, [M-C<sub>6</sub>H<sub>2</sub>F<sub>7</sub>NO<sub>2</sub>]<sup>+</sup>), 124 (48 %, [M-C<sub>6</sub>H<sub>2</sub>F<sub>7</sub>NO<sub>2</sub>]<sup>2+</sup>). **IR:** ν = 2961 (m), 2921 (m), 2845 (m), 1741 (w), 1723 (w), 1518 (w), 1457 (w), 1375 (m), 1259 (m), 1090 (m), 1011 (s), 867 (w), 785 (s), 690 (w), 663 cm<sup>-1</sup> (w)

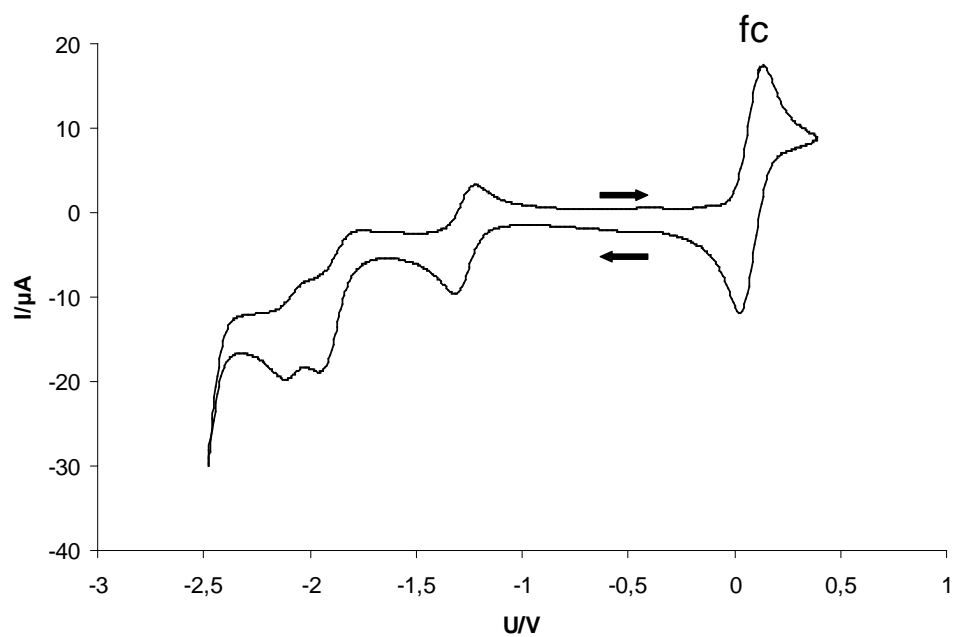
## Cyclic Voltammetry

Cyclic voltammetry was measured on a MaterialsM 510 potentiostat using a Schlenk measuring cell with three platinum wires as electrodes. Measurements were conducted in dry dichloromethane and THF with tetra-*n*-butylammonium hexafluorophosphate (0.1 M) as conducting salt, an electrolyte concentration of  $5 \times 10^{-4}$  M and a scan rate of 0.1 V/s was used for all measurements.

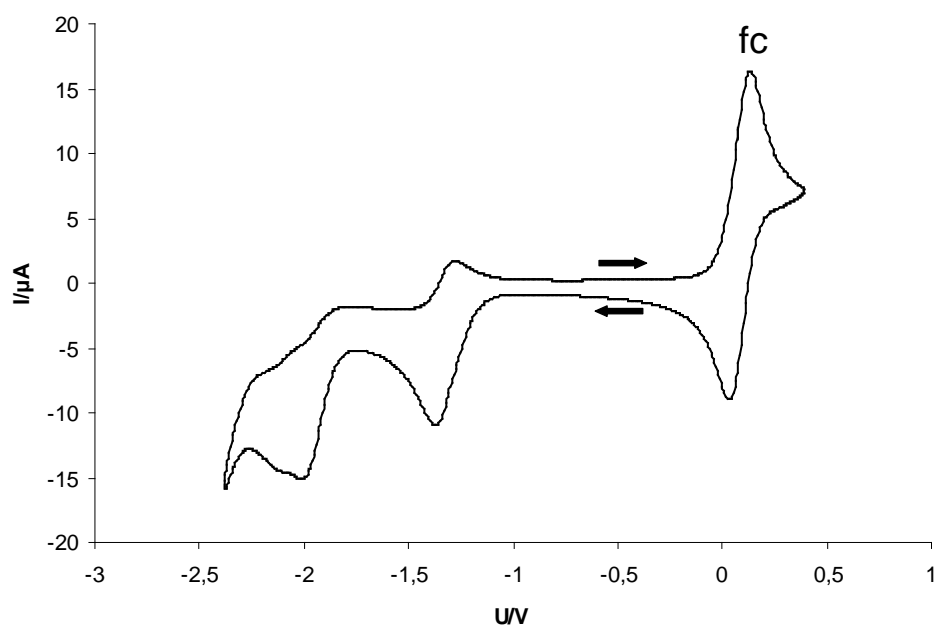
Compound	$E_0$ vs ferrocene in $\text{CH}_2\text{Cl}_2$	$E_{\text{LUMO}}$	$E_0$ vs ferrocene in THF
<b>1a</b>	-1.714	-3.1 eV	n.d.
<b>1b</b>	-1.771	-3.1 eV	n.d.
<b>2</b>	irreversibel reduction	-	n.d.
<b>3a</b>	-1.352	-3.4 eV	-1.364 -2.056
<b>3b</b>	-1.409	-3.4 eV	-1.468 -2.145

**Table S1.**  $E_0$  obtained from CVs.

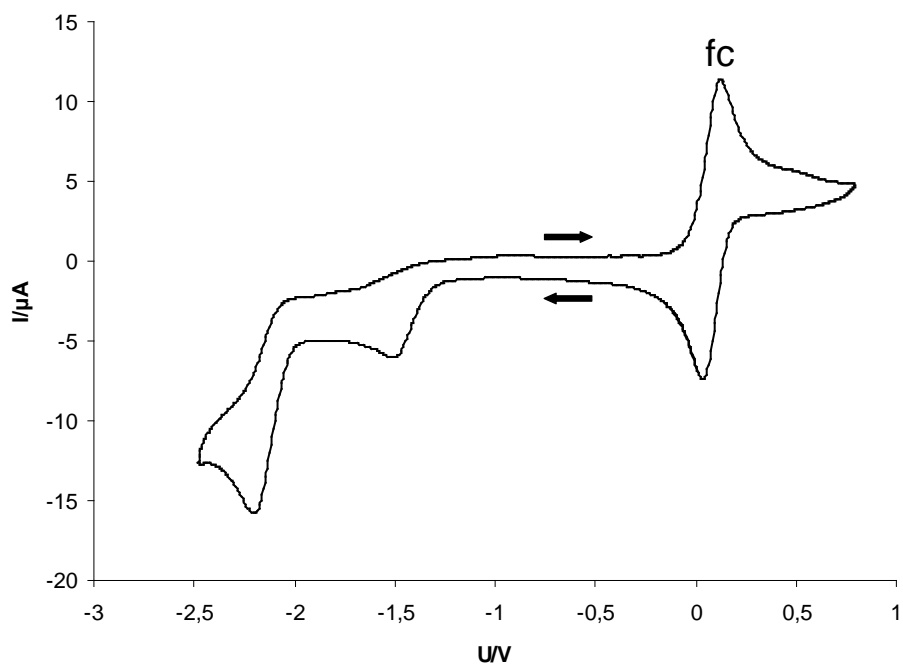




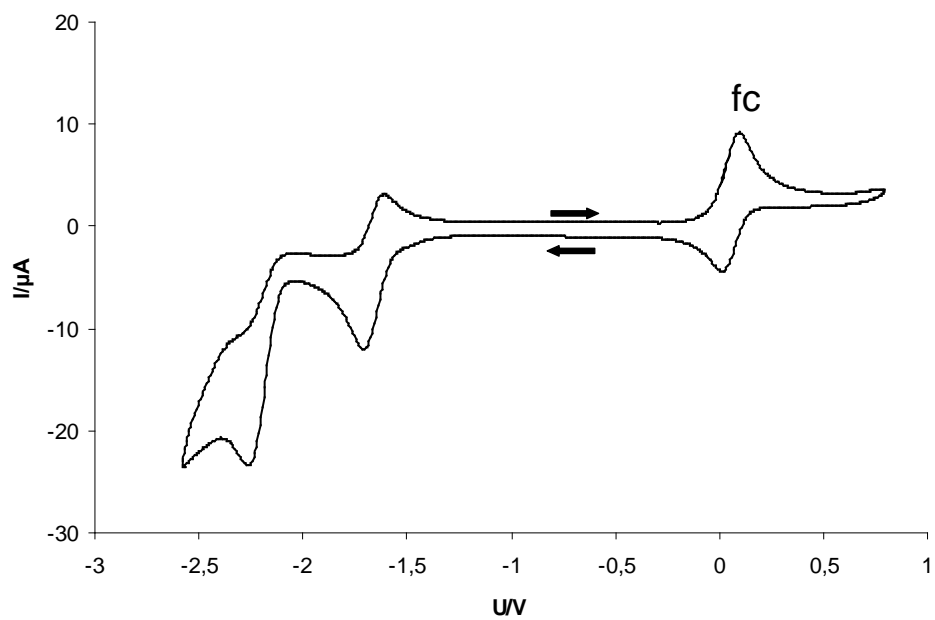
**Figure S1. 3a** in CH<sub>2</sub>Cl<sub>2</sub>



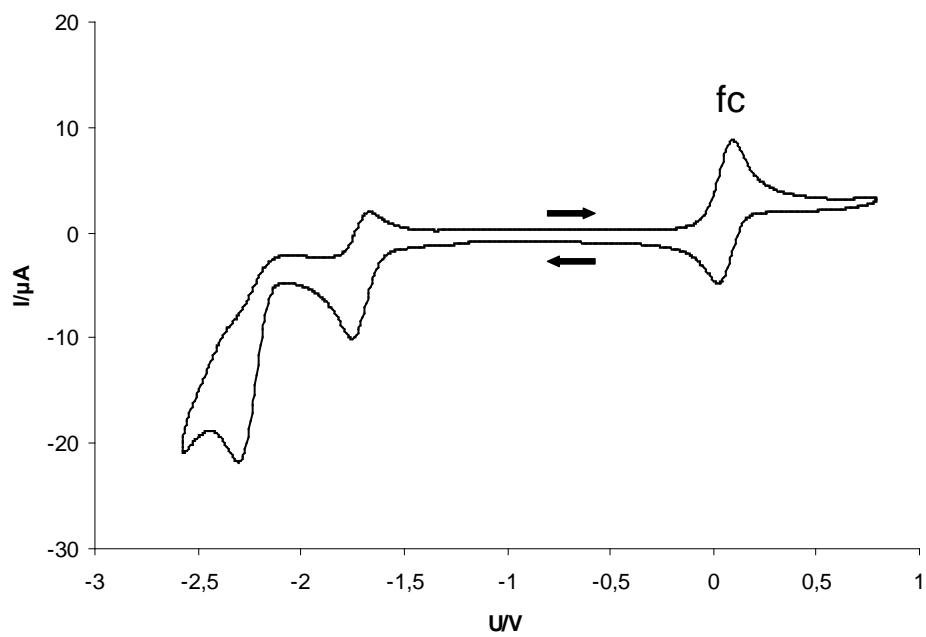
**Figure S2. 3b** in CH<sub>2</sub>Cl<sub>2</sub>



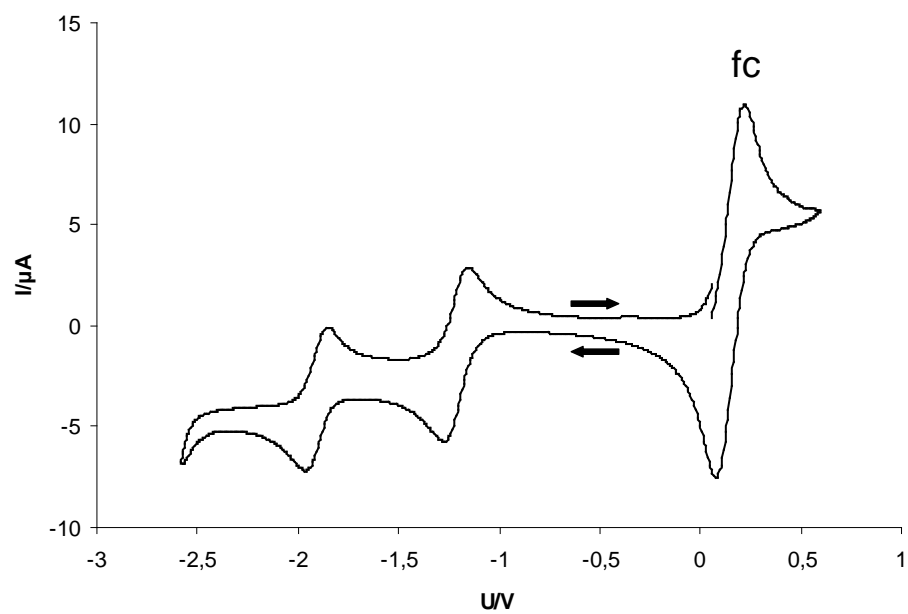
**Figure S3. 2** in  $\text{CH}_2\text{Cl}_2$



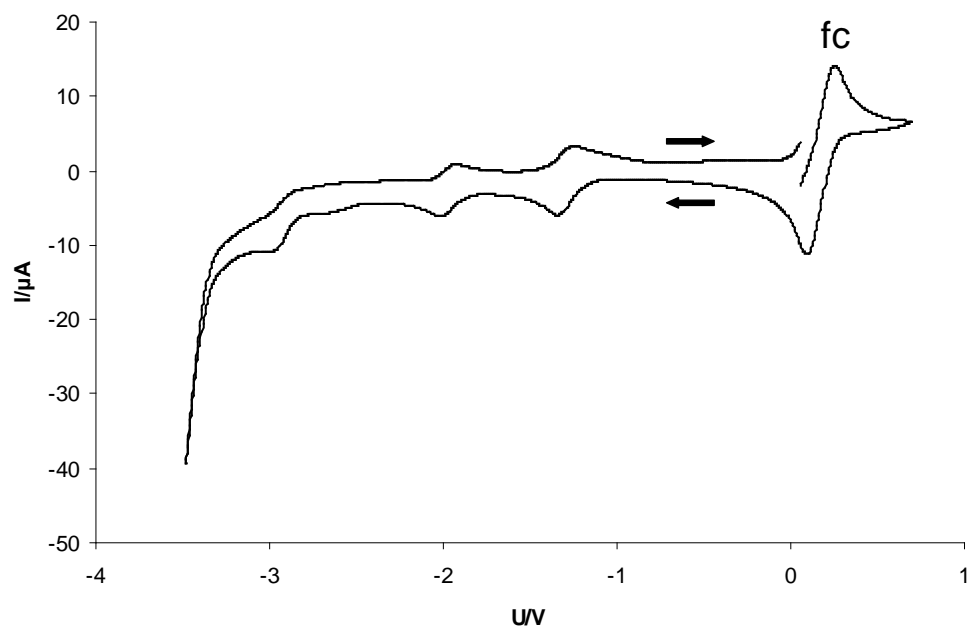
**Figure S4. 1a** in  $\text{CH}_2\text{Cl}_2$



**Figure S5. 1b** in CH<sub>2</sub>Cl<sub>2</sub>



**Figure S6. 3a** in THF.



**Figure S7. 3b** in THF

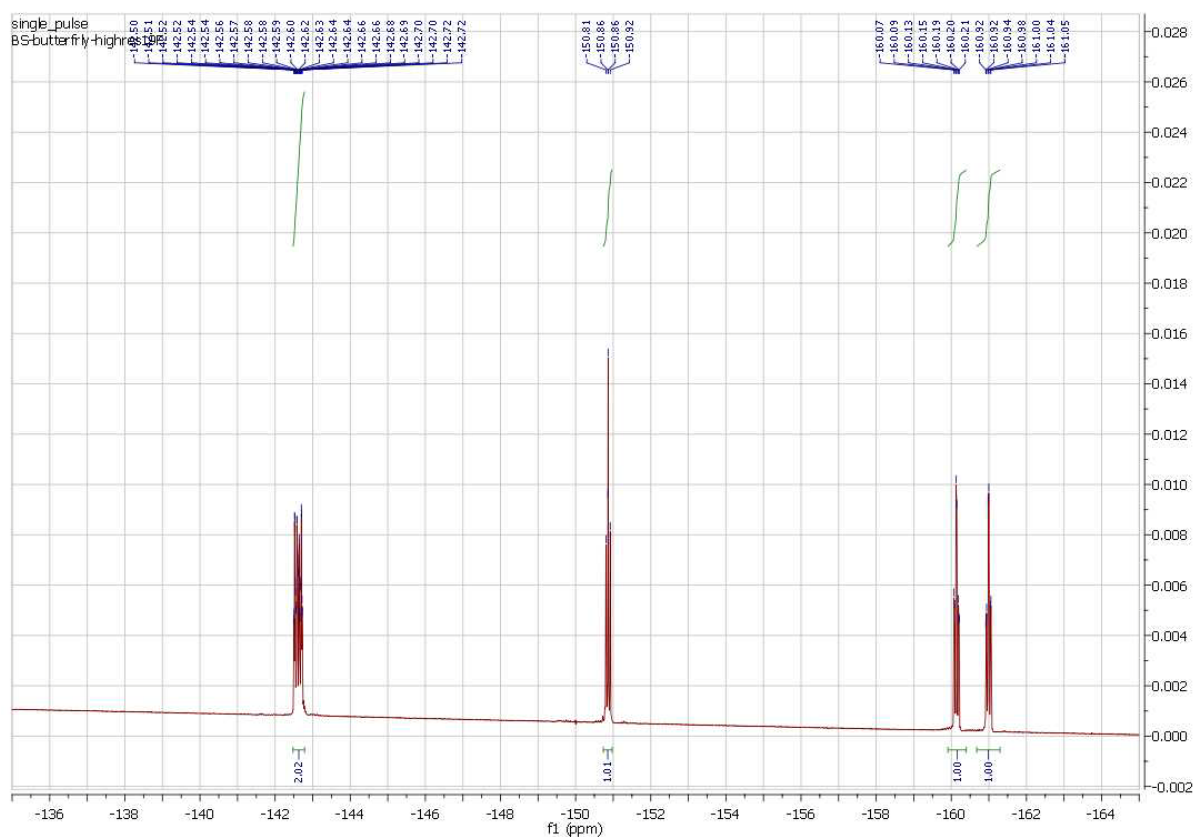


Figure S8.  $^{19}\text{F}$ -NMR spectrum of 2

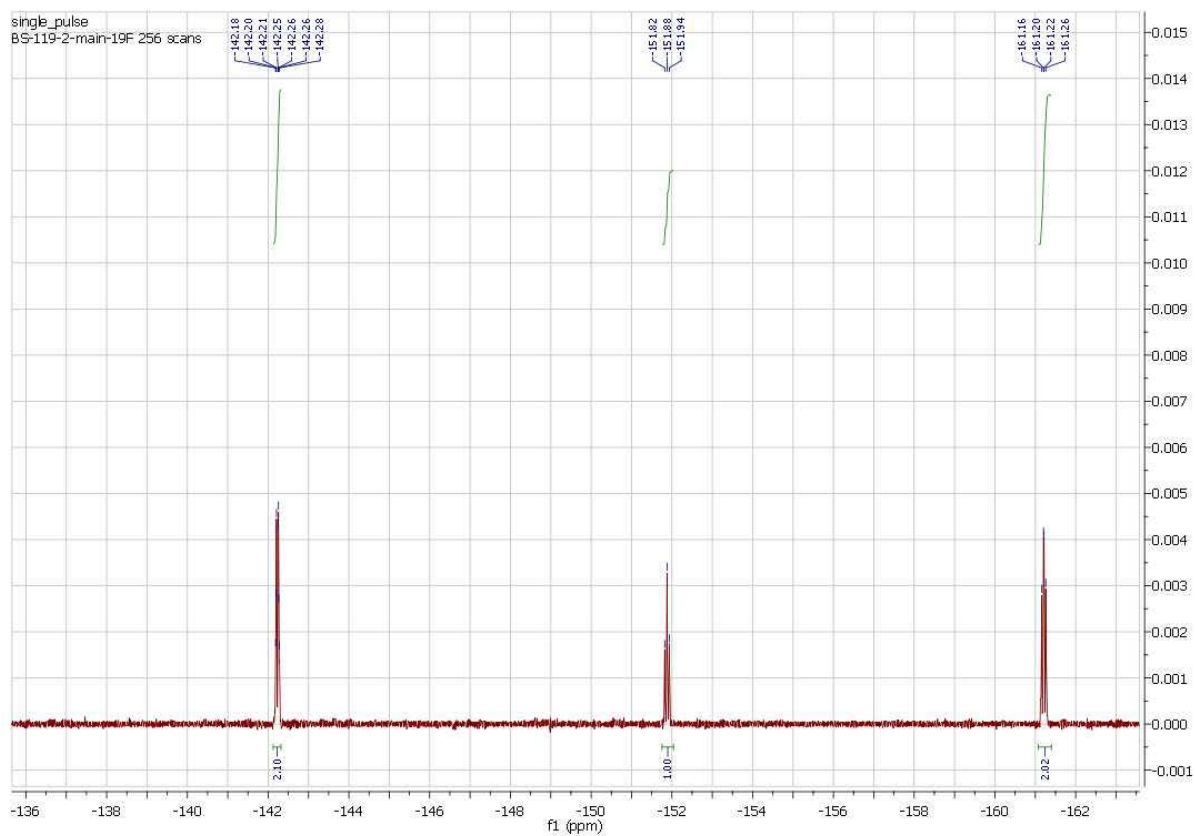


Figure S9.  $^{19}\text{F}$ -NMR spectrum of 1a

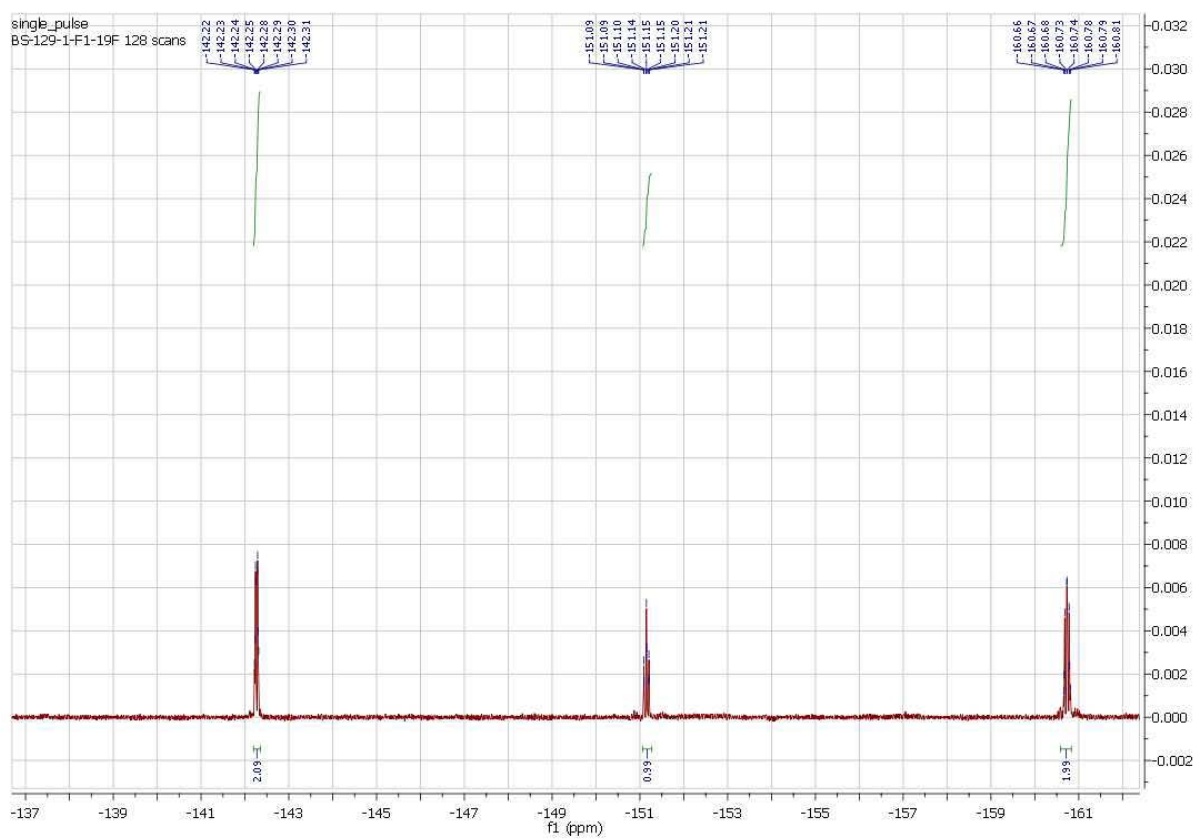
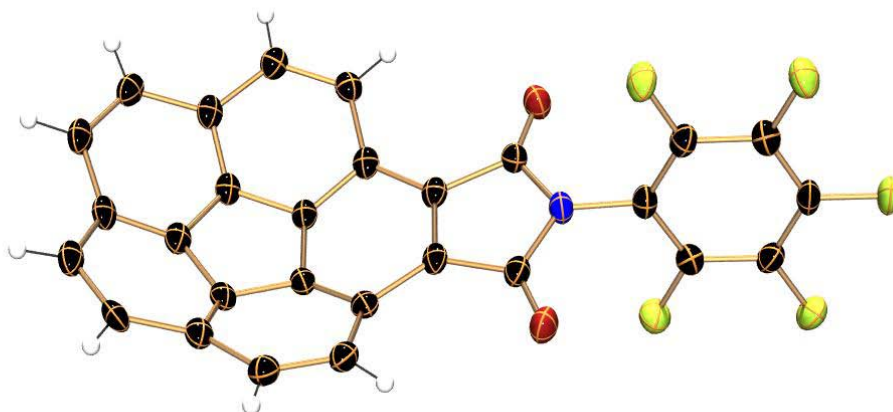
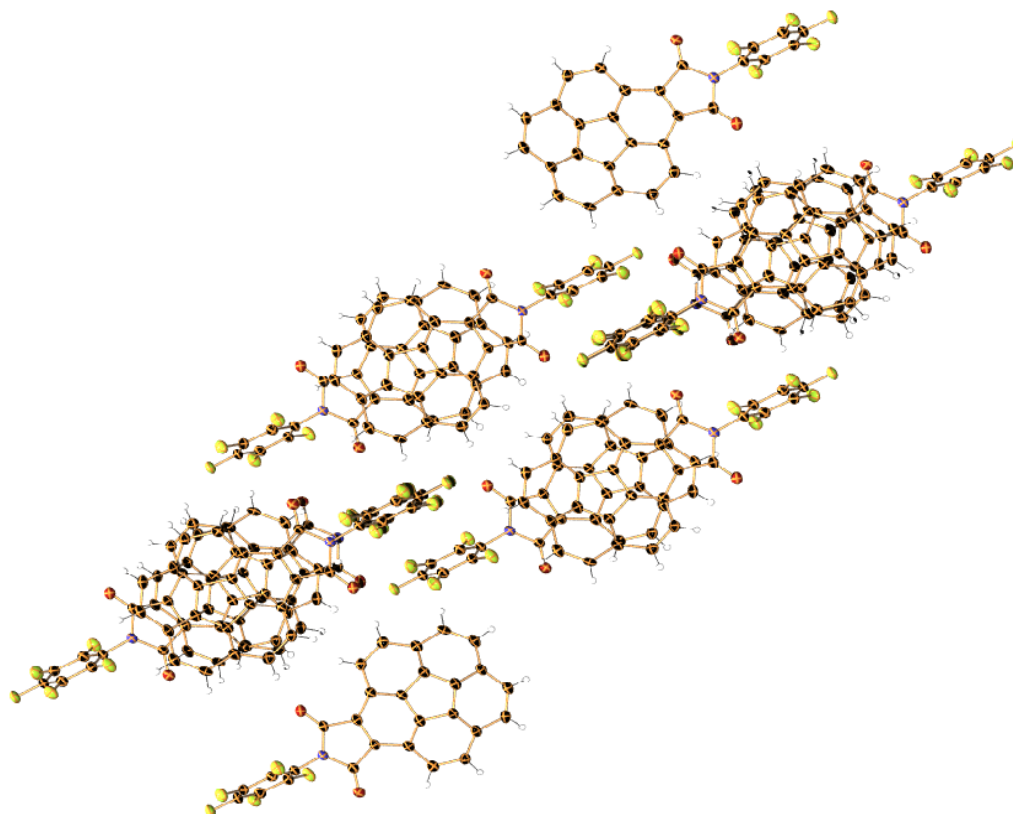


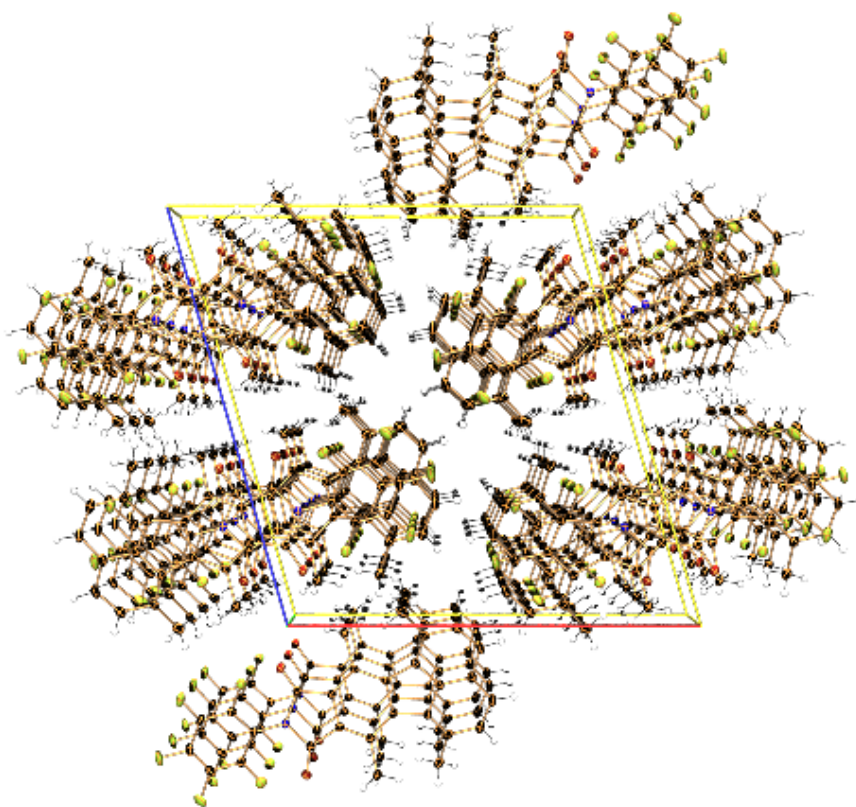
Figure S10.  $^{19}\text{F}$ -NMR spectrum of 3a



**Figure S11.** 50 % probability ellipsoids representation of the asymmetric unit of **3a**.



**Figure S12.** Columnar packing of **3a**.



**Figure S13.** Columnar packing of **1a**.

**References:**

[S1] K. Bynum, R. Prip, R. Callahan and R. Rothchild, *J. Fluorine Chem.*, 1998, **90**, 39-46.