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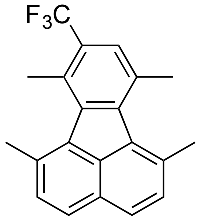
1. General

Melting points were determined on a Gallenkamp Melting Point Apparatus or Stanford Research Systems MPA100. IR spectra were recorded on a Nicolet iS10 MFR FT-IR Sp spectrometer or a JASCO FT IR-4100 spectrometer (signals are denoted as following, s (strong), m (middle) and w (weak)). ^{1}H, ^{19}F and ^{13}C-NMR spectra were measured on a JEOL ECS 400/500 spectrometer or on a Bruker Instruments AVIII 700 at 23 °C. $CDCl_3$ and CD_2Cl_2 were used as solvents and the residual solvent peak was taken as an internal standard (^{1}H-NMR: $CDCl_3$ 7.26, CD_2Cl_2 5.30 ppm; ^{13}C-NMR: $CDCl_3$ 77.0 ppm, CD_2Cl_2 54.0 ppm; always proton-decoupled), ^{19}F-NMR spectra were referenced against external $CFCl_3$. Mass spectra were measured on a MAT CH7A (EI, 80 eV, 3 kV) or on a on a JEOL JMS-777V. High-resolution masses were determined by peak match method against perfluorokerosene. Gel permeation chromatography (GPC) was performed on JAIGEL 1H and 2H using a JAI Recycling Preparative HPLC LC-908W. TLC analysis was performed using Merck Silica gel 60 F_{254}.

2. Synthesis

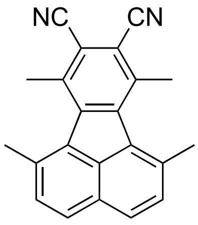
2.1. 1,6,7,10-Tetramethyl-8- (trifluoromethyl)fluoranthene (1)



A flask was charged with 68 mL methanol and potassium hydroxide (27.5 g, 492.2 mmol, 23.0 eq.) was added portion wise. The solution was headed to 80 °C for 10 min and afterwards allowed to slowly cool to room temperature. 3-Pentanone (14.5 g, 171.3 mmol, 8.0 eq.) and 3,8-dimethylacenaphthylene-1,2-dione (4.5 g, 21.4 mmol, 1.0 eq.) were added portion wise to the cooled solution. The mixture was allowed to stir at room temperature for 2 h and then cooled to 0 °C. A cooled solution of *conc.* hydrochlorid acid (58 g) in water (116.5 g) was added dropwise to the reaction mixture. Once the suspension turned green yellow it was extracted two times with dichloromethane (100 mL). The combined organic fractions were washed with water (100 mL), dried over anhydrous sodium sulfate, filtered and evaporated. The residue was dissolved in acetic anhydride (52 mL) and degassed trifluoropropyne (9.0 g, 96.3 mmol, 2.0 eq.) was condensed into the flask. The mixture was allowed to warm to room temperature and consequently heated to 80 °C for seven days. The cooled reaction mixture was evaporated under reduced pressure, leaving a viscose liquid that was purified by column chromatography using silica gel and *n*-pentane. The product was obtained as pale yellow crystals 1.62 g (23 %).

Mp: 69-71 °C; **^{1}H NMR** (700 MHz, CDCl$_3$): δ = 7.71 (d, ^3J = 8.2 Hz, 1H), 7.71 (d, ^3J = 8.2 Hz, 1H), 7.71 (d, ^3J = 8.2 Hz, 1H), 7.38 (d, ^3J = 8.2 Hz, 1H), 7.36 (d, ^3J = 8.2 Hz, 1H), 2.84 (s, 3H), 2.83 (s, 3H), 2.78 (s, 3H), 2.77 ppm (s, 3H); **^{19}F NMR** (376 MHz, CDCl$_3$): δ = 59.53 (s, 3 F) ppm. **^{13}C{^{1}H} NMR** (176 MHz, CDCl$_3$): δ = 142.6, 142.0, 134.0, 133.9, 133.2, 133.1, 132.7, 131.8, 131.6, 129.0, 128.3 (q, ^3J = 5.6 Hz), 128.2 (q, ^1J = 28.6 Hz), 127.8, 127.0, 126.6, 126.6, 125.4 (q, ^1J = 272.3 Hz), 24.8, 24.8, 24.1, 19.8 ppm; **^{13}C{^{1}H, ^{19}F} NMR** (176 MHz, CDCl$_3$): δ = 142.8, 142.2, 134.3, 134.3, 133.6, 133.4, 133.1, 132.1, 132.0, 129.3, 128.6, 128.3, 128.2, 127.3, 126.9, 126.8, 125.4, 25.2, 25.0, 24.4, 19.9 ppm; **MS** (EI, 40 °C): m/z = 326.1 (100 %, [M]$^{+\cdot}$), 311.1 (77 %, [M-CH$_3$]$^+$); **IR**: v = 3043 (w), 2953 (w), 2921 (w), 2863 (w), 1894 (w), 1613 (w), 1595 (w), 1505 (m), 1463 (m), 1440 (m), 1414 (m), 1397 (w), 1363 (m), 1350 (m), 1307 (m), 1283 (s), 1207 (s), 1190 (m), 1162 (m), 1143 (s), 1103 (s), 1049 (m), 1027 (m), 974 (m), 886 (m), 870 (w), 834 (s), 821 (m),795 (m), 718 (m), 698 (w), 673 (w), 641 (m), 627 (m), 613 (w), 545 (m) cm^{-1}.

2.2 1,6,7,10-Tetramethylfluoranthene-8,9-dicarbonitrile (7)



In a 100 mL Schlenk flask 3,8-dimethylacenaphthylene-1,2-dione (300 mg, 1.43 mmol, 1.0 eq.), pentan-3-one (0.81 mL, 7.62 mmol, 5.3 eq.) were suspended in methanol (16.5 mL). A solution of potassium hydroxide (660 mg, 12.00 mmol, 8.4 eq.) in methanol (3.3 mL) was added by syringe and the mixture was stirred for one hour at room temperature. The yellow solution was diluted with 30 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 a solution of dicyanoacetylene (217 mg, 2.85 mmol, 2.0 eq.) in 1,2-dichloroethane (2.6 mL), additional 1,2-dichloroethane (5 mL) and three drops of acetic anhydride were added to the crude solid. The yellow solution was stirred at 50 °C for 15 hours. The cooled reaction mixture was evaporated under reduced pressure, leaving a solid residue that was filtrated through a short plug of silica gel with dichloromethane as eluent. The product was obtained as a yellow solid 385 mg (88 %).

Mp: gradually darkens above 267 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.86 (½ AB, ^3J = 8.2 Hz, 2H), 7.47 (½ AB, ^3J = 8.2 Hz, 2H), 2.92 (s, 6H), 2.84 ppm (s, 6H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ = 143.75 (2C), 135.73 (2C), 135.44 (2C), 134.09 (1C), 132.39 (2CH), 132.01, 129.04 (2CH), 126.70, 116.34 (2CN), 115.37 (2C), 25.17 (2C), 22.66 ppm (2C); **MS** (EI, 120 °C): *m/z* 308.1326 (found), 308.1314 (calc'd), 308 (100 %, $[M]^{+\cdot}$), 293 (72 %, $[M\text{-}CH_3]^+$), 277 (17 %, $[293\text{-}CH_3]^+$); **IR**: ν = 2964 (w), 2926 (w), 2216 (s), 1608 (m), 1456 (s), 1438 (m), 1409 (s), 1262 (s), 1022 (s), 1197 (m), 1153 (m), 1022 (s), 844 (s), 790 (m), 627 (s) cm^{-1}.

3. Computational details

The optimization of the fluoranthenes was carried out with the Gaussian 03 program, using gas-phase density functional theory calculations at B3LYP/6-311G(d,p) level of theory. The following input was used for all calculations.

```
#p opt freq=noraman b3lyp/6-311g(d,p) geom=connectivity pop=minimal
```

Obtained dipoles for the optimized fluoranthenes in the gas phase are given in Debye.

1: 3.4372

2: 5.8324

3: 2.4950

4: 0.7326

5: 2.317

6: 4.9054

7: 9.2635

4. Crystallographic details

Compound reference	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Chemical formula	$C_{21}H_{17}F_3$	$C_{22}H_{16}F_6$	$C_{23}H_{14}F_9$	$C_{48}H_{28}F_{24}$	$C_{24}H_{14}F_{12}$	$C_{32}H_{16}F_{10}$	$C_{22}H_{16}N_2$
Formula Mass	326.36	394.35	462.35	1060.70	530.36	590.45	308.37
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic
a/Å	21.1643(12)	16.028(5)	8.943(2)	12.479(2)	11.817(3)	30.365(11)	12.017(2)
b/Å	11.9365(6)	12.352(4)	9.827(2)	11.3269(19)	21.237(4)	12.085(4)	7.1071(14)
c/Å	12.8317(8)	17.520(5)	21.451(5)	29.181(5)	8.2580(16)	13.365(5)	35.635(7)
α/°	90	90	90	90	90	90	90
β/°	106.5350(19)	104.455(19)	97.064(5)	101.941(2)	97.474(2)	90	92.848(5)
ɣ/°	90	90	90	90	90	90	90
Unit cell volume/Å^3	3107.6(3)	3358.8(18)	1870.8(7)	4035.5(12)	2054.9(7)	4905(3)	3039.7(10
Temperature/K	100(2)	108(2)	100(2)	123(2)	153	133(2)	133(2)
Space group	$P2_1/c$	$I2/a$	$P2_1/c$	$P2_1/c$	$P2_1/c$	Pccn	$I2/a$
Z	8	8	4	4	4	8	8
No. of reflections measured	23923	19536	14069	8738	7879	36886	14214
No. of independent reflections	5485	4176	3819	7359	4015	4318	4509
R_{int}	0.0588	0.0229	0.0241	0.0255	0.0162	0.0556	0.0227
Final R_1 values (I > 2σ(I))/	0.0567	0.0352	0.0474	0.0505	0.0504	0.0663	0.0462
Final $wR(F^2)$ values (I > 2σ(I))	0.1301	0.0883	0.1089	0.1387	0.050	0.1364	0.1194
Final R_1 values (all data)	0.0929	0.0516	0.0538	0.0585	0.0504	0.0914	0.0596
Final $wR(F^2)$ values (all data)	0.1460	0.1009	0.1116	0.1453	0.0599	0.1477	0.1313
Goodness of fit on F^2	1.1018	1.040	1.218	0.992	3.246	1.093	1.062
CCDC	1522468	1522469	1522467	1522470	1522473	1522471	1522472

Table 1 Crystallographic data and structure refinement parameters for **1**-**7**.

5. Observed contacts

Observed contacts in the solid state structure of compound **1**

C-H···F contact 2.546 H7-F5
C-H···F contact 2.736 H18A-F6
C-H···F contact 2.786 H18B-F6
C-H···F contact 2.812 H17B-F2
C-H···F contact 2.829 H28-FF1
C-H···F contact 2.875 H39A-F3
C-H···F contact 2.921 H38C-F4
C-H···F contact 2.923 H29-F2
C-H···F contact 2.942 H19C-F1
C-H···F contact 2.990 H17C-F3

C-H···π contact 2.531 (Benz-Methyl···Benz-Centroid) H20B-
C-H···π contact 2.893 (Naphtha-H···Benz-Centroid) H25-

Observed contacts in the solid state structure of compound **2**

C-H···F contact 2.649 H22B-F5
C-H···F contact 2.817 H22C-F1
C-H···F contact 2.871 H20A-F6
C-H···F contact 2.736 H19A-F6
C-H···F contact 2.742 H21C-F6
C-H···F contact 3.046 H19B-F6
C-H···F contact 2.817 H3-F2
C-H···F contact 2.539 H5-F4

C-H···π contact 3.226 (Benz-Methyl···Benzene) H19C
C-H···π contact 3.336 (Benz-Methyl···Naphtalene) H22A
C-H···π contact 2.974 (Methyl···Benzene)
C-H···π contact 2.975 (Naphtha-Methyl···Benzene) H20B-

Observed contacts in the solid state structure of compound **3**

C-H···F contact 2.604 H22C-F3
C-H···F contact 2.627 H16-F1
C-H···F contact 2.678 H21C-F5
C-H···F contact 2.757 H22A-F5
C-H···F contact 2.813 F1-H21B
C-H···F contact 2.825 H1SC-F2
C-H···F contact 2.842 H16-F4

C-H···F contact 2.858 H22C-F6

C-H···F contact 2.883 H18C-F4

C-H···F contact 2.919 H18B-F2

C-H···F contact 2.960 (benz-methyl···disordered-CF3)

Naphthalene-Naphthalene π···π distance 3.831
Naphthalene five membered ring π···π stacking 3.845

C-H···π contact 2.929 (Naphtha-H···Naphtha)

C-H···π contact 2.965 (Naphtha-H···Naphtha)

C-H···π contact 3.093 (Naphtha-H···Naphtha)

C-H···π contact 2.929 (Naphtha-H···Naphtha)

Observed contacts in the solid state structure of compound **4**

C-H···π contact **2.833** (Naphtha-Methyl···Naphtha-Centroid) H38c-

C-H···π contact **3.201** (Naphtha-Methyl···Naphtha-Centroid) H24c-

C-H···F contact **2.475** H2b-F5 “inner layer”

C-H···F contact **2.815** H24b-F12 “inner layer”

C-H···F contact **2.850** H24c-F1 “inner layer”

C-H···F contact **2.886** H32-F1 “inner layer”

C-H···F contact **2.906** H24b-F3 “inner layer”

C-H···F contact **2.780** H8a-F20 “inner layer”

C-H···F contact **2.780** H8c-F6 “inner layer”

C-H···F contact **2.763** H25-F6 “inner layer”

C-H···F contact **2.913** H8a-F11 “inner layer”

C-H···F contact **2.877** H16-F9 “inner layer”

C-H···F contact **2.946** H25b-F5 “inner layer”

C-H···F contact **2.723** H2a-F18 “inner layer”

C-H···F contact **2.944** H40c-F17 “inner layer”

C-H···F contact **2.533** H43b-F21 “inner layer”

C-H···F contact **2.795** H24a-F11 “inner layer”

C-H···F contact **2.706** H13c-F13 “inner layer”

C-H···F contact **2.946** H31a-F22 “inter layer”

C-H···F contact **2.861** H40c-F2 “inter layer”

C-H···F contact **2.620** H43c-F10 “inter layer”

Observed contacts in the solid state structure of compound **5**

C-H···F contact **2.586** H2-F9

C-H···F contact **2.817** H6-F10

C-H···F contact **2.531** F10-H6

C-H···F contact **2.833** H5-F1

C-H···F contact **2.547** H9-F7

C-H···F contact **2.631** H10-F1

C-H···F contact **2.684** H13-F4

C-H···F contact **2.890** H12-F5

Observed contacts in the solid state structure of compound **6**

C-H···π contact 3.621 (Aromatic···Naphtha) H8-

C-H···π contact 3.089 (Naptha-Methyl···Benzene) H18B-

C-H···π contact 3.007 (Benz-Methyl···Naphtha) H19b-

C-H···F contact 2.399 H20B-F8A

C-H···F contact 2.528 H17B-F5

C-H···F contact 2.546 H18a-F5

C-H···F contact 2.591 H20A-F10

C-H···F contact 2.785 H20C-F5

C-H···F contact 2.801 H17B-F4

C-H···F contact 3.064 H7-F4

C-H···F contact 3.042 H5-F3