Electronic Supplementary Information

Perfluoro-1,1'-biphenyl and perfluoronaphthalene and their derivatives as π-acceptors for anions

Hai Yi, Markus Albrecht,* Arto Valkonen and Kari Rissanen

Content

Experimental section..................................................................................................................... 2
Methods of $^{19}$F NMR titration for 1 or 2 .......................................................................................... 5

$^{19}$F NMR titration of acceptor 1 with tetrabutylammonium bromide (TBA·Br) ...................... 6
$^{19}$F NMR titration of acceptor 1 with tetrabutylammonium chloride (TBA·Cl) ...................... 7
$^{19}$F NMR titration of acceptor 1 with tetrabutylammonium fluoride (TBA·F) ....................... 8
$^{19}$F NMR titration of acceptor 1 with tetrabutylammonium iodide (TBA·I) ......................... 9
$^{19}$F NMR titration of acceptor 1 with tetrabutylammonium nitrate (TBA·NO$_3$) ............ 10
$^{19}$F NMR titration of acceptor 1 with tetrabutylammonium tetrafluoroborate (TBA·BF$_4$) .... 11
$^{19}$F NMR titration of acceptor 2 with tetrabutylammonium bromide (TBA·Br) ................. 12
$^{19}$F NMR titration of acceptor 2 with tetrabutylammonium chloride (TBA·Cl) ................. 13
$^{19}$F NMR titration of acceptor 2 with tetrabutylammonium fluoride (TBA·F) ................. 14
$^{19}$F NMR titration of acceptor 2 with tetrabutylammonium iodide (TBA·I) ....................... 15
$^{19}$F NMR titration of acceptor 2 with tetrabutylammonium nitrate (TBA·NO$_3$) ............ 16
$^{19}$F NMR titration of acceptor 2 with tetrabutylammonium tetrafluoroborate (TBA·BF$_4$) .... 17

Thermal ellipsoid (50 % probability) diagram of the structure 3............................................. 18
Thermal ellipsoid (50 % probability) diagram of the structure 4............................................. 18
Experimental section

General experiment conditions

All commercially available reagents were used as received. Solvents were distilled and used without further purification. $^1$H (300 MHz or 400 MHz) and $^{19}$F (282 or 376 MHz) NMR spectra were obtained with a Varian Mercury 300 or Inova 400 spectrometer in deuterated solvents. The mass spectrometric data were recorded with a Finnigan SSQ 7000 and a Thermo Deca XP system by using EI (70 eV) or ESI, and the infrared spectra were measured with a PerkinElmer FTIR spectrometer (Spectrum 100). The sample was measured in KBr (4000–650 cm$^{-1}$). Elemental analyses were performed with a CHN-O-Rapid Vario EL system from Heraeus. HRMS were performed with a Thermo Scientific LTQ XL system. The melting points were measured with a Büchi B-540 system and were not corrected.

Single crystal X-ray data were collected at 173(2) K using Agilent SuperNova diffractometer (3) and at 123(2) K using a Bruker-Nonius KappaCCD diffractometer with an APEX-II detector (4) and utilizing monochromatized Mo-Kα ($\lambda = 0.71073$ Å) radiation. The data collection, data reduction and multi-scan absorption correction for 3 were made by program CrysAlisPro.$^{1a}$ COLLECT$^{1b}$ software was used for the data collection ($\theta$ and $\omega$ scans), DENZO-SMN$^{1c}$ for the processing and SADAB$^{1d}$ for multi-scan absorption correction for data of 4. The structures were solved by direct methods with SIR2004$^{1e}$ and refined by full-matrix least-squares methods with WinGX-software,$^{1f}$ which utilizes the SHELXL-97 module.$^{1f}$ All C–H hydrogen positions were calculated and refined as a riding atom model with 1.2 or 1.5 times the thermal parameter of the C atoms. H-atom bonded to O in 4 was found from the electron density map and restrained (by DFIX, s = 0.02) to a distance of 0.84 Å from O atom with thermal parameter of 1.5 times the O atom parameter. CCDC 1014200 (3) and 1014201(4).

Synthesis of compounds

2,2',3,3',5,5',6,6'-Octafluoro-4,4'-dimethyl-1,1'-biphenyl 5. Under Nitrogen atmosphere, PFBP (2.3 g, 7.0 mmol) was dissolved in THF (7.0 mL) and cooled to 0 °C. Methyllithium (14.0 mmol, 1.6 M sol. in diethyl ether) was added dropwise into the solution. The mixture was stirred overnight at the same temperature and then was allowed to warm to room temperature. After completion of reaction, the mixture was washed with saturated NaCl aqueous solution (3 x 20 mL) and extracted with ethyl acetate (3 x 15 mL). The organic layers were combined and dried with Na$_2$SO$_4$, filtered. Then the organic solution was removed under vacuum, finally the residua were obtained and separated with column chromatography on a silica gel using Hexane as eluent. Compound 5 was obtained as a white solid with yield of 88% (2.0 g, 6.2 mmol). m.p.: 142.3-143.9 °C; $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 2.29$ (t, $J = 2.1$ Hz, 6H); $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta = -140.29$ (dd, $J = 16.4$ Hz, $J = 8.2$ Hz, 4F), -142.90 (d, $J = 9.9$ Hz, 4F); EI-MS: m/z: 326.3 (52.77%), 325.4 (56.73%), 324.3 (63.83%), 162.6 (100%), 160.9 (86.05%); IR(KBr, cm$^{-1}$):

4,4'-Bis(bromomethyl)-2,2',3,3',5,5',6,6'-octafluoro-1,1'-biphenyl 6. A mixture of compound 5 (1.6 g, 5.0 mmol) and N-Bromosuccinimide (1.8 g, 10.0 mmol) in CCl₄ (10.0 mL) was refluxing for 10 h. After completion of reaction, the mixture was washed with saturated NaCl aqueous solution (3 x 20 mL) and extracted with ethyl acetate (3 x 15 mL). The organic layers were combined and dried with Na₂SO₄ filtered. The solvent was evaporated and the residue was purified by column chromatography on a silica gel using hexane as eluent to afford the 6 as a white solid (1.2 g, 2.4 mmol, 48%). m.p.: 146.4-147.6 °C; ¹H NMR (300 MHz, CDCl₃): δ = 4.51 (s, 4H); ¹³C NMR (282 MHz, CDCl₃): δ = -137.45 (dd, J = 16.4 Hz, J = 8.5 Hz, 4F), -141.57 (d, J = 8.7 Hz); EI-MS: 405.0 (8.90%), 403.4 (14.96%), 324.5 (100.00%), 316.0 (97.35%), 256.2 (25.52%); IR(KBr, cm⁻¹): 1470, 1321, 1268, 1222, 1167, 1120, 1068, 1026, 929, 861, 805, 759, 721; Anal. Calcd. for C₁₄H₈Br₂F₈: C, 4.0 mmol; Found: C, 8.40 mmol.

1,1'-(Perfluoro-[1,1'-biphenyl]-4,4'-diyl)bis(methylene)bis(1,4-diazabicyclo[2.2.2]octan-1-ium) bromide 3. Compound 6 (1.0 g, 2.0 mmol) was dissolved in dichloromethane (2.0 mL), then DABCO (0.4 g, 4.0 mmol) was added and stirred at room temperature. After 10 min, white precipitate was generated from the solution. The mixture was continued to stir overnight and the white solid was filtered and dried under vacuum to obtain pure compound 3 (1.3 g, 1.9 mmol, 95%). m.p.: 270 °C decomposition; ¹H NMR (300 MHz, DMSO-d₆): δ = 3.05 (t, J = 6.9 Hz, 12H), 4.75 (s, 4H); ¹³C NMR (282 MHz, DMSO-d₆): δ = -138.03 (dd, J = 12.1 Hz, J = 7.9 Hz, 4F); ESI-MS: 274.1 [3-3Br⁺²], 627.1 [3-Br⁺³]; IR(KBr, cm⁻¹): 3417, 2954, 2889, 2798, 2594, 2317, 2191, 2030, 1971, 1654, 1469, 1381, 1334, 1264, 1188, 1057, 992, 936, 886, 844, 793, 722, 663.

Crystal data for 3: Colourless plates from MeOH/Et₂O, C₂₀H₂₈Br₂F₈N₄, F.W. = 708.34, crystal size 0.15 × 0.10 × 0.03 mm, monoclinic, space group C2 (no. 5), a = 13.0391(5), b = 6.8246(3), c = 15.9891(10) Å, α = γ = 90°, β = 92.828(5), V = 1421.08(12) Å³, Z = 2, Dcalc = 1.655 Mg·m⁻³, µ = 2.928 mm⁻¹, F(000) = 708, 2711 collected reflections (θmax = 25.25°) of which 2013 independent (Rint = 0.0245) and 1774 with I > 2σ(I), Tm = 0.9173, Tm = 0.6678, full-matrix least-squares on F² with 1 restraint and 190 parameters, GOF = 1.052, R₁ = 0.0382 [I > 2σ(I)], wR² (all data) = 0.1038, largest peak/hole = 0.646 / -0.358 e.Å⁻³, Flack parameter = 0.015(15).

1,2,3,4,5,6,8-Heptafluoro-7-methylphenanthrene 7. Under Nitrogen atmosphere, PFN (1.9 g, 7.0 mmol) was dissolved in Et₂O (7.0 mL) and cooled to 0 °C. Methyllithium (7.0 mmol, 1.6 M sol. in diethyl ether) was added dropwise into the solution. The mixture was stirred overnight at the same temperature and then was allowed to warm to room temperature. After completion of reaction, the mixture was washed with saturated NaCl aqueous solution (3 x 20 mL) and extracted with ethyl acetate (3 x 15 mL). The organic layers were combined and dried with Na₂SO₄ filtered. Then the organic solution was removed under vacuum, finally the residua were obtained and separated with column chromatography on a silica gel using Hexane as eluent. Compound 7 was obtained as a white solid with yield of 82% (1.5 g, 5.7 mmol). m.p.: 53.1-53.9 °C; ¹H NMR (400 MHz, CDCl₃): δ = 2.41 (t, J = 2.4 Hz, 3H); ¹³C NMR (376 MHz, CDCl₃): δ = -121.62 (d, J = 18.8 Hz, 0.5F), -121.80 (d, J = 18.8 Hz, 0.5F), -137.27 (d, J = 12.8 Hz, 1F), -145.08 (dd, J = 35.0 Hz, J = 16.9 Hz, 1F), -146.57 (td, J = 17.3 Hz, J = 4.1 Hz, 0.5F), -146.73 (td, J =
2-(Bromomethyl)-1,3,4,5,6,7,8-heptafluoronaphthalene 8. A mixture of compound 7 (1.3 g, 5.0 mmol) and N-Bromosuccinimide (0.9 g, 5.0 mmol) in CCl$_4$ (10.0 mL) was refluxing for 6 h. After completion of reaction, the mixture was washed with saturated NaCl aqueous solution (3 x 20 mL) and extracted with ethyl acetate (3 x 15 mL). The organic layers were combined and dried with Na$_2$SO$_4$, filtered. The solvent was evaporated and the residue was purified by column chromatography on a silica gel using hexane as eluent to obtain the 8 as a white solid (0.7 g, 2.0 mmol, 39%). m.p.: 71.8-73.2 °C; $^1$H NMR (400 MHz, CDCl$_3$); δ = 4.65 (t, J = 1.6 Hz, 2H); $^{19}$F NMR (376 MHz, CDCl$_3$); δ = -120.01 (d, J = 19.2 Hz, 0.5F), -120.19 (d, J = 19.2 Hz, 0.5F), -138.96 (d, J = 16.2 Hz, 1F), -143.29 (t, J = 16.9 Hz, 0.5F), -143.47 (t, J = 16.9 Hz, 0.5F), -145.42 (t, J = 16.9 Hz, 0.5F), -145.57 (t, J = 16.9 Hz, 0.5F), -147.98 (m, 1F), -151.89 (t, J = 16.9 Hz, 1F), -154.75 (m, 1F); ESI-MS: 347.6 (2.11%), 346.1 (4.10%), 267.0 (32.92%), 265.5 (100.00%); IR(KBr, cm$^{-1}$): δ = 3422, 2949, 2655, 2335, 2098, 1742, 1651, 1473, 1396, 1265, 1217, 1177, 1107, 1055, 1014, 948, 869, 778, 715.

1-((Perfluorophenalen-2-yl)methyl)-1,4-diazabicyclo-[2.2.2]octan-1-ium bromide 4. Compound 8 (0.5 g, 1.5 mmol) was dissolved in dichloromethane (1.0 mL), then DABCO (0.2 g, 1.5 mmol) was added and stirred at room temperature. After 10 min, white precipitate was generated from the solution. The mixture was continued to stir overnight and the white solid was filtered and dried under vacuum to obtain pure compound 4 (0.7 g, 1.5 mmol, 97%). m.p.: 260 °C decompose; $^1$H NMR (300 MHz, DMSO-d$_6$); δ = 3.02 (dt, J = 9.3 Hz, J = 5.1 Hz, 6H), 3.47 (m, 6H), 4.79 (s, 2H); $^{19}$F NMR (282 MHz, DMSO-d$_6$); δ = -112.27 (dd, J = 68.8 Hz, J = 17.5 Hz, 1F), -133.03 (d, J = 17.2 Hz, 1F), -144.04 (dt, J = 68.8 Hz, J = 17.2 Hz, 1F), -147.18 (dt, J = 55.8 Hz, J = 16.9 Hz, 1F), -149.37 (dt, J = 55.8 Hz, J = 18.3 Hz, 1F), -150.92 (t, J = 19.7 Hz, 1F), -154.76 (t, J = 18.3 Hz, 1F); ESI-MS: 379.1 [4-Br$^+$]; IR(KBr, cm$^{-1}$): 2980, 2893, 2594, 2187, 2170, 1976, 1656, 1614, 1533, 1494, 1404, 1327, 1264, 1174, 1113, 1058, 1031, 982, 930, 887, 849, 785, 726, 672; HRMS (ESI) m/z Calcd. for C$_{15}$H$_3$N$_2$BrF$_7$ (M-H): 457.0145; Found: 457.0153.

Crystal data for 4: Colourless plates from MeOH, C$_{15}$H$_3$BrF$_7$N$_2$O, F.W. = 491.25, crystal size 0.26 × 0.20 × 0.07 mm, orthorhombic, space group $Pbca$ (no. 61), $a = 13.6470(3)$, $b = 12.4533(2)$, $c = 22.0643(4)$ Å, $\alpha = \beta = \gamma = 90^\circ$, $V = 3749.83(12)$ Å$^3$, $Z = 8$, $D_{calc} = 1.740$ Mgm$^{-1}$, $\mu = 2.272$ mm$^{-1}$, $F(000) = 1968$, 21666 collected reflections ($\theta_{max} = 25.25^\circ$) of which 3389 independent ($R_{int} = 0.0659$) and 2345 with $I > 2\sigma(I)$, $T_{max} = 0.8571$, $T_{min} = 0.5896$, full-matrix least-squares on $F^2$ with 1 restraint and 266 parameters, GOF = 1.037, $R1 = 0.0470$ [$I > 2\sigma(I)$], wR2 (all data) = 0.1189, largest peak/hole = 0.720 / −0.694 e.Å$^{-3}$. 

17.3 Hz, $J = 4.1$ Hz, 0.5F), -150.23 (m, 1F), -155.11 (t, $J = 18.8$ Hz, 1F), -156.44 (m, 1F); EI-MS: 268.1 (12.45%), 85.4 (34.96%), 83.3 (44.68%), 71.5 (53.44%), 57.5 (100.00%); IR(KBr, cm$^{-1}$): 3422, 2949, 1653, 1472, 1406, 1262, 1172, 1104, 1056, 1000, 947, 901, 844, 770, 777, 671; Anal. Calcd. for C$_{15}$H$_3$F$_7$·0.5H$_2$O: C, 47.67; H, 1.45; Found: C, 47.68; H, 1.68.
Methods of $^{19}$F NMR titration for 1 or 2

In each $^{19}$F NMR titration, the amount of each receptor 1 or 2 was 0.025 mmol, the volume of the deuterated solution (CDCl$_3$) in the NMR tube was 0.6 mL. The amount of tetrabutylammonium chloride (TBA-Cl), tetrabutylammonium bromide (TBA-Br), tetrabutylammonium fluoride (TBA-F), tetrabutylammonium iodide (TBA-I), tetrabutylammonium nitrate (TBA-NO$_3$), tetrabutylammonium tetrafluoroborate (TBA-BF$_4$) in each NMR tube was successive increased. All NMR spectra were processed at room temperature.
Figure S1. $^{19}$F NMR titration of acceptor 1 with tetrabutylammonium bromide (TBA·Br)
**Figure S2.** $^{19}$F NMR titration of acceptor 1 with tetrabutylammonium chloride (TBA·Cl)
Figure S3. $^{19}\text{F}$ NMR titration of acceptor 1 with tetrabutylammonium fluoride (TBA·F)
Figure S4. $^{19}$F NMR titration of acceptor 1 with tetrabutylammonium iodide (TBA·I)
Figure S5. $^{19}$F NMR titration of acceptor 1 with tetrabutylammonium nitrate (TBA·NO$_3$)
Figure S6. $^{19}$F NMR titration of acceptor 1 with tetrabutylammonium tetrafluoroborate (TBA·BF$_4$)
Figure S7. $^{19}$F NMR titration of acceptor 2 with tetrabutylammonium bromide (TBA·Br)
Figure S8. $^{19}$F NMR titration of acceptor 2 with tetrabutylammonium chloride (TBA·Cl)
Figure S9. $^{19}$F NMR titration of acceptor 2 with tetrabutylammonium fluoride (TBA·F)
**Figure S10.** $^{19}$F NMR titration of acceptor 2 with tetrabutylammonium iodide (TBA·I)
Figure S11. $^{19}$F NMR titration of acceptor 2 with tetrabutylammonium nitrate (TBA·NO$_3$)
Figure S12. $^{19}$F NMR titration of acceptor 2 with tetrabutylammonium tetrafluoroborate (TBA·BF$_4$)
**Figure S13.** Thermal ellipsoid (50 % probability) diagram of the structure 3.\(^1\)

**Figure S14.** Thermal ellipsoid (50 % probability) diagram of the structure 4.\(^1\)

---