

Supplementary information:

Modulating the charge injection in organic field-effect transistors: Fluorinated oligophenyl self-assembled monolayers for high work function electrodes

Oliver Fenwick,^a Colin Van Dyck,^{b,c} Kathiresan Murugavel,^d David Cornil,^b Federica Reinders,^d Sébastien Haar,^a Marcel Mayor,^{d,e} Jérôme Cornil^{b*} and Paolo Samori.^{a*}*

^aISIS & icFRC, Université de Strasbourg & CNRS, 8, allée Gaspard Monge, 67000 Strasbourg, France.

^bLaboratory for Chemistry of Novel Materials, University of Mons, Place du Parc 20, B-7000 Mons, Belgium.

^cDepartment of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, USA

^dDept. of Chemistry, University of Basel, St Johannis-Ring 19, CH-4056 Basel, Switzerland.

^eKarlsruhe Institute of Technology, INT, P.O. Box 3640, D-76021 Karlsruhe, Germany.

Contents

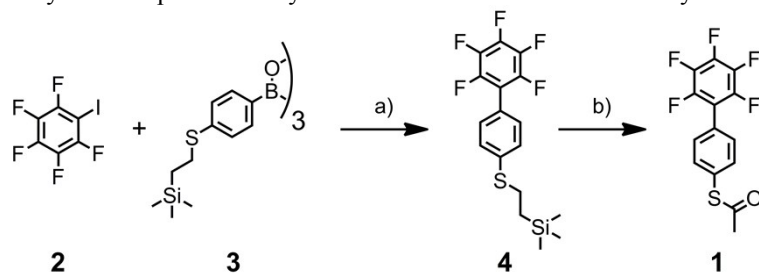
1. Synthesis S-(2',3',4',5',6'-pentafluoro-[1,1'-biphenyl]-4-yl) ethanethioate.....	SI-1
2. Scanning tunneling microscopy of PFBT monolayers.....	SI-3
3. Ambient photoelectron spectroscopy data.....	SI-3
4. Water contact angle data.....	SI-4

1. Synthesis of *S*-(2',3',4',5',6'-pentafluoro-[1,1'-biphenyl]-4-yl) ethanethioate

The acetyl protected 2',3',4',5',6'-pentafluorobiphenyl-4-thiol **1** was synthesized in a two step reaction sequence in an overall yield of 58%. First pentafluoroiodobenzene **2** and the boroxine **3** were exposed to Suzuki coupling conditions to provide the trimethylsilylethyl protected biphenylthiol **4** after column chromatography in 61% yield. Transprotection to the acetyl protected target structure **1** was achieved almost quantitatively by treatment of **4** with silver tetrafluoroborate in the presence of an excess of acetylchloride. The compounds were characterized by ¹H- and ¹⁹F-NMR spectroscopy, mass spectrometry and elemental analysis.

General Remarks

All commercially available starting materials were of reagent grade and used as received. Dry *N,N*-dimethylformamide (DMF) was purchased from *Fluka*, stored over 4 Å molecular sieves and handled under argon. The solvents for chromatography, crystallization and extraction were of technical grade. Column chromatography purifications were carried out on silica gel 60 (particle size 0.040-0.063 mm) from *Fluka*. Deuterated solvents were purchased from Cambridge Isotope Laboratories. ¹H-, ¹⁹F- and ¹³C-NMR spectra were recorded with a *Bruker* DMX 400 instrument (¹H resonance 400 MHz, ¹⁹F resonance 377 MHz, ¹³C resonance 101 MHz) at 298 K. The Electron Impact (EI) mass spectra were recorded on a *Finnigan* MAT 95Q by H. Nadig. GC-MS were recorded with a *Shimadzu* GCMS-2020 SE equipped with a *Zebron* 5 MS Inferon column enabling temperatures up to 350°C. Elemental analyses were performed by W. Kirsch on a *Perkin-Elmer* Analysator 240.



Scheme 1: Synthesis of the fluorinated biphenylethanethioate **1**. Reaction and conditions: a) Pd(PPh₃)₄, Ag₂O, Cs₂CO₃, DMF, 130°C, 61%; b) AgBF₄, CH₃COCl, CH₂Cl₂, 0°C to RT., 98%.

Trimethyl(2-((2',3',4',5',6'-pentafluoro-[1,1'-biphenyl]-4-yl)thio)ethyl)silane (**4**):

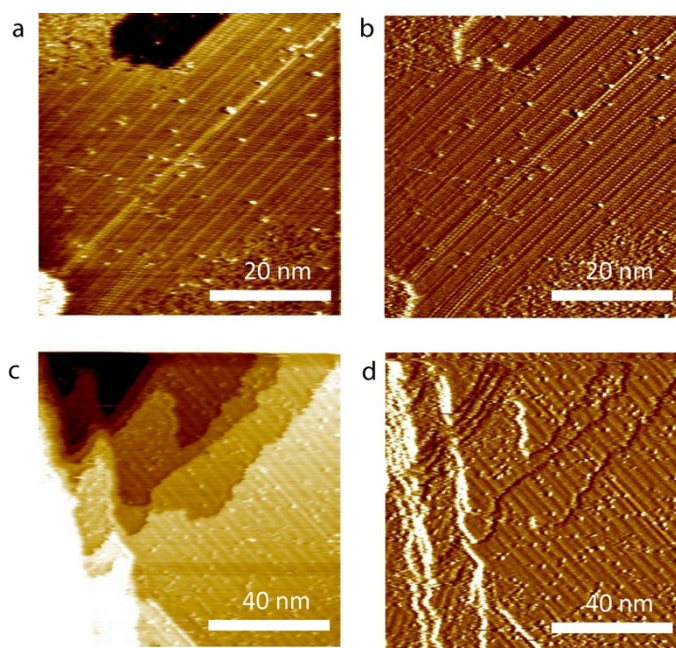
2,3,4,5,6-pentafluoro-1-iodobenzene (0.9 g, 3 mmol) and 4-thio(ethylsilane)phenylboronic acid trimer (0.755 g, 1.07 mmol) were dissolved in DMF (20 mL) and the reaction mixture was degassed with Ar. To this solution, Pd(PPh₃)₄ (173 mg, 0.15 mmol, 5 mol%), Cs₂CO₃ (2 g, 6 mmol) and Ag₂O (0.855 g, 3.6 mmol) were added. The reaction mixture was heated to 130°C and stirred for 24 h. After cooling to RT, the reaction mixture was diluted with EtOAc and filtered through a celite plug. The organic layer was washed with water several times, washed with brine, dried over MgSO₄, filtered and concentrated. Further purification of the residue by column chromatography (silica gel, cyclohexane) provided **4** as colorless solid (0.7 g, 61% yield): ¹H-NMR (400 MHz, CDCl₃) δ 7.36 (qd, *J* = 8.7, 7.5, 1.4 Hz, 4H), 3.07 – 2.99 (m, 2H), 1.03 – 0.95 (m, 2H), 0.08 (s, 9H); ¹⁹F-NMR (376 MHz, CDCl₃) δ -143.30 (dd, *J* = 23.1, 7.9 Hz), -155.71 (t, *J* = 21.0 Hz), -162.12 – -162.29 (m); **MS**: (EI, *m/z*): 376.1 (12.33%, M⁺), 348.1 (22.93%), 333 (18.3%), 275 (6.6%), 166.5 (1.72%), 101.1 (14.82), 73.1 (100%); **EA**: Anal. calcd. for C₁₁H₁₇F₅SSi: C 54.24, H 4.55, found C 54.38, H 4.83.

S-(2',3',4',5',6'-pentafluoro-[1,1'-biphenyl]-4-yl) ethanethioate (**1**):

4 (0.3 g, 0.79 mmol) was dissolved in 20 mL dry CH₂Cl₂ under a protection atmosphere of argon. The solution was cooled to 0°C and acetyl chloride (1.7 mL, 23.9 mmol) followed by AgBF₄ (0.47 g, 2.3 mmol) were added. The reaction mixture was stirred for 2 hours while warming up to RT. The reaction mixture was neutralized with sat. NaHCO₃, diluted with CH₂Cl₂, washed with water and brine. After drying over anhydrous MgSO₄ and filtration the solvent was removed under reduced pressure providing the NMR and GCMS pure product as colorless solid (0.24 g, 95% yield): ¹H-NMR (400 MHz, CDCl₃) δ 7.57 – 7.52 (m, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 2.47 (s, 3H); ¹⁹F-NMR (376 MHz, CDCl₃) δ -142.74 – -142.89 (m), -154.61 (t, *J* = 21.0 Hz), -161.76 (td, *J* = 22.5, 8.0 Hz); ¹³C-NMR (101 MHz, CDCl₃) δ 193.2, 144.2, 140.6, 136.7, 134.47, 130.87, 129.61, 127.48, 115.04, 30.36; **MS**:

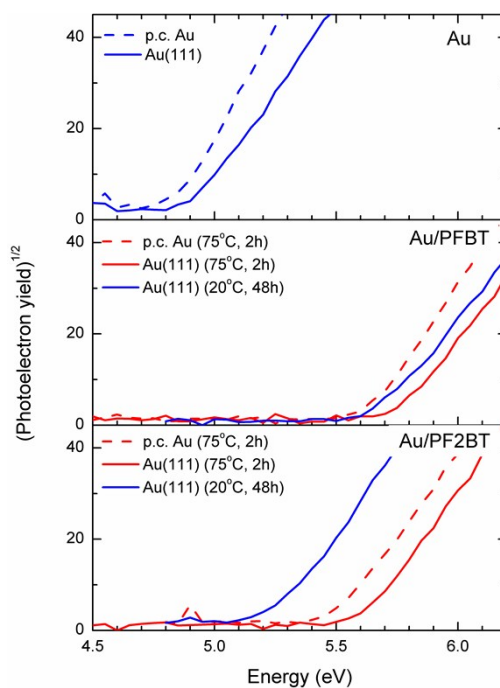
(GCMS, m/z): 318.3 (5.72, M⁺), 276.3 (100%); **EA**: Anal. calcd. for C₁₄H₇F₃O₁S₁ C 52.83, H 2.22, found C 52.58, H 2.35.

2. Scanning tunneling microscopy of PFBT monolayers



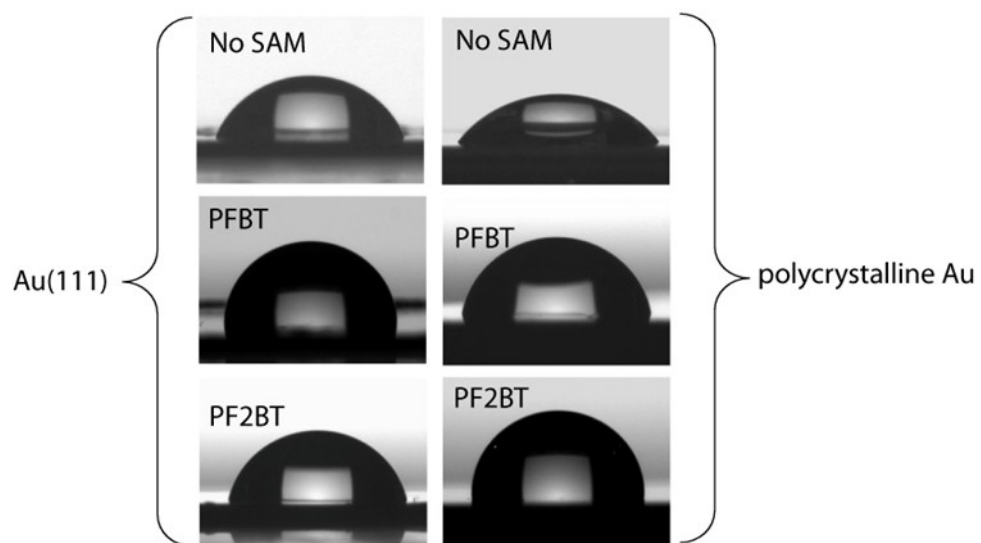
Supplementary figure 1- Scanning tunneling micrographs recorded in constant current mode of long range order in PFBT SAMs formed at 75°C. **a** Height (full colour scale represents 0.3 nm), and **b** error (current) signal recorded over a 50 x 50 nm area with a tip bias of 20 mV and a current set-point of 6.5 pA. **c** Height (full colour scale represents 1.3 nm), and **d** error (current) signal recorded over a 100 x 100 nm area with a tip bias of 20 mV and a current setpoint of 5.0 pA.

3. Ambient photoelectron spectroscopy



Supplementary figure 2 – Typical ambient ultraviolet photoelectron yields of the modified Au(111) (solid lines) and polycrystalline (p.c.) gold surfaces (dashed lines) showing changes in the gold work function depending on the treatment. Room temperature treatments are shown in blue and treatments at 75°C are shown in red.

4. Water contact angle



Supplementary figure 3 – Typical water contact angle measurements of the SAM-modified gold surfaces for both Au(111) surfaces and polycrystalline (p.c.) gold surfaces.