

Electronic Supplementary Information (ESI) for the article entitled:

Light-induced reversible modification of the work function of a new perfluorinated biphenyl azobenzene chemisorbed on Au (111)

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Synthesis of the terminally fluorinated azo-biphenyl rod 1

The synthesis is displayed in scheme 1 (main text). The numbering of the structures corresponds to the one used in scheme 1 of the main text. The *para*-pentafluoroaniline **5** is assembled by a *Suzuki-Miyaura* cross-coupling between the commercially available 4-(N-Boc-amino)phenylboronic acid pinacol (**2**) and iodopentafluorobenzene (**3**). The coupling with caesium carbonate as base and Pd(PPh₃)₄ as catalyst in toluene at reflux for 30 hours gave the corresponding coupling product **4** in a yield of 60%. It is noteworthy that the use of Cs₂CO₃ instead of K₂CO₃ increased the isolated yield, while no influence of the presence of water was observed. Caesium bases such as caesium carbonate and caesium hydroxide were reported to exhibit a greater accelerating effect than sodium or potassium salts.¹ Acidic removal of the BOC-protection group with an excess of trifluoroacetic acid followed by the treatment of the crude product with triethylamine gave the free amine **5** after workup without further purification. The aniline derivative **5** was isolated as a colourless solid in almost quantitative yield. The required 1-bromo-4-nitrosobenzene was obtained by treating 4-bromoaniline with Oxone[®] following a literature protocol.^{2,3} The *Mills* condensation between the aniline **5** and 1-bromo-4-nitrosobenzene in acetic acid at room temperature provided the azo intermediate **6** as orange solid in very good 89% isolated yield after column chromatography. The trimeric boroxine **7** was synthesized following a reported protocol.⁴ The *Suzuki-Miyaura* cross-coupling between the boroxine **7** and the bromine functionalized azo derivative **6** was performed with Pd(PPh₃)₄ as catalyst, K₂CO₃ as base in a toluene/ethanol mixture at 60°C for 45 minutes. The TMS-ethynyl protected target structure **8** was isolated as orange solid in excellent 98% yield after work up and column chromatography. The TMS-ethynyl protected thiophenol derivative **8** was dissolved in CH₂Cl₂ in the presence of an excess of acetyl chloride. An excess of silver tetrafluoroborate was added and an immediate color change, from the initial orange solution to dark blue and then dark red was observed. The reaction mixture was stirred for another 20 minutes at room temperature, before being quenched with water and worked up to provide the target structure **1** as orange solid in 83% isolated yield after column chromatography. It is noteworthy that several attempts to transprotect **8** to **1** with TBAF failed and we profited from reports using AgBF₄ as deprotection agent.^{5,6}

¹ A. De Meijere, F. Diederich, *Metal-Catalyzed Cross-Coupling Reactions*, Wiley-VCH, 2004.

² B. Priewisch, K. Rück-Braun, *The Journal of Organic Chemistry* 2005, 70, 2350-2352.

³ B. C. Yu, Y. Shirai, J. M. Tour, *Tetrahedron* 2006, 62, 10303-10310.

⁴ S. Grunder, R. Huber, S. Wu, C. Schönenberger, M. Calame, M. Mayor, *Eur. J. Org. Chem.* 2010, 5, 833-845.

⁵ H. Grundberg, M. Andergran, U. J. Nilsson, *Tetrahedron Lett.* 1999, 40, 1811-1814.

⁶ Y. Shirai et al., *J. Org. Chem.* 2009, 74, 7885-7897.

Experimental Part

General Remarks: All commercially available starting materials were of reagent grade and used as received. Dry ethanol and dry toluene were 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 , ^{19}F and ^{13}C NMR spectra were recorded with a *Bruker* DMX 400 instrument (^1H resonance 400 MHz, ^{19}F resonance 377 MHz, ^{13}C resonance 101 MHz) or a *Bruker* DRX 500 instrument (^1H resonance 500 MHz, ^{13}C resonance 125 MHz) at 298 K. The Electron Impact (EI) mass spectra were recorded on a *Finnigan* MAT 95Q by H. Nadig. Elemental analyses were performed by W. Kirsch on a *Perkin-Elmer* Analysator 240.

4-Boc-amino-(2',3',4',5',6'-pentafluoro[1,1'-biphenyl]) (4): A mixture of 4-Boc-amino-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene) (**2**, 102 mg, 0.32 mmol, 1.0 eq.), iodopentafluorobenzene (**3**, 0.06 mL, 0.45 mmol, 1.4 eq.), caesium carbonate (814 mg, 2.50 mmol, 7.8 eq.) and dry toluene (40 mL) was degassed by purging argon through the solution. Then $\text{Pd}(\text{PPh}_3)_4$ (34 mg, 0.03 mmol, 9 mol%) was added under an argon atmosphere and the reaction mixture was heated to reflux for 30 hours. Afterwards water was added to the reaction mixture, which was extracted with ethyl acetate (3x). The collected organic layers were washed with water (3x) and brine and dried over MgSO_4 . The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel, dichloromethane/*n*-hexane 2:1, ethyl acetate/*n*-hexane 1:5) to obtain 4-Boc-amino-(2',3',4',5',6'-pentafluoro[1,1'-biphenyl]) (**4**, $\text{C}_{17}\text{H}_{14}\text{F}_5\text{NO}_2$, 69 mg, 60%) as a colourless solid. **TLC:** $R_f=0.56$ (dichloromethane/*n*-hexane 2:1), $R_f=0.41$ (ethyl acetate/*n*-hexane 1:5); **$^1\text{H-NMR}$:** (400 MHz, CDCl_3 , δ/ppm): 7.50 (d, $^3J_{\text{HH}} = 8.7$ Hz, 2H), 7.36 (d, $^3J_{\text{HH}} = 8.6$ Hz, 2H), 6.59 (s, 1H), 1.54 (s, 9H); **$^{19}\text{F-NMR}$:** (377 MHz, CDCl_3 , δ/ppm): -143.7 (dd, $^3J_{\text{FF}} = 23.3$ Hz, $^4J_{\text{FF}} = 8.3$ Hz, 2F), -156.4 (t, $^3J_{\text{FF}} = 21.2$ Hz, 1F), -162.6 (td, $^3J_{\text{FF}} = 22.9$ Hz, $^4J_{\text{FF}} = 8.4$ Hz, 2F); **$^{13}\text{C-NMR}$:** (101 MHz, CDCl_3 , δ/ppm): 181.6, 152.5, 139.4, 130.9, 118.4, 81.0, 28.3; **MS:** (EI, *m/z*): 359.1 (7%, M^+), 303.0 (76%), 285.0 (49%), 259.0 (100%), 57.1 (98%), 41.0 (19%); **EA:** calculated: C 56.83, H 3.93, N 3.90, found: C 56.68, H 3.92, N 3.85.

2',3',4',5',6'-Pentafluoro-[1,1'-biphenyl]-4-amine (5): A mixture of 4-Boc-amino-(2',3',4',5',6'-pentafluoro[1,1'-biphenyl]) (**4**, 1.97 g, 5.48 mmol, 1.0 eq.) was dissolved in dichloromethane (300 mL). Then trifluoroacetic acid (10.0 mL, 131 mmol, 24 eq.) was added and the reaction mixture was heated to reflux for 1 hour. The mixture was then cooled to room temperature and neutralized carefully with a water/triethylamine mixture (1:5). The phases were separated and the organic layer was washed with water (3x) and brine before being dried over MgSO_4 . The solvent was removed under reduced pressure. Without further purification 2',3',4',5',6'-pentafluoro-[1,1'-biphenyl]-4-amine (**5**, $\text{C}_{12}\text{H}_6\text{F}_5\text{N}$, 1.39 g, 98%) was obtained as a colourless solid. **$^1\text{H-NMR}$:** (400 MHz, CDCl_3 , δ/ppm): 7.22 (d, $^3J_{\text{HH}} = 8.5$ Hz, 2H), 6.77 (d, $^3J_{\text{HH}} = 8.6$ Hz, 2H), 3.87 (s_{br}, 2H); **$^{19}\text{F-NMR}$:** (377 MHz, CDCl_3 , δ/ppm): -145.0 (dd, $^3J_{\text{FF}} = 23.6$ Hz, $^4J_{\text{FF}} = 8.4$ Hz, 2F), -158.6 (t, $^3J_{\text{FF}} = 20.8$ Hz, 1F), -164.1 (td, $^3J_{\text{FF}} = 23.7$ Hz, $^4J_{\text{FF}} = 8.2$ Hz, 2F); **MS:** (EI, *m/z*): 259.1 (100%, M^+); **EA:** calculated: C 55.61, H 2.33, N 5.40, found: C 55.63, H 2.63, N 5.23.

1-(4-Bromophenyl)-2-(2',3',4',5',6'-pentafluoro-[1,1'-biphenyl]-4-yl)diazene (6): Crude 1-bromo-4-nitrosobenzene (1.76 g) and 2',3',4',5',6'-pentafluoro-[1,1'-biphenyl]-4-amine (**5**, 1.39 g, 5.38 mmol) were dissolved in acetic acid (200 mL) and stirred at room temperature for 29 hours. The reaction mixture was carefully neutralized with a saturated aqueous NaHCO_3 -solution. Then an extraction with dichloromethane (3x) was performed and the collected organic layers were washed with water (3x) and brine before being dried over MgSO_4 . The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel, dichloromethane/*n*-hexane 1:5) to afford azo compound **6** ($\text{C}_{18}\text{H}_8\text{BrF}_5\text{N}_2$, 2.05 g, 89% over two steps) as an orange solid. **TLC:** $R_f=0.48$ (dichloromethane/*n*-hexane 1:5); **$^1\text{H-NMR}$:** (400 MHz, CDCl_3 , δ/ppm): 8.03 (d, $^3J_{\text{HH}} = 8.5$ Hz, 2H), 7.84 (d, $^3J_{\text{HH}} = 8.7$ Hz, 2H), 7.68 (d, $^3J_{\text{HH}} = 8.6$ Hz, 2H), 7.60 (d, $^3J_{\text{HH}} = 8.3$ Hz, 2H); **$^{19}\text{F-NMR}$:** (377 MHz, CDCl_3 , δ/ppm): -143.0 (dd, $^3J_{\text{FF}} = 22.9$ Hz, $^4J_{\text{FF}} = 8.1$ Hz, 2F), -154.7 (t, $^3J_{\text{FF}} = 21.0$ Hz, 1F), -161.9 (td, $^3J_{\text{FF}} = 22.2$ Hz, $^4J_{\text{FF}} = 7.9$ Hz, 2F); **$^{13}\text{C-NMR}$:** (101 MHz, CDCl_3 , δ/ppm): 152.5, 151.3,

132.5, 131.1, 129.1, 126.0, 124.5, 123.2; **MS**: (EI, m/z): 426.0 (48%, M⁺), 243.0 (100%), 224.0 (23%), 182.9 (21%), 155.0 (42%); **EA**: calculated: C 50.61, H 1.89, N 6.56, found: C 50.35, H 1.92, N 6.76.

1-(2',3',4',5',6'-Pentafluoro-[1,1'-biphenyl]-4-yl)-2-(4'-((2-(trimethylsilyl)ethyl)thio)-[1,1'-biphenyl]-4-yl)diazene (8): Boroxine **7** (116 mg, 0.23 mmol, 0.4 eq.), azo compound **6** (250 mg, 0.59 mmol, 1.0 eq.), potassium carbonate (161 mg, 1.17 mmol, 2.0 eq.), dry ethanol (20 mL) and dry toluene (20 mL) were added into a flask and the reaction mixture was degassed by purging argon through the solution. Afterwards Pd(PPh₃)₄ (34 mg, 0.03 mmol, 5 mol%) was added and the reaction mixture was stirred at 60 °C for 45 minutes. After dilution with dichloromethane the organic layer was washed with water (3x) and brine before being dried over MgSO₄. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel, dichloromethane/cyclohexane 1:2) to obtain azo compound **8** (C₂₉H₂₅F₅N₂SSi, 319 mg, 98%) as an orange solid. **TLC**: R_f = 0.53 (dichloromethane/cyclohexane 1:2); **¹H-NMR**: (400 MHz, CDCl₃, δ/ppm): 8.05 (d, ³J_{HH} = 8.7 Hz, 2H), 8.03 (d, ³J_{HH} = 8.6 Hz, 2H), 7.76 (d, ³J_{HH} = 8.6 Hz, 2H), 7.61 (d, ³J_{HH} = 8.4 Hz, 2H), 7.60 (d, ³J_{HH} = 8.6 Hz, 2H), 7.40 (d, ³J_{HH} = 8.4 Hz, 2H), 3.03 (m, 2H), 0.99 (m, 2H), 0.07 (s, 9H); **¹⁹F-NMR**: (377 MHz, CDCl₃, δ/ppm): -143.0 (dd, ³J_{FF} = 23.0 Hz, ⁴J_{FF} = 8.2 Hz, 2F), -154.9 (t, ³J_{FF} = 20.9 Hz, 1F), -162.0 (td, ³J_{FF} = 22.8 Hz, ⁴J_{FF} = 8.1 Hz, 2F); **¹³C-NMR**: (126 MHz, CDCl₃, δ/ppm): 152.8, 151.6, 143.5, 137.7, 137.2, 131.1, 128.9, 128.7, 127.5, 127.5, 123.7, 123.1, 29.3, 16.8, -1.73; **MS**: (EI, m/z): 556.2 (35%, M⁺), 528.2 (27%), 257.1 (36%), 243.0 (20%), 73.0 (100%); **EA**: calculated: C 62.57, H 4.53, N 5.03, found: C 62.59, H 4.75, N 4.91.

S-(4'-((2',3',4',5',6'-Pentafluoro-[1,1'-biphenyl]-4-yl)diazenyl)-[1,1'-biphenyl]-4-yl) ethanethioate (1): Compound **8** (18 mg, 0.03 mmol, 1.0 eq.) and acetyl chloride (1 mL) were dissolved under an argon atmosphere in dry dichloromethane (5 mL). Then silver tetrafluoroborate (76 mg, 0.39 mmol, 12 eq.) was added and the reaction mixture turned immediately from orange to dark blue and then dark red. After stirring at room temperature for 20 minutes the reaction mixture was quenched with water. The phases were separated and the organic layer was washed with water (3x) and brine before being dried over MgSO₄. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel, dichloromethane/*n*-hexane 1:1) to obtain target structure **1** (C₂₆H₁₅F₅N₂OS, 13 mg, 83%) as an orange solid. **TLC**: R_f = 0.22 (dichloromethane/*n*-hexane 1:1); **¹H-NMR**: (400 MHz, CDCl₃, δ/ppm): 8.06 (d, ³J_{HH} = 8.4 Hz, 2H), 8.05 (d, ³J_{HH} = 8.3 Hz, 2H), 7.78 (d, ³J_{HH} = 8.5 Hz, 2H), 7.72 (d, ³J_{HH} = 8.4 Hz, 2H), 7.61 (d, ³J_{HH} = 8.4 Hz, 2H), 7.53 (d, ³J_{HH} = 8.3 Hz, 2H), 2.47 (s, 3H); **¹⁹F-NMR**: (377 MHz, CDCl₃, δ/ppm): -142.7 (dd, ³J_{FF} = 23.4 Hz, ⁴J_{FF} = 8.4 Hz, 2F), -154.6 (t, ³J_{FF} = 20.6 Hz, 1F), -161.7 (m, 2F); **¹³C-NMR**: ¹³C-shifts determined from HSQC and HMBC experiments; due to C-F coupling, C-atoms adjacent to F-atoms were not identified; (126 MHz, CDCl₃, δ/ppm): 128.7, 152.7, 152.0, 143.0, 141.2, 127.5, 194.0, 123.3, 123.4, 128.0, 127.9, 131.1, 134.9, 30.1; **MS**: (EI, m/z): 498.1 (58%, M⁺), 456.1 (62%), 243.0 (40%), 185.0 (100%), 152.0 (58%), 43.0, (21%); **UV/Vis**: (CHCl₃, λ_{max}/nm, (ε/L · mol⁻¹ · cm⁻¹)): 243 (20400), 355 (42500), 439 (1800).