

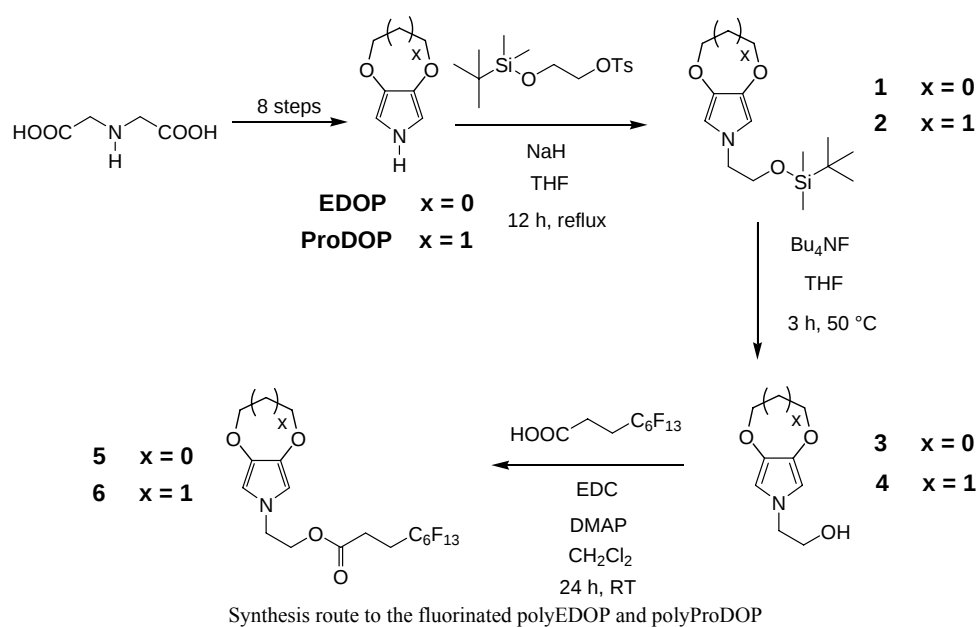
## Electronic Supporting Information

# One methylene unit to control super oil-repellency properties of conducting polymers

Thierry Darmanin and Frederic Guittard\*

### General

All chemicals were purchased from Sigma-Aldrich. NMR spectra were realized with a Bruker W-200 MHz. The mass spectra were obtained with a Thermo TRACEGC of Thermofischer Corp. fitted with an Automass III Multi spectrometer (electron ionisation at 70 eV). The retention time of the compounds were determined with a 5890 series II gas chromatography from Hewlett Packard equipped with a capillary column HP5 (30 m, 0.32 mm) and with this following programming: heating from 60°C to 250°C at 10°C/mn and 10 min at 250°C and using heptane as standard reference. The melting points were determined with a Büchi-510 melting point apparatus. Electrochemical experiments were performed with an Autolab PGSTAT 30 potentiostat from Eco Chemie B. V. equipped with General Purpose Electrochemical System GPES software. A three-electrode cell equipped with either a platinum disk (area = 7.1 mm<sup>2</sup>) or a gold plate (area = a few cm<sup>2</sup>) as working electrode, a glassy carbon rod as counter-electrode and a SCE reference electrode was used. Electrochemical grade of tetrabutylammonium hexafluorophosphate was chosen. Gold plates (deposition of Cr + Au 1500 Å on silicon wafers) were purchased from Neyco. Static and dynamic contact angle measurements were performed with a Krüss DSA-10 contact angle goniometer at 21 ± 1°C. An average of five measurements with water, diiodomethane and hexadecane was made to determine the hydrophobicity and the oleophobicity of the surfaces. The sliding angle and the hysteresis were measured by the tilted-drop method with a 6 µl water droplet. With this method the advancing and the receding angles were measured just before the water droplet rolls off the surface. Scanning Electron Microscopy images were performed with a JEOL 6700F microscope.



## Experimental

### Synthesis of 1 and 2.

3,4-ethylenedioxyproline (EDOP) and 3,4-propylenedioxyproline (ProDOP) were synthesized from iminodiacetic acid in a eight steps reaction developed by Merz *et al.*<sup>1</sup> using 1,2-dibromoethane or 1,3-dibromopropane. Dry sodium hydride (0.25 g, 10 mmol) was carefully added to a solution of EDOP (1 g, 8 mmol) or ProDOP (1.1 g, 8 mmol) in anhydrous THF at 0°C. After stirring for 1 hr at 0°C, 2-*tert*-butyldimethylsilyloxyethyl tosylate (3.2 g, 10 mmol) was added and the reaction mixture was refluxed for 12 hr. After cooling at room temperature and solvent evaporation, aqueous NH<sub>4</sub>Cl was carefully added and the solution was extracted with diethyl ether and dried (MgSO<sub>4</sub>). Removal of solvent and purification by column chromatography (silica gel; eluent: hexane) gave **1** (retention time: 14.7 mn) or **2** (retention time: 15.8 mn).

### Synthesis of 3.

Tetrabutylammonium fluoride (1M in THF) was added to a solution of **1** in THF. After stirring during 3 hr at 50°C and solvent evaporation, the purification by column chromatography (silica gel; eluent: ethyl acetate) afforded **3** (retention time: 10.5 mn) as a colourless liquid.

Yield 65 %;  $\delta_{\text{H}}$ (250 MHz, CDCl<sub>3</sub>) 6.12 (2 H, s), 4.17 (4 H, s), 3.79 (4 H, m), 1.79 (1 H, s);  $\delta_{\text{C}}$ (50 MHz, CDCl<sub>3</sub>) 132.24, 101.35, 65.74, 62.77, 52.53; MS (70 eV): *m/z* 169 (M<sup>+</sup>, 100%), 138 (74); Elem. Anal.: Found: C, 56.85; H, 6.58; N, 8.17. C<sub>8</sub>H<sub>11</sub>NO<sub>3</sub> requires C, 56.80; H, 6.55; N, 8.28.

### Synthesis of 4.

Tetrabutylammonium fluoride (1M in THF) was added to a solution of **2** in THF. After stirring during 3 hr at 50°C and solvent evaporation, the purification by column chromatography (silica gel; eluent: ethyl acetate) afforded **4** (retention time: 12.1 mn) as a colourless liquid.

Yield 70 %;  $\delta_{\text{H}}$ (250 MHz, CDCl<sub>3</sub>) 6.22 (2 H, s), 3.96 (4 H, t, <sup>3</sup>*J*<sub>HH</sub> 5.0 Hz), 3.75 (4 H, m), 2.11 (2 H, quint, <sup>3</sup>*J*<sub>HH</sub> 5.0 Hz), 2.07 (1 H, s);  $\delta_{\text{C}}$ (50 MHz, CDCl<sub>3</sub>) 138.75, 106.21, 72.38, 62.56, 52.51, 35.07; MS (70 eV): *m/z* 183 (M<sup>+</sup>, 100%), 152 (63). Elem. Anal. Found: C, 59.08; H, 7.21; N, 7.63. C<sub>9</sub>H<sub>13</sub>NO<sub>3</sub> requires C, 59.00; H, 7.15; N, 7.65.

### Synthesis of 5.

4-dimethylaminopyridine (DMAP) (30 mg) and N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC) (0.3 mg, 1.5 mmol) were added to a solution of 4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononanoic acid (0.59 g, 1.5 mmol) in dichloromethane. After stirring during 30 mn at room temperature, **3** (0.25 g, 1.5 mmol) was added. After a day, the solvent was removed and the crude was purified by column chromatography (silica gel; eluent: dichloromethane) to yield **5** (retention time: 15.6 mn) as a white solid.

Yield 68 %; mp 46-47 °C;  $\delta_{\text{H}}$ (250 MHz, CDCl<sub>3</sub>) 6.07 (2 H, s), 4.29 (2 H, t, <sup>3</sup>*J*<sub>HH</sub> 5.4 Hz), 4.17 (4 H, s), 3.92 (2 H, t, <sup>3</sup>*J*<sub>HH</sub> 5.4 Hz), 2.64 (2 H, t, <sup>3</sup>*J*<sub>HH</sub> 7.1 Hz), 2.44 (2 H, tt, <sup>3</sup>*J*<sub>HH</sub> 7.1 Hz, <sup>3</sup>*J*<sub>HF</sub> 18.4 Hz);  $\delta_{\text{C}}$ (50 MHz, CDCl<sub>3</sub>) 170.76, 132.46, 101.37, 65.76, 64.63, 48.67, 26.40 (t, <sup>2</sup>*J*<sub>CF</sub> 21.9 Hz), 25.37 (t, <sup>3</sup>*J*<sub>CF</sub> 3.7 Hz);  $\delta_{\text{F}}$ (188 MHz, CDCl<sub>3</sub>) -81.16, -115.15, -122.33, -123.34, -123.96, -126.60; FTIR (KBr):  $\nu$  2922, 2864, 1740, 1556, 1188, 1144; MS (70 eV): *m/z* 543 (M<sup>+</sup>, 5%), 151 (82), 138 (100); Elem. Anal. Found: C, 37.55; H, 2.65; N, 2.57. C<sub>17</sub>H<sub>14</sub>F<sub>13</sub>NO<sub>4</sub> requires C, 37.58; H, 2.60; N, 2.58.

**Synthesis of 6.**

DMAP (30 mg) and EDC (0.3 mg, 1.5 mmol) were added to a solution of 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecanoic acid (0.72 g, 1.5 mmol) in dichloromethane. After stirring during 30 mn at room temperature, **4** (0.27 g, 1.5 mmol) was added. After a day, the solvent was removed and the crude was purified by column chromatography (silica gel; eluent: dichloromethane) to yield **6** (retention time: 17.7 mn) as a white solid.

Yield 60 %; mp 68-69 °C; (250 MHz, CDCl<sub>3</sub>) 6.20 (2 H, s), 4.30 (2 H, t, <sup>3</sup>J<sub>HH</sub> 5.4 Hz), 3.98 (4 H, t, <sup>3</sup>J<sub>HH</sub> 5.0 Hz), 3.90 (2 H, t, <sup>3</sup>J<sub>HH</sub> 5.4 Hz), 2.65 (2 H, t, <sup>3</sup>J<sub>HH</sub> 7.4 Hz), 2.48 (2 H, tt, <sup>3</sup>J<sub>HH</sub> 7.4 Hz, <sup>3</sup>J<sub>HF</sub> 18.7 Hz), 2.13 (2 H, quint, <sup>3</sup>J<sub>HH</sub> 5.0 Hz); δ<sub>C</sub>(50 MHz, CDCl<sub>3</sub>) 170.73, 139.11, 106.23, 72.45, 64.50, 48.67, 35.10, 26.31 (t, <sup>2</sup>J<sub>CF</sub> 21.4 Hz), 25.35 (t, <sup>3</sup>J<sub>CF</sub> 4.0 Hz); δ<sub>F</sub>(188 MHz, CDCl<sub>3</sub>) -81.20, -115.10, -122.32, -123.30, -123.95, -126.57; FTIR (KBr): ν 2964, 2936, 2864, 1748, 1548, 1182, 1146; MS (70 eV): m/z 557 (M<sup>+</sup>, 22%), 165 (100), 152 (85); Elem. Anal. Found: C, 38.75; H, 2.91; N, 2.45. C<sub>18</sub>H<sub>16</sub>F<sub>13</sub>NO<sub>4</sub> requires C, 38.79; H, 2.89; N, 2.51.