

# Spider-web-like fiber toward highly oleophobic fluorinated materials with low bioaccumulative potential



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## ABSTRACT

Original fluorinated (*F*-butyl, *F*-hexyl and *F*-octyl) EDOT derivatives containing thioester connectors are synthesized and used as monomers for the elaboration of liquid-repellent surfaces by electrodeposition. Their surface morphology varies as a function of the fluorinated chain length, due to the increase in the insolubility of the oligomers formed in the first instances. Superhydrophobic surfaces are obtained with *F*-octyl and *F*-hexyl chains but only the surfaces produced from the monomer containing *F*-butyl chains are highly oleophobic. These high contact angles can be explained by their surface morphology (spider-web-like structure) which favors the “pinning effect”. This work allows the decrease in the bioaccumulative potential of fluorinated materials with an increase in their oil-repellent properties.

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## 1. Introduction

The tuning in the surface wettability is fundamental in a theoretical point of view and for applications in very large domains in chemistry, physics, biology or mathematics [1–6]. In particular, superhydrophobic properties have attracted many researchers with more than 700 papers just for the last year [7–10]. Biomimetic approaches showed that the effect of different parameters on the change of the surface hydrophobicity and oleophobicity are extremely important [11–16]. Various experiments on superhydrophobic or superhydrophilic plants and insects showed the crucial role of the surface morphology, which plays a key role in the surface wettability. Others important parameters include the intrinsic liquid-repellent properties of the materials present at the extreme surface as well as the surface roughness/topography [17–19].

In order to reproduce such phenomena in laboratory, many processes were employed going from top-down approaches to bottom-up approaches [20–23]. The electrodeposition of conjugated polymers is one of the more promising methods to deposit liquid-repellent polymer layers containing micro- and/or nanostructures [7]. This electrochemical method is based on the oxidation of a monomer to produce the corresponding polymer and its deposition on a working electrode. The surface morphology or/and wettability can be controlled by insertion or removal of doping agents in the polymer structure [24–27], or by the grafting of a hydrophobic

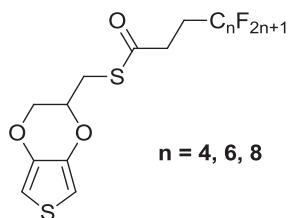
substituent on the monomer before polymerization [28–33]. The main advantages of the last method are the possibility to produce very quickly very stable polymer films in one-step and on large substrates, with an easy control of the surface morphology by adapting the electrochemical conditions. Moreover, the surface morphology can also be modified by playing on the structure of the monomer. EDOT derivatives and analogues are special monomers due to their exceptional polymerization ability, the possibility to produce polymer films in few seconds and to lead to a large variety of surface morphologies including fibers, spherical structures or cauliflower-like structures [32,33].

Fluorinated substituents, especially long fluorinated chains, are very often used to increase both the surface hydrophobicity and oleophobicity. However, in order to find alternatives to long fluorinated chains, due to their bioaccumulation potentials, it is extremely important to investigate the possibility to replace long fluorinated chains to reach water and oil-repellent properties. Indeed, it was demonstrated that the bioaccumulation potential in depending on the fluorinated chain length and fluorinated chain lengths lower than seven methylene units can be considered as non-persistent [34,35].

Previously, it has been demonstrated the importance of the connectors between the polymer backbone and the fluorinated chains to control the surface oleophobicity [32b]. Here, in order to tune the surface morphology and the oleophobic properties of PEDOT films, the original fluorinated EDOT derivatives containing a thioester spacer between the fluorinated chain and the EDOT moiety, represented in Scheme 1 (EDOT-S-F<sub>n</sub>), were synthesized and used as monomer to elaborate liquid-repellent surfaces. The polymer

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**Scheme 1.** Fluorinated EDOT derivatives used in this report (EDOT-S-F<sub>n</sub> with *n* = 4, 6 and 8).

films, electrodeposited at constant potential, were analysed by static and dynamic contact angle measurements with various probe liquids, optical profilometry and scanning electron microscopy.

## 2. Experimental

### 2.1. Synthesis of the monomers

(2,3-Dihydrothieno[3,4-*b*][1,4]dioxin-2-yl)methanethiol was synthesized in three steps from 3,4-dimethoxythiophene using the procedure reported by Sallé et al. [36], except that we preferred to pass through the substitution of a chlorine group rather than a tosylate one (see Scheme 2). Then, the fluorinated monomers were obtained by esterification in the presence of EDC.

EDC (1.2 eq.) and a catalytic quantity of 4-dimethylaminopyridine were added to 5 mL of a solution of anhydrous dichloromethane containing the corresponding semifluorinated acid (1.2 eq.). After stirring for 30 min, (2,3-dihydrothieno[3,4-*b*][1,4]dioxin-2-yl)methanethiol (1 eq.) was added. After 24 h at 50 °C, the solvent was removed and the crude product was purified by column chromatography (eluent, cyclohexane/ethyl acetate 9:1).

EDOT-S-F<sub>8</sub>. Yield 48.8%. m.p. 72.7 °C. 250 MHz <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.51 (tt, 2H, <sup>3</sup>J<sub>HF</sub> = 14.7 Hz, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz), 2.93 (t, 2H, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz), 3.19 (dd, 1H, <sup>2</sup>J<sub>HH</sub> = 14.2 Hz, <sup>3</sup>J<sub>HH</sub> = 6.4 Hz), 3.28 (dd, 1H, <sup>2</sup>J<sub>HH</sub> = 14.2 Hz, <sup>3</sup>J<sub>HH</sub> = 5.9 Hz), 3.96 (dd, 1H, <sup>2</sup>J<sub>HH</sub> = 11.7 Hz, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz), 4.20 (dd, 1H, <sup>2</sup>J<sub>HH</sub> = 11.7 Hz, <sup>3</sup>J<sub>HH</sub> = 2.2 Hz), 4.26 (m, 1H), 6.34 (d, 1H, <sup>4</sup>J<sub>HH</sub> = 3.8 Hz), 6.36 (d, 1H, <sup>4</sup>J<sub>HH</sub> = 3.8 Hz). 50 MHz <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 26.40 (t, <sup>2</sup>J<sub>CF</sub> = 24.2 Hz), 29.22, 34.54 (t,

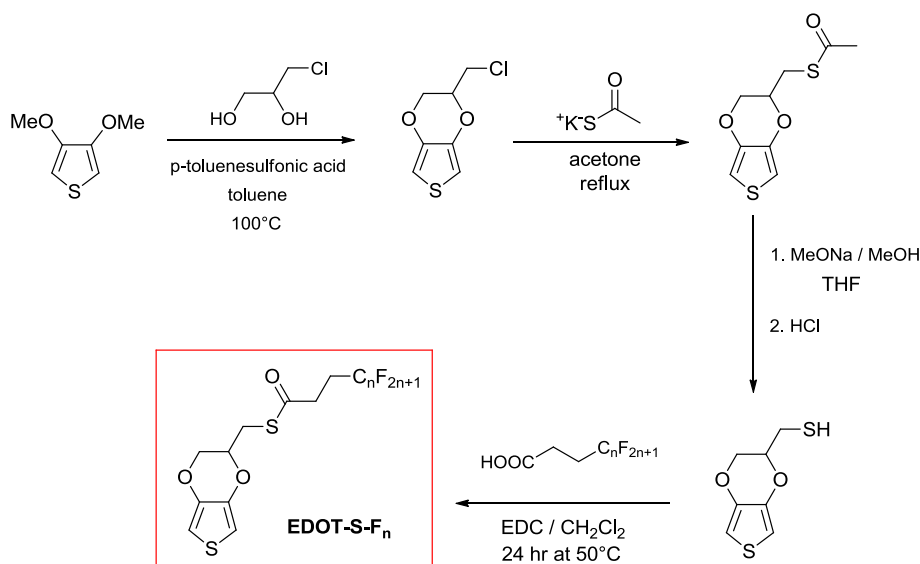
<sup>3</sup>J<sub>CF</sub> = 3.7 Hz), 66.80, 72.20, 99.95, 100.11, 140.90, 141.10, 195.59. 200 MHz <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ -126.15, -123.46, -122.72, -121.92, -114.46, -80.77. IR ν<sub>max</sub> (cm<sup>-1</sup>): 2955, 2925, 2854, 1699, 1491, 1241, 1202, 1148 cm<sup>-1</sup>. MS (70 eV, *m/z*): 662 (M<sup>+</sup>, 38%), 475 (C<sub>11</sub>H<sub>4</sub>F<sub>17</sub>O<sup>+</sup>, 25%), 154 (C<sub>7</sub>H<sub>6</sub>O<sub>2</sub>S<sup>+</sup>, 49%), 73 (C<sub>2</sub>H<sub>1</sub>OS<sup>+</sup>, 100%).

EDOT-S-F<sub>6</sub>. Yield 49.5%. m.p. 51.7 °C. 250 MHz <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.51 (tt, 2H, <sup>3</sup>J<sub>HF</sub> = 14.6 Hz, <sup>3</sup>J<sub>HH</sub> = 7.8 Hz), 2.93 (t, 2H, <sup>3</sup>J<sub>HH</sub> = 7.8 Hz), 3.19 (dd, 1H, <sup>2</sup>J<sub>HH</sub> = 14.2 Hz, <sup>3</sup>J<sub>HH</sub> = 6.5 Hz), 3.28 (dd, 1H, <sup>2</sup>J<sub>HH</sub> = 14.2 Hz, <sup>3</sup>J<sub>HH</sub> = 5.8 Hz), 3.96 (dd, 1H, <sup>2</sup>J<sub>HH</sub> = 11.7 Hz, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz), 4.20 (dd, 1H, <sup>2</sup>J<sub>HH</sub> = 11.7 Hz, <sup>3</sup>J<sub>HH</sub> = 2.2 Hz), 4.26 (m, 1H), 6.34 (d, 1H, <sup>4</sup>J<sub>HH</sub> = 3.8 Hz), 6.36 (d, 1H, <sup>4</sup>J<sub>HH</sub> = 3.8 Hz). 50 MHz <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 26.36 (t, <sup>2</sup>J<sub>CF</sub> = 25.3 Hz), 29.22, 34.54 (t, <sup>3</sup>J<sub>CF</sub> = 3.3 Hz), 66.80, 72.19, 99.95, 100.11, 140.90, 141.10, 195.58. 200 MHz <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ -126.17, -123.52, -122.93, -121.93, -114.45, -80.79. IR ν<sub>max</sub> (cm<sup>-1</sup>): 2955, 2925, 2854, 1697, 1493, 1237, 1192, 1142 cm<sup>-1</sup>. MS (70 eV, *m/z*): 562 (M<sup>+</sup>, 45%), 375 (C<sub>9</sub>H<sub>4</sub>F<sub>13</sub>O<sup>+</sup>, 25%), 154 (C<sub>7</sub>H<sub>6</sub>O<sub>2</sub>S<sup>+</sup>, 50%), 73 (C<sub>2</sub>H<sub>1</sub>OS<sup>+</sup>, 100%).

EDOT-S-F<sub>4</sub>. Yield 46.9%. m.p. 28.9 °C. 250 MHz <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.51 (tt, 2H, <sup>3</sup>J<sub>HF</sub> = 14.7 Hz, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz), 2.93 (t, 2H, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz), 3.19 (dd, 1H, <sup>2</sup>J<sub>HH</sub> = 14.2 Hz, <sup>3</sup>J<sub>HH</sub> = 6.5 Hz), 3.28 (dd, 1H, <sup>2</sup>J<sub>HH</sub> = 14.2 Hz, <sup>3</sup>J<sub>HH</sub> = 5.9 Hz), 3.96 (dd, 1H, <sup>2</sup>J<sub>HH</sub> = 11.7 Hz, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz), 4.20 (dd, 1H, <sup>2</sup>J<sub>HH</sub> = 11.7 Hz, <sup>3</sup>J<sub>HH</sub> = 2.2 Hz), 4.26 (m, 1H), 6.34 (d, 1H, <sup>4</sup>J<sub>HH</sub> = 3.8 Hz), 6.36 (d, 1H, <sup>4</sup>J<sub>HH</sub> = 3.8 Hz). 50 MHz <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 26.27 (t, <sup>2</sup>J<sub>CF</sub> = 23.0 Hz), 29.22, 34.52 (t, <sup>3</sup>J<sub>CF</sub> = 3.3 Hz), 66.80, 72.19, 99.95, 100.10, 140.89, 141.09, 195.57. 200 MHz <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ -126.05, -124.43, -114.71, -81.07. IR ν<sub>max</sub> (cm<sup>-1</sup>): 2955, 2925, 2854, 1693, 1489, 1237, 1187, 1129 cm<sup>-1</sup>. MS (70 eV, *m/z*): 462 (M<sup>+</sup>, 45%), 275 (C<sub>7</sub>H<sub>4</sub>F<sub>9</sub>O<sup>+</sup>, 28%), 154 (C<sub>7</sub>H<sub>6</sub>O<sub>2</sub>S<sup>+</sup>, 51%), 73 (C<sub>2</sub>H<sub>1</sub>OS<sup>+</sup>, 100%).

### 2.2. Electrochemical experiments

The monomer (0.01 M) was added to 10 mL of anhydrous acetonitrile containing 0.1 M of tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>), previously introduced in a glass cell and degassed with argon. A three-electrode system was introduced in the cell and connected to a potentiostat (Autolab from Metrohm). A carbon rod and a saturated calomel electrode were used as counter-electrode and reference electrode, respectively. For the experi-



**Scheme 2.** Chemical route to the monomers.

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