

## Supporting Information

### **Highly hydrophobic Films with Various Adhesion by Electrodeposition of Poly(3,4-Bis(Alkoxy)Thiophene)s**

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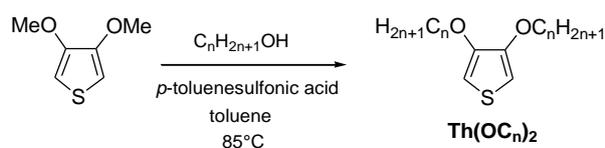
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### Monomer characterization

The monomer retention times (r.t.) were determined with a 5890 series II gas chromatography from Hewlett-Packard (capillary column HP5, 30 m, 0.32 mm; heating program: 60-250°C at 10°C/min). The melting points (m.p.) were determined with a Perkin-Elmer Jade DSC using the following protocol: heating from 30 to 70°C, cooling until -20°C, and then heating to 70°C (scan rate 10°C/min). The melting points were recorded during the second heating phase. <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained with a Bruker W-200 MHz spectrometer. The monomer mass spectra were obtained by electron ionization at 70 eV with a Thermofischer Corp. Thermo TRACEGC fitted with an Automass III Multi spectrometer. Infrared spectra in KBr were recorded using a Perkin-Elmer Spectrum 100 FT-IR spectrometer.

### Monomer synthesis

The monomers were synthesized using a modification of a procedure established in the literature.<sup>1-2</sup> Briefly, 1-alkanol (11.0 mmol) was added to 5 mL of toluene containing 0.8 g (5.5 mmol) of 3,4-dimethoxythiophene and 40 mg of *p*-toluenesulfonic acid monohydrate (Scheme ESI<sub>1</sub>). After stirring for 24 h at 85°C, the solvent was removed and the product was separated by column chromatography (silica gel; eluent: hexane/ethyl acetate 9:1). The characterization details are given in ESI.



**Scheme ESI<sub>1</sub>.** Synthetic way to the monomers  $\text{Th}(\text{OC}_n)_2$  with  $n = 8, 10$  and  $12$ .

### **3,4-bis(octyloxy)thiophene (ThO(C<sub>8</sub>)<sub>2</sub>).**

Yield 35 %; r.t. 19.6 mm; white solid. m.p. 28.3°C;  $\delta_{\text{H}}$ (200 MHz, CDCl<sub>3</sub>) 6.16 (2 H, s), 3.97 (4 H, t, *J* 6.8), 1.82 (4 H, quint, *J* 6.8), 1.42 (4 H, m), 1.29 (16 H, m), 0.88 (6 H, t, *J* 6.4);  $\delta_{\text{C}}$ (50 MHz, CDCl<sub>3</sub>): 147.54, 96.83, 70.56, 31.79, 29.33, 29.21, 29.00, 25.96, 22.64, 14.07; FTIR (KBr):  $\nu_{\text{max}}/\text{cm}^{-1}$  2946, 2924, 2854, 1564, 1500, 1467, 1372, 1202, 1153 cm<sup>-1</sup>; MS (70 eV): *m/z* 341 (M<sup>+</sup>, 1), 256 (C<sub>14</sub>H<sub>24</sub>O<sub>2</sub>S<sup>+</sup>, 2), 116 (C<sub>4</sub>H<sub>4</sub>O<sub>2</sub>S<sup>+</sup>, 100).

### **3,4-bis(decyloxy)thiophene (ThO(C<sub>10</sub>)<sub>2</sub>).**

Yield 25 %; r.t. 24.7 mm; white solid; m.p. 39.5°C;  $\delta_{\text{H}}$ (200 MHz, CDCl<sub>3</sub>) 6.16 (2 H, s), 3.97 (4 H, t, *J* 6.8), 1.81 (4 H, quint, *J* 6.8), 1.26 (24 H, m), 0.88 (6 H, t, *J* 6.4);  $\delta_{\text{C}}$ (50 MHz, CDCl<sub>3</sub>): 147.57, 96.86, 70.58, 31.90, 29.70, 29.57, 29.39, 29.33, 29.03, 25.97, 22.68, 14.10; FTIR (KBr):  $\nu_{\text{max}}/\text{cm}^{-1}$  2953, 2912, 2847, 1567, 1507, 1463, 1369, 1204, 1160 cm<sup>-1</sup>; MS (70 eV): *m/z* 396 (M<sup>+</sup>, 2), 256 (C<sub>14</sub>H<sub>24</sub>O<sub>2</sub>S<sup>+</sup>, 2), 116 (C<sub>4</sub>H<sub>4</sub>O<sub>2</sub>S<sup>+</sup>, 100).

### **3,4-bis(dodecyloxy)thiophene (Th(OC<sub>12</sub>)<sub>2</sub>)**

Yield 23 %; r.t. 37.6 mm; white solid; m.p. 45.8°C;  $\delta_{\text{H}}$ (200 MHz, CDCl<sub>3</sub>) 6.16 (2 H, s), 3.97 (4 H, t, *J* 6.8), 1.81 (4 H, quint, *J* 6.8), 1.42 (H, m), 1.26 (32 H, m), 0.88 (6 H, t, *J* 6.4);  $\delta_{\text{C}}$ (50 MHz, CDCl<sub>3</sub>): 147.55, 96.84, 70.57, 31.91, 29.67, 29.64, 29.60, 29.58, 29.39, 29.35, 29.01, 25.97, 22.68, 14.10; FTIR (KBr):  $\nu_{\text{max}}/\text{cm}^{-1}$  2940, 2915, 2847, 1567, 1509, 1464, 1370, 1203, 1159 cm<sup>-1</sup>; MS (70 eV): *m/z* 453 (M<sup>+</sup>, 15), 116 (C<sub>4</sub>H<sub>4</sub>O<sub>2</sub>S<sup>+</sup>, 100).

### **Electropolymerization**

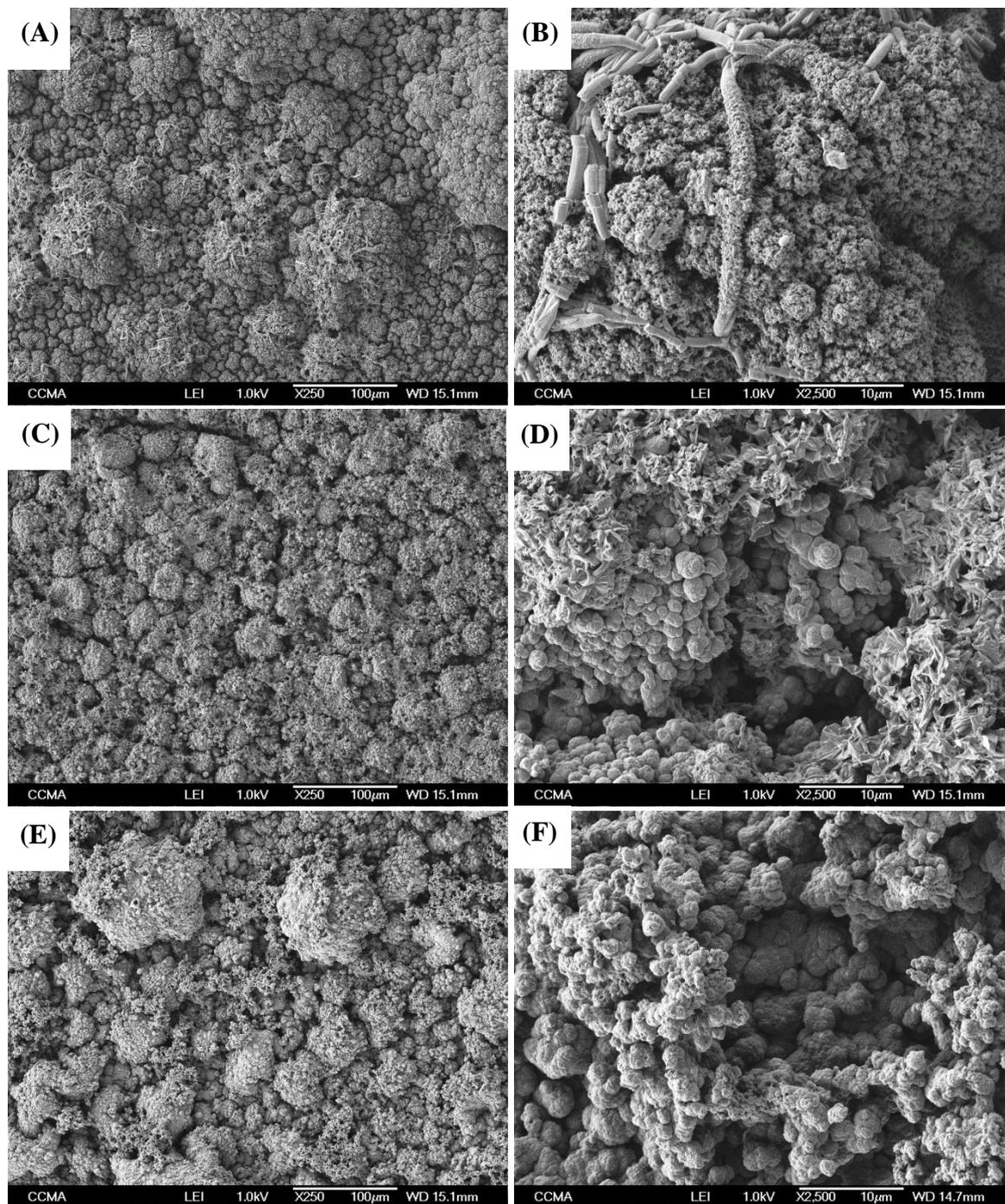
Polymer electrochemical depositions were performed using a three-electrode cell connected to Autolab PGSTAT 30 potentiostat from Eco Chemie B. V. A platinum disk working electrode was used for cyclic voltammetry experiments and gold plates for the surface characterization. The two others electrodes were a glassy carbon rod as counter-electrode and a saturated calomel reference (SCE) electrode. For the experiments, the cell was purged with argon and 10 mL of anhydrous acetonitrile containing 0.1 M of supporting electrolyte was added. After 20 mn under argon, 0.02 M of monomer was added and the solution was purged for 20 mn.

### **Surface characterization**

The superhydrophobic properties were evaluated by static and dynamic contact angles of water. The measurements were performed with a Krüss DSA-10 contact angle goniometer. The values given in this report correspond to an average of five measurements. The static contact angles were obtained with the sessile drop method using 2  $\mu\text{l}$  deionized water droplets (mean of five measurements). The dynamic contact angles were evaluated with the tilted-drop method using 6  $\mu\text{l}$  water droplets. The surface inclination gave the sliding angle when the droplet rolled off the surface. Just before the water droplet rolled off the surfaces, the advanced and receding angles were obtained due to the droplet deformation.

To analyse the surface morphology, the surface were characterized by scanning electron microscopy with a JEOL 6700F microscope. Roughness profiles of the surface were achieved by optical profilometry with a WYKO NT1100 optical profilometer. A field of view of 0.5x and an objective of 50x were used for the measurements given analysed areas of 239  $\mu\text{m}$  x 182  $\mu\text{m}$ . The arithmetic mean roughness (Ra) and the quadratic mean roughness (Rq) were also assessed.

Complementary SEM images



**Fig.** ESI<sub>3</sub> SEM images of polyTh(OC<sub>8</sub>)<sub>2</sub> ((A) x 250 and (B) x 2500), polyTh(OC<sub>10</sub>)<sub>2</sub> ((C) x 250 and (D) x 2500) and polyTh(OC<sub>12</sub>)<sub>2</sub> ((E) x 250 and (F) x 2500) obtained with NaClO<sub>4</sub>; Q<sub>s</sub> ≈ 1000 mC.cm<sup>-2</sup>.

## References

- 1 a) M. Leclerc and G. Daoust, *J. Chem. Soc., Chem. Commun.*, 1990, **3**, 273; b) G. Daoust, and M. Leclerc, *Macromolecules*, 1991, **24**, 455; c) F. Goldoni, B.M.W. Langeveld-Voss, E.W. Meijer, *Synth. Commun.*, 1998, **28**, 2237.
- 2 M. Refczyńska and M. Skompska, *J. Phys.: Conference Series*, 2009, **146**, 012013; b) M. Refczyńska, J. Mieczkowski and M. Skompska, *Electrochim. Acta*, 2008, **53**, 2984.