Supporting Information

Superoleophobic Surfaces with Short Fluorinated Chains?

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Monomer synthesis

**Synthesis of (2,3-dihydrothieno[3,4-b][1,4]dioxin-2-yl)methanamine (EDOT-NH₂)**

2-(chloromethyl)-2,3-dihydrothieno[3,4-b][1,4]dioxine (0.3 g, 1.6 mmol) and potassium phtalimide (0.4 g, 2.2 mmol) were added to 5 mL of DMF. The mixture was heated at 100°C for 24 hrs. Then, the solution was poured in 100 mL of water and the product was extracted with chloroform. The organic layer was washed with cold 0.1 N sodium hydroxide and water and dried over Na₂SO₄. Then, the obtained product and hydrazine hydrate (0.16 g, 3.2 mmol) were added to 10 mL of methanol and the mixture heated at 50°C for 1 hr. 25 mL of water were added and the methanol was extracted under vacuum. 2 mL of concentrated HCl were slowly added and the solution was heated at 60°C for 1 hr. After filtration, the filtrate was neutralized with 2 N sodium hydroxide. After solvent evaporation, the product was purified by column chromatography (silica gel; eluent: methanol/ dichloromethane 1:4).

Yield 33 %; Slightly yellow liquid; δ_H (200 MHz, CD₃OD): 6.40 (1 H, d, J 3.6), 6.36 (1 H, d, J 3.6), 4.23 (1 H, dd, J 11.3, J 2.0), 4.11 (1 H, m), 3.92 (1 H, dd, J 11.3, J 7.4), 2.88 (2 H, d, J 5.9); δ_C (50 MHz, CD₃OD): 143.07, 142.96, 100.54, 100.36, 76.03, 67.66, 42.58; FTIR (KBr): v_max/cm⁻¹ 3371, 2951, 2924, 2870, 1662, 1578, 1486, 1187, 1057, 1022 cm⁻¹; MS (70 eV): m/z 171 (M⁺, 30), 154 (C₇H₆O₂S⁺, 100), 142 (C₆H₅O₂S⁺, 47).

**Synthesis of EDOT-NH-OFₙ**

Finally, the fluorinated monomers were synthesized by amidification reaction in presence of semi-fluorinated acid, EDC and DMAP. The corresponding semifluorinated acid (1.5 mmol), EDC (0.3 g, 1.5 mmol) and DMAP (40 mg) were added to 20 mL of dichloromethane. After stirring during 30 mn at room temperature, (2,3-dihydrothieno[3,4-b][1,4]dioxin-2-yl)methanamine (0.2 g, 1.3 mmol) was added. After stirring for a day at 50°C, the solvent was removed and the crude was purified by column chromatography (silica gel; eluent: ethyl acetate/cyclohexane 50:50) to yield the products.

N-((2,3-dihydrothieno[3,4-b][1,4]dioxin-2-yl)methyl)-
4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecanamide (EDOT-NH-F₈).
Yield 52%; m.p. 72.4 °C; δ_H (200 MHz, CDCl₃): 6.35 (1 H, d, J 3.8), 6.34 (1 H, d, J 3.8), 5.99 (1 H, m), 4.27 (1 H, m), 4.20 (1 H, dd, J 11.7, J 2.2), 3.92 (1 H, dd, J 11.7, J = 7.5), 3.72 (1 H, ddd, J 14.4, J 6.5, J 3.8), 3.47 (1 H, ddd, J 14.4, J 6.8, J 5.6), 2.52 (4 H, m); δ_C (50 MHz, CDCl₃): 170.19, 141.16, 140.94, 100.10, 99.92, 72.44, 66.11, 39.72, 26.99 (t, J 4.6), 26.65 (t, J 21.0); δ_F (CDCl₃): -80.77, -114.65, -121.94, -122.75, -123.51, -126.99; FTIR (KBr): ν_max/cm⁻¹ 3355, 2955, 2928, 2850, 1653, 1542, 1490, 1260, 1237, 1195, 1146, 1097, 1026 cm⁻¹; MS (70 eV): m/z 645 (M⁺, 25), 530 (C₁₀H₉F₉NO⁺⁺, 85), 154 (C₇H₆O₂S⁺, 100).

N-((2,3-dihydrothieno[3,4-b][1,4]dioxin-2-yl)methyl)-4,4,5,5,6,6,7,8,9,9,9-tridecafluorononanamide (EDOT-NH-F₆).
Yield 58%; m.p. 58.7 °C; r.t. 17.6 min; δ_H (200 MHz, CDCl₃): 6.35 (1 H, d, J 3.8), 6.34 (1 H, d, J 3.8), 5.98 (1 H, m), 4.27 (1 H, m), 4.20 (1 H, dd, J 11.7, J 2.2), 3.92 (1 H, dd, J 11.7, J 7.5), 3.72 (1 H, ddd, J 14.4, J 6.5, J 3.8), 3.47 (1 H, ddd, J 14.4, J 6.8, J 5.6), 2.52 (4 H, m); δ_C (50 MHz, CDCl₃): 170.17, 141.16, 140.93, 100.10, 99.92, 72.44, 66.10, 39.72, 26.94 (t, J 4.3), 26.65 (t, J 21.9); δ_F (CDCl₃): -80.80, -114.66, -121.94, -122.91, -123.50, -126.20; FTIR (KBr): ν_max/cm⁻¹ 3351, 2955, 2928, 2854, 1653, 1544, 1490, 1261, 1226, 1201, 1148, 1072, 1026 cm⁻¹; MS (70 eV): m/z 545 (M⁺, 24), 430 (C₁₀H₉F₉NO⁺⁺, 95), 154 (C₇H₆O₂S⁺, 100).

N-((2,3-dihydrothieno[3,4-b][1,4]dioxin-2-yl)methyl)-4,4,5,5,6,6,7,7,7-nonafluoroheptanamide (EDOT-NH-F₄).
Yield 67%; m.p. 42.5 °C; r.t. 16.3 min; δ_H (200 MHz, CDCl₃): 6.35 (1 H, d, J 3.7), 6.34 (1 H, d, J 3.7), 5.99 (1 H, m), 4.27 (1 H, m), 4.20 (1 H, dd, J 11.7, J 2.2), 3.92 (1 H, dd, J 11.7, J 7.5), 3.72 (1 H, ddd, J 14.4, J 6.5, J 3.8), 3.47 (1 H, ddd, J 14.4, J 6.8, J 5.6), 2.52 (4 H, m); δ_C (50 MHz, CDCl₃): 170.17, 141.16, 140.93, 100.10, 99.92, 72.43, 66.10, 39.72, 26.95 (t, J 4.0), 26.55 (t, J 21.7); δ_F (CDCl₃): -81.04, -114.91, -122.91, -123.50, -126.20; FTIR (KBr): ν_max/cm⁻¹ 3335, 2959, 2924, 2854, 1658, 1555, 1487, 1260, 1229, 1201, 1134, 1097, 1020 cm⁻¹; MS (70 eV): m/z 445 (M⁺, 33), 330 (C₁₀H₉F₉NO⁺⁺, 100), 154 (C₇H₆O₂S⁺, 53).