Electronic Supplementary Material (ESI) for Soft Matter

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-NH_2)

2-(chloromethyl)-2,3-dihydrothieno[3,4-*b*][1,4]dioxine (0.3 g, 1.6 mmol) and potassium phtalimide (0.4 g, 2.2mmol) 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 Na_2SO_4. 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, CD_3OD): 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, CD_3OD): 143.07, 142.96, 100.54, 100.36, 76.03, 67.66, 42.58; FTIR (KBr): ν_{max}/cm^{-1} 3371, 2951, 2924, 2870, 1662, 1578, 1486, 1187, 1057, 1022 cm^{-1}; MS (70 eV): *m*/*z* 171 (M^+, 30), 154 ($C_7H_6O_2S^+$, 100), 142 ($C_6H_5O_2S^{+\bullet}$, 47).

Synthesis of EDOT-NH-OF_n

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-F_8).**

Yield 52 %; m.p. 72.4 °C; δ_H(200 MHz, $CDCl_3$): 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, $CDCl_3$): 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($CDCl_3$): -80.77, -114.65, -121.94, -122.75, -123.51, -126.16; 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 ($C_{10}H_9F_9NO^{+\bullet}$, 85), 154 ($C_7H_6O_2S^+$, 100).

_N_-((2,3-dihydrothieno[3,4-*b*][1,4]dioxin-2-yl)methyl)-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononanamide (EDOT-NH-F_6).

Yield 58 %; m.p. 58.7 °C; r.t. 17.6 mn; δ_H(200 MHz, $CDCl_3$): 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, $CDCl_3$): 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($CDCl_3$): -80.80, -114.66, -121.94, -122.91, -123.50, -126.20; FTIR (KBr): ν_{max}/cm^{-1} 3351, 2955, 2924, 2854, 1653, 1544, 1490, 1261, 1226, 1201, 1148, 1072, 1026 cm^{-1}; MS (70 eV): *m*/*z* 545 (M^+, 24), 430 ($C_{10}H_9F_9NO^{+\bullet}$, 95), 154 ($C_7H_6O_2S^+$, 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-F_4).

Yield 67 %; m.p. 42.5 °C; r.t. 16.3 mn; δ_H(200 MHz, $CDCl_3$): 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, $CDCl_3$): 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($CDCl_3$): -81.04, -114.91, -124.50, -126.07; 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 ($C_{10}H_9F_9NO^{+\bullet}$, 100), 154 ($C_7H_6O_2S^+$, 53).