

Supporting Information

Super oil-repellent surfaces from conductive polymers

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Synthesis of the monomers

2-(2,3-dihydro-[1,4]dioxino[2,3-c]pyrrol-6-yl)ethoxytert-butyldimethylsilane (1).

EDOP was synthesized from iminodiacetic acid in an eight steps process developed by Merz et al¹. Dry sodium hydride (0.25 g, 10 mmol) was carefully added to a solution of EDOP (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 NH₄Cl was carefully added and the solution was extracted with diethyl ether and dried (MgSO₄). Removal of solvent and purification by column chromatography (silica gel; eluent: hexane) gave **(1)** (Retention time: 14.7 mn); Yield 73 %.

2-(2,3-dihydro-[1,4]dioxino[2,3-c]pyrrol-6-yl)ethanol (2).

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 **(2)** (Retention time: 10.5 mn) as a colourless liquid.

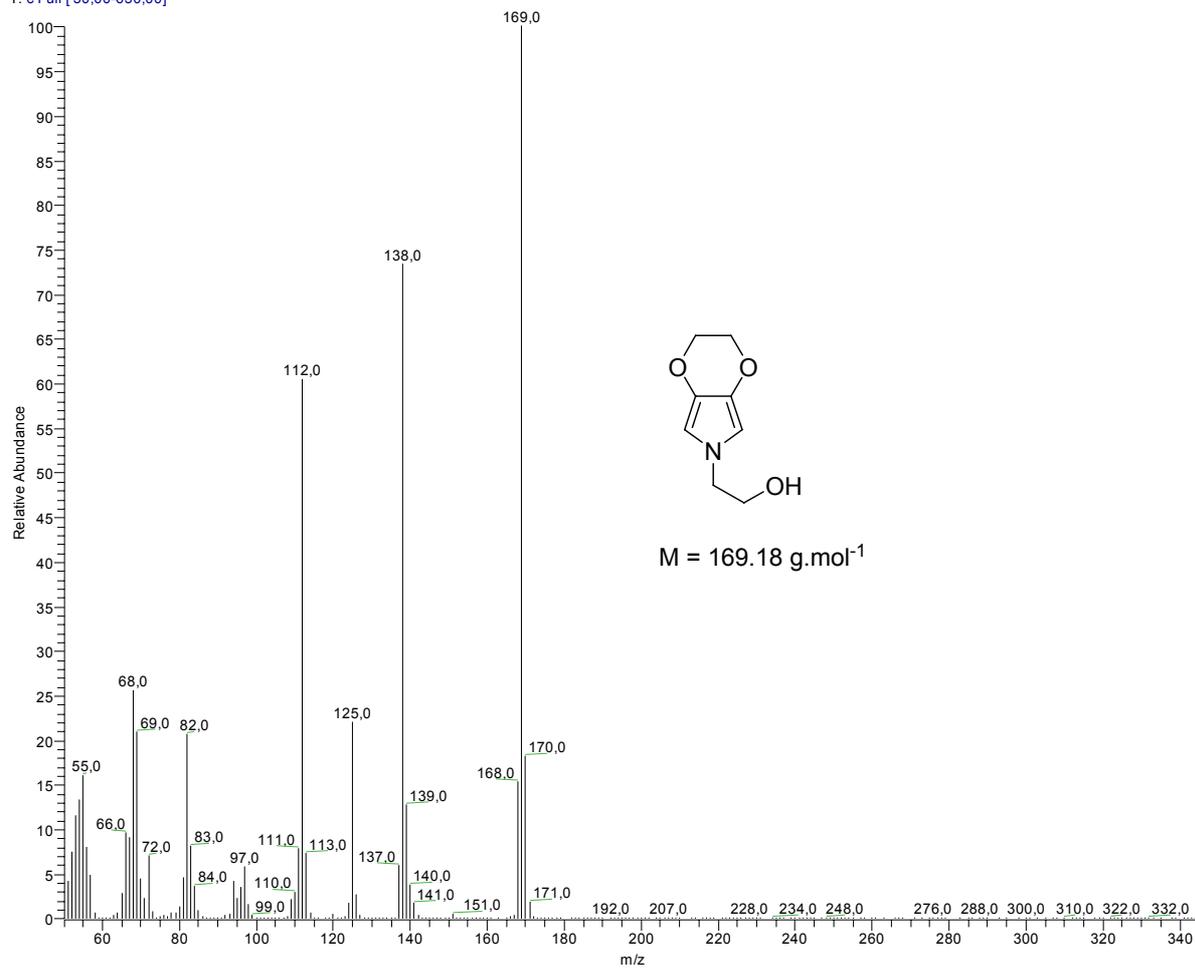
Yield 65 %; δ_{H} (250 MHz, CDCl₃) 1.79 (1 H, s), 3.79 (4 H, m), 4.17 (4 H, s) and 6.12 (2 H, s); δ_{C} (50 MHz, CDCl₃) 52.53, 62.77, 65.74, 101.35 and 132.24; m/z 169 (M⁺, 100%), 138 (C₇H₈NO₂⁺, 74); Found: C, 56.85; H, 6.58; N, 8.17. C₈H₁₁NO₃ requires C, 56.80; H, 6.55; N, 8.28%;

2-(2,3-dihydro-[1,4]dioxino[2,3-c]pyrrol-6-yl)ethyl 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptafluoroundecanoate (3).

DMAP (30 mg) and N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC) (0.3 mg, 1.5 mmol) were added to a solution of 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptafluoroundecanoic acid (0.72 g, 1.5 mmol) in dichloromethane. After stirring during 30 mn at room temperature, **(2)** (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 **(3)** (Retention time = 16.6 mn) as a white solid.

Yield 75 %; m.p. 71-72 °C; δ_{H} (250 MHz, CDCl₃) 2.44 (2 H, tt, J_{HH} 7.1, J_{HF} 18.4), 2.63 (2 H, t, $^3J_{\text{HH}}$ 7.1), 3.92 (2 H, t, J_{HH} 5.4), 4.17 (4 H, s), 4.29 (2 H, t, J_{HH} 5.4) and 6.07 (2 H, s); δ_{C} (50 MHz, CDCl₃) 25.37 (t, J_{CF} 3.7), 26.40 (t, J_{CF} 21.9), 48.67, 64.63, 65.76, 101.37, 132.46 and 170.76; δ_{F} (188 MHz, CDCl₃) -126.54 (2 F, m), -123.97 (2 F, m), -123.15 (2 F, m), -122.32 (6 F, m), -115.15 (2 F, m) and -81.16 (3 F, m); ν_{max} (film)/cm⁻¹ 2922, 2864, 1740, 1556, 1200 and 1148; m/z 643 (M⁺, 22), 151 (C₈H₉NO₂⁺, 100), 138 (C₇H₈NO₂⁺, 93); Found: C, 35.58; H, 2.21; N, 2.15. C₁₉H₁₄F₁₇NO₄ requires C, 35.47; H, 2.19; N, 2.18%.

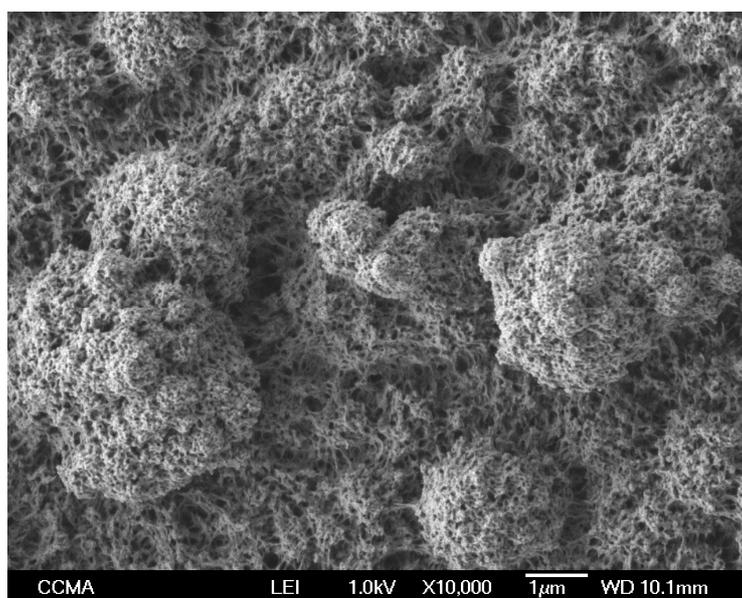
TD135 #2717 RT: 11.03 AV: 1 SB: 793 10,01-10,93, 11,34-12,75 NL: 1,28E6
T: c Full [50,00-650,00]



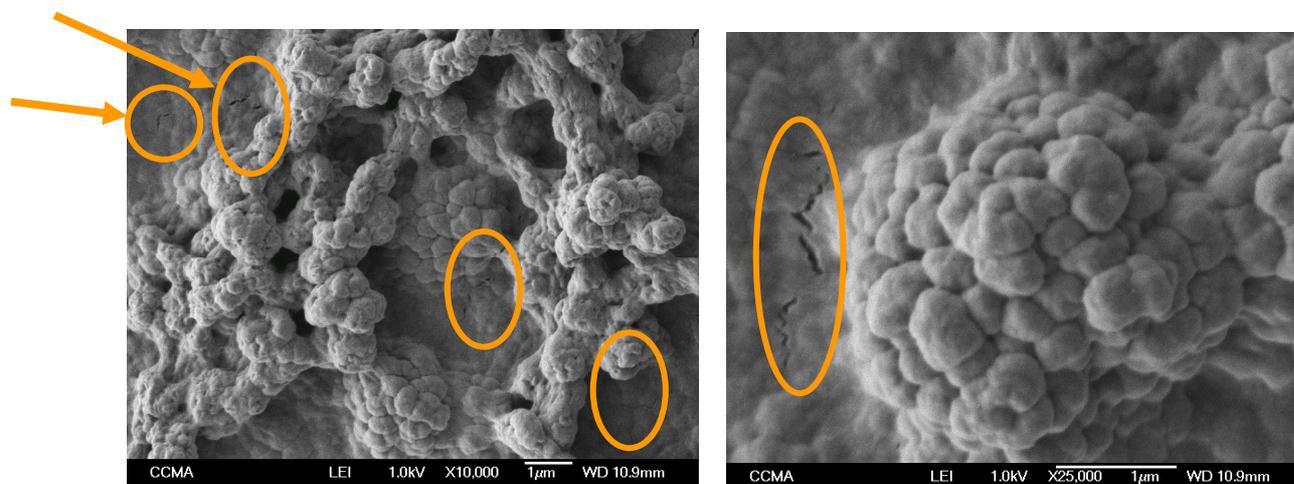
Mass spectrum of (2)

Contact angles with oils of superoleophobic surfaces reported in the literature.

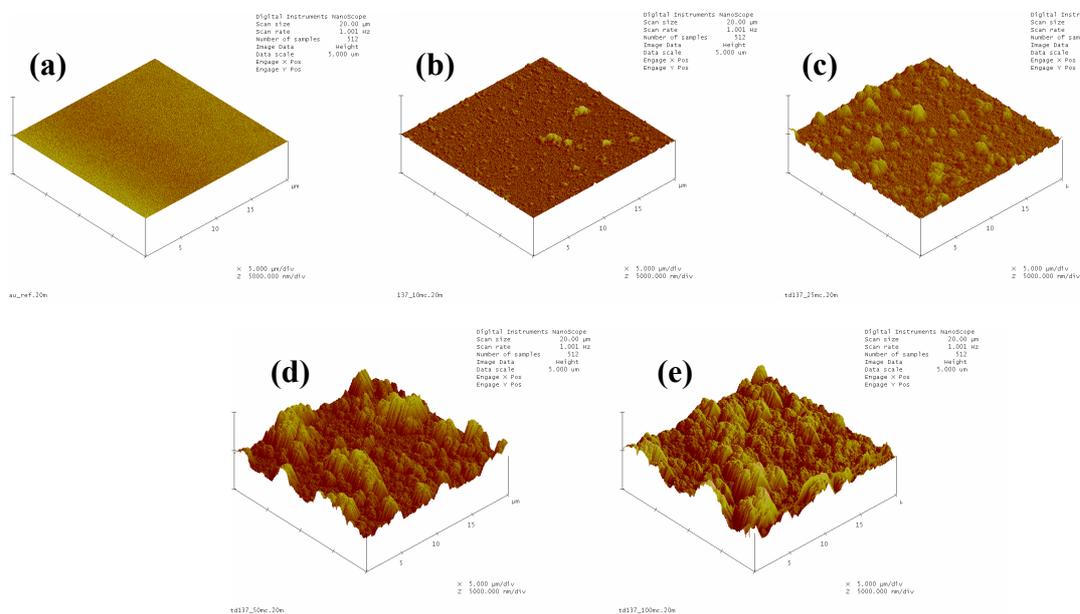
Reference	Oil	γ_L (mN/m)	Contact angle
[19-20]	rapeseed oil	35	150
	hexadecane	27.5	135.5
[21]	salad oil	not available in the pub	130
[22]	oil used : not identified	not available in the pub	150.0
[23]	hexadecane	27.5	140
[24]	hexadecane	27.5	150.7
[25]	hexadecane	27.5	140
[26]	rapeseed oil	35	161
[27]	octane	21.6	163
[28]	oil used : not identified	not available in the pub	140
[29]	salad oil	not available in the pub	142.8
[30]	diiodomethane (not oil)	50	152
[31]	hexadecane	27.5	135
[55]	hexadecane	27.5	135
present work	hexadecane	27.5	147



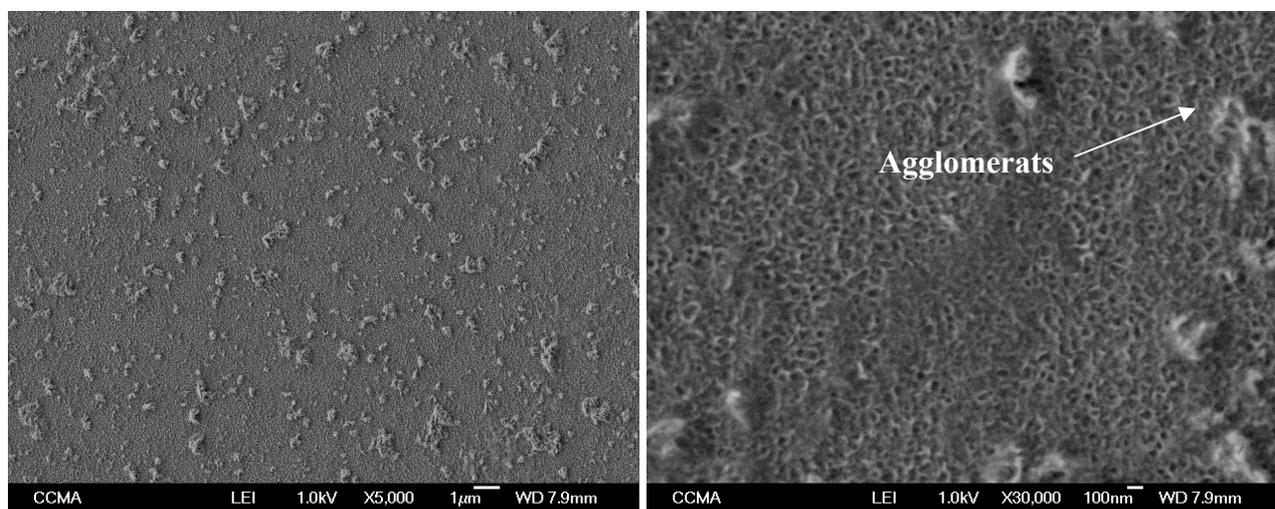
SEM images of poly(3) electrodeposited on gold from an acetonitrile solution containing $\text{Bu}_4\text{N}^+\text{ClO}_4^-$; the scale bar represents 1 μm .



SEM images of poly(3) surface obtained with $\text{Bu}_4\text{N}^+\text{CH}_3\text{PhSO}_3^-$ salt: same surface, two different magnifications. Circles indicate small fractures of the surface.



AFM images of poly(3) electrodeposited with various deposition charges Q_s (mC.cm⁻²): (a) 0; (b) 10; (c) 25; (d) 50 et (e) 100.



SEM images of the polymer surface for $Q_s = 10 \text{ mC.cm}^{-2}$; the scale bar represents (a) 1 μm , (b) 100 nm.