

Electronic supplementary information for:

Solution-Processed Superhydrophobic Conjugated Polymer Films

Daniel Nyström,^a Per Antoni,^a Steven Holdcroft,^b Anders Hult,^a Eva Malmström^a and George Vamvounis^{*a,c}

^a *School of Chemical Science and Engineering, Fibre and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Sweden*

^b *Department of Chemistry, Simon Fraser University, Burnaby, B.C., Canada*

^c *School of Chemistry and Molecular Biosciences, University of Queensland, Brisbane, QLD, Australia, e-mail: g.vamvounis@uq.edu.au*

Supporting Information:

Synthesis:

Poly(9,9-dihexylfluorene-2,7-diyl-alt-2-(2-thiophen-3-ethoxy)tetrahydropyran-2,5-diyl) (PFT-THP): To a purged solution (with nitrogen) of 2,5-dibromo-3-(2-hydroxy)ethylthiophene (0.204g, 0.55 mmol), 9,9-dihexylfluorene-2,7-bis(trimethyleneborate) (0.277g, 0.55 mmol) and an 1 ml of an aqueous solution of 2.4M K₂CO₃ in THF (6 ml) was added 3 mole % of Pd(PPh₃)₄ (0.0187g, 0.00162 mmol) to a vial and sealed. The solution was heated for 72 hours at 40°C. The solution was then diluted with CHCl₃ and washed with water (2 times). The organic phase was dried with MgSO₄ and most of the solvent was removed under reduced pressure. The remaining polymer solution (~2ml) was then precipitated into methanol to afford a bright yellow product. After filtration, 0.256 g (86 % yield) of polymer was obtained. Flash chromatography with CHCl₃ was performed to remove catalyst residues, followed by precipitation. 400MHz ¹H NMR, PPM (CD₂Cl₂) δ 7.8-7.5 (m, 6H), 7.46 (s, 1H), 4.67 (m, 1H), 4.1 (m, 1H), 3.8(m, 2H), 3.5 (m, 1H), 3.0 (br, s, 2H), 2.1 (s, 4H), 1.9-0.49 (m, 28H). ¹³C NMR δ 142.28, 140.56, 139.58, 136.76, 133.56, 128.50, 126.35, 124.76, 124.10, 120.09, 98.94, 67.69, 62.21, 55.69, 40.71, 31.87, 31.08, 30.049, 25.93, 24.22, 22.95, 19.87, 14.14. FTIR (KBr), cm⁻¹: 3150 (C-H stretch, aromatic), 2929 (CH₂ in-phase vibration), 2860 (CH₂ out of phase vibration), 1465 (C=C stretch, ring), 1135, 1133, 819 (C-H out of plane bending). GPC: M_w 9395, PDI 2.36.

Poly(9,9-dihexylfluorene-2,7-diyl-alt-2-(2-thiophen-3-ethanol)-2,5-diyl): A mixture of poly(9,9-dihexylfluorene-2,7-diyl-alt-2-(2-thiophen-3-ethoxy)tetrahydropyran-2,5-diyl) (PFT-THP) (0.200 g, 0.437 mmol), 2 ml 10% hydrochloric acid solution, and 20 ml of THF was heated under reflux for 48 hours. The reaction mixture was eluted with CHCl₃ and washed with 10% Na₂CO₃ solution and water (2 times). Evaporation under reduced pressure resulted in the title compound in quantitative yields. 400MHz ¹H NMR, PPM δ 7.8-7.5 (m, 7H), 4.0 (m, 2H), 3.0 (m, 2H), 2.1 (s, 4H), 1.9-0.49 (m, 20H). FTIR (neat), cm⁻¹: 3366 (-OH stretch), 3045 (C-H stretch, aromatic), 2922 (CH₂ in-phase vibration), 2851 (CH₂ out of phase vibration), 1462 (C=C stretch, ring), 1028, 819 (C-H out of plane bending).

Poly(9,9-dihexylfluorene-2,7-diyl-alt-3-ethylperfluorooctanoate thiophene-2,5-diyl) (PFT-F): To a THF solution of poly(9,9-dihexylfluorene-alt-2-(2-thiophen-3-ethanol)) (0.043 g, 0.0094 mmol), triethylamine (0.038 g, 0.038 mmol) and catalytic amounts of dimethylaminopyridine, pentadecafluorooctanoyl chloride (0.081 g, 0.0188 mmol) was added. The reaction was left to proceed over night at room temperature under stirring. The target was purified via precipitation in methanol and isolated via filtration. 400MHz ¹H NMR, PPM δ 7.8-7.5 (m, 7H), 4.7 (m, 2H), 3.2 (m, 2H), 2.0 (s, 4H), 1.6 (br, s, 2H), 1.1(br, s, 10H), 0.8 (m, 8H). FTIR (neat), cm⁻¹: 3040 (C-H stretch, aromatic), 2924 (CH₂ in-phase vibration), 2853 (CH₂ out of phase vibration), 1779 (C=O stretch), 1463 (C=C stretch, ring), 1202 (C-F stretch), 1143, 1011, 814 (C-H out of plane bending).

Filmcasting:

Smooth films were prepared by solvent casting in dry air. Porous films were obtained by dissolving the polymers in the casting solvent, followed by sonication to ensure complete dissolution, and the polymer films were then cast under humid conditions (60-90% relative humidity). The concentration of the polymer solutions were between 2-30 mg/ml solvent.