

Supporting Information

Nucleoside surface as platform for the control of surface hydrophobicity

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Materials

All chemical products were purchased from Sigma-Aldrich. Electrochemical grade of tetrabutylammonium hexafluorophosphate was chosen. Gold plates (deposition of Cr + Au 1500 Å on silicon wafers) were purchased from Neyco.

Monomer synthesis

Synthesis of 2-(4-bromobutyl)-2,3-dihydrothieno[3,4-*b*][1,4]dioxine (EDOT-Br). EDOT-OH¹ (1.9 g, 8.9 mmol) was dissolved in dichloromethane (100 mL). Triethylamine (1.8 g, 17.8 mmol, 2 eq) was added (Scheme 1). The mixture was cooled at 0 °C. Methanesulfonyl chloride (1.2 g, 10.6 mmol, 1.2 eq) was added carefully. The mixture was allowed to warm up at room temperature. After 4 h, methanol (10 mL) was added. The mixture was stirred for 30 mn. All volatiles were removed under reduced pressure. The residual oil was dissolved in DMF (100 mL) and potassium bromide (5.3 g, 44.5 mmol, 5 eq) was added. The mixture stirred overnight at 95 °C. The reaction was then allowed to cool at room temperature and most part of the volatiles were removed under reduced pressure. Dichloromethane (100 mL) was added. The organic layer was washed with water (2X30 mL), brine (30mL) and dried over MgSO₄. The solvents were removed under reduced pressure. **EDOT-Br** is finally purified on column (90/10, cyclohexane/dichloromethane).

Yield: 57%; Colorless oil; δ_{H} (200 MHz, CDCl₃, ppm): 6.3 (s, 2H), 4.11-4.18 (m, 2H), 3.86-3.92 (m, 1H), 3.53-3.60 (m, 2H), 1.6-1.85 (m, 6H); δ_{C} (50 MHz, CDCl₃, ppm): 142, 141.6, 99.4, 73.4, 68.3, 44.6, 32.3, 29.9, 22.4.

Synthesis of 5'-azido-5'-deoxy-uridine. 5'-azido-5'-deoxyuridine was prepared following procedure described in the literature (Scheme 2). Uridine (5 g, 20.5 mmol) was dissolved in acetone. H₂SO₄ (200 mg, 2.05 mmol, 0.1 eq) was added and the mixture was stirred at room temperature overnight. 1 mL of triethylamine was added and all volatiles were removed under vacuum. The formed compound was dissolved in DCM (50 mL) and triethylamine (6.2 g, 61.5 mmol, 3 eq) was added. Methanesulfonyl chloride (4.7 g, 41 mmol, 2 eq) was added dropwise at 0 °C. The mixture was stirred 4 h at room temperature. Methanol (10 mL) was added. The mixture was stirred for 30 mn. All volatiles were removed under reduced pressure. The residual oil was dissolved in DMF (100 mL) and sodium azide (6.7 g, 5 eq, 102.5 mmol) was added. The mixture was stirred overnight at 95 °C. The reaction was then allowed to cool at room temperature and most part of the DMF was removed under reduced pressure. Finally, the residual compound was dissolved in MeOH (40 mL) and HCl water solution (10 mL, 1M). The mixture was stirred overnight at room temperature. All volatiles were removed under reduced pressure. **5'-Azido-5'-deoxyuridine** was finally purified on column (100/0 to 90/10, dichloromethane/methane).

Yield: 54%.

Synthesis of uridine-EDOT (EDOT-U-OH): Uridine (352 mg, 1.44 mmol, 1 eq) and EDOT-Br (400 mg, 1.44 mmol) were dissolved in DMF. Potassium carbonate (398 mg, 2.88 mmol, 2 eq) was added. The mixture was stirred at 90 °C overnight. The mixture was then allowed to cool down at room temperature (Scheme 3). The DMF was removed under reduced pressure. **EDOT-U-OH** is finally purified on column (50/50, cyclohexane/ethyl acetate).

Yield: 87%; Colorless oil; δ_{H} (200 MHz, CDCl₃, ppm): 7.24 (d, *J* = 8 Hz, 1H), 6.28 (s, 2H), 5.76 (d, *J* = 8 Hz, 1H), 5.64 (s, 1H), 4.57-4.99 (m, 2H), 3.59-4.14 (m, 8H), 1.41-1.64 (m, 6H); δ_{C} (50 MHz, CDCl₃, ppm): 162.8, 156.6, 151.5, 142, 141.6, 139.1, 101.8, 99.4, 99.3, 92.7, 85.4, 74.8, 73.5, 70.2, 68.3, 61.7, 40.8, 30.2, 27.2, 22.3; MS: 441.2.

Synthesis of 5'-azido-5'-deoxyuridine-EDOT (EDOT-U-N₃): 5'-azido-5'-deoxyuridine (417 mg, 1.55 mmol) and EDOT-Br (430 mg, 1.55 mmol, 1 eq) were dissolved in DMF. 428 mg of

potassium carbonate was added. The mixture was stirred at 90 °C overnight. The mixture was then allowed to cool down at room temperature. The DMF was removed under reduced pressure. **EDOT-U-N₃** is finally purified on column (50/50, cyclohexane/ethyl acetate). Yield: 24%; Colorless oil; δ_{H} (200 MHz, CDCl₃, ppm): 7.55 (d, $J = 8$ Hz, 1H), 6.29 (s, 2H), 5.82 (d, $J = 8$ Hz, 1H), 5.73 (s, 1H), 3.63-4.20 (m, 10H), 1.42-1.65 (m, 6H); δ_{C} (50 MHz, CDCl₃, ppm): 162.6, 156.7, 151.3, 141.9, 141.6, 137.8, 102.2, 99.3, 91.7, 82.3, 74.6, 73.5, 70.3, 68.3, 51.6, 40.9, 30.2, 27.2, 22.3; MS: 466.07.

General procedure for electropolymerization

In a glass cell containing a solution 0.1 M of tetrabutylammonium perchlorate (Bu₄NClO₄) in anhydrous acetonitrile, 0.01 M of monomer was inserted. Three electrodes were put inside the solution. A 2 cm² gold plates (purchased from Neyco), glassy carbon rods, and saturated calomel electrodes (SCE) were used as working, counter, and reference electrodes, respectively. The three electrodes were connected to an Autolab potentiostat (Metrohm). Before each experiment, the solution was degassed under argon. After the deposition, the samples were cleaned in three different acetonitrile solutions in order to remove the remaining salts.

General procedure for PEDOT surface modification

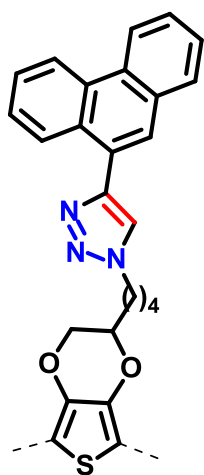
PEDOT-U-N₃ modified substrate was immersed in 50/50 water/THF solution (5 mL). CuSO₄ (100 mg, 0.6 mmol), sodium ascorbate (100 mg, 0.5 mmol) and the corresponding alkyne (100 mg, from 0.19 to 0.91 mmol depending on the alkyne structure) were then added. The mixture was shaken 3 h. The substrate was then successively washed 3 times with water and 3 times with ethanol and dried.

Surface characterization

The apparent and dynamic contact angles were obtained with a DSA30 goniometer of Krüss. Apparent contact angles were measured using the sessile drop method and the dynamic one was obtained with the tilted drop method. In this last method, a surface, on which a 4 μ L water droplet or 2 μ L diiodomethane droplet was placed, is inclined until the droplet rolls off. The maximum surface inclination is called sliding or tilting angle (α). The advancing and receding contact angles and, as a consequence, the hysteresis (H) are taken just before the droplet rolls off the surface. Indeed, the droplet is deformed by the gravity when the surface is inclined. The angle in the moving direction is the advanced contact angle and that in the opposite direction is the receding contact angle. If the droplet does not move, the hysteresis cannot be determined the substrate is called sticky (the adhesion is extremely high).

Procedure for PEDOT-Phenan surface elaboration

PEDOT-N₃¹ substrate was immersed in 50/50 water/THF solution (5 mL). CuSO₄ (100 mg, 0.6 mmol), sodium ascorbate (100 mg, 0.5 mmol) and the phenanthrene acetylene (100 mg, 0.49 mmol) were then added. The mixture was shaken 3 h. The substrate was then successively washed 3 times with water and 3 times with ethanol and dried.



PEDOT-Phenan

Figure SI 1. Structure of the PEDOT-Phenan surface W/O nucleoside