

Supporting Information

Morphology-Dependent Electrical Memory Characteristics of a Well-Defined Brush Polymer Bearing Oxadiazole-Based Mesogens

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Details of Monomer Synthesis

An oxadiazole-containing monomer was synthesized in a five-step reaction as shown in Scheme 1. In the first step, a solution of 4-bromobenzoyl chloride (5.05 g, 23.0 mmol) in 30 mL THF was added to a solution of benzoic hydrazide (3.10 g, 23.0 mmol) and sodium bicarbonate (1.91 g, 23.0 mmol) in 40 mL deionized (DI) water under stirring. The solution at room temperature was stirred for additional 30 min. Then, the precipitate in the solution was filtered, washed with water several times, and then dried at 40 °C under vacuum for 1 day, giving the target product, *N'*-benzoyl-4-bromobenzohydrazide (**1**). In the second step, the obtained compound **1** was further converted to 2-(4-bromophenyl)-5-phenyl-1,3,4-oxadiazole (**2**). Phosphorus oxychloride (POCl₃) (40 mL) was added to a solution of

the compound **1** (7.00 g, 22.0 mmol) in dry toluene (80 mL) and then refluxed with stirring for 6 h. From the reaction medium, the used toluene and excess POCl₃ were removed by vacuum distillation. The resulting product was washed, dried, and recrystallized from ethanol, producing the target product **2**. Yield: 6.0 g (91%). ¹H NMR (δ (ppm), 300 MHz, CDCl₃): 7.58–7.49 (m, 3H, Ar), 7.70 (d, 2H, Ar), 8.01 (d, 2H, Ar), 8.15–8.09 (m, 2H, Ar); ¹³C NMR (δ (ppm), 75.46 MHz, CDCl₃): 122.8, 123.7, 126.4, 127.0, 128.3, 129.1, 132.0, 132.4, 163.9, 164.8.

In the third step, the compound **2** (6.00 g, 20.0 mmol) was dissolved together with (4-(methoxycarbonyl)phenyl)boronic acid (3.80 g, 20.9 mmol) and tetrakis(triphenylphosphine)palladium(0) (Pd(pph₃)₄; 0.60 g, 0.5 mmol) in the toluene (140 mL). To the solution, potassium carbonate solution (2 M, 55 mL) was added and stirred for 2 days at 90 °C. Then the reaction mixture was cooled to room temperature and extracted with CHCl₃. The organic layer was separated, washed with brine (150 mL) twice, and dried with MgSO₄. After the solvent was evaporated off, the residue was purified by chromatography on silica gel with a mixture of hexane and ethyl acetate (2:1 in volume) as the eluent, giving the product 4'-(5-phenyl-1,3,4-oxadiazol-2-yl)-[1,1'-biphenyl]-4-carboxylate (**3**) in white powder. Yield: 5.54 g (78%). ¹H NMR (δ (ppm), 300 MHz, CDCl₃): 3.9 (s, 3H, COOCH₃), 7.55 (m, 3H, Ar), 7.73 (d, 2H, Ar), 7.81 (d, 2H, Ar), 8.19–8.14 (m, 4H, Ar), 8.26–8.23 (d, 2H, Ar); ¹³C NMR (δ (ppm), 75.46 MHz, CDCl₃): 52.2, 123.5, 123.9, 127.1, 127.2, 127.5, 128.0, 129.1, 130.2, 131.8, 132.4, 143.2, 144.1, 164.3, 164.7, 166.8.

In the fourth step, the compound **3** (5.39 g, 15.0 mmol) was dissolved in a mixture of THF (60 mL) and ethanol (180 mL). To the solution, a solution of sodium hydroxide (1.70 g, 30 mmol) in small amount of water was slowly added. The reaction mixture was stirred at 70 °C for 3 h and then cooled to room temperature. To the reaction mixture, water

was added and then insoluble solids were removed out by filtration. To the filtrate, 0.5N HCl aqueous solution was added until the solution's pH value was reached to 2. The precipitation was filtered, washed with water three times, and dried under vacuum, giving the target product 4'-(5-phenyl-1,3,4-oxadiazol-2-yl)-[1,1'-biphenyl]-4-carboxylic acid (**4**) in pinkish solid. Yield: 2.74 g (53%). ¹H NMR (δ (ppm), 300 MHz, DMSO-*d*₆): 7.68–7.65 (m, 3 H, Ar), 7.95 (d, 2H, Ar), 8.03 (d, 2H, Ar), 8.07 (d, 2H, Ar), 8.18–8.14 (m, 2H, Ar), 8.23 (d, 2H, Ar), 13.1 (s, 1H, COOH); ¹³C NMR (δ (ppm), 75.46 MHz, CDCl₃): 122.9, 123.3, 126.7, 127.0, 127.3, 127.8, 129.4, 130.0, 130.4, 132.0, 142.1, 142.7, 163.7, 164.0, 167.0.

On the other hand, 9-hydroxynonyl acrylate (**5**) was synthesized as follows. Nonane-1,9-diol (1.80 g, 11.2 mmol) was dissolved together with a small amount of hydroquinone in THF (45 mL) and cooled to 0 °C with stirring by using an ice-bath. To the solution at 0 °C, triethylamine (1.6 mL) was added. Then, using a dropping funnel, acryloyl chloride (0.83 mL, 10.2 mmol) was added drop-wise to the solution with stirring over 30 min. The reaction mixture was stirred at 0 °C for additional 4 h. The stirring of the reaction mixture was continued at room temperature for another 12 h. After NaHCO₃ aqueous solution was added, the reaction mixture was extracted with ethyl acetate three to four times. The organic layer was separated and dried over MgSO₄. After the solvent was removed out by distillation, the residue was purified by chromatography on silica gel with a mixture of hexane and ethyl acetate (1:1 in volume) as the eluent, producing the target product **5** in clear, colorless oil. Yield: 1.56 g (65%). ¹H NMR (δ (ppm), 300 MHz, CDCl₃): 1.47–1.26 (m, 10H, -CH₂-), 1.54 (t, 2H, -CH₂-), 1.67 (t, 2H, -CH₂-), 3.64 (t, 2H, CH₂OH), 4.15 (t, 2H, CH₂CO₂), 5.8 (d, 1H, CH=CH₂), 6.1 (q, 1H, CH=CH₂), 6.4 (d, 1H, CH=CH₂); ¹³C NMR (δ (ppm), 75.46 MHz, CDCl₃): 25.7, 25.9, 28.6, 29.1, 29.3, 29.4, 32.7, 63.0, 64.7, 128.6, 130.4, 166.4.

In the final step, the compounds **4** (2.74 g, 8.0 mmol) and **5** (1.73 g, 8.1 mmol) were dissolved with *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC; 1.53 g, 8.0 mmol) and 4-(dimethylamino)pyridine (DMAP; 0.49 g, 4.0 mmol) in anhydrous dimethylformamide (DMF; 40 mL) and stirred at 40 °C for 1 day. Then, the used solvent was removed out from the reaction mixture by distillation. The residue was purified by chromatography on silica gel with a mixture of hexane and ethyl acetate (3:1 in volume) as the eluent and recrystallized with a mixture of hexane and ethyl acetate, giving the target monomer, 9-(acryloyloxy)nonyl 4'-(5-phenyl-1,3,4-oxadiazol-2-yl)-[1,1'-biphenyl]-4-carboxylate (**6**). Yield: 3.02 g (74.0%). ¹H NMR (δ (ppm), 300 MHz, CDCl₃): 1.49–1.32 (m, 10H, -CH₂-), 1.67 (t, 2H, -CH₂-), 1.80 (t, 2H, -CH₂-), 4.16 (t, 2H, CH₂CO₂), 4.36 (t, 2H, CH₂CO₂), 5.8 (d, 1H, CH=CH₂), 6.1 (q, 1H, CH=CH₂), 6.4 (d, 1H, CH=CH₂), 7.59–7.54 (m, 3H, Ar), 7.7 (d, 2H, Ar), 7.8 (d, 2H, Ar), 8.18–8.14 (m, 4H, Ar), 8.26 (d, 2H, Ar); ¹³C NMR (δ (ppm), 75.46 MHz, CDCl₃): 25.9, 26.0, 28.6, 28.7, 29.1, 29.2, 29.4, 64.7, 65.2, 123.5, 123.9, 127.0, 127.1, 127.5, 127.9, 128.6, 129.1, 130.1, 130.2, 130.4, 131.8, 143.2, 144.0, 164.3, 164.7, 166.2, 166.3.

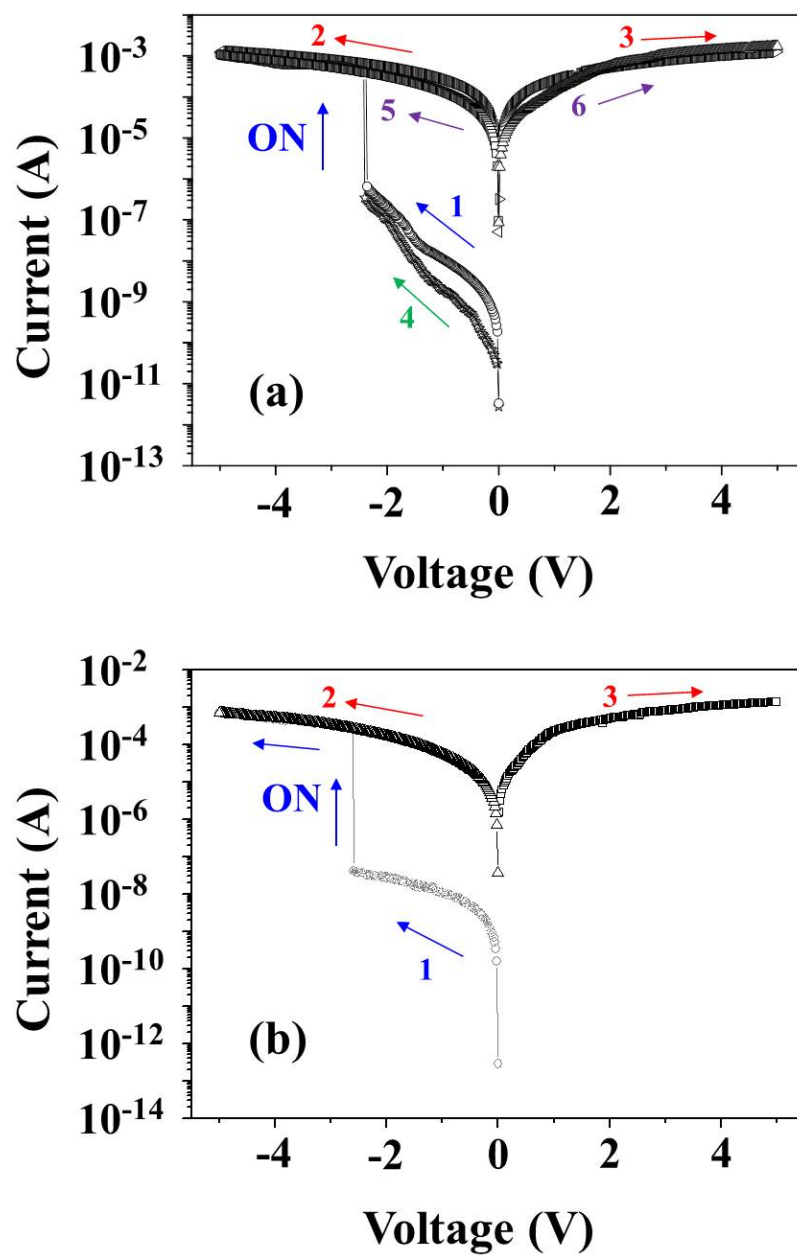


Figure S1. I - V curves of the ITO/ PPOXBPA(30 nm thick)/Al devices: (a) as-cast film; (b) thermally annealed film. The voltage was swept from 0 to -5.0 V.