Electronic Supplementary Information

Template-free Perpendicular Growth of Poly(3,4-ethylenedioxythiophene) Fiber Array by Bipolar Electrolysis under Iterative Potential Application

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1. *Gradient potential distribution on BPE surface*

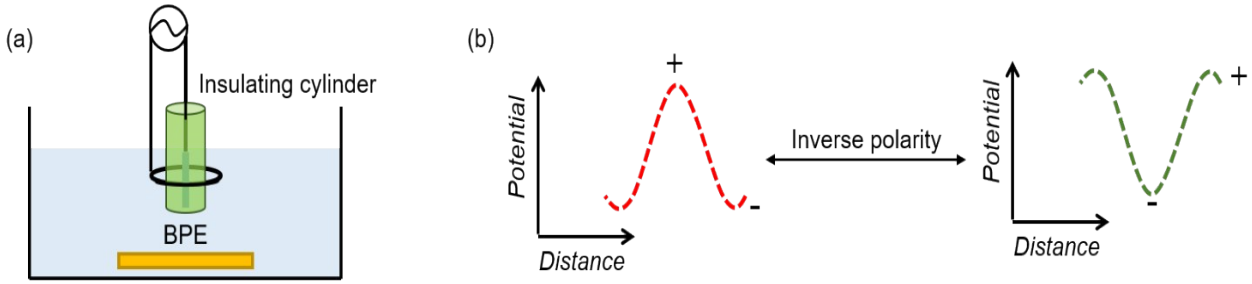


Figure S1. (a) Schematic illustration of the cell configuration and (b) Potential distribution on BPE surface under the alternating current (AC) application.

2. *Microstructure of PEDOT films formed under the application of 50 V*

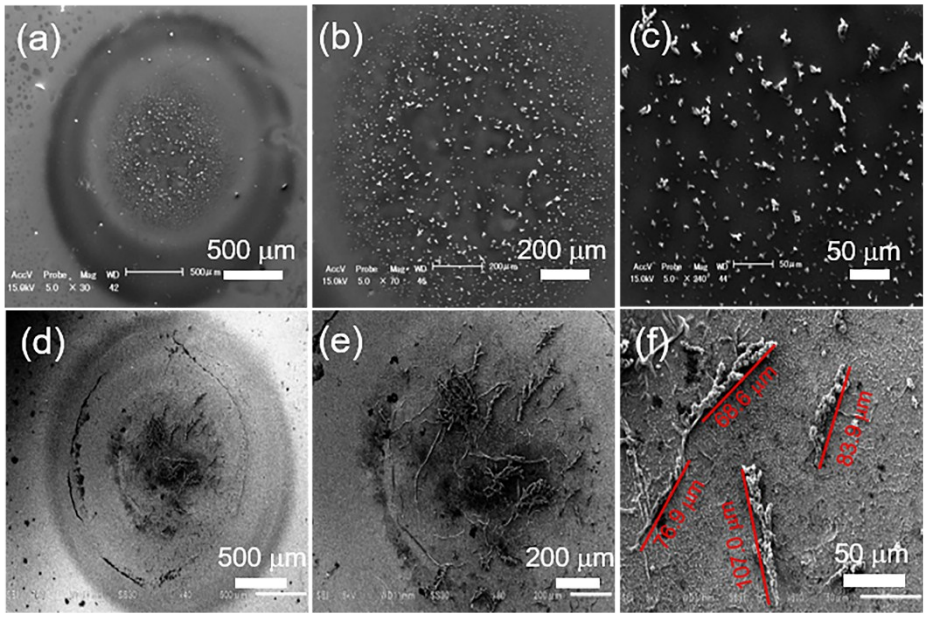


Figure S2. Various magnitudes of SEM images of the PEDOT films formed under the application of (a-c) 50 V (30 min) and (d-f) 100 V (5 min).

3. *PEDOT fiber array formed when the voltage was swept from high to low during growth*

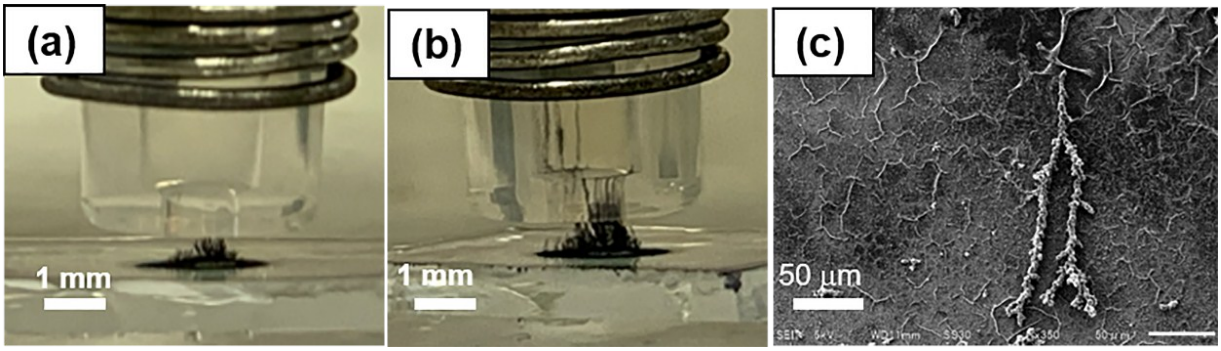


Figure S3. Photographs of the PEDOT array after applying 100 V for 30 min (a), and subsequent application of 50 V for 30 min (b) (60 min-polymerization in total). (c) SEM image of resultant PEDOT fiber in 60 min.

4. *PEDOT fiber array formation with driving electrodes at the lower position*

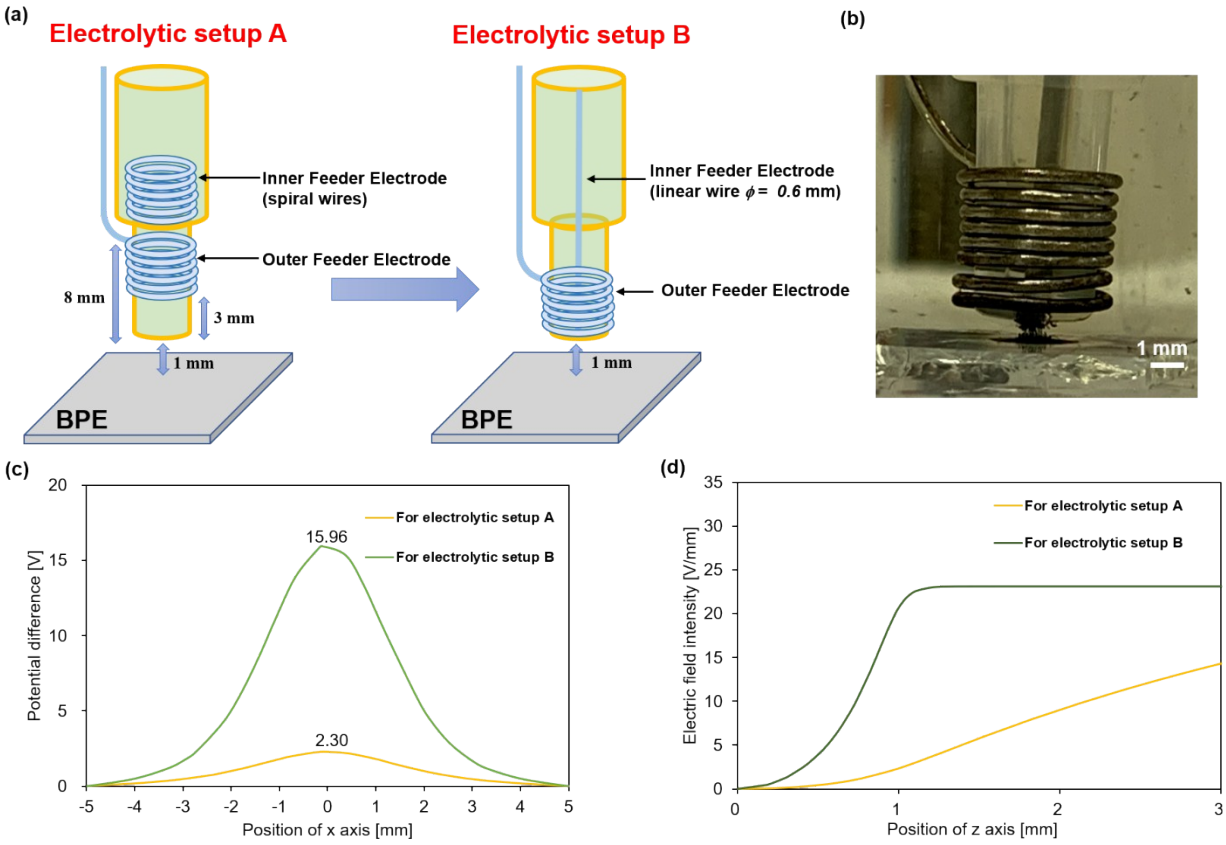


Figure S4. (a) Schematic illustration for previous and repurposed electrolytic setups. (b) Photograph of the PEDOT fiber array grown by using electrolytic setup B. Simulations of potential distribution of (c) ΔV_{BPE} on BPE and (d) Electric field intensity in the z direction.

5. *Microscope Analyses of the PEDOT film*

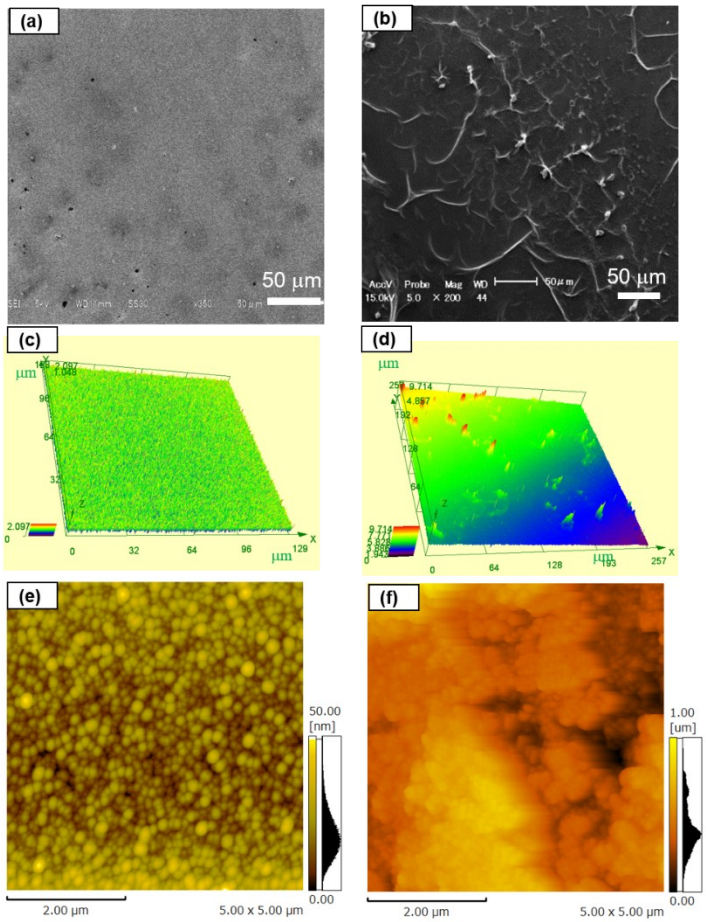


Figure S5. SEM images, laser microscope images and AFM images of pristine ITO surface (a, c, e) and formed film (b, d, f) (color bar presents local height distribution in laser microscope images).

6. *AC-bipolar electropolymerization*

6.1 Effect of applied frequencies

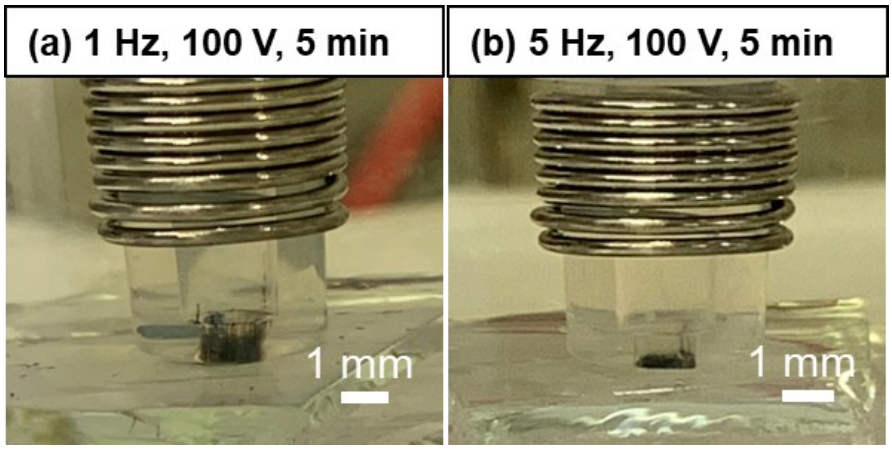


Figure S6. Photographs of PEDOT fiber arrays in 5 min with (a) 1 Hz and (b) 5 Hz.

6.2 Effect of concentrations of EDOT

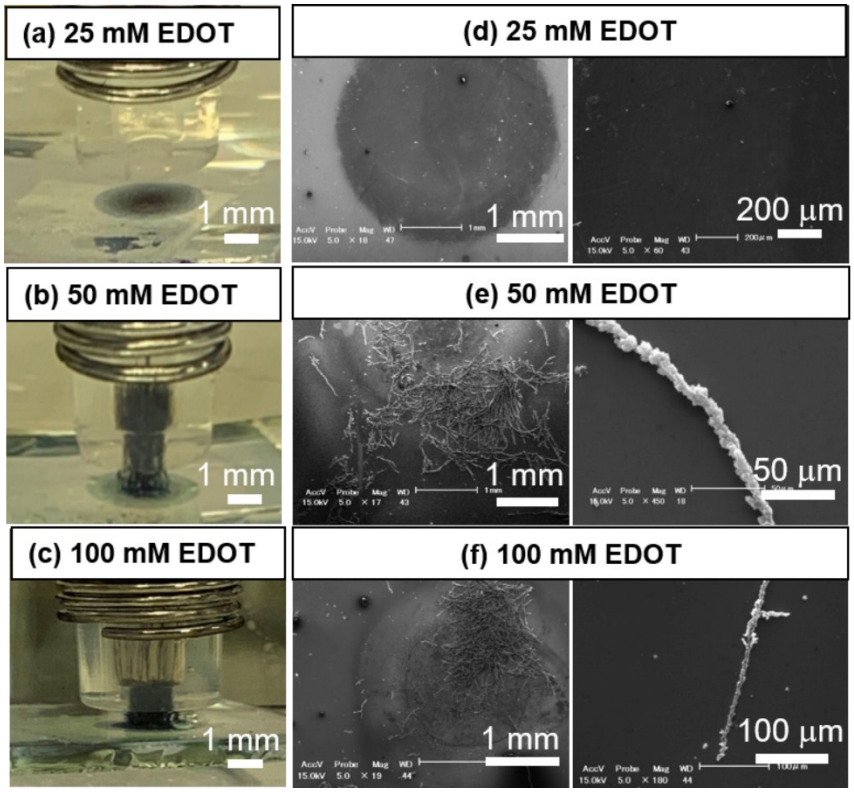


Figure S7. Photograph of PEDOT fiber arrays (left) and SEM images (right) under different EDOT monomer concentrations (a, d) 25 mM, (b, e) 50 mM and (c, f) 100 mM.

6.3 Effect of supporting electrolytes

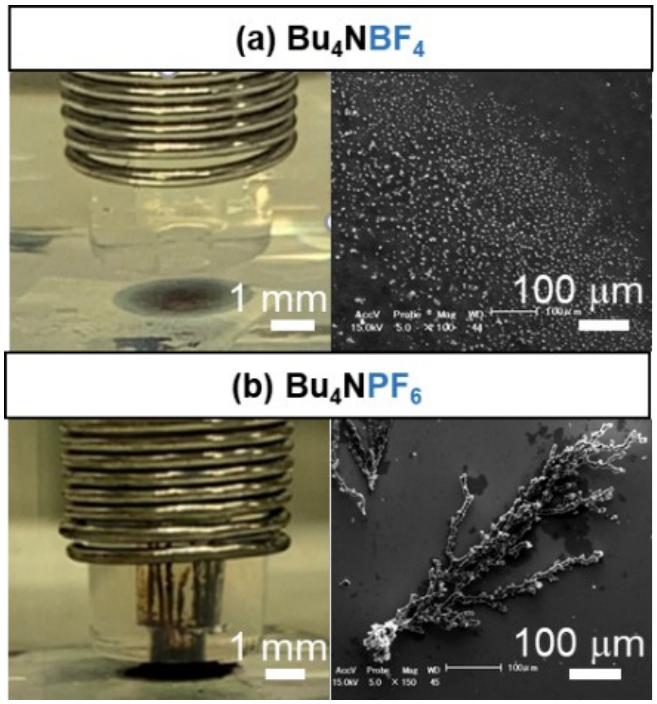


Figure S8. Photographs (left) of PEDOT fiber arrays with 150 V and SEM images (right) using different electrolytes (a) Bu_4NBF_4 and (b) Bu_4NPF_6.

6.4 Effect of solvents

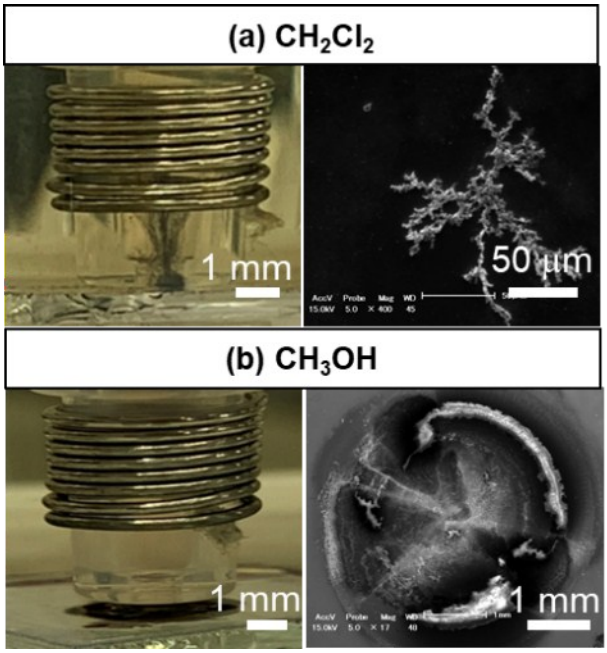


Figure S9. Photographs of PEDOT fiber arrays (left) and SEM images (right) under the application of 150 V using different solvents (a) CH_2Cl_2 and (b) CH_3OH.

6.5 Effect of BPE materials

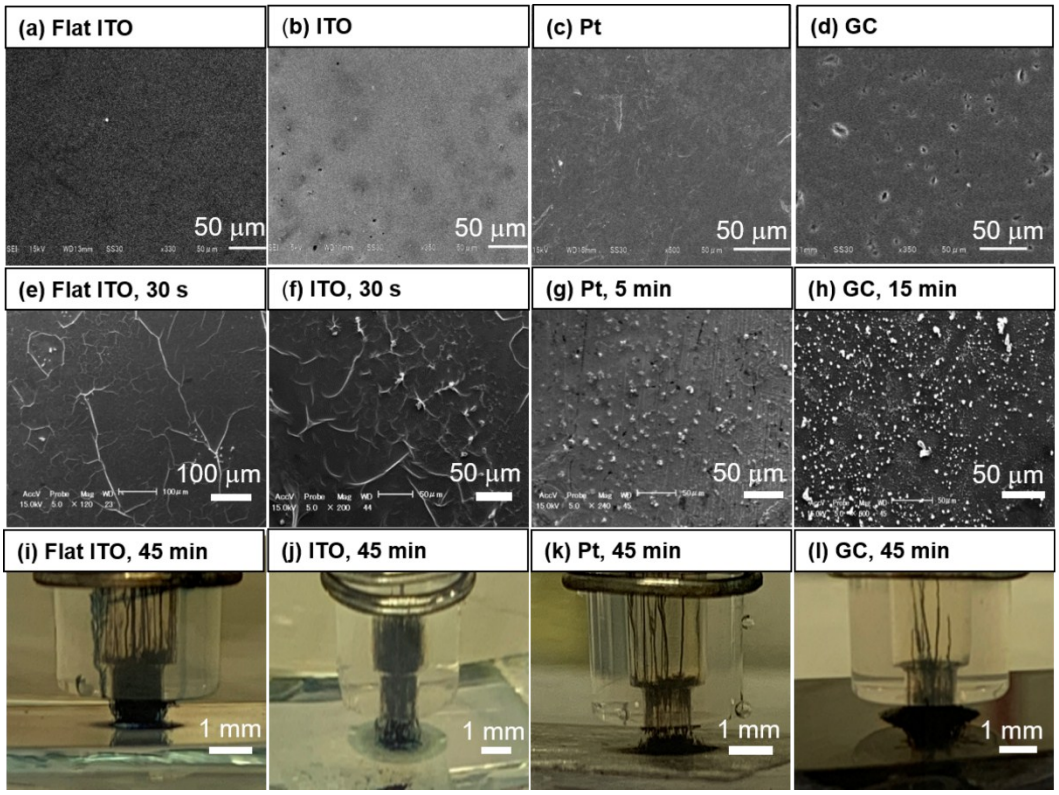


Figure S10. SEM images of pristine substrate surfaces (a-d) and films on different substrate surface formed during the induction period (e-h). (i-l) Photographs of PEDOT fiber arrays formed on different substrates.

6.6 The effect of diameters of insulating cylinder

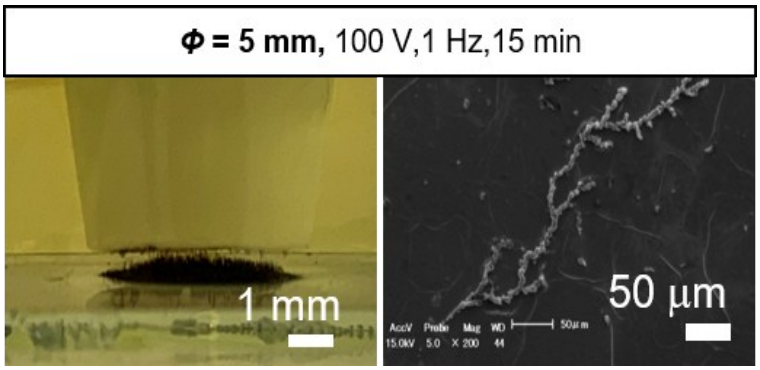


Figure S11. Photograph (left) and SEM image (right) of the PEDOT fiber array under the application of 100 V with a cylinder (ϕ = 5 mm).

7. Surface roughness of BPE materials measured by 3D laser microscope

Supplementary Table 1. Surface roughness of the substrates used in this study

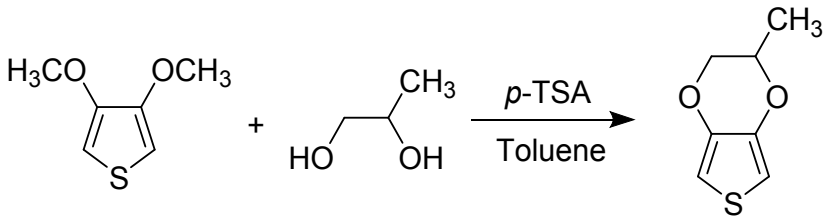
Substrate	Surface roughness (μm)
Flat ITO	0.120
ITO	1.513
Pt	3.133
GC	4.139

8. Synthesis of EDOT-derivatives

The monomers EDOT-C_1, EDOT-C_{10} and EDOT-Cl were prepared by a *p*–toluenesulfonic acid (*p*-TSA)-catalyzed transetherification reaction between 3,4-dimethoxythiophene and 1,2-propanediol, 1,2-dodecanediol or 3-chloropropane-1,2-diol, respectively, according to the previously reported procedure.[1] The nuclear magnetic resonance data of these monomers corresponded to the previous report.

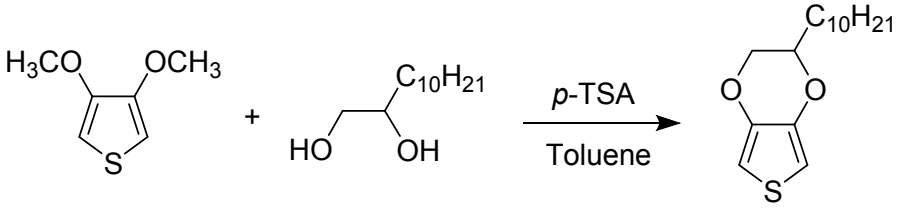
8.1 EDOT-C_1

A mixture of 3,4-dimethoxythiophene (1.00 g, 7 mmol), *p*-toluenesulfonic acid (0.34 g, 1.8 mmol), 1,2-propanediol (1.31 g, 17.3 mmol) in toluene (30 mL) was reflux for 48 h under an N_2 atmosphere. The system was cooled to room temperature, filtrated with celite, extracted with dichloromethane, and then washed with 5% NaOH solution and brine. The collected organic phase was dried over anhydrous $MgSO_4$ and concentrated under vacuum. The crude product was purified by silica gel chromatography (eluent hexane/ethyl acetate, 4/1) to yield 0.22 g as a greenish yellow oil (17%). ^{1}H NMR (270 MHz, $CDCl_3$, ppm): 6.27 (s, 2H), 4.25 (m, 2H), 3.85 (dd, 1H), 1.35(t, 3H).



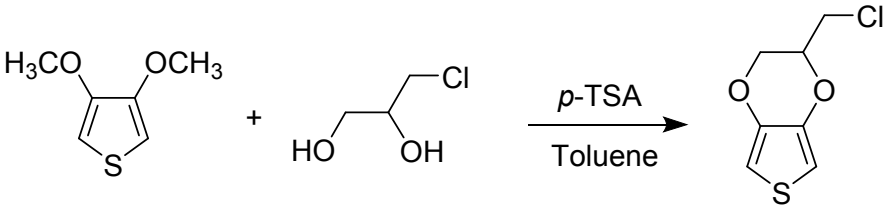
8.2 EDOT-C_{10}

A mixture of 3,4-dimethoxythiophene (1.08 g, 7.5 mmol), *p*-toluenesulfonic acid (0.15 g, 0.8 mmol), 1,2-dodecanediol (2.26 g, 11.2 mmol) in toluene (30 mL) was reflux for 67 h under an N_2 atmosphere. The system was cooled to room temperature, filtrated with celite, extracted with dichloromethane, and then washed with 5% NaOH solution and brine. The collected organic phase was dried over anhydrous $MgSO_4$ and concentrated under vacuum. The crude product was purified by silica gel chromatography (eluent hexane/ethyl acetate, 8/1) to yield 1.74 g as a yellow oil (83%). ^{1}H NMR (270 MHz, $CDCl_3$, ppm): 6.32 (s, 2H), 4.16 (m, 2H), 3.86 (dd, 1H), 1.40 (m, 18H), 0.88 (t, 3H).



8.3 EDOT-Cl

A mixture of 3,4-dimethoxythiophene (1.00 g, 7.0 mmol), *p*-toluenesulfonic acid (0.20 g, 1.1 mmol), 3-chloropropane-1,2-diol (1.53 g, 13.9 mmol) in toluene (30 mL) was reflux for 70 h under an N_2 atmosphere. The system was cooled to room temperature, filtrated with celite, extracted with dichloromethane, and then washed with 5% NaOH solution and brine. The collected organic phase was dried over anhydrous $MgSO_4$ and concentrated under vacuum. The crude product was purified by silica gel chromatography (eluent hexane/ethyl acetate, 6/1) to yield 0.75 g as a yellow oil (57%). ^{1}H NMR (270 MHz, $CDCl_3$, ppm): 6.36 (s, 2H), 4.26 (m, 2H), 4.15 (dd, 1H), 3.7 (m, 2H).



9. Reference

1. D. W. Breiby, E. J. Samuelsen, L. Groenendaal, and B. Struth, *J. Polym. Sci. Part B: Polym. Phys.*, 2003, **41**, 945-952.