Supporting Information

for

Effect of Ion-Chelating Chain Lengths in Thiophene-Based Monomers on in Situ Photoelectrochemical Polymerization and Photovoltaic Performances

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1. Experimental details

Synthesis. All reagents and solvents were purchased from Sigma-Aldrich Co. and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-300 (300 MHz) FT-NMR system operated at 300 MHz and 75 MHz, respectively. Melting point measurement (OptiMelt, Stanford Research System), elemental analyzer (Vario MICRO, Analysensysteme GMBH) and mass spectrometer (Applied Biosystems, Proteomics Analyzer 4700) were used for characterization of synthesized compounds. Compounds were synthesized referring published papers.[1,2,3]

Toluene-4-sulfonic acid 2-[2-(2-methoxy-ethoxy)-ethoxy]-ethyl ester. A solution of tosyl chloride (57.8 mmol) in 50 mL of CH_2Cl_2 was added to stirred solution of triethylene glycol monomethyl ether(61 mmol) and triethylamine (91.3 mmol) in 100 mL of CH_2Cl_2 at 0 ℃. The mixture was stirred at 0 ℃ for 5 h, before being poured into a stirred solution of HCl in ice water. The aqueous layer was separated and extracted with CH_2Cl_2. The combined organic extracts were washed with water, dried over magnesium sulfate and the solvent was evaporated under reduced pressure to yield pale yellow oil. The crude residue was purified by flash column chromatography (hexane:EtOAc=7:3) to yield the pale yellow oil tosylate with 93 % of yield, ^{1}H NMR (DMSO d_6) δ 7.76-7.79 (d, 2H), 7.46-7.49 (d, 2H), 4.08-4.11 (t, 2H), 3.54-3.57 (t, 2H), 3.33-3.47 (m, 8H), 3.23 (s, 3H), 2.41 (s, 3H). All data was identical to literature values.[2]

1,4-Dibromo-2,5-bis-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-benzene. A solution of KOH (50 mmol) in ethanol (30 mL) was slowly added into a solution of 1,4-dibromo-2,5-hydroxybenzene (24.5 mmol) in THF (60 mL) under nitrogen atmosphere. After stirring for 3 h at room temperature, a solution of tosylated TEG (50 mmol) in THF (30 mL) was added slowly. The temperature was increased to 50 ℃ and then, the mixture was stirred for 24 h. The reaction mixture was poured into aqueous sodium chloride and ether was added for extraction. Combined organic layer was dried with MgSO4 and concentrated under reduced pressure. The crude was purified by flash column chromatography (hexane:EtOAc=1:1). The resulting compound was obtained as pale yellow oil with 91 % of yield, ^{1}H NMR ($CDCl_3$) δ 7.31(s, 2H), 3.76-3.80(t, 4H), 3.61-3.66(m, 12H), 3.52-3.54(t, 4H), 3.42-3.46(t,

4H), 3.36(s, 6H); ^{13}C NMR ($CDCl_3$) δ 150.3, 119.2, 111.4, 71.9, 71.1,70.7, 70.6, 70.2, 69.6, 59.0; Elem. anal. calcd for C, 42.87; H, 5.76; found for C, 42.87; H, 5.76; m/e calcd for $C_{20}H_{32}Br_2O_8$, 558.0464, found for 559.0440 ([M]+).

1,4-bis[2-(3,4-ethylenedioxy)thienyl]-2,5-bis{2-[2-(2-methoxyethoxy)ethoxy] ethoxy}benzene (bis-EDOT-TBO4). *n*-Butyl lithium (30 mmol) was dropwised into a solution of EDOT (30 mmol) in THF (75 mL) at -78 °C under nitrogen. The color of solution was changed from transparent to yellow within 1h. After that, the resulting solution was transferred into a stirring solution of $ZnCl_2$ (33 mmol) in THF (75 mL) over a 20-min period. The mixture was stirred under nitrogen for 1 h. The resulting EDOT–ZnCl complex was then dropwised to a solution of 1,4-Dibromo-2,5-bis-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-benzene (6.91 mmol) and $Pd(PPh_3)_4$ (0.03 mmol) in THF (50 mL). The solution was stirred at 50 °C under nitrogen for 3 days. It was then cooled to room temperature and quenched by 1 M HCl. The mixture was extracted with CH_2Cl_2, dried over magnesium sulfate, and filtered through *Celite*; the resulting pale yellow liquid was concentrated under reduced pressure at room temperature. The product was finally recrystallized from CH_2Cl_2 and yield was 84 %, mp 85.0-86.2; ^{1}H NMR ($CDCl_3$) δ 7.69 (s, 2H), 6.36 (s, 2H) 4.31-4.29 (m, 4H), 4.26-4.24 (m, 4H), 4.22-4.20 (t, 4H), 3.96-3.93 (t, 4H), 3.77-3.74 (m, 4H), 3.69-3.63 (m, 8H), 3.55-3.52 (m, 4H), 3.37 (s, 6H); ^{13}C NMR (CDCl3) δ 148.9, 141.2, 138.7, 121.1, 113.9, 113.2, 99.5, 71.9, 70.8, 70.7, 70.5, 69.7, 69.1, 64.9, 64. 3, 60.0; Elem. Anal. calcd for C, 56.29; H, 6.20; S, 9.39; found for C, 56.28; H, 6.16, S, 9.37; m/e calcd for $C_{32}H_{42}O_{12}S_2$, 682.2118, found for 683.4300 ([M]+).

1,4-bis[2-(3,4-ethylenedioxy)thienyl]-2,5-bis[2-(2-methoxyethoxy)ethoxy]benzene (bis-EDOT-TBO3). The product was pale yellow crystal and yield was 76 %, ^{1}H NMR ($CDCl_3$) δ 7.69 (s, 2H), 6.36 (s, 2H) 4.31-4.29 (m, 4H), 4.26-4.24 (m, 4H), 4.22-4.20 (t, 4H), 3.96-3.93 (t, 4H), 3.77-3.74 (m, 4H), 3.69-3.63 (m, 8H), 3.55-3.52 (m, 4H), 3.37 (s, 6H).

1,4-bis[2-(3,4-ethylenedioxy)thienyl]-2,5-bis-2-{2-[2-(2-methoxyethoxy)ethoxy] ethoxy}ethoxybenzene (bis-EDOT-TBO5) The product was brown oil and yield was 79 % ^{1}H NMR ($CDCl_3$) δ 7.69 (s, 2H), 6.36 (s, 2H) 4.31-4.29 (m, 4H), 4.26-4.24 (m, 4H), 4.22-

4.20 (t, 4H), 3.96-3.93 (t, 4H), 3.77-3.74 (m, 4H), 3.69-3.63 (m, 8H), 3.55-3.52 (m, 4H), 3.37 (s, 6H).

Fabrication of sDSCs. TiO_2 compact layer or blocking layer was prepared via spin-coating of a solution of 0.25 M titanium(IV) isopropoxide (TIP) in ethanol followed by sintering at 500 ℃. Nanoporous TiO_2 electrodes were prepared on a fluorine-doped SnO_2 (FTO) (Pilkington, SnO_2:F, 8 ohm/sq) from the colloidal Nanoxide-T paste (Solaronix) by doctor-blade techniques. The films were annealed at 500 ℃ for 30 min in air. The resulting TiO_2 films (thickness is around 6 μm, measured by a profiler, α-step 500, KLA Tencor) were cut into pieces. Then, the electrodes were immersed into 0.3 mM D205 (Mitsubishi-chemicals) in acetonitrile/*tert*-butanol (1:1) for 18 h. A solutions of 0.1 M LiTFSI in acetonitrile was prepared before use. The dye-coated TiO_2 film as a working electrode, a platinum foil as a counter electrode, and Ag/AgCl as a reference electrode (SP-200, Biologic potentiostat) were employed. A concentration of 0.01 M monomers in LiTFSI electrolyte was used for the photoelectrochemical polymerization. The photoelectrochemical polymerization was achieved by using the constant potential (+0.2 V vs Ag/AgCl) under light irradiation of a 150 W Xe lamp (22 mW cm^{-2}, λ> 520 nm) for each optimized time. The sheet resistances of the different PEDOT hole conductors were measured by four-probe-type resistance meter. After in situ photoelectrochemical polymerization, the resulting TiO_2/dye/PEDOT electrode was rinsed by acetonitrile and then dried. After that, a few drops of EMIm-TFSI with 0.2 M TBP and 0.2 M LiTFSI were added on the surface. Silver paste (Elcoat) was covered on PEDOT-coated electrode.

Photoelectrochemical measurement. A 450 W xenon light source (Model No. 94022A, Oriel) was used to apply an illumination power of 100 $mWcm^{-2}$ (the equivalent of one sun at AM1.5) to the surface of the solar cell to simulate solar light irradiation. The incident light intensity was calibrated with reference to a Si solar cell equipped with an IR-cutoff filter (KG-5, Schott). Comparison of the simulated light to the true solar spectrum in the region 350–750 nm determined a spectral mismatch of less than 2%. The *I-V* characteristics were obtained by measuring the photocurrent generated by the cells (under an applied

external bias) using a Keithley model 2400 digital source meter (Keithley, USA). The voltage step and delay time for the measurement were 10 mV and 40 ms, respectively.

Recombination resistances and electron life-time. The recombination resistances and electron life-times of devices were measured using a computer-controlled potentiostat (SP-200, BioLogic) under dark conditions. To measure the recombination resistance, the frequency range examined was 0.5 Hz–500 kHz at room temperature, and the impedance spectra were recorded at a potential of –0.75 V with an amplitude set at 50 mV. The measured spectra were fit to an appropriate simplified circuit using the Z-fit software provided by BioLogic. The electron lifetimes (τ_n) in devices were calculated based on the fallowing equation from the corresponding Bode plot.

$$R_S + \left[\begin{array}{c} R1 \\ Q1 \end{array}\right] + \left[\begin{array}{c} R2 \\ Q2 \end{array}\right]$$

$$\tau_n = \frac{1}{2\pi f_{min}}$$

2. Calculation of the binding constant of TEG-Li^+ complexes

We assumed that the binding ability of TEGs was independent from binding nearby TEGs. The concentration of host was not the concentration of monomer but the concentration of TEGs. Under this assumption, host-guest 1:1 complex system was applied for our system.

$$[TEG] + [Li^+] \overset{K_a}{\leftrightarrow} [TEG{:}\,Li^+] \qquad \text{Equation (1)}$$

$$K_a = \frac{[TEG{:}\,Li^+]}{[TEG][Li^+]} \qquad \text{Equation (2)}$$

If the binding ability of TEGs is strong, equilibrium will be closed to the product, [TEG:Li^+]. It means that K_a will be higher. However, there are two unknown parameters such as [TEG] and [Li^+] to calculate the K_a value. Therefore, we used two mass formulas to replace these unknown parameters as written below.

$$[TEG]_t = [TEG] + [TEG{:}\,Li^+] \quad \text{Equation (3)}$$

$$[Li^+]_t = [Li^+] + [TEG{:}\,Li^+] \quad \text{Equation (4)}$$

Here, $[TEG]_t$ and $[Li^+]_t$ are the total concentration of TEGs and Li^+s, which are determined by feeding amounts of monomers and Li salts. On the one hand, K_a can be related with peak shift (δ) of ^{1}H-NMR using the equation as below.

$$\delta = f_{TEG}\delta_{TEG} + f_{Li^+}\delta_{Li^+} + f_{TEG:Li^+}\delta_{TEG:Li^+} \quad \text{Equation (5)}$$

Here, f_x is the mole faction of each components, $[x]/[x]_t$. Since we already assumed independency of changes with host and guest, δ_{TEG} and δ_{Li+} are almost zero. $\Delta\delta$ is the difference of δ from the final δ to the initial δ, and $f_{teg:Li+}$ is the [TEG:Li^+]/$[TEG]_t$. The simplified equation are written below.

$$\Delta\delta = \delta_c \frac{[TEG{:}\,Li^+]}{[TEG]_t}, \delta_c = \delta_{TEG:Li^+} - \delta_{TEG} \quad \text{Equation (6)}$$

Here, δ_c is the constant value of ^{1}H-NMR peak shift at $f_{teg:Li+}$ = 1, which is also the unknown parameter. The equation 3 and 4 can be inserted to the equation (2).

$$K_a = \frac{[TEG{:}\,Li^+]}{([TEG]_t - [TEG{:}\,Li^+])([Li^+]_t - [TEG{:}\,Li^+])}$$

Equation (7)

The equation (7) can be derived as the [TEG:Li^+] using the quadratic formula (the equation (8) and (9)) to substitute into the [TEG:Li^+] in the equation (6), which results in the relationship between $\Delta\delta$ and K_a.

$$[TEG{:}\,Li^+]^2 - \left([TEG]_t + [Li^+]_t + \frac{1}{K_a}\right)[TEG{:}\,Li^+] + [TEG]_t[Li^+]_t = 0$$

Equation (8)

$$\therefore [\text{TEG}{:}\,Li^+] = \frac{\left([TEG]_t + [Li^+]_t + \frac{1}{K_a}\right) - \sqrt{([TEG]_t + [Li^+]_t + \frac{1}{K_a})^2 + 4[TEG]_t[Li^+]_t}}{2}$$

Equation (9)

Finally, resulting equation (the equation (10)) written below was used for fitting with two parameters such as $\Delta\delta$ and $[Li^+]_t$. Here, δ_c and $1/K_a$ are the unknown parameter and remained values are constant.

$$\Delta\delta - \delta_c \frac{\left([TEG]_t + [Li^+]_t + \frac{1}{K_a}\right) - \sqrt{([TEG]_t + [Li^+]_t + \frac{1}{K_a})^2 + 4[TEG]_t[Li^+]_t}}{2[TEG]_t}$$

Equation (10)

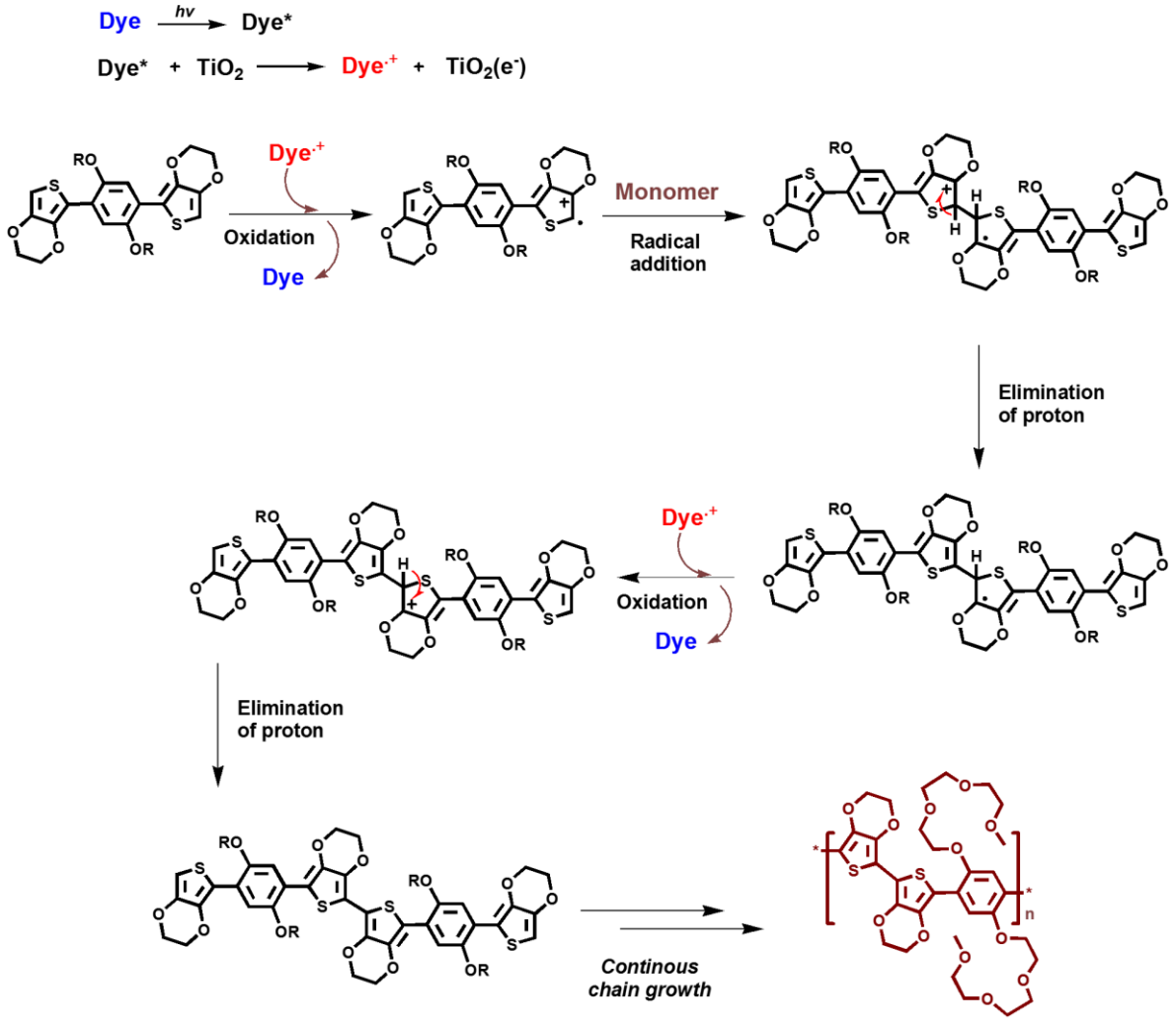

Figure S1. Detailed in situ PEP mechanism.

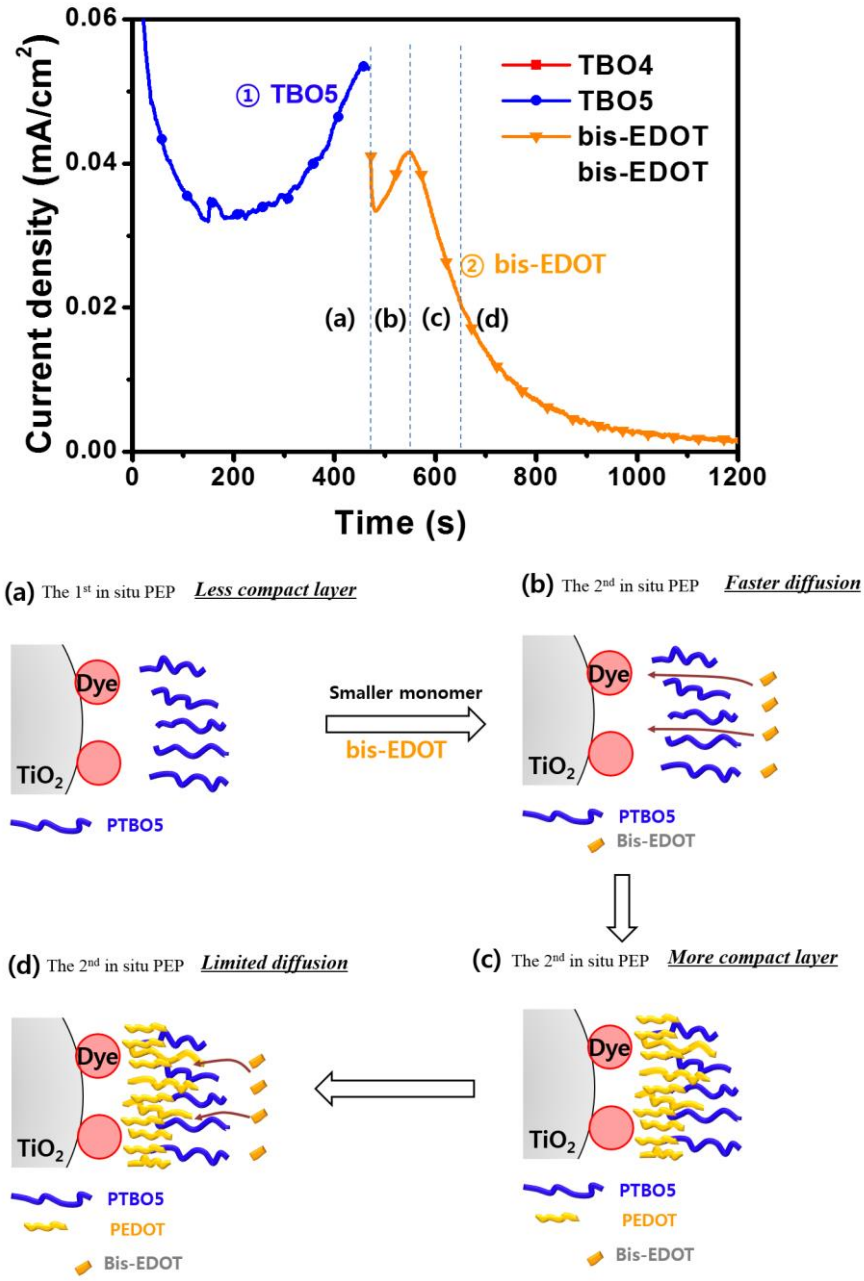

Figure S2. The sequential in situ PEP curve obtained from TBO5, followed by bis-EDOT and illustration of the process. (a) The 1st in situ PEP of PTBO5, (b) faster diffusion of bis-EDOT through less compact polymer layer (PTBO5), (c) formation of more compact layer (PEDOT) by 2nd in situ PEP, (d) termination of 2nd in situ PEP resulting from limited diffusion of bis-EDOT.

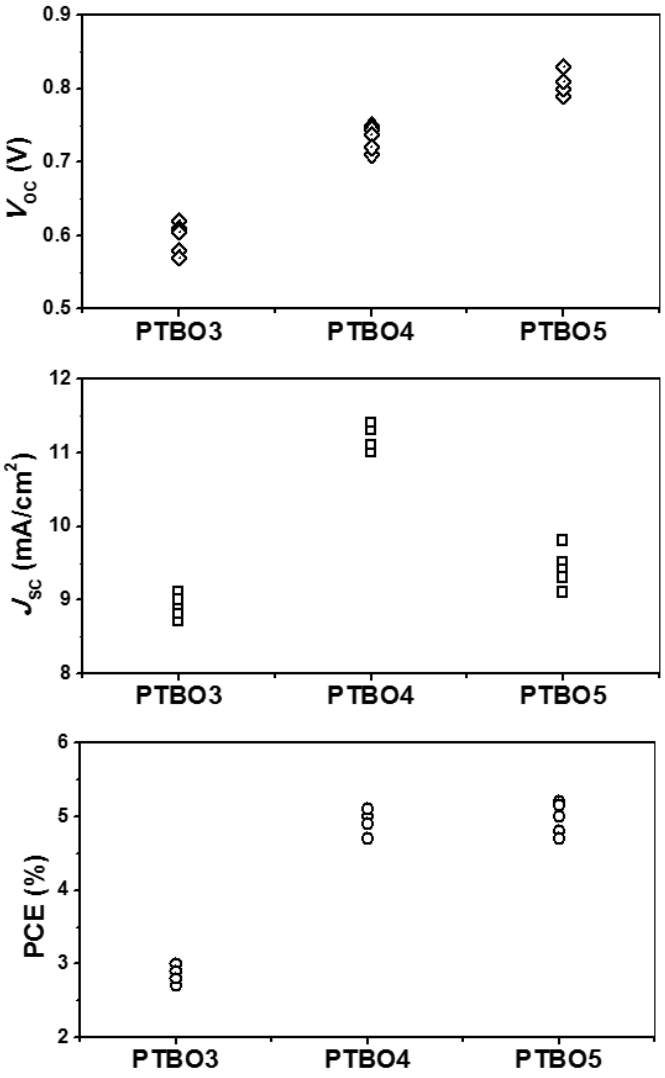

Figure S3. Reproducibility of the photovoltaic parameters obtained 5 devices.

References

1. Sotzing, G. A.; Reynolds, J. R.; Steel, P. J. Poly(3,4-ethylenedioxythiophene) (PEDOT) Prepared via Electrochemical Polymerization of EDOT, 2,2′-Bis(3,4-ethylenedioxythiophene) (BiEDOT), and their TMS Derivatives. *Adv. Mater.* **1997**, *9*, 795−798.
2. Gentilini, C.; Boccalan, M.; Pasquato, L. Straightforward Synthesis of Fluorinated Amphiphilic Thiols. *Eur. J. Org. Chem.* **2008**, 3308−3313.
3. Sotzing, G. A.; Reynolds, J. R. Electrochromic Conducting Polymers via

Electrochemical Polymerization of Bis(2-(3,4-ethylenedioxy)thienyl) Monomers. *Chem. Mater.* **1996**, *8*, 882−889.

4. Irvin, J. A.; Schwendeman, I.; Lee, Y.; Abboud, K. A.; Reynolds, J. R. Low-Oxidation-Potential Conducting Polymers Derived from 3,4-Ethylenedioxythiophene and Dialkoxybenzenes. *J. Polym. Sci.: Part A: Poly. Chem.* **2001**, *39*, 2164−2178.