Electronic Supporting Information

for

A Novel Hole Transport Material for Iodine-Free Solid State Dye-Sensitized Solar Cells

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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]

2,2'-Bis(3,4-ethylenedioxythiophene) (bis-EDOT) To a three-necked round bottom flask containing 30 mL of anhydrous THF under nitrogen purge was added EDOT (7.0 mmol). The solution was cooled to -78°C in a dry ice/2-propanol bath. 2.5 M n-BuLi in hexane (7.0 mmol) was added to the solution and the mixture was stirred for 45 min, after which, CuCl$_2$ (7.0 mmol) was added in one portion. The solution was slowly warmed to 45°C and was stirred for a further 2 h. The solution was evaporated and then poured into water and CH$_2$Cl$_2$. The mixture was extracted three times by CH$_2$Cl$_2$. Organic layer was filtered on celite and dried over magnesium sulfate. Concentrated compound was passed through a dry flash silica column using CHCl$_3$ as the eluent. Evaporation of CHCl$_3$, gave white solid of Bis-EDOT with 70 % of yield, mp 183-185 °C; ^{1}H NMR (CDCl$_3$) δ 6.93 (s, 2H), 4.34-4.32 (m, 4H), 4.25-4.23 (m, 4H); All data was identical to literature values.[1]

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$_2$Cl$_2$ was added to stirred solution of triethylene glycol monomethyl ether(61 mmol) and triethylamine (91.3 mmol) in 100 mL of CH$_2$Cl$_2$ 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$_2$Cl$_2$. 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 exraction. Combined organic layer was dried over $MgSO_4$ 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, ^1H 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 (MALDI-mass) calcd for $C_{20}H_{32}Br_2O_8$, 558.0464, found for 559.0440 ([M]+).

1,4-bis[2-(3,4-ethylenedioxy)thienyl]benzene (bis-EDOT-B) Bis-EDOT-B was synthesized in a similar manner as bis-EDOT-TB. EDOT (10 mmol), THF (70 mL), *n*-butyl lithium (10 mmol), $ZnCl_2$ (11 mmol), Pd($PPh_3)_4$ (0.01 mmol) and 1,4-dibromobenzene (4.9 mmol) were used. After quenching with water, hexane was added for precipitation. The crude was filtered and washed with hexane. The product obtained after column chromatography ($CHCl_3$) was pale yellow solid, 81 % of yield, ^1H NMR ($CDCl_3$) δ 7.70 (s, 4H), 6.29 (s, 2H), 4.32-4.30 (m, 4H), 4.26-4.24 (m, 4H); All data was identical to literature values.[3]

1,4-bis[2-(3,4-ethylenedioxy)thienyl]-2,5-bis{2-[2-(2-methoxyethoxy)ethoxy] ethoxy}benzene (bis-EDOT-TB) *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; ^1H 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 (MALDI-mass) calcd for $C_{32}H_{42}O_{12}S_2$, 682.2118, found for 683.4300 ([M]+).

Fabrication of DSSCs. TiO_2 compact layer or blocking layer were 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 *cis*-bis(isothiocyanato)(2,2'-bipyridyl-4,4'-dicarboxylato)(2,2'-bipyridyl-4,4'-di-nonyl)ruthenium(II) (known as Z-907, Solaronix) in acetonitrile/*tert*-butanol (1:1) for 18 h. A solution of 0.1 M LiTFSI in acetonitrile was prepared prior to use. The dye-coated TiO_2 film as a working electrode, a platinum coil 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 photo-electropolymerization. The photo-electropolymerization 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 photo-electropolymerization, 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.

Cyclic voltammetry measurements. The potentiostat (SP-200, BioLogic) was used for electropolymeriation and electrochemical study. The electropolymerized polymer on FTO was immersed into supporting electrolyte which is 0.1 M tetrabutylammonium perchlorate (TBAP) in acetonitrile. To check stability of polymer films in supporting electrolyte, ten cycles was scanned from -0.5 V to 0.1 V. Then, electrochemical property was measured in the same range of voltage as acetonitrile of 1.0 M LiTFSI was added sequentially.

Sheet resistance measurement. The photo-electropolymerization was carried out on dyed TiO_2 and then the samples were rinsed with acetonitrile and dried prior to use. 4-point probe type resistance meter (Keithley, USA) was used to measure the sheet resistance of polymer-coated TiO_2 films.

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.

Electrochemical impedance spectrophotometer measurement. The impedance values were obtained by potentiostat (SP-200, BioLogic) under dark conditions. The frequency ranges 1 Hz to 1 MHz at room temperature, and then spectra were recorded under condition of -0.6 V potentials and 10 mV voltage amplitude. Fitting process was done by appropriate simplified circuit using the Z-fit software provided by BioLogic.

2. ^{1}H-NMR spectra of bis-EDOT-TB and calculation of the binding constant
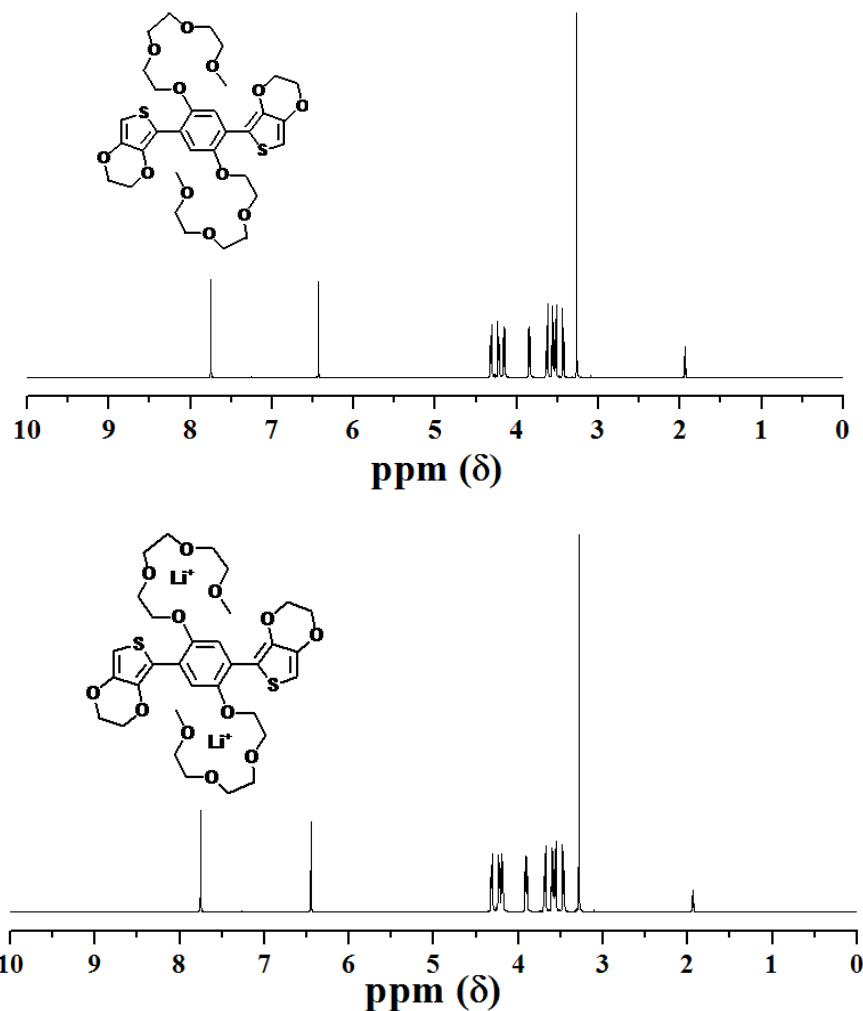
Fig. S1 Representative ^{1}H-NMR spectra: before and after addition of LiTFSI (0.02 M) in solution of bis-EDOT-TB (0.01 M)/CD$_3$CN.

Calculation of the binding constant of TEG-Li$^+$ complex

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.

$$[TEG] + [Li^+] \underset{\longleftarrow}{\overset{K_a}{\longrightarrow}} [TEG\!:\!Li^+]$$

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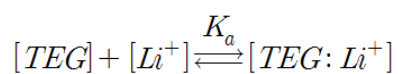
Here, K_a is the binding constant of TEG-Lithium ion complexes and K_a and total concentration of TEGs ($[TEG]_t$) and Li^+($[Li^+]_t$) are defined to equation below.

$$K_a = \frac{[TEG:Li^+]}{[TEG][Li^+]}$$

$$[TEG]_t = [TEG] + [TEG:Li^+]$$

$$[Li^+]_t = [Li^+] + [TEG:Li^+]$$

The relationship between the peak shift (δ) of 1H-NMR and K_a was described below expressed by mole fractions.

$$\delta = f_{TEG}\delta_{TEG} + f_{Li^+}\delta_{Li^+} + f_{TEG:Li^+}\delta_{TEG:Li^+}$$

Here, f_x is the mole faction of each components, $[x]/[x]_t$. Since we already assumed independency of changes with host and guest, we can simplify the equation further.

$$\Delta\delta = \delta_c \frac{[TEG:Li^+]}{[TEG]_t} , \delta_c = \delta_{TEG:Li^+} - \delta_{TEG}$$

To calculate the $\Delta\delta$, the equation of [TEG:Li$^+$] consisting of [Li$^+$]$_t$ is needed and it can be derived by the quadratic formula.

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

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

$$\therefore [TEG\!:\!Li^+] = \frac{([TEG]_t + [Li^+]_t + 1/K_a) - \sqrt{([TEG]_t + [Li^+]_t + 1/K_a)^2 + 4[TEG]_t[Li^+]_t}}{2}$$

Finally, resulting equation 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.

$$\Delta\delta = \delta_c \frac{([TEG]_t + [Li^+]_t + 1/K_a) - \sqrt{([TEG]_t + [Li^+]_t + 1/K_a)^2 + 4[TEG]_t[Li^+]_t}}{2[TEG]_t}$$
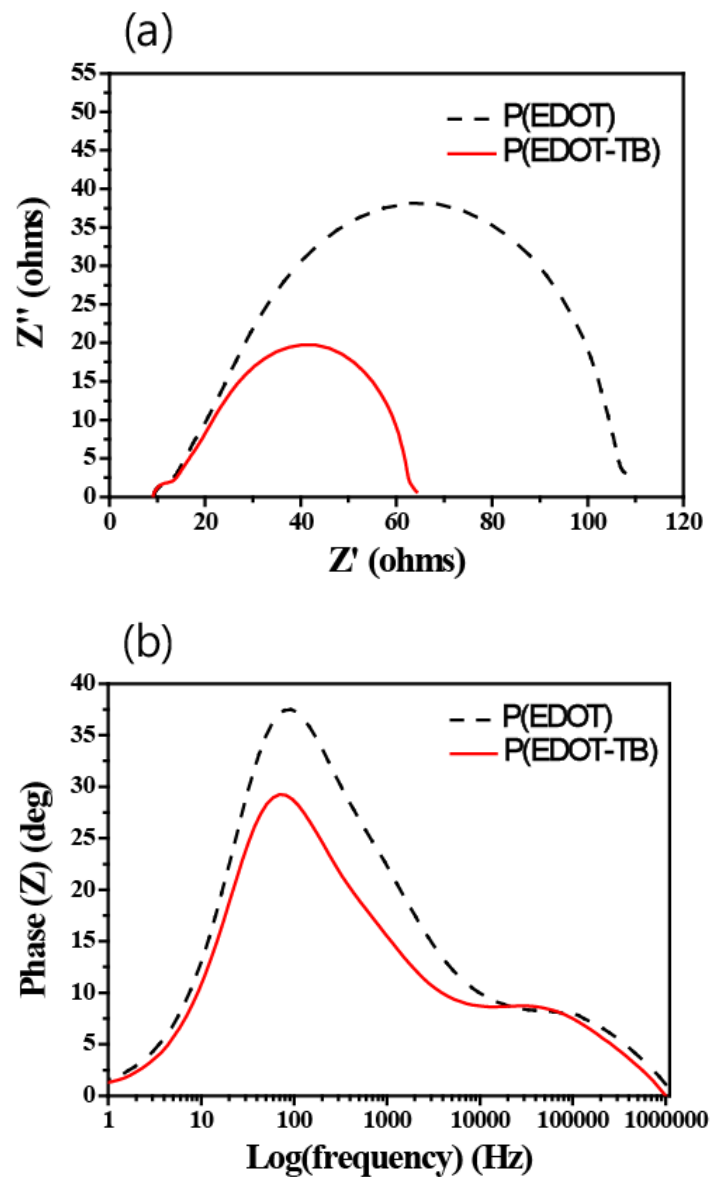
### 3. Cyclic voltammograms of PEDOT at a variety concentration of LiTFSI
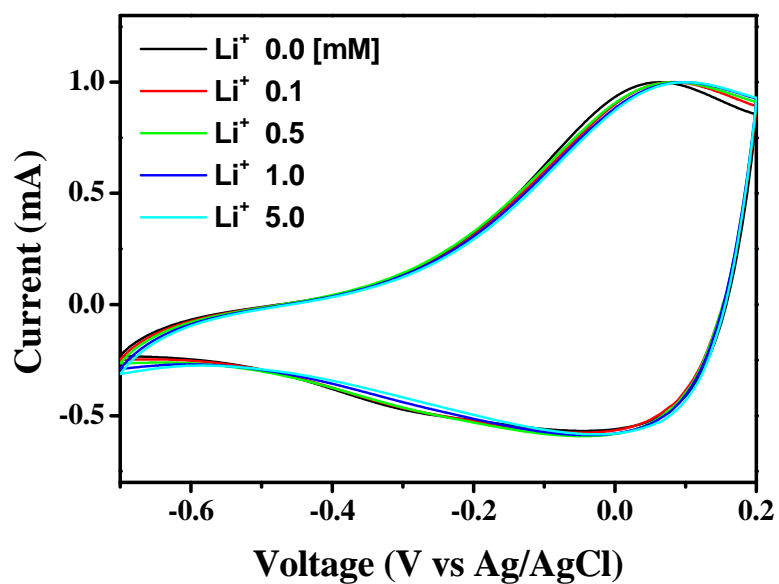
Fig. S2 Effect of LiTFSI concenetrations (0 ~ 5.0 mM) on oxidation potentials of **PEDOT** formed on the surface of FTO in cyclic voltammeter. Tetrabuthylamonium perchlorate (TBAP, 0.1 M) was used as electrolyte in CH_3CN.

4. Electrochemical impedance spectroscopy (EIS) data

Fig. S3 Representative electrochemical impedence spectroscopy (EIS) data of device-A and device-B (a) Nyquist plot (b) Bode plot

5. Device performance of PEDOT-based DSSCs for 20 min and 30 min in PEPs
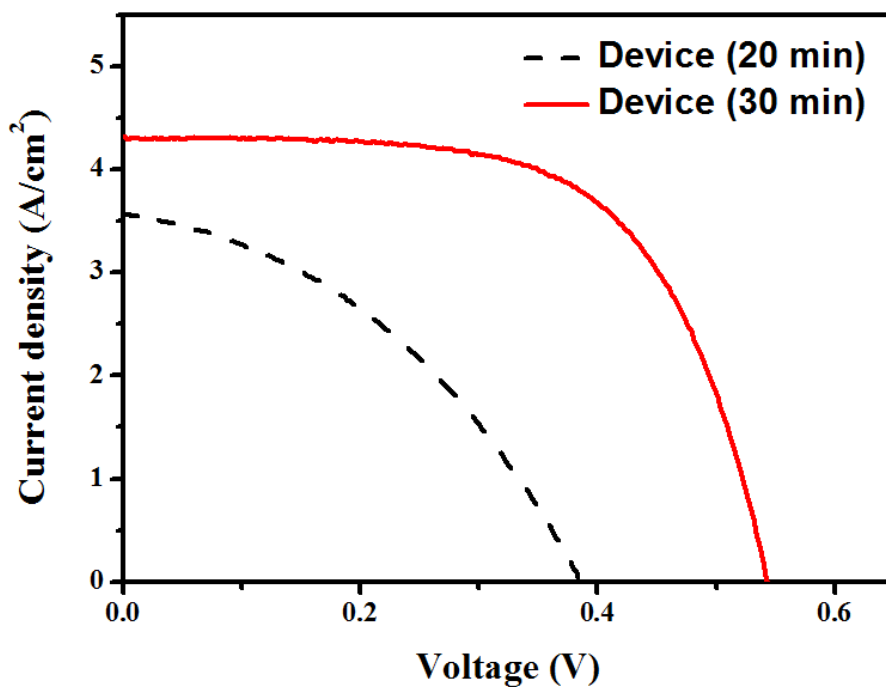
Fig. S4 Representative photocurrent–voltage curves for s-DSSCs prepared from 20 min and 30 min in PEP of **bis-EDOT**.

Table S1 Photocurrent–voltage characteristics[a] for DSSCs for 20 min and 30 min of PEP

Entry	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	η (%)
Device (20 min)	0.385	3.6	40	0.6
Device (30 min)	0.543	4.5	60	1.5

[a] Values obtained using the average over 4 devices for each experiment
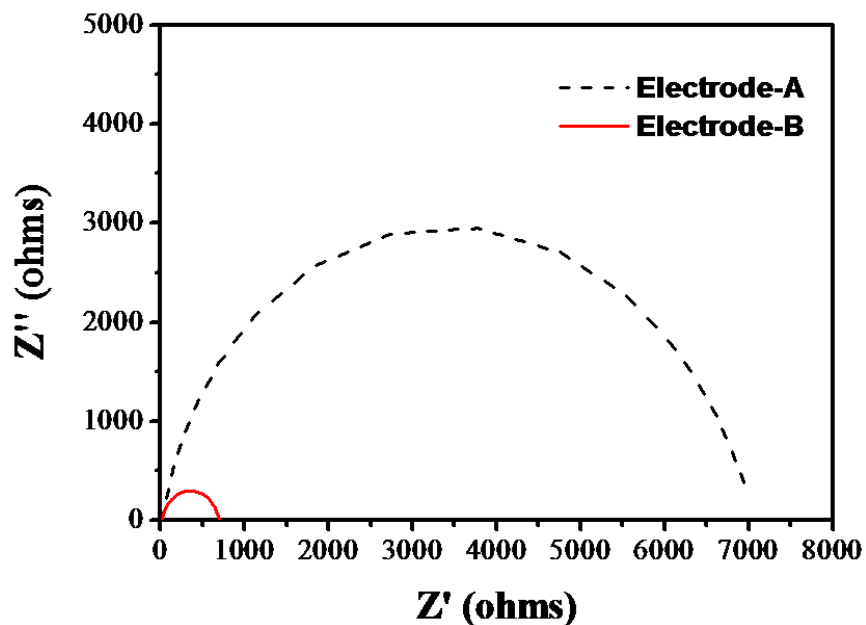
6. Resistance of devices without compact TiO$_2$ layer

Fig. S5 Representative EIS curves at 0 V for electrode-A (**PEDOT**) and electrode-B (**PEDOT-TB**).
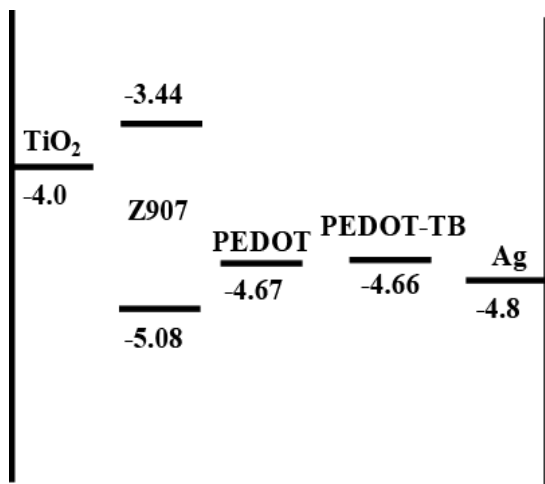

Fig. S6 The energy diagram of the devices.

7. Reference for supporting information

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2. Gentilini, C.; Boccalan, M.; Pasquato, L. *Eur. J. Org. Chem.* **2008**, 3308.
3. (a) Sotzing, G. A.; Reynolds, J. R. *Chem. Mater.* **1996**, *8*, 882. (b) Irvin, J. A.; Schwendeman, I.; Lee, Y.; Abboud, K. A.; Reynolds, J. R. *Journal of Polymer Science: Part A: Polymer Chemistry*, **2001**, *39*, 2164.