Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplementary Information

Design of Organic Redox Mediator and Optimization of Organic Counter Electrode for Efficient Transparent Bifacial Dye-Sensitized Solar Cells

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Synthesis and characterization of the redox couples

The synthesis started commercially from available aryl-isothiocyanate which was transformed into the corresponding 1-aryltetrazol-5-thiol (AT) by cycloaddition reaction with sodium azide in refluxing ethanol according to the known procedures.[1] The oxidized species, bis(1-aryltetrazol-5-yl) disulfide (BAT), were prepared by oxidation of the mercaptan AT with hydrogen peroxide, and thiolate form AT^- was obtained by deprotonation of AT with sodium bicarbonate. Structures of this redox couple were proved by the combination of ^1H NMR spectroscopy, mass spectroscopy (ESI-MS) and elemental analyses.

General procedure for synthesis of thiolate forms (AT^-): A mixture of 0.05 mole of the isothiocyanate and 0.075 mole of sodium azide dissolved in 100 mL of water was refluxed for a period of 6 hours. The mixture was cooled and filtered from any insoluble material present. The filtrate was then extracted twice with ether to remove any unreacted isothiocyanate. The aqueous layer was cooled and acidified with concentrated hydrochloric acid to pH 2.5 and the corresponding mercaptan compound precipitated out at this stage. This precipitation was filtered, washed with water, and then dried under vacuum at 40 ℃ for 12 h to give the purified mercaptan compound. After that, the mercaptan was deprotonated with an excess of sodium bicarbonate in ethanol. The mixture was stirred for 2 h at room temperature, and then filtered. The crude product was obtained by evaporation of the solvent in the filtrate. The pure sodium thiolate ($AT^- Na^+$) was obtained after recrystallization from a mixture of chloroform and ethanol.

Sodium 1-phenyl-tetrazole-5-thiolate ($AT^- Na^+$): white powder, yield 65 %, ^1H NMR ($CDCl_3$): $\delta = 7.38$ (d, 2H, J = 8.4 Hz, ArH), 7.66 (d, 2H, J = 8.4 Hz, ArH). MS (ESI): negative ion: m/z = 177.3 $[M-Na]^-$, calculated 177.2. Anal. Calcd. for $C_7H_5N_4NaS$: C, 42.00; H, 2.52; N, 27.99; S, 16.02 %; Found: C, 41.96; H, 2.50; N, 27.91; S, 15.72 %.

General procedure for synthesis of oxidized species (BAT): 1 mL of 30% hydrogen peroxide was added dropwise to 0.01 mole of the corresponding mercaptan compound in 50 mL of ethanol. The mixture was stirred at 30 °C for 12 h and the disulfide precipitated out at this stage. The reaction mixture was cooled to 0 °C. The crude product was collected after filtration.

Recrystallization from a mixture of chloroform and ethanol gave the purified oxidized species BAT.

Bis(1-*p*-phenyl-tetrazol-5-yl) disulfide (BAT): white powder, yield 80 %, ^{1}H NMR ($CDCl_3$): δ = 7.33 (d, 2H, J = 8.4 Hz, ArH), 7.51 (d, 2H, J = 8.4 Hz, ArH). MS (ESI): positive ion: m/z = 355.6 $[M+H]^+$, calculated 355.4. Anal. Calcd. For $C_{14}H_{10}N_8S_2$: C, 47.44; H, 2.84; N, 31.62; S, 18.09 %; Found: C, 47.10; H, 2.83; N, 31.33; S, 17.89 %.

Preparation of counter electrode

The platinized counter electrode (CE) was prepared by depositing 10 *u*L cm^{-2}, 5 mM H_2PtCl_6 solution in isopropanol to the F-doped tin oxide conducting glass substrate (Nippon) followed by heating in air at 400 °C for 30 min.

The highly porous poly(3,4-ethylenedioxythiophene) ($PEDOT_{HP}$) and ultra thin PEDOT ($PEDOT_{UT}$) films were obtained through electropolymerization using a bath solution consisting of 0.01 mol L^{-1} ethylenedioxythiophene (EDOT) and 0.1 mol L^{-1} lithium bis-trifluoromethanesulfonylimide (LiTFSI) in acetonitrile, and using a three-electrode system, i.e., a FTO glass as the working electrode, a platinum foil as the counter electrode, and Ag/AgCl as the reference electrode. The $PEDOT_{HP}$ and $PEDOT_{UT}$ CEs were prepared by applying a constant potential until a charge capacities of 100 mC cm^{-2} and 2 mC cm^{-2} was reached, respectively. Then the conducting polymer electrodes were washed by ethanol for three times, and dried in a vacuum oven for 30 min.

Preparation of photoelectrode and fabrication of dye-sensitized solar cells

FTO glass plates with high transparency in the visible range purchased from Nippon sheet glass. It was first cleaned in a detergent solution using an ultrasonic bath for 15 min, and then rinsed with water and ethanol. Photoelectrodes consisted of a TiO_2 film with a double-layer structure. A compact blocking underlayer of dense titanium dioxide was deposited onto a cleaned FTO glass substrate by immersing the FTO glass plates into a 40 mM aqueous $TiCl_4$ solution, which was washed with water and ethanol. Depositions of a 12 μm thick transparent layer (PST-18NR, JGC Catalysts and Chemicals Ltd., Japan) of nanocrystalline TiO_2 were printed layer by layer. The electrodes coated with the TiO_2 pastes were gradually heated under an airflow at 325 °C for 5 min, at 375 °C for 5 min, and at 450 °C for 15min, and finally, at 500 °C for 15 min. After sintering, The TiO_2 “double-layer” film thus produced is once again treated with 40mM $TiCl_4$ solution, as described previously, then rinsed with water and ethanol and sintered at 500 °C for 30 min. After cooling to 80 °C, the TiO_2 electrode was immersed into a 0.3 mM N719 dye solution in a mixture of acetonitrile and *tert*-butyl alcohol (volume ratio, 1:1) and kept at room temperature for 20–24 h to assure complete sensitizer uptake. The sensitized semiconductor films were washed with the same solvent as used in the dye-bath, dried and sealed with the prepared counter electrode as mentioned above using a hot-melt film (Surlyn, Solaronix) through heating the system at 120 °C. The electrolyte solution was then introduced through two holes predrilled in the counter electrode, and the cell was sealed with thermoplastic Surlyn covers and a glass coverslip.

Table S1. Calculated energy values of the redox potentials $E^{c}_{1/2}{}^{a}$ for the AT^{-}/BAT and T^{-}/T_2 mediators.

Redox couple	$-E_{HOMO}$ [eV]	$-E_{LUMO}$ [eV]	$E^{c}_{1/2}$ [eV]
AT^{-}/BAT	5.499	2.809	4.154
T^{-}/T_2	1.183	3.011	2.097

[a] DFT calculations were performed using the Gaussian 09 programme.[2] In particular, The geometries and the electronic structures were calculated at B3LYP/6-31+G(d) level. $E^{c}_{1/2}$ is estimated from the middle value of the HOMO and LUMO energies ($E^{c}_{1/2}$ = -(HOMO + LUMO)/2).

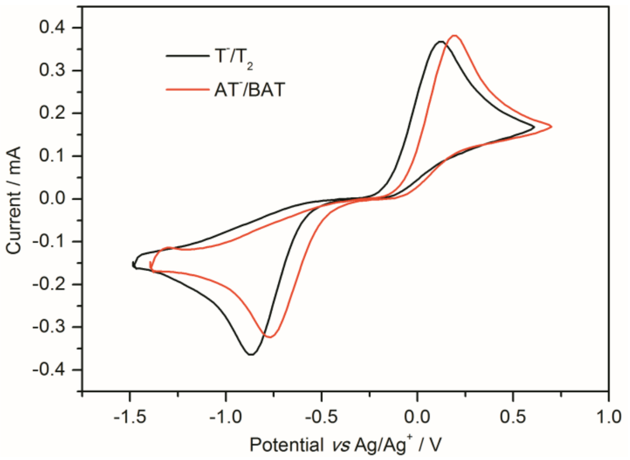

Fig. S1 Cyclic voltammograms of different organic redox couples.

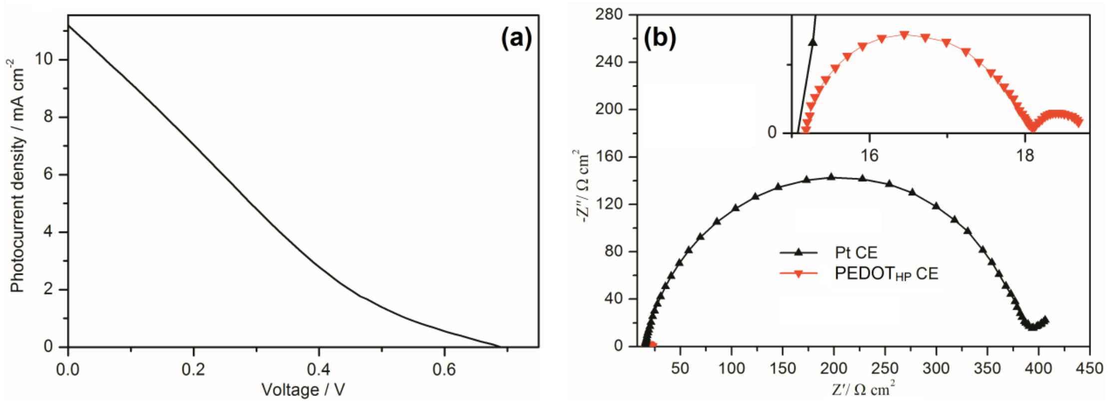

Fig. S2 (a) Current density versus applied potential curves of AT$^-$/BAT based DSCs using Pt CE, (b) impedance spectra of AT$^-$/BAT based symmetric cells using Pt or PEDOT$_{HP}$ CEs with 0 V bias voltage.

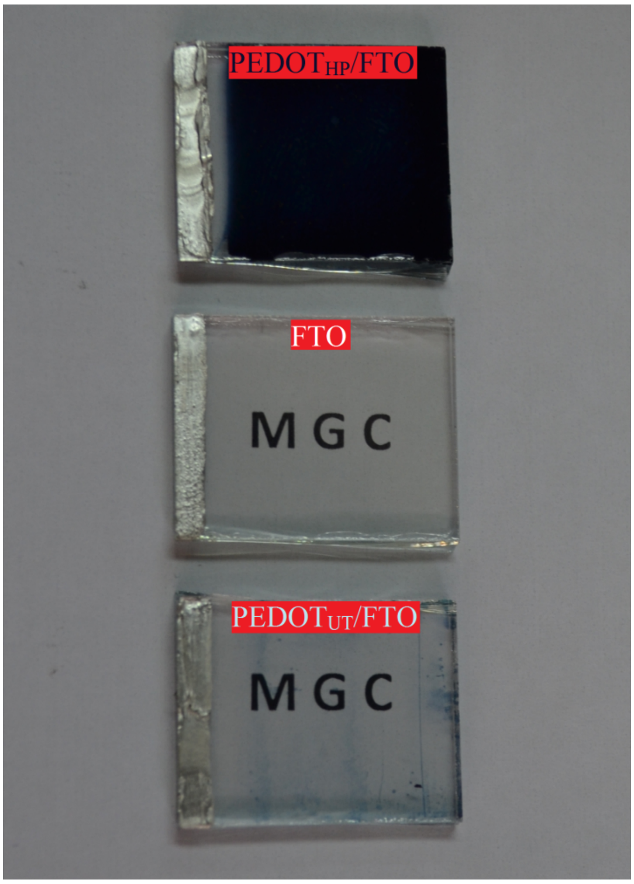

Fig. S3 Digital photographs of PEDOT$_{HP}$ coated FTO and PEDOT$_{UT}$ coated FTO glasses.

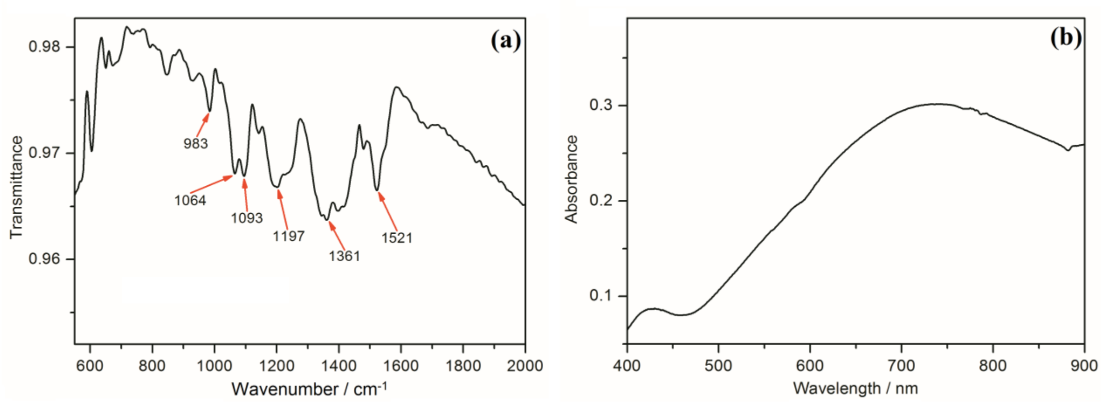

Fig. S4 (a) ATR-FTIR, (b) UV-vis spectrum of the transparent $PEDOT_{BE}$ film deposited onto the FTO substrate. Similar to the reported FTIR spectrum for $PEDOT_{BE}$.[3,4] the four characteristic bands at 1361 cm^{-1}, 1197 cm^{-1}, 1093 cm^{-1} and 1064 cm^{-1} are assigned to thiophene ring stretch, and the peaks at 1521 cm^{-1} and 983 cm^{-1} are corresponding to the stretche of the cyclic ether. According to the literature,[5] the 700-800 nm absorption band is ascribed to the PEDOT.

Notes and references

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