Electronic Supplementary Material (ESI) for ChemComm.

Solution processable, cross-linked sulfur polymers as solid electrolytes in dye-sensitized solar cells

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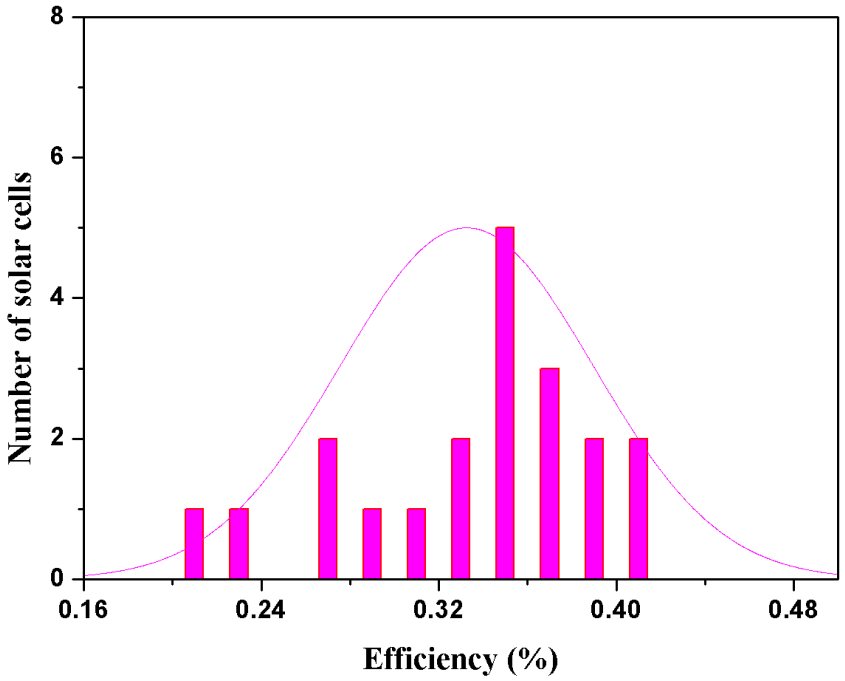

Figure S1. Histogram of efficiencies from DSSCs based on polymeric sulfur with 2000 nm thick TiO_2

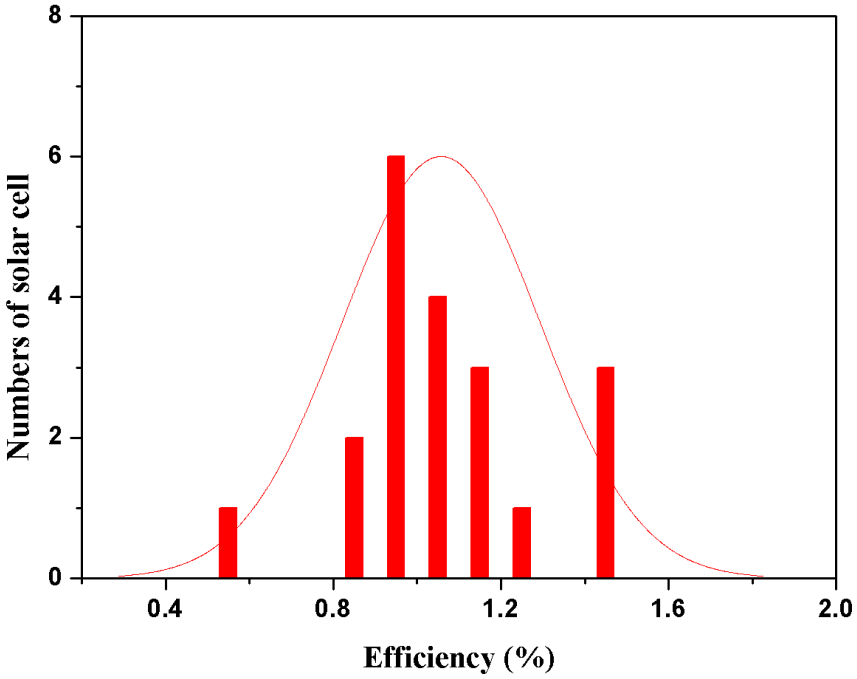

Figure S2. Histogram of efficiencies from DSSCs based on polymeric sulfur with 500 nm thick TiO_2

Experimental Section:

Chemicals Used

All chemicals were purchased from Sigma-Aldrich unless otherwise indicated. The company Dyenamo AB supplied the dye LEG4[1].

Device Fabrication

Fluorine-doped tin dioxide (FTO) substrates (Pilkington TEC15) were dipped into a Zn-HCl solution (Zinc powder and 2M hydrochloric acid) for etching process. After that step, the substrates were cleaned in an ultrasonic bath using deionized water (15 min), acetone (30 min), and ethanol (30 min), respectively. A spray pyrolysis deposition (SPD) technique was applied to obtain a compact layer of TiO_2 as a blocking layer on top of the FTO substrate. The solution used in the SPD process was 0.2 M Ti-isopropoxide and 2M acetylacetone in isopropanol. In order to generate the nano-porous TiO_2 film, a TiO_2 paste (Dyesol DSL 18NR-T) mixed with terpineol (2:1 mass ratio) was deposited on the compact layer of TiO_2 using a screen-printing method. After sintering on a hotplate at 500 °C for 30 min and cooling to room temperature, the

substrate was immersed into a solution of 0.2 M aqueous $TiCl_4$ at 70 °C for 30 min. Then, the substrates were rinsed with deionized water and ethanol and annealed on a hotplate at 500 °C for 30 min. After being cooled to 90 °C, the hot TiO_2 film was immersed into a dye bath for 18h. After the sensitization, the electrodes were rinsed with ethanol and dried in an N_2 gas flow. The surfaces of the dried substrates were covered by an HTM solution containing additives for 30 s and then spin-coated for 30s at 2000 rpm to form a uniform HTM layer. Afterwards, the cells were left in air overnight in the dark and a 200 nm thick Ag layer was deposited on the top of HTM layer by thermal evaporation in a vacuum chamber (Leica EM MED020).

Device Characterization

Current-voltage characteristics of the ssDSSCs were studied under 100 mW cm^{-2} (AM 1.5) radiation using a Keithlley Model 2400 source meter. The light source was calibrated by a certified reference solar cell (Fraunhofer ISE). A black mask with an aperture area of 0.126 cm^2 was placed on the top of the cell during the measurements. Incident photo-to-current conversion efficiency (IPCE) spectra were recorded by a computer-controlled setup comprised of a xenon lamp (Spectral Products ASB-XE-175), a monochromator (Spectral Products CM110) and a Keithley multimeter (Model 2700), calibrated by a certified reference solar cell (Fraunhofer ISE). The electron lifetime data were recorded through monitoring photovoltaic transients at different light intensities by applying a small square-wave modulation to a base light intensity. The photovoltaic response was fitted using first-order kinetics in order to obtain the time constants[2].

UV-vis absorption measurement

UV-vis absorption measurement was performed through a Lambda 750 UV-vis spectrophotometer. The signal of FTO/TiO_2 substrate was used as calibration.

Conductivity measurement

Non-conductive glass substrates were carefully cleaned by deionized water, acetone and ethanol respectively. Remaining organic residues were removed by airbrushing for 10min. A diluted TiO_2 paste (Dyesol DSL 18NR-T) with terpineol (1:3, mass ratio) was used to form thin layer TiO_2 film by spin-coating process. The thickness of the film is ca. 500 nm

measured through a DekTak profilometer. The concentrations of Li-TFSI in HTM solutions were the same as used for the photovoltaic devices. *J-V* characteristics were recorded on a Keithley 2400 Semiconductor Characterization System. Measurements were carried out following the procedure described in a previously published paper[4].

1. Gabrielsson, E.; Ellis, H.; Feldt, S.; Tian, H.; Boschloo, G.; Anders, H.; Licheng, S., Convergent/Divergent Synthesis of a Linker-Varied Series of Dyes for Dye-Sensitized Solar Cells Based on the D35 Donor. *Advanced Energy Materials* **2013**, *3*, 16471656.
2. Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H., Dye-Sensitized Solar Cells. *Chemical Reviews* **2010**, *110*, 6595-6663.
3. Boschloo, G.; Hagfeldt, A., Photoinduced absorption spectroscopy as a tool in the study of dye-sensitized solar cells. *Inorganica Chimica Acta* **2008**, *361*, 729-734.
4. Zhang, J.; Yang, L.; Shen, Y.; Park, B.-W.; Hao, Y.; Johansson, E. M. J.; Boschloo, G.; Kloo, L.; Gabrielsson, E.; Licheng, S.; Jarboui, A.; Perruchot, C.; Jouini, M.; Vlachopoulos, N.; Anders, H., Poly(3,4-ethylenedioxythiophene) Hole-Transporting Material Generated by Photoelectrochemical Polymerization in Aqueous and Organic Medium for All-Solid-State Dye-Sensitized Solar Cells. *The Journal of Physical Chemistry C* **2014**, 580190662.