Supporting information

Efficient dye regeneration at low driving force achieved in triphenylamine dye LEG4 and TEMPO redox mediator based dye-sensitized solar cells

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(b)

Figure S1. (a) The comparison of DSSCs performance for TEMPO-based solar cells with spray pyrolysis blocking layer and with the $TiCl_4$ pretreatment blocking layer. LEG4- $TiCl_4$ treatment: the FTO glass was put into a 40 mM $TiCl_4$ solution for 30 min before screen printed with mesoporous TiO_2 ; LEG4-SP blocking: the compact TiO_2 layer was first deposited by spray pyrolysis, and the mesoporous TiO_2 was then screen printed on the top of compact TiO_2 . (b) The SEM image of the spray pyrolysis TiO_2 compact layer, with a thickness measured to be around 160 nm.



Figure S2. Cyclic voltammogram of 2 mM TEMPO in 0.1 M TBAPF₆ ACN with a microelectrode as the working electrode, the scan rate is 10 mV s⁻¹. Precisely weighted ferrocyanide was used as a reference to calculate the surface area of the microelectrode according to equation¹:

 $I_{lim} = 4nFDCr$

Where *D* is the diffusion coefficient of the redox species, *C* is its concentration of the redox species and *r* is the radius of the microelectrode. The calibrated radius was then used to calculate the diffusion coefficients of interested compounds. TEMPOBF₄, Co(bpy)₃(PF₆)₂ and Co(bpy)₃(PF₆)₃ were done in the same way (data not shown here) and the results are listed in Table 1.









Figure S3. Cyclic voltammogram (CV) of TEMPO, and D149-/LEG4- sensitized film. (a) CV of TEMPO, and TEMPO with Fc/Fc⁺ as an internal reference in 0.1 M TBAPF₆ ACN solutions. A platinum working electrode was used in combination with a graphite rod as the counter electrode and Ag/AgCl (3 M NaCl aqueous) as reference electrode. The cyclic voltammogram was first conducted with only 2 mM TEMPO in the system. Then, Fc/Fc⁺ was added to above solution. The redox potential was read as half of the oxidation peak potential and reduction peak potential. The scan rate is 10mV s⁻¹. (b) Cyclic voltammogram of LEG4-/D149- sensitized TiO₂ film with a 10 mV s⁻¹ scan rate. Fc/Fc⁺ was used to calibrate the reference electrode potential before and after measurements

Table S1. Effects of Li⁺ concentration in TEMPO electrolytes on the solar cell performance

Code	Voc (mV)	Jsc (mA cm ⁻²)	FF	EF (%)
LEG4-T	865	7.00	0.78	4.70
LEG4-T-0.5	900	7.40	0.78	5.22
LEG4-T-0.1	965	7.74	0.73	5.43



Figure S4. Effects of Li⁺ concentration on the performance of DSSCs and the charge extraction measurements. (a) I-V curves of DSSCs with different Li⁺ concentration in the electrolyte. (b) The corresponding charge extraction measurement. Three electrolyte concentrations were used here: LEG4-T-0.1 (0.1 M LiTFSI, 0.5 M NMBI, 1 M TEMPO, 0.05 M TEMPOBF₄ in ACN), LEG4-T-0.5 (0.5 M LiTFSI, 0.5 M NMBI, 1 M TEMPO, 0.05 M TEMPOBF₄ in ACN), LEG4-T-0.5 (0.5 M NMBI, 1 M TEMPO, 0.05 M TEMPOBF₄ in ACN), LEG4-T (1.2 M LiTFSI, 0.5 M NMBI, 1 M TEMPO, 0.05 M TEMPOBF₄ in ACN). The shift in charge extraction amount is considered to be a positive conduction band shift caused by Li⁺.²



Figure S5. Absorption spectrum of D149 and LEG4 sensitized TiO₂ film on FTO.

Analysis of the electron transfer kinetics in the regeneration reaction

The Marcus equation reads:

$$k_{et} = \frac{H_{AB}^2}{\sqrt{4\pi\lambda k_B T}} \exp\left(-\frac{\left(\Delta G^0 + \lambda\right)^2}{4\lambda k_B T}\right),$$

where k_{et} is the rate constant for the electron transfer reaction, H_{AB} the electronic coupling, ΔG^0 the thermodynamic free energy of reaction and λ the reorganization energy.

 ΔG^0 for regeneration of oxidized LEG4 by TEMPO is -0.18 eV, while for D149 it is -0.25 eV. Assuming $\lambda = 0.5$ eV and equal electronic coupling, $k_{\rm et}$ (LEG4)/ $k_{\rm et}$ (D149) = 0.46; For $\lambda = 1.0$ eV, $k_{\rm et}$ (LEG4)/ $k_{\rm et}$ (D149) = 0.33. Experimentally found: $k_{\rm et}$ (LEG4)/ $k_{\rm et}$ (D149) \approx 5. Differences in $H_{\rm AB}$ and / or λ can account for the observed trend in the rate constants.

References

- (1) Baur, J. E.; Wightman, R. M. Diffusion Coefficients Determined with Microelectrodes. *J. Electroanal. Chem. Interfacial Electrochem.* **1991**, *305*, 73–81.
- (2) Wang, H.; Peter, L. M. Influence of Electrolyte Cations on Electron Transport and Electron Transfer in Dye-Sensitized Solar Cells. *J. Phys. Chem. C* **2012**, *116*, 10468–10475.