Supporting Information

Influence of Ionic Liquid on Recombination and Regeneration Kinetics in Dye-sensitized Solar Cells

Feng Li^[a], James Robert Jennings^[a], Xingzhu Wang^[a], Li Fan^[a], Zhen Yu Koh^[a], Hao Yu^[b], Lei Yan^[b] and Qing Wang^[a]*

- Department of Materials Science and Engineering, Faculty of Engineering, NUSNNI-NanoCore, National University of Singapore, Singapore 117576
- College of Chemistry and Key Laboratory of Low Dimensional Materials and Application Technology of Ministry of Education, Xiangtan University, Xiangtan 411105, Hunan Province, P. R. China

*E-mail: <u>qing.wang@nus.edu.sg</u>, Tel: ++(65) 6516-7118.

Part 1. Information on the recently developed organic D-A-π-A dye CBTC. The manuscript has been accepted by *Chem. Commun.*, 2014, 50, 3965-3968 (DOI: 10.1039/C4CC00577E).

Part 2. Figure. **SI-1**. Electron diffusion length L_n calculated using $L_n = d\sqrt{R_{ct}/R_t}$ where *d* is the film thickness and R_{ct} and R_t are the recombination resistance and electron transport resistance derived from IS data.



Part 3. Figure. SI-2. *j*-V characteristics of cells based on $[Co(bpy)_3]^{2+/3+}$ redox mediator under both 0.95 SUN and 0.15 SUN.



Part 4. Calibration of electron density n during TA measurements.

To obtain $k_{rg}[Red]$ and $k_{edr}n^{\chi}$, the electron density *n* during TA measurements is needed. Here the electron density following the laser pulse is used as the reference, which can be determined by:

$$n_{\rm peak} = n_{\rm bg} + \Delta n_{\rm laser} \tag{SI.1}$$

where n_{bg} is the background electron density with only 627 nm background illumination but no laser pulse and Δn_{laser} is the extra electron density injected into the film due to dye excitation by the laser pulse. n_{bg} can be easily calculated using Eq.1 from the main article. In order to determine Δn_{laser} , the OD change at 970 nm (where only electrons absorb) caused by varying the background light intensity was recorded for Z907 cells (CBTC⁺ absorbs at 970 nm) and correlated to *n* obtained from integrated $C_{\mu} \sim V_{oc}$ plots. Fig. **SI-3a** is an example of the $n \sim \Delta 0D$ plots, from which it is estimated that $\Delta OD = 1$ approximately corresponds to Δn of 2.13×10^{21} cm⁻³ (linear fit). With this correlation, and comparing $\Delta 0D_{0,e^{-},970}$ fitted from 970 nm TA (Fig.**SI-3b** and Eq.**5**) to $\Delta 0D_{0,e^{-},850}$ determined from 850 nm TA (Eq.**4**) measured under identical conditions, Δn_{laser} can be linked to $\Delta 0D_{0,e^{-},850}$. Note that $\Delta 0D$ at t = 0.2 s (period of laser pulses) is practically zero as shown in Fig.**SI-3b**, thus the application of Eq.**SI.1** is validated. Given that the TiO₂ electrodes used for CBTC cells are identical to those used for Z907 cells, this correlation should also apply for CBTC cells.



Figure SI-3. (a) Electron density *n* versus Δ OD measured at 970 nm for Z907 cells under various 627 nm background illumination levels. (b) An example for 970 nm TA of Z907 cells, measured under identical conditions to 850 nm TA. Red line is the fit to Eq.**5**.

Part 5. Table **SI-1**. Table of EDR rate constant k_{edr} and reaction order χ obtained from the fits of Fig.**5a** to $k_{obs,D^+} = k_{rg}[Red] + k_{edr}n^{\chi}$. Note that the large error in k_{edr} is misleading as discussed in our previous work.[1]

| Label | C-R-I | C-IL-I | Z-R-I | Z-IL-I |
|--------------------------------------|----------|----------|----------|----------|
| k _{edr} / cm ^{-3χ} | 1.12E-97 | 2.47E-84 | 1.85E-50 | 1.25E-78 |
| σ _k | 1.08E-96 | 2.26E-83 | 5.13E-49 | 3.00E-77 |
| X | 5.6181 | 4.87 | 2.9779 | 4.5347 |
| σχ | 0.2321 | 0.22 | 0.6581 | 0.5719 |
| Label | C-R-Co | C-IL-Co | Z-R-Co | Z-IL-Co |
| $k_{ m edr}$ / $cm^{-3\chi}$ | 2.38E-60 | 2.28E-63 | 1.56E-39 | 1.28E-68 |
| σ _k | 1.77E-58 | 1.17E-61 | 1.72E-38 | 3.98E-67 |
| x | 3.5236 | 3.689 | 2.351 | 3.8883 |
| σχ | 1.773 | 1.2281 | 0.2592 | 0.7259 |

Part 6. Figure. **SI-4**. Comparison of pseudo first-order rate constant for EDR ($k_{edr}n^{\chi}$) of different cells calculated using the fitting results from Fig.**5a** in the main text.



References

 Li, F., J.R. Jennings, and Q. Wang, Determination of Sensitizer Regeneration Efficiency in Dye-Sensitized Solar Cells. ACS Nano, 2013. 7(9): p. 8233-8242.