Electronic Supplementary Information

The combination of a polymer/carbon composite electrode with a high-absorptivity ruthenium dye achieves an efficient dye-sensitized solar cell based on a thiolate/disulfide redox couple†

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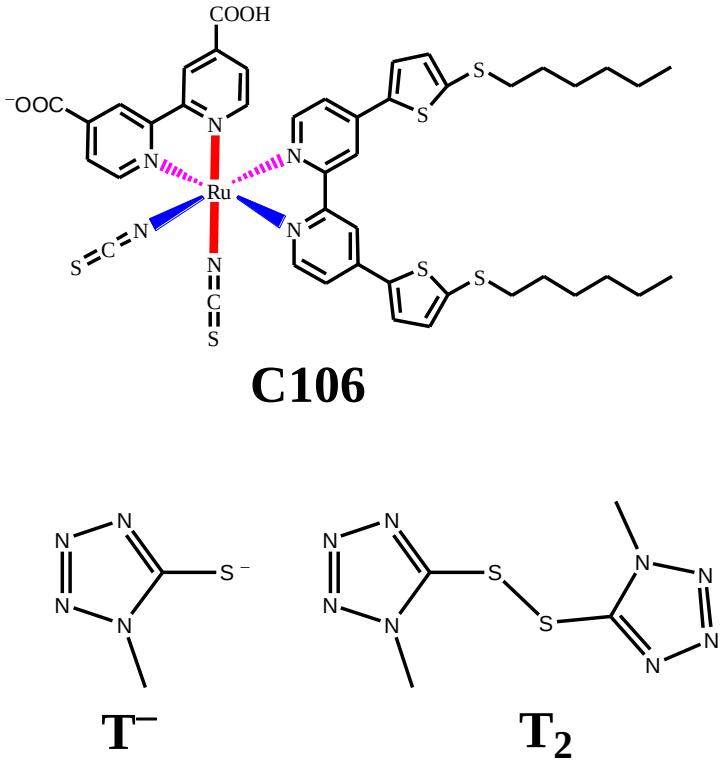


Fig. S1 Molecular structures of the C106 dye and the thiolate/disulfide redox couple.

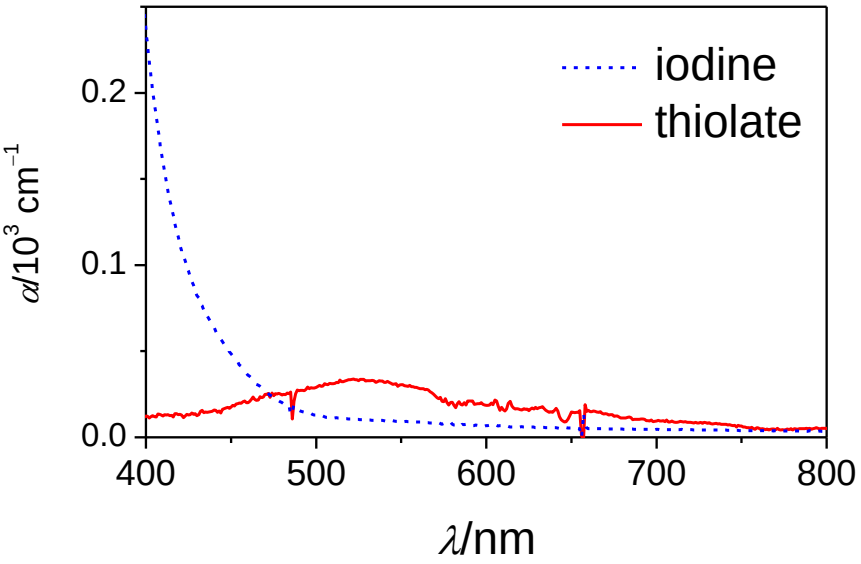


Fig. S2 Absorption coefficients (α) of 4000-fold diluted thiolate and iodine electrolytes.

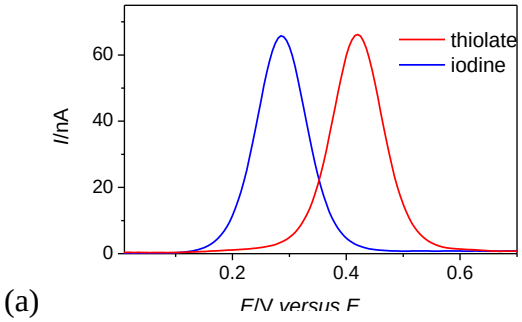
The details of fitting of TAS and emission decay

(1) The absorption decays were fitted by a stretched exponential function $\Delta A \propto A_0 \exp[-(t/\tau)^{\alpha}]$, where A_0 is a pre-exponential factor, α is the stretching parameter and τ is the characteristic time. Using the gamma function $\Gamma(x)$, the average time ($<\tau>$) of this charge transfer reaction was calculated through $<\tau>=(\tau/\alpha)\Gamma(1/\alpha)$.

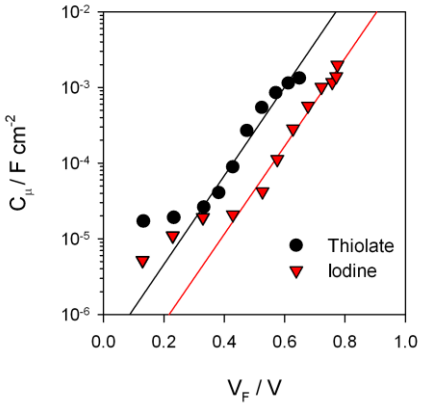
(2) The time-correlated emission decay traces are well fitted with a stretch exponential function of

$$I = I_0 \exp\left[-\left(\frac{t}{\tau}\right)^{\alpha}\right], \qquad (1)$$

where I_0 is the initial emission amplitude on alumina, α is the stretch parameter and τ denotes the lifetime. The photoluminescence average lifetimes ($\bar{\tau}$) of the C106 dye molecules anchored on alumina in contact with the thiolate and iodine electrolytes were calculated with $\bar{\tau} = (\tau/\alpha)\Gamma(1/\alpha)$ where $\Gamma(x)$ is gamma function. The interfacial electron injection rate constant (k_{inj}) can be derived by $k_{inj} = 1/\bar{\tau}_{titania} - 1/\bar{\tau}_{alumina}$, where $\bar{\tau}_{titania}$ and $\bar{\tau}_{alumina}$ represent the photoluminescence average lifetimes on titania and alumina films, respectively. In consideration of the non-injection deactivation rate constant $k_d = 1/\bar{\tau}_{alumina}$, the yield of electron injection (η_{inj}) was estimated through $\eta_{inj} = k_{inj}/(k_{inj} + k_d)$.



(a)



(b)

Fig. S3 (a) Square-wave voltammogram of ferrocene in acetonitrile measured with a homemade thiolate or iodine reference electrode. (b) Chemical capacitance of TiO_2 in DSC with thiolate and iodine as redox electrolytes.

Changes in the redox energy level were measured employinga reference electrode composed of a platinum wire dipped in a DSC electrolyte-filling glass tube, the lower end of which is sealed with a porous ceramic frit, to measure the square-wave voltammogram, Fig. S3(a) of ferrocene dissolved in 0.1 M 1,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide acetonitrile. In our experiments, a 5-μm-radius platinum ultramicroelectrode was used as working electrode and a platinum foil as auxiliary electrode. On the basis of voltammetric measurements, we further calculated $E_{F,redox}$ of the thiolate and iodine electrolytes being −0.42 and −0.29 V *versus* Fc^+/Fc, respectively. So the Fermi level of thiolate electrolyte is ~0.13V more negetive than the iodine counterpart.

The position of the conduction band relative to the redox couple was estimated from chemical capacitance measurements:[S1,S2]

$$C_{\mu} = \frac{N_t e^2}{k_B T_c} \exp\left[\frac{E_{F,redox} - E_c}{k_B T_c}\right] \exp\left[\frac{eV}{k_B T_c}\right] \quad \text{(S1)}$$

where $N_t \sim 2\times10^{20}$ is the density of accessible interband states of titania, T_c is a characteristic temperature describing the distribution profile of surface states, e is the elementary charge and V_F is the potential bias in our impedance measurements free from series resistance drop. As shown in Fig. S3(b), the semilogarithmic plots of C_{μ} against V_F for thiolate and iodine electrolytes exhibit comparable slopes, indicative similar T_c. In comparison with iodine congener, the thiolate electrolyte possesses an ~0.14 V smaller value of $E_c - E_{F,redox}$. Combining with the difference of Fermi level between these two electrolytes, the absolute value of E_c in thiolate is ~10 mV more negative than in iodine electrolyte.

References

(1) Bisquert, J. *Phys. Chem. Chem. Phys.*, **2003**, *5*, 5360.

(2) Fabregat-Santiago, F.; Mora-Seró, I.; Garcia-Belmonte, G.; Bisquert, J. *J. Phys. Chem. B*, **2003**, *107*, 758.