

Electronic Supplementary Information

Probing energy losses from dye desorption in cobalt complex based dye-sensitized solar cells

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List of Contents

1. Photophysical and electrochemical parameters for dye M26.....	S1
2. Variation of light absorption spectrum of the M26 sensitized TiO ₂ film under HCl treatment.....	S3
3. Absorption coefficient and light harvesting efficiency at the wavelength of 630 nm.....	S3
4. Details on the fits to the curves of electron density versus the Fermi-level.....	S4
5. Derivation of equation 5.....	S6
6. Reaction-diffusion model for simulating DSCs and numerical details.....	S7
7. Effect of the conduction band edge shift on absorbed photon conversion efficiency.....	S12
8. Dependence of recombination constant on dye loading.....	S12
References	S13

1. Photophysical and electrochemical parameters for dye M26

Table 1 Photophysical and electrochemical data for dye M26.

Dye	$\lambda_{\max}/\text{nm}^a$	$\lambda_{\max}/\text{nm}^b$	$\varepsilon/10^3 \text{ M}^{-1} \text{ cm}^{-1}$	E_{0-0}/eV^c	HOMO /V vs NHE ^d	LUMO /V vs NHE ^e
M26	532	489	19.2	2.16	0.99	-1.17

^aAbsorption spectra of dye M26 in dichloromethane (DCM). ^bAbsorption spectra of dye N26 anchoring in TiO₂ film. ^c E_{0-0} was estimated from the intersection of the normalized absorption and emission spectra in dichloromethane (DCM) solution. ^dHOMO is estimated as the average of anodic and cathodic peak potentials. ^eLUMO is calculated by reducing optical transition energy (E_{0-0}) from oxidation potential (HOMO)

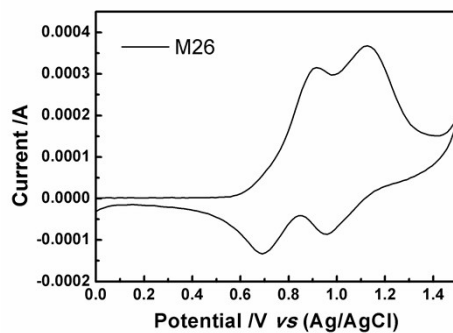


Fig. S1 Cyclic voltammograms of M26 sensitized electrodes.

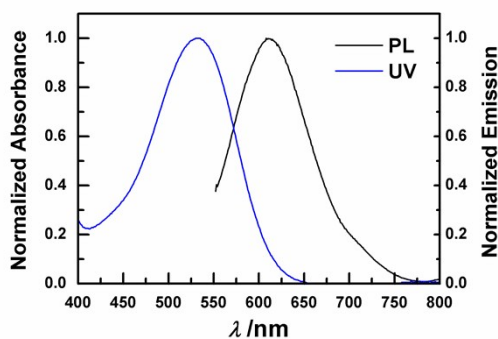


Fig. S2 Normalized absorption and emission spectra of the dyes in DCM.

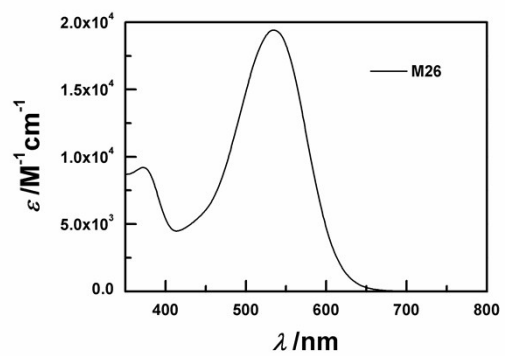


Fig. S3 Absorption spectra of dye M26 in DCM.

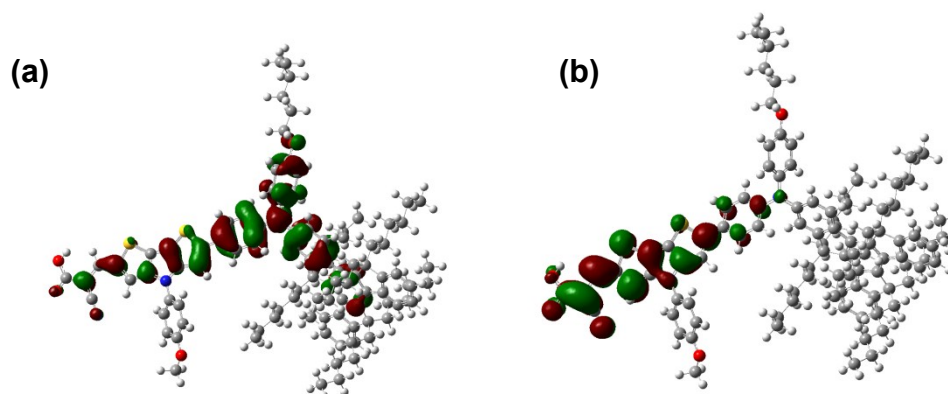


Fig. S4 Isodensity surface plots for the HOMO (a) and LUMO (b) of dye M26.

2. Variation of light absorption spectrum of the M26 sensitized TiO₂ film under HCl treatment

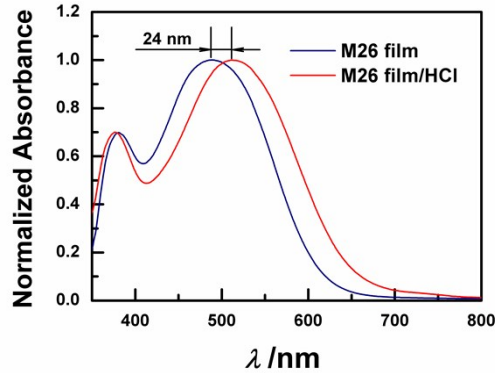


Fig. S5 Absorption spectra of dye M26 sensitized TiO₂ film and its light response after treated with HCl solution

3. Absorption coefficient and light harvesting efficiency at the wavelength of 630 nm

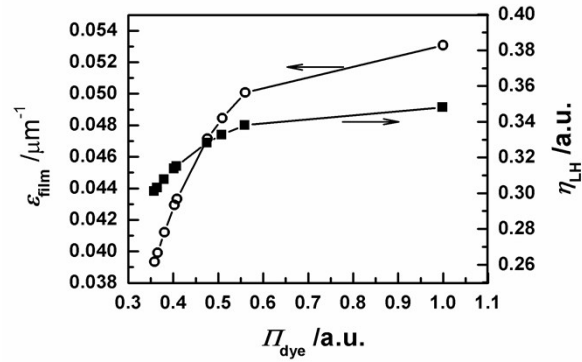


Fig. S6 Dependence of absorption coefficient and light harvesting efficiency on normalized dye loading. Wavelength of incident LED is 630 nm.

4. Details on the fits to the curve of electron density versus the Fermi-level using biexponential distribution function

To make good fits to the $n-E_{F,n}$ curves, biexponential distribution equation is simplified as follows,

$$n = \sum_{i=s,d} P_i \exp\left(\alpha_i \frac{E_{F,n}}{k_B T}\right) \quad (S1)$$

where prefactor P_i is given by

$$P_i = N_{T,i} \exp\left(\alpha_i \frac{-E_c}{k_B T}\right) \quad (S2)$$

Here subscripts “s” and “d” in eqn (S1) stand for deep and shallow traps, respectively. As illustrated in Fig. S8, the $n-E_{F,n}$ curve is well fitted by eqn (S1). The fitting results are summarized in Table S2. One can see that α_s is nearly invariant to Π_{dye} . Thereby, the shift of the conduction band edge (ΔE_c) with respect to Π_{dye} can be estimated by assuming the invariance of the density of shallow trap states. That is given by

$$\Delta E_c = \frac{k_B T}{\bar{\alpha}_s} \ln \frac{P_s^1}{P_s^2} \quad (S3)$$

where $\bar{\alpha}_s$ is the average of α_s , which equals to 0.498 according to fitting results.

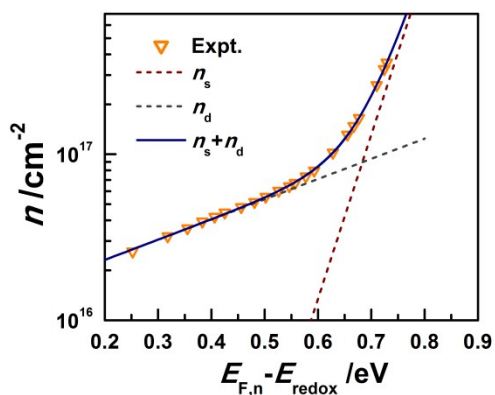


Fig. S7 Best fits to the $n-E_{F,n}$ curve of the DSCs with relative dye loading of 0.47 using a biexponential distribution function. Gray and red dashed lines represent the fitted distributions of the electrons at deep-trapping states (n_d), shallow-trapping states (n_s), respectively.

Table 2 Fitted parameters for the $n-E_{F,n}$ curves.

Π_{dye}	$P_s / 1 \times 10^{10}$	α_s	$P_d / 1 \times 10^{16}$	α_d	R^2
1.00	0.55	0.497	3.05	0.045	0.997
0.64	0.87	0.497	1.98	0.045	0.999
0.52	1.18	0.500	2.38	0.042	0.999
0.47	1.52	0.499	1.81	0.051	0.999
0.43	2.51	0.496	1.70	0.058	0.999
0.40	2.78	0.496	1.50	0.058	0.999
0.34	3.03	0.506	1.68	0.050	0.998
0.33	4.04	0.498	1.37	0.063	0.998
0.31	6.47	0.496	1.47	0.052	0.999

5. Derivation of Equation 4

The rate of recombination reaction between injected electrons and the oxidized species in electrolyte can be formulated as follows,

$$U_{\text{rec}} = k_r n_c^\beta \quad (\text{S4})$$

where U_{rec} represents recombination rate, n_c is the density of the conduction band electrons, β is ideality factor, k_r is recombination rate constant. When DSC is at open circuit, the injected electrons are absolutely consumed by the combination reaction. Thereby, eqn (S4) can be rewritten as

$$I_0 \eta_{\text{inj}} \eta_{\text{LH}} = k_r N_c^\beta \exp\left[\frac{q\beta}{k_B T} (E_{\text{F,n}} - E_c)\right] \quad (\text{S5})$$

where I_0 is illumination intensity, η_{inj} is electron injection efficiency, η_{LH} is light harvesting efficiency, E_c is the conduction band edge, N_c is the density of the conduction band, k_B is the Boltzmann constant, T is the absolute temperature and q is elementary charge. Note that n_c in eqn (S5) is expressed as the function of the Fermi-level. By replacing the Fermi-level with V_{oc} , one can find,

$$V_{\text{oc}} = E_c + \frac{k_B T}{\beta q} \ln \frac{I_0 \eta_{\text{LH}} \eta_{\text{inj}}}{k_r N_c} \quad (\text{S6})$$

If the variation of V_{oc} , i.e. ΔV_{oc} , is relative to the band edge shift, light absorption efficiency, or other kinetic factors, ΔV_{oc} is decomposed into follows,

$$\Delta V_{\text{oc}} = \Delta E_c - \Delta E_k + \Delta E_{\text{LH}} \quad (\text{S7})$$

where ΔE_k is given by

$$\Delta E_k = \frac{k_B T}{q} \Delta \frac{\ln k_r}{\beta} \quad (\text{S8})$$

and ΔE_{LH} is written as

$$\Delta E_{\text{LH}} = \frac{k_{\text{B}}T}{q} \Delta \frac{\ln \eta_{\text{LH}}}{\beta} \quad (\text{S9})$$

It is seen that we exclude the contribution of η_{inj} to ΔV_{oc} in eqn (S7). This is justified for the DSCs under the treatment of dye desorption.

6. Reaction-diffusion model for simulating DSCs and numerical details

Reaction-diffusion model was employed in this work for mimicking the j - V response of cobalt complex based DSCs at different dye loading. Briefly, this model describes four photoelectrochemical processes: (1) the injection of photo-generated electrons, (2) the diffusion of the injected electrons across TiO_2 film, (3) interfacial recombination reaction, and (4) the recovery of electron receptors at counter electrode. When cobalt complex based DSCs operate at steady state, the transport of conduction band electrons is formulated by a time-independent equation in one dimension,^[S1]

$$D_{\text{c}} \frac{\partial^2 n_{\text{c}}}{\partial x^2} - U_{\text{rec}} + G_{\text{in}} = 0 \quad (\text{S10})$$

where D_{c} is the diffusion coefficient of conduction band electrons, U_{rec} is the recombination rate, G_{in} is the rate of electron injection. Normally, n_{c} is estimated according to the quasi-Fermi level of TiO_2 , that is

$$n_{\text{c}} = N_{\text{c}} \exp\left(\frac{E_{\text{F,n}} - E_{\text{c}}}{k_{\text{B}}T}\right) \quad (\text{S11})$$

where E_c is the energy level of the band edge, N_c is the density of the states at the conduction band, k_B is the Boltzmann constant, and T is the absolute temperature.

The recombination reaction is assumed to satisfy the empirical relation,^[S2] which is written as

$$U_{\text{rec}} = k_r n_{\text{ox}} n_c^b \quad (\text{S12})$$

where n_{ox} is the concentration of electron receptor in electrolyte, k_r is rate constant of recombination reaction, and b is the apparent reaction order.

Considering the exponential decay of the absorption of dye-soaked TiO_2 film, electron injection rate in eqn (1) is given by

$$G_{\text{in}} = I_0 \eta_{\text{inj}} \varepsilon_{\text{film}} \exp(-\varepsilon_{\text{film}} x) \quad (\text{S13})$$

where I_0 is incident photon flux, η_{inj} is electron injection efficiency, and $\varepsilon_{\text{film}}$ is adsorption coefficient.

The kinetic equations for the diffusion-reaction of the redox shuttles in electrolyte are given as eqns (S14) and (S15),

$$D_{\text{ox}} \frac{\partial^2 n_{\text{ox}}}{\partial x^2} - U_{\text{rec}} + G_{\text{in}} = 0 \quad (\text{S14})$$

$$D_{\text{re}} \frac{\partial^2 n_{\text{re}}}{\partial x^2} - G_{\text{in}} = 0 \quad (\text{S15})$$

where n_{ox} and n_{re} represents the mole concentrations for the oxidized form (receptor) and the reduced form (donor) in redox shuttles, respectively.

Eqns (S10), (S14), and (S15) in this work are employed for determining density profiles of the conduction band electrons and redox couples at steady condition. In the numerical calculations, we

applied reflective boundary conditions for n_c , n_{ox} , and n_{re} , i.e. $\nabla n_c|_{x=d} = 0$, $\nabla n_{re}|_{x=0} = 0$, $\nabla n_{ox}|_{x=0} = 0$. At the contact between TiO₂ film and TCO sheet ($x=0$), the interfacial density of the conduction band electron (n_c^0) is related to its Fermi-level ($E_{F,n}^0$). And the latter depends on bias voltage (V) and the energy level of counter electrode ($E_{F,redox}$) by the expression of $E_{F,n}^0 = qV + E_{F,redox}$, where q is the elementary charge. According to the definition, $E_{F,redox}$ is written as

$$E_{F,redox} = k_B T \ln \left(\frac{n_{ox}^{eq} - n_{ox}^{CE}}{n_{ox}^{CE}} \right) \quad (S16)$$

where n_{ox}^{CE} and n_{ox}^{eq} are the concentrations of the receptors at counter electrode ($x=d+d_{el}$) under illumination and in the dark, respectively. Current density is estimated by the expression of $j=qD_c \nabla n_c^0$ after calculating the density profiles. The absorbed photon conversion efficiency (η_{APCE}) at short circuit is then obtained,

$$\eta_{APCE} = \frac{j}{I_0(1 - \exp(-\varepsilon_{film}d))} \quad (S17)$$

These equations were solved numerically in one dimension by using Clark-Nicolson method. Experimental data of E_c , b , ε_{film} , d , and η_{APCE} etc. at a given dye loading were employed for solving k_r via a relaxation iteration scheme. To be specific, an initial value of k_r is estimated to yield a numerical result of η_{APCE}^n by solving the equation set. Subsequently, the obtained η_{APCE}^n is applied for generating a new guess of k_r^n with the aid of standard relaxation form.

$$k_r^n = k_r \times \left[1 + \xi \left(\eta_{APCE}^n - \eta_{APCE}^{expt} \right) / \eta_{APCE}^{expt} \right] \quad (S18)$$

where $\eta_{\text{APCE}}^{\text{expt}}$ is the experimental data of η_{APCE} , ζ is the relaxation factor. In our simulations, the value of ζ is chosen as 0.5. The k_r^n is then used to calculate next η_{APCE}^n . Such process is repeated until the following criterion of convergence reaches,

$$\left| 1 - \frac{\eta_{\text{APCE}}^n}{\eta_{\text{APCE}}} \right| \leq 10^{-4} \quad (\text{S19})$$

As k_r is calculated, we also obtain the density profiles of the conduction band electrons (n_c) and electron receptors (n_{ox}). The diffusion length (L_n) is usually defined by^[S3]

$$L_n = \sqrt{D_c \tau_n} \quad (\text{S20})$$

where τ_n is the electron lifetime depending on the density of the conduction band electrons,

$$\tau_n = (k_r n_c^{\beta-1} n_{\text{ox}})^{-1} \quad (\text{S21})$$

As shown above, n_c varies with the position of the device. It implies τ_n has to be estimated as its average over the TiO_2 film. Therefore, L_n is calculated by inserting eq S1 into eq 20. Usually, charge collection efficiency is correlated to the ratio between L_n and film thickness. It follows that L_n/d is expressed as

$$\frac{L_n}{d} = \sqrt{\frac{D_c}{d \int_0^d k_r n_c^{\beta-1} n_{\text{ox}} dx}} \quad (\text{S22})$$

The employed parameters in the simulations are summarized in Table 3.

Table 3. Parameters used in the simulation^a

Parameter	Symbol	Value	Unit
Conduction band edge	E_c	Expt.	eV
Reaction order of recombination	b	Expt.	–
Absorption coefficient	$\varepsilon_{\text{film}}$	Expt.	μm^{-1}
Film thickness	d	Expt.	μm
Absorbed photon conversion efficiency	η_{APCE}	Expt.	–
Light intensity	I_0	Expt.	cm^{-2}
Density of the Conduction band	N_c	7×10^{20}	cm^{-3}
Density of the Shallow Trapping states	N_s	2×10^{20}	cm^{-3}
Diffusion coefficient of the conduction band electrons	D_c	0.5	$\text{cm}^2 \text{s}^{-1}$
Diffusion coefficient for electron receptors	D_{ox}	3.6×10^{-5}	$\text{cm}^2 \text{s}^{-1}$
Diffusion coefficient for electron donors	D_{re}	4.4×10^{-5}	$\text{cm}^2 \text{s}^{-1}$
Porosity	p	0.6	–
Thickness of electrolyte layer	d_{el}	10	μm
Temperature	T	293.15	K

^a Experimental data are shown in the text.

7. Effect of the conduction band edge shift on absorbed photon conversion efficiency

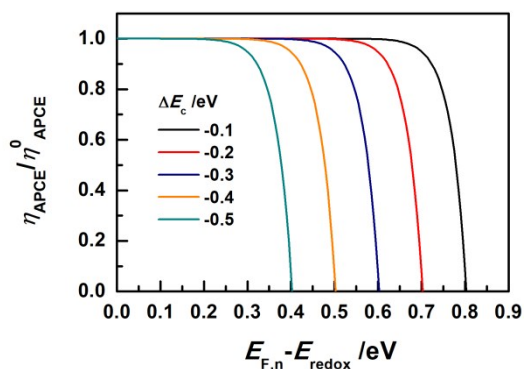


Fig. S8 Simulation results on the relation between positive band edge shift and the reduction of absorbed photon conversion efficiency. The η_{APCE}^0 stands for the η_{APCE} at the original band edge (E_c^0). Simulation parameters: $b=0.72$, $E_c^0=1.11$ V, $k_r=1.26 \times 10^{-11}$ cm^{3b} s⁻¹, and $I_0=20$ mW cm⁻².

8. Dependence of recombination constant on dye loading

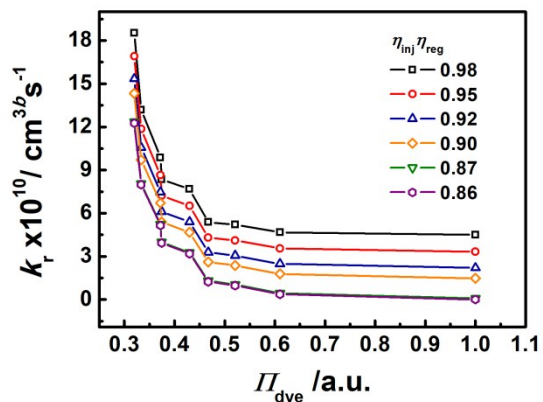


Fig. S9 Dependence of recombination constant on dye loading. Note that the experimental value of η_{APCE} is 0.857 at $\Pi_{\text{dye}}=1.0$, which means $\eta_{\text{inj}} \eta_{\text{reg}}$ is in the range from 1.0 to 0.857.

References

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- (S3) J. Bisquert and I. Mora-Seró, *J. Phys. Chem. Lett.*, 2010, **1**, 450–456.