

New insight into the regeneration kinetics of organic dye sensitised solar cells

Supporting information

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Detailed description of the assembly of the cells:

TiO₂ (DSL18NRT) films were tape-cast onto the transparent conductive F:SnO₂ (FTO) glass substrates, LOF Tec 15. They were heated to 450 °C in air for 30 min to give a layer thickness of 7 μm. The standard TiCl₄ treatment was applied using a 30 mM TiCl₄-tetrahydrofuran (THF) complex in water at 70 °C for 30 min.¹ After reheating to 450 °C for 30 min, the films were allowed to cool to ≈100 °C and then immersed in the dye solution for 2h. Dye solution used was 0.0625mM

5-[[4-[4-(2,2-Diphenylethenyl)phenyl]-1,2,3-3a,4,8b-hexahydrocyclopent[b]indol-7-yl]methylene]-2-(3-ethyl-4-oxo-2-thioxo-5-thiazolidinylidene)-4-oxo-3-thiazolidineacetic acid (D149) with 0.03125mM chenodeoxycholic acid (Cheno) in acetonitrile and tert-butanol (1:1 vol:vol) and 0.26 mM

(E)-2-((E)-(5-carboxy-3,3-dimethyl-1-octylindolin-2-ylidene)methyl)-4-((1-ethylbenzo[cd]indol-2-yl)methylene)-3-oxocyclobut-1-enolate (VG5) with 52mM chenodeoxycholic acid (Cheno) in ethanol. Counter electrodes were prepared by drilling 0.8 mm holes through FTO glass before platinising them with H₂PtCl₆ (5mM) in 2-propanol. Cells were sealed with 25 μm Surlyn gasket. Electrolyte was injected into the cells through the holes on the counter electrode. Holes were sealed with a glass cover slip and Surlyn. The cell active area was 1 cm × 1 cm. Silver paint was applied onto the tin oxide on the four sides the cells to reduce series resistance. Transparent conductive fluorine:SnO₂ (FTO) glass, LOF Tec 15, was purchased from Hartford Glass (Indiana, USA). TiO₂ nanoparticle paste DSL18NRT was purchased from DyeSol (NSW, Australia).

Detailed description of the experimental setup²:

The current-voltage characteristics of the cells were measured using a solar simulator based made by a 150W Xenon lamp with AM 1.5 filter (Sci Tech).

A pump stimulated the injection of about 3 μC of charge, corresponding to less than 1 electron per particle. The pulse intensity was about 0.8 mJ cm⁻², pulse width 3ns, using a repetition rate of 4Hz (opetek Opolette 355II).

The transient absorption was recorded using a Si photodiode (Hamamatsu S3071), a Costronics preamplifier-amplifier and a Tektronix TDS 1012 oscilloscope. The probe was constituted by a 100W quartz halogen lamp (Bentham IL1) driven by constant current power supply (Bentham 605). Before the sample the probe was attenuated by neutral density filters to 1 sun intensity while after the sample scattering was virtually eliminated by short/long pass filters and the probe wavelength was selected by band-pass filters.

Derivation and sensitivity analysis of equation 2

We start with the standard equation for the rate equation.

$$k_{et} = \frac{2\pi}{\hbar} |H_{AB}|^2 \frac{1}{\sqrt{4\pi\lambda k_b T}} \exp\left(-\frac{(\lambda + \Delta G^\circ)^2}{4\lambda k_b T}\right)$$

In comparing VG5 and D149 we start by asserting that the main influence on the ratio of the rates shown in figure 2b will be λ and ΔG inside the exponential. We assert that changes in the coupling factor between the dye and iodide (H_{AB}) will be not be large enough to contribute relative to the exponential of changes in ΔG. We further start with the idea that the reorganization energy (λ) will be similar, so we treat it as the same for both dyes. We test the sensitivity to different λ below.

Under these conditions, the ration of the rate constants will be equation S1.

$$k_1/k_2 = \exp(-(\lambda + \Delta G_1)^2 / 4\lambda k_b T) / \exp(-(\lambda + \Delta G_2)^2 / 4\lambda k_b T) \quad (S1)$$

where subscript 1 refers to D149. By the following steps we arrive at equation S2.

$$k_1/k_2 = \exp\left(\frac{-(\lambda+\Delta G_1)^2}{4\lambda k_b T} + \frac{(\lambda+\Delta G_2)^2}{4\lambda k_b T}\right)$$

$$\ln(k_1/k_2) = \left(\frac{-(\lambda+\Delta G_1)^2}{4\lambda k_b T} + \frac{(\lambda+\Delta G_2)^2}{4\lambda k_b T}\right) = \frac{(\lambda+\Delta G_2)^2 - (\lambda+\Delta G_1)^2}{4\lambda k_b T}$$

$$\ln(k_1/k_2) = \frac{(\lambda^2 + 2\lambda\Delta G_2 + \Delta G_2^2) - (\lambda^2 + 2\lambda\Delta G_1 + \Delta G_1^2)}{4\lambda k_b T}$$

$$\ln(k_1/k_2) = \frac{(+2\lambda\Delta G_2 + \Delta G_2^2 - 2\lambda\Delta G_1 - \Delta G_1^2)}{4\lambda k_b T} \quad (S2)$$

We now apply $\Delta G_1 = \Delta G_2 + D$. From the electrochemical data we will set $D = -0.3$ eV. But some manipulation, we solve for ΔG_2 in terms of the "knowns" k_1/k_2 and D , and the unknown λ arriving at equation S3:

$$\ln(k_1/k_2) = \frac{(+2\lambda\Delta G_2 + \Delta G_2^2 - 2\lambda(\Delta G_2 + D) - (\Delta G_2 + D)^2)}{4\lambda k_b T}$$

$$\ln(k_1/k_2) = \frac{((+2\lambda\Delta G_2 + \Delta G_2^2 - 2\lambda\Delta G_2 - 2\lambda D - \Delta G_2^2 - 2\Delta G_2 D - D^2))}{4\lambda k_b T}$$

$$\ln(k_1/k_2) = \frac{((- 2\lambda D - 2\Delta G_2 D - D^2))}{4\lambda k_b T}$$

$$-2D\Delta G_2 = 4\lambda k_b T * \ln(k_1/k_2) + 2\lambda D + D^2$$

$$-\Delta G_2 = 4\lambda k_b T * \ln(k_1/k_2)/2D + \lambda + 0.5*D$$

$$\Delta G_2 = (4k_b T * \ln(k_1/k_2)/2D - 1) * \lambda - 0.5*D \quad (S3)$$

now inserting $D = -0.3$, and $k_1/k_2 = 20$, and $k_b T = 0.1$ (in eV) gives equation S4.

$$\Delta G_2 = (0.1 * 3 / (-0.6) - 1) * \lambda - 0.5 * -0.3$$

$$\Delta G_2 = -0.5 \lambda + 0.15 \quad (S4)$$

Using a reasonable range for λ , 0.3 to 0.7 eV, we find ΔG_2 runs from 0 to -0.2 eV. Recall ΔG_2 is the free energy of the electron transfer step. We find thus that ΔG_2 is much smaller than the ΔG for the complete reaction, which is ~0.43 eV. This agrees with the conclusion of others that the more positive redox potential of $I_2^{\bullet-}/I^-$ controls the forward rate constant of regeneration, and thus the ΔG of the electron transfer step depend on the E_{ox} of the dye and the E_{ox} of $I_2^{\bullet-}/I^-$.

To test the sensitivity of equation 4 to possible differences in reorganization energy between the dyes, we solve the equation of k_1/k_2 again using $\lambda_{VG5} = 0.5$ and letting λ_{D149} range from 0.3 to 0.7. We arrive at equation S5.

$$k_1/k_2 = (1 + \delta/\lambda)^{0.5} * \exp\left\{\frac{((0.5+\delta+\Delta G_2-0.3)^2)/(0.1*(0.5+\delta)) - ((0.5+\Delta G_2)^2/0.1*0.5)}{4\lambda k_b T}\right\} \quad (S5)$$

where δ is the difference in λ between D149 and VG5, and we have already inserted $D = -0.3$, $k_b T = 0.1$, and $\lambda_{VG5} = 0.5$. The first term in equation 5 comes from the $(4\pi\lambda k_b T)^{-0.5}$ term in the Marcus rate equation. The results are shown in figure S1. The contour plot shows that a $\lambda_{VG5} = 0.5$ and a $k_1/k_2 = 20$ predicts ΔG_2 near -0.1 over a wide range of λ_{D149} . Thus equation S4 is not very sensitive to the differences in reorganization energy.

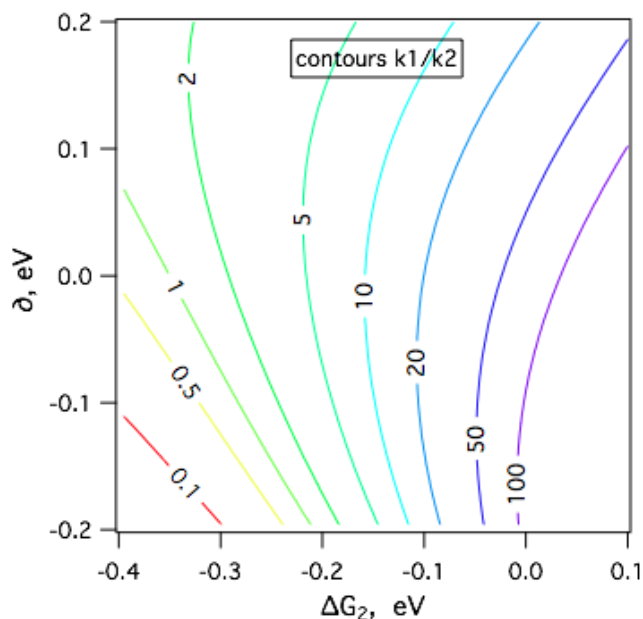


Figure S1. Contour plot of k_1/k_2 dependence on ΔG_2 and δ , where δ is the difference in λ between VG5 and D149 and the $\lambda_{VG5} = 0.5$.

We also tested the sensitivity of equation S4 to errors in the measured difference in the redox potential of the two dyes. We let the difference between D149 to VG5 range from -0.2 to -0.4 eV. The results are plotted in figure S2. Here again, $k_1/k_2 = 20$ predicts ΔG_2 near -0.1.

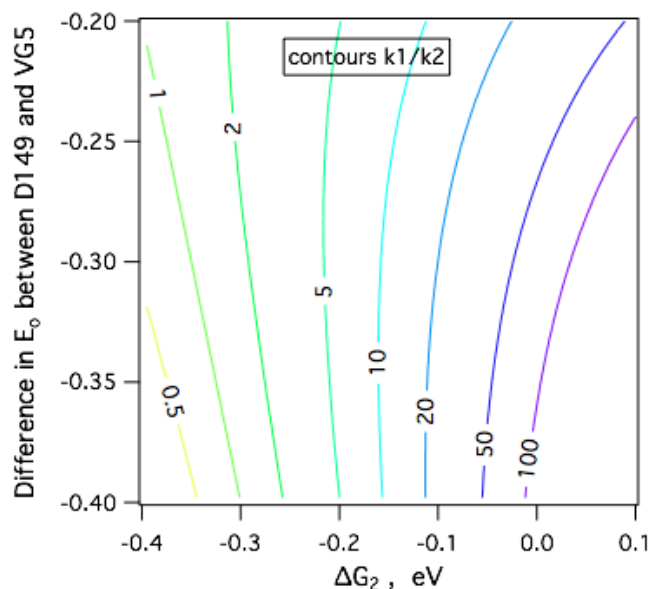


Figure S2. Contour plot of k_1/k_2 dependence on ΔG_2 and D , the difference in redox potential between D149 and VG5. Reorganization energy is set to 0.5 eV for both dyes.

In summary once k_1/k_2 is measured, the main factor determining ΔG_2 is the reorganization energy of the two dyes. Via equation S4, Reasonable values for the reorganization given quite small values for ΔG_2 as pointed out in the text. Evidence for small reorganization values (<0.7 eV) can be taken from the small stokes shifts of these dyes.

References

1. B. C. O'Regan, J. R. Durrant, P. M. Sommeling and N. J. Bakker, *The Journal of Physical Chemistry C*, 2007, **111**, 14001-14010.
2. A. Y. Anderson, P. R. F. Barnes, J. R. Durrant and B. C. O'Regan, *The Journal of Physical Chemistry C*, 2011, **115**, 2439-2447.