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

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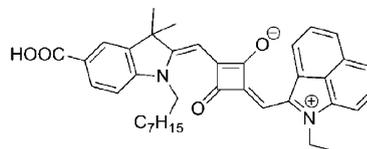
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**The order of regeneration for DSCs based on two organic dyes has been investigated by transient absorption spectroscopy on devices under operating conditions and determined to be 2nd order in iodide. The results shed light on the mechanism and limits to the regeneration rate relative to oxidation potential.**

Since 1991, when the first high efficiency dye sensitized solar cell (DSC) was reported,<sup>1</sup> significant advances have been made in the understanding of the processes underlying the functioning of these devices. Still much effort is required to obtain a mechanistically detailed picture useful for further optimization of efficiency. One direction in which researchers have moved is the synthesis of new sensitizers with an enhanced absorption in the NIR to better match the solar emission spectrum. However, knowledge of the kinetics of DSCs based on organic sensitizers is yet limited compared to the well established organometallics based DSCs. In this paper we address this issue by providing new mechanistic insight into the regeneration of two organic dyes, D149 and VG5, by iodide. We determine the reaction order, in iodide, of the regeneration for these two dyes by transient absorption spectroscopy, analogous to the previous work by Anderson *et al.*<sup>2</sup> The order of the reaction is important in determining the reaction mechanism and also in numerical modelling.

When a photon is absorbed by a dye molecule (S) in its ground state, anchored to a TiO<sub>2</sub> anatase nanoparticle, an electron is first promoted to an excited state and then injected into the conduction band of the semiconductor. The thus oxidised dye (S<sup>+</sup>) needs to be regenerated by an iodide ion. Dye structure/regeneration relationships have not been widely reported. For example, not enough data are available to clearly establish the relationship between dyes redox potentials and regeneration.

Work published by Anderson *et al.*<sup>2</sup> provides a robust method to quantify the order of the regeneration reaction and the rate constants for a DSC under operational conditions. Here we used the same method. Two series of cells were used, based, respectively, on the dyes D149 and VG5, with varying



**Fig. 1** Structure of the near-IR asymmetric squaraine dye VG5.

concentrations of iodide. The former dye is a well established organic sensitizer which has shown 9% efficiency, one of the highest energy efficiencies for organic dye based DSCs.<sup>3</sup>

The latter is a newly sensitized near-IR asymmetric squaraine dye (Fig. 1) which has shown a limited efficiency (1.1%), but its strong absorption at 780 nm makes it a useful system for studies on NIR dyes.<sup>4</sup> All electrolytes were prepared in MPN. Electrolytes for the VG5 series began with 1 M LiI and 10 mM I<sub>2</sub>. Varying I<sup>-</sup> concentrations, as listed in Fig. 3a, were provided by substituting LiClO<sub>4</sub> for LiI. The electrolyte composition for D149 series began with 0.6 M 1-methyl-3-propylimidazolium iodide (PMII), 0.1 M LiI, 50 mM I<sub>2</sub> and 50 mM TBP. Varying I<sup>-</sup> concentrations, as listed in Fig. 3b, were provided by substituting PMITFSI and LiClO<sub>4</sub> for the iodide salts. A plot of the variation of photocurrent with varying iodide can be seen in Fig. 2. Details regarding the preparation of the devices can be found in the ESI.†

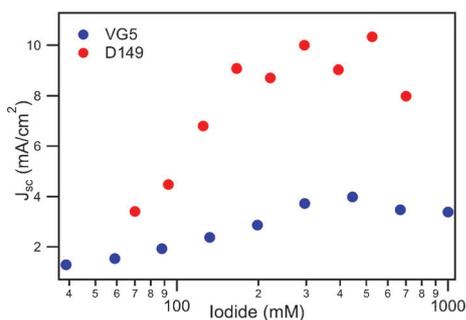
As can be observed, the short circuit photocurrent decreases with decreasing iodide concentration below about 300–400 mM iodide. The plateau at high iodide concentration indicates regeneration redundancy; beyond this concentration the increase in the regeneration rate does not cause an increase in the photocurrent. For the VG5 series the drop in photocurrent above 650 mM can be attributed to the low iodine concentration, cells of higher iodine concentration do not show this feature.

The experimental set-up for measuring the regeneration rate constant is similar to the one used by Anderson *et al.*<sup>2</sup> For a detailed description see the ESI.† The transient absorption experiment was conducted on fully working devices, at short circuit, under 1 sun bias light. The excitation wavelengths chosen for VG5 and D149 were, respectively, 780 nm and 530 nm, corresponding to the maxima of the absorption spectra of the two dyes. Photo-oxidized dyes (“dye cations”) were probed at 650 nm and 990 nm for VG5 and D149 respectively. The laser energy was adjusted to provide less than 1 electron per particle from each pump pulse. Steady state photocurrent

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**Fig. 2** Short circuit photocurrent vs. iodide concentration. Logarithmic scale is used to highlight the differences at low iodide concentrations.

from each cell was measured during the experiments; measurements were performed at  $\sim 29^\circ\text{C}$ .

The decay of the dye cation absorption is shown in Fig. 3. Double exponential decays were fit to the data as explained by Anderson *et al.*<sup>2</sup> Briefly, the absorption contains both dye cations and electrons in varying proportions. From previous assignment we know that the slower decay is that of the electrons.<sup>5</sup> We fit a double exponential to the decay to separate the electron signal from the earlier decay of the dye cation. In the VG5 data the second decay is hardly visible due to the low contribution from electrons at 650 nm. The decay parameters obtained from the transient absorption, and the measured photocurrents, allow us to calculate the rate of regeneration according to the following equation<sup>5</sup>

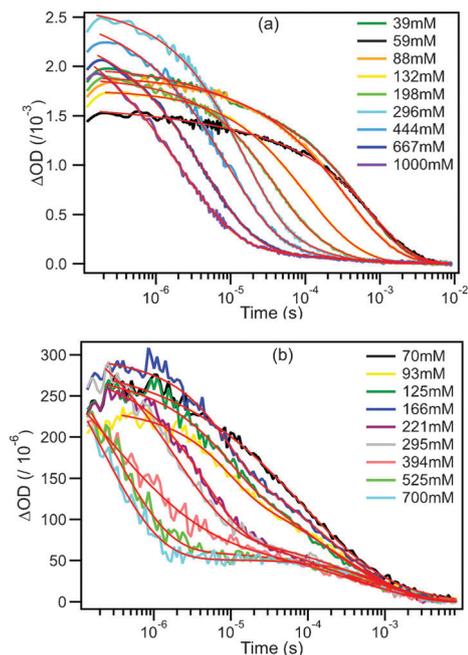
$$\nu_{\text{rg}} = K_{\text{rg}}[I]_{\text{free}}^\gamma = \frac{J_{\text{sc}}K_{\text{obs}}}{J_{\text{max}}} \quad (1)$$

where  $\nu_{\text{rg}}$  is the regeneration rate,  $k_{\text{rg}}$  the regeneration constant,  $\gamma$  the order of regeneration in iodide,  $J_{\text{sc}}$  the short-circuit photocurrent,  $k_{\text{obs}}$  the observed rate constant (inverse of  $\tau_{\text{obs}}$ ) and  $J_{\text{max}}$  the theoretical maximum current for the cell. A plot of the regeneration rate vs. free iodide (Fig. 4) is used to determine  $k_{\text{rg}}$  and the order.  $J_{\text{max}}$  for each dye was estimated from the maximum  $J_{\text{sc}}$  from the series. However, as  $J_{\text{max}}$  is the same for each iodide concentration, it does not affect the determination of the order of regeneration. The values obtained from the best fit of the data shown in Fig. 4, including the error estimates shown, are:

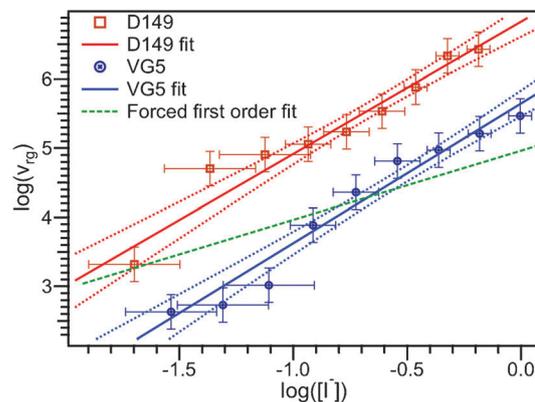
$$\begin{aligned} \gamma_{\text{VG5}} &= 2.02 \pm 0.24 \\ \gamma_{\text{D149}} &= 1.91 \pm 0.28 \end{aligned}$$

where the confidence intervals are one standard deviation. The main source of error in these values is the actual concentration of free iodide in the pores, especially for low iodide concentrations. This uncertainty accounts for some deviations from an ideal second order at low iodide concentrations. To account for this we have included up to  $\pm 40\%$  error in  $[I^-]$ . Although the errors in the fits of the transient data (Fig. 3) were very small, we have included  $\pm 50\%$  error in the  $\nu_{\text{rg}}$  to account for possible effects of differing dye loading and light intensity on  $J_{\text{max}}$  and  $J_{\text{sc}}$ . Even given these very generous error estimates the fits return almost exactly second order behaviour for both dyes. In fact, the first order behaviour for both dyes can be rejected at the 98% confidence level.

Previous work has found regeneration to be first order in iodide for ruthenium and osmium based dyes.<sup>2,6,7</sup> From the



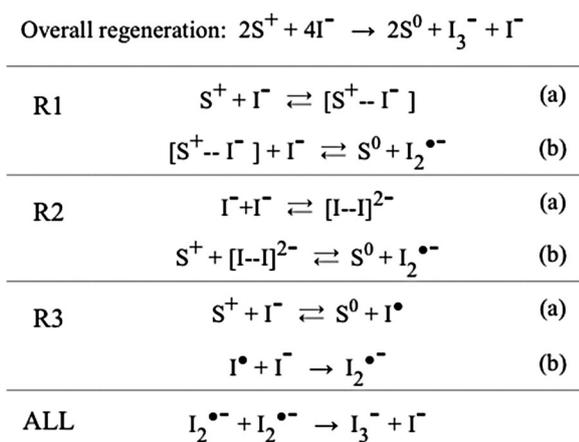
**Fig. 3** (a) Transient absorption decays for VG5 containing cells. Pump 780 nm, probe 650 nm. (b) Transient absorption decays for D149 containing cells. Pump 530 nm, probe 990 nm. Fits in both panels are double stretched exponentials.



**Fig. 4** Rate of regeneration vs. free iodide concentration. Linear fits performed using both X and Y error bars shown. Dotted lines are confidence bands at one  $\sigma$ . Dashed line is a fit through VG5 forced to be first order in iodide.

above results we hypothesize that for most organic dyes, the reaction order in iodide will be two. The possible reaction schemes for regeneration lend credence to this proposal (Scheme 1). The first order behaviour requires either mechanism R1 or R3. Meyer *et al.* have shown that only very strongly oxidizing dyes can use R3.<sup>8</sup> Clifford *et al.*<sup>9</sup> provided evidence for the formation of a  $[S-I]$  complex (R1a) in some Ru-bipyridine dyes. For the R1 mechanism to be first order in iodide, the complex formation in R1a has to be effectively irreversible. This can be understood in terms of the localized Ru-centered HOMO in Ru dyes.

The second order process observed here leaves two possibilities for the regeneration mechanism. R1 can give second order if R1a forms an equilibrium such that the concentration of  $(S^+ - I^-)$  is a



Scheme 1

linear function of  $[I^-]$ . A weaker  $I^-$  binding to the oxidized dye is certainly compatible with the more delocalized positive charge on the organic dyes used here. R2 appears to be implicitly second order, though we assume  $[I \cdots I]^{2-}$  formation, if any, would be related to the surface of the  $TiO_2$ , which could perturb the order. In fact both pathways require the formation of an iodide dimer. The difference lies in whether the dimer assembles only in the presence of  $S^+$ , in a two step process, or it assembles independent of  $S^+$  in a one step process.

Dyes used in DSCs typically have large driving forces for regeneration. Typical oxidation potentials are near 1 V vs. NHE which is 0.7 V more oxidizing than the redox potential of the electrolyte. This driving force is thought to be needed due to the slow kinetics of iodide oxidation. For example, regeneration by the one electron couple  $Co(II)/Co(III)$  has been found to be more than an order of magnitude faster.<sup>10</sup> The slow kinetics of iodide oxidation have been hypothesized to stem from the high energy of the  $I_2^{\bullet-}$  intermediate.<sup>11</sup>

The regeneration rates measured above can shed some light on this question. The oxidation potential of D149 is 1.04 V vs. NHE<sup>12</sup> whereas that of VG5 is 0.73 V.<sup>4</sup> This means that the difference in  $\Delta G$  for the overall regeneration reaction is 0.3 V. We find that the regeneration rate of D149 is  $\sim 20$  times faster than that of VG5. With the measured difference in  $\Delta G$ , the ratio of the rates, and some assumptions, we can estimate the absolute  $\Delta G$  of the electron transfer step (R1b or R2b). We assume that the electron transfer reorganization energy,  $\lambda$ , and electronic coupling for the two dyes are similar. With this information we can solve the Marcus equation for the relation between  $\lambda$  and the electron transfer  $\Delta G$  for one of the dyes. The result is the linear relationship  $\Delta G_{VG5} = 0.15 - 0.5\lambda$  (derivation in ESI†).

Choosing a range of  $\lambda$  between 0.3 and 0.8 eV, we find  $\Delta G_{VG5}$  to be between 0 and  $-0.25$  eV. Recall this is the  $\Delta G$  for the electron transfer step, not for the complete reaction. These values are clearly much lower in magnitude than the total  $\Delta G$  of  $-0.43$  eV for VG5. (The electrolyte potential is 0.3 V vs. NHE.) In this case we can estimate that these low driving forces for the electron transfer step are consistent with a reaction limited by the high energy of the  $I_2^{\bullet-}$  intermediate.<sup>11</sup> The results suggest that the potential of  $I^-/I_2^{\bullet-}$  is in the range

of 0.7–0.5 V vs. NHE in our electrolyte, consistent with previous estimates.<sup>11</sup>

If these results prove to be general, they have the following implication: the rate constant of R1b/R2b can only be increased by increasing the oxidation potential of the dye, which leads to an unwanted blue shift in the absorption, or by decreasing the potential of  $I_2^{\bullet-}$  in the electrolyte. This latter strategy will require either a solvent that stabilizes  $I_2^{\bullet-}$  more effectively than the current ones, perhaps water, or specific molecules in the solvent which act as shuttles, carrying the  $I_2^{\bullet-}$  until it disproportionates. We believe that this latter possibility has never been considered previously, but it may be the function of some of the empirically discovered additives that improve efficiency for some dyes.

Of course, the other approach to increase the rate of R1b/R2b is to increase the concentration of the reactants, either  $[I \cdots I]^{2-}$  or  $[S^+ \cdots I^-]$ . Most likely this has already been pursued empirically in choosing those dyes with high regeneration efficiencies. The lack of such binding in R1a might explain the failure of some promising dyes to perform.

These issues may be critical for the further improvement of DSCs. The decrease in the regeneration rate for VG5 did not limit the photocurrent because the regeneration rate was still sufficiently fast, relative to recombination, at easily accessible iodide concentrations. However, the VG5 LUMO potential is too low to produce efficient injection in high band edge, high voltage electrolytes. Raising the LUMO level without losing red absorption will also raise the HOMO, and must decrease the driving force for regeneration. One of the two strategies for increasing the regeneration rate mentioned above will probably be required with NIR dyes and iodine electrolytes.

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## Notes and references

- B. O'Regan and M. Grätzel, *Nature*, 1991, **353**, 737–740.
- A. Y. Anderson, P. R. F. Barnes, J. R. Durrant and B. C. O'Regan, *J. Phys. Chem. C*, 2011, **115**, 2439–2447.
- S. Ito, S. M. Zakeeruddin, R. Humphry-Baker, P. Liska, R. Charvet, P. Comte, M. K. Nazeeruddin, P. Péchy, M. Takata, H. Miura, S. Uchida and M. Grätzel, *Adv. Mater.*, 2006, **18**, 1202–1205.
- C. Barolo, S. Martiniani, *et al.*, in preparation.
- A. Y. Anderson, P. R. F. Barnes, J. R. Durrant and B. C. O'Regan, *J. Phys. Chem. C*, 2010, **114**, 1953–1958.
- M. Alebbi, C. A. Bignozzi, T. A. Heimer, G. M. Hasselmann and G. J. Meyer, *J. Phys. Chem. B*, 1998, **102**, 7577–7581.
- I. Montanari, J. Nelson and J. R. Durrant, *J. Phys. Chem. B*, 2002, **106**, 12203–12210.
- J. M. Gardner, J. M. Giaimuccio and G. J. Meyer, *J. Am. Chem. Soc.*, 2008, **130**, 17252–17253.
- J. N. Clifford, E. Palomares, M. K. Nazeeruddin, M. Grätzel and J. R. Durrant, *J. Phys. Chem. C*, 2007, **111**, 6561–6567.
- D. Zhou, Q. Yu, N. Cai, Y. Bai, Y. Wang and P. Wang, *Energy Environ. Sci.*, 2011, **4**, 2030–2034.
- G. Boschloo and A. Hagfeldt, *Acc. Chem. Res.*, 2009, **42**, 1819–1826.
- R. Jose, A. Kumar, V. Thavasi and S. Ramakrishna, *Nanotechnology*, 2008, **19**, 424004.