Catalysis of Recombination and Its Limitation on Open Circuit Voltage for Dye Sensitized Photovoltaic Cells Using Phthalocyanine Dyes

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Decreasing the cost of electricity from sunlight is one of the great challenges of the 21st century. Dye sensitized (DS) solar cells are one of the promising technologies, due in part to the inexpensive materials and processes used in fabrication. The present state-of-the-art DS cells achieve 10% energy efficiency using one of a small group of ruthenium bipyridyl (RuBpy) dyes. The efficiency of DS cells could be improved significantly if dyes with greater red and near-infrared absorption could be used. Many hundreds of dyes have been tested for this purpose, including both metal complex and all organic dyes. Despite this large effort, none of these dyes have surpassed the best RuBpy dyes (e.g., N719) introduced more than a decade ago. It is apparent that there is large need for improved “design rules” to help guide dye synthesis. This paper examines a heretofore little discussed problem with many, if not most, organic dyes that have shown promise in DS cells. We find, by measurement of a series of phthalocyanine dyes and by examination of the literature, that most organic dyes tested have shown significantly lower output voltages than equivalent cells made using N719 or its analogues. For the ruthenium phthalocyanines (RuPc) examined in this paper, we demonstrate that the voltage reduction occurs because the RuPc dyes are catalyzing the electron/electrolyte recombination reaction at both the TiO2 and SnO2 surfaces. We propose that this problem holds in varying degree for most other organic dyes. If so, then it is imperative to determine the molecular basis of this catalysis in order to develop design rules to avoid it.

Phthalocyanines are often suggested as a substitute for, or in addition to, the established RuBpy dyes. Phthalocyanines show large and tunable absorption in the red and near-infrared and good thermal and chemical stability. Ten years ago it was already shown that RuPc1 (bis(3,4-dicarboxyphyrinato)-1,4,8,11,15,18,22,25-octamethylphthalocyaninato)ruthenium(II)) could sensitize TiO2 with reasonable quantum efficiency. However, the resulting open circuit voltage was significantly lower than that found for the standard ruthenium polypyridyl dyes (e.g., N719). Since 1999, phthalocyanine based DS cells have been investigated by several laboratories, always with decreased Voc’s relative to ruthenium polypyridyl analogues. To further the study of RuPcs, we have retested RuPc1, along with several others including (4-carboxyphyrinato)(4-methoxyphyrinato)-2,9(10),16(17),23(24)(tetra-tert-butylphthalocyaninato)ruthenium(II) (RuPc2) and (4-carboxyphyrinato)(4-4′-(N,N-diphenylamino)-1′-phenyl) pyridinato)-2,9(10),16(17),23(24)(tetra-tert-butylphthalo-cyaninato)ruthenium(II) RuPc3 (Structures in Figure 1 and Supporting Information).

Figure 1 compares typical IVs for RuPcs compared to N719 in an identical cell. TiO2 films (4 µm) synthesized as previously described, including TiCl4 treatment. N719 was absorbed from 1 mM solution in acetonitrile/tert-butyl alcohol. RuPcs were absorbed from 0.02 mM solution in CH3Cl2 with 40 mM chenodeoxycholic acid (RuPc1) or 0.05 mM chenodeoxycholic acid (RuPc3). Electrolyte: propylene carbonate, 0.5 M LiI, 20 mM iodine. Inset: RuPc3 structure and energy levels.

Similar to nearly all low voltages are due to the LiI electrolyte used; this electrolyte is required to achieve high quantum efficiency with these RuPc dyes. An identical Voc decrease occurs in a standard electrolyte (iodolyte R150 purchased from Solaronix) where RuPc1 gives 566 mV compared to 750 mV for N719; however, the photocurrent for the RuPc1 is only 0.9 mA in this electrolyte.

In DS cells, a decrease in the voltage can come about because of a decrease in the band offset (TiO2 conduction band relative to iodine/iodide potential) or because of an increased recombination rate constant. A shift in the band edge can be detected by a shift in the cell capacitance (or charge density) as a function of voltage. Figure 2 shows the capacitance vs voltage for RuPc1 and N719 cells with identical TiO2 and electrolyte. The data for the RuPc cell lie along the same curve as that from the N719 cell, so we can be confident no shift in the conduction band edge has occurred. Data for other RuPcs were similar.

In the absence of a decrease in the band offset, the loss of voltage must be caused by an increase in recombination. Pseudo-first-order recombination rate constants (kRecomb) were determined from small perturbation photovoltage transient decay (Figure 2, inset). Figure 3 shows kRecomb as a function of voltage for N719 and three RuPcs. The data shows that, at any given voltage, kRecomb in the RuPc cell is ~100 times faster than in N719 cells. Because kRecomb in DS cells is a function of the charge density, they can only be usefully compared at constant charge density. Here this condition is satisfied at when the voltage is the same in both cells (Figure 2).
The recombination rate constants shown in Figure 3 include recombination from the TiO₂ surface and also from the underlying SnO₂ electrode. In cells with N719, it has been found that the recombination from the SnO₂ to the iodine/iodide electrolyte is slow and can be ignored under normal conditions. However, by comparing the forward bias current of bare SnO₂ films in electrolytes containing dissolved N719 or RuPc dyes, we find that RuPc dyes can also catalyze the recombination reaction at SnO₂ (Figure S1 in Supporting Information). Although the current through the SnO₂ is not the major effect for our dye/electrolyte combination, the degree of this catalysis is highly variable and should probably be examined for all new candidate dyes.

The combined effect of the acceleration of the recombination on the TiO₂ and SnO₂ is to lower the Vₘₚₖ dramatically. The overall recombination reaction in these cells is the two electron reduction of iodine to iodide. Because of the high-energy intermediates (I⁻ or I₂⁻), this reaction is normally slow on both the TiO₂ and SnO₂. The acceleration of the recombination by RuPcs could have several causes. Iodine is known to form a complex with phthalocyanine.⁹ Even a weak complex between RuPc and iodine can cause a large increase in the local concentration of I₂ near the TiO₂ surface because almost all iodine in the cell is complexed as triiodide (I₃⁻). Triiodide is thought not to be active in the recombination reaction. It has also been shown that I⁻ can complex with some porphyrins, resulting in static quenching by reduction of the I⁻ to I₂⁻ (see Supporting Information). The RuPcs might show a greater tendency to bind I₃⁻ than N719 because the aromatic surface is more accessible for the Pc ring and more sterically hindered for the N719 bipyridines. It has also been suggested that decreasing the distance between the site of iodide oxidation and the TiO₂ surface can speed up recombination.¹⁰ In N719, iodide oxidation is thought to take place on the thiocyanate side of the molecule, away from the TiO₂ binding site. The dyes RuPc1 and RuPc2 clearly do not share this asymmetry, and calculations show that the HOMO of RuPc3 does not extend onto the triphenylamine.

If the problem with RuPcs is inherent in the structure, then it might be shared by other dyes. A survey of the literature concerning organic dyes in DS cells shows that nearly all of these dyes show lower Vₘₚₖ’s relative to N719. Because few publications include a direct comparison to N719, using an identical electrolyte, we have had to extrapolate from our experience to make these comparisons. Not withstanding this disadvantage, we have found cases of lowered Vₘₚₖ for almost all classes of organic dyes used in DS cells, including porphyrins,¹¹ coumarins,¹² perylenes,¹³ cyaines,¹⁴ merocyanines,¹⁵ and azulene¹⁶ (Table S1 in Supporting Information). In addition, Bignozzi et al. have published a similar list of metal centered dyes with lower Vₘₚₖ’s.¹⁷ It is critical for DS cells that the barrier to the use of more red absorbing dyes be understood and surmounted. We plan further experiments with a wider range of dye classes in order to quantify the variation of recombination rate constants with dye molecular structure.

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Supporting Information Available: Chemical structures of RuPc dyes and N719, synthetic procedures and NMR of RuPc1 and RuPc3, dark current IVs for SnO₂ films in electrolytes with and without dyes, table of Vₘₚₖ’s for a range of dyes, and discussion of reductive quenching vs recombination. This material is available free of charge via the Internet at http://pubs.acs.org.

References