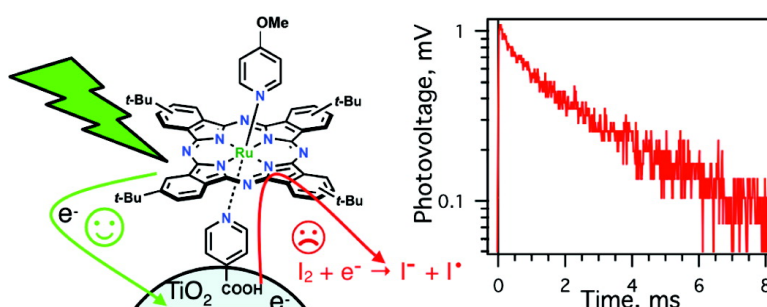Communication

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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.[1] 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[2] 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 TiO_2 and SnO_2 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-dicarboxypyridine)(1,4,8,11,15,18,22,25-octamethyl-phthalocyaninato)ruthenium(II)) could sensitize TiO_2 with reasonable quantum efficiency.[3] 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 V_{oc}'s relative to ruthenium polypyridyl analogues.[4] To further the study of RuPcs, we have retested **RuPc1**, along with several others including (4-carboxypyridine)-(4-methoxypyridine)-2,9(10),16(17),23(24)-(tetra-*tert*-butylphthalocyaninato)ruthenium(II) (**RuPc2**) and (4-carboxypyridine)-[4-(4′-(N,N-diphenylamino)-1′-phenyl) pyridine]-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 and N719 in otherwise identical DS cells. The RuPc dyes give V_{oc}'s that are 120−200 mV lower that for N719. Results for several other RuPc dyes were
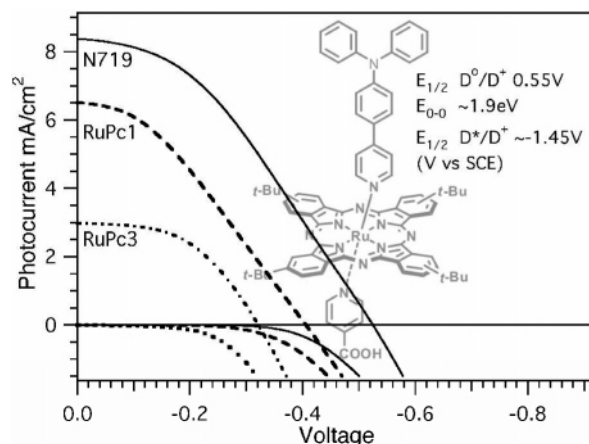

Figure 1. Typical dark and "1 sun" IVs for RuPcs compared to N719 in an identical cell. TiO_2 films (4 μm) synthesized as previously described, including $TiCl_4$ treatment.[6] N719 was absorbed from 1 mM solution in acetonitrile/*tert*-butyl alcohol. RuPcs were absorbed from 0.02 mM solution in CH_2Cl_2 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. The overall low voltages are due to the LiI electrolyte used; this electrolyte is required to achieve high quantum efficiency with these RuPc dyes.[5] An identical V_{oc} 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 (TiO_2 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.[7] Figure 2 shows the capacitance vs voltage for **RuPc1** and N719 cells with identical TiO_2 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 (k_{pfo}) were determined from small perturbation photovoltage transient decays (Figure 2, inset).[8] Figure 3 shows k_{pfo} as a function of voltage for N719 and three RuPcs. The data shows that, at any given voltage, k_{pfo} in the RuPc cell is ~100 times faster than in N719 cells. Because k_{pfo} 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).

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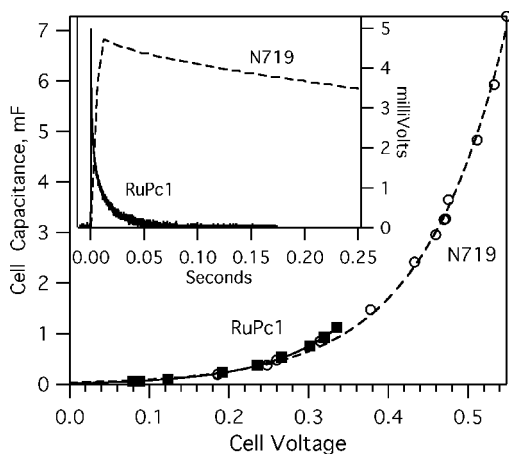§ Institute of Chemical Research of Catalonia and Catalan Institution for Research and Advanced Studies (ICREA).

Figure 2. Cell capacitance as a function of V_{oc} for cells with **RuPc1** or N719. Cell construction as in Figure 1. Capacitance determined from photovoltage transient peaks.[7] Inset: typical photovoltage transients taken at $V_{oc} = 300$ mV for both cells.
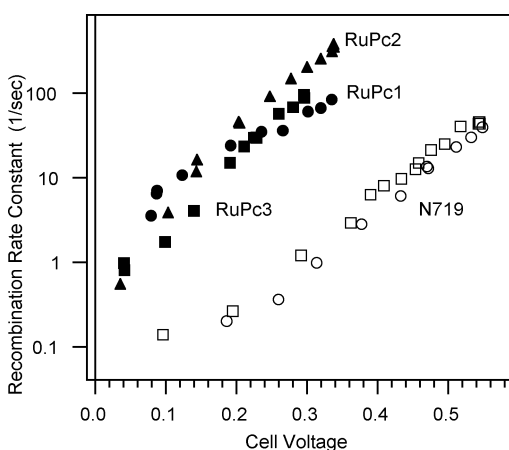

Figure 3. Recombination rate constants (k_{pfo}) as a function of V_{oc} for dye sensitized cells with N719 and RuPcs. V_{oc} controlled by varying bias light intensity. Cell construction as in Figure 1.

The recombination rate constants shown in Figure 3 include recombination from the TiO_2 surface and also from the underlying SnO_2 electrode. In cells with N719, it has been found that the recombination from the SnO_2 to the iodine/iodide electrolyte is slow and can be ignored under normal conditions. However, by comparing the forward bias current of bare SnO_2 films in electrolytes containing dissolved N719 or RuPc dyes, we find that RuPc dyes can also catalyze the recombination reaction at SnO_2 (Figure SI1 in Supporting Information). Although the current through the SnO_2 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 recombination on the TiO_2 and SnO_2 is to lower the V_{oc} 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 $I_2^{•−}$), this reaction is normally slow on both the TiO_2 and SnO_2. The acceleration of the recombination by RuPcs could have several causes. Iodine is known to form a complex with phthalocyanine.[9a] Even a weak complex between RuPc and iodine can cause a large increase in the local concentration of I_2 near the TiO_2 surface because almost all iodine in the cell is complexed as triiodide ($I_3^−$). Triiodide is thought not to be active in the recombination reaction. It has also been shown that $I_3^−$ can complex with some porphyrins, resulting in static quenching by reduction of the $I_3^{−}$[9b] (see Supporting Information). The RuPcs might show a greater tendency

to bind I_2 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 TiO_2 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 TiO_2 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 V_{oc}'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 V_{oc} for almost all classes of organic dyes used in DS cells, including porphyrins,[11a] coumarins,[11b] perylenes,[11c] cyanines,[11d] merocyanines,[11e] and azulene[11f] (Table S1 in Supporting Information). In addition, Bignozzi et al. have published a similar list of metal centered dyes with lower V_{oc}'s.[11g]

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.

Supporting Information Available: Chemical structures of RuPc dyes and N719, synthetic procedures and NMR of **RuPc2** and **RuPc3**, dark current IVs for SnO_2 films in electrolytes with and without dyes, table of V_{oc}'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.

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