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Efficient Non-corrosive Electron-Transfer Mediator Mixtures for Dye-Sensitized Solar Cells

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Dye-sensitized solar sells (DSSC) are considered to be a viable alternative to amorphous silicon solar devices due to comparable efficiency, transparency, and low cost.[1] In these cells, the primary event is electron injection from a photoexcited dye adsorbed on the surface of a wide band-gap semiconductor (TiO_2, SnO_2, NiO) into the semiconductor's conduction band. The resulting oxidized dye is reduced by a redox couple mediating the transport of holes from the photoanode to the "dark" cathode. Until now, the best efficiencies have been obtained with polypyridine Ru(II) dyes used in conjunction with I^-/I_3^- as mediator.[2,3] As a mediator, I^-/I_3^- has ideal kinetic properties; specifically, the regeneration of the dye by I^- is very fast and the recombination of I_3^- with photoinjected electrons in the TiO_2 is extremely slow.[4] The main drawback of the I^-/I_3^- system is its corrosivity toward most high conductivity metals. This feature limits the durability in the DSSC of metallic fingers necessary to overcome the large ohmic losses in the conductive glass contact of cells exceeding a few square centimeters[5] in areas. Thus finding an efficient non-corrosive electron-transfer mediator is an important step toward the practical application of DSSCs.

Kinetically fast couples, such as ferrocene/ferrocenium, efficiently reduce the oxidized dye, but due to the fast recombination of injected electrons with Fe(III), such systems are totally unsuccessful as mediators in DSSCs.[4] Recently, certain polypyridine Co(II) complexes have been shown to be moderately efficient mediators in solar cells;[6,7] however, compared to I^-/I_3^-, they exhibit slower dye reduction and faster recombination with photoinjected electrons.[8] In this communication, we wish to report the photoelectrochemical characterization of mediator mixtures in which a co-mediator, characterized by a fast electron transfer reaction, is used in conjunction with the previously studied $Co(DTB)_3^{2+}$ complex[7] (DTB = 4,4′-di-*tert*-butyl-2,2′-bipyridine).

Phenothiazine (PTZ) and ferrocene (Fc), both of which have a small reorganizational energy associated with the electron transfer, are the first co-mediators to be considered.[9] Each has a potential which falls between 0.22 and 0.75 V vs SCE, respectively, the potential of $Co(DTB)_3^{2+/3+}$, and the approximate potential for oxidation of the dye, $[Ru(dnbpy)(H_2Dcbpy)(NCS)_2]$ (Z907).[10] Because of facile charge-transfer kinetics, it might be anticipated that the photooxidized dye would predominantly be reduced by the co-mediator. The oxidized form (Fc^+ or PTZ^+) could then be rapidly intercepted by the Co(II), preventing the direct charge recombination between the oxidized co-mediator and the electrons in the TiO_2. Since the $Co(DTB)_3^{2+}/Co(DTB)_3^{3+}$ couple is characterized by a very slow *heterogeneous* electron-transfer on semiconductor oxides,[11] the parasitic recombination between conduction band electrons and Co(III) is inefficient. Consequently, Co(III) created in the second electron-transfer step would be free to diffuse to the counter electrode. By choosing a suitable Co(II)/co-mediator ratio, it should therefore be possible to create a mediator mixture characterized by a faster dye recovery *and* a low recombination rate between the photoinjected electrons and oxidized mediator.

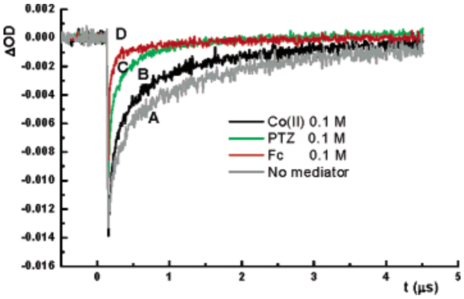

Figure 1. Decay kinetic of photooxidized Z907 adsorbed on TiO_2 in the presence of various electron mediators: (A) no mediator; (B) 0.1 M $Co(DTB)_3^{2+}$; (C) 0.1 M PTZ; (D) 0.1 M Fc. Differential absorbance changes were measured at 480 nm using a 532 nm laser excitation (1 mJ/cm^2/pulse, pulse width ≈ 10 ns).

Nanosecond transient absorption measurements (Figure 1) confirmed faster dye regeneration by both PTZ and Fc relative to $Co(DTB)_3^{2+}$, despite their higher redox potentials. In presence of 0.1 M Co(II), the lifetime of the Ru(III) was ~390 ns, whereas in the presence of the same concentration of PTZ or Fc, substantially shorter lifetimes were found (98 and 56 ns, respectively).

The best photoconversion efficiencies were determined using a co-mediator/Co(II) ratio of 1:2, employing 0.15 M $Co(DTB)_3^{2+}$ in acetonitrile. No oxidant was added to the electrolytic mixtures. Prior to recording photoaction spectra or $i-V$ curves, the oxidized forms of the electron relays were created inside the cell by irradiation for 10−15 min at short circuit until a stationary current was achieved. Under these conditions, IPCEs reached maximum values of 75% for the Fc/Co(II) and more than 80% for the PTZ/Co(II) (inset Figure 2a)—performances comparable to an equivalent I^-/I_3^- cell. The $i-V$ curves recorded using parafilm-sealed cells (Supporting Information S1) (Figure 2a) showed a consistent increase in the photovoltaic output of the PTZ/Co(II)-mediated cell with respect to an equivalent cell based on the Co(II)/(III) couple. It must be noted that both the V_{oc} (0.65 V) and the Fill Factor (0.63) of the PTZ/Co(II) cell were considerably larger than the ones obtained from the I^-/I_3^- electrolyte. The lower J_{sc} obtained in the case of the cobalt-based electrolytes was probably the result of mass transport limitations caused by the slow Co(III) diffusion. This limitation could be surmounted by building cells without the parafilm spacer in which the diffusive path was substantially

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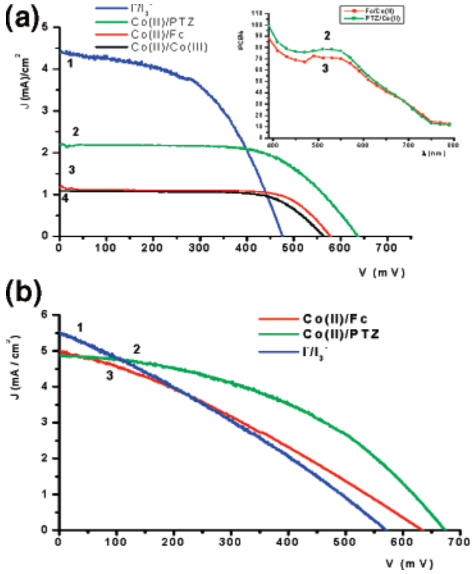

Figure 2. $i-V$ curves recorded under 0.1 W/cm^2 Xe lamp irradiation. (a) Cells sealed with parafilm spacer: (1) 0.3/0.03 M LiI/I_2 in ACN; (2) 0.15/0.075 M Co(II)/PTZ + 0.5 M Li^+ in ACN; (3) 0.15/0.075 M Co(II)/Fc + 0.5 M Li^+ in ACN; (4) 0.3/0.03 M Co(II)/Co(III) in ACN. Inset shows photoaction spectra of (2) and (3) mediated DSSC. (b) Cells without spacer: (1) 0.3/0.03 M LiI/I_2 in methoxypropionitrile (MPN); (2) 0.15/0.075 M Co(II)/PTZ + 0.5 M Li^+ in MPN; (3) 0.15/0.075 M Co(II)/Fc + 0.5 M Li^+ in MPN; 0.1 M 4-*tert*-butylpyridine was added to all electrolytic solutions. The poorer fill factors in the data for Figure 1b relative to 1a are likely due to a combination of electrical shorting between the TiO_2 layer and the cathode without the spacer and the fact that, typically, fill factors are better in acetonitrile solvent than in methoxypropionitrile.

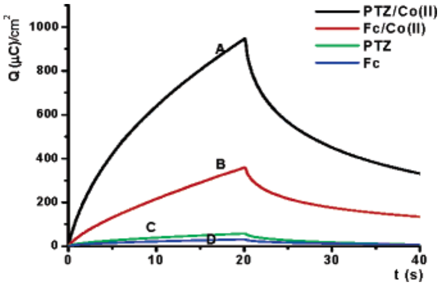

Figure 3. Chronocoulometry of 10^{-5} M co-mediator in ACN/$TBAPF_6$ 0.1 M: (A) PTZ + 10^{-3} M Co(II); (B) Fc + 10^{-3} M Co(II); (C) PTZ; (D) Fc.

reduced (Supporting Information S1). Under these conditions (Figure 2b), the PTZ/Co(II) mixture almost equalled I^-/I_3^- in J_{sc} (5 mA/cm^2) and surpassed it both in V_{oc} (0.68 V) and in Fill Factor (0.35).

It is evident from the data reported in Figure 2 that the Co(II)/Fc mixture gave poorer overall photovoltaic performances than the equivalent Co(II)/PTZ mixture. One explanation could lie in a less efficient interception of Fc^+ by Co(II) centers, resulting in a larger steady-state concentration of Fe(III) which undergoes recombination on the TiO_2.

To clarify the point, chronocoulometry (Figure 3) using FTO working electrodes was performed. Here Fc^+ or PTZ^+ is electrochemically generated at an FTO working electrode in the presence of an excess of $Co(DTB)_3^{2+}$. The oxidized co-mediator accepts an electron from the Co(II), whereupon it can be reoxidized at the FTO. Thus each co-mediator molecule exchanges multiple electrons, the number depending on the rate of electron exchange with Co(II).[11] This catalytic cycle is possible because of the electrochemical inertness of $Co(DTB)_3^{2+}$ on FTO which results in a negligible direct faradic contribution from Co(II) oxidation even at high overpotentials.

The ratio of the charge exchanged during the electrochemical oxidation of PTZ or Fc in the presence and in the absence of the same Co(II) excess allows the number of Co(II) centers intercepted by each PTZ^+ or $(Fc)^+$ cation to be determined. PTZ^+ was found to intercept 16 Co(II) centers, while under the same conditions, Fc^+ oxidized only 11 Co(II) ions. Thus Fc^+ is reduced less efficiently by Co(II), and it has a larger probability of recombining with injected electrons. Similar conclusions result from I_{cat} versus $[Co(DTB)_3^{2+}]$ studies, details of which are included in Supporting Information S2.

Analogous behavior extends to other species having small reorganization energies (Supporting Information S3) and appropriate potentials, such as the iron complex $Fe(DMB)_3^{2+}$ ($E_{1/2}{}^{2+/3+} = 0.92$ V vs SCE; DMB = 4,4′-dimethyl-2,2′-bipyridine).

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Supporting Information Available: Sensitizers and mediators preparation, cell assembly, additional photoelectrochemical, electrochemical, and spectroscopic measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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