Solvatochromic Dye-Sensitized Solar Cells

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About ten years ago, Gratzel and coworkers reported the first dye-sensitized solar cells with efficiencies comparable to solid-state solar cell.¹ Since then many dye molecules have been synthesized to achieve broad spectral sensitization and optimization of energy conversion efficiencies. In this work, we report a unique way to tune the spectral sensitization by varying the solvent. This approach provides a direct method for studying the solvation of the surface bond sensitizers and for controlling interfacial energetics.

Coordination compounds with cyano and polypyridyl ligands, such as $Ru(bpy)(CN)_4$, are known to be highly solvatochromic.^{2,3} The UV-Visible absorbance spectra and emission spectra for this molecule change dramatically in different solvents.

In this paper we demonstrate that solvatochromic solar cells can be achieved by anchoring the $[\text{Ru}(\text{dcb})(\text{CN})_4]^2$ (dcb = 4, 4'-(COOH)₂ -2,2'-bipyridine) onto nanocrystalline TiO₂ films. Distinct solvatochromism of the dye-sensitized TiO₂ surface is shown in Figure 1. The MLCT (metal-to-ligand charge transfer) absorption maximum for surface bound $[\text{Ru}(\text{dcb})(\text{CN})_4]^2$ blue-shifts ~ 60 nm in acetonitrile compared to dimethylformamide. The solvatochromic photoaction spectra based on $[\text{Ru}(\text{dcb})(\text{CN})_4]^2$ in regenerative solar cells with 0.5 M LiI/0.05M I₂ electrolytes are shown in Figure 2. The shifts of photoaction spectra peak maxima follow the absorbance spectra in the indicated solvents. The light conversion efficiencies also change in different solvents.

The electrochemical, photoelectrochemical and photophysical properties of the dye-sensitized nanocrystalline TiO_2 surface will be discussed to further understand the loss mechanisms in light conversion process. This work opens a new direction for photosensitization mechanistic studies.

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Figure 1. The absorbance spectra of $[Ru(dcb)(CN)_4]^2$ /TiO₂ in 0.5 M LiClO₄ acetonitrile (-) or dimethylformamide (---) solutions.



Figure 2. The normalized photoaction spectra of $[\text{Ru}(\text{dcb})(\text{CN})_4]^2$ /TiO₂ in 0.5 M LiI/0.05 M I₂ acetonitrile (-**-**) or dimethylformamide (-**-**) electrolytes. The insets are the unnormalized spectra in 0.5 M LiI/0.05 M I₂ acetonitrile (-**-**), dimethylformamide (-**-**) or tetrahydrofuran (-**-**) electrolytes.