Dual Pathways for TiO_2 Sensitization by $Na_2[Fe(bpy)(CN)_4]$

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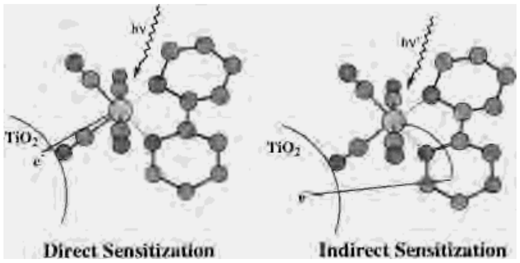
Semiconductor sensitization is an attractive approach for the conversion of light into electricity.[1] Sensitization of n-type semiconductors to visible light has been accomplished by electron transfer from the excited or the ground states of molecular compounds to the solid.[1] Here, we report the first example of a compound designed to sensitize semiconductors to visible light by two distinct charge-transfer pathways. The compound is $Na_2[Fe(bpy)(CN)_4]$, where bpy is 2,2′-bipyridine, and the charge-transfer pathways are shown schematically:



For the direct injection pathway, the electron is optically excited from the $(d\pi)^6$ iron center directly to Ti(IV) sites on the semiconductor surface. For indirect sensitization, the injection process involves interfacial electron transfer from a $(d\pi)^5(\pi^*)^1$ metal-to-ligand charge-transfer (MLCT) excited state. About 10 years ago it was shown that metal cyanides, such as ferrocyanide, $Fe(CN)_6^{4-}$, bind to TiO_2 through ambidentate cyano ligands and that intervalence charge-transfer bands, M → Ti(IV), appear in the visible region.[2] More recently, sensitization of the same semiconductor by the MLCT excited states of Fe(II) polypyridyl compounds was realized.[3] By designing both intervalent and MLCT-mediated electron transfer into one molecular compound, broad spectral sensitization can be realized for solar energy conversion applications. Furthermore, since the two sensitization pathways have distinct dynamics and efficiencies, time-dependent optoelectronic responses can be systematically controlled and fine-tuned at the molecular level for other applications.[4]

$K_4[Fe(CN)_6]$ was purchased from Aldrich. $Na_2[Fe(bpy)(CN)_4]$ was prepared by a published procedure.[5] Mesoporous, ∼10 μm thick nanocrystalline TiO_2 (anatase) films and aqueous colloidal solutions were prepared by a previously described sol−gel technique.[6] Unless otherwise stated, the Fe(II) compounds were attached to TiO_2 in pH 2 aqueous solution.

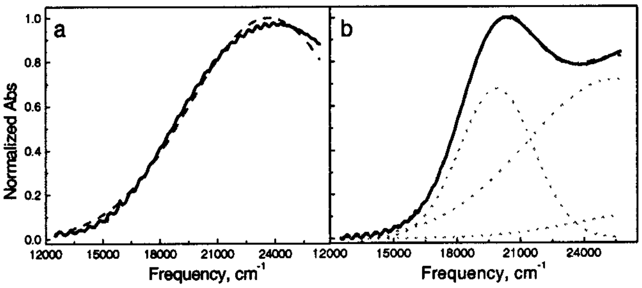


Figure 1. Visible absorption spectrum of (a) $Fe(CN)_6^{4-}/TiO_2$ and (b) $Fe(bpy)(CN)_4^{2-}/TiO_2$ in 0.5 M $LiClO_4$ acetonitrile solution (solid lines). Superimposed on the data are the results of spectra fitting. See the text for more details.

Shown in Figure 1 are typical absorption spectra of the sensitized materials in 0.5 M $LiClO_4$ acetonitrile solution. Normalized absorption spectra were independent of the sensitizer surface coverage within experimental error. The $Fe(CN)_6^{4-}$ sensitized material, abbreviated $Fe(CN)_6^{4-}/TiO_2$, displays a broad absorption band with a maximum at ∼420 nm that has been previously assigned to an Fe(II) → Ti(IV) intervalence charge transfer, IT, transition.[2] The $Fe(bpy)(CN)_4^{2-}$ sensitized material, $Fe(bpy)(CN)_4^{2-}/TiO_2$, displays a visible absorption spectral envelope that is well modeled as a sum of MLCT and IT bands. The MLCT absorption maximum of $Fe(bpy)(CN)_4^{2-}/TiO_2$ is observed at higher energy than $Fe(bpy)(CN)_4^{2-}$ in acetonitrile solution. This spectral shift presumably reflects a more polar, aqueous-like surface environment[5a−c] and/or inductive electron withdrawal from the Fe(II) center by the semiconductor surface through the ambidentate cyano ligands.[5d] The solvatochromic MLCT bands of $Fe(bpy)(CN)_4^{2-}$ are excellent indicators of the electron density on the iron center.[5] The absorption maximum measured for the low-energy MLCT band in water is the same, within experimental error, as that measured for $Fe(bpy)(CN)_4^{2-}/TiO_2$ in acetonitrile.[7]

Superimposed on the data in Figure 1 are the results of spectral fitting. The individual MLCT and IT components are shown and, for $Fe(bpy)(CN)_4^{2-}/TiO_2$, their algebraic sum. The $Fe(CN)_6^{4-}/TiO_2$ absorption spectrum is well modeled by a single Gaussian distribution, while $Fe(bpy)(CN)_4^{2-}/TiO_2$ requires at least two. The absorption spectrum of $Fe(bpy)(CN)_4^{2-}/TiO_2$ was modeled assuming that (1) the ∼7500 cm^{-1} energy separation between the two MLCT bands observed in fluid solution is preserved for $Fe(bpy)(CN)_4^{2-}/TiO_2$,[7] (2) the MLCT absorption maximum on the surface corresponds to that observed in aqueous solution, (3) the $Fe(bpy)(CN)_4^{2-}/TiO_2$ IT band has the same fwhm as $Fe(CN)_6^{4-}/TiO_2$, and the absorption maximum frequency is blue-shifted by the calculated and known ∼1600 cm^{-1} increase in the $Fe^{III/II}$

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(7) In fluid solution $Fe(bpy)(CN)_4^{2-}$ displays two MLCT bands; see ref 5, for example. For $Fe(bpy)(CN)_4^{2-}/TiO_2$ in acetonitrile, only the lower energy band is observed and the higher energy band is obscured by the fundamental absorption edge of the semiconductor. In dimethylformamide the high-energy MLCT absorption band of $Fe(bpy)(CN)_4^{2-}/TiO_2$ is more clearly resolved: Yang, M. Unpublished results.

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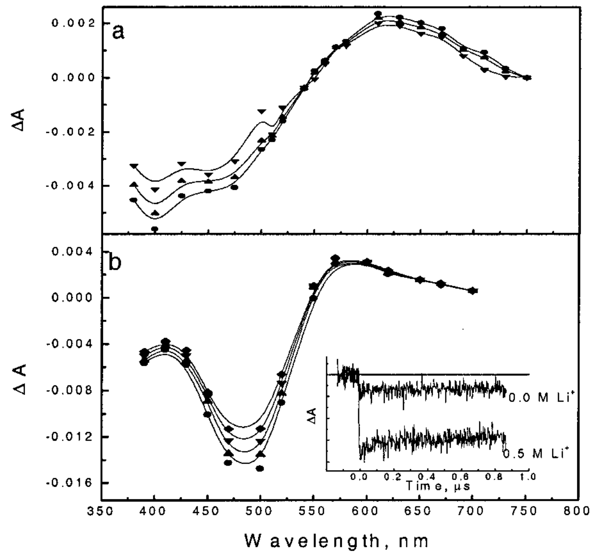

Figure 2. Transient absorption difference spectra of (a) $Fe(CN)_6^{4-}/TiO_2$ and (b) $Fe(bpy)(CN)_4^{2-}/TiO_2$ in acetonitrile after pulsed 532.5 nm (fwhm 8 ns, ~4 mJ/pulse) excitation. The spectra are shown at delay times of 0.2 (circles), 0.5 (triangles), 1.0 (upside-down triangles), and 1.5 μs (diamonds, for $Fe(bpy)(CN)_4^{2-}/TiO_2$ only). The inset in part b shows single wavelength kinetic traces for a different sample of $Fe(bpy)(CN)_4^{2-}$ bound to TiO_2 from ethanol. The kinetic traces were monitored at 440 nm in 0.0 and 0.5 M $LiClO_4$ acetonitrile solution.

reduction potential.[8] With these assumptions and constraints, the simulated and measured absorption spectra agree well. The IT-to-MLCT band intensity ratio was then adjusted until the best fit was obtained, approximately 1:1 in Figure 1. When $Fe(bpy)(CN)_4^{2-}$ was anchored to TiO_2 from ethanol, the ratio decreased to 1:2.

Figure 2 displays the transient absorption difference spectra ΔA observed after pulsed 532 nm light excitation of the sensitized materials in neat acetonitrile under an argon atmosphere at 25 °C. The difference spectra of $Fe(CN)_6^{4-}/TiO_2$ shows a prompt bleach of the ground-state absorption band with a weak positive absorption at longer wavelengths (Figure 2a). The visible region of the $Fe(bpy)(CN)_4^{2-}/TiO_2$ difference spectra is dominated by a bleach of the charge-transfer bands (Figure 2b). The difference spectra are reasonably assigned to an interfacial charge-separated state [$TiO_2(e^-)$, Fe^{III}]. Under all experimental conditions explored, the rate of interfacial charge separation could not be time-resolved, indicating that $k_{inj} > 10^8\ s^{-1}$. Charge recombination was complete within milliseconds with no evidence for decomposition, which is consistent with previous observations.[2,9,10]

Determination of the absorbed photon-to-injected electron quantum yield, ϕ_{inj}, by comparative actinometry requires knowledge of extinction coefficients.[11] For the sensitized mesoporous films, this is problematic because of the ill-defined path length. To circumvent this problem, the extinction coefficients of aqueous pH 2 colloidal TiO_2 solutions in standard cuvettes were measured to be 5000 $M^{-1}\ cm^{-1}$ at 420 nm for $Fe(CN)_6^{4-}/TiO_2$ and 5000 $M^{-1}\ cm^{-1}$ at 440 nm for $Fe(bpy)(CN)_4^{2-}/TiO_2$.[12] It was assumed that these extinction coefficients translate to the thin films in acetonitrile and that neither the Fe(III) state or the injected electron absorb significantly enough at 420 or 440 nm to influence the observed transients. With these assumptions, the injection quantum yields for $Fe(CN)_6^{4-}/TiO_2$ were within experimental error of unity, $\phi_{inj} = 0.8 \pm 0.2$, as expected for a direct IT charge-transfer transition. The rather large standard deviation reflects sample-to-sample deviation. Interestingly, $Fe(bpy)(CN)_4^{2-}$ bound to TiO_2 from ethanol displayed injection quantum yields that could be reversibly increased by a factor of 4 when 1.0 M $LiClO_4$ was added to the acetonitrile (Figure 2b, inset). When the sensitizer was anchored to TiO_2 in pH 2 water where the injection quantum yield was high and ionic strength independent, $\phi_{inj} = 0.7 \pm 0.2$. The high quantum yield measured by nanosecond comparative actinometry indicates that there is little recombination of the injected electron with the Fe(III) center on time scales less than 1 ns under these conditions.

The photoaction spectrum, photocurrent yield versus excitation wavelength, of $Fe(bpy)(CN)_4^{2-}/TiO_2$ was measured in a two-electrode arrangement with 0.5 M LiI/0.05 M I_2 in acetonitrile. When the injection quantum yields and charge collection efficiencies are wavelength-independent, the photoaction and absorptance, $\alpha = 1 - T$, spectra should be superimposeable.[13] The data suggest that is not the case, and there appears to be less MLCT contribution to the photocurrent than one would expect on the basis of the absorptance spectra. The maximum IPCE of ~0.15 is lower than the high injection quantum yield measured spectroscopically. The low IPCE most probably results from inefficient iodide oxidation after electron injection, $E°(Fe^{III/II}) = 0.56$ V vs NHE in water,[8] which allows a greater fraction of the injected electrons to recombine.[14] We emphasize, however, that the comparative actinometry and photoelectrochemical measurements were performed under different experimental conditions of irradiance and electrolyte, so direct comparisons should be made with this in mind.

In summary, the optical and interfacial electron-transfer properties of $Fe(bpy)(CN)_4^{2-}$ anchored to nanocrystalline TiO_2 have been studied by steady state and nanosecond absorption measurements. The data provide strong evidence that semiconductor sensitization by $Fe(bpy)(CN)_4^{2-}$ occurs by a combination of two discrete charge-transfer mechanisms. The high quantum yield for electron injection alone indicates that the absorbed light is quantitatively converted to interfacial charge-separated states regardless of whether the absorbed photon is channeled directly to the semiconductor or to an MLCT excited state. The appearance of cation-dependent electron injection yields signals that the MLCT excited-state pathway is operative, since the direct intervalence transfer pathway, by definition, must have an ionic strength independent of the absorbed photon-to-injected electron yield of unity. The work here demonstrates that ambidentate cyano ligands serve as novel molecular−semiconductor linkages that hold the excited-state proximate to the surface and provide a unique pathway for interfacial electron transfer. By combining two interfacial charge-transfer pathways in one sensitizer, broad spectral sensitization may be realized for solar energy conversion.

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