Metal-to-Particle Charge Transfer and its Role in Dye-Sensitized Solar Cells

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GMF tutorial meeting
Prussian Blue

\[ Fe_{3}^{IV} \left[ Fe^{III} (CN)_{6} \right]_{4} \cdot xH_{2}O \]

Intervalence Charge Transfer (IVCT) band

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Robin-Day classification


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Efficient Visible Light Sensitization of TiO$_2$ by Surface Complexation with Fe(CN)$_6^{4-}$

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A coloured charge-transfer complex formed by adsorption of Fe(CN)$_6^{4-}$ at the surface of TiO$_2$ particles and electrodes upon photoexcitation injects electrons into the conduction band of this semiconductor with a quantum yield of at least 37%.

The deeply orange coloured surface complex is formed when TiO$_2$ colloid (particle size 12 nm, prepared as previously described$^9$) or powder (Degussa P25, a mixture of ca. 75% anatase and 25% rutile) is added to a deaerated aqueous solution of K$_4$Fe(CN)$_6$. The reaction takes place readily at

$$[\text{Fe(CN)}_6^{4-}]_{\text{TiO}_2} \xrightarrow{\text{hv}} \text{e}^-_{\text{cb}} (\text{TiO}_2) + [\text{Fe(CN)}_6^{3-}]_{\text{TiO}_2}$$  (1)  Very rapid

$$[\text{Fe(CN)}_6^{3-}]_{\text{TiO}_2} + \text{e}^-_{\text{cb}} (\text{TiO}_2) \rightarrow [\text{Fe(CN)}_6^{4-}]_{\text{TiO}_2}$$  (2)  $2 \cdot 10^5 \text{ s}^{-1}$

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Photocurrent action spectrum

Figure 2. Photocurrent action spectrum obtained with Fe(CN)$_6^{4-}$-loaded anatase electrodes; conditions: 10$^{-2}$ M HClO$_4$, 10$^{-2}$ M hydroquinone electrode potential 0.2 V (S.C.E.), solution deaerated with Ar. Insert: Photocurrent–potential curve obtained under the same conditions at $\lambda$ 440 nm.


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Note: No measurable change in the absorption spectrum when the concentration of LiClO$_4$ was varied from 0 to 1.0 M.
What if some cyanides are substituted with 2,2’-bipyridines?

*Fitted with two Gaussians
*Both MLCT

The spectra blueshift by 100 cm\(^{-1}\) and increase in intensity by about 10% when 0.5 M LiClO\(_4\) added

Note: oxidation potentials are strongly sensitive to solvent, while MPCT bands position are not.

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Inorg. Chem. 2000, 39, 3738-3739
Transient absorption spectra

Figure 3. Transient absorption difference spectra of Fe(bpy)(CN)$_4^{2-}$/TiO$_2$ in (a) neat acetonitrile at delay times of (■) 0 µs, (●) 0.2 µs, (▲) 0.4 µs, (▼) 0.6 µs, and (●) 0.8 µs and in (b) 0.5 M LiClO$_4$ acetonitrile recorded at delay times of (■) 0 µs, (●) 0.2 µs, (▲) 0.4 µs, (▼) 0.6 µs, and (●) 0.8 µs. The insets in panels a and b are kinetic traces collected at 500 nm under the corresponding conditions. The samples were excited with a pulsed 532.5 nm light (12 mL/pulse, fwhm 8 ns) at 25 °C under an argon atmosphere.

*Ground state recovery (2$^\text{nd}$ order equal-concentration kinetic model) - $k_{obs} = 3 \pm 2 \cdot 10^9 \text{s}^{-1}$

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Incident Photon-to-Current Conversion Efficiency

Figure 4. (a) Photoaction spectra of (■) Fe(bpy)(CN)$_4^{2-}$/TiO$_2$, (●) Fe(dpdb)(CN)$_4^{2-}$/TiO$_2$, and (▲) Fe(dmb)(CN)$_4^{2-}$/TiO$_2$, obtained at room temperature in LiI/I$_2$ acetonitrile solutions. The IPCE is the incident-photon-to-current efficiency. Additional details are given in the text. (b) Comparison of $1 - T$ spectrum of Fe(bpy)(CN)$_4^{2-}$/TiO$_2$ in 0.5 M LiClO$_4$ acetonitrile to the photoaction spectrum of Fe(bpy)(CN)$_4^{2-}$/TiO$_2$ in 0.5 M LiI/0.05 M I$_2$ acetonitrile.

What is the energy of an acceptor state?

Figure 1. UV−vis spectra of 2 nm TiO₂ nanoparticles in 50:50 water/ethylene glycol (solid line) and the resulting Fe³⁺(CN)₆⁴⁻−TiO₂(particulate) system (dotted line) at 298 K.

\[ h\nu_{\text{max}} = \Delta G_b^0 + \lambda + \sqrt{4\lambda k_B T} \]

\[ \Delta G_b^0 = E_C + eE_{M(CN)_n}^{0^0} + k_B T \ln \frac{K_{\text{red}}}{K_{\text{ox}}} \]

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J. Am. Chem. Soc. 2003, 125, 4637-4642
What is the energy of an acceptor state?

<table>
<thead>
<tr>
<th>M(CN)$_n^4$−</th>
<th>$\lambda_{\text{max}}^a$</th>
<th>$\epsilon_{\text{max}}^b$</th>
<th>$E^0^c$</th>
<th>$\Delta G^0^d$</th>
<th>$\lambda_{\text{max-calcd}}^e$</th>
<th>$\lambda_{\text{max-calcd}}^f$</th>
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</thead>
<tbody>
<tr>
<td>Fe$^{II}$C(CN)$_6^4$−</td>
<td>430</td>
<td>5000</td>
<td>0.36</td>
<td>0.50</td>
<td>700</td>
<td>530</td>
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<tr>
<td>Ru$^{II}$(CN)$_6^4$−</td>
<td>390</td>
<td>sh</td>
<td>0.86</td>
<td>1.00</td>
<td>540</td>
<td>440</td>
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<tr>
<td>Mo$^{IV}$(CN)$_6^4$−</td>
<td>438</td>
<td>1300</td>
<td>0.73</td>
<td>0.87</td>
<td>580</td>
<td>460</td>
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<tr>
<td>W$^{IV}$(CN)$_6^4$−</td>
<td>480</td>
<td>1500</td>
<td>0.46</td>
<td>0.60</td>
<td>660</td>
<td>510</td>
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</tbody>
</table>

$^a$ Room temperature. $^b$ Calculated on the basis of the metal cyanide concentration. $^c$ vs NHE ref 35. $^d$ Calculated from eq 14 using $E_{cb} \approx -0.1$ eV and $k_BT \ln(K_{\text{red}}/K_{\text{ox}}) = 0.24$ eV. $^e$ Calculated from eq 13 using $\lambda = 1.0$ eV. $^f$ Calculated using eqs 13 and 14 with $\lambda = 1.0$ eV, $E_{cb} = +0.4$ eV, and $k_BT \ln(K_{\text{red}}/K_{\text{ox}}) = 0.24$ eV.

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Observation

Oxidation potential depends on solvent

$E_C \rightarrow E_T$

$TiO_2$

$\text{MPCT}$

Absorbance

Wavelength

$\text{Inorg. Chem. 2000, 39, 3738-3739}$

$\text{Inorg. Chem. 2002, 41, 1254-1262}$

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Observation

$E_T$ - $E_C$ anodic shift of oxidation potential

$TiO_2$

200-500 mV anodic shift of oxidation potential

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Inorg. Chem. 2000, 39, 3738-3739
What about the spatial location of the acceptor state?

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What about the spatial location of the acceptor state?

\[ f_{osc} = \left(4.61 \times 10^{-9}\right) \varepsilon_{max} \Delta \nu_{1/2} \]

\[ f_{osc} = \left(\frac{8\pi^2 m_e c v_{max}}{3he^2}\right) |\mu_{12}|^2 = \left(1.08 \times 10^{-5}\right) v_{max} |\mu_{12}|^2 \]

\[ (H_D) = \left(9.2 \times 10^4\right) v_{max} f_{osc} = \left(4.0 \times 10^{-4}\right) v_{max} \int \varepsilon(v) dv \]

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Johannes Stark
Physics Nobel Prize laureate...
but unfortunately a strong supporter of Nazi regime.

https://en.wikipedia.org/wiki/Johannes_Stark
Stark/Electroabsorption Spectroscopy

\[
\bar{F}_{int} = f\bar{F}_{ext}
\]

\[
f = \frac{3D_S}{2D_S + 1}
\]

\[
\Delta A(\nu) = \left\{ A_\chi A(\nu) + \frac{B_\chi \nu}{15hc} \frac{d[A(\nu)/\nu]}{d\nu} + \frac{C_\chi \nu}{30h^2c^2} \frac{d^2[A(\nu)/\nu]}{d\nu^2} \right\} \bar{F}_{int}^2
\]

Figure 1. Electroabsorption (a) 77 K absorption spectrum with fit to gaussian curve. (b) Electroabsorption spectra (\(\chi = 54.7^\circ\)) with fit to equation (5). (c) Fit to equation (5) (thick solid line) along with zeroth (solid, thin), first (dotted), and second (dashed) derivative contributions.


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Stark/Electroabsorption Spectroscopy

![Graphs showing Stark/Electroabsorption Spectroscopy](image)

**TABLE 3: Spectral Data and Stark Fitting Results for \( \text{M(CN)}_n^{4-}/\text{TiO}_2 \) Systems at 77 K in 50:50 Water–Ethylene Glycol**

| \( \text{M(CN)}_n^{4-} \) | \( h\nu_{\text{max}, 77\text{K}} \) \( \times 10^3 \) cm\(^{-1} \) | \( |\mu_{12}| \) e\(\text{\AA}\) | \( |\Delta\mu_{12}|^a \) e\(\text{\AA}\) | \( |\Delta\mu_{ab}| \) e\(\text{\AA}\) | \( H_{ab}\) \( \times 10^3 \) cm\(^{-1} \) | \( \text{Tr}(\Delta\alpha)^c \) \( \) A\(^3\) | \( c_6^d \) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Fe(II)(CN)\(_6^4\) | 24.9             | 0.7             | 4.7             | 5.0             | 3.8             | 600             | 0.02            |
| Ru(II)(CN)\(_6^4\) | 28.9             | 0.6             | 4.1             | 4.2             | 4.3             | 700             | 0.02            |
| Mo(IV)(CN)\(_8^4\) | 21.9             | 0.4             | 4.5             | 4.6             | 1.9             | 1000            | 0.01            |
| W(IV)(CN)\(_8^4\)  | 19.4             | 0.5             | 4.6             | 4.7             | 2.2             | 800             | 0.01            |

\(^a\) The estimated uncertainties are \( \approx 15\% \). \(^b\) Electronic-coupling element between the charge-transfer centers. \(^c\) Polarizability change between the ground and excited states (50\% uncertainty). \(^d\) Degree of delocalization between the charge-transfer centers.

*J. Phys. Chem. B 2007, 111, 6695-6702*
DFT and TD-DFT calculations

**Figure 1.** Optimized geometrical structure of the \([\text{Fe(CN)}_6]^{4-}\)/TiO\(_2\) system in the monodentate configuration. Main bond distances (Å) are reported. Grey = Ti, red = O, turquoise = N, brown = C and yellow = Fe atoms.

**Figure 2.** G03/B3LYP energy levels (eV) of the noninteracting \([\text{Fe(CN)}_6]^{4-}\) (left) and TiO\(_2\) (right) and interacting \([\text{Fe(CN)}_6]^{3-}/\text{TiO}_2\) (middle) systems in water solution. Blue (red) colors refer to states that are mostly localized on the dye (nanoparticle). Values in parentheses refer to TDDFT excitation energies.

DFT and TD-DFT calculations

Figure 3. Calculated optical absorption spectrum of [Fe(CN)₆]⁴⁻/TiO₂. Two of the orbitals involved in the transitions that maximally contribute to the intensity of the MPCT band are also shown.


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How to make an efficient solar cell based on MPCT?

Highest Occupied Molecular Orbital
Acceptor States
Extinction Coefficient
Recombination
Improving Optical and Charge Separation Properties of Nanocrystalline TiO$_2$ by Surface Modification with Vitamin C

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Scheme 1. Molecular Structure of Ascorbic Acid before (a) and after (b) Binding to the Surface of Nanocrystalline TiO$_2$

Figure 3. Absorption spectra and surface structure of 0.05 M TiO$_2$ nanoparticles with different sizes before (TiO$_2$) and after surface modification with ascorbic acid (0.05 M TiO$_2$).
Thank You for Your Attention!