TiO$_2$-Based Photovoltaics: The Grätzel Cell

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- extended previously known concept of semiconductor sensitization
- inexpensive and easy to manufacture
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O’Regan, B.; Gratzel, M. Nature 1991, 335, 737
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- highest overall conversion efficiency currently reported is ca. 12%
- broad-based utility tied to cost reductions, significant improvements in overall efficiency, and scalability

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• Potential benefits:
  ✓ substantial reduction in cost (particularly for multi-component cells)
  ✓ expands palette of possible chromophores
  ✓ scalable
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![Relative abundance of the chemical elements in Earth’s upper continental crust](image-url)
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Ru,Os

CB

Fe

LF

CT

CT

LF

VB

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   - Paradigm shift for Fe(II) complexes?
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- sought to decrease the density of states by preparing a high-symmetry analog
An $O_h$ Symmetry Fe(II) Polypyridyl Complex

Single-crystal x-ray structure of $[\text{Fe(dcpp)}_2](\text{PF}_6)_2$. The bond distances and angles in the primary coordination sphere indicate that the molecule possesses nearly perfect $O_h$ symmetry.

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- basic structural motif is based on an analogous Ru(II) complex reported by Schramm et al. (*Inorg. Chem.* 2009, **48**, 5677)

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- high symmetry is possibly linked to some interesting properties...

Optical Properties of \([\text{Fe}(\text{dcpp})_2]^{2+}\)
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- $[\text{Fe(dcpc)}_2]^2^+$ is navy blue color in both the solid-state and in solution
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Electronic absorption spectra for $[\text{Fe(dcpp)}_2](\text{PF}_6)_2$ in CH$_3$CN solution. Corresponding spectra for $[\text{Fe(bpy)}_3](\text{PF}_6)_2$ and $[\text{Fe(terpy)}_2](\text{PF}_6)_2$ are included for comparison.
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- MLCT lifetime still too short ($75 \pm 15 \text{ fs}$)...

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**Synthetic Elaboration of dcpp Ligand**

- extension of $\pi$ system to stabilize the MLCT state
- functionalization to allow for binding to surface of semiconductor

\[ \begin{align*}
\text{CrO}_3 & \quad \text{H}_2\text{SO}_4 \\
\text{CH}_3\text{COCl} & \quad \text{CHCl}_3 \\
\text{DMAP (cat.), NH}_3\text{OH-}\text{HCl} & \quad \text{CH}_2\text{Cl}_2 \text{ or DMF, r.t.}
\end{align*} \]
• **Important physical properties of** \([\text{Fe(dcpped)}_2]^{2+}\):

  ➤ **Fe**\(^{II/III}\) oxidation couple is \(~600\) mV positive that of comparable Fe(II) polypyridyl complexes

  ➤ reduction potential of dcpp ligand is \(~700\) mV more positive than that of other polypyridyl ligands

  ➤ excited-state lifetime of lowest-energy excited state is nearly 4-fold shorter than that of (barrier-less) \([\text{Fe(bpy)}_3]^{2+}\) under similar solution conditions
Electronic Structure of \([\text{Fe(dcpp)}_2]^{2+}\)

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• suggests the real possibility of developing an Fe(II) analog of $[\text{Ru(bpy)}_2]^{2+}$
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