## TiO<sub>2</sub>-Based Photovoltaics: The Grätzel Cell

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- broad-based utility tied to cost reductions, significant improvements in overall efficiency, and scalability



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Ru,Os CB Fe

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- change the nature/energy of the lowest-energy excited state(s) of low-spin Fe(II) complexes
- paradigm shift for Fe(II) complexes?

# Excited-state Evolution of Fe(II) Complexes
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- sought to decrease the density of states by preparing a highsymmetry analog



Single-crystal x-ray structure of  $[Fe(dcpp)_2](PF_6)_2$ . The bond distances and angles in the primary coordination sphere indicate that the molecule possesses nearly perfect  $O_h$  symmetry.

Jamula, L; Brown, A.; Guo, D.; McCusker, J.K., submitted for publication.



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

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Electronic absorption spectra for [Fe(dcpp)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> in CH<sub>3</sub>CN solution. Corresponding spectra for [Fe(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> and [Fe(terpy)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> are included for comparison.

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- MLCT lifetime still too short (75 ± 15 fs)...



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- functionalization to allow for binding to surface of semiconductor



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  - ➡ Fe<sup>II/III</sup> 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
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- suggests the real possibility of developing an Fe(II) analog of [Ru(bpy)<sub>2</sub>]<sup>2+</sup>





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- 2-D femtosecond electronic absorption (w/G. Scholes, Toronto)