RESEARCH HIGHLIGHT

Are we on a path to solar cells that utilize iron?

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By mass, iron is the most common element on earth and the most widely utilized metal in industry. Over 30 years of research have shown that iron is a poor choice for practical applications in solar energy conversion. Hematite and other ferric oxide polymorphs are competent for water oxidation in photoelectrochemical cells, but just barely. Photovoltaics based on iron oxide or sulfide materials are inefficient and the inclusion of even trace iron in silicon significantly lowers the efficiency of today's commercial photovoltaics. In dve-sensitized solar cells (DSSCs), inclusion of an iron center in a dye molecule results in devices with poor efficiencies that are of no practical value.1 Iron-based materials and compounds function for light-driven electron transfer and catalysis, but just well enough to give some hope to highly optimistic scientists in academic labs. In the final analysis, iron consistently continues to disappoint and one can safely conclude that it is best to keep iron out of solar cells. Until now Harlang et al.² found that the iron compound shown in Figure 1 harvests sunlight through most of the visible region with subsequent excited state electron transfer to a TiO₂ semiconductor with efficiencies >90%. Such a breakthrough in efficiency is remarkable, particularly when one considers the decades of prior research that failed to accomplish anything even close. This breakthrough raises the question, are we on a path to solar cells that utilize iron? Before addressing this question, it is worthwhile to consider the impact an iron center has on a dye molecule.

Many molecular compounds that contain iron, such as hemes or $Fe(bpy)_3^{2+}$ (where bpy is 2,2'-bipyridine), absorb sunlight effectively in the visible region. However, the excited states formed upon light excitation do not luminesce as would a free base porphyrin or $Ru(bpy)_3^{2+}$. Instead, the excited states deactivate through unwanted reactions that include photochemistry or intersystem crossing/internal conversion to non-luminescent high-spin states. Inorganic photochemists have recognized that this behavior results from the population of metal-centered states, sometimes called 'ligand field' or 'dd' states, which

are anti-bonding with respect to iron-ligand bonds. Attempts to raise the energy of these metal-centered states so they are not populated by sunlight have been unsuccessful. Heme carbonyl compounds, for example, photo-release carbon monoxide with quantum yields of unity even though CO is a strong field ligand that destabilizes the ligand field states. Chelating ligands such as bpy can lower the quantum yields for ligand loss photochemistry, yet Monat et al.³ have shown that unproductive population of high-spin metal-centered states occurs quantitatively on femtosecond time scales with such compounds. In a new approach, Harlang et al. circumvented these issues with strong, σ -donating anionic N-heterocyclic carbene (NHC) chelating ligands that suppress these unwanted deactivation pathways. Indeed when this compound was immobilized on an Al₂O₃ insulator and illuminated with visible light, the desired excited state was found to live for 37 ps, a value that remains a record to date. The time constant for excited state electron injection into the mesoporous TiO₂ thin films commonly used in DSSCs was found to be about 3 ps, which is consistent with >90% reported yield.² Indeed, a variety of spectroscopic measurements provided strong evidence of



Figure 1 Chemical structure of the N-heterocyclic carbene Fe(II) compound that efficiently transfers electrons to TiO₂ when illuminated with visible light. Taken without permission from Harlang *et al.*²

nearly quantitative excited state interfacial electron transfer to TiO₂. It is abundantly clear that an iron compound has finally been discovered that efficiently transfers electrons when illuminated with visible light!

So, are we on a path to solar cells that utilize iron? The answer to this question lies in part on the ability of DSSCs to compete with traditional Si photovoltaics, as well as with emerging technologies such as the lead-based perovskites. If so, some challenging science still remains. The nearly quantitative vield of injected electrons were measured spectroscopically and NOT by measurement of the electrons in an external circuit where they could provide electrical power. After excited state injection into TiO2, the oxidized iron compound is not efficiently 'regenerated' by the redox mediators commonly used in DSSCs. In addition, the solar light harvesting extends only through the orange region (to about 600 nm) without appreciable absorption in the red or near infrared regions. The challenges of enhanced light harvesting and more favorable energetics for regeneration are, to some extent, orthogonal. Alternative iron compounds that utilize this novel NHC ligand and have the formal Fe^{III/II} reduction potentials necessary for regeneration by iodide will have blue-shifted absorption spectra. Thus, unless alternative redox mediators for DSSCs are identified, it would appear that both the ground and the excited state reduction potentials will need to be tuned. While challenging, there is good precedence for optimization of dye energetics through synthetic design and the probability for success is quite high. In this regard, it is interesting to note that independent calculations by Mukherjee et al.4 predicted a priori that iron carbene compounds would indeed be useful for solar energy conversion. With synthesis guided by theory, the possibility for efficient DSSCs based on iron seems highly likely.

Aside from practical applications, the report by Harlang *et al.* raises some interesting fundamental questions that will certainly inspire future research. Indeed, while an early study of dye sensitization with iron compounds revealed nothing of practical utility they remain highly impactful to the scientific community interested in efficient energy conversion with low-cost earth-abundant materials.¹ The radical departure of Harlang's iron

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carbene compound from the bipyridine and porphyrin ligands that have historically dominated the field opens new opportunities for exploitation and characterization of the excited states that almost certainly represent ongoing research in many laboratories around the world. In addition, the symmetric bis-tridentate structure reported would not have been predicted to result in such efficient excited state electron transfer. The two carboxylic acid groups cannot simultaneously bind to the same TiO2 nanocrystallite, and a dogma asserts that a useful dve molecule should contain only a single dipole oriented toward the semiconductor surface. Hence it is unclear why two orthogonal dipoles did not lower the injection yields measured for this iron compound. Likewise, recombination of the injected electron with the oxidized iron compound was unexpectedly fast and suggests that alternative recombination pathways, perhaps through high-spin states, is operative for this iron compound. Such fascinating, yet poorly understood behavior coupled with the real possibility of practical application makes for a very bright future for iron utilization in solar cells.

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