

Heteroleptic N-heterocyclic carbene complexes of iron as photosensitizers for light-induced water reduction

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Photocatalytic water splitting using sunlight allows producing hydrogen and oxygen in a sustainable way as sunlight is an eternal abundant energy source. This contribution will demonstrate that iron-based photosensitizers (PS) can increase the degree of sustainability in photocatalytic hydrogen production, while at the same time offering interesting photophysical properties.

A typical system for photocatalytic proton reduction consists of a molecular photosensitizer and a catalytic center. By harvesting light with the PS an electron is transferred to a MLCT state, promoting the electron transfer to the catalytic center. Here protons of water are reduced to hydrogen. For the reduction of the photosensitizer a sacrificial electron donor like EDTA or TEA is used.

To replace noble metals in transition metal photosensitizers by inexpensive and easily available iron-based complexes both their stability under irradiation and the lifetimes of the excited states have to be tailored. Based on first attempts using NHC-ligands^[1-3] new photosensitizers with iron and a heteroleptic ligand environment are introduced here (Figure 1).

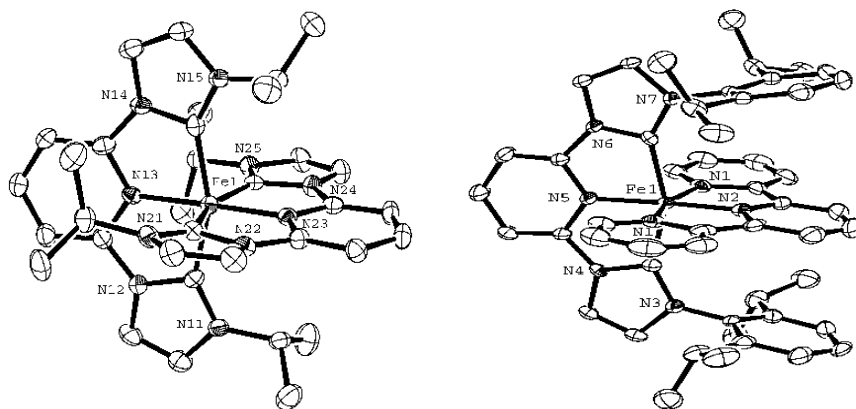


Figure 1. Examples of heteroleptic iron NHC-complexes used for photocatalytic proton reduction.

Strongly coordinating NHC-ligands enlarge the lifetime of the MLCT-state, whereas the terpyridine ligands improve light absorption in the visible range. Consequently, these new complexes exhibit highly interesting photophysical properties. Figure 2 shows the extended visible absorption as well as unprecedented luminescence spectra. Such properties will be discussed in the context of (TD-)DFT calculations to understand the transition and time resolved spectroscopy to identify the accessible excited states and their according lifetime.

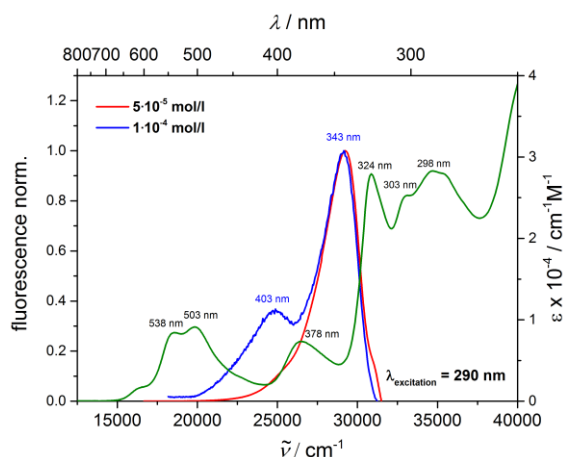


Figure 2. Optical absorption (green) and concentration dependent luminescence (red, blue) spectra of a selected heteroleptic iron-NHC complex.

The presented complexes are the first iron photosensitizers applied in the photocatalytic proton reduction (Figure 3). By comparison to established iridium the potential of such photosensitizers is proved. Moreover X-ray absorption spectroscopy (XAS) measurements of solid samples and of the reaction mixture after catalysis prove the structural identity and photostability by both identical XANES and EXAFS spectra shown in Figure 3.^[4] In a final outlook, strategies to improve the efficiency of such photosensitizers will be presented, which in turn will enable MLCT emitters based on iron in the near future.

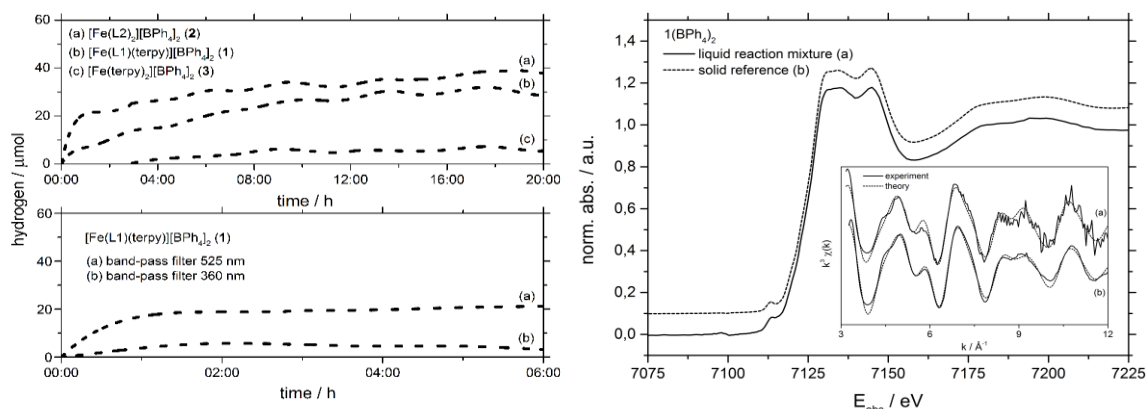


Figure 3. Catalytic activity of the iron NHC-complexes in photocatalytic proton reduction (top left). Band pass filter experiments prove the activity in the visible spectral range (bottom left). Such complexes exhibit exceptional photostability as shown by XAS measurements (right).

References:

- [1] Y. Liu, T. Harlang, S. E. Canton, P. Chábera, K. Suárez-Alcántara, A. Fleckhaus, D. A. Vithanage, E. Göransson, A. Corani, R. Lomoth et al., *Chem. Commun.* **2013**, 49, 6412.
- [2] L. A. Fredin, M. Pápai, E. Rozsályi, G. Vankó, K. Wärnmark, V. Sundström, P. Persson, *J. Phys. Chem. Lett.*, **2014**, 2066.
- [3] T. Duchanois, T. Etienne, M. Beley, X. Assfeld, E. A. Perpète, A. Monari, P. C. Gros, *Eur. J. Inorg. Chem.* **2014**, 3747.
- [4] P. Zimmer, P. Müller, L. Burkhardt, R. Schepper, A. Neuba, J. Steube, F. Dietrich, U. Flörke, S. Mangold, M. Gerhards, M. Bauer, *Eur. J. Inorg. Chem.* **2014**, 3747.