How to find your catalyst: Solvatochromism as tool for the molecular localization of a Photomolecular Device

Benedikt Bagemihl¹, Miftahussurur Hamidi Putra², Axel Groß² and Sven Rau¹

Email: benedikt.bagemihl@uni-ulm.de, miftahussurur.putra@uni-ulm.de

Introduction

In the photomolecular device \( \text{RutpphZMX}_2 \), activity in photocatalytic hydrogen production is governed by fast electron transfer via the tetrapyridophenazine (tpphz) bridging ligand to the reductive metal center \([1,2]\). In order to identify the localization of this catalyst in soft-matter liquid media environments, we investigated its properties in different solvents. Previously not observed transitions in unpolar aromatic solvents may serve as an \textit{in situ} marker for the localization of the catalyst.

Theoretical Results

Theoretical parameters: DFT for geometry optimization and TDDFT for absorption spectra. Calculated by Gaussian 16 package. Simulation parameter: B3LYP with vdW-BJ, def2svp basis set, and SMD implicit solvent model. \( ^* \)R = Methyl, Nonyl, tert-Butyl

Synthesis and Experimental Results

New substitution pattern: \( R = \text{CF}_3 \) & \( R = \text{Nonyl} \) as Photomolecular devices with electron-withdrawing or solubilizing peripheral ligands.

Synthesis of the Ruthenium Dyads

NMR, MS, Emission/ Absorption characterization

Conclusion

- It was possible to observe spectra of the Dyads in very unpolar, ‘toluene-like’ solvent
- The calculated spectra match the experimental data, but only when the anion PF\(_6\) is included
- The position of the anion seems highly important for the exact positions of the MLCT bands
- Especially the position of the MLCT (Pt \( \rightarrow \) tpphz) in the spectra seems indicative for the chemical environment of the Dyad such as Anion and Solvent.

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Toluene spectra were recorded by pre-dissolution in 2 drops of DCM and addition of excess of Toluene prior to heating to 80 °C for 1/2 hour.