

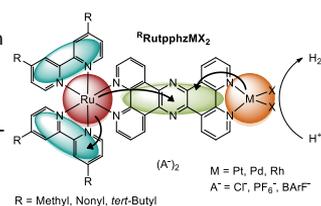
How to find your catalyst: Solvatochromism as tool for the molecular localization of a Photomolecular Device

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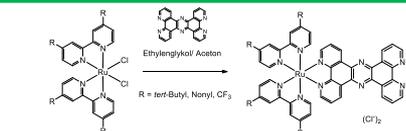
Introduction

In the photomolecular device $^R\text{Ru}t\text{pphzMX}_2$, 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 unipolar aromatic solvents may serve as an *in situ* marker for the localization of the catalyst.

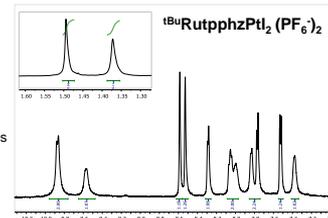
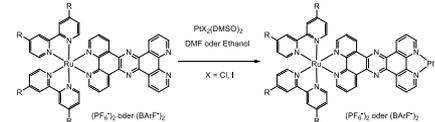


[1] M. G. Pfeiffer et al., *Angew. Chemie - Int. Ed.* **2015**, *54*, 6627–6631.
[2] L. Zedler, A. K. Mengelle et al., *Angew. Chemie Int. Ed.* **2019**, 13140–13148.

Synthesis and Experimental Results

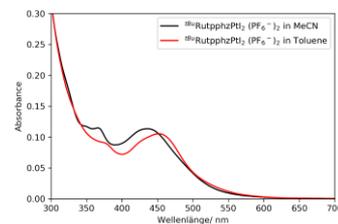


New substitution pattern: R = CF₃ & R = Nonyl as Photomolecular devices with electron-withdrawing or solubilizing peripheral ligands.



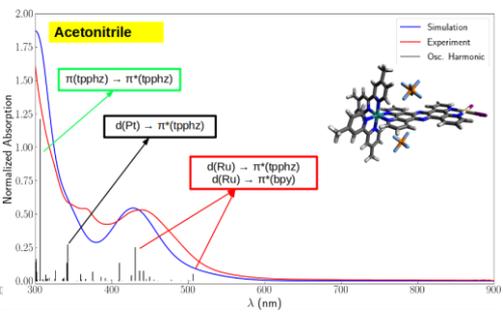
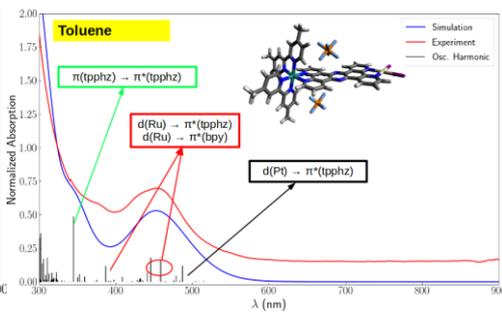
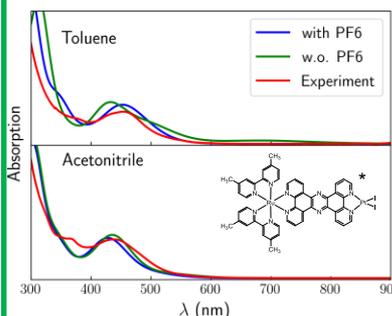
Synthesis of the Ruthenium Dyads ✓

NMR, MS, Emission/Absorption characterization* ✓



*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 ½ hour.

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 was used instead of *tert*-Butyl or Nonyl to save computational costs

Conclusion

- It was possible to observe spectra of the Dyads in very unipolar, 'toluene-like' solvent
- The calculated spectra match the experimental data, but only when the anion PF₆⁻ 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 → tpphz) in the spectra seems indicative for the chemical environment of the Dyad such as Anion and Solvent.

Acknowledgement

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