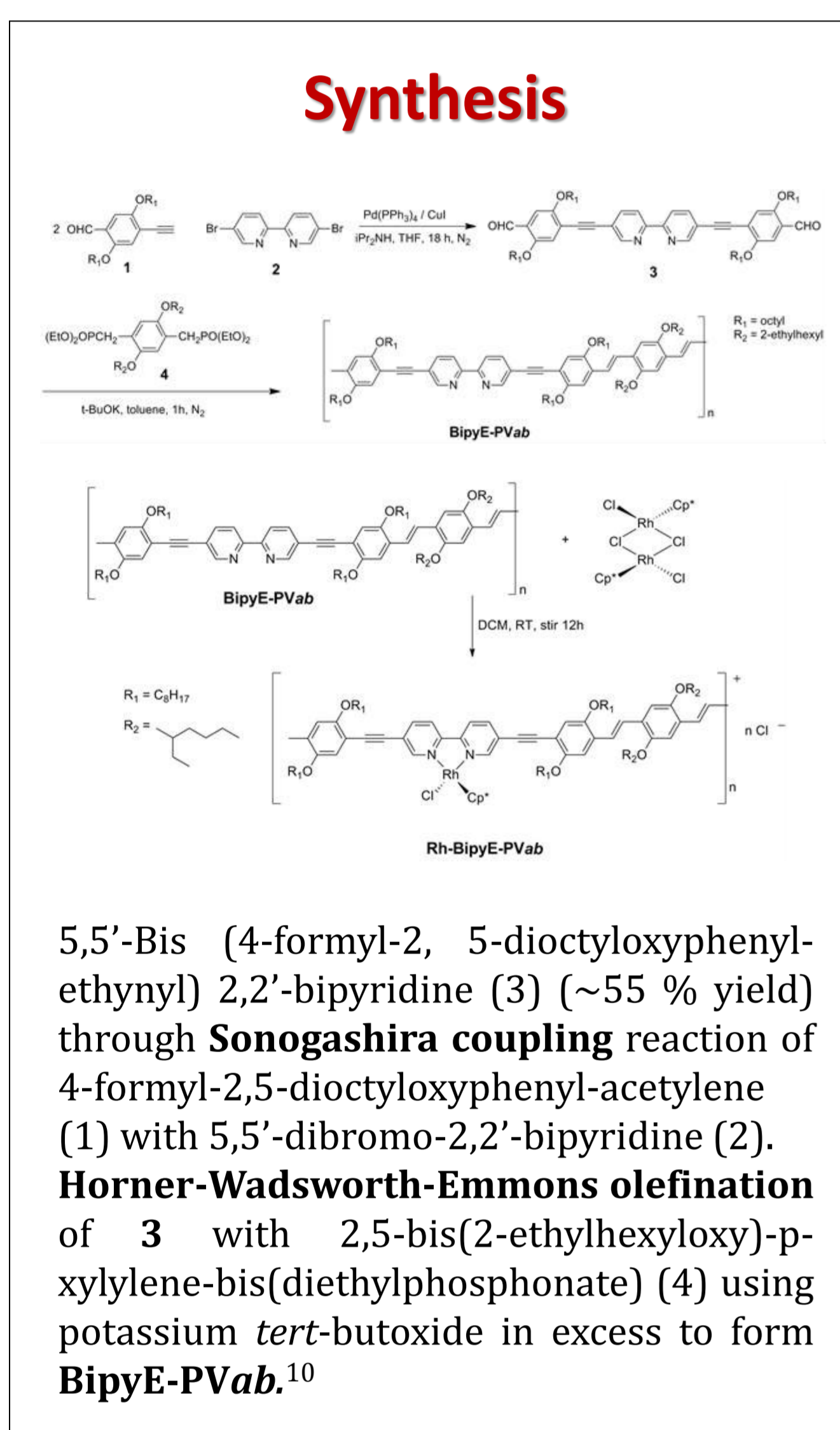


Introduction

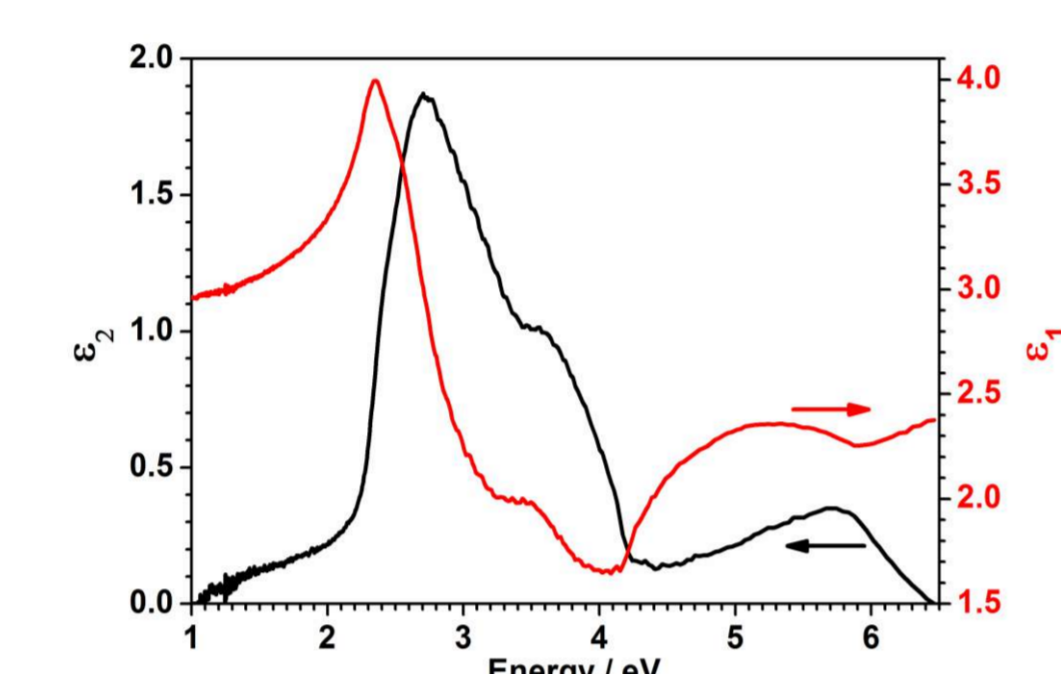
In the field of artificial photosynthesis,^{1,2} the coupling of photocatalytic and enzymatic processes has recently gained increasing attention.³⁻⁷ One possible merging point is the combination of photocatalytic cofactor reduction steps with enzymatic carbon dioxide reduction.⁸⁻⁹

A bipyridine-containing poly(arylene-ethynylene)-*alt*-poly(arylene-vinylene) copolymer with a redox-active rhodium cyclopentadienyl-complex as the active site for catalytic substrate conversion is presented¹⁰ and applied in photochemical regeneration of NADH.

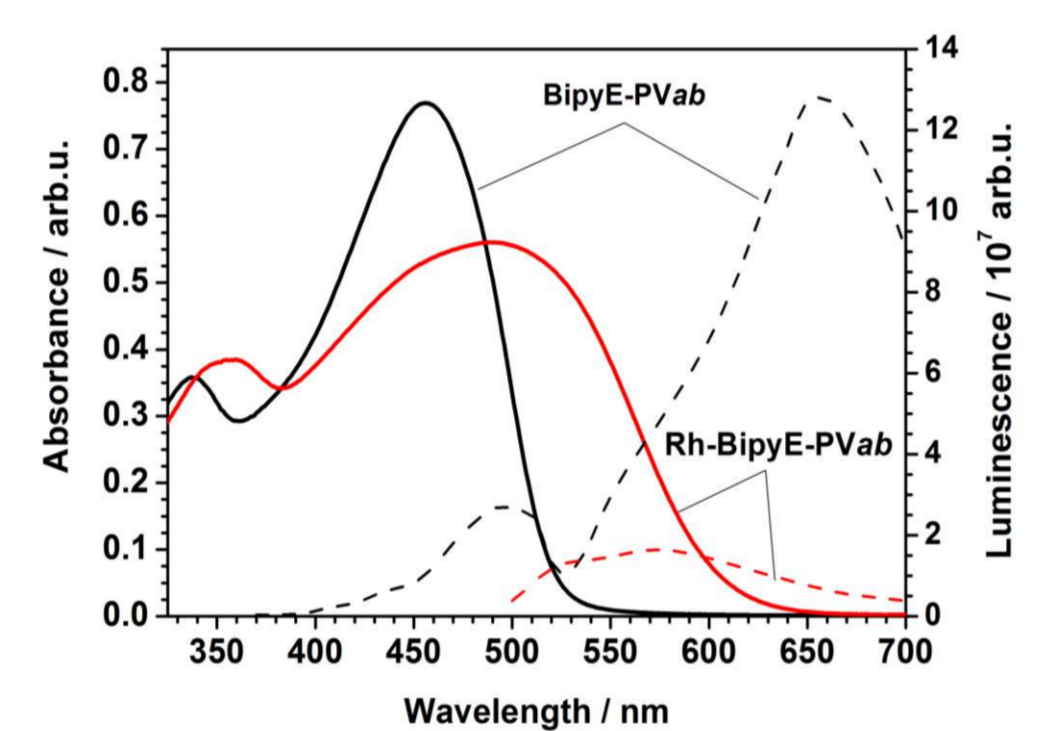
It works as both immobilizing agent and photosensitizer and thus, in contrast to similar systems with free rhodium complexes in solution, could minimize the contact of the catalyst compound with the NADH-binding site of enzymes applied in photoenzymatic redox systems¹¹⁻¹³ and enables separation of the catalyst from the reaction solution and reusability of the precious metal compound.



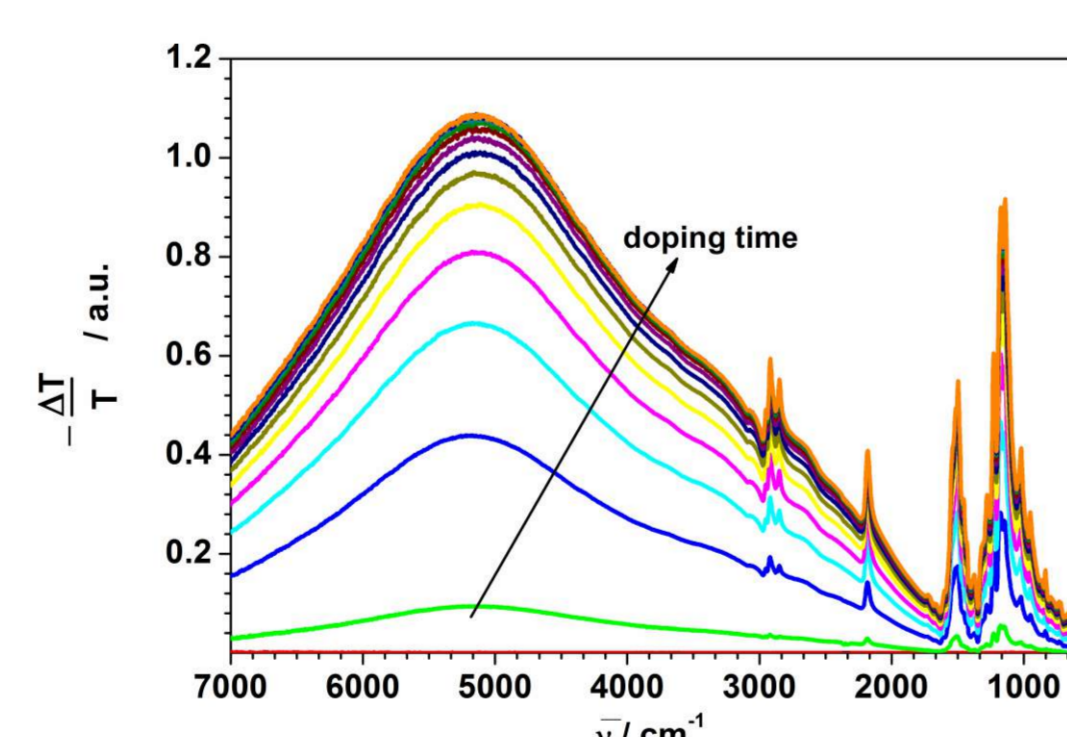
Spectroscopic Characterization



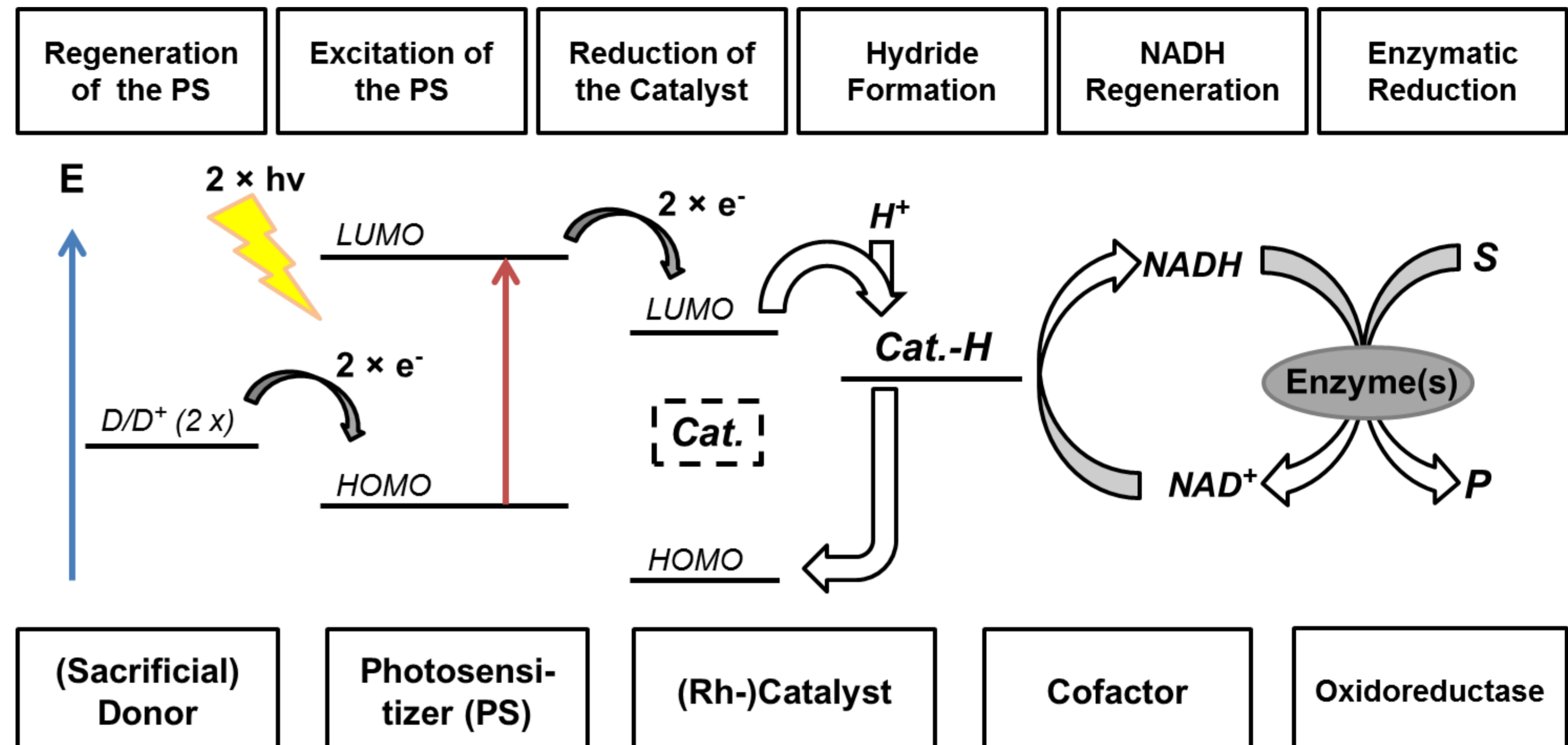
Spectroscopic ellipsometry of the spin-coated pristine polymer film of **BipyE-PVab** shows two main absorption maxima at 460 nm (2.7 eV) and 348 nm (3.5 eV), respectively. An additional broad absorption band can be found at 218 nm (5.7 eV). The optical **bandgap** is found at 2.1 eV.



UV-Vis absorption (solid line) and **emission** spectra (dashed line) of the **BipyE-PVab** polymer (black) and the metallated polymer **Rh-BipyE-PVab** (red) in dichloromethane solution. The metallated polymer **Rh-BipyE-PVab** shows a red shift in absorbance by about 50 nm and a much broader absorption as the bare **BipyE-PVab** polymer. Upon complexation, the polymer emission is quenched almost completely.

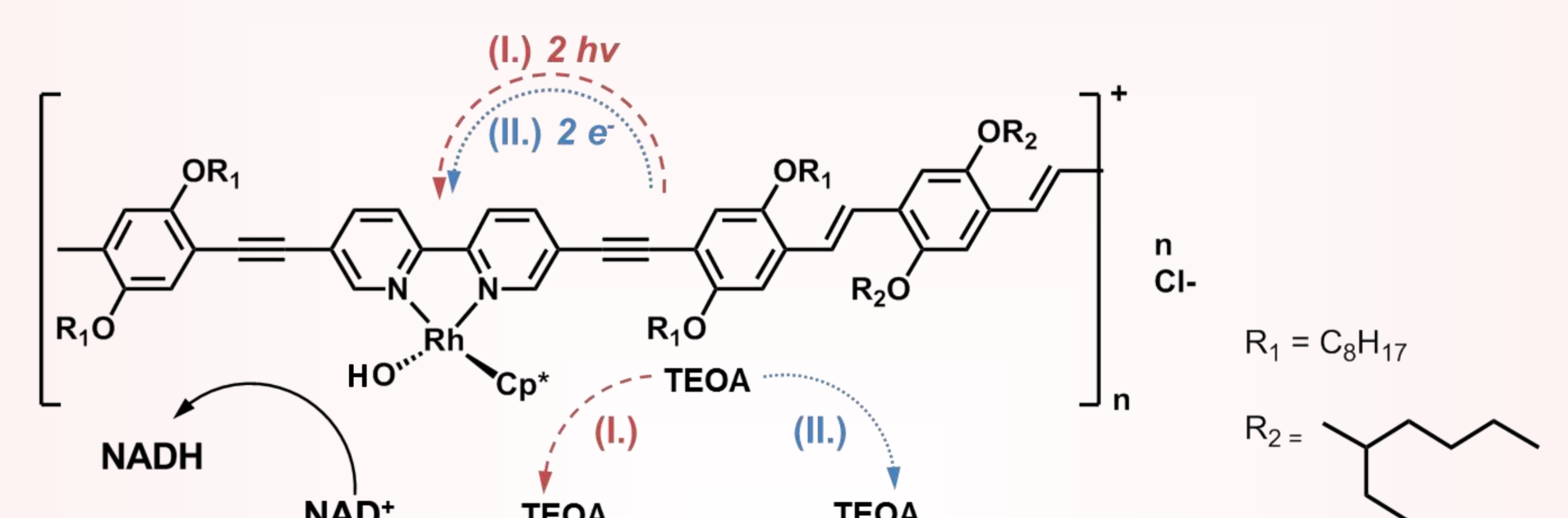


ATR-FTIR measurement of the chemical doping-process of **BipyE-PVab** by iodine vapour. With increasing time of exposure, the formation of a broad polaron absorption can be observed.



Conclusions

- Two probable **catalytic pathways** proposed for the reaction:
- The first possibility **(I)** involves direct excitation of the rhodium subunit or energy transfer from the irradiated polymer **BipyE-PVab** to the Rh centre in **Rh-BipyE-PVab** and subsequent reductive quenching of the excited state by TEOA. This would have to occur twice at the same Rh-site for later reduction of NAD⁺ to NADH.



- The second one **(II)** involves (oxidative) quenching of the photoexcited polymer chain by a rhodium centre. This is accompanied by electron transfer to the rhodium active site, possibly also involving a different polymer chain. As iodine vapor with an estimated redox potential of 0.35 ± 0.1 V¹⁶ is sufficient to oxidize the **BipyE-PVab** polymer backbone and the bandgap measured by ellipsometry with 2.1 eV rank this pathway the most probable one. After two electron transfer steps to the rhodium centre a proton can be taken up from the solution and the active Rh-hydride complex is formed at the active bipyridyl-coordination site of the rhodium polymer. The hydride is then transferred to NAD⁺.

- In a photoenzymatic reaction the amount of L-glutamate formed per repetition unit of the **Rh-BipyE-PVab** polymer (M=1560 g mol⁻¹) was used to estimate a TN per rhodium centre, which is 3.2 after 22h (TOF= 0.145 h⁻¹).¹⁷

- Photochemical quantum yield: Φ = 1.0 × 10⁻⁴ (±0.1 × 10⁻⁴).

- Amount of NADH formed per unit area and time : 1.8 μmol cm⁻² h⁻¹.

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References:

- (1) Oberholzer, M.; Probst, B.; Bernasconi, D.; Spingler, B.; Alberto, R. *Eur. J. Inorg. Chem.* **2014**, 2014, 3002.
- (2) Faunce, T.; Styring, S.; Wasielewski, M. R.; Brudvig, G. W.; Rutherford, A. W.; Messinger, J.; Lee, A. F.; Hill, C. L.; deGroot, H.; Fontecave, M.; MacFarlane, D. R.; Hankamer, B.; Nocera, D. G.; Tiede, D. M.; Dau, H.; Hillier, W.; Wang, L.; Amal, R. *Energy Environ. Sci.* **2013**, 6, 1074.
- (3) Knör, G. *Chem. - A Eur. J.* **2009**, 15, 568.
- (4) Kim, J. H.; Nam, D. H.; Park, C. B. *Curr. Opin. Biotechnol.* **2014**, 28, 1.
- (5) Sakai, T.; Mersch, D.; Reinsner, E. *Angew. Chemie Int. Ed.* **2013**, 52, 12313.
- (6) Oppelt, K. T.; Wöb, E.; Stiftinger, M.; Schöfberger, W.; Buchberger, W.; Knör, G. *Inorg. Chem.* **2013**, 52, 11910.
- (7) Siu, E.; Won, K.; Park, C. B. *Biotechnol. Prog.* **2007**, 23, 293.
- (8) Dibenedetto, A.; Stufano, P.; Nocito, F.; Aresta, M. *ChemSusChem* **2011**, 4, 1311.
- (9) Aresta, M.; Dibenedetto, A.; Angelini, A. J. *CO₂ Util.* **2013**, 3-4, 65.
- (10) Oppelt, K. T.; Gasiorowski, J.; Egbe, D. A. M.; Kollender, J. P.; Himmelsbach, M.; Hassel, A. W.; Sariciftci, N. S.; Knör, G. *J. Am. Chem. Soc.* **2014**, 136, 12721.
- (11) Poizat, M.; Arends, I. W. C. E.; Hollmann, F. J. *Mol. Catal. B Enzym.* **2010**, 63, 149.
- (12) Liu, J.; Antonietti, M. *Energy Environ. Sci.* **2013**, 6, 1486.
- (13) Liu, J.; Cazelles, R.; Chen, Z. P.; Zhou, H.; Galarneau, A.; Antonietti, M. *Phys. Chem. Chem. Phys.* **2014**, 16, 14699.
- (14) Kollender, J. P.; Mardare, A. I.; Hassel, A. W. *ChemPhysChem* **2013**, 14, 560.
- (15) Gasiorowski, J.; Kollender, J. P.; Hingerl, K.; Sariciftci, N. S.; Mardare, A. I.; Hassel, A. W. *Phys. Chem. Chem. Phys.* **2014**, 16, 3739.
- (16) Boschloo, G.; Hagfeldt, A. *Acc. Chem. Res.* **2009**, 42, 1819.
- (17) Kim, J. H.; Lee, S. H.; Lee, J. S.; Lee, M.; Park, C. B. *Chem. Commun.* **2011**, 47, 10227.