Transition metal phosphino complexes, copper chromophores and nanoparticles in the field of photocatalytic water splitting

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The main focus of my work is the coordination of different phosphines like tetradentate phosphines *cis, trans, cis*-1,2,3,4-tetrakis-(diphenylphosphino)cyclobutane (dppcb)[1], *trans, trans, trans*-1,2,3,4-tetrakis-(di-o-anisylphosphino)cyclobutane (*o*-MeO-dppcb) and *cis, trans, cis*-1,2,3,4-tetrakis(diphenylphosphino)buta-1,3-diene (dppbd)[2] as well as bidentate phosphines of the form PNP^{rest} with thiolate and dithiolate co-ligands to transition metals. I synthesized two copper chromophores with tetradentate phosphines $[Cu_2(dppcb)(mercaptopyridine)_4](BF_4)_2$ and $[Cu_2(o\text{-}MeO\text{-}dppcb)\text{-}(mercaptopyridine)_4](BF_4)_2$ with long excited state lifetimes of 1 µs (Fig. 1).

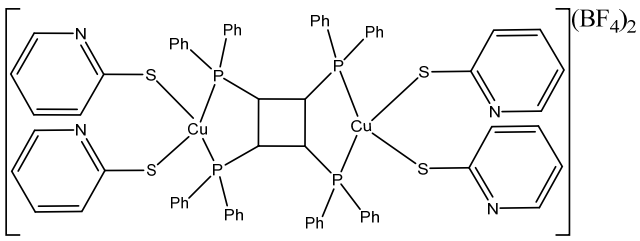

Figure 1.: $[Cu_2(dppcb)(mercaptopyridine)_4](BF_4)_2$

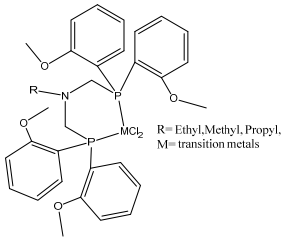

Figure.:PNP-rest

Also a bidentate phosphine copper complex with PNP^{Et} $[Cu(PNP^{Et})(mercaptopyrdine)_2]$ was synthesized which shows a very long lifetime of 6.2 µs. In the field of water reduction catalysts, I produced $[Au(PNP^{Et})(mercaptopyrdine)_2]$ and a $[Au(PNP^{Me})mercaptopyrdine)_2]$ complexes with activity in photocatalytic water splitting. In the field of nanoparticles a PEG-mercaptopyridine with 0,52% and 0,26% palladium was prepared and tested with Eosin Y as chromophore for its photochemical catalysis. These nanoparticles produce only a low amount of hydrogen, because we believe they build a cluster and the size is too big. In other experiments with PEG-palladium nanoparticles we achieve a turn over number of 20.000.

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[1] W. Oberhauser, C. Bachmann, T. Stampfl, R. Haid, C. Langes, H. Kopacka, A. Rieder, P. Brüggeller, *Inorganica Chimica Acta* **1999**, *290*, 167.

[2] J. Prock, K. Ehrmann, W. Viertl, R. Pehn, J. Pann, H. Roithmeyer, M. Bendig, A. Rodríguez Villalón, H. Kopacka, A. Dumfort et P. Brüggeller, *Eur. J. Inorg. Chem.* **2018**, *34*, 133+**Titelseite**.