

Dinuclear Complexes with Bridging Phenanthroline-5,6-dithiolates

Elisa Erdmann, Alexander Villinger and Wolfram W. Seidel*

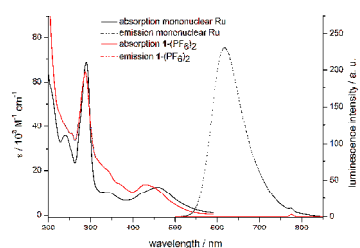


Fig. 1: Comparison of absorption and emission spectra of mononuclear Ru complex and dinuclear complex **1-(PF₆)₂**. Photoluminescence quenching caused by energy transfer (ϕ_{en} going from 13% to 0.05%).

To avoid the rare and expensive metals Ru and Ir it was possible to isolate a complex based on Cu(I) with PP and NN coordination (**3-BF₄**). Such complexes [Cu(NN)(PP)]⁺ with phenanthroline derivatives as NN building blocks exhibit quantum yields up to 30% [2] and are active photocatalysts for hydrogen generation with lifetimes of about 6.9 μ s [3].

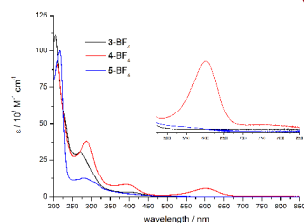


Fig. 3: UV-vis absorption spectra of the mononuclear **3-BF₄** (black) and the dinuclear complexes **4-BF₄** (red) and **5-BF₄** (blue) in CH₃CN.

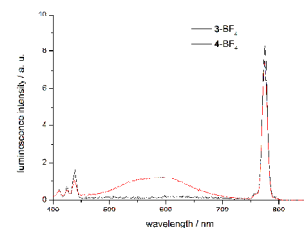


Fig. 4: Emission spectra of mononuclear Cu(I) complex **3-BF₄** (black) and dinuclear Cu(I)-Co(III) complex **4-BF₄** (red). Absolute photoluminescence quenching in **3-BF₄** could be related to the absence of substituents at the phen building block.

Charge and energy transfer are the key elements in photocatalysis. Their understanding and optimization are of crucial importance. We use the directional ligand phenanthroline-5,6-dithiolate (**phendt²⁻**) providing a strong electronic cooperativity between two metal centres. Due to the different coordination sites dinuclear complexes are accessible by a consecutive coordination sites strategy. Ru/Ir(phendt)Ni like **1-(PF₆)₂** show an energy transfer by the DEXTER mechanism.[1] To realize an electron transfer we isolated Co(III) complexes (**2-PF₆**). A drastic drop of the luminescence quantum yield going from mononuclear to the dinuclear complexes could be detected in **1-(PF₆)₂** and **2-PF₆** independent of the second coordinated metal centre.

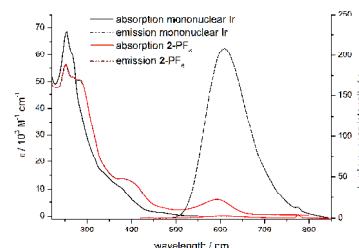
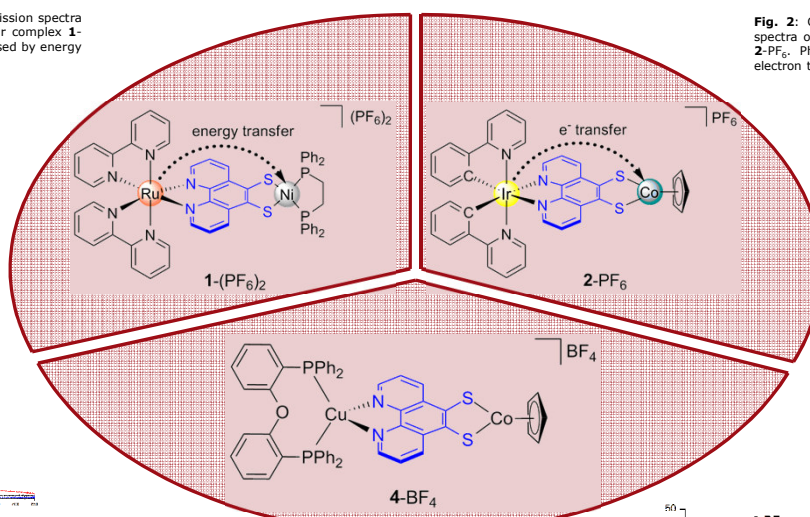
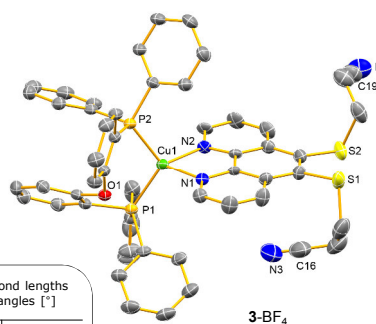


Fig. 2: Comparison of absorption and emission spectra of mononuclear Ir complex and dinuclear **2-PF₆**. Photoluminescence quenching caused by electron transfer (ϕ_{en} going from 9.1% to 0.15%).



Dinuclear complexes are accessible by a successive synthesis route. After coordination of the photosensitizer to the N,N'-phenanthroline a second metal centre can coordinate selectively by removing the cyanoethyl protective groups under basic conditions with *tert*-BuOK. The investigated synthetic strategy could also be applied in Cu(I) complexes with chelating phosphine ligands.



Selected bond lengths [Å] and angles [°]	
Cu1-N1	2.028
Cu1-N2	2.062
Cu1-P1	2.234
Cu1-P2	2.231
S1-S2	3.234
N1-Cu1-N2	81.45

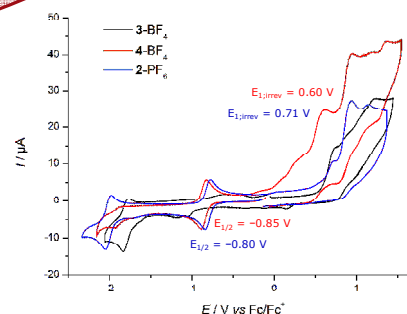
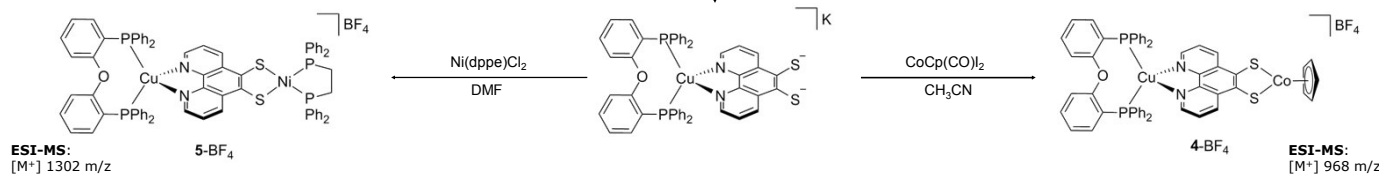


Fig. 5: Cyclic voltammetry of **3-BF₄** (black), **4-BF₄** (red) and **2-PF₆** (blue) in CH₃CN (0.15 M *n*-Bu₄NPF₆, 100 mV/s).

Comparison of the redox potentials of the Cu(I) complexes **3-BF₄** and **4-BF₄** show an additional reversible potential at -0.85 V from the redox pair Co(III)/Co(II) similar to the signal in **2-PF₆**. Moreover the irreversible potential at 0.60 V is in the range of the potential of Co-dithiolate moiety.



[1] D. Schallenberg, A. Neubauer, E. Erdmann, M. Tänzler, A. Villinger, S. Lochbrunner, W. W. Seidel, *Inorg. Chem.* **2014**, *53*, 8859.

[2] N. Armadori, G. Accorsi, M. Holler, O. Moudam, J.-F. Nierengarten, Z. Zhou, R. T. Wegh, R. Welter, *Adv. Mater.* **2006**, *18*, 1313.

[3] S.-P. Luo, E. Mejía, A. Friedrich, A. Pazidis, H. Junge, A.-E. Surkus, R. Jackstell, S. Denurra, S. Gladiali, S. Lochbrunner, M. Beller, *Angew. Chem. Int. Ed.* **2013**, *52*, 419.