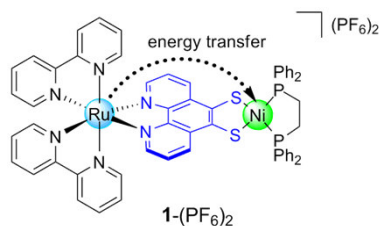


# Electron Cascade via a Phenanthroline-5,6-dithiolate Bridge

Elisa Erdmann, Alexander Villinger, Wolfram W. Seidel\*



Charge and energy transfer are key elements in photocatalysis. A variety of polynuclear complexes with Ru(II) or Ir(III) chromophores have shown remarkable potential of charge separation or energy transfer.[1] To achieve light-driven charge separation ligands with different coordination sites are particular interesting, because they are directional. Phenanthroline-5,6-dithiolate combines the rigid structure of the phenanthroline with a dithiolate function in 5,6-position as classical donor groups. We synthesised the first dinuclear complex  $1-(PF_6)_2$  with the specific bridging ligand and the electrochemical properties disclose an oxidation potential at 0.47 V for the oxidation of the metal dithiolate moiety (Fig. 4).[2]

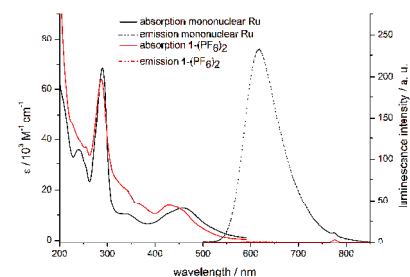
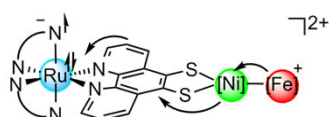


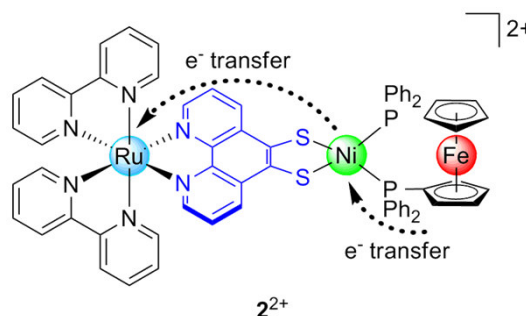
Fig. 1: Comparison of absorption and emission spectra of mononuclear Ru complex and dinuclear complex  $1-(PF_6)_2$ . Photoluminescence quenching caused by energy transfer ( $\phi_{PL}$  going from 13% to 0.05%).

The replacement of dppe by the ferrocene diphos ligand (dppf) leads to the first trinuclear complex  $2-Cl_2$  with three different metal centres. Nickel phosphine complexes especially with non-innocent ligands like dithiolates are potentially active in hydrogen evolution.[3] Comparison of  $1-(PF_6)_2$  with  $2-Cl_2$  shows the benefits of the three metal electron cascade for the generation of a long distance charge separated state. The first excited state of the photosensitizer is based on the bipyridine and the electron hole at the Ru can be filled with an electron coming from the dppf ligand above the Ni centre and the bridging ligand.



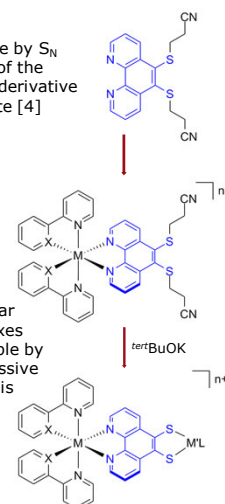
idea

pioneer



synthesis

- Accessible by  $S_N$  reaction of the bromine derivative by thiolate [4]



- Dinuclear complexes accessible by a successive synthesis route

properties

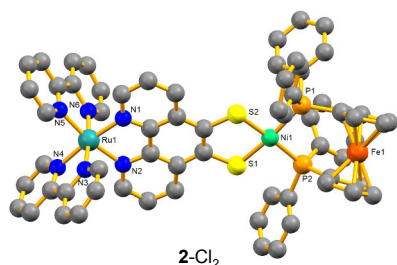


Fig. 3: Molecular structure of  $2^+$  in the crystal. Selected bond lengths [Å] and angles [°]: Ru1-Ni1 8.295(10), Ni1-Fe1 4.184(7), S1-Ni1-S2 89.3(2), P1-Ni1-P2 97.3(2).

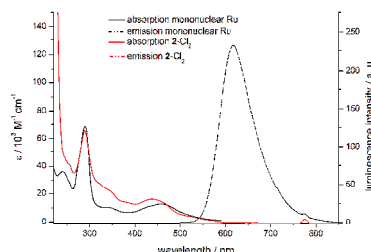


Fig. 3: Comparison of absorption and emission spectra of mononuclear Ru complex and dinuclear complex  $2-Cl_2$ . Effective photoluminescence quenching is shown ( $\phi_{PL}$  going from 13% to 0.2%).

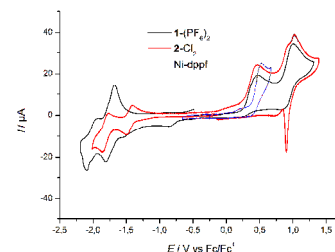


Fig. 4: Comparison of cyclic voltammetry of  $1-(PF_6)_2$  (black),  $2-Cl_2$  (red) and Ni(dppf)(Cl) $_2$  (blue) in  $CH_2Cl_2$  (0.15 M *n*-Bu $_4$ NPF $_6$ , 100 mV/s).

- Emission spectra show a very effective photoluminescence quenching
- Oxidation of the NiS $_2$  moiety and dppf moiety are comparable and similar to the potential in  $1-(PF_6)_2$
- By comparison of  $E^*$  representing the oxidation power of photoexcited Ru $^{III}$ -bipy $^{\cdot-}$  an exergonic electron transfer from the Ni-dithiolate moiety to the Ru centre is possible

	$E_{1/2}$ (ground state)	$E^*$ (excited state)
	reduction	oxidation
Ru	(-1.49 V)	+0.99 V
$1-(PF_6)_2$	-1.74 V	(+0.47 V)
$2-Cl_2$	-1.45 V	(+0.47 V)
	reduction	oxidation
		-1.27 V
		+0.54 V
		+0.81 V

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