Universität Rostock

Traditio et Innovatio

Dinuclear Ru and Ir Complexes with Bridging Phenanthroline-5,6-dithiolate

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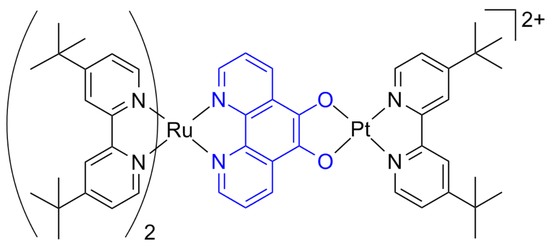
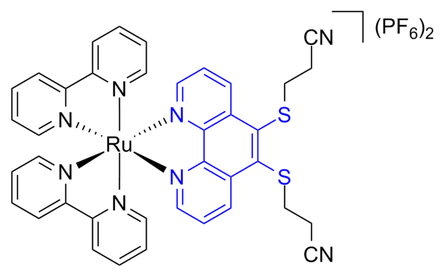
Introduction



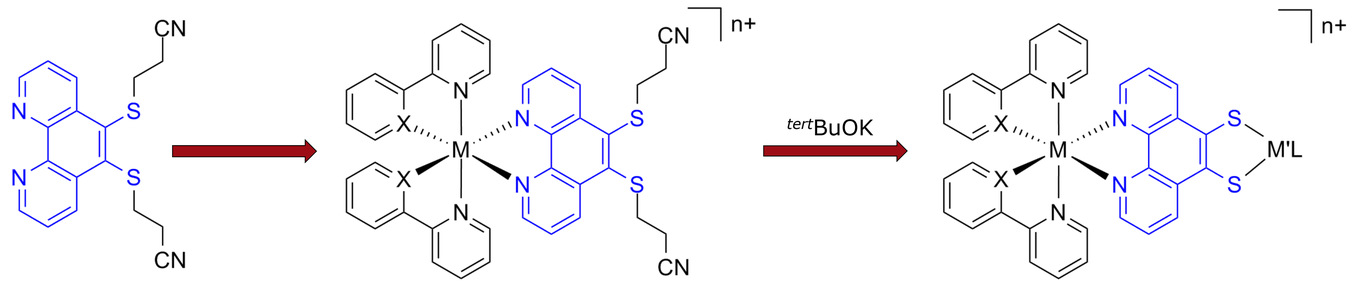
I

Charge and energy transfer are the key elements in photocatalysis, and their understanding and optimization are of crucial importance. Bridging two metal centers by phenanthroline-5,6-diolate has been thoroughly investigated by PIERPONT and EISENBERG proving the strong intermetallic electronic cooperativity in those systems (**I**). [1,2] Phenanthroline derivatives with sulfur substitution in the 5,6-position and respective monomolecular complexes with Ru(II) have been reported for example by HUDHOMME (**II**).[3]



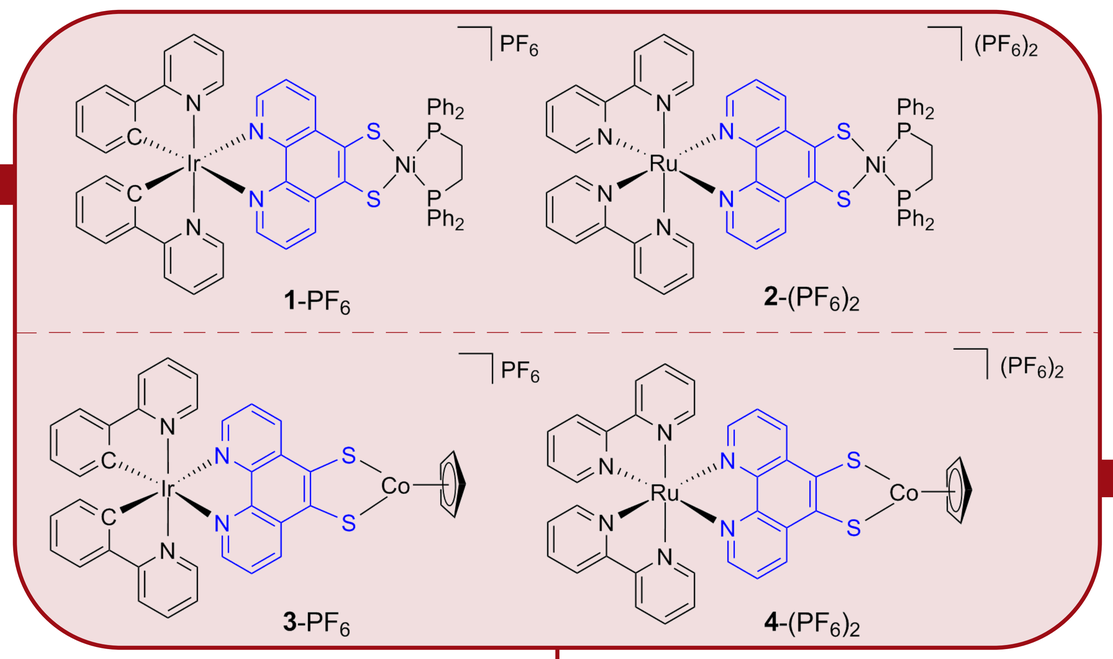
II

We use the directional ligand phenanthroline-5,6-dithiolate providing an intermetallic electronic cooperativity. Due to the different coordination sites and with the cyanoethyl protective group, dinuclear complexes are easily accessible by a consecutive coordination strategy.



A drastic drop of the luminescence quantum yield going from mononuclear to the dinuclear complexes could be detected independent of the second coordinated metal centre.

Energy transfer



1-PF_6 **2**-$(PF_6)_2$ **3**-PF_6 **4**-$(PF_6)_2$

Low-temperature luminescence measurements of **1**-PF_6 and **2**-$(PF_6)_2$ show the typical luminescence rigidochromic effect and only a partial luminescence recovery for the dinuclear complexes relating to ambient temperature solution and the mononuclear prototypes. The excited state potentials were calculated using the zero–zero energy E_{00} values.

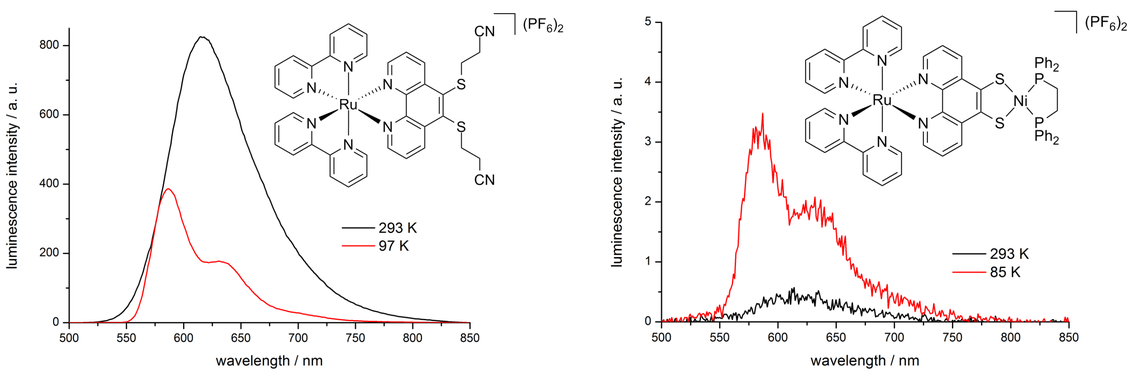


Fig. 1: Low temperature emission spectra of mononuclear and the related dinuclear complex **2**-$(PF_6)_2$.

	τ_{PL}	Φ_{PL}
Ru	2.3 µs	0.13
Ru/Ni	400 ns	0.0005
Ir	490 ns	0.091
Ir/Ni	440 ns	0.0064

The similarity of the determined lifetimes and the difference in quantum yields in Ir complexes disclose the existence of a second, much faster deactivation channel. So we expect a fast DEXTER energy transfer.[4]

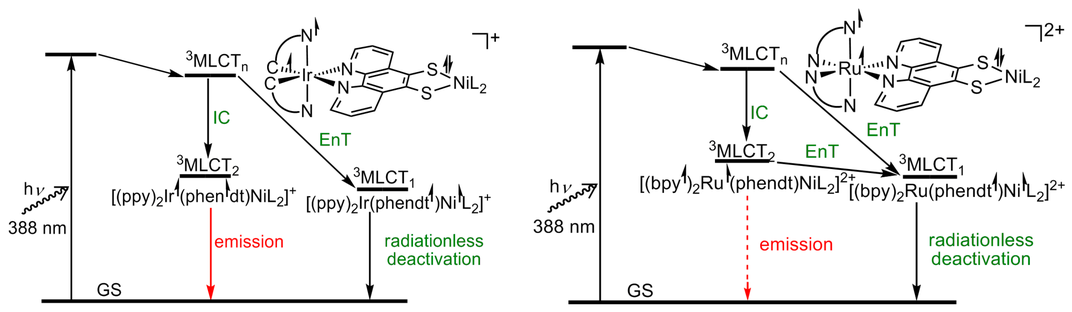


Fig. 2: Qualitative energy diagram for charge transfer states in **1**-PF_6 (left) **2**-$(PF_6)_2$ (right) upon excitation.

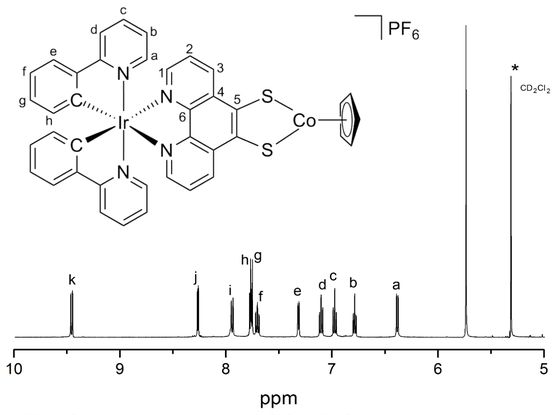


Fig. 3: ^{1}H NMR spectra of **3**-PF_6 for characterisation.

Electron transfer

New complexes with Co(III) (**3**-PF_6 and **4**-$(PF_6)_2$) at the dithiolate moiety have a strong affinity to act as electron acceptor and force an electron transfer.

3-PF_6 and **4**-$(PF_6)_2$ show besides efficient luminescence quenching an additional redox potential from the Co^{III}/Co^{II} redox pair. Comparison of E^* representing the reducing power of the photoactivated Ir^{IV}-$phen^-$ system render an electron transfer to the Co complex moiety possible.

	$E_{1/2}$ (ground state)		E^* (excited state)	
	reduction	oxidation	reduction	oxidation
Ir	(-1.52 V)	+0.87 V		-1.46 V
Ir/Co	-2.01 V	(+0.71 V)	+0.57 V	
Ru	(-1.49 V)	+0.99 V		-1.27 V
Ru/Co	-1.79 V	(+0.51 V)	+0.57 V	

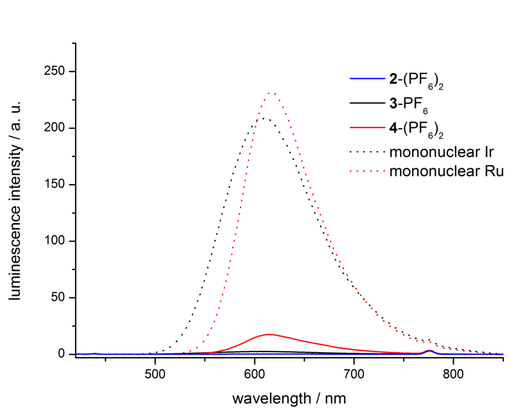


Fig. 4: Emission spectra of **2**-$(PF_6)_2$ (blue), **3**-PF_6 (black) and **4**-$(PF_6)_2$ (red) compared to the mononuclear species Ir (black dotted) and Ru (red dotted).

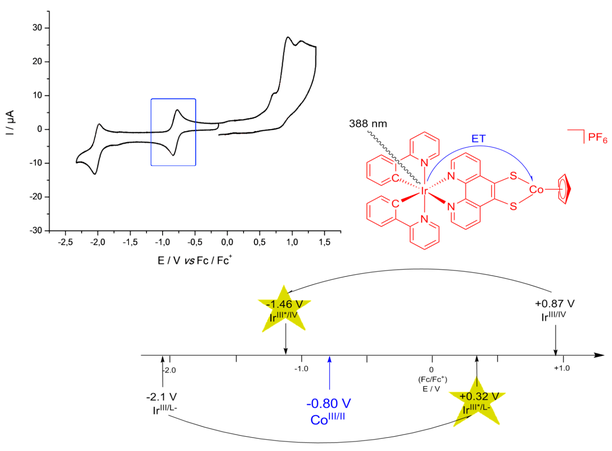


Fig. 5: Cyclic voltammetry of **3**-PF_6 (top) and redox potentials of the excited state (bottom).

[1] G. A. Fox, S. Bhattacharya, C. G. Pierpont, *Inorg. Chem.* **1991**, *30*, 2895.
[2] W. Paw, R. Eisenberg, *Inorg. Chem.* **1997**, *36*, 2287.
[3] B. Chesneau, A. Passelande, P. Hudhomme, *Org. Lett.* **2009**, *11*, 649.
[4] D. Schallenberg, A. Neubauer, E. Erdmann, M. Tänzler, A. Villinger, S. Lochbrunner, W. W. Seidel, *Inorg. Chem.* **2014**, *53*, 8859.

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