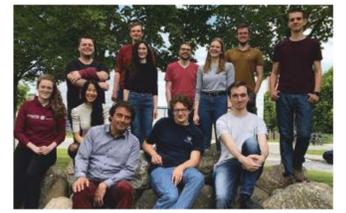


New Alkyne Complex Based Framework for Visible Light induced Electron Transfer

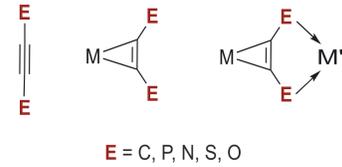


Seidel Group

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Introduction

- W(II)-alkyne complexes bearing donor atoms in both α -positions
- combines redox-active complex moiety with a potentially chelating unit
- valuable building blocks for polynuclear compounds with a short metal-metal distance and interesting redox behaviour
- so far, we were able to form heterobimetallic complexes using C, P, N, S or O as donor atoms [1]



This project

- this project is focused on the new C,N_{py} -donor combination to mimic the phenyl pyridine ligand [2]
- in the literature, only C,C - or $N_{py}N_{py}$ -bridged heterobimetallic alkyne complexes are known [3]
- within these new complexes the potential light induced electron transfer from the tungsten-centre towards the photocentre is investigated

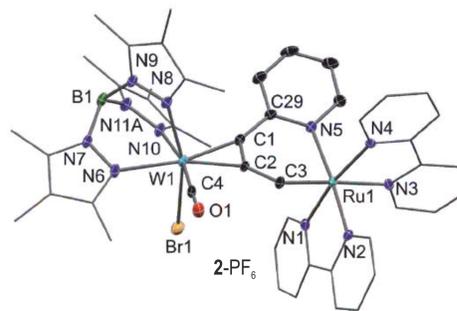
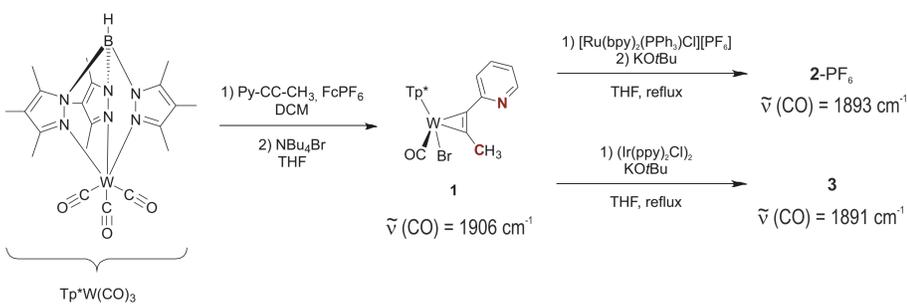
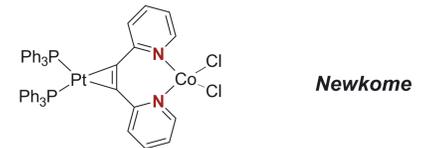
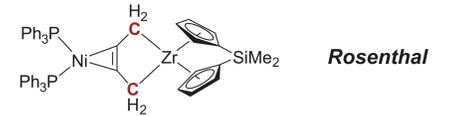


Fig. 1: Molecular structure of 2' in the crystal. Selected bond lengths [Å] and angles [°]: W1-C4 1.945(4), C1-C2 1.323(5), C2-C1-C29 135.7(4), C1-C2-C3 128.2(4), N5-Ru1-C3 94.04(12).

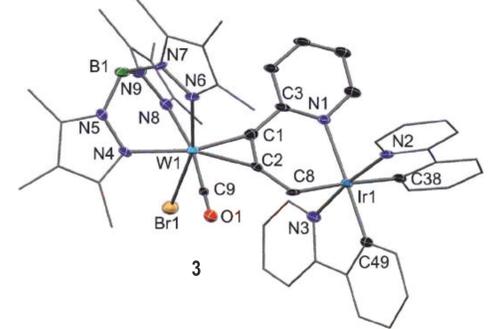
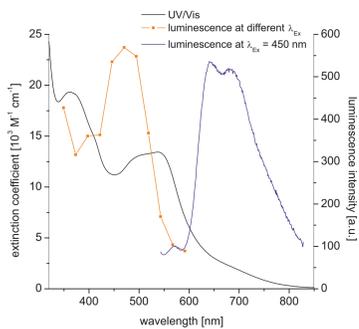
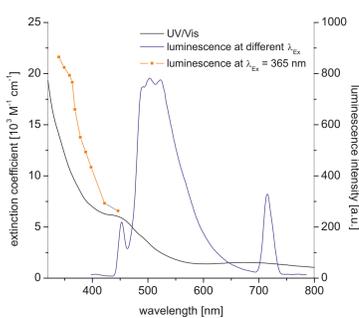


Fig. 2: Molecular structure of 3 in the crystal. Selected bond lengths [Å] and angles [°]: W1-C9 1.932(10), C1-C2 1.312(13), Ir1-W1 5.001, C1-C2-C8 137.2(10), C2-C1-C3 128.9(9), N1-Ir1-C8 91.8(3).



	Φ [%]
2-PF ₆	0.006
3	0.3
$Ir(ppy)_3$	73.0
$[Ru(bpy)_3]^{2+}$	9.5



The drastically quenched quantum yields suggest an electron transfer from the W(II) towards the photo-excited metal-centre.

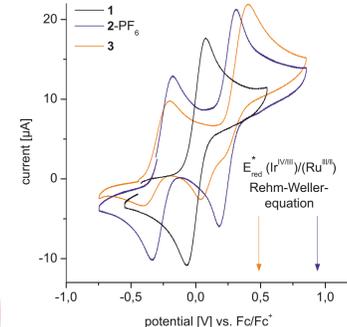
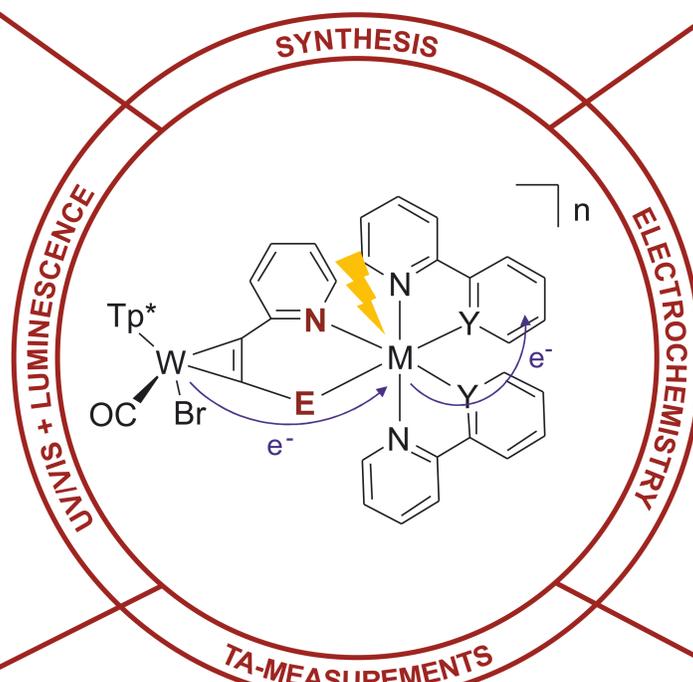


Fig. 4: CV measurements of 1, 2-PF₆ and 3 in CH_2Cl_2 vs. Fc/Fc^+

- oxidation is metal based
1: W-based
2-PF₆ and 3
1. oxidation W-based
2. oxidation Ru/Ir-based
- reduction is ligand based
2-PF₆: bpy-based
3: py-based

Rehm-Weller equation: redox potential for the photoexcited Ir(IV)- or Ru(III)-centre

	$E_{1/2}(Ox)$ [V]	$E_{1/2}(Red)$ [V]
1	+0.002	
2-PF ₆	-0.26; +0.25	-1.42
3	-0.33; +0.22	-1.55

$E_{1/2}^*(Ru^{III}) = 0.49\text{ V}$
 $E_{1/2}^*(Ir^{IV}) = 0.85\text{ V}$

The electron transfer from W(II) to the photoexcited metal centres is thermodynamically possible.

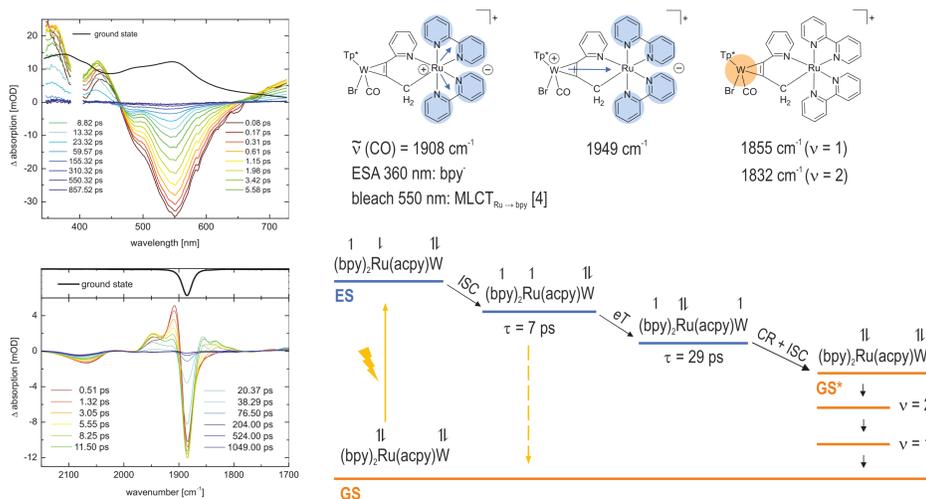


Fig. 5: fs-TA measurements of 2-PF₆ in CH_3CN ; pump pulses at 400 nm; TA-UV/Vis (top) and TA-IR (bottom).

ISC: Intersystem crossing; eT: electron transfer; CR: charge recombination
GS: ground state; ES: excited state

The light induced electron transfer from W(II) towards Ru(III) leads to charge separated state between the W(III) and the bipyridyle ligand ($\tau = 29\text{ ps}$).

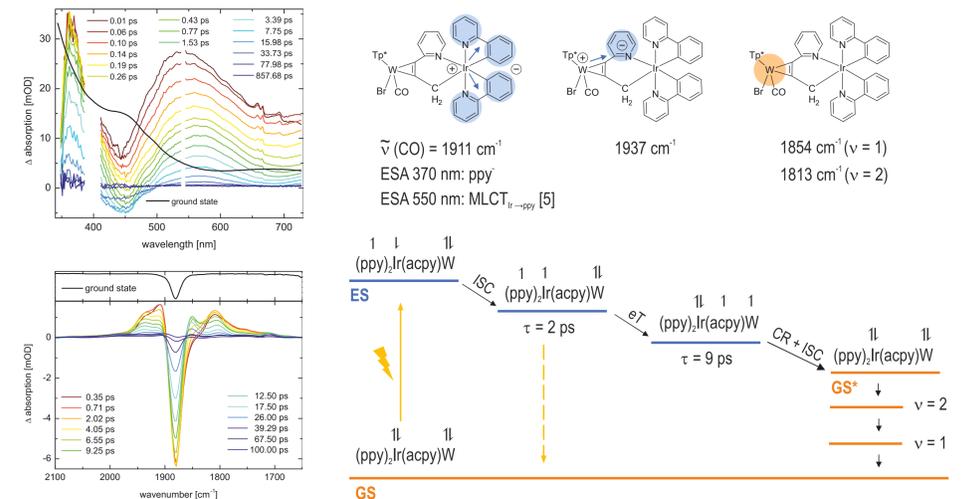


Fig. 6: fs-TA measurements of 3 in CH_3CN ; pump pulses at 400 nm; TA-UV/Vis (top) and TA-IR (bottom).

ISC: Intersystem crossing; eT: electron transfer; CR: charge recombination
GS: ground state; ES: excited state

The light induced electron transfer from W(II) towards the Ir(IV) leads to a charge separation between the W(III) and the pyridine ligand ($\tau = 9\text{ ps}$).

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