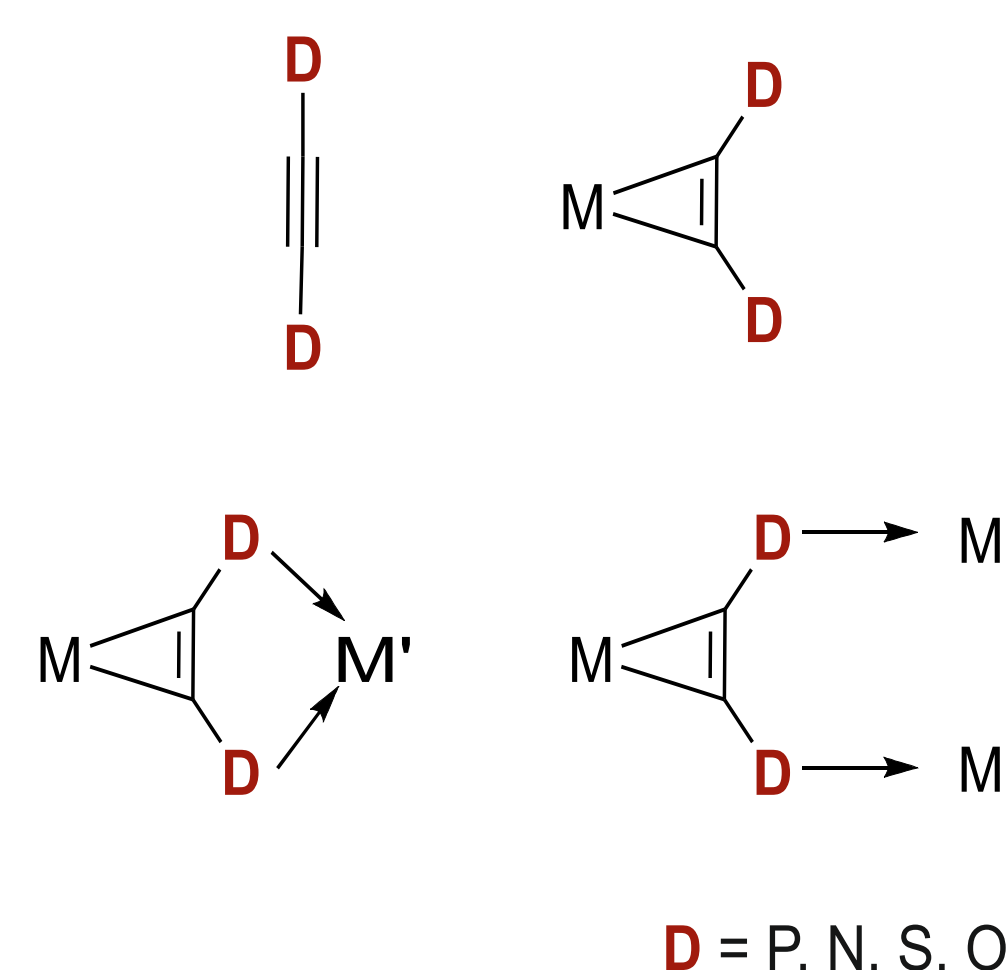


New Alkyne Complex Based Framework for Visible Light induced Electron Transfer

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Introduction

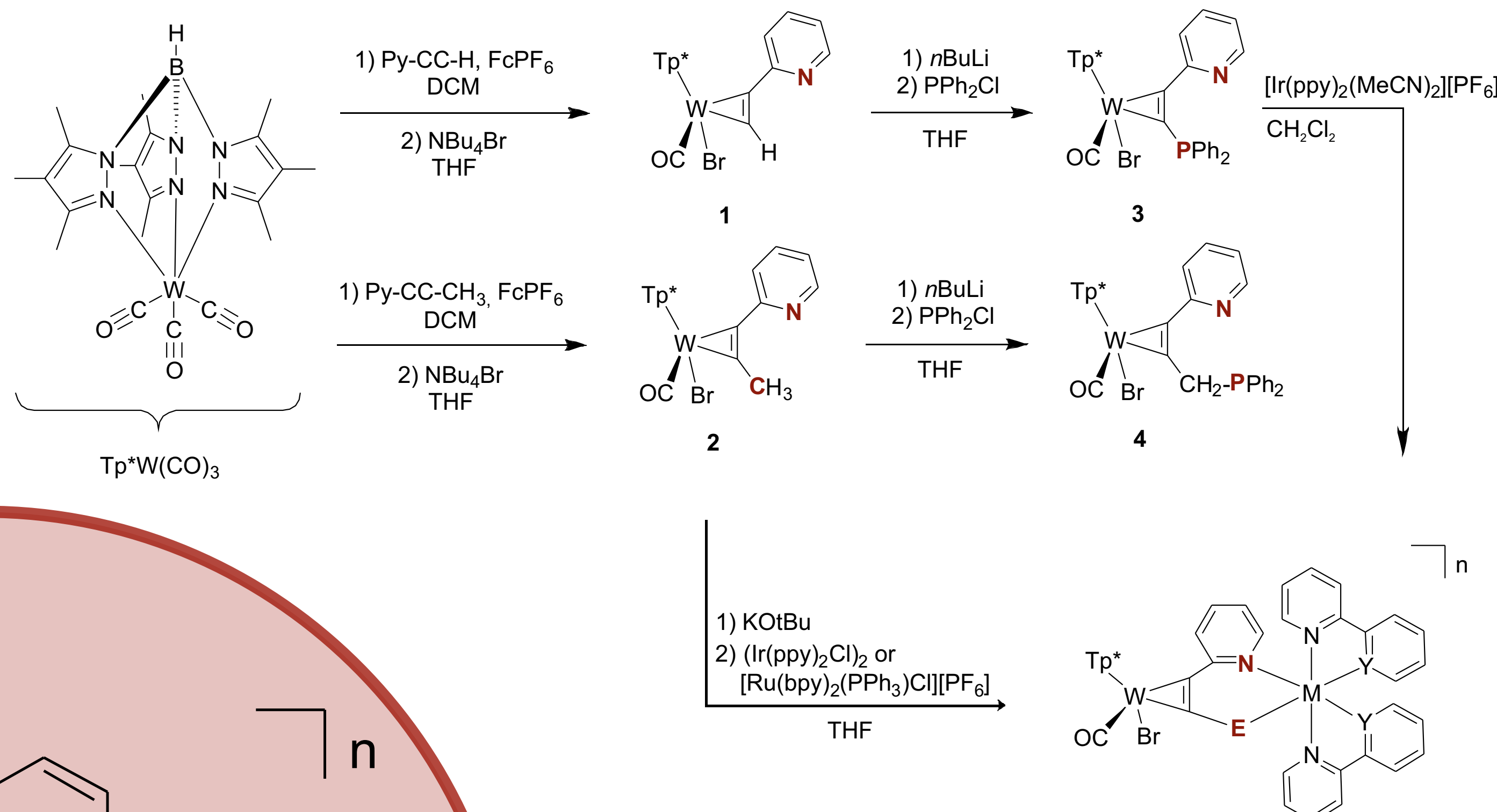


- W(II)-alkyne complexes bearing donor atoms in both α -positions
→ combines redox-active complex moiety with a potentially chelating unit
→ valuable building blocks for polynuclear compounds with a short metal-metal distance and interesting redox behaviour
→ so far, we were able to form heterobimetallic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

This project

- coordination of the alkyne complex via a cyclometallating pyridinyl propyne donor to an Ir(III) or Ru(II) centre, to mimic the phenyl pyridine ligand
- for comparison, we also used two different phosphine groups in place of the carbanion, since phosphines are also suitable donor atoms for photoactive polypyridine substituted complexes [2]

Synthesis



- 5 E = PPh₂, M = Ir, Y = C, n = +1
- 6 E = CH₂PPh₂, M = Ir, Y = C, n = +1
- 7 E = CH₂, M = Ir, Y = C, n = 0
- 8 E = CRu, M = N, Y = , n = +1

UV/vis and luminescence measurements

- UV/vis of **5-PF₆**: shoulder 450 nm is assigned to W(II) to pyridine transitions; weak absorption at 710 nm due to d-d-transitions associated with the W(II)-centre
- UV/vis of **6-PF₆**: shoulder at 500 nm is assigned to W(II) to pyridine transitions; absorption features being associated with the W alkyne complex moiety cannot be observed in the visible range
- compared to the mononuclear Ir(ppy)₃ the quantum yield of **5-PF₆** and **6-PF₆** is quenched to 0.3 and 0.15 %, respectively, due to the electron transfer from the W(II)-centre

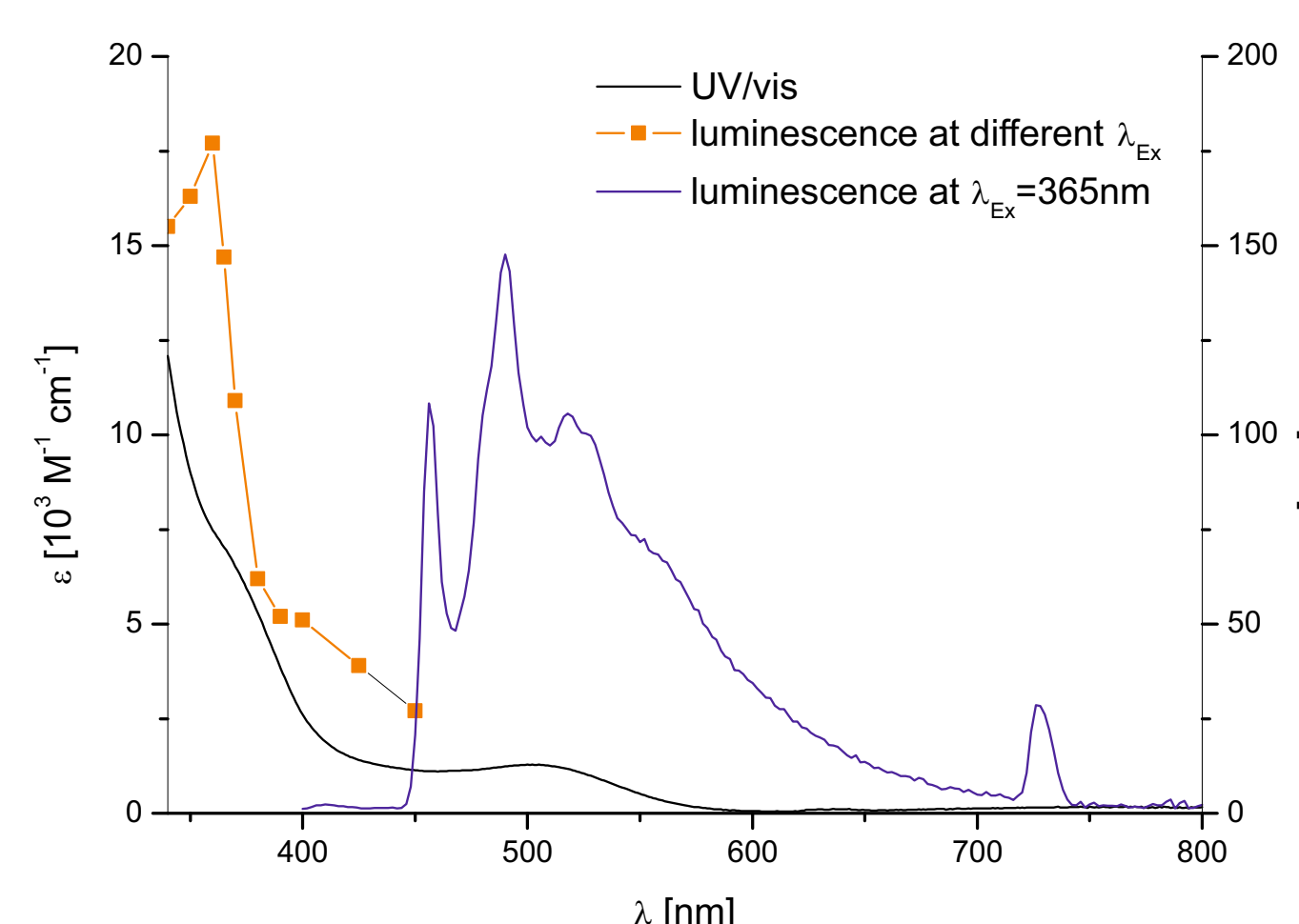


Fig. 1: Absorption spectra (black), luminescence spectra at -196 °C (blue) and excitation spectra (orange dotted) of **5-PF₆**. λ_{exc} = 360 nm, λ_{em} = 500 nm, in 2-Me-THF.

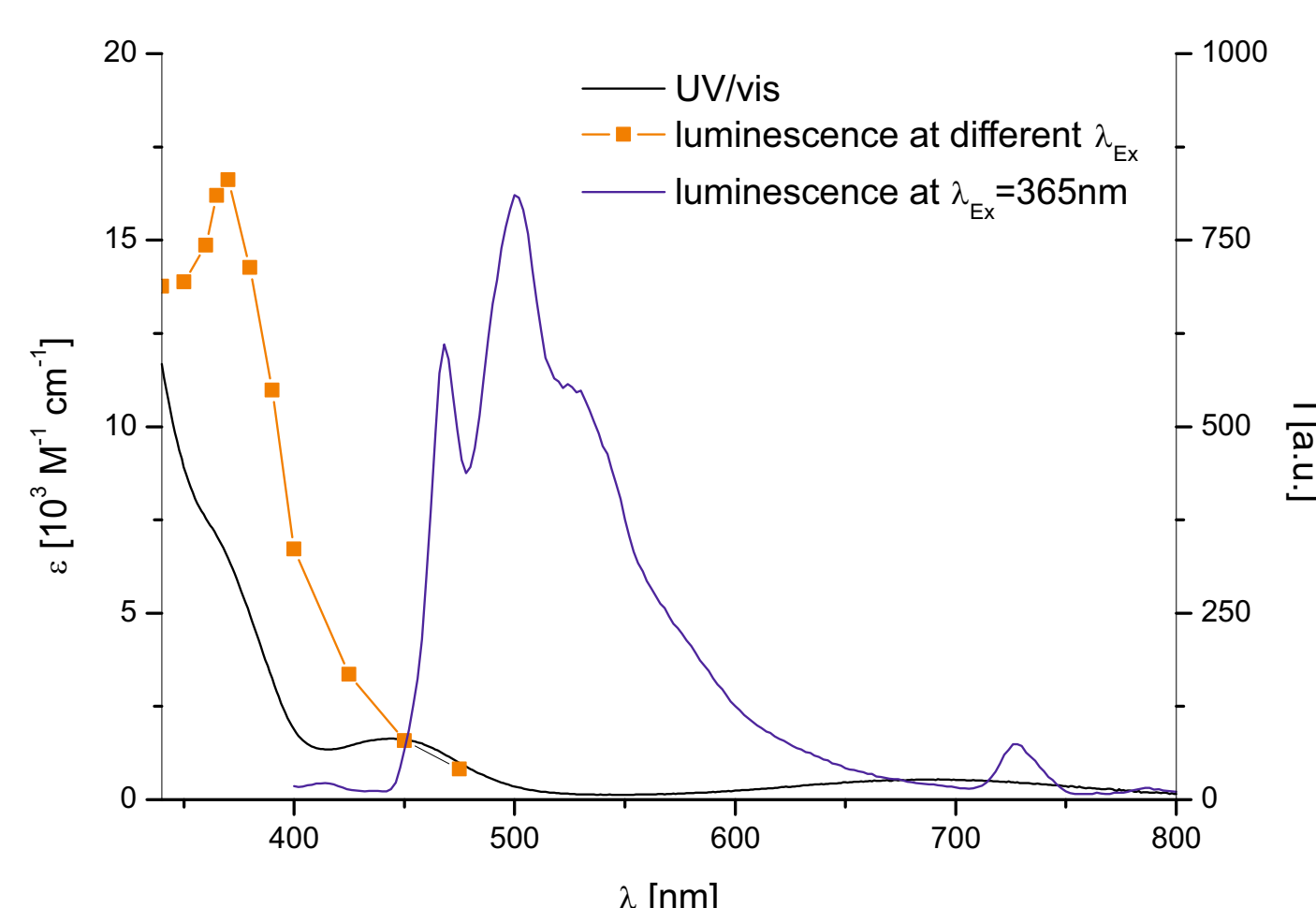


Fig. 2: Absorption spectra (black), luminescence spectra at -196 °C (blue) and excitation spectra (orange dotted) of **6-PF₆**. λ_{exc} = 360 nm, λ_{em} = 500 nm, in 2-Me-THF.

- UV/vis of **7**: shoulder 450 nm is assigned to W(II) to pyridine CT transitions; weak absorption at 710 nm due to d-d-transitions associated with the W(II)-centre
- quantum yield is quenched drastically compared to the mononuclear Ir(ppy)₃ (to 0.3 %), due to the electron transfer from the W(II)-centre
- UV/vis of **8-PF₆**: transitions between 300 and 420 nm are ligand based π - π^* -transitions, while the absorption around 470 nm are assigned to Ru to bipyridine CT transitions
- compared to the mononuclear [Ru(bpy)₂(ppy)][PF₆] the quantum yield is quenched (to 40 %)

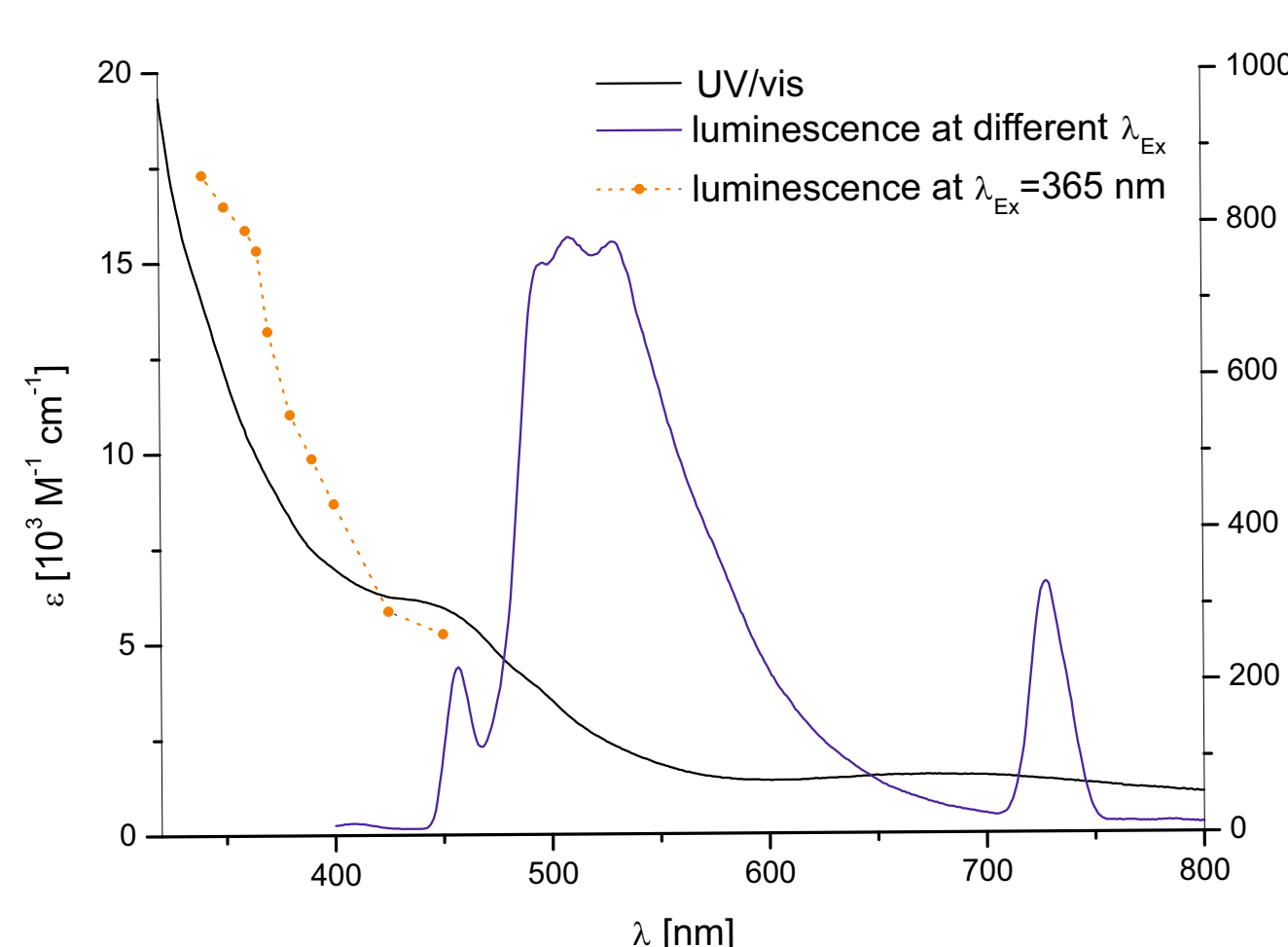


Fig. 3: Absorption spectra (black), luminescence spectra at -196 °C (blue) and excitation spectra (orange dotted) of **7**. λ_{exc} = 360 nm, λ_{em} = 510 nm, in 2-Me-THF.

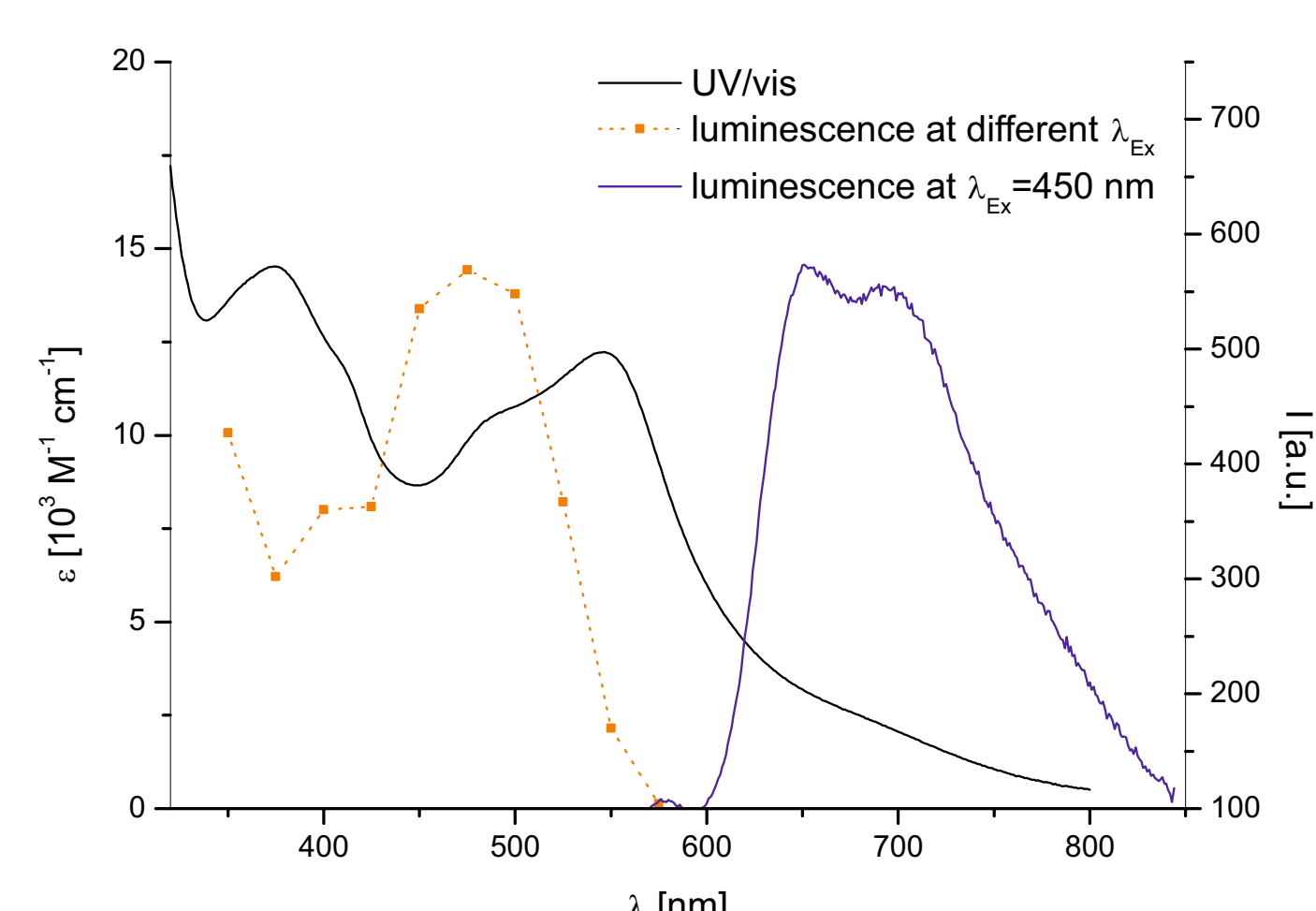


Fig. 4: Absorption spectra (black), luminescence spectra at -196 °C (blue) and excitation spectra (orange dotted) of **8-PF₆**. λ_{exc} = 470 nm, λ_{em} = 650 nm, in 2-Me-THF.

TA measurements

- the predominant broad excited state absorption between 500 and 650 nm, which is typical for a ³MLCT state Ir(IV)(ppy)₂ [4], decreases with a time constant of 5.2 ps
- the resulting state can be assigned to the charge separated W(III)-ppy complex formed by a W(II) to Ir(IV) electron transfer due to the bleach feature at 450 nm

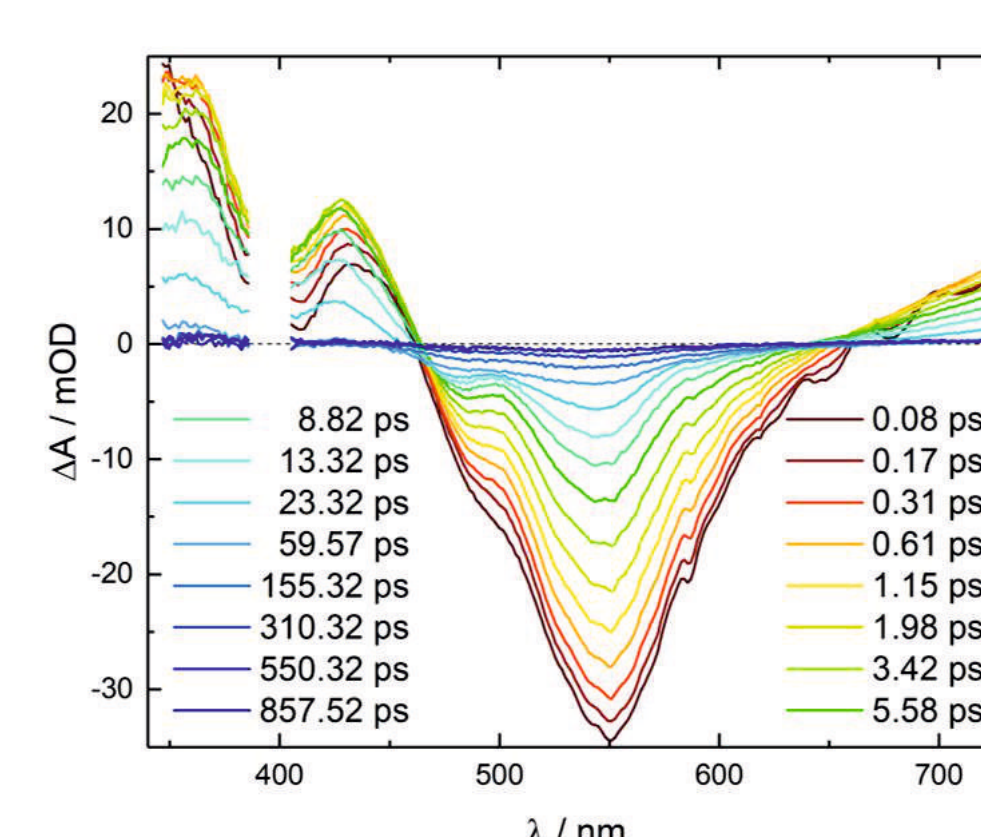


Fig. 6: fs-TA measurements of **8-PF₆** in CH₃CN; 70 fs pump pulses at 490 nm.

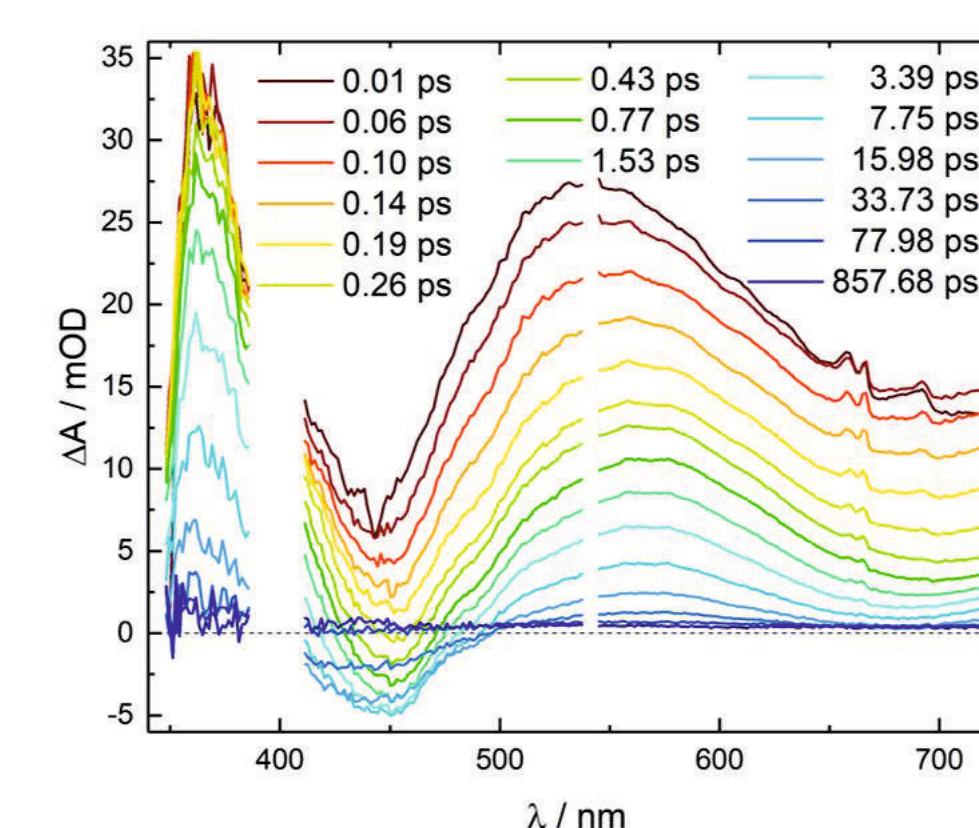


Fig. 5: fs-TA measurements of **7** in CH₂Cl₂; 70 fs pump pulses at 360 nm.

- the ground state bleach between 520 and 650 nm is due to a ³MLCT state Ru(III)(bpy)₂ [5] and decreases with a time constant of 4.1 ps
- the species with a life time of 18 ps is assigned to the intermediate charge separated W(III)-ppy state

CV measurements

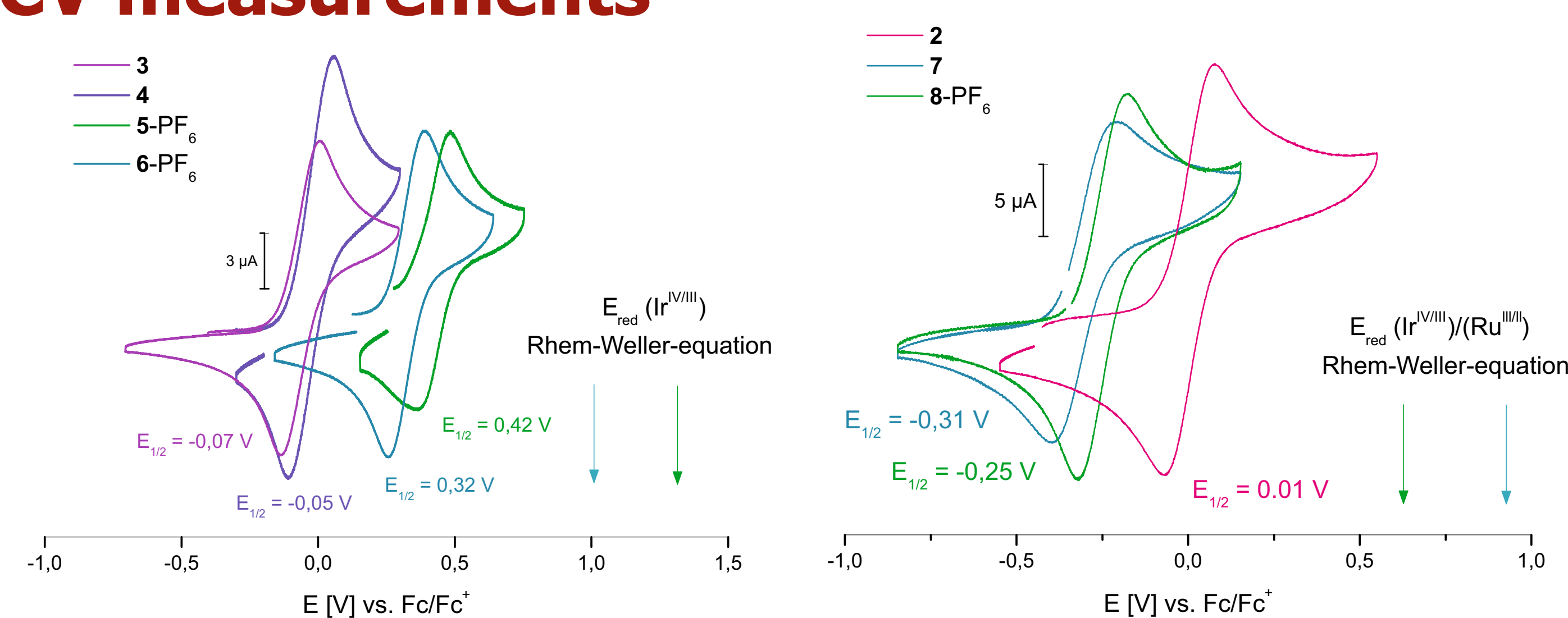


Fig. 7: CV measurements of **2 - 8-PF₆** in CH₂Cl₂ vs. Fc/Fc⁺

- the coordination of the Ir(ppy)₂-moiety via the neutral donors leads to the formation of cationic complexes and a lower electron density at the tungsten centre, resulting in higher redox potentials for **5-PF₆** and **6-PF₆** of 0.42 and 0.32 V, respectively
- coordination to either the Ir(ppy)₂- or Ru(bpy)₂-moiety via the neutral pyridine- and the anionic carbon-donor leads to lower redox potentials compared to the mononuclear complex, indicating a higher electron density at the W(II) centre
- the estimated redox potentials for the photoexcited Ir(VI)- or Ru(III)-centre, via the Rehm-Weller equation reveals that such a transfer is certainly thermodynamically possible

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