

Dinuclear Complexes with Bridging Phenanthroline-5,6-dithiolate

FROM SYNTHESIS TO ELECTROCHEMICAL AND PHOTOPHYSICAL BEHAVIOR

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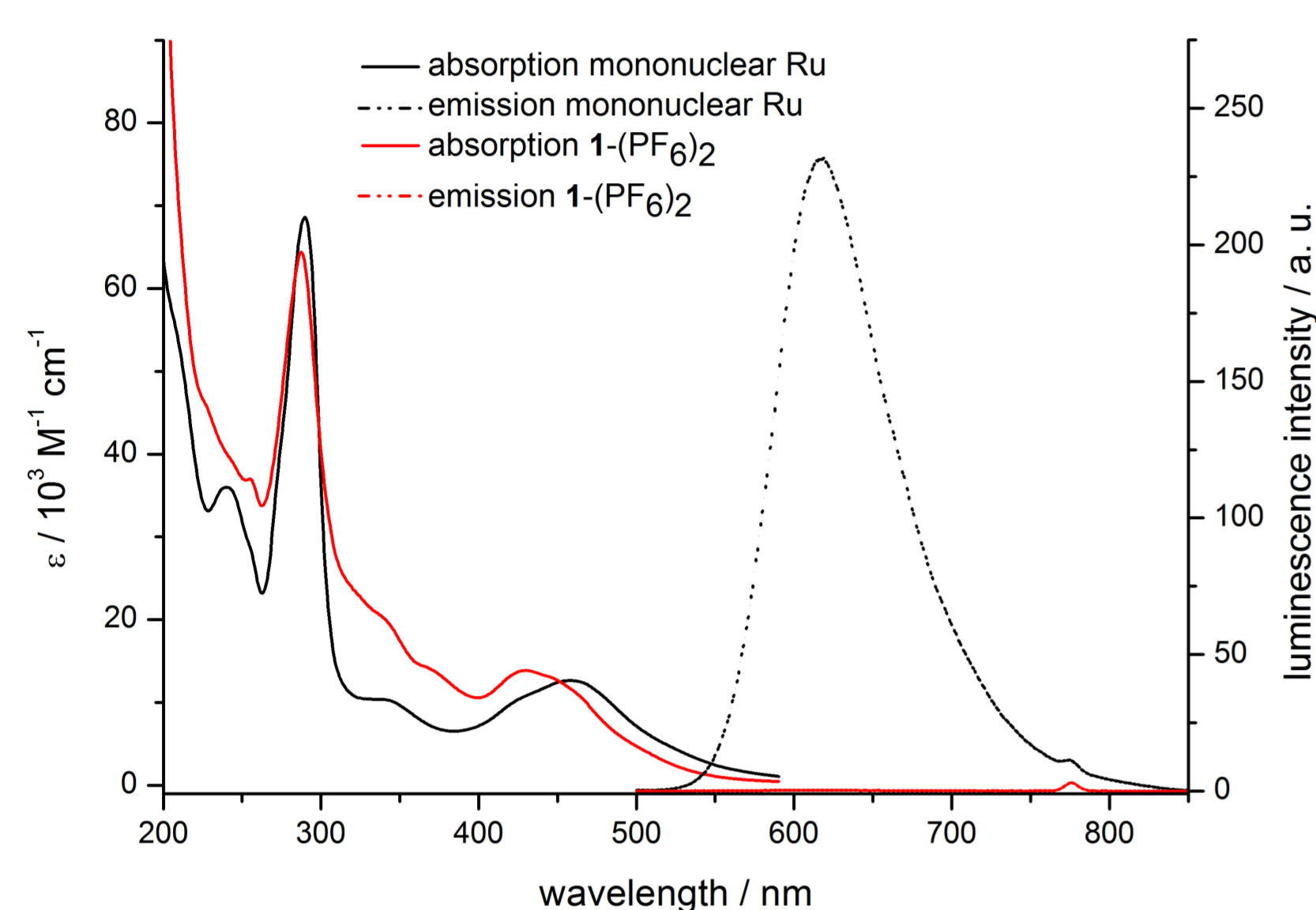
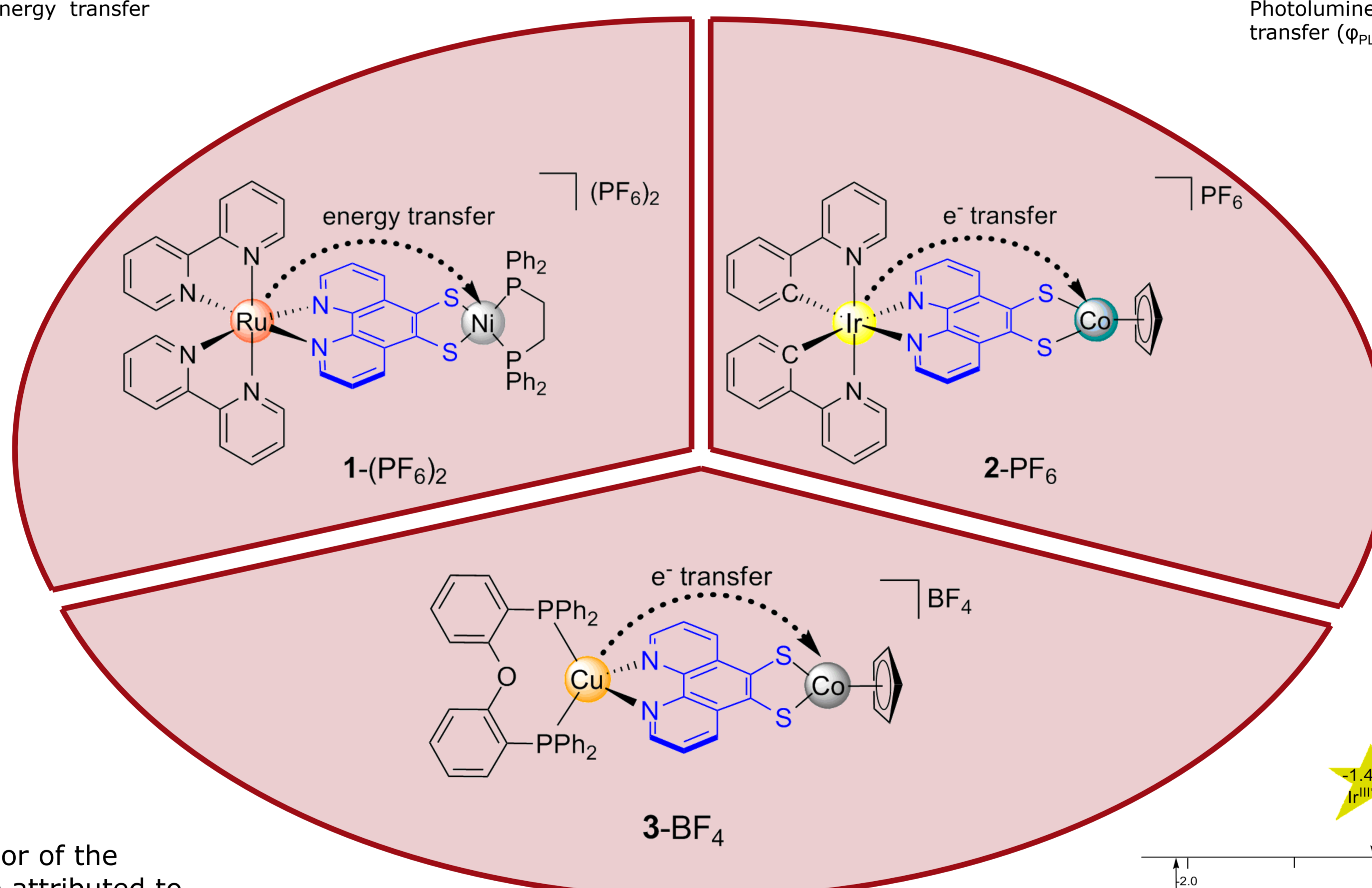


Fig. 1: Comparison of absorption and emission spectra of mononuclear Ru complex and dinuclear complex **1**-(PF₆)₂. Photoluminescence quenching caused by energy transfer (ϕ_{PL} going from 13% to 0.05%).

We use the bridging ligand **phendt**²⁻ providing a strong intermetallic electronic cooperativity. With respect to light-driven charge separation, directional ligands with different coordination sites are very interesting. Therefore, 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.



Charge and energy transfer are the key elements in photocatalysis, and their understanding and optimization are of crucial importance. A variety of polynuclear complexes with Ru(II) or Ir(III) chromophores have shown remarkable potential of charge separation or energy transfer.[1] The close connection of a photosensitizer and an active catalyst by a rigid ligand could have considerable advantages. We synthesized new dinuclear complexes with bridging phenanthroline-5,6-dithiolate (**phendt**²⁻) and investigated the electrochemical and photophysical properties.

All complexes show a drastic drop of the luminescence quantum yield going from mononuclear to the dinuclear complexes. Accordingly, the complexes Ru/Ir(phendt)Ni like **1**-(PF₆)₂ show an energy transfer by DEXTER mechanism.[2]

The different luminescence behavior of the Ru(bpy)₂²⁺ and Ir(ppy)₂⁺ could be attributed to differing orbital contributions to the emissive state. According to the frontier orbital ordering, the emissive state in the Ru complex **1**²⁺ is predominantly localized on the bpy and could serve as a rationale for an accessible energy transfer path.

In the Ir complex **2**⁺ a presumed localization of the emissive state on the **phendt** bridging ligand acts with the additional charge as a barrier for the energy transfer. However, the Co(III) dithiolate moiety in complexes **2**⁺ and **3**⁺ has a strong affinity to act as electron acceptor and force an effective electron transfer in **2**⁺ from the photoexcited Ir[ppy]₂ to the Co(III) across **phendt**.

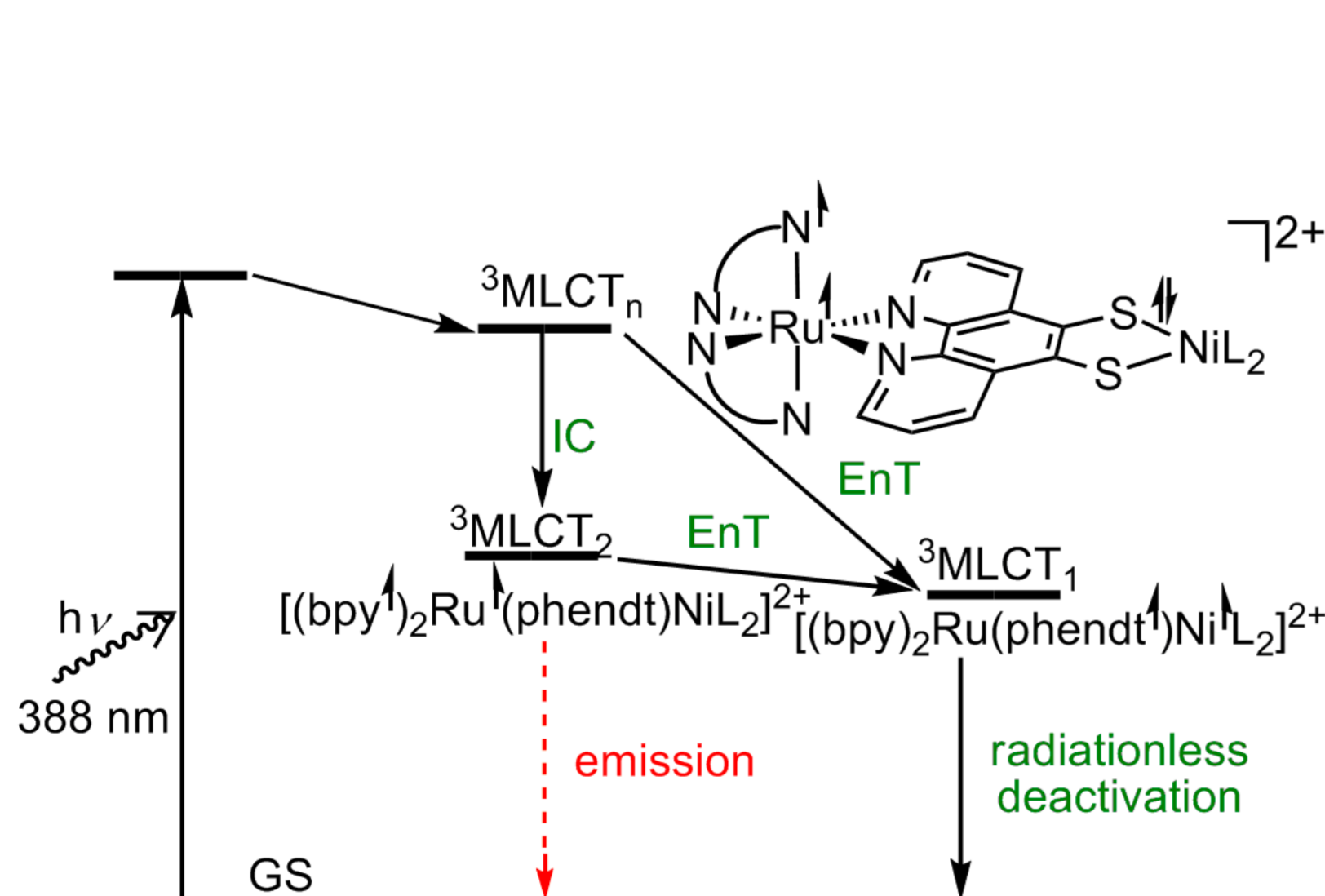


Fig. 4: Qualitative energy diagram for charge transfer states in **1**-(PF₆)₂ upon excitation show effective energy transfer.

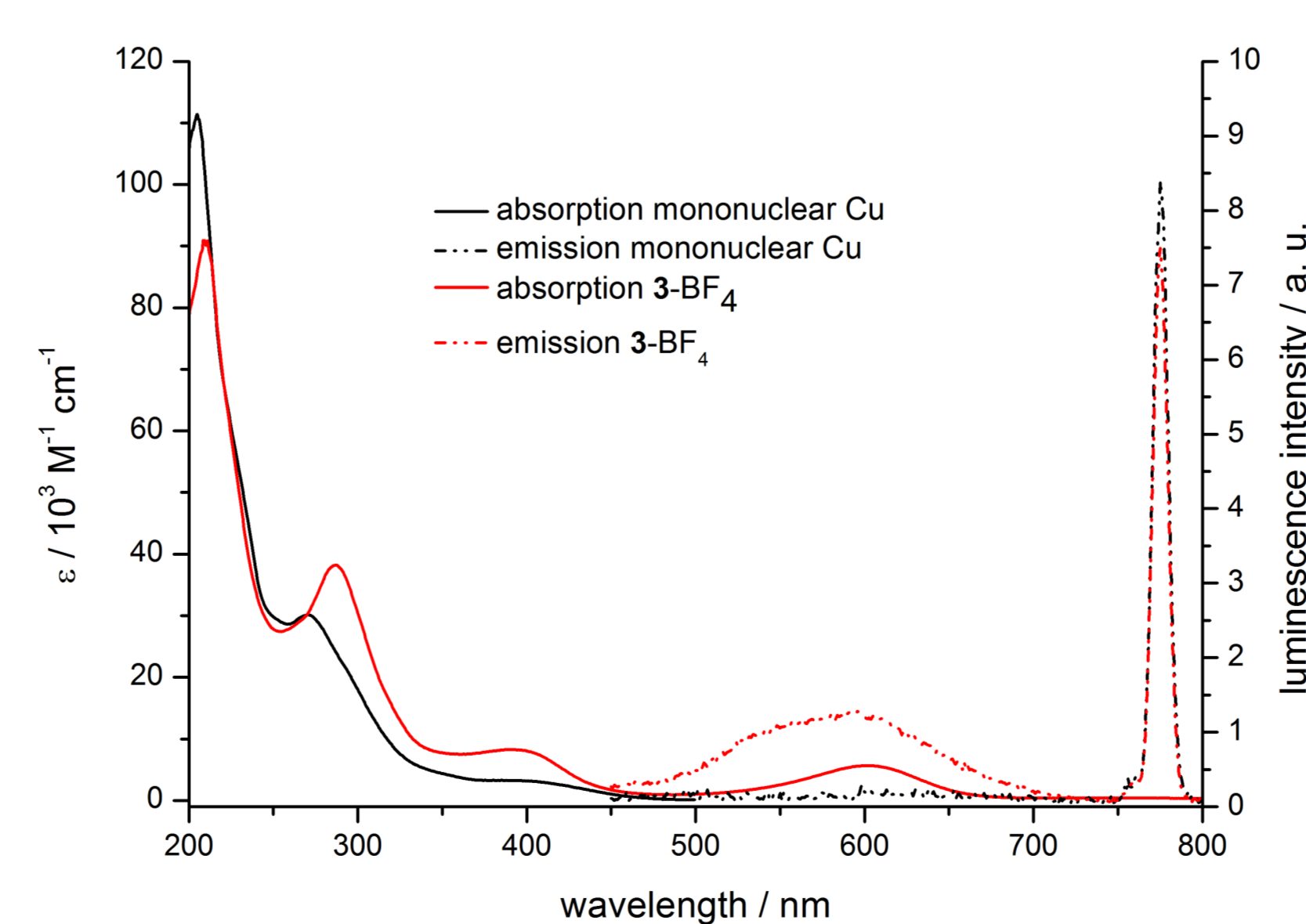


Fig. 5: Comparison of absorption and emission spectra of mononuclear Cu complex and dinuclear complex **3**-BF₄. Photoluminescence quenching in mononuclear complex caused by fast relaxation of the ³MLCT (ϕ_{PL} of **3**-BF₄: 0.16%).

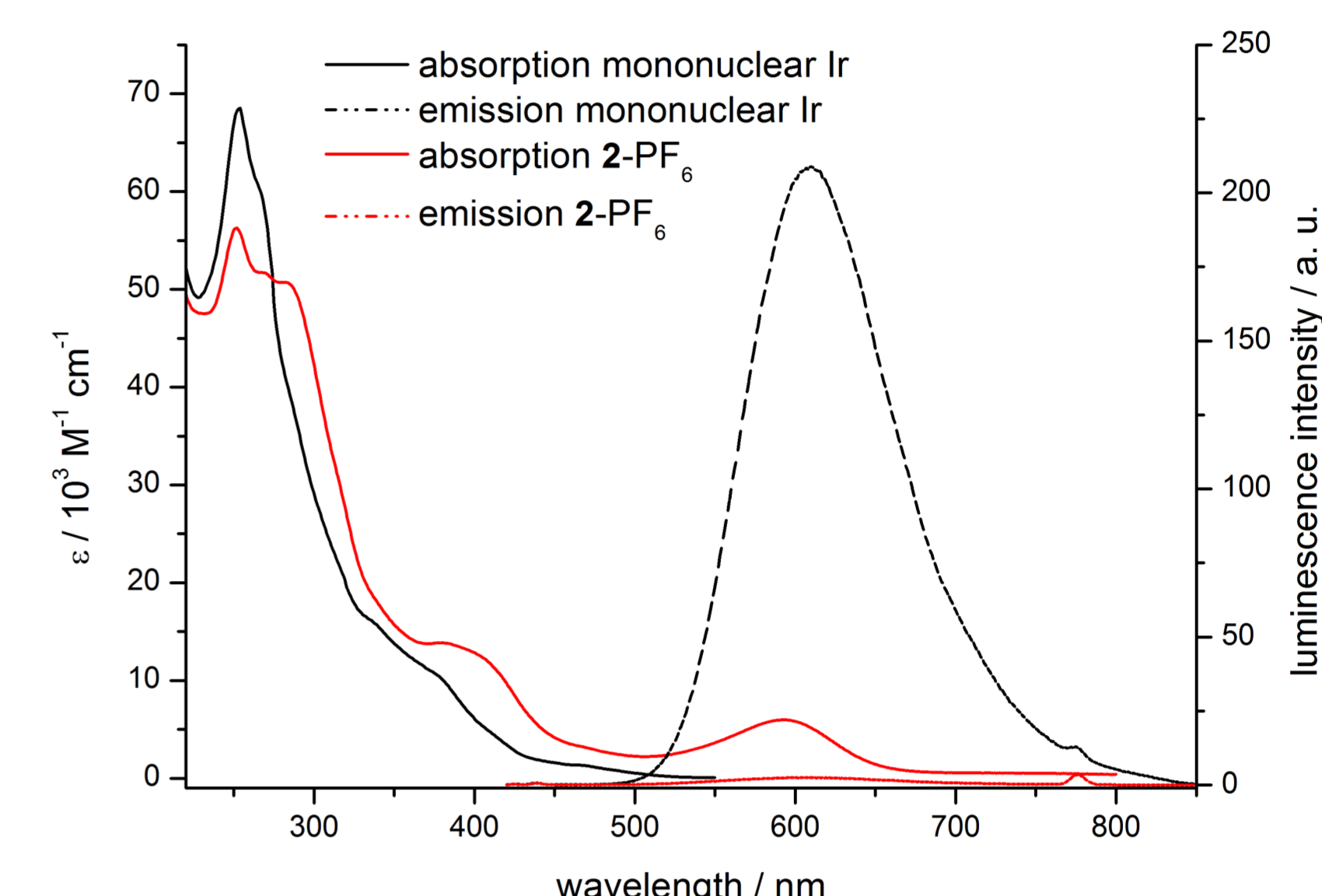


Fig. 2: Comparison of absorption and emission spectra of mononuclear Ir complex and dinuclear **2**-PF₆. Photoluminescence quenching caused by electron transfer (ϕ_{PL} going from 9.1% to 0.15%).

To force charge separation Co(III) complexes were isolated with Ru(II), Ir(III) and Cu(II) photosensitizer (**2**-PF₆ and **3**-BF₄) showing appropriate excited state redox potentials.[3]

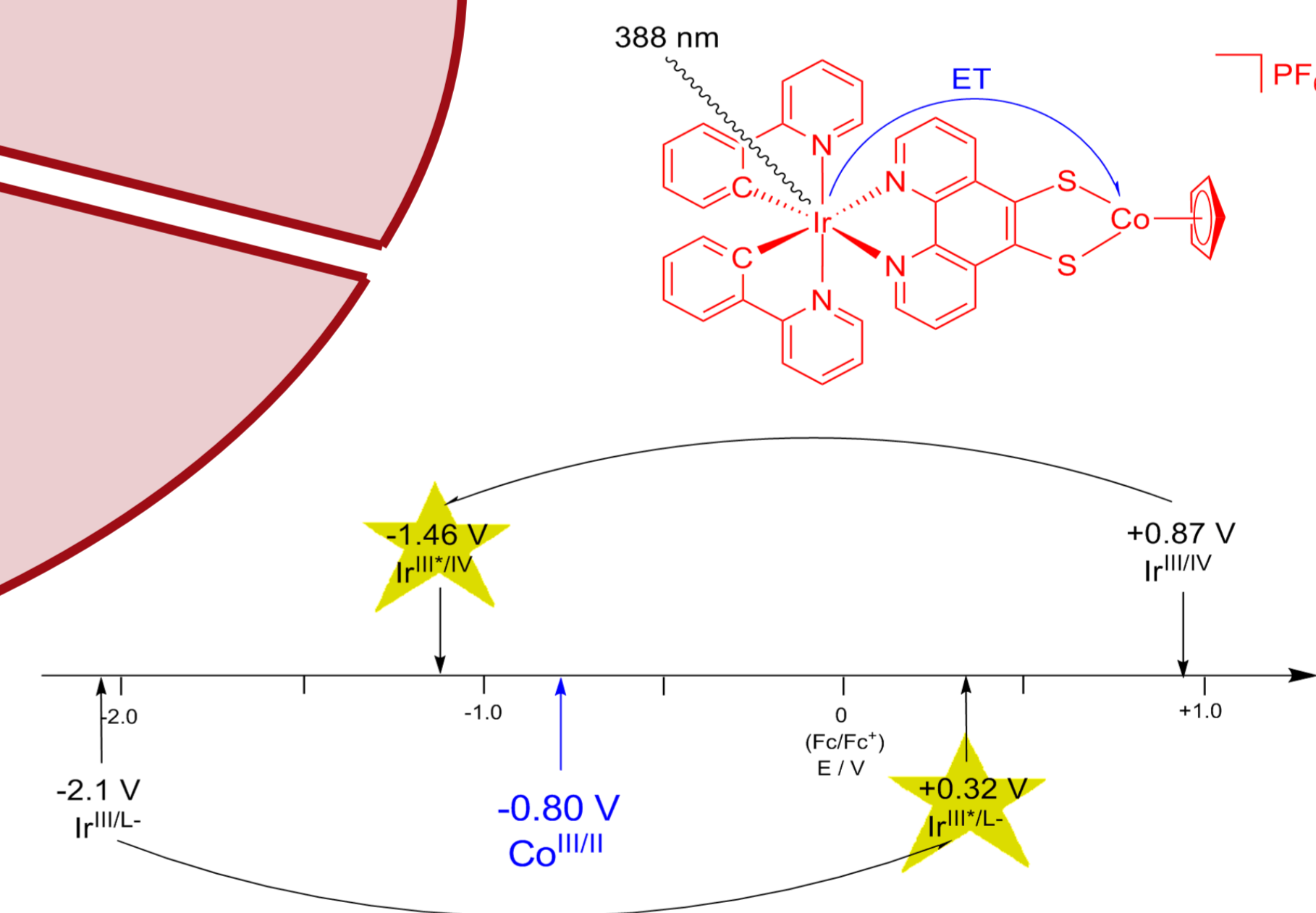


Fig. 3: Redox potentials of the ground and the excited state of **2**-PF₆ render an electron transfer from the photoexcited Ir chromophore to the Co dithiolate moiety possible.

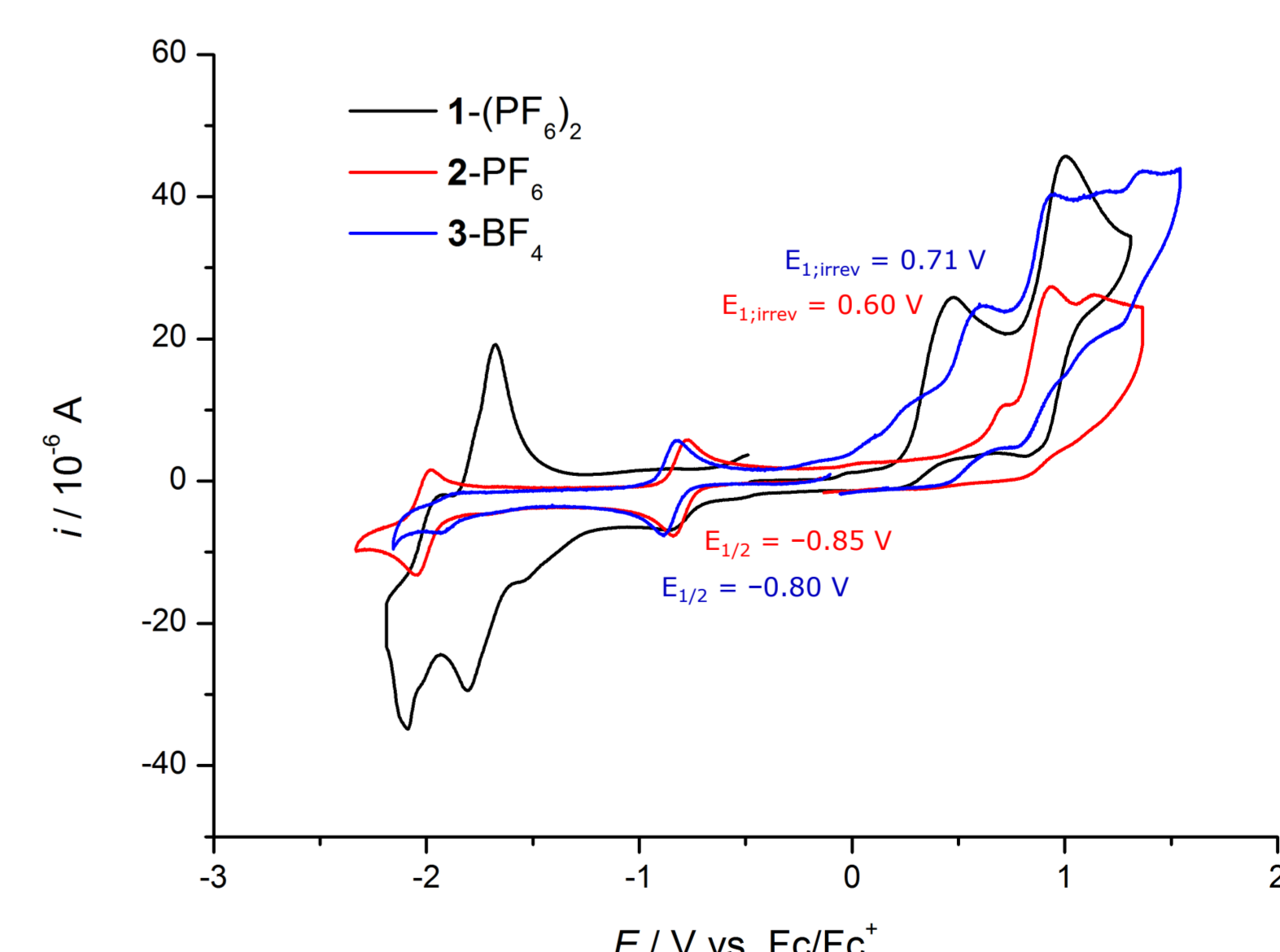


Fig. 6: Comparison of cyclic voltammetry of **1**-(PF₆)₂ (black), **2**-PF₆ (red) and **3**-BF₄ (blue) in CH₃CN (0.15 M *n*-Bu₄NPF₆, 100 mV/s). **2**-PF₆ and **3**-BF₄ show an additional reversible potential at -0.8 V from the redox pair Co(III)/Co(II). Moreover, the irreversible potential at about 0.60 V is in the range of the potential of Co-dithiolate moiety.

- [1] (a) G. F. Manbeck, K. J. Brewer, *Coord. Chem. Rev.* **2013**, *257*, 1660.
 (b) S. Ladouceur, E. Zysman-Colman, *Eur. J. Inorg. Chem.* **2013**, 2985.
 [2] D. Schallenberg, A. Neubauer, E. Erdmann, M. Tänzler, A. Villinger, S. Lochbrunner, W. W. Seidel, *Inorg. Chem.* **2014**, *53*, 8859.
 [3] E. Erdmann, S. Tschierlei, W. W. Seidel, *in preparation*.