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Light emission with a twist: Ultrafast evolution of chiral excited states determines the circularly-polarized luminescence of a chiral OLED complex

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Circularly-polarized luminescence (CPL) has promising applications in the fields of optical data storage, biosensing and for the creation of more efficient OLED displays [1]. In this respect, chiral lanthanide complexes are particularly attractive CPL emitters due to their intense and long-lived emission lines, and their exceptional degree of circular polarization. However, despite the impressive progress in the synthesis of CPL complexes, the direct resolution and analysis of their chiral luminescent states has remained a formidable experimental challenge, due to a lack of ultrafast spectroscopic techniques with sufficient chiral sensitivity.
To address this gap, we have developed an ultrafast circular dichroism (CD) instrument that combines ultrasensitive broadband detection with sub-picosecond time resolution to resolve the dynamics of chiral photoexcited states [2]. We now apply this technique to resolve the CPL mechanism of the prototypical CsEu((+)-hfbc)4 (hfbc = 3-heptafluoro-butylyrylcamphorate), which achieves record-breaking CPL emission purity by coupling the metal-centered (MC) luminescent states to a chiral ligand sphere [3]. In this mechanism, the ligands serve two roles. First, they act as photosensitizers providing efficient energy transfer (EnT) to the MC states. Second, the chiral ligand system breaks the spherical symmetry of the Eu(III) ion to induce its CPL activity. [4]
Combining ultrafast CD and transient absorption measurements with TDDFT calculations, we resolve the complete EnT mechanism and the associated chiral structural evolution that determine the CPL emission properties of the complex.We find that the initially excited ligand-centered singlet exciton states undergo a sub-picosecond intersystem crossing to populate a triplet state localized on a single ligand, from where EnT to the MC states proceeds in 150 ps. Quite remarkably, we observe an increase in optical activity of the ligand system upon EnT, which we assign to an ultrafast structural change to an achiral square antiprismatic geometry. Our findings thus support the predicted chirality transfer to the emissive states [4]: as the first coordination sphere of the excited Eu(III) is indeed achiral, its CPL is induced by the second coordination sphere, provided by the helical arrangement of hfbc-ligands. Our results demonstrate that it is now possible to determine the stereochemistry of electronically excited states, opening the path to directly capture the CPL mechanisms of chiral luminescent molecules and materials to further improve their designs.

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Authors: Ms MÜLLER, Livia (Department of Chemistry, University of Basel, Switzerland); Mr PUPPIN, Michele (Lausanne Centre for Ultrafast Science, Ecole Polytechnique Fédérale de Lausanne, Switzerland); Mr PESCITELLI, Gennaro (Department of Chemistry and Industrial Chemistry, University of Pisa, Italy); Mr ZINNA, Francesco (Department of Chemistry and Industrial Chemistry, University of Pisa, Italy); Mr OPPERMANN, Malte (Department of Chemistry, University of Basel, Switzerland)

Presenter: Ms MÜLLER, Livia (Department of Chemistry, University of Basel, Switzerland)

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