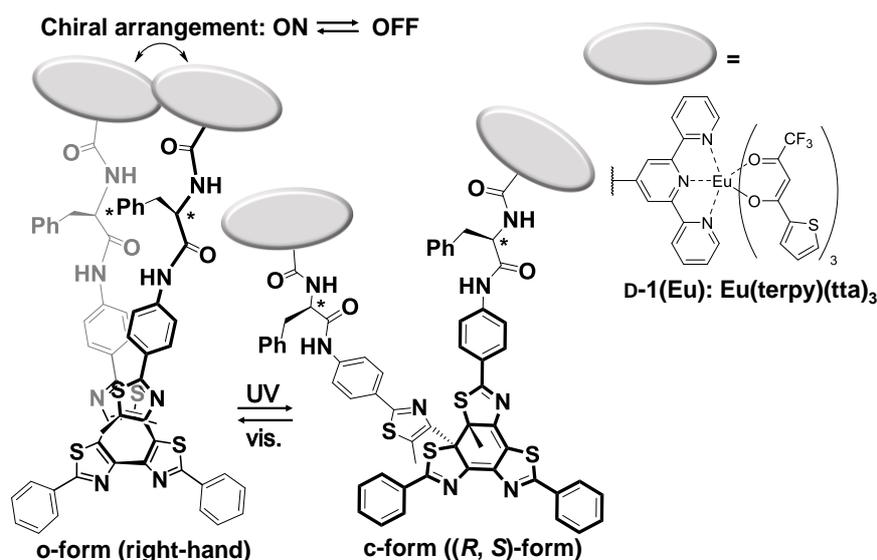


# HIERARCHICAL CONTROL OF CHIRALITY AND EMERGENCE OF CIRCULARLY POLARIZED LUMINESCENCE

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Circularly polarized luminescence (CPL) is of increasing interest as an important chiroptical phenomenon, which provides the differential emission intensity of right- and left-circularly polarized light.<sup>[1]</sup> Organic fluorophores with chiral chemical structures often exhibit CPL, which could be further controlled by their supramolecular chiral assemblies.<sup>[2]</sup> The chiral supramolecular assemblies were demonstrated as a platform of chiral recognition, wherein sensitized CPL could be utilized as a detection mechanism of analyte.<sup>[3]</sup> Recently, we also reported a chiroptical photoswitch composed of a chiral photochromic scaffold bearing two pyrene units, demonstrating dynamic CPL modulation.<sup>[4]</sup> We further replace the pyrene units with europium-complex units to demonstrate dynamic on-off photoswitching of CPL with a binuclear complex system. The coordination unit (**Eu(terpy)(tta)<sub>3</sub>**) has intrinsically chiral coordination system with asymmetric  $\beta$ -diketonato ligands, which is arranged closely in a chiral fashion by a photoresponsive ligand with a one-handed helical structure (Figure 1). Chiral arrangement of the **Eu(terpy)(tta)<sub>3</sub>** unit with a close contact may transfer chiral information to the inherently chiral coordination unit in a remote manner, leading to an enrichment of one-handed enantiomeric coordination structure. Furthermore, the photoinduced helical to non-helical transformation of the main framework switches off the close arrangement of the coordination units. The labile coordination character of lanthanide ions should facilitate the racemization in the ring-closed form, diminishing CPL activity. The present helical photochromic  $\text{Eu}^{3+}$  dinuclear complex therefore achieves not only the photoswitching of emission intensity owing to the change in electronic structure of ligands, but also the modulation of CPL activity in conjunction with the change in chiral coordination structures.<sup>[5]</sup>



**Figure 1.** Photoswitching reaction of dinuclear complex.

- [1] J. Kumar, et al., *J. Phys. Chem. Lett.*, **2015**, 6, 3445. [2] J. Kumar et al., *Angew. Chem. Int. Ed.*, **2015**, 54, 5943.  
[3] R. Sethy et al., *Angew. Chem. Int. Ed.*, **2017**, 56, 15043. [4] Y. Hashimoto, et al., *Chem. Commun.*, **2016**, 52, 5171.  
[5] Y. Hashimoto et al., submitted.