MEROCYANINE DYSPROSIUM(III) COMPLEXES : MAGNETIC ANISOTROPY AND PHOTOCHROMISM

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Single Molecule Magnets (SMM), which at low temperature behave as tiny magnets at the molecular scale, have attracted enormous interest in recent years, and the switching of their magnetic characteristics is raising more and more attention.[1] So far, a total, robust, and reversible photo-switching process has not been reached with 4f-based SMM. For mononuclear 4f complexes, the magnetic ground state splitting caused by the crystal field is the origin of the barrier to slow magnetic relaxation and the magnetic properties of these complexes are then sensitive to minute changes in their coordination environments. Consequently, mononuclear lanthanide complexes based on spiropyran (SP) ligands are ideal candidates for the photo-control of slow relaxation of magnetization since SP to merocyanine (MC) isomerization will lead to drastic modifications in the lanthanide ion environment. Our recent work demonstrated the feasibility of this approach and underlines the challenges associated with the combination of efficient light-switching and targeted magnetic behavior within the same entity.[2]

Reaction of dysprosium(III) hexafluoroacetylacetonate precursors with a SP ligand that spontaneously transforms into MC upon coordination provides a complex with SMM behavior, which has rather high-energy barrier to slow relaxation of magnetization (Δ= 215 K) and significant hysteretic behavior. Ab initio calculations demonstrate that the strong merocyanine metal O-M bond drives the anisotropy of the system.[2a] Then, by changing the type of dysprosium(III) precursors, a second type of MC complexes was obtained, which combine SMM behavior with an unusual *trans* to *cis* photoisomerization of the merocyanine ligand (figure 1).[2b]

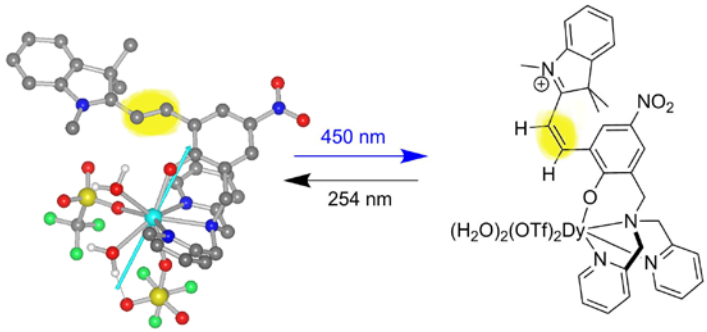

Figure 1. A Dysprosium(III) MC complex (with its magnetic anisotropy axis) *trans* to *cis* photoisomerization.

[1] G. Cosquer, B. K. Breedlove, M. Yamashita, *Dalton Trans.* **2015**, *44*, 2936-2942.

[2] a) P. Selvanathan, G. Huang, T. Guizouarn, T. Roisnel, G. Fernandez-Garcia, F. Totti, B. Le Guennic, G. Calvez, K. Bernot, L. Norel, S. Rigaut, *Chem. Eur. J.* **2016**, *22*, 15222-15226. b) P. Selvanathan, V. Dorcet, T. Roisnel, K. Bernot, G. Huang, B. Le Guennic, L. Norel, S. Rigaut, *Dalton Trans.* Accepted.