

Are room-temperature molecular photomagnets possible and how to reach them?

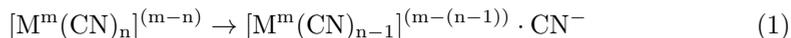
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Visible light photoexcitation of some molecules/molecular solids can lead to a dramatic change of their magnetization. This is the so called photomagnetic effect and the relevant compounds are called photomagnets. In other words, photomagnets belong to a class of photoresponsive compounds that become paramagnetic, ferromagnetic or simply change their magnetic properties upon illumination – a property that is hardly accessible in conventional magnetic solids such as metal alloys and oxides.

The first examples of photomagnetism in molecular compounds are related to the discovery of the light-induced excited spin state trapping (LIESST) effect in some octahedral Fe^{II} spin crossover (SCO) compounds[1] followed by the report of the light-induced shift of the magnetic ordering temperature in K_{0.2}Co_{1.4}[Fe(CN)₆]·6.9H₂O Prussian Blue analog (PBA) due to the charge transfer induced spin transition (CTIST).[2] Similar photomagnetic behavior was also observed for some octacyanomolybdate(IV)-based systems[3] including the recent report of the LIESST-like behavior of [Mo^{IV}(CN)₈]⁴⁻ itself in a [Mo^{IV}(CN)₈Zn₂{tren}₂] compound.[4] Various photomagnetic building blocks were successfully used in the design and construction of multifunctional photomagnetic compounds.[5,6] However, only a handful, mostly based on Fe^{II} and Mo^{IV} centers, were shown to be intrinsically photomagnetic.

During the talk I will focus on multiple photomagnetic experiments for various cyanometallate-based compounds ranging from simple salts to bimetallic coordination polymers, that show photomagnetic switching associated with the photodissociation reaction occurring in the solid state (see also Figure 1):



In order to confirm this photodissociation mechanism, the aforementioned photomagnetic studies are accompanied by single crystal X-ray diffraction structural analysis and/or UV-vis-IR spectroscopy studies before and after irradiation. Thanks to the slow relaxation of the photoinduced CN-dissociated state and very strong magnetic coupling interactions between the photoexcited paramagnetic cyanometallates and the early transition metal ions, these unique coordination complexes hold great promise as building blocks for the construction of room-temperature photomagnets. This is partly confirmed by several examples of coordination polymers based on Mn^{II}, showing the highest photo-induced magnetic ordering temperatures exceeding the boiling point of liquid nitrogen for [Mn^{II}(imH)₂][W^{IV}(CN)₈]_n [7] and approaching 130 K for [Mn^{II}(pydz)][W^{IV}(CN)₈]_n. [8] Changing Mn^{II} to V^{II} should shift the current 130 K limit to room temperature.[9]

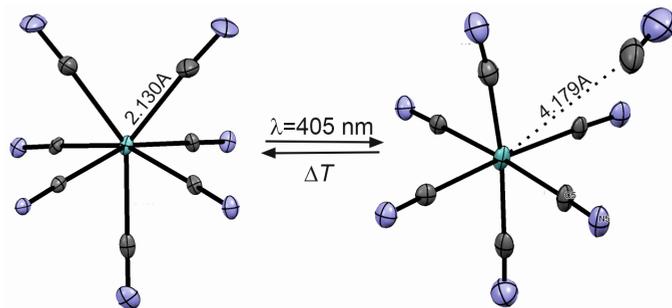


Figure 1. An example of the reversible photo-induced ligand dissociation in the solid state upon violet light irradiation of the polycrystalline sample of potassium heptacyanomolybdate(III) dihydrate.

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