Photomagnetic effects in low–dimensional copper octacyanidometallate assemblies

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Research on new photomagnetic materials – compounds which magnetic properties can be switched by irradiation, are of great interest in the study of magnetochemistry. Two main classes of photomagnetic materials have been broadly studied: electron transfer and spin crossover photomagnets. Much attention was drawn to the Cu^{II}–$[Mo^{IV}(CN)_8]$ assemblies due to their ability to reveal the light–induced metal–to–metal charge–transfer (MMCT) effect: $Cu^{II}(S=½)$–$Mo^{IV–LS}(S=0)$–$Cu^{II}(S=½)$ → $Cu^{I}(S=0)$–$[Mo^{V–LS}$–$Cu^{II}](S_{total}=1)$ and/or the light–induced excited spin–state trapping (LIESST) phenomenon in the Mo(IV) centre: $Cu^{II}(S=½)$–$Mo^{IV–LS}(S=0)$–$Cu^{II}(S=½)$ → $[Cu^{II}$–$Mo^{IV–HS}$–$Cu^{II}](S_{total}=2)$.[1]

In this presentation we will summarize research on two new ionic systems: $\{[Cu(tren)]_2(\mu$–tn)$\}\cdot[Mo(CN)_8]\cdot 7.5H_2O$ (**1**) and $\{[Cu(tren)]_2(\mu$–tn)$\}\cdot[Mo(CN)_8]\cdot\{[Cu(tren)]_2[Mo(CN)_8]\}\cdot 9H_2O$ (**2**), where tren = (tris(2–aminoethyl)amine and tn = 1,3–diaminopropane, and two trinuclear reference samples: $[Cu(tn)_2]_2[Mo(CN)_8]\cdot 2H_2O$ (**3**) and $[Cu(tren)]_2[Mo(CN)_8]\cdot 5.25H_2O$ (**4**).[2] Optical spectroscopy, supported by quantum chemical calculations, confirmed the presence of the Mo(IV) to Cu(II) charge transfer bands for CN^-–bridged compounds (**2** – **4**). Additionally, detailed descriptions of energy level diagrams of **1** – **4** with the frontier molecular orbitals and possible optical transitions were made. Magnetic studies indicated paramagnetic behaviour with weak antiferromagnetic interactions at low temperature. Finally, photomagnetic studies of **1** – **4** showed the increase of magnetization after irradiation with 473 and 410 nm light at 10 K. Data analysis suggests that the photomagnetic effect in **1** has the LIESST origin, while other cyanido–bridged compounds prefer the MMCT mechanism.

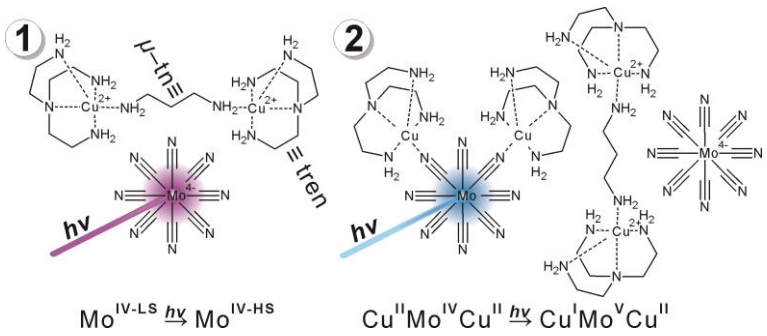

Figure 1. Scheme of structure and photomagnetic effect in **1** and **2**.

1) O. Stefanczyk, K. Nakabayashi, S. Ohkoshi, *Springer Series in Chemical Physics*, **2021**, *125*, 149. 2) T. Pai, O. Stefanczyk, K. Kumar, C. Mathonière, B. Sieklucka, S. Ohkoshi, *Inorg. Chem. Front.*, **2022**, DOI: 10.1039/D1QI01469B