

**Doctoral thesis:** Synthesis and characterization of porous photomagnetic systems

**Author:** mgr Michał Magott

**Supervisor:** dr hab. Dawid Pinkowicz, prof. UJ

## Abstract in English

The interaction of light with matter has been an object of interest of physical sciences for centuries. In the case of a special class of chemical compounds, referred to as *photomagnetic systems*, absorption of light can induce a change in magnetic moment, which then can be reversed by raising a temperature. Materials exhibiting a *photomagnetic effect*, as defined in this way, may in the future find applications in information storage and processing, or be used as molecular sensors.

This dissertation describes attempts to obtain new systems exhibiting the photomagnetic effect, in which the effect of light would be coupled to the chemical state of matter, dependent on its porous properties. In the included **publications P1-P5** three different synthetic strategies are described, leading to coordination polymers combining photomagnetism and porosity. In the first trial, a linear inorganic anion was used as a photomagnetic building block in the construction of heterotrimetallic coordination polymers containing large solvent-filled cavities in their structure. As an alternative strategy a long organic linker was used, which favoured the formation of porous organic-inorganic hybrid systems. Finally, the inherent photomagnetism of octacyanomolybdate(IV) and octacyanotungstate(IV) was exploited to introduce photomagnetic functionality into known porous coordination polymers based on octacyanoniobate(IV).

During the studies presented in this dissertation, a number of new discoveries concerning photomagnetic and porous systems were described. Detailed measurements were carried out for the anion  $[(\text{CN})_7\text{Mo}^{\text{IV}}-\text{CN}-\text{Pt}^{\text{IV}}(\text{NH}_3)_4-\text{NC}-\text{Mo}^{\text{IV}}(\text{CN})_7]^{4-}$  and its photomagnetic properties were observed for the first time, as well as its potential as a secondary building block in the construction of photomagnetic coordination polymers. Photoswitching between the antiferromagnetically interacting state and the ferromagnetically interacting state was demonstrated for the  $\text{Fe}^{\text{II}}-\text{M}^{\text{IV}}(\text{CN})_8$  ( $\text{M} = \text{Nb}, \text{Mo}, \text{W}$ ) family. In this series of compounds, a different relaxation process was observed for systems based on octacyanomolybdate(IV) or octacyanotungstate(IV), indicating greater application potential for the latter, for which the photomagnetic effect was completely reversible. Detailed sorption and structural studies for the  $\{[\text{Mn}^{\text{II}}(\text{imH})(\text{H}_2\text{O})_2]_2[\text{Mo}^{\text{IV}}(\text{CN})_8] \cdot 4\text{H}_2\text{O}\}_n$  system previously reported in the literature showed that coordination polymers based on cyanide bridges can compete with metal-organic frameworks in applications based on water adsorption. For this particular system, a significant volume change associated with the so-called "gate-opening" process, complete stability of the crystal lattice over 50 dehydration-hydration cycles, humidity sensing by electron paramagnetic resonance spectroscopy and large adsorption of water vapor accompanied by low-temperature desorption were demonstrated. In addition, a magnetic sponge effect was observed for this system at helium temperatures in the activated state – the shift of the critical temperature of the light-induced magnetic ordering depending on the degree of hydration, which was observed for the first time for a photomagnet.

The most important discovery described in this dissertation is the observation of the photomagnetic sponge effect - in the case of the two coordination polymers studied, the photomagnetic effect resulting in magnetic ordering was activated only after guest molecules were completely removed from the crystal structure. This type of behaviour has never been reported in the literature. Therefore, it can be expected that some of the systems described so far,

which were concluded to not show a photomagnetic effect, may become photomagnets after the removal or replacement of guest molecules. At the same time, in the case of the compound  $\{[\text{Mn}^{\text{II}}(\text{imH})(\text{H}_2\text{O})_2][\text{W}^{\text{IV}}(\text{CN})_8] \cdot 4\text{H}_2\text{O}\}_n$  which lacks photomagnetic activity, the transformation to the anhydrous phase of  $\{[\text{Mn}^{\text{II}}(\text{imH})]_2[\text{W}^{\text{IV}}(\text{CN})_8]\}_n$  resulted in the appearance of the light-induced magnetic ordering with a record high critical temperature of  $T_c = 93$  K. This is the first example of a high-temperature photo-induced ferrimagnet, in which a magnetic hysteresis loop can be induced by irradiation even at temperatures higher than the boiling point of liquid nitrogen (77 K).

In summary, this dissertation opens new pathways for the synthesis of porous photomagnetic systems and describes the first demonstration of chemical control over photomagnetism by adsorption/desorption of guest molecules in a coordination polymer. Thus, the dissertation predominantly describes the magnetic properties of matter (usually outside the typical area of interest of chemists), but the study was conducted for environmentally sensitive chemical compounds obtained by solution synthesis (clearly different from the systems typically analysed by physicists). In order to make the thesis more accessible to both potential groups of readers, the fourth chapter provides a brief description of photomagnetism as it is understood in this work, and a short introduction to the study of porosity as applied to coordination polymers. Chapters five and six play a clarifying role, allowing the reader to get an idea of how the characterization of the studied compounds was carried out. Chapter seven describes in Polish the most important results presented in **publications P1-P5**, which form the core of this dissertation. Finally, chapter eight summarizes the achieved results and outlines plans for further research, which are based on results presented in this dissertation.