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Optical activity and switchable luminescence in octacyanido-based bimetallic layered magnets

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Molecule-based magnets constructed of octacyanidometallates and complexes of 3d/4f metal ions are now attracting a considerable attention as they reveal the wide range of magnetic phenomena including ferromagnetism, metamagnetism, charge transfer or spin transitions, and slow relaxation of magnetization.^[1] The implementation of other physical functionalities, including chirality, luminescence, ionic conductivity, microporosity, or photoinduced phase transitions into magnetic octacyanido-based material results in extraordinary cross-effects, such as a magnetization-induced second harmonic generation, or photoswitchable second harmonic light, occurring when chirality is combined with photoinduced magnetic ordering.^[2,3] In this context, we focus on searching for new synthetic pathways towards $[M(CN)_8]$ -bridged magnets with additional optical functionalities, which were found to be the most promising in the interactions with magnetic phenomena.^[3] Here, we present two novel types of two-dimensional bimetallic cyanido-bridged networks combining magnetic ordering with embedded optical functionalities: (a) chiral $\{[Mn^{II}(R\text{-mpm})_2]_2[Nb^{IV}(CN)_8]_4\cdot 4H_2O}$ and $\{[Mn^{II}(S\text{-mpm})_2]_2[Nb^{IV}(CN)_8]_4\cdot 4H_2O}$ (mpm = α -methyl-2-pyridine-methanol) ferrimagnets with $T_c = 23.5$ K revealing natural optical activity due to the chiral crystal structure, and magnetic optical activity in the presence of external magnetic field, with the strong enhancement in the magnetically ordered phase,^[4] and (b) $\{[Tb^{III}(Box)_2]_2(dmf)_2\cdot 2H_2O}$ (Box = bis(oxazoline)) ferrimagnets with $T_c = 2.4$ K exhibiting visible green to red luminescence switchable by excitation light.^[5]

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Primary author: Dr CHORAŻY, Szymon (Department of Chemistry, The University of Tokyo)

Co-authors: Prof. SIEKLUCKA, Barbara (Faculty of Chemistry, Jagiellonian University, Kraków); Dr GORLICH, Edward (Institute of Physics, Jagiellonian University, Kraków); Dr NAKABAYASHI, Koji (Department of Chemistry, The University of Tokyo); Dr RAMS, Michał (Institute of Physics, Jagiellonian University, Kraków); Dr PODGAJNY, Robert (Faculty of Chemistry, Jagiellonian University, Kraków); Prof. OHKOSHI, Shin-ichi (Department of Chemistry, The University of Tokyo); Dr NITEK, Wojciech (Faculty of Chemistry, Jagiellonian University, Kraków)

Presenter: Dr CHORAŻY, Szymon (Department of Chemistry, The University of Tokyo)

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