

Supramolecular Systems on the Platform of p-Sulfonatothiacalix[4]arene Containing Photochromic Mononitrosyl Ru (II) and Paramagnetic Aqua Gd and Dy Complexes

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Design of molecular compounds which combine two or more physical properties is currently one of the most rapidly developing areas of chemistry and physics of new materials. For the synthesis of multifunctional compounds, a combinatorial approach is commonly used, which is a combination of molecular building blocks responsible for different properties in the same crystal lattice. The existence of different functional blocks in a single molecule provides an opportunity to manage one of the properties affecting on other by external factors. Calix[n]arenes can act as metal-assembling and cluster-forming macrocyclic ligands due to excellent complex ability stipulated by the presence of upper and lower rims, and cavity. They are of interest as a promising platform for poly- and heterometallic systems [1]. Herein we for the first time present the synthesis, structure and properties two bifunctional supramolecular heterometallic systems on the platform of p-sulfonatothiacalix[4]arene (TCAS): $[\text{RuNO}(\text{NH}_3)_4\text{OH}]^{2+} \cdot [\text{RuNO}(\text{NH}_3)_4\text{H}_2\text{O}]^{3+} \cdot \text{Gd}^{3+}(\text{H}_2\text{O})_6 \cdot 2[\text{TCAS}]^{4-} \cdot 4\text{H}_2\text{O}$ (**1**) and $[\text{RuNO}(\text{NH}_3)_4\text{OH}]^{2+} \cdot [\text{RuNO}(\text{NH}_3)_4\text{H}_2\text{O}]^{3+} \cdot \text{Dy}^{3+}(\text{H}_2\text{O})_6 \cdot 2[\text{TCAS}]^{4-} \cdot 4\text{H}_2\text{O}$ (**2**), which exhibit photochromism and magnetism. **1** and **2** are isostructural. Their structures differ only by conformations of calixarenes and mutual arrangement of mononitrosyl cations. The independent part of the unit cells of **1** and **2** includes two TCAS tetra-anions arranged head-to-head to each other. Such arrangement is stabilized by Gd(Dy)³⁺ linkage. In the case of **1**, the Gd(III) ion links two SO₃⁻ groups of the opposite TCAS anions, while the Dy(III) ion binds three SO₃⁻ groups from two neighboring TCAS anions in **2**. Guest $[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{OH})]^{2+}$ cation is inserted into the cavity of TCAS *via* its N=O moiety in **2** and *via* NH₃ ligand in **1**. Photochromic properties of the compounds were investigated by IR spectroscopy. The populations of two long-lived metastable states (MS1, MS2) under light irradiation were 16% and 14% for **1**, and 20% and 15% for **2**, respectively. At low temperature (2K) **1** shows the reversible photomagnetic effect under light irradiation.

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