QUEST FOR MULTICOLORED AND WHITE-LIGHT EMISSION IN LANTHANIDE(III)-RUTHENIUM(II) COORDINATION NETWORKS

Tomasz Charytanowicz, Barbara Sieklucka, and Szymon Chorazy

Faculty of Chemistry, Jagiellonian University, Krakow, Poland

Significant scientific attention is devoted to lanthanide(III)-based inorganic materials due to their attractive photoluminescent properties, including switchable multicolored and white light emission, sensitized near-infrared, and up-conversion luminescence.[1] On the other hand, cyanido complexes of transition metals represent a pretty interesting group of molecular building blocks for the construction of novel molecular materials,[2] including novel solid luminophores, due to their synthetic simplicity and their fruitful utility in the enhancement of the 4f-metal-centered emission properties through a metal-to-metal energy transfer.[3] Moreover, the polycyanidometallates themselves can be emissive which can alter and enhance the overall luminescence of the material.[4] In this context, we present a family of three-dimensional $KLn^{III}[Ru(CN)_6]\cdot nH_2O$ coordination frameworks. The mono-lanthanide compounds (Ln = Ce, Sm, Tb) reveal blue, red, and green emission colors, respectively, at room temperature due to the d-f or f-f electronic transitions of the Ln(III) complexes. We combined all three lanthanide ions in a single-phase material. Our studies resulted in a broad set of heterometallic systems, including the $KTb_{0.997}Ce_{0.003}[Ru(CN)_6]\}\cdot 4.4H_2O$ (**TbCeRu**) $KSm_{0.998}Ce_{0.002}[Ru(CN)_6]\}\cdot 4.1H_2O$ (**SmCeRu**), and $KSm_{0.4}Tb_{0.599}Ce_{0.001}[Ru(CN)_6]\cdot 4.5H_2O$ (**SmTbCeRu**). Each compound shows the tuning of emission with the excitation wavelength. **TbCeRu** and **SmCeRu** exhibit switchable luminescence from blue to green and blue to red, respectively. For **SmTbCeRu**, the emission color varies from red, through orange and white, to blue, as the excitation wavelength increase.[5] We discuss the mechanisms applied for achieving multicolored and white light emission in such heterometallic inorganics.

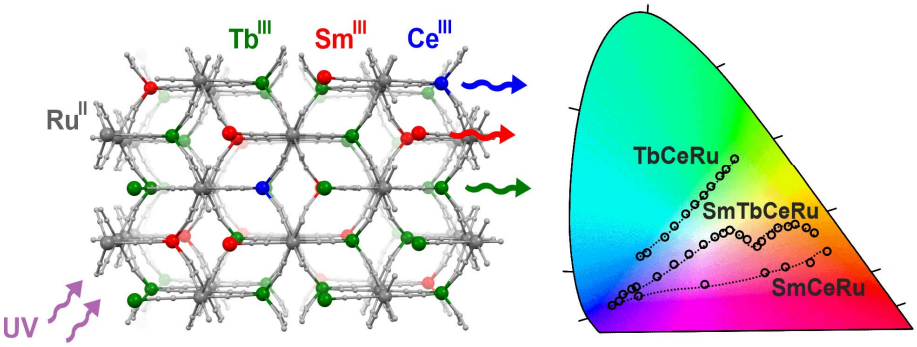

Figure 1. Structural scheme of the **SmTbCeRu** coordination network (left) and the chromaticity diagram for the emissions of **TbCeRu**, **SmCeRu**, and **SmTbCeRu** (right).

[1] J. Rocha, L. Carlos, F. Almeida Paz, D. Ananias, *Chem. Soc. Rev.*, **2011**, *40*, 926.

[2] S. Chorazy, T. Charytanowicz, D. Pinkowicz, --J. Wang, K. Nakabayashi, S. Klimke, F. Renz, S. Ohkoshi, B. Sieklucka, *Angew. Chem. Int. Ed*., **2020**, *59*, 15741.

[3] J. Wang, J. J. Zakrzewski, M. Heczko, M. Zychowicz, K. Nakagawa, K. Nakabayashi, B. Sieklucka, S. Chorazy, S. Ohkoshi, *J. Am. Chem. Soc.*, **2020**, *142*, 3970.

[4] K. Kumar, S. Chorazy, K. Nakabayashi, H. Sato, B. Sieklucka, S. Ohkoshi, *J. Mater. Chem. C*, **2018**, *6*, 8384.

[5] T. Charytanowicz, B. Sieklucka, S. Chorazy, *Inorg. Chem.*, **2023**, *62*, 1627.