

PHOTOLUMINESCENCE AND SWITCHABLE DIELECTRIC PROPERTIES IN HYBRID MATERIALS BASED ON A DICYANIDO-BIS(2,2'-PHENYLPYRIDINATE)RHODATE(III) ION

Kinga Szczecińska, Tomasz Charytanowicz, Jan Rzepiela, Szymon Chorazy

Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, 30-387 Kraków, Poland

Dielectric materials are extensively studied to enhance their applications, ranging from pure capacitors to tunable electronic devices and actuators.^[1,2] The other heavily explored functionality, employed, e.g. in chemical sensing and optoelectronics, is photoluminescence which is usually realized by the employment of lanthanide ions or other emissive metal complexes.^[3-5] The strategy to combine those two functionalities is to utilize the molecular building blocks approach, in which each of the selected building blocks bears at least one of the desired functionality. Thus, combining proper molecular precursors can lead to multifunctional materials that combine luminescence and dielectric properties sensitive to external stimuli. For the latter case, the promising molecular building block is a 1,4-diazabicyclo[2.2.2]octane (DABCO) which is a polar cation inducing switchable dielectric properties in numerous materials.^[6]

Our work aimed to combine a unique luminescent dicyanido-bis(2,2'-phenylpyridinate) rhodate(III) anion, $[\text{Rh}(\text{ppy})_2(\text{CN})_2]^-$ with N-alkylated DABCO derivatives of varying chain lengths (C_1 - C_4), to obtain luminescent dielectric materials. We present a series of the crystalline compounds with the general formula of $[\text{R}(\text{DABCO})][\text{Rh}(\text{ppy})_2(\text{CN})_2]$ ($\text{R}=\text{CH}_3$ - (1), C_2H_5 - (2), C_3H_7 - (3), C_4H_9 - (4)). All synthesized hybrid materials exhibit pronounced UV-light-induced emission at low temperatures due to the presence of the LMCT emission bands of the metal complex, as well as the thermal variation of dielectric characteristics originating from the presence of the polar $\text{R}(\text{DABCO})^+$ cations.

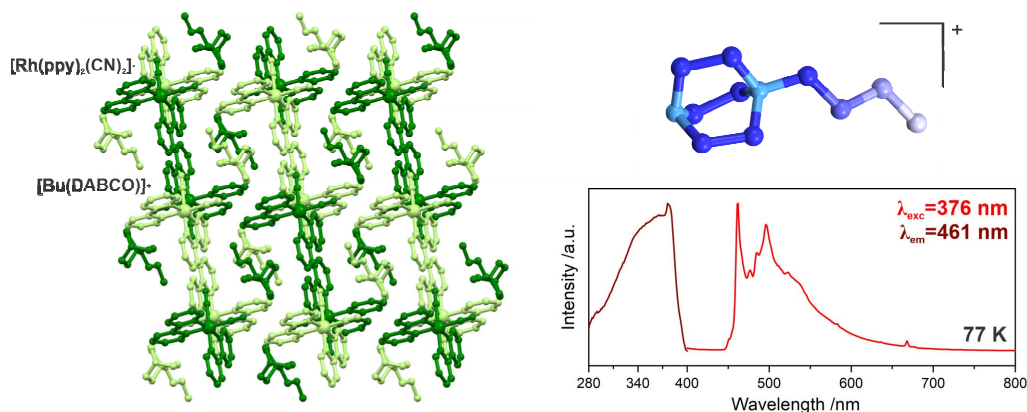


Figure 1. Scheme of the utilized N-alkylated DABCO cations (top, right), the crystal structure of **4** (left), and the related emission properties (bottom, right).

[1] Y.-L. Liu, W. Zhang, *Chem. Commun.*, **2017**, 53, 6077.

[2] Y. Mao et al., *Angew. Chem. Int. Ed.*, **2022**, 61, e202204135.

[3] M. Wyczesany, J. Zakrzewski, B. Sieklucka, S. Chorazy, *J. Mater. Chem. C*, **2022**, 10, 12054..

[4] M. A. Noorshida, L. M. Voirrey, P. Jennison, I. V. Sazanowich, C. A. Hunter, J. A. Weinstein, M. D. Ward, *Dalton Trans.*, **2012**, 41, 2408

[5] J. J. Zakrzewski, M. Liberka, M. Zychowicz, S. Chorazy, *Inorg. Chem. Front.*, **2021**, 8, 452.

[6] A. Cizman et al., *Dalton Trans.*, **2020**, 49, 10394.