

Three-dimensional polycyanidocuprate(I)-based frameworks showing single-molecule magnet behavior and NIR emission

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Multifunctionality including proton conductivity, humidity-sensitive magnetism, photomagnetism and photoluminescent single-molecule magnet, have increasingly show promising prospects in lanthanide-based cyanido-bridged metal assemblies.¹ Promotion of photoluminescent single-molecule magnet materials within cyanido-bridged frameworks have been acquired by taking advantages of both emission and large magnetic anisotropy from lanthanide(III) ions as functional centers.² Moreover, designing contactless temperature sensors and further SMM-based devices with a self-monitored temperature is of great interest in regard to ratiometric luminescence thermometry.³ In this regard, our group presents the three-dimensional cyanido-bridged metal assemblies, [Ln(2,2'-bipyridine N,N'-dioxide)₂(H₂O)] [Cu₂(CN)₅]·5H₂O (Ln=Nd, **1**; Yb, **2**; Nd_xYb_y, **3**). These compounds exhibit sensitized photoluminescence in near-infrared (NIR) range together with slow relaxation of magnetization. With great enhancement in absorption in visible range through dehydration, the NIR luminescent emission can be greatly promoted at the same time. This characteristic could lead to promising application in the aspect of optical thermometry based on the thermally sensitized luminescence of IR emissive f-block metal ions. The distinctive temperature-dependence of Nd and Yb photoluminescence makes the trimetallic system favorable candidates to work as ratiometric luminescent molecular thermometer with good performance in the range of 50-350 K.

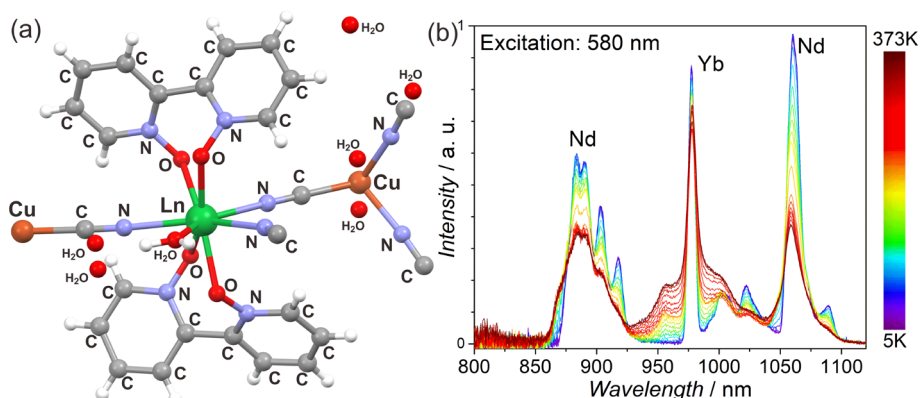


Figure. (a) Crystal structures of [Ln(2,2'-bipyridine N,N'-dioxide)₂(H₂O)] [Cu₂(CN)₅]·5H₂O; (b) Temperature dependence of photoluminescence for dehydrated [Nd_{0.7}Yb_{0.3}] species.

[1] a) S. Ohkoshi et al., *Dalton Trans.*, 2011, 40, 6825-6833. b) S. Ohkoshi et al. *Nature Photon.*, 2014, 8, 65. c) M. Komine and S. Ohkoshi et al., *Inorg. Chem.*, 2021, 60, 2097. [2] S. Chorazy and S. Ohkoshi et al., *Chem. Eur. J.*, 2016, 22, 7371 [3] a) J. Wang, J. and S. Ohkoshi et al., *Chem. Sci.*, 2021, 12, 730. b) M. Liberka and S. Chorazy, *Inorg. Chem.*, 2021, 60, 4093. c) J. Wang and S. Ohkoshi et al., *J. Am. Chem. Soc.*, 2020, 142, 3970.