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Near-Infrared Luminescent and Magnetic Cyano-Bridged Coordination Polymers Nd(phen)$_n$(DMF)$_m$[M(CN)$_8$] (M = Mo, W)

Jérôme Long,[†] Elena Chelebaeva,[†] Joulia Larionova,*[,†] Yannick Guari,[†] Rute A. S. Ferreira,[‡] Luis D. Carlos,*[,‡] Filipe A. Almeida Paz,[§] Alexander Trifonov,[⊥] and Christian Guérin[†]

[†]Institut Charles Gerhardt Montpellier, UMR 5253, Chimie Moléculaire et Organisation du Solide, Université Montpellier II, Place E. Bataillon, 34095 Montpellier Cedex 5, France

[‡]Department of Physics, CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal

[§]Department of Chemistry, CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal

[⊥]G. A. Razuvaev Institute of Organometallic Chemistry of the Russian Academy of Science, Tropinina 49, GSP-44S, 603950 Nizhny Novgorod, Russia

S *Supporting Information*

ABSTRACT: New cyano-bridged coordination polymers [Nd(phen)$_2$(DMF)$_2$(H$_2$O)Mo(CN)$_8$]$\cdot$2H$_2$O (**1**) and [Nd(phen)(DMF)$_5$M(CN)$_8$]$\cdot x$H$_2$O [M = Mo (**2**), W (**3**); phen = 1,10-phenanthroline] have one-dimensional structures with variable number of phenanthroline ligands. Compounds exhibit photoluminescence in the near-infrared region and ferromagnetic Nd^{3+}−M^{5+} interactions.

The design and study of multifunctional molecular materials exhibiting different physical properties have attracted a great deal of attention because of their fundamental interest and their potential applications.[1] Efforts have been focused on investigations of magnetoluminescent coordination polymers[2] and, in particular, those presenting luminescence in the near-infrared (NIR) region because of interesting applications in fields ranging from biomedical applications to telecommunications.[3] Along this line of thought, one of the promising families of coordination polymers is cyano-bridged networks in which the luminescent lanthanide ions are associated with *n*d ($n = 3-5$) cyanometallate building blocks in order to enhance magnetic anisotropy and magnetic interactions.[4] Indeed, numerous one-, two-, and three-dimensional cyano-bridged compounds presenting mainly magnetic properties have been reported in the last 30 years,[5] but the luminescent properties of these compounds have rarely been exploited.[6] To the best of our knowledge, only two compounds based on an association of NIR-emissive lanthanides (Yb^{3+} and Nd^{3+}) with cyanometallates have been reported, but the diamagnetism of the transition-metal ions results in the absence of magnetic interactions.[7] Our strategy to obtain magnetoluminescent materials relies on associating paramagnetic [M(CN)$_8$]$^{3-}$ (M = Mo, W) building blocks (which do not act as luminescence quenchers, contrary to most of the hexacyanometallates) with an NIR-emissive Nd^{3+} coordinated to an antenna ligand in order to enhance luminescence. In this Communication, we report the first examples of the NIR-emissive one-dimensional cyano-bridged compounds [Nd(phen)$_2$(DMF)$_2$(H$_2$O)Mo(CN)$_8$]$\cdot$2H$_2$O (**1**) and [Nd(phen)(DMF)$_5$M(CN)$_8$]$\cdot x$H$_2$O [M = Mo (**2**), W (**3**); DMF = dimethylformamide] sensitized by one or two phenanthroline ligands presenting ferromagnetic interactions between the spin carriers. Red crystals of **1** have been obtained by the slow diffusion of the DMF layer to a 0.1 mmol (0.044 g) solution of [Nd(H$_2$O)$_6$](NO$_3$)$_3$ in water, 0.2 mmol (0.036 g) of phenanthroline, and a 0.1 mmol (0.103 g) solution of [(N(C$_4$H$_9$)$_4$]$_3$[Mo(CN)$_8$]$\cdot$2H$_2$O[8] in methanol (see the Supporting Information, SI). A mixture of 0.2 mmol (0.088 g) of [Nd(H$_2$O)$_6$](NO$_3$)$_3$ and 0.4 mmol (0.072 g) of phenanthroline in 10 mL of CH$_3$CN/DMF (3:2) was added to a solution of [(N(C$_4$H$_9$)$_4$]$_3$[M(CN)$_8$]$\cdot$2H$_2$O (M = Mo, W)[8] in 5 mL of the same solvent mixture. Slow diffusion of diethyl ether yields yellow crystals of **2** and **3**.

The crystal structures belong to two distinct structural families: [Nd(phen)$_2$(DMF)$_2$(H$_2$O)Mo(CN)$_8$]$\cdot$2H$_2$O (**1**) and [Nd(phen)(DMF)$_5$M(CN)$_8$]$\cdot x$H$_2$O (M^{5+} = Mo and $x = 1.5$ for **2**; M^{5+} = W and $x = 0$ for **3**, as determined from the X-ray diffraction studies). The common structural feature of these compounds concerns the presence of one-dimensional coordination polymers $_{\infty}^{1}$[Nd(phen)$_2$(DMF)$_2$(H$_2$O)Mo(CN)$_8$] (in **1**) and $_{\infty}^{1}$[Nd(phen)(DMF)$_5$M(CN)$_8$] (in **2** and **3**) (Figures 1 and 2). Besides the common bridging cyanide group, while in compound **1** the Nd^{3+} center is coordinated to two N,N′-chelated phenanthroline molecules and two DMF and one water solvent moieties (Figure 1c), in compounds **2** and **3**, the coordination sphere is filled instead with DMF molecules (five in total) and only one phenanthroline molecule (Figure 2b).

Because the five spatially close DMF molecules seem to impose a significant steric impediment around the Nd^{3+} coordination environment, $_{\infty}^{1}$[Nd(phen)(DMF)$_5$W(CN)$_8$] (in **3**) deviates more from linearity than that present in **1** (Figures 1a and 2a). Close packing of individual polymers to produce the crystal structures of **1**−**3** is clearly mediated by various supramolecular interactions, namely, close $\pi-\pi$ contacts (Figures S1 and S2 in the SI) and O−H$\cdots$(N,O) hydrogen-bonding interactions. Because of the extra phenanthroline molecule in **1**, the number of $\pi-\pi$ contacts is also significantly higher than that in **2** and **3**, with offset contacts occurring parallel to both the *a* and *b* axes of the unit cell (Figure S1 in the SI). In addition, the

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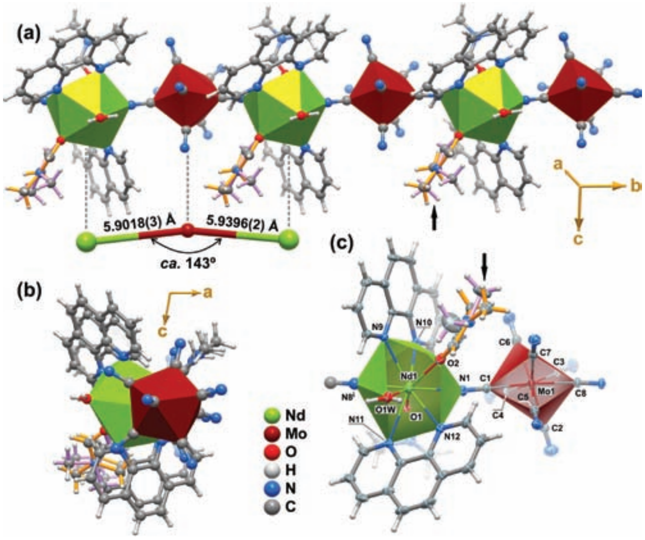

Figure 1. (a and b) Mixed ball-and-stick and polyhedral perspective views of **1**. The two locations for the disordered coordinated DMF molecule are pointed out by the black arrows and are represented in different colors. (c) Representation of the asymmetric unit (thermal ellipsoids of non-hydrogen atoms are drawn at the 50% probability level).

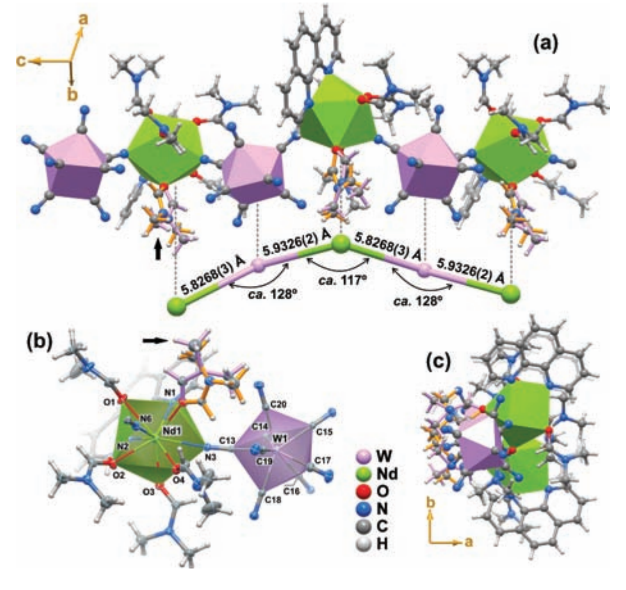

Figure 2. (a and c) Mixed ball-and-stick and polyhedral perspective views of **3** (identical geometrical details were registered for **2**). The two locations for the disordered coordinated DMF molecule are pointed out by the black arrows and are represented in different colors. (b) Representation of the asymmetric unit (thermal ellipsoids of non-hydrogen atoms are drawn at the 30% probability level).

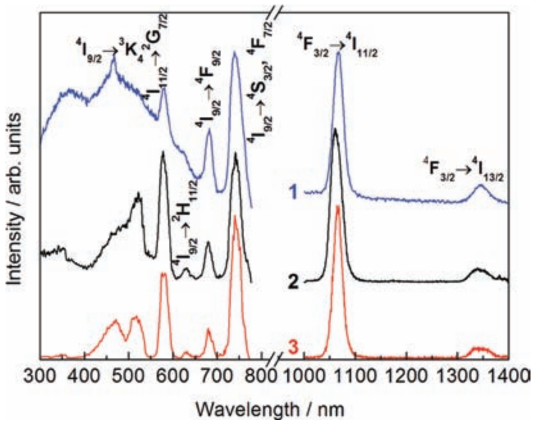

Figure 3. Excitation (left) and emission (right) spectra of **1**−**3** monitored around 1060 nm and excited at 465−488 nm, respectively.

presence of both coordinated and uncoordinated water molecules in **1** promotes the existence of O−H···(N,O) hydrogen bonds, which further strengthen the connections between adjacent polymers (Table S3 in the SI). In **2** and **3**, van der Waals interactions between neighboring DMF molecules arise as the main contacts between adjacent polymers (Figure S2 in the SI), creating an hydrophobic environment that seems to significantly minimize the number of O−H···(N,O) hydrogen bonds. The structural differences between the two families of coordination polymers can be explained by (i) the presence of water for **1** during the synthesis and (ii) the in situ complexation of lanthanide and phenanthroline in the presence of DMF, which acts as a competitive ligand, prior to the assembly reaction with the cyanometallate in the cases of **2** and **3**.

The photoluminescence features of all of the crystals were acquired at room temperature (see the SI). Figure 3 shows the excitation (left) and emission (right) spectra of all of the cyano-bridged compounds. The excitation spectra exhibit large bands ascribed to the organic ligand excited states and a series of narrow lines attributed to the intra-4f^3 $^4I_{9/2} \rightarrow {}^3K_4$, $^2G_{7/2}$, $^2H_{11/2}$, $^4F_{9/2,7/2}$, $^4S_{3/2}$ transitions. In **1**, the presence of two phenanthroline ligands induces an enlargement in the broad-band spectral region (300−650 nm) and a decrease of the intra-4f^3 transition relative intensity, boosting the ligand sensitization process relative to direct intra-4f^3 excitation. Under ligand excitation, all of the crystals display NIR emission ascribed to the $\mathrm{Nd}^{3+\,4}F_{3/2} \rightarrow {}^4I_{11/2,13/2}$ transitions (right spectra in Figure 3). For all crystals, the absence of emission from the phenanthroline ligand triplet states in the UV−vis spectral region points out the presence of an efficient ligand-to-Nd^{3+} energy-transfer mechanism.

The magnetic properties of these compounds were investigated using a SQUID magnetometer working in the 1.8−350 K temperature range with applied fields of up to 7 T.[9] At room temperature, the χT values are in good agreement with the theoretical value of 2.01 cm^3 K mol^{-1} expected for one Nd^{3+} ion ($^4I_{9/2}$, $S = {}^3/_2$, $L = 5$, and $g = {}^8/_{11}$) and one M^{5+} ion ($S = {}^1/_2$ and $g = 2$).[10] χT decreases with the temperature, reaches a minimum value, and then increases (Figure 4). The presence of the minima can be explained by thermal depopulation of the Stark sublevels of the Nd^{3+} ion, and the abrupt increase observed below 10 K reflects a ferromagnetic Nd^{3+}−M^{5+}interaction. The field dependences of the magnetization at 1.8 K show values of 2.42, 2.42, and 2.17 μ_B for **1**−**3** at 70 kOe, consistent with a ferromagnetic interaction between the M^{5+} and Nd^{3+} ions (effective spin $S = {}^1/_2$ and $g = 2.18$), leading to a theoretical value of 2.09 μ_B.[10] While the exchange interaction between the M^{5+} and Nd^{3+} ions seems to be similar for **2** and **3**, **1** presents a stronger interaction, as suggested by the higher value of χT at 1.8 K as well as the steeper slope of the magnetization curve. This behavior may arise from significant changes in the M−CN−Ln angle between the two different structures. Note that no evidence of slow relaxation of the magnetization has been observed with

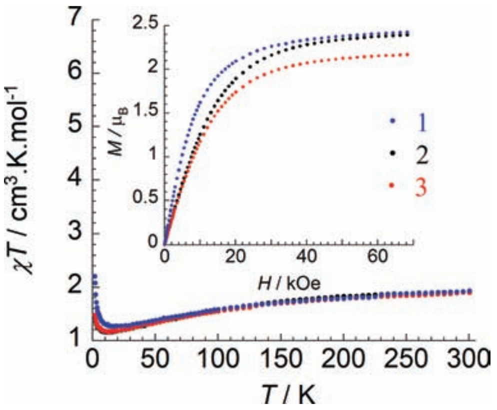

Figure 4. (a) Temperature dependence of the χT product for **1**−**3** with an applied field of 1000 Oe. Inset: Field dependence of the magnetization, *M*, for **1**−**3** at 1.8 K.

alternating-current magnetic measurements even with the presence of a static direct-current field.

To summarize, new one-dimensional cyano-bridged coordination polymers based on luminescent lanthanide ion Nd^{3+} and the $[M(CN)_8]^{3-}$ building block have been synthesized and characterized. Adjustment of the number of phenanthroline ligands in the coordination sphere of the lanthanide can be reached by modulating the experimental conditions. These compounds display the Nd^{3+} typical NIR emission enhanced by the presence of the phenanthroline ligand and ferromagnetic interactions between Nd^{3+} and M^{5+} ions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Additional information on the crystallographic studies of compounds **1**−**3** (technical section detailing the structure solution and refinement procedures, tabulated geometrical data for the metallic coordination environments, and hydrogen-bonding interactions in **1**) and CIF files of all structures. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: joulia.larionova@univ-montp2.fr (J.L.), lcarlos@ua.pt (L.D.C.). Fax: (33) 467143852 (J.L.), (351) 234378197 (L.D.C.).

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