Holmium, thulium and lutetium-octamolybdate \([\text{Mo}_8\text{O}_{28}]^{8-}\) 1D chains: luminescence investigation of europium doped lutetium-octamolybdate†

Anna M. Kaczmarek, †a Rik Van Deun †a and Kristof Van Hecke †a, *b

In this work we report a novel lanthanide octamolybdate 1D chain type of structure formed with holmium, thulium and lutetium. This is a rare case of compounds built out of \([\text{Mo}_8\text{O}_{28}]^{8-}\) units. These compounds were prepared in a mild reaction synthesis starting from the commonly used heptamolybdate polyoxometalate (POM) \([\text{INH}_4\text{d[Mo}_7\text{O}_{24}]\]. Interestingly, in our previous study we have employed a very similar synthesis route for lanthanides with a larger ionic radius and obtained heptamolybdate clusters. For the lanthanides with a smaller ionic radius (Ho\(^{3+}\), Tm\(^{3+}\) and Lu\(^{3+}\)) no crystals could be obtained under those conditions. Only when doubling the amount of the lanthanide salt, single crystals suitable for measurements were obtained. These crystals revealed yet a very different structure from those previously observed. Lanthanide octamolybdate 1D chains were formed. Doubling the amount of the salt for other lanthanide ions still yielded heptamolybdate compounds previously reported by us. The lutetium octamolybdate compound was doped with 1–7.5% of Eu\(^{3+}\) ions yielding emission colors ranging from blue to strong red. Additionally in these materials the excitation wavelength was varied, and it was observed that the materials emission color was excitation-wavelength dependent.

1. Introduction

To date, lanthanide materials have found many interesting applications relaying on their luminescence, catalytic and magnetic properties.\(^1\)–\(^6\) The luminescence properties of these ions result from transitions within the partially filled 4f shells. These transitions are parity-forbidden; therefore lanthanides have low molar absorption coefficients and relatively long decay times.\(^3\) To overcome the problem of low molar absorption coefficients various inorganic materials, where the lanthanide can be excited through a charge-transfer band, or hybrid materials, such as beta-diketonate complexes, crown ether complexes or Metal Organic Frameworks (MOFs), have been designed. Also, lacunary or defect polyoxometalates (POMs) can act as inorganic polydentate O-donor ligands, forming LnPOM complexes with novel properties differing from inorganic phosphors and hybrid materials obtained with organic ligands.\(^7\)–\(^8\)

POMs are clusters of early transition metals (such as Mo, W, V, and As) in a high oxidation state and they show a large variety in their size, shape and nuclearity. POMs can be divided into iso-polyanions and hetero-polyanions. Among some of the most known POMs are the Keggin-type, Dawson-type and Anderson-type POMs.\(^7\) Lanthanides can bind to POMs forming either mono- or multinuclear compounds.\(^9\) In LnPOMs the emission can be sensitized by photo-excitation of the O→M (M = Mo, W, V, As) ligand-to-metal charge transfer band of the POM and intramolecular energy transfer from the resulting O→M excited state to excited energy levels of the lanthanides. POMs bonded to lanthanide ions have shown an interesting variety of structures ranging from mononuclear sandwich types structures, to multinuclear clusters, 1D-chains and even 3D frameworks.\(^7,8\)

Previously, we have reported a series of tetranuclear LnPOMs assembled from the well-known \([\text{Mo}_7\text{O}_{24}]^{6-}\) unit.\(^10\) In those materials we also implemented low-percentage lanthanide doping, which yielded good visible and near-infrared luminescence. Throughout the lanthanide series of these LnPOMs we could only obtain single crystals of tetranuclear LnPOMs constructed from lanthanide ions with a larger ionic radius (Ln\(^{3+}\) = La–Dy). For Er\(^{3+}\) and Yb\(^{3+}\) we obtained a mononuclear sandwich type structure. On the other hand, for Ho\(^{3+}\), Tm\(^{3+}\) and Lu\(^{3+}\) no single crystals could be obtained when applying the same synthesis conditions. In this work we

† Electronic supplementary information (ESI) available. CCDC 1887985–1887987. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9dt00695h
show that 1D-chains can be obtained for these lanthanides when reacting with the [MoO$_3$]$_6^{2-}$ unit; yet it is necessary to increase (double) the ratio of Ln$^{3+}$/[MoO$_3$]$_6^{2-}$. Surprisingly, the 1D chains no longer consist of the [MoO$_3$]$_6^{2-}$ units, but instead the [MoO$_2$]$_8^{8-}$ unit. Two types of octamolybdate anions can be found in the literature: [MoO$_3$]$_6^{2-}$ and the abovementioned [MoO$_2$]$_8^{8-}$. The existence of compounds built of the [MoO$_2$]$_8^{8-}$ unit is much more common. [MoO$_2$]$_8^{8-}$ has eight isomers: α, β, γ, δ, ε, ζ, η, and θ, where each of these isomers can be viewed as distorted arrays of cubic close-packed oxygen atoms with Mo atoms occupying the interstitial sites. Some examples of structures found in the literature with the [MoO$_2$]$_8^{8-}$ unit and lanthanide ions are discussed. For example Kitamura et al. has reported employing β-octamolybdate as a building block to obtain [Ln[MoO$_3$]$_6$]$_2^{2-}$ and [Ln[N(NO$_3$)$_2$]$_2$[MoO$_2$]$_8$]$^{10-}$ (Ln$^{3+}$ = Y, La, Ce, Pr, Nd, Gd, Yb) as tetra-n-butylammonium salts. In another study by Khelifa et al. [La[n$_2$NO$_3$][dmso]-][β-MoO$_2$]$_8$ was synthesized employing the [[Cu$_6$H$_6$][N][MoO$_3$]] salt. It is known that the hexamolybdate cluster [MoO$_3$]$_6^{2-}$ can be easily converted to the octamolybdate cluster [MoO$_2$]$_8^{8-}$. The lanthanide complex formed a honeycomb-like structure. Baldovi et al. have reported [Ln[β-MoO$_2$]$_8$]$_2^{2-}$ (Ln$^{3+}$ = Tb, Dy, Ho, Er, Tm, Yb), which consists of a Ln$^{3+}$ ion trapped between two [β-MoO$_2$]$_8^{8-}$ moieties. Lu et al. reported a pillar-layered organic–inorganic hybrid based on a lanthanide polymer and octamolybdate cluster: [[La(H$_2$O)$_2$][diptic]]{[La(H$_2$O)][diptic]}, [MoO$_3$]$_6$-10H$_2$O where H$_2$diptic = pyridine-2,6-dicarboxylic acid. Other interesting structures, such as [[Ce[pda][H$_2$O]]{[Ce[pda][H$_2$O]]$_2$}, [MoO$_2$]$_8$-10H$_2$O and Na$_2$[Nd[diptic]$_2$[H$_2$O]$_2$][MoO$_2$]$_8$]8H$_2$O have also been reported. As can be seen different synthetic routes and starting reagents have been employed to obtain lanthanide octamolybdate [MoO$_2$]$_8^{8-}$ complexes and frameworks.

On the other hand, to the best of our knowledge, polyoxometalate structures built from the octamolybdate [MoO$_2$]$_8^{8-}$ units are quite rarely reported. We have found a few cases of such compounds, but none consisted of lanthanide ions. Zhang et al. reported purely inorganic [Mn(H$_2$O)$_2$]MoO$_2$]$_6$-1D chains using the (NH$_4$)$_6$MoO$_2$-4H$_2$O salt and Mn(Alc)$_2$-4H$_2$O as the starting reagents. This was the first example of a purely inorganic polymer built from the [MoO$_2$]$_8^{8-}$ units alternately linked by Mn(H$_2$O)$_2^{2+}$ ions. Wang et al. reported the synthesis of several polyoxomolybdate based compounds, including [Co$_3$L$_3$][H$_2$Mo$_2$O$_2$]-4DMA-2H$_2$O, where L = 1,3-bis(1H-imidazole-4-carboxoamido)metaphenylene and DMA = N$_2$N-dimethylacetamide. This compound was synthesized under mixed solvent conditions, employing the (NH$_4$)$_6$MoO$_2$-4H$_2$O salt, Co salt and ligands. Budantseva et al. reported a series of M$_n$[Mo$_2$O$_2$]$_3$(MoO$_2$]$_8$]-2H$_2$O (M = NH$_4$, K, Rb, Cs, Tl). The compounds were obtained by a hydrothermal synthesis also using ammonium paramolybdate as the reactant.

Several different, very interesting, 1D chain like structures are known from the literature employing different POM building units and lanthanide ions. For example a 1D zigzag chain like structure of [La(H$_2$O)$_3$Al(OH)$_3$MoO$_2$]$_{18}$-4H$_2$O built from Anderson-type [Al(OH)$_3$]MoO$_2$]$_{18}$- and La connectors has been reported by Shivaiah et al.

Another interesting example is the ([α-x-PW$_{11}$O$_{39}$]Tm$_{2}$(C$_2$O$_4$)(H$_2$O)]$_{28}^{28-}$ 1D chain like motif formed by unusual divancant di-Tm-containing [([α-x-PW$_{11}$O$_{39}$]$_{11}$–Keggin POM) subunits connected to each other through oxalate linkers as reported by Zhang et al. These chains are interestingly aligned in two different spatial orientations. Also, a 1D chain like structure containing peroxisopolyoxomolybdate [H$_3$L$_2$(H$_2$O)$_{24}$]MoO$_4$[([Mo$_3$O$_{22}$O$_2$])$_{2}$]$^{38-}$ was formed by [La$_2$(MoO$_4$)(H$_2$O)$_{14}$][([Mo$_3$O$_{22}$O$_2$])$_{2}$]$^{38-}$ units connected by additional La$^{3+}$ cations. Other 1D chain like structures can be found by the reader in the review by Ma et al.

Here we report a novel series of 1D chain like structures built from the [MoO$_2$]$_8^{8-}$ POM unit obtained for Ho$^{3+}$, Tm$^{3+}$, and Lu$^{3+}$ ions. We have additionally doped the LuPOM 1D chains with a low percentage of Eu$^{3+}$ ions in order to achieve red light emission. It was observed that varying the excitation wavelength of several of the compounds influenced the change in emission color.

2. Experimental section

2.1. Synthesis

All chemicals (analytical-grade) were purchased from Sigma-Aldrich or VWR and used without further purification. The octamolybdate POMs were prepared as described below.

0.4 mmol (NH$_4$)$_6$MoO$_2$-4H$_2$O dissolved in 6 mL of distilled water and 1 mL of methanol was heated up to 80 °C until all solid products were completely dissolved. The heating was switched off and after cooling down the solution to room temperature 0.4 mmol of Ln(NO$_3$)$_3$-6H$_2$O (Ln = Ho$^{3+}$, Tm$^{3+}$, Lu$^{3+}$) dissolved in 2 mL of distilled water were added dropwise with vigorous stirring. The solution was left to stir for 30 min. The solution was next filtered and the precipitate was discarded.

The filtrate was set up for crystallization through vapor diffusion of methanol into the water–methanol solution of the LnPOMs (at 7 °C). Crystals suitable for measurements were obtained after 1–5 days. Their chemical formula can be written as (NH$_4$)$_6$Ln[MoO$_2$]$_8$-xH$_2$O (where Ln = Ho$^{3+}$, Tm$^{3+}$, Lu$^{3+}$). They were filtered off and dried in air for further analysis (PXRD, XRF and luminescence spectroscopy). To prepare the Eu$^{3+}$ doped compounds a similar synthetic procedure was followed, just that an appropriate mixture of Ln(NO$_3$)$_3$-6H$_2$O and Eu(NO$_3$)$_3$·6H$_2$O was used (for example, 1% Eu(NO$_3$)$_3$·6H$_2$O and 99% Lu(NO$_3$)$_3$·6H$_2$O, in total 0.4 mmol to obtain 1% Eu:LuPOM).

2.2. Characterization

For the structures of the octamolybdate 1D-chains, X-ray intensity data were collected at 100 K, on a Rigaku Oxford Diffraction Supernova Dual Source (Cu at zero) diffractometer equipped with an Atlas CCD detector using ω scans and MoKα (λ = 0.71073 Å) and CuKα (λ = 1.54184 Å) radiation, for the Lu-, TmPOMs and HoPOM, respectively. The images were interpreted and integrated with the program CrysalisPro. Using
Olex2 the structures were solved by direct methods using the ShelXS structure solution program and refined by full-matrix least-squares on $F^2$ using the ShelXL program package. All atoms were refined anisotropically. For both structures, hydrogen atoms of coordinated, as well as solvent water molecules, could not be located from a difference Fourier electron density map and hence were not included in the refinements. CSD reference numbers: CSD 1887985 (HoPOM), 1887986 (TmPOM) and 1887987 (LuPOM). Powder XRD patterns were recorded using a Thermo Scientific ARL XTRA diffractometer equipped with a Cu Ka ($\lambda = 1.5405$ Å) source, a goniometer and a Peltier cooled Si (Li) solid-state detector. Before measurements the crystals were crushed in a mortar to form a fine powder. For determining the Ln$^{3+}$ concentrations a Rigaku NEX CG Energy Dispersive X-ray Fluorescence (EDXRF) spectrometer was used. Low energy “soft” X-rays (1–50 keV) are emitted from an X-ray tube. The NEX CG software was used to calculate the concentration of the Ln$^{3+}$ elements. Thermogravimetry (TGA) and differential thermal analysis (DTA) were performed on a Stanton Redcroft 1500 apparatus under air flow, and the temperature region is from 20 °C to 1200 °C with a heating rate of 10 °C min$^{-1}$. The luminescence of solid samples was recorded. Dried crystals were put between quartz plates (Starna cuvettes for powdered samples, type 20/C/Q/0.2). Luminescence measurements were performed on an Edinburgh Instruments FLSP920 UV-vis-NIR spectrometer. A 450 W Xe lamp was used as the steady state excitation source. Luminescence decay times were recorded using a 60 W pulsed Xe lamp, operating at a frequency of 100 Hz. A Hamamatsu R928P photomultiplier tube was used to detect the emission signals in the near UV to visible range. In order to compare the measurements, the same amounts of powders were used, as well as the same settings for each measurement (same slit size, step, and dwell time). All of the excitation spectra are recorded observing the strongest f-f emission peak. All emission spectra in the manuscript have been corrected for detector response. For all of the compounds the luminescence decay curves were measured when excited into the broad LMCT band and monitored at the appropriate wavelength ($^5D_0 \rightarrow ^7F_2$ transition peak). All of the decay curves could be well fitted using a biexponential function (eqn (1)).

$$I = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right)$$

where $I$ represents the luminescence intensity and $A_1$ and $A_2$ are constants, $t$ is time and $\tau_1$ and $\tau_2$ are the luminescence lifetimes.

3. Results and discussion

3.1. Synthesis and characterization

All 1D chain LnPOMs were obtained under mild reaction conditions, employing a simple 30-minute synthesis. Single crystals were obtained through vapor diffusion of methanol into the solution of the LnPOM. In this work we show that Ln$^3+$(Mo$_5$O$_{26}$) (Ln$^{3+}$ = Ho, Tm, Lu) 1D chains can be obtained using the (NH$_4$)$_6$Mo$_5$O$_{26}$·4H$_2$O salt. We have employed a very similar synthesis for the preparation of a series of tetracnuclear LnPOMs (Ln$^{3+}$ = La–Dy), whereas for Er$^{3+}$ and Yb$^{3+}$ mononuclear sandwich type structures could only be obtained.

When attempting to obtain tetracnuclear or mononuclear sandwich type POMs for Ho$^{3+}$, Tm$^{3+}$, and Lu$^{3+}$ using this synthesis no single crystals suitable for analysis could be obtained. Only upon doubling the amount of the Ln$^{3+}$ nitrate salt single crystals of LnPOMs for Ho$^{3+}$, Tm$^{3+}$, and Lu$^{3+}$ could be obtained. When using the same approach for Ln$^{3+}$ = La–Dy, Er, Yb the same compounds were obtained as previously reported by us (tetracnuclear or mononuclear type structures).

To characterize the obtained HoPOM, TmPOM and LuPOM compounds we have used single crystal diffractometry (see below). All of the Eu$^{3+}$ doped LuPOM compounds were characterized using powder XRD (PXRD) to confirm that after Eu$^{3+}$ doping the LuPOM structure remained unchanged. The compiled PXRD pattern of the compounds can be found in Fig. 1. The samples were also analyzed by FT-IR (Fig. S1†). Their IR spectra recorded in the 650–4000 cm$^{-1}$ range are virtually identical strongly suggesting a common structure of all these compounds. The IR spectra show the O–H and N–H absorption bands as well as typical frequencies for Mo–O bonds. The characteristic absorptions around 906 and 847 cm$^{-1}$ are attributed to the Mo–O$_2$ and Mo–O$_n$–Mo vibrations, respectively. The Mo–O$_2$–Mo absorption is not visible in our spectrum as it starts only from 650 cm$^{-1}$ (and the absorption is expected around 630 cm$^{-1}$). These vibrations are somewhat red shifted compare to those of [γ-Mo$_5$O$_{26}$]$.^{17}$ The bonds at around 3400–3500 cm$^{-1}$ and 3187 cm$^{-1}$ are attributed to the $\nu_{ad}$(H$_2$O) and $\nu_{as}$(NH$_3$) vibrations, respectively. The bonds at around

![Fig. 1. Powder XRD diffractograms of LuPOM and Eu$^{3+}$ doped LuPOMs.](image)
1625 cm$^{-1}$ and 1420 cm$^{-1}$ are attributed to (H$_2$O) and (NH$_3$) deformation vibrations. The exact Eu$^{3+}$ doping percentages were determined using XRF. A table overviewing the results can be found in the ESI (Table S1†).

3.2. Crystal structures

Compounds HoPOM, TmPOM and LuPOM are isostructural and crystallize in the triclinic space group $P1$; therefore only compound LuPOM will be described in detail. The data collection and refinement statistics for all three compounds are presented in Table S2.† The asymmetric unit of LuPOM consists of one lutetium ion and two halves of the [Mo$_8$O$_{28}$]$^{8-}$ polyoxometalates. The two polyoxometalates are attached through a bridging oxygen atom and the lutetium ion is coordinated to one of the polyoxometalates by two oxygen atoms. The [Mo$_8$O$_{28}$]$^{8-}$ unit has $C_1$ symmetry and is composed of eight molybdenum atoms, which impose an octahedral geometry at their highest oxidation state (+6). Four types of oxygen atoms exist in the [Mo$_8$O$_{28}$]$^{8-}$ units – terminal oxygen Ot, double-bridged oxygen O(µ2), three-bridging oxygen O(µ3), and four-bridging oxygen O(µ4). The lutetium ion is surrounded by eight oxygen atoms, two from the same [Mo$_8$O$_{28}$]$^{8-}$ unit and six oxygen atoms from six water molecules. Every second [Mo$_8$O$_{28}$]$^{8-}$ unit is linked to two such eight-coordinated Lu$^{3+}$ ions. A 1D polymeric chain is generated along the [101] direction. The crystal structure of the LuPOM is presented in Fig. 2 and 3.

3.3. Luminescence properties

The room temperature luminescence properties of the HoPOM, TmPOM, and LuPOM, as well as the Eu$^{3+}$ doped LuPOM 1D chains, were investigated. In the case of the HoPOM and TmPOM no characteristic $f$-$f$ transitions of Ho$^{3+}$ or Tm$^{3+}$, respectively, were observed in the spectra (see ESI Fig. S2a and b†). Only the O $→$ Mo charge transfer bands were detected in the excitation and emission spectra. Lu$^{3+}$ is a silent lanthanide; therefore no emission from the LuPOM was expected (Fig. S2c†). We doped the LuPOM compound with different percentages of Eu$^{3+}$ ions (1%, 2.5%, 5%, and 7.5%) in an attempt to obtain red-emitting LuPOM 1D chains. A strong emission signal from Eu$^{3+}$ could be obtained for the LuPOM doped with 7.5% Eu$^{3+}$ ions. A combined excitation–emission spectrum of this sample is presented in Fig. 4. In the excitation band a strong broad band between 250 and 400 nm, with a maximum at 317.0 nm is observed. Several additional $f$-$f$ transition peaks were detected in the excitation spectrum (see assignment of peaks in Table 1). The emission spectra consist of the characteristic Eu$^{3+}$ $f$-$f$ transition peaks: $^5D_0 \rightarrow ^7F_0$, $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_2$, $^5D_0 \rightarrow ^7F_3$, and $^5D_0 \rightarrow ^7F_4$. The decay time of this compound was also investigated. The decay profile could be well fitted with a biexponential function, as there were short and long components present. The long decay component can be assigned to the Eu$^{3+}$ emission, whereas the short component most likely belongs to the POM matrix. The decay values were calculated to be 7.956 µs and 155.590 µs. The decay profile can be found in the ESI, Fig. S3a†.
As mentioned earlier we also doped the LuPOM material with 1%, 2.5%, and 5% Eu$^{3+}$ ions. In the emission spectra of these samples aside from the characteristic Eu$^{3+}$ peaks we observed the presence of a broad charge transfer band, which indicates incomplete energy transfer to the Eu$^{3+}$ ions upon lower doping (Fig. 5). The excitation spectra for the 1%, 2.5%, and 5% Eu$^{3+}$ doped samples are presented in Fig. S3a–c.† A shift of the maximum of the LMCT band towards lower wavelength values can be observed upon higher Eu$^{3+}$ doping (from 354.0 nm for 1% Eu:LuPOM, 352.0 nm for 2.5% Eu:LuPOM, 332.0 nm for 5% Eu:LuPOM and 317.0 nm for 7.5% Eu:LuPOM). For the samples doped with 2.5% and 5% Eu$^{3+}$ ions we investigated varying the excitation wavelength, which resulted in tuning the emission color from orange/pink to dark blue. These two samples were chosen, as there are strong f–f Eu$^{3+}$ transition peaks visible in the emission spectra and an important contribution from the LMCT band. The different colors obtained upon changing the excitation wavelength have been visualized in the CIE 1931 space color diagrams in Fig. 6.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Assignment of peaks labeled in Fig. 4 (7.5% Eu:LuPOM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Label</td>
<td>Wavelength (nm)</td>
</tr>
<tr>
<td>----------</td>
<td>-----------------</td>
</tr>
<tr>
<td>Excitation</td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>317.0</td>
</tr>
<tr>
<td>b</td>
<td>393.3</td>
</tr>
<tr>
<td>c</td>
<td>414.9</td>
</tr>
<tr>
<td>d</td>
<td>463.5</td>
</tr>
<tr>
<td>Emission</td>
<td></td>
</tr>
<tr>
<td>e</td>
<td>578.9</td>
</tr>
<tr>
<td>f</td>
<td>593.3</td>
</tr>
<tr>
<td>g</td>
<td>614.7</td>
</tr>
<tr>
<td>h</td>
<td>649.3</td>
</tr>
<tr>
<td>i</td>
<td>698.3</td>
</tr>
</tbody>
</table>

Fig. 5  Emission spectra with rainbows fitted underneath the curves of (a) 1% Eu:LuPOM, (b) 2.5% Eu:LuPOM, and (c) 5% Eu:LuPOM (in all cases the emission spectrum was recorded when excited into the maximum of the LMCT band).

Fig. 6  CIE 1931 space color diagrams for (a) 2.5% Eu:LuPOM and (b) 5% Eu:LuPOM showing a change of color when exciting at different wavelengths.
The exact CIE coordinates are given in Table S3† for 2.5% Eu:LuPOM and Table S4† for 5% Eu:LuPOM. Emission maps presenting the emission spectra at different wavelengths can be found in Fig. 7 and 8 for 2.5% Eu:LuPOM and 5% Eu:LuPOM, respectively. The decay times of these compounds were also investigated, and similar to what was observed for the 7.5% Eu:LuPOM the decay profiles could be fitted well using a biexponential function, where shorter and longer components were visible. An overview of the decay time values for all the compounds has been presented in Table 2. The decay profiles of 5% Eu³⁺, 2.5% Eu³⁺ and 1% Eu³⁺ doped LuPOMs are presented in Fig. S4b–d.†

Table 2 Luminescence decay times of Eu³⁺ doped LuPOM samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>τ₁ (µs)</th>
<th>τ₂ (µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% Eu:LuPOM</td>
<td>5.255</td>
<td>26.828</td>
</tr>
<tr>
<td>2.5% Eu:LuPOM</td>
<td>7.613</td>
<td>121.613</td>
</tr>
<tr>
<td>5% Eu:LuPOM</td>
<td>7.668</td>
<td>124.705</td>
</tr>
<tr>
<td>7.5% Eu:LuPOM</td>
<td>7.956</td>
<td>155.590</td>
</tr>
</tbody>
</table>

4. Conclusions

In this work we report a novel series of 1D chain like structures built from [Mo₈O₂₈]⁶⁻ POM units obtained for Ho³⁺, Tm³⁺, and Lu³⁺. These 1D chains are obtained employing the (NH₄)₆Mo₇O₂₄·4H₂O salt and lanthanide nitrate salts, under mild reaction conditions. To the best of our knowledge, this is a rare example of compounds built from the [Mo₈O₂₈]⁶⁻ unit, and the first series of compounds with this POM unit built from lanthanide ions. Also, they are among the few examples of 1D chain like structures built from POM units reported in the literature. The HoPOM and TmPOM did not show the characteristic f–f transitions of these lanthanides when excit- ing into the LMCT band. Yet, the LuPOM compound could be doped with up to 7.5% Eu³⁺ ions without changing the structure yielding red or varying orange/pink to dark blue emission colors.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

A. M. K. acknowledges Ghent University’s Special Research Fund (BOF) for a Postdoctoral Mandate (project BOF15/PDO/ 091). K. V. H. thanks the Hercules Foundation (project AUGE/11/029 “3D-SPACE: 3D Structural Platform Aiming for Chemical Excellence”) and the Special Research Fund (BOF) – UGent (project 01N03217) for funding.

References


