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# Amplified Luminescence in Organo-Curium Nanocrystal Hybrids

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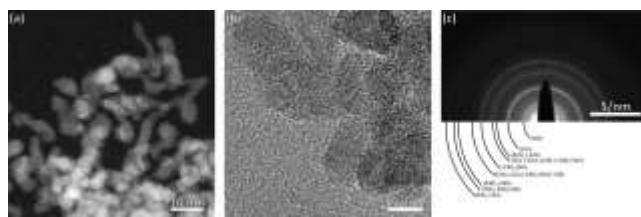
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**ABSTRACT:** We present the first report of ligand-sensitized actinide luminescence in a lanthanide nanoparticle host. Here, we demonstrate amplified luminescence of  $^{248}\text{Cm}^{3+}$  doped in a  $\text{NaGdF}_4$  lattice, achieved through optical pumping of a surface-localized metal chelator (3,4,3-LI[1,2-HOPO]), capable of sensitizing  $\text{Cm}^{3+}$  excited states. We provide evidence for  $\text{Cm}^{3+} \rightarrow \text{Eu}^{3+}$  energy transfer and subsequent europium emission. Taken together, the data suggest the possibility of using such materials in theranostic applications, with a ligand-sensitized actinide or radio-lanthanide serving the dual roles of a nuclear decay source for radiotherapeutics, and as a luminescent center or energy transfer conduit to another emissive metal ion, for biological imaging.

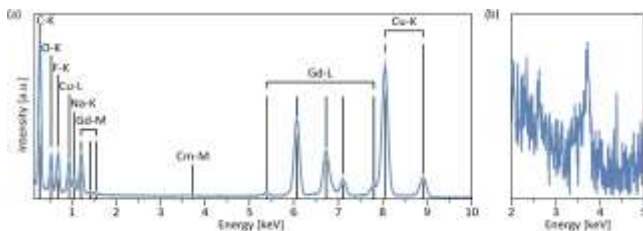
The exploration of lanthanide luminescence in nanoparticle structures over the last decade has found much of its motivation behind their potential use in lasing, spectral conversion and biomedical imaging applications.<sup>1-6</sup> The result has been a broad body of literature produced in the areas of sensitized lanthanide luminescence, lanthanide spectral conversion, and actinide photospectroscopy in lanthanide host materials.<sup>3, 6-13</sup> Additionally, significant investigations have delved into creating *f*-element materials capable of serving the dual purpose of targeted radiotherapeutics and photoluminescent cell/tissue-imaging agents.<sup>1, 14-17</sup> Less work has considered the prospect of combining these research areas, through the synthesis of ligand-sensitized lanthanide nanoparticles with highly radioactive actinide co-dopants for radiotherapy applications. The dearth of research in this area motivated an investigation into the luminescent properties of curium-doped  $\text{NaGdF}_4$  nanoparticles featuring a surface-bound chelator, 3,4,3-LI(1,2-HOPO), hereafter 3,4,3. To our knowledge, this study marks the first of its kind, with an actinide being successfully doped into the hexagonal  $\text{NaGd(Y)F}_4$ -type lattices that have become common host

crystals for studies in solid-state lanthanide luminescence. Nanoparticles were synthesized from metal acetate precursors in a 1-oleic acid/1-octadecene mixture and were decorated with 3,4,3 by substitution of 1-oleate ligands, following methods adapted from the literature.<sup>18</sup> While we utilize a low-activity  $^{248}\text{Cm}^{3+}$  isotope for the sake of safety, these results should be applicable to the more radioactive  $^{243}\text{Cm}^{3+}$  and  $^{244}\text{Cm}^{3+}$  isotopes, if not other actinides and lanthanide radioisotopes as well.

The Cm-doped  $\text{NaGdF}_4$  formed ill-defined nanoparticles without distinct surface facets. Many nanoparticles were approximately spherical and up to 10 nm in size (Figure 1a), but several larger nanoparticles seem to have formed by coalescence. The presence of distinct necking-like features supports our hypothesis (Figure 1b). This is in accordance with reports of a low surface energy.<sup>19</sup> Electron diffraction patterns over large areas confirmed the hexagonal  $\beta\text{-NaGdF}_4$  phase (Figure 1c).<sup>20</sup> Using energy-dispersive X-ray spectroscopy (EDS), the Cm-content was quantified as being below 1% (Figure 2a, 2b).

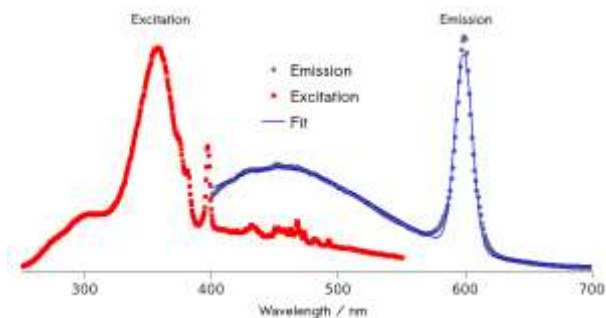


**Figure 1.** (a) High-angle annular dark field scanning TEM (HAADF-STEM) image of several nanoparticles; (b) High-resolution TEM (HRTEM) image of a few nanoparticles, (c) electron diffraction pattern of a large area.



**Figure 2.** (a) Typical EDS spectrum of Cm-NaGdF<sub>4</sub>. Cu and C peaks are due to the grid onto which the nanoparticles were deposited, whereas oxygen is a common residual gas in the microscope column; (b) Close-up of the weak Cm-M peak. The energy scale is the same as in (a), but the intensity scale has been stretched approximately 40-times.

Excitation at 357 nm into the ligand band of 3,4,3-modified, Cm-doped nanoparticles results in a broad, ligand-centered emission (453 nm) derived from 3,4,3 singlet/triplet relaxation, and a narrow emission peaking at 598 nm ( ${}^6D_{7/2} \rightarrow {}^8S_{7/2}$ ) arising from Cm<sup>3+</sup> excited state decay (Figure 1). Excitation spectra acquired by monitoring the 598-nm signal reveal that luminescence at this wavelength responds to excitation over the range 300–360 nm (ligand), while also demonstrating a sensitivity to *f-f* transitions originating from direct excitation of the curium center between *ca.* 390–500 nm, with a peak at 397 nm assigned to Cm<sup>3+</sup>  ${}^8S_{7/2} \rightarrow {}^6I_1$  (Figure 3).<sup>9</sup>



**Figure 3.** Steady-state photoluminescence (PL) of Cm-doped NaGdF<sub>4</sub>-3,4,3 nanoparticles. Red: Excitation spectrum measured at Cm<sup>3+</sup> ( ${}^6D_{7/2} \rightarrow {}^8S_{7/2}$ ) emission at 598 nm. The peak at 350 nm is due to ligand absorption; the strong narrow excitation band at *ca.* 400 nm is the result of direct light absorption by Cm<sup>3+</sup>. Blue: PL spectrum representing a summation of ligand and Cm<sup>3+</sup> ion emission.

Further evidence of surface-bound ligand sensitization is seen through comparison of luminescence in the washes of the ligand-modification reactions with the nanoparticle suspension. Following a series of centrifugation/wash cycles to remove excess 3,4,3, a residual luminescence assigned to formation of the 3,4,3-LI(1,2-HOPO)-Cm molecular complex is observed, with roughly 1/40<sup>th</sup> the emission intensity of the nanoparticle sample being present in the supernatant of the third wash. In addition, formation of the molecular complex in the washes is also evidenced by a significant (12 nm) shift in the Cm<sup>3+</sup> emission band observed in the washes at wavelengths previously reported for Cm<sup>3+</sup>-3,4,3 ( $\sim$  610 nm),<sup>21</sup>

which is notably distinct from the 598-nm emission wavelength of the sensitized nanocrystals (SI). Bathochromic Cm(III) fluorescence shifts, observed with the transition from the lowest energy crystal field level of the first excited  ${}^6D_{7/2}$  multiplet to the ground multiplet of the  ${}^8S_{7/2}$  state, have been qualitatively associated with trends in the nephelauxetic effect.<sup>22</sup> The large  $\sim$ 16-nm shift ( $\sim$ 450 cm<sup>-1</sup>) observed upon complexation of the free Cm(III) ion by 3,4,3 in aqueous solution is characteristic of strong ligand interactions that result in diminished electrostatic repulsion effects. Within the nanocrystals, the fluorescence shift is much less pronounced ( $\sim$ 4 nm or  $\sim$ 120 cm<sup>-1</sup>) as the Cm ions interact with fluoride anions and the larger organic ligand is kept at the particle surface. While relatively small compared to several crystalline matrices, including Cs<sub>2</sub>NaYCl<sub>6</sub>,<sup>22-23</sup> this shift is consistent with those observed in crystalline halides CmF<sub>3</sub> and CmCl<sub>3</sub> ( $\sim$ 90 and  $\sim$ 82 cm<sup>-1</sup>, respectively),<sup>24</sup> prior to corrections made for the crystal field splitting of the  ${}^6D_{7/2}$  multiplet. This is further confirmation of the constrained environment of the Cm ions within the nanoparticle host.

Co-substitution with Eu<sup>3+</sup> reveals that Cm<sup>3+</sup>  $\rightarrow$  Eu<sup>3+</sup> energy transfer is also possible, with direct photoexcitation of the curium ions at 400 nm resulting in the appearance of the europium  ${}^5D_0 \rightarrow {}^7F_2$  emission band at 612 nm. Population of europium's  ${}^5D_1$  manifold presumably arises from energetic exchange between the resonant  ${}^6D_{7/2}$  and  ${}^5D_0$  states in curium and europium centers, respectively (SI).

Measurements of quantum yields for the sensitization efficiency of the Cm-only system reveal a quantum yield of approximately 0.4% for the Cm<sup>3+</sup> emission; factoring in ligand emission results in a total luminescence quantum yield of 1.2%. While these values are low, the curium doping levels employed here (0.075%) are far lower than those typically used in correspondent lanthanide luminescence studies. In past work, Eu<sup>3+</sup> doping levels of 5% in NaGdF<sub>4</sub> with this ligand set, were used.<sup>25</sup> Despite the  $\sim$ 70-fold dopant excess used in those studies relative to the curium investigations here, the sensitized-europium system was found to display a quantum efficiency only an order of magnitude ( $\Phi = 3.3\%$ ), greater than what we observe for the curium system.<sup>25</sup> It is worth noting that the 5% doping level used for the europium study did not place the system in a concentration-quenching regime, suggesting a significantly higher efficiency for ligand-curium energy transfer relative to the europium nanoparticle analog, a finding consistent with an earlier study of luminescence in the 3,4,3-LI(1,2-HOPO)-Cm molecular complex.<sup>21</sup>

Time-dependent luminescence was investigated through pulsed excitation of the ligand band at 350 nm, with concurrent monitoring of sample emission at 598 nm (SI). We observed a triexponential luminescence decay, with rates of  $k_1 = 647$  s<sup>-1</sup>,  $k_2 = 139$  s<sup>-1</sup>, and  $k_3 = 8.4$  s<sup>-1</sup>, with their weighted-average yielding a mean decay time of 1.26 ms (normalized weights for the respective decay

phases are  $c_1 = 0.29$ ,  $c_2 = 0.55$ ,  $c_3 = 0.16$ ). Notably, this average lifetime is much longer than those of the Cm aquo ion and the 3,4,3-Cm molecular complex (65 and 383  $\mu\text{s}$ , respectively, in  $\text{H}_2\text{O}$ )<sup>21</sup> and more consistent with that of Cm embedded in a solid  $\text{ThO}_2$  crystalline host matrix (1380  $\mu\text{s}$ ).<sup>22</sup> Incorporating past measurements of the 3,4,3 triplet state decay allowed determining the ligand-curium energy transfer efficiency as 0.22 (SI).

Our experiments confirm interstitial doping of actinides in  $\text{NaGdF}_4$  hosts is indeed possible, opening up the potential for synthesizing radioactive, luminescent nanocrystals for therapeutic and diagnostic medical applications. Additionally, the particular system examined in this manuscript allows for the possibility of bio-imaging tissues at relatively low excitation powers, with the high extinction coefficient of 3,4,3 permitting relatively efficient photon absorption and  $\text{Cm}^{3+}$  luminescence relative to direct  $f\text{-}f$  actinide excitation.

## ASSOCIATED CONTENT

**Supporting Information.** Experimental procedures, quantum yield data, time-resolved luminescence, energy transfer calculations, and  $\text{Eu}^{3+}$ - $\text{Cm}^{3+}$  excitation spectra are included in the Supporting Information. This material is available free of charge via the internet at <http://pubs.acs.org>.

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### Notes

RJA and PA are listed as inventors on a patent application filed by the Lawrence Berkeley National Laboratory and describing inventions related to the research results presented here. The authors declare no other competing financial interests.

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