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Article

# <sup>1</sup>O<sub>2</sub> Generating Luminescent Lanthanide Complexes with 1,8-Naphthalimide-Based Sensitizers

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Supporting Information

ABSTRACT: Lanthanide ion (Ln<sup>III</sup>) complexes with two new 1,8-naphthalimide-based ligands, Nap-dpe and Nap-cbx, were isolated, and their photophysical properties were explored. Upon excitation at 335 nm, Nap-dpe and Napcbx sensitize visible and near-infrared emitting Ln<sup>III</sup> ions (Ln<sup>III</sup> =  $Eu^{III}$ ,  $Nd^{III}$ , and  $Yb^{III}$ ) and generate singlet oxygen ( $^{1}O_{2}$ ). The quantum yields of Eu<sup>III</sup> luminescence for [Eu(Nap- $(bx)_{3}^{3+}$  and  $[Eu(Nap-dpe)_{3}^{3+}]^{3+}$  are 16.7% and 8.3%, respectively, with <sup>1</sup>O<sub>2</sub> generation efficiencies of 41% and 59%, respectively. The efficiencies of  ${}^{1}O_{2}$  generation for the NIR emitting complexes  $[Ln(Nap-dpe)_3]^{3+}$  are 59% and 56%, respectively, and those for  $[Ln(Nap-cbx)_3]^{3+}$   $(Ln^{III} = Nd^{III},$ 



Yb<sup>III</sup>) are 64% and 61%, respectively. In an oxygen-free environment, the quantum yields of Eu<sup>III</sup> luminescence for [Eu(Nap- $(\mathbf{bx})_3$ <sup>3+</sup> and  $[\mathrm{Eu}(\mathbf{Nap-dpe})_3]^{3+}$  increase to 20% and 18%, respectively.

# INTRODUCTION

Ln<sup>III</sup> ion luminescence is based on 4f-4f transitions. Due to shielding of the 4f orbitals by the filled 5s and 5p orbitals, these transitions are not significantly altered by the ion's environment. This leads to characteristic emission with high color purity making luminescent Ln<sup>III</sup> complexes great candidates for application as imaging agents,<sup>1,2</sup> as sensors,<sup>3</sup> as anti-counterfeiting inks,<sup>4</sup> and in optics.<sup>5,6</sup> However, direct excitation of Ln<sup>III</sup> ions is inefficient due to the parity-forbidden nature of the f-ftransitions, which leads to low extinction coefficients. A sensitizer (or antenna) is coordinated to the metal ion to promote Ln<sup>III</sup>-centered emission, in a process called the antenna effect. As illustrated in Figure 1, a photon is absorbed by the antenna and generates a ligand-based singlet (<sup>1</sup>S) excited state. After intersystem crossing (ISC), a triplet (<sup>3</sup>T) excited state is populated, which then transfers energy to the Ln<sup>III</sup> excited state. This excited state decays by luminescence. Using an organic ligand as a sensitizer is advantageous because it can be tailored to a specific application or property. For example, our group has isolated several functionalized pybox (pyridine-bis(oxazoline)) ligands that lead to highly luminescent visible Ln<sup>III</sup> emitters in organic solvents.<sup>8</sup> When para-functionalized with a glycol tail, the new complexes display efficient luminescence in water, which is valuable for imaging in biological systems.

Our group is now interested in luminescent Ln<sup>III</sup> complexes with additional properties.<sup>10</sup> As illustrated in Figure 1, the <sup>3</sup>T state of the ligand can be used to also generate singlet oxygen (<sup>1</sup>O<sub>2</sub>), a cytotoxic species.<sup>11</sup> Examples of luminescent Ln<sup>III</sup> compounds capable of generating <sup>1</sup>O<sub>2</sub> are Tb<sup>III</sup> DOTA-based complexes functionalized with either naphthyl or azaxanthonyl pendants. These complexes display Tb<sup>III</sup> emission efficiencies as high as 24% and  ${}^{1}O_{2}$  generation efficiencies ( $\phi_{1O2}$ ) as high as 12%.<sup>12</sup> Although the complexes are good Tb<sup>III</sup> sensitizers, their <sup>1</sup>O<sub>2</sub> generation efficiencies fall well below the efficiencies of organic photosensitizers.<sup>13</sup> More recently, Maury and coworkers described a tris-picolinato-1,4-7-triazacyclononane macrocycle with  $\phi_{1O2}$  = 80% when complexed to Gd<sup>III</sup>. However, when the Gd<sup>III</sup> ion was exchanged for Yb<sup>III</sup>, only luminescence was observed, due to the competition between the two energy transfer pathways.<sup>14</sup> This group also recently described helicenic complexes of Ln<sup>III</sup>, and in this case, good efficiencies of both metal-centered emission and <sup>1</sup>O<sub>2</sub> generation were observed.<sup>15</sup> As shown in Figure 1, the  ${}^{3}T$  state is responsible for generation of both <sup>1</sup>O<sub>2</sub> and Ln<sup>III</sup> luminescence, and competing nonradiative processes lead to quenching of the excited states. A good understanding of the interplay between the two properties is important to enable researchers to use compounds with phototoxic properties for therapeutic applications and to track them *in situ* through Ln<sup>III</sup>-centered luminescence. Thus, we aimed to isolate Ln<sup>III</sup> complexes that display efficient luminescence and, in addition, efficiently generate  ${}^{1}O_{2}$ . We chose naphthalimide as the  ${}^{1}O_{2}$  generating functional group.

1,8-Naphthalimide is known for its near unit quantum yield of ISC and high  $\phi_{102}$  in acetonitrile.<sup>16</sup> 1,8-Naphthalimide-based compounds are also efficient photosensitizers of  ${}^{1}O_{2}$ , with reported  $\phi_{102}$  in the range 5–82%,<sup>16–19</sup> and are proposed for biological sensing,  $2^{20-23}$  as anti-inflammatory drugs,  $2^{4}$  and as anticancer therapeutics.  $2^{5-28}$  For example, the derivatives

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**Figure 1.** Energy level diagram showing the energy transfer (ET) pathways for both  $Ln^{III}$  ion sensitization and  ${}^{1}O_{2}$  generation. Energy  $h\nu$  is absorbed by the ligand to populate a singlet excited state ( ${}^{1}S$ ). Intersystem crossing (ISC) leads to population of a triplet excited state ( ${}^{3}T$ ). This state can then transfer energy to populate the emissive \**f* excited state, which decays by luminescence (L) to the ground state, *f*. Alternatively, the energy transfer leads to  ${}^{1}O_{2}$  generation, which decays to triplet oxygen  ${}^{3}O_{2}$  by emitting at 1270 nm. Nonradiative (NR) (dash-dot lines) pathways lead to quenching of excited states. Competing radiative processes are fluorescence (F) and phosphorescence (P). Energy levels are not drawn to scale.

amonafide and mitonafide were tested in clinical trials as anticancer agents.<sup>29,30</sup> 1,8-Naphthalimide and its derivatives intercalate between DNA base pairs and form strong van der Waals interactions,<sup>31</sup> resulting in reduced gene expression.<sup>32</sup> Selected derivatives are reported to bind and disable topoisomerase II (the enzyme responsible for DNA packaging)<sup>33</sup> or tubulin,<sup>34</sup> or nitroreductase,<sup>35</sup> considerably hindering cell function. Naphthalimide derivatives are often used as fluorescent reporters.<sup>17,24,26,36,37</sup> Hideg and co-workers described an example used to infiltrate chlorophyll-containing mesophyll cells of tobacco leaves and to detect <sup>1</sup>O<sub>2</sub> *in vitro* by luminescence in the range 500–600 nm.<sup>38</sup>

1,8-Naphthalimide is easily functionalized,<sup>39</sup> and many groups have investigated ways to increase its potency by adding heavy atoms,<sup>40,41</sup> extending conjugation,<sup>18</sup> or incorporating multiple cytotoxic motifs.<sup>42</sup> Some of these methods do increase the efficiency of ISC, but can result in shortening the lifetime of the <sup>1</sup>S excited states. This leads to decreased fluorescence efficiency,<sup>18,40,43</sup> and thus decreased signal-to-noise ratio,<sup>44</sup> preventing *in situ* and *in vivo* bioimaging. The long-lived luminescence of Ln<sup>III</sup> ions, which is a result of the forbidden nature of the *f*-*f* transitions, circumvents these two barriers inherent to organic fluorophores.

Luminescent Ln<sup>III</sup> complexes with 1,8-naphthalimide-based ligands have been reported, but their <sup>1</sup>O<sub>2</sub> generating properties have not been explicitly explored.<sup>6,45–52</sup> Ward and co-workers studied a Eu<sup>III</sup> DOTA-based complex featuring a 1,8-naphthalimide pendant that in solution displays concurrent ligand- and Eu<sup>III</sup>-centered emission as a white light emitter, and they determined a Eu<sup>III</sup> emission efficiency ( $\phi^{Eu}$ ) of 12%.<sup>53</sup> Pischel and co-workers discussed a polyamine-derivatized naphthalimide chromophore for Eu<sup>III</sup> luminescence with  $\phi^{Eu} = 11\%$ .<sup>54</sup> More recently, two 1,8-naphthalimidopyridine-*N*-oxides were shown to sensitize Eu<sup>III</sup> luminescence, with  $\phi^{Eu}$  of 42% and 29%.<sup>6</sup>

To expand our knowledge of compounds that generate  ${}^{1}O_{2}$  and that simultaneously display  $Ln^{III}$ -centered luminescence, we isolated two new 1,8-naphthalimide-based compounds, Napdpe and Nap-cbx, shown in Scheme 1, in which a  $Ln^{III}$  chelator

#### Scheme 1. Compounds Nap-dpe and Nap-cbx Studied Here



is present at the imide nitrogen atom. These ligands are easily synthesized, as discussed below, with direct communication of the two functional groups involved in the sensitization process; this synthetic strategy has proven successful in our group for other families of sensitizers.<sup>35–57</sup> We report here their ability to sensitize  $Ln^{III}$  luminescence in the visible and NIR and concurrently generate  ${}^{1}O_{2}$ .

#### RESULTS AND DISCUSSION

Nap-dpe and Nap-cbx were synthesized through condensation of 4-aminopyridine-2,6-diethyl ester or 4-aminopyridine-2,6dicarboxamide with 1,8-naphthalic anhydride in 34% and 46% yields, respectively (Figure S1; details of synthesis can be found in the Supporting Information). We confirmed their isolation by NMR and FT-IR spectroscopy and mass spectrometry (Figures S2-S8). Both compounds display broad absorption in the ultraviolet (UV) region with maxima at 334 nm. Exciting at  $\sim$ 330 nm results in fluorescence bands with maxima at 380 nm (Figures S9 and S10). Quantum yields of fluorescence ( $\phi^{\text{F}}$ ) are 2 and 5% for Nap-cbx and Nap-dpe (Table 1), respectively, and are similar to other naphthalimide derivatives.<sup>18,58-60</sup> Upon complexation to Gd<sup>III</sup>, which cannot be sensitized by these ligands due to its high lying emissive state  $({}^{3}P_{7/2}$  at 32,200 cm<sup>-1</sup>),<sup>61</sup> the emission spectra do not change appreciably (Figures S11 and S12). Instead, a slight red-shift of the emission maxima and an increase in emission efficiency to 6% for  $[Gd(Nap-dpe)_3]^{3+}$  and 7% for  $[Gd(Nap-cbx)_3]^{3+}$  are observed, consistent with planarization of the ligand upon coordination<sup>62</sup> and some phosphorescence contribution, due to improved ISC. In degassed solutions, fluorescence efficiencies increase slightly to  $\phi^F = 7\%$  for both **Nap**-based compounds and to 9% for both Gd<sup>III</sup> complexes, confirming that fluorescence decreases because of the simultaneous generation of  ${}^{1}O_{2}$  in aerated solution (vide infra).

To assess the adequacy of **Nap-dpe** and **Nap-cbx** as sensitizers for Ln<sup>III</sup> emission, the energies of their singlet (<sup>1</sup>S) and triplet (<sup>3</sup>T) excited states were determined through fluorescence and phosphorescence spectroscopy of the Gd<sup>III</sup> complexes (Table 1, Figures S13 – S18).<sup>63</sup> The <sup>1</sup>S and <sup>3</sup>T states are located at 25,700 and 18,300 cm<sup>-1</sup>, respectively, for  $[Gd(Nap-dpe)_3]^{3+}$  and 26,500 and 21,200 cm<sup>-1</sup>, respectively, for  $[Gd(Nap-cbx)_3]^{3+}$ . As expected, the <sup>3</sup>T excited state for both complexes is lower than what is reported for the <sup>3</sup>T state for chelators diethylpyridine-2,6-dicarboxylate (23,260 cm<sup>-1</sup>)<sup>64</sup> and *N,N,N',N'*-tetraethylpyridine-2,6-dicarboxamide (20,600 cm<sup>-1</sup>).<sup>65</sup> Using the INDO/ S-CIS method<sup>66</sup> and ORCA,<sup>67</sup> as implemented within LUMPAC,<sup>68</sup> we modeled the ground state geometry of the Table 1. Quantum Yields of Fluorescence ( $\phi^{F}$ ) for Nap-cbx and Nap-dpe and Their Gd<sup>III</sup> Complexes and Experimental and Calculated Singlet (<sup>1</sup>S) and Triplet (<sup>3</sup>T) State Energies

		$\operatorname{Experimental}^b$		$Calculated^{c}$	
Compound	$\phi^{{\scriptscriptstyle \mathrm{F}}^a}$ [%]	<sup>1</sup> S [cm <sup>-1</sup> ]	${}^{3}T [cm^{-1}]$	<sup>1</sup> S [cm <sup>-1</sup> ]	${}^{3}T [cm^{-1}]$
Nap-cbx	$2 \pm 07 \pm 1^{d}$				
Nap-dpe	$5 \pm 17 \pm 2^{d}$				
[Gd( <b>Nap-cbx</b> ) <sub>3</sub> ] <sup>3+</sup>	$7 \pm 09 \pm 1^{d}$	$26,500 \pm 60$	21,200 ± 50	31,840	21,115
$[Gd(Nap-dpe)_3]^{3+}$	$6 \pm 09 \pm 0^{d}$	$25,700 \pm 150$	$18,300 \pm 10$	26,231	18,035

<sup>*a*</sup>Measured at 25.0  $\pm$  0.1 °C. <sup>*b*</sup>Measured at 77 K in 1:1 dichloromethane:acetonitrile, reported as the 0–0 transition. <sup>*c*</sup>Calculated using the INDO/S-CIS method<sup>66</sup> and ORCA,<sup>67</sup> as implemented within LUMPAC.<sup>68</sup> <sup>*d*</sup>Degassed solutions of 1:1 dichloromethane:acetonitrile.



**Figure 2.** Ground state geometries of (a)  $[Gd(Nap-cbx)_3]^{3+}$  and (b)  $[Gd(Nap-dpe)_3]^{3+}$ . Hydrogen atoms are omitted for clarity. Insets show a tricapped trigonal prismatic coordination geometry around the  $Gd^{III}$ .

complexes (vide infra), as shown in Figure 2. The calculated <sup>1</sup>S and <sup>3</sup>T excited state energies are 26,231 cm<sup>-1</sup> and 18,035 cm<sup>-1</sup> for  $[Gd(Nap-dpe)_3]^{3+}$  and 31,840 cm<sup>-1</sup> and 21,115 cm<sup>-1</sup> for  $[Gd(Nap-cbx)_3]^{3+}$  (Table 1), respectively, which compare favorably with the experimental values. These energies indicate that both ligands are capable of sensitizing Eu<sup>III</sup>, which has its emissive state at 17,300 cm<sup>-1</sup>, in addition to Yb<sup>III</sup> and Nd<sup>III</sup>, with their emissive states at 11,500 cm<sup>-1</sup> and 11,600 cm<sup>-1</sup>, respectively.

The stoichiometry of the complexes in solution was determined through emission titrations of  $Eu(NO_3)_3$  with aliquots of either ligand (Figures S19 and S20). The stability constants for the 1:1, 2:1, and 3:1 ligand-to-metal species for the **Nap-dpe** complexes are  $8.02 \pm 0.07 (\log \beta_1)$ ,  $14.01 \pm 0.24 (\log \beta_2)$  $\beta_2$ ), and 19.00  $\pm$  0.20 (log  $\beta_3$ ) and are comparable to the values reported for diethylpyridine-2,6-dicarboxylate coordinating to Ln<sup>III</sup>, which are in the range 6.8–7.0 for log  $\beta_1$ , 12.8–14.0 for log  $\beta_2$ , and 16.3–18.0 for log  $\beta_3$ .<sup>71</sup> The stability constants for the **Nap-cbx** complexes are  $8.64 \pm 0.12 (\log \beta_1)$ ,  $14.67 \pm 0.11 (\log \beta_1)$  $\beta_2$ ), and 19.80  $\pm$  0.24 (log  $\beta_3$ ) (Table S1). These values are similar to the values reported for N,N,N',N'-tetraethylpyridine-2,6-dicarboxamide coordinating to Ln<sup>III</sup>, which are in the range of 7.3–8.5 for  $\log \beta_1$ , 13.8–16.0 for  $\log \beta_2$ , and 21.0–22.9 for  $\log \beta_2$  $\beta_3$ .<sup>65</sup> Speciation diagrams for both systems (Figure S21) confirm the presence of the 3:1 complex as the main metal-containing species at the appropriate conditions. The formation of the 3:1 complexes was further assessed through speciation studies using <sup>1</sup>H NMR spectroscopy with the diamagnetic La<sup>III</sup> analogs (Figures S22 and S23). It is noteworthy that while the speciation diagrams (Figure S21) indicate the possible presence of a small amount of the 2:1 ligand-to-metal ion complex in solution, as discussed below, emission lifetime measurements of the Eu<sup>III</sup> analogs show that the decay curves can be fit to a single exponential, which is consistent with the presence of one emissive species in solution.<sup>72–74</sup>

Attempts to isolate X-ray quality single crystals to confirm structure are ongoing. Nonetheless, the ground state geometry of each complex (Figure 2) was modeled using SPARKLE/ $PM3^{75}$  implemented in MOPAC2016.<sup>76</sup> In both cases, each Gd<sup>III</sup> ion is bound to three ligands through the nitrogen atom of the pyridine rings and the carbonyl oxygen atoms of the carboxamide or ester, respectively, resulting in a coordination number of 9. The coordination polyhedra (insets, Figure 2) are, in both cases, distorted tricapped trigonal prisms. To validate the calculated geometry, we compared calculated bond lengths and dihedral angles in these structures with known complexes for which crystallographic data is available. We obtained Gd–N and Gd–O bond distances around 2.5 and 2.6 Å, respectively, for both complexes, similar to what is observed for related dipicolinato-based complexes.<sup>77,78</sup> We calculated dihedral



**Figure 3.** Normalized emission spectra of the (a)  $[Ln(Nap-cbx)_3]^{3+}$  complexes  $[Ln = Eu^{III} (blue), Nd^{III} (light blue), or Yb^{III} (navy)]$  and of the (b)  $[Ln(Nap-dpe)_3]^{3+}$  complexes  $[Ln = Eu^{III} (red), Nd^{III} (pink), or Yb^{III} (dark red)]$  in 1:1 dichloromethane: acetonitrile measured at 25.0 ± 0.1 °C ( $\lambda_{exc} = 335$  nm).

Table 2. Difference in Energy ( $\Delta E$ ) between <sup>3</sup> T and <sup>5</sup> D <sub>0</sub> of Eu <sup>111</sup> , Quantum Yield of Eu <sup>111</sup> Luminescence ( $\phi^{Eu}$ ), Observed Lifet	ime
( $\tau$ ), Intrinsic Quantum Yield ( $\phi_{Eu}^{Eu}$ ), and Sensitization Efficiency ( $\eta_{sens}$ ) for the Eu <sup>III</sup> Complexes in Aerated and Degassed	
Solutions	

Compound	$\Delta E (^{3}T - {}^{5}D_{0}) [cm^{-1}]$	$\phi^{ ext{Eu}}  [\%]^{a}$	$\tau [\mathrm{ms}]^a$	$\phi {}^{{}_{\mathrm{Eu}}}{}_{{}_{\mathrm{Eu}}} [\%]$	$\eta_{sens}$ [%]
[Eu(Nap-dpe) <sub>3</sub> ] <sup>3+</sup>	~1,000	$8.3 \pm 0.0$	$0.51 \pm 0.01;$	22	38
		$17.7 \pm 0.2^{b}$	$0.81 \pm 0.02^{b}$	35 <sup>c</sup>	51 <sup>c</sup>
			$1.08 \pm 0.08^{d}$		
[Eu(Nap-cbx) <sub>3</sub> ] <sup>3+</sup>	~4,000	$16.7 \pm 0.1$	$0.68 \pm 0.01;$	32	52
		$20.4 \pm 0.5^{b}$	$0.85 \pm 0.03^{b}$	39 <sup>c</sup>	53 <sup>c</sup>
			$1.10 + 0.04^{d}$		

<sup>*a*</sup>Measured at 25.0  $\pm$  0.1 °C in 1:1 dichloromethane:acetonitrile. <sup>*b*</sup>Degassed 1:1 dichloromethane:acetonitrile <sup>*c*</sup>Calculated from data collected in degassed solutions. <sup>*d*</sup>Degassed 1:1 dichloromethane:acetonitrile at 77 K.

angles between the naphthalimide and pyridyl groups of about  ${\sim}51^\circ$  , which are comparable to experimental values in similar compounds.  $^6$ 

To characterize the photophysical properties of the complexes,  $[Ln(Nap-dpe)_3]^{3+}$  and  $[Ln(Nap-cbx)_3]^{3+}$  were isolated by reacting Nap-dpe or Nap-cbx with  $Ln(NO_3)_3$ 

(Ln<sup>III</sup> = Nd<sup>III</sup>, Eu<sup>III</sup>, Gd<sup>III</sup>, and Yb<sup>III</sup>) in 1:1 dichloromethane:acetonitrile. After filtration and subsequent solvent evaporation, the salts [Ln(Nap-dpe)<sub>3</sub>](NO<sub>3</sub>)<sub>3</sub> or [Ln(Nap-cbx)<sub>3</sub>](NO<sub>3</sub>)<sub>3</sub> precipitated as white powders in 91–98% yield (details in Supporting Information). Their isolation was confirmed through high resolution mass spectrometry (Figures S24 – S31). After redissolving them in 1:1 dichloromethane:acetonitrile, the complexes display the characteristic metal-based emission colors upon excitation. The emission spectra of [Eu(Nap-cbx)<sub>3</sub>]<sup>3+</sup> and [Eu(Nap-dpe)<sub>3</sub>]<sup>3+</sup> (Figure 3) show the <sup>5</sup>D<sub>0</sub>  $\rightarrow$  <sup>7</sup>F<sub>J</sub> (J = 0-4) transitions of Eu<sup>III</sup> luminescence. The presence of the <sup>5</sup>D<sub>0</sub>  $\rightarrow$  <sup>7</sup>F<sub>0</sub> band for both complexes suggests a low symmetry environment around the metal ion.<sup>2</sup> The emission spectra of [Yb(Nap-cbx)<sub>3</sub>]<sup>3+</sup>, [Yb(Nap-dpe)<sub>3</sub>]<sup>3+</sup>, [Nd(Nap-cbx)<sub>3</sub>]<sup>3+</sup>, and [Nd(Nap-dpe)<sub>3</sub>]<sup>3+</sup> display the characteristic NIR emission bands for Yb<sup>III</sup> (<sup>2</sup>F<sub>5/2</sub>  $\rightarrow$  <sup>2</sup>F<sub>7/2</sub>) and Nd<sup>III</sup> (<sup>4</sup>F<sub>3/2</sub>  $\rightarrow$  <sup>4</sup>I<sub>J</sub> (J = 9/2, 11/2, and 13/2)). Quantum efficiencies of sensitized Eu<sup>III</sup> emission ( $\phi^{Eu}$ )

Quantum efficiencies of sensitized Eu<sup>III</sup> emission ( $\phi^{Eu}$ ) are 8.3% for [Eu(**Nap-dpe**)<sub>3</sub>]<sup>3+</sup> and 16.7% for [Eu(**Nap-cbx**)<sub>3</sub>]<sup>3+</sup> (Table 2) and are comparable to reported  $\phi^{Eu}$  for naphthalimide-based complexes (*vide supra*).<sup>53,54</sup> We attribute the lower emission efficiency of [Eu(**Nap-dpe**)<sub>3</sub>]<sup>3+</sup> to the narrower gap between the <sup>3</sup>T excited state and the <sup>5</sup>D<sub>0</sub> emissive state,<sup>79</sup> which results in a low sensitization efficiency ( $\eta_{sens}$ ) of 38% (Table 2) compared to 52% for [Eu(**Nap-cbx**)<sub>3</sub>]<sup>3+</sup> and also explains the residual ligand band seen in the region 500–550 nm in the emission spectrum of the former complex (Figure 3b, S32).

The luminescence lifetimes  $(\tau)$  for both Eu<sup>III</sup> complexes are 0.51 ms for  $[Eu(Nap-dpe)_3]^{3+}$  and 0.68 ms for  $[Eu(Nap-dpe)_3]^{3+}$  $(\mathbf{cbx})_{3}^{3+}$  in aerated solution at 298 K. Both  $\tau$  could be fit as single-exponential decays (Figures S33 and S34, Table S2), indicating one unique coordination environment around the  $Eu^{III}$  ions.<sup>72-74</sup> The slightly longer lifetime of  $[Eu(Nap-cbx)_3]^{3+1}$ is consistent with a higher intrinsic quantum yield ( $\phi^{Eu}_{Eu}$ = 32%) compared to [Eu(Nap-dpe)<sub>3</sub>]<sup>3+</sup> ( $\phi^{Eu}_{Eu}$ = 22%) and indicates slightly better shielding from vibrational quenching.<sup>80</sup> Nap-dpe shows slightly lower sensitization efficiency, consistent with the lower energy gap between the  ${}^{3}T$  state and the  ${}^{5}D_{0}$  level of Eu<sup>III</sup>. Finally, this lower gap leads to a certain degree of back-energy transfer from  ${}^{5}D_{0}$  to  ${}^{3}T$ , as can be seen by the small increase in the emission lifetimes when the solutions of the complexes are cooled to 77 K (Table 2 and Figures S45 and S46, Table S3). This repopulation of the <sup>3</sup>T and lower sensitization efficiency are advantageous for a more efficient <sup>1</sup>O<sub>2</sub> generation for the  $[Eu(Nap-dpe)_3]^{3+}$  complex, as discussed below.

Quantum yields of Yb<sup>III</sup> and Nd<sup>III</sup> luminescence emission and emission lifetimes could not be determined reliably due to weak emission.

All compounds discussed here generate  ${}^{1}O_{2}$ . Its formation was evaluated by monitoring the phosphorescence at 1270 nm from the  ${}^{1}O_{2} \rightarrow {}^{3}O_{2}$  transition (Figures S35 and S36). The  ${}^{1}O_{2}$ generation efficiencies ( $\phi_{102}$ ) for Nap-cbx and Nap-dpe are 60% and 56% (Table 3), respectively, comparable to values reported for other naphthalimide derivatives.<sup>16,18</sup> All metal complexes generate  ${}^{1}O_{2}$  with efficiencies comparable to Napcbx and Nap-dpe, as summarized in Table 3. They are 41% for [Eu(Nap-cbx)<sub>3</sub>]<sup>3+</sup>, 59% for [Eu(Nap-dpe)<sub>3</sub>]<sup>3+</sup>, 59% and 56% for [Nd(Nap-dpe)<sub>3</sub>]<sup>3+</sup> and [Yb(Nap-dpe)<sub>3</sub>]<sup>3+</sup>, respectively, and 64% and 61% for [Nd(Nap-cbx)<sub>3</sub>]<sup>3+</sup> and [Yb(Nap-cbx)<sub>3</sub>]<sup>3+</sup>, respectively. The largest  $\phi_{102}$  are observed for the Gd<sup>111</sup> complexes, which are 72% for [Gd(Nap-dpe)<sub>3</sub>]<sup>3+</sup> and 68% for [Gd(Nap-cbx)<sub>3</sub>]<sup>3+</sup>. These values are similar to values of  $\phi_{102}$  for

Table 3. Quantum Yields of Singlet Oxygen Generation  $(\phi_{102})$  at 25.0 ± 0.1 °C in 1:1 Dichloromethane:Acetonitrile

Compound	$\phi$ <sub>102</sub> [%]	Compound	$\phi$ <sub>102</sub> [%]
Nap-cbx	60 ± 1	Nap-dpe	$56 \pm 2$
$[Gd(Nap-cbx)_3]^{3+}$	68 ± 4	[Gd(Nap-dpe) <sub>3</sub> ] <sup>3+</sup>	$72 \pm 2$
$[Eu(Nap-cbx)_3]^{3+}$	$41 \pm 5$	[Eu(Nap-dpe) <sub>3</sub> ] <sup>3+</sup>	$59 \pm 2$
$[Nd(Nap-cbx)_3]^{3+}$	64 ± 1	[Nd(Nap-dpe) <sub>3</sub> ] <sup>3+</sup>	59 ± 5
$[Yb(Nap-cbx)_3]^{3+}$	$61 \pm 3$	[Yb(Nap-dpe) <sub>3</sub> ] <sup>3+</sup>	$56 \pm 2$

Gd<sup>III</sup> complexes, reported by Maury and co-workers,<sup>14,15</sup> and to a variety of naturally occurring  ${}^{1}O_{2}$  photosensitizers, such as clorin- $e_{6}$  (64% in phosphate buffer),<sup>81</sup> chlorophyll *a* (44% in ethanol),<sup>82</sup> riboflavin (48% in methanol),<sup>83</sup> porfimer sodium (89% in phosphate buffer),<sup>81</sup> and lutetium texaphyrin (23% in methanol).<sup>84</sup>

As mentioned, all Ln<sup>III</sup> complexes generate <sup>1</sup>O<sub>2</sub>, while concurrently displaying metal-centered emission. While not demonstrated here, this should facilitate luminescence imaging. To further characterize the concurrent processes of <sup>1</sup>O<sub>2</sub> generation and metal-centered luminescence, the emission of Eu<sup>III</sup>, Nd<sup>III</sup>, and Yb<sup>III</sup> in the complexes was evaluated in degassed solutions. For all complexes, luminescence emission intensity increased under anaerobic conditions (Figures S37–S42).<sup>15,54</sup> In the absence of O<sub>2</sub>, we observed an increase of  $\phi^{Eu}$  to 17.7% for [Eu(Nap-dpe)<sub>3</sub>]<sup>3+</sup> and 20% for [Eu(Nap-cbx)<sub>3</sub>]<sup>3+</sup> (Table 2), as the <sup>3</sup>T state is only involved in sensitization of Eu<sup>III</sup> emission but not in <sup>1</sup>O<sub>2</sub> generation.<sup>15,54</sup> The increased emission intensity also leads to an increase in both Eu<sup>III</sup> lifetimes to 0.81 and 0.85 ms for [Eu(Nap-dpe)<sub>3</sub>]<sup>3+</sup> and [Eu(Nap-cbx)<sub>3</sub>]<sup>3+</sup>, respectively (Figures S43 and S44), higher  $\phi_{Eu}^{Eu}$  of 39% for [Eu(Nap-cbx)<sub>3</sub>]<sup>3+</sup> and 35% for [Eu(Nap-dpe)<sub>3</sub>]<sup>3+</sup>, and higher  $\eta_{sens}$  of 53% and 51% for [Eu(Nap-cbx)<sub>3</sub>]<sup>3+</sup> and [Eu(Nap-dpe)<sub>3</sub>]<sup>3+</sup>, respectively.

Despite the expectation that efficiencies of NIR emission would be larger in degassed solutions, quantum yields of Yb<sup>III</sup> and Nd<sup>III</sup> luminescence emission and emission lifetimes under these conditions are still too weak to be determined reliably.

#### CONCLUSIONS

We isolated two new sensitizing ligands based on 1,8naphthalimide, Nap-dpe and Nap-cbx, and their lanthanide compounds then demonstrated their ability to concurrently display Ln<sup>III</sup>-centered emission in the visible and NIR and generate <sup>1</sup>O<sub>2</sub> in solution upon excitation at 335 nm. The compounds with the largest <sup>1</sup>O<sub>2</sub> generation efficiencies while sensitizing Ln<sup>III</sup> luminescence are [Nd(Nap-cbx)<sub>3</sub>]<sup>3+</sup> (64%) and  $[Eu(Nap-dpe)_3]^{3+}$  (59%). We identified that the complexes' ability to generate <sup>1</sup>O<sub>2</sub> efficiently impacts the luminescence efficiency, as is expected, due to the involvement of the <sup>3</sup>T excited state of the ligand in both processes. While their lack of solubility in water prevents them from being used for bioimaging and therapy purposes, the work presented here expands our knowledge of compounds displaying the superior properties of emissive Ln<sup>III</sup> complexes, while simultaneously generating a cytotoxic species.

# EXPERIMENTAL SECTION

All commercially obtained reagents were of analytical grade and were used as received. Solvents were dried and purified by standard methods unless otherwise noted. All synthetic steps were completed under  $N_2$  unless otherwise specified. The detailed synthetic procedures of the ligands and their  $Ln^{III}$  complexes are provided in the Supporting Information.

Ε

**Preparation of Ln(NO<sub>3</sub>)<sub>3</sub> Solutions.** The stock solutions of lanthanide(III) nitrate (Ln = Eu<sup>III</sup>, Gd<sup>III</sup>, Nd<sup>III</sup>, or Yb<sup>III</sup>) nitrate were prepared by dissolving the nitrate salt in spectroscopic grade 1:1 dichloromethane:acetonitrile. The concentration of the metal was determined by complexometric titration with EDTA (0.01 M) using xylenol orange as indicator.<sup>85</sup>

**NMR Spectroscopy.** All NMR spectra were recorded on Varian 400 and 500 MHz spectrometers with chemical shifts reported ( $\delta$ , ppm) in deuterated chloroform (CDCl<sub>3</sub>) against tetramethylsilane (TMS, 0.00 ppm) at 25.0 ± 0.1 °C.

**Infrared Spectroscopy.** All FT-IR spectra were measured on a Nicolet 6700 FT-IR in ATIR mode. The IR data for each sample were collected in the range 4000–590 cm<sup>-1</sup>, with 32 scans at 4 cm<sup>-1</sup> resolution per spectrum. A background correction for  $CO_2$  and  $H_2O$  was conducted.

**Mass Spectrometry.** Electrospray ionization mass spectra (ESI-MS) were collected in positive ion mode on a Waters Micromass ZQ quadrupole in the low-resolution mode for the ligands and on an Agilent model G6230A with a QTOF analyzer in the high-resolution mode for the metal complexes. The samples were prepared by diluting acetonitrile solutions to a concentration of ~1 mg/mL and passing through a 0.2 mm microfilter.

**Absorption Spectroscopy.** Absorption spectra were measured on a PerkinElmer Lambda 35 spectrometer equipped with deuterium and tungsten halogen lamps (PerkinElmer) and a concave grating with 1053 lines/mm. The absorption spectra were collected using a scan speed of 480 nm/min in the range 225–600 nm with a photodiode detector. All spectra were background corrected, using solvent as the blank. Spectra of the ligands and their complexes were collected using concentrations between  $9.0 \times 10^{-5}$  M and  $1.25 \times 10^{-4}$  M.

**Speciation Studies.** For speciation studies using emission spectroscopy, spectra were measured in 1:1 dichloromethane:acetonitrile at 25.0  $\pm$  0.1 °C using a constant concentration of Eu(NO<sub>3</sub>)<sub>3</sub> (1 × 10<sup>-4</sup> M). Solutions of the ligand and Eu(NO<sub>3</sub>)<sub>3</sub> were prepared with stoichiometries between 1:0.25 and 1:3.5 (Eu<sup>III</sup>:ligand), and their emission spectra were measured under the same experimental conditions. The concentration of Eu<sup>III</sup> in solution remained constant,  $1 \times 10^{-4}$  M. Fitting and refinement of the data were performed using HypSpec2014.<sup>86</sup> The speciation diagrams were generated using HySS.<sup>87</sup>

For speciation studies using NMR spectroscopy, solutions of Napdpe and Nap-cbx were prepared in a deuterated solvent mixture (1:1 CDCl<sub>3</sub>:CD<sub>3</sub>CN) with ratios of 0:1, 1:1, 2:1, and 3:1 (La<sup>III</sup>:Nap-dpe or La<sup>III</sup>:Nap-cbx). The concentration of ligand, Nap-dpe or Nap-cbx, was kept constant at  $1 \times 10^{-3}$  M. All NMR spectra were recorded on a Varian 400 spectrometer with chemical shifts reported ( $\delta$ , ppm) against tetramethylsilane (TMS, 0.00 ppm) at 25.0 ± 0.1 °C.

Excitation and Emission Spectroscopy. Emission and excitation spectra of Nap-dpe and Nap-cbx and their Ln<sup>III</sup> complexes were obtained on a Fluorolog-3 fluorimeter (Horiba FL3-22-iHR550), with 1200 grooves/mm excitation monochromator gratings blazed at 330 nm and 1200 grooves/mm or 600 grooves/mm emission monochromator gratings blazed at 500 or 1000 nm for UV-vis or NIR range, respectively. An ozone-free xenon lamp of 450 W (Ushio) was used as the radiation source. The excitation spectra were corrected for instrumental function and measured between 250 and 600 nm. The emission spectra were measured in the range 350-800 nm using a Hamamatsu 928P detector and in the range 800-1600 nm using a Hamamatsu 5509-73 detector cooled with liquid N2. All emission spectra were also corrected for instrumental function. The ligands' <sup>1</sup>S and  ${}^{3}T$  energies were obtained at  $\sim 77$  K by deconvoluting the fluorescence and phosphorescence spectra of the analogous gadolinium complexes into their Franck-Condon progression and are reported as the 0-0 transition.<sup>63</sup> Spectra of the ligands and their complexes were collected using solution concentrations of 9.5  $\times$  10  $^{-5}$  M to 1.25  $\times$  10  $^{-4}$ M

**Emission Efficiency Measurements.** The emission and  ${}^{1}O_{2}$  generation quantum yields of the samples were determined by the dilution method using eq 1.<sup>88</sup>

$$\phi_x = \frac{\text{grad}_x}{\text{grad}_{std}} \times \frac{n_x^2}{n_{std}^2} \times \frac{I_{std}}{I_x} \phi_{std}$$
(1)

Article

*Grad* is the slope of the plot of the emission area as a function of the absorbance, *n* is the refractive index of the solvent (n = 1.3870 was determined experimentally for the acetonitrile/dichloromethane mixture; see below), *I* is the intensity of the excitation source at the excitation wavelength used, and  $\phi$  is the quantum yield for sample, *x*, and standard, *std*. All data are the average of at least three independent measurements.

Standards for emission quantum yield measurements were quinine sulfate ( $\phi$  = 55%, 5 × 10<sup>-6</sup> M in aqueous 0.5 M H<sub>2</sub>SO<sub>4</sub>),<sup>8</sup>  $Cs_3[Eu(dpa)_3]$  ( $\phi = 24\%$ , 7.5 × 10<sup>-5</sup> M in aqueous TRIS/HCl buffer  $(0.1 \text{ M}, \text{pH} \sim 7.4))$ , <sup>90,91</sup> and 2,2':5',2"-terthiophene ( $\phi = 74\%$ , <sup>92</sup> 1 ×  $10^{-4}~M$  in air-saturated acetonitrile) for ligand and  $Gd^{\rm III}$  complex fluorescence, Eu<sup>III</sup> emission, and <sup>1</sup>O<sub>2</sub> emission, respectively. The excitation wavelengths for both sample and quantum yield standard were chosen to ensure a linear relationship between the intensity of emitted light and the concentration of the absorbing/emitting species  $(A \le 0.05)$ . <sup>1</sup>O<sub>2</sub> emission efficiencies should be determined with both sample and standard in the same solvent, due to different oxygen contents and <sup>1</sup>O<sub>2</sub> lifetimes, yet this is not always the case.<sup>92,93</sup> We used the two slightly different solvent systems due to solubility issues. However, the mol fractions of O<sub>2</sub> are not very different, at 0.662 in acetonitrile and 0.709 in dichloromethane.<sup>94</sup> In addition, the  ${}^{1}O_{2}$ lifetimes are also very similar, with values of 5.4  $\times$  10<sup>-5</sup> s in acetonitrile<sup>95</sup> and  $5.5 \times 10^{-5}$  s in dichloromethane.<sup>94</sup> Determination of the emission efficiency of 2,2':5',2"-terthiophene in 1:1 acetonitrile:dichloromethane yielded a value of 77  $\pm$  3%, which is experimentally equivalent to the value we used for the standard in acetonitrile and within the range 65-81% reported by different authors for this standard in a variety of solvents.<sup>92,93,96,97</sup>

The intrinsic quantum yield  $(\phi_{Eu}^{Eu})$  was determined using eq 2.<sup>98</sup>

$$\phi_{Eu}^{Eu} = \frac{A_{rad}}{A_{tot}} \tag{2}$$

 $A_{tot}$  is the total emission rate  $(A_{tot} = k_R + k_{NR} = 1/\tau_{exp})$ , where  $k_R$  is the radiative rate constant,  $k_{NR}$  is the nonradiative decay constant,  $\tau_{exp}$  is the observed excited state lifetime, and  $A_{rad}$  is the radiative emission rate, determined using eq 3.

$$A_{rad} = A_{MD,0} \times n^3 \left( \frac{I_{tot}}{I_{MD}} \right)$$
(3)

 $I_{tot}$  and  $I_{MD}$  are the total integrated emission spectrum and the area of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  transition, respectively, and  $A_{MD,0}$  is the Einstein coefficient of spontaneous emission  $(A_{MD,0} = 14.65 \text{ s}^{-1}).^{99}$ 

The sensitization efficiency ( $\eta_{sens}$ ) was determined using eq 4.<sup>98</sup>

$$\eta_{sens} = \frac{\phi^{Eu}}{\phi^{Eu}_{Eu}} \tag{4}$$

 $\phi^{Eu}$  is the efficiency or quantum yield of sensitized emission.

**Refractive Index Measurements.** Refractive indices were measured on a Leica MARK II ABBE refractometer with a built-in light source for the measuring prism with an accuracy of  $\pm 0.0001$  in  $n_D$  mode at 25.0  $\pm$  0.2 °C. The average value of three independent measurements (1.3870  $\pm$  0.0004) was used in determining the quantum yield as the refractive index for a 1:1 acetonitrile:dichloromethane solution. This value is in agreement with the value reported by Tsierkezos.<sup>100</sup>

**Ground-State Geometries and Excited State Calculations.** The Sparkle/PM3 model was used to determine the complexes' ground state geometries.<sup>75</sup> In this model the lanthanide ion is replaced by a +3e point charge.<sup>101</sup> The RHF wave functions were optimized using the Broyden–Fletcher–Goldfarc–Shanno (BFGS) procedure with a convergence criterion of 0.15 kcal/mol·Å and the semiempirical PM3 with a convergence criterion of  $10^{-6}$  kcal/mol for the SCF. In the MOPAC2016 package<sup>76</sup> the keywords GNORM = 0.25, PRECISE, GEO-OK, XYZ, T = 10D, and ALLVEC were used. The excited state calculations were preformed using ORCA software  $^{67}$  using the INDO/ S-CIS  $^{66}$  method.

### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b02431.

Synthesis details, NMR spectra, FT-IR spectra, mass spectra, absorption, excitation, and emission spectra, fluorescence and phoporescnece spectra, (PDF)

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#### Notes

The authors declare no competing financial interest.

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