



# Switchable photoluminescence of europium(III) complexes with chromonylhydrazones

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**Europium(III) complexes bearing 4-hydroxy- or 4-methyl-*N'*-(6-methyl-4-oxo-4*H*-chromen-3-yl)methylene)benzohydrazide (HL<sup>1</sup> or HL<sup>2</sup>) showed characteristic Eu<sup>III</sup> <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>*J*</sub> (*J* = 0–4) luminescence both in acetonitrile and in solid states with relatively high Φ<sub>tot</sub> values. The luminescence was quenched not only by adding triethylamine in acetonitrile, but also by heating the solid sample, and recovered by adding perchloric acid in solution or by diffusion of HCl vapor to the resulting solid sample.**

Certain lanthanoid(III) complexes exhibit intense luminescence with high color purity when compared to luminescent organic compounds or transition-metal complexes and can be applied to bioprobes,<sup>1–3</sup> optical devices, and electroluminescent materials.<sup>4,5</sup> However, photoluminescent materials for switching devices using photo-,<sup>6–9</sup> thermo-<sup>10–12</sup> and acidochromic behaviors<sup>13,14</sup> have also been studied extensively over the past decade. In particular, lanthanoid(III) complexes showing similar responsiveness to external stimuli usually require a complicated molecular structure,<sup>15–18</sup> and it is often difficult to design and prepare these ligands to obtain stimuli-responsive chromic properties.

Hydrazone compounds are widely used as convenient ligands in transition-metal complexes, because they are easily prepared in high yields through condensation reactions of the

corresponding hydrazine and carbonyl compounds under relatively mild reaction conditions. Within these hydrazones, a large number of transition-metal complexes having characteristic chromic behaviors have been reported to date.<sup>19–23</sup> For example, an acetonitrile solution of a platinum(II) complex with 2-(diphenylphosphino)benzaldehyde-2-pyridyl-hydrazone showed absorption and emission color changes by the addition of base (*i.e.*, deprotonation) or acid (*i.e.*, reprotonation).<sup>24</sup> More interestingly, this compound showed reversible changes following heating and exposure to HCl vapor in the solid state. Considering the lanthanoid(III) complexes of hydrazones, some europium(III) complexes bearing 2,6-diformylpyridine-bis(benzoylhydrazone)<sup>25,26</sup> or 7-methoxychromone-3-carbaldehyde-(4'-hydroxy) benzoylhydrazone<sup>27,28</sup> were synthesized and their luminescent properties reported. Apart from hydrazone complexes, highly intriguing europium(III) complexes, which exhibit switchable photoluminescence property in response to exposure of acidic/basic vapor, have recently been reported.<sup>29,30</sup> However, examples of lanthanoid(III) complexes which showed reversible color changes or photoluminescence properties by external stimuli both in solution and in solid states are very limited. Therefore, it would be interesting if some lanthanoid(III) complexes with certain hydrazones exhibit a switchable (on/off) sharp and intense luminescence in response to external stimuli both in solution and in solid states.

Herein, we report the synthesis and structural and spectroscopic characterization of europium(III) complexes with two kinds of chromonylhydrazones, 6-methylchromone-3-carbaldehyde-(4'-hydroxy or 4'-methyl)benzoylhydrazone (*i.e.*, HL<sup>1</sup> or HL<sup>2</sup>) (Scheme 1). The isolated complex salts were [Eu(HL<sup>1</sup>)<sub>3</sub>]Cl<sub>3</sub> (**1Cl**), [Eu(HL<sup>1</sup>)<sub>3</sub>](OTf)<sub>3</sub> (**1OTf**) and [Eu(HL<sup>2</sup>)<sub>3</sub>](OTf)<sub>3</sub> (**2OTf**). These complexes exhibited reversible color change and turn-on/off behavior in the Eu<sup>III</sup> <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>*J*</sub> (*J* = 0–4) luminescence by addition of acids or bases in acetonitrile, as well as by heating or diffusion of acidic vapor in the solid states. This switching was induced by deprotonation of only one N–H proton in the tris(hydrazone)-type complexes.

The hydrazones, HL<sup>1</sup> and HL<sup>2</sup>, were prepared by a reaction of 6-methyl-3-formylchromone with *p*-hydroxybenzohydrazide and *p*-methylbenzohydrazide, respectively, in methanol at room

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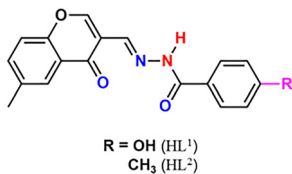
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Scheme 1 Structures of the hydrazones, HL<sup>1</sup> and HL<sup>2</sup>.

temperature (see: supplementary information (SI)). The complex salt, **1Cl**, was prepared by a reaction of EuCl<sub>3</sub>·6H<sub>2</sub>O and HL<sup>1</sup> in a 1 : 3 molar ratio in 2-methoxyethanol and obtained as a crystalline product by addition of diisopropyl ether into the reaction mixture. The corresponding trifluoromethanesulfonate (OTf<sup>-</sup>) salt, **1OTf**, was similarly prepared using a mixed acetonitrile and chloroform solution of Eu(OTf)<sub>3</sub> and HL<sup>1</sup> in a 1 : 3 molar ratio. The other hydrazone compound, **2OTf**, was also obtained from an acetone solution of Eu(OTf)<sub>3</sub> and HL<sup>2</sup> in a 1 : 3 molar ratio. All complexes were crystallized with some solvent molecules of crystallization (see: Table S1). Single-crystal X-ray diffraction (SC-XRD) analysis revealed that the molecular structures of the Eu<sup>III</sup> complex cations in **1Cl**, **1OTf** and **2OTf** are similar. In particular, the Eu<sup>III</sup> ion was coordinated by three HL<sup>1</sup> or HL<sup>2</sup> ligands having the O,N,O tridentate mode (Fig. 1 and Fig. S2). In the crystal structures of these complexes, all N–H protons formed hydrogen bonds with the Cl<sup>-</sup> or OTf<sup>-</sup> anions. Although the crystal structures were successfully analyzed at 188 or 100 K, these crystals were highly efflorescent due to the loss of the solvating molecules at ambient condition. Therefore, characterization of the products by elemental analysis and FT-IR spectroscopy (Fig. S1) were performed with the samples dried and then left in air for a while at room temperature, confirming the purity of the bulk samples. In this study, the corresponding gadolinium(III) (**1Gd-Cl**, **1Gd-OTf** and **2Gd-OTf**) and yttrium(III) (**2Y-OTf**) complexes were also prepared and fully characterized by elemental analysis, FT-IR and ESI-MS spectroscopy (Fig. S4–S8) as well as the SC-XRD study for **1Gd-Cl** and **2Gd-OTf**, which revealed that their crystal structures were isomorphous to those of the corresponding europium(III) complexes (Table S1).

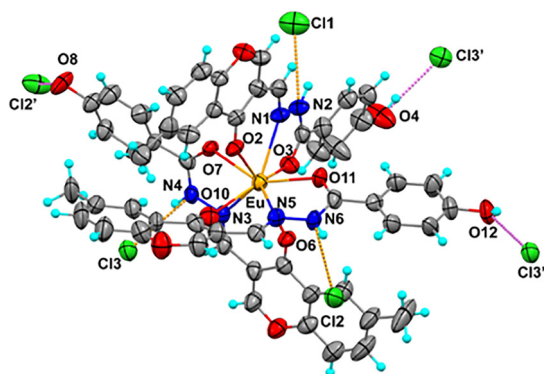


Fig. 1 An ORTEP drawing (the thermal ellipsoids at 50% probability level) of the Eu<sup>III</sup> cationic complex and the surrounding Cl<sup>-</sup> anions those bound to the cation with hydrogen bonds in **1Cl**.

To confirm the possibility of deprotonation from the hydrazone N–H moiety in **1OTf**, titration of triethylamine (TEA) in acetonitrile was performed by monitoring its UV-vis absorption spectrum. To ensure full protonation at the N–H moiety of three hydrazone ligands in **1OTf**, an equivalent amount (1.0 eq.) of HClO<sub>4</sub> was added, prior to the titration. As shown in Fig. 2a, the spectrum of an acetonitrile solution of **1OTf** with a 1.0 eq. HClO<sub>4</sub> exhibited an intense absorption band at 310 nm. Following addition of TEA, the absorption gradually decreased and the absorption shoulder around 380 nm became larger. After addition of 4.0 eq. of TEA, the solution was inversely titrated with HClO<sub>4</sub>, resulting in the recovery of the original spectrum (Fig. 2b). The **2OTf** complex showed a similar behavior in spectral changes to **1OTf** (Fig. S9). Proton NMR measurement was conducted in acetonitrile-*d*<sub>3</sub> using analogous **2Y-OTf**: addition of TEA to the solution caused the N–H signal to disappear (Fig. S10). Therefore, deprotonation and reprotonation reversibly occurred at the N–H moiety.

Photoluminescence spectra of **1Cl** and **1OTf** in acetonitrile and the solid states were examined, which showed five sharp peaks derived from the Eu<sup>III</sup>-centered excited states at 583.5, 593, 616.5, 654.5 and 699 nm, attributed to the <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>*J*</sub> (*J* = 0–4) transitions (Fig. S11a–c) and those of **2OTf** (see Fig. S13d and e). Photoluminescence quantum yield (Φ<sub>tot</sub>), luminescence lifetime (τ<sub>obs</sub>) and photosensitization efficiency (η<sub>sens</sub>) are summarized in Table 1. These europium(III) complexes in solid states showed relatively high Φ<sub>tot</sub>, indicating that the hydrazone ligands (*i.e.*, HL<sup>1</sup> and HL<sup>2</sup>) are good photosensitizers. The energy gap between the S<sub>0</sub> and T<sub>1</sub> states of HL<sup>1</sup> and HL<sup>2</sup> were estimated by the phosphorescence spectra of the corresponding gadolinium(III) complexes (**1Gd-Cl** and **2Gd-OTf**) in the solid states (the 0–0 vibronic bands at 514 and 520 nm) as 19 500 cm<sup>-1</sup> and 19 200 cm<sup>-1</sup>, respectively (Fig. S14), which is enough to transfer the energy to the <sup>5</sup>D<sub>0</sub> excited state of the Eu<sup>III</sup> center.

The luminescence spectral change of **1OTf** in acetonitrile by addition of TEA were examined (Fig. 3). Similar to the above-mentioned titration with absorption spectra, 1.0 eq. HClO<sub>4</sub> was added to the sample solution beforehand (Fig. S13), ensuring full protonation at three hydrazone N–H moieties of **1OTf**. At 616.5 nm, the luminescence intensity remained nearly unchanged until 1.0 eq. TEA was added to the mixed sample solution. However, addition of more than 1 eq. TEA gradually decreased the <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>*J*</sub> luminescence, and by 2.0 eq. TEA, the

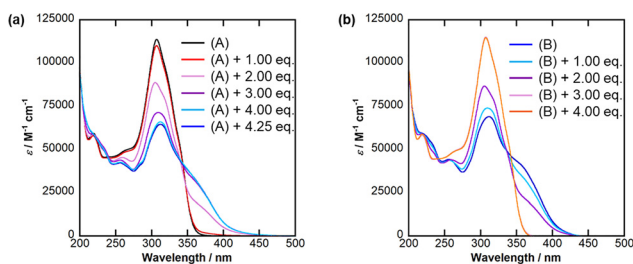
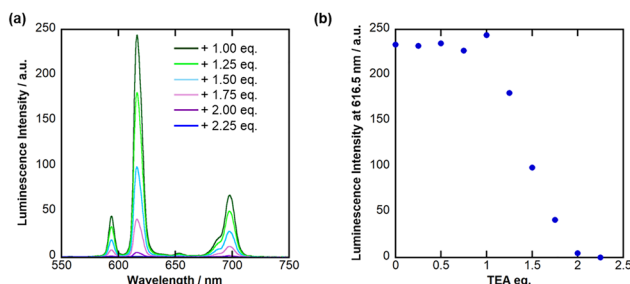


Fig. 2 Absorption spectral change of (a) **1OTf** and 1.0 eq. HClO<sub>4</sub> in acetonitrile (solution (A)) by addition of TEA and that of (b) **1OTf**, 1.0 eq. HClO<sub>4</sub> and 4.0 eq. TEA in acetonitrile (solution (B)) by addition of HClO<sub>4</sub>.



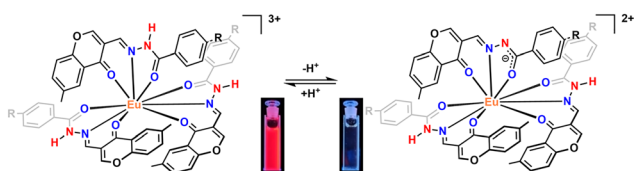
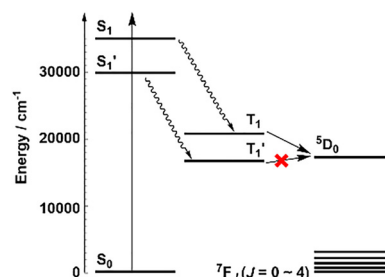
**Table 1** Photophysical properties of the Eu<sup>III</sup> complexes in acetonitrile and in the solid state

Complex	Sample states	$\Phi_{\text{tot}}$	$\Phi_{\text{Eu}}$	$\tau_{\text{obs}}/\text{ms}$	$k_{\text{r}}^{\text{Eu}}/\text{s}^{-1}$	$k_{\text{nr}}^{\text{Eu}}/\text{s}^{-1}$	$\eta_{\text{sens}}$
<b>1Cl</b>	Solid	0.56	0.56	0.76	76.9	546	> 0.99
	Solid	0.57	0.57	0.53	71.3	140	> 0.99
<b>1OTf</b>	In CH <sub>3</sub> CN	0.03	0.32	0.70	45.0	974	0.09
	Solid	0.40	0.57	0.74	77.2	587	0.70
<b>2OTf</b>	In CH <sub>3</sub> CN	0.01	> 0.34	0.74	46.5	888	0.02

**Fig. 3** (a) Photoluminescence ( $\lambda_{\text{ex}} = 360$  nm) spectral change of **1OTf** ( $9.7 \times 10^{-5}$  M) with 1.0 eq. HClO<sub>4</sub> in acetonitrile by titration of TEA. (b) The plots of the luminescence intensity at 616.5 nm during the titration of TEA (0–2.25 eq.).

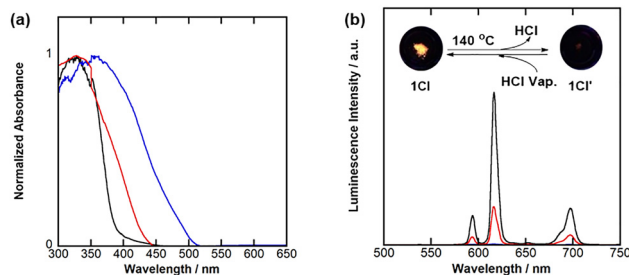
luminescence was nearly quenched (Fig. 4 and Table S2). Hence, only one deprotonation forming  $[\text{Eu}(\text{L}^1)(\text{HL}^1)_2]^{2+}$  from  $[\text{Eu}(\text{HL}^1)_3]^{3+}$  was enough to quench the  $^5\text{D}_0 \rightarrow ^7\text{F}_j$  luminescence. When the hydrazone ligand was reprotonated (by addition of HClO<sub>4</sub>), the luminescent bands were recovered (Fig. S14). Therefore, the deprotonation and reprotonation process, which induces a switching of photoluminescent behavior, is fully reversible. An analogous hydrazone complex of **2OTf** exhibited a similar reversible photoluminescent property (Fig. S15–S17). Furthermore, the stability tests toward the addition of acid and base were conducted on **1OTf** and **2OTf** in acetonitrile. No significant changes in luminescence intensities were observed upon the repeated deprotonation/reprotonation for up to 10 cycle times (Fig. S18), which indicated the high stabilities of **1OTf** and **2OTf** in solution.

To explain the mechanism of quenching by deprotonation, phosphorescence spectra of the analogous gadolinium(III) complexes, **1Gd-OTf** and **2Gd-OTf**, were examined. In acetonitrile, however, both complexes gave no phosphorescence spectra even at 77 K. We assume that the excitation energy,  $\Delta(\text{S}_0\text{--}\text{S}_1)$ , and the phosphorescent energy,  $\Delta(\text{S}_0\text{--}\text{T}_1)$ , of the neutral hydrazone complexes in the solid states and in acetonitrile are nearly the same, because the excitation peak maximum of **1OTf** in the solid state and in acetonitrile are

**Fig. 4** Schematic representation of the successive deprotonation/reprotonation for **1OTf** and **2OTf**. Inserted pictures show the luminescence color change with an acetonitrile solution of **1OTf** on irradiation by UV light ( $\lambda_{\text{ex}} = 365$  nm,  $c = 9.7 \times 10^{-5}$  M).**Fig. 5** Proposed excited energy diagram of the hydrazone ( $\text{S}_1$ ,  $\text{T}_1$ ) and hydrazone ( $\text{S}'_1$ ,  $\text{T}'_1$ ) europium(III) complex.

almost the same (Fig. S11f). However, an acetonitrile solution of **1Gd-OTf** or **2Gd-OTf** with 1.0 eq. HClO<sub>4</sub> and 2.25 eq. TEA showed a broad phosphorescence band around 640 nm (Fig. S21). In particular, these bands were remarkably red shifted from those of the above-mentioned **1Gd-Cl** and **2Gd-OTf** in the solid states, and the phosphorescent energy in the deprotonated complexes,  $\Delta(\text{S}_0 - \text{T}'_1)$  are lower than the  $^5\text{D}_0 \rightarrow ^7\text{F}_j$  luminescent energy (Fig. 5). This finding suggests that deprotonation from one HL<sup>1</sup> in **1OTf** (or one HL<sup>2</sup> in **2OTf**) induced stabilization of the triplet excited state in the complex,  $\Delta(\text{S}_0 - \text{T}'_1)$  being  $15\,570\text{ cm}^{-1}$ . Then, the energy transfer from the deprotonated ligand triplet ( $\text{T}'_1$ ) state to the Eu<sup>III</sup>  $^5\text{D}_0$  excited state resulted in up-conversion. Considering **1OTf** and **2OTf**, the quenching of the Eu<sup>III</sup>  $^5\text{D}_0 \rightarrow ^7\text{F}_j$  luminescence can be controlled by reversible deprotonation/reprotonation through the  $\text{S}_1$  and  $\text{T}_1$  excited states of the hydrazone ligands.

Quenching of luminescence in the Eu<sup>III</sup> complexes by removing the hydrazone N–H proton in the solid state has also been examined with **1Cl**. After heating the powdered sample of **1Cl** at  $140^\circ\text{C}$  for 5 minutes, the diffuse reflectance spectrum showed a clear redshift in the band (Fig. 6a). To confirm the origin of this redshift, which may related to the deprotonation from the N–H group as a release of HCl molecule, the electrical conductivity of the sample solution in methanol was measured. Titration with an methanolic AgNO<sub>3</sub> solution gave, owing to the precipitation of AgCl by the dissolved Cl<sup>−</sup> anions in solution, an increase of the electric conductivity of the sample solution just after the stoichiometric point. The results for the original and the heated samples indicated that approximately one-thirds of the original amount of Cl<sup>−</sup> ion in **1Cl** was released as HCl gas on heating (Fig. S20). In the heated sample, the emission bands

**Fig. 6** (a) Diffuse reflectance spectra and (b) photoluminescence spectra ( $\lambda_{\text{ex}} = 365$  nm) of **1Cl** before (black) and after (blue) heating the sample and, then, exposure to HCl vapor (red).

