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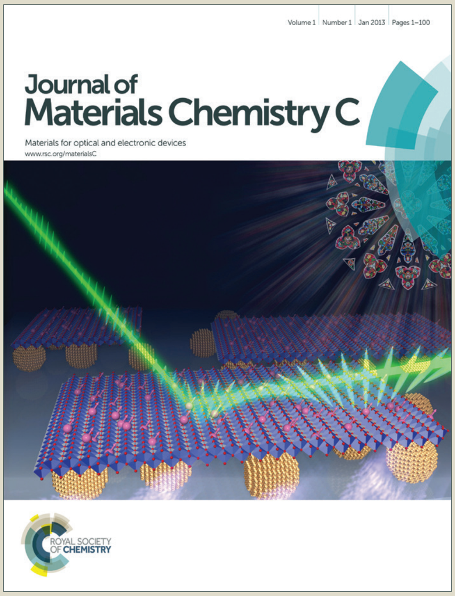

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ARTICLE

Relationship between interlayer anions and photoluminescence of layered rare earth hydroxides

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The effect of interlayer anions on the photoluminescence of layered rare earth hydroxides was investigated with the rare earth (RE)-doped layered gadolinium hydroxynitrate as a representative base matrix for efficient and stable anion-exchange reactions. Eu^{3+}, Tb^{3+}, and Ce^{3+} were employed as RE activator ions for red, green, and blue emissions, respectively. The excitation and emission behaviors of $Gd_{1.80}RE_{0.20}(OH)_5X\cdot nH_2O$ (LGdH:RE) were systematically compared for various interlayer inorganic and organic anions, where X = F^-, Cl^-, I^-, OH^-, ClO_3^-, S^{2-}, CO_3^{2-}, SO_4^{2-}, terephthalate, 2-naphthoate, and dodecylsulfate members were obtained by the exchange reaction of corresponding X = NO_3^- members. Interestingly, a close relationship was found between the UV-Vis absorption spectra of aqueous solutions containing X anions and the excitation behavior of LGdH:RE. Thus, NO_3^-, I^-, and S^{2-} anions showing high absorbance in aqueous solution consistently shielded the excitation light for the $^8S_{7/2} \rightarrow {}^6I_J$ transition of Gd^{3+} and the 4f → 5d interconfigurational transitions of Tb^{3+} and Ce^{3+} to turn off the corresponding emissions from LGdH:Eu, LGdH:Tb, and LGdH:Ce. In contrast, the effect of terephthalate and 2-naphthoate, despite high absorbance in aqueous solutions, was significantly different depending on the RE activator ion. It is proposed that an identical interlayer anion in the gallery of LRHs can filter or sensitize the UV energy for excitation of RE^{3+}-doped LRHs and its role (whether as a filter, a sensitizer, or just a spacer) is determined by the nature of the activator ions.

Introduction

A family of lamella compounds containing pure rare earth hydroxocation layers have recently been developed.[1] These materials, called the layered rare earth hydroxides (LRHs), are repersented by the general formula $RE_2(OH)_5X\cdot nH_2O$ or $[RE_2(OH)_5(H_2O)_n]X$ (RE = rare earths and X = interlayer organic and inorganic anions). Alternate stacking of $[RE_2(OH)_5(H_2O)_n]^+$ hydroxocation layers and charge-compensating $X_{1/q}{}^{q-}$ anion layers constructs a typical two-dimensional structure of these LRHs.[2]

Because high accessibility of diverse guest molecules to their galleries can be the subject of study for numerous ion-exchange reactions,[3] LRHs are an emerging class of host materials for a wide range of active molecules. As layered materials generally show rich interlayer chemistry,[4] the intercalation of guest molecules significantly influences the structural, chemical, thermal, catalytic characteristics of LRH layers as well as interlayer guests themselves. These features have been investigated for several purposes such as building blocks for self-assembled hierarchical superstructures,[5] catalysts for green chemistry,[6] and detectors of organic and inorganic anions for bio-[7] and environmental applications.[8] In addition, the layered gadolinium hydroxide matrix has attracted significant attention because its magnetic resonance (MR) relaxation properties show potential utility as a positive contrast agent for MR imaging.[9] The silica spheres embossed with fluorescent and MR active $GdPO_4$:Eu nanoparticles, which are derived by assembling the delaminated gadolinium hydroxide doped with Eu^{3+} on the particle surface, have demonstrated potential application as a dual imaging agent in cellular labeling for both fluorescent and MR imaging.[10]

Most importantly, the large field of applications of LRHs is based on their abundant and attractive optical properties arising from the 4f electronic shells of rare earths in two-dimensionally stacked layers.[1b,11] The varied substitution capacity of rare earth activators has endowed this family with a photofunctional switchability and rich color-tunability in both solid-state and composite films.[12,13] These hydroxides have also been used as precursors for controlling the morphology of down-conversion oxide phosphors such as $Y_{2-x}Gd_xO_3$:Eu and $Gd_{2-x}Eu_xO_3$ and up-conversion fluoride phosphor materials such as β-$NaYF_4$:RE and for fabricating phosphor films.[14-16] Their exfoliated hydroxocation nanosheets are not only useful for preparing color-tunable colloidal hybrid solutions, but also for constructing several film types, including transparent functional films, orientation-controlled and self-assembled luminescent films, and heterogeneous multilayer films.[17-19] Furthermore, the photoluminescence (PL) properties of LRHs or their rare earth-doped matrices show a sensitive dependence on organic anions in the interlayer.[20] It was also suggested that LRHs function as

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† Electronic Supplementary Information (ESI) available: Additional XRD patterns and FT-IR spectra of $Gd_{1.80}RE_{0.20}(OH)_5X\cdot nH_2O$ (LGdH:RE) where RE = Eu, Tb, and Ce and X = NO_3^-, F^-, Cl^-, I^-, OH^-, ClO_3^-, S^{2-}, CO_3^{2-}, SO_4^{2-}, terephthalate, 2-naphthoate, and dodecylsulfate. XRD patterns measured as a function of reaction time during the exchange reaction of $Gd_{1.80}Ce_{0.20}(OH)_5NO_3\cdot nH_2O$ with Cl^- and vice versa. See DOI: 10.1039/x0xx00000x

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both a host matrix and an inorganic antenna for an organic sensitizer to induce a synergistic effect on photoluminescence.[21]

Thus, the interlayer gallery of the LRH framework offers a suitable space for enormous optical filter and sensitizer molecules, and the concomitant modification of the coordination environment for rare earth sites in the layer could make unexpected changes to the luminescence property of LRHs possible. However, the understanding of interrelationship between the PL of (RE^{3+} doped-) LRH and host matrix, activator ion, and interlayer anion is currently limited to a few special example pairs of activator and interlayer organic anions. The improvement in luminescence efficiency induced after the exchange reaction can also be quite different depending on the activator and interlayer anion in the starting host matrix before the exchange. In this respect, a systematic investigation for the overall host-activator, host-interlayer anion, activator-interlayer anion, and host-activator-interlayer anion combinations is required to guide future research aiming to optimize the PL of LRHs for various applications.

In this paper, we devoted special attention to establishing the role of diverse interlayer organic and inorganic anions (X) in luminescence behavior on the basis of the identical matrix $Gd_2(OH)_5X{\cdot}nH_2O$. Three different dopants, Eu^{3+}, Tb^{3+}, and Ce^{3+}, which are generally used for red, green, and blue emissions, respectively, were employed as activator ions. General NO_3^-, F^-, Cl^-, I^-, OH^-, ClO_3^-, S^{2-}, CO_3^{2-}, and SO_4^{2-} ions and terephthalate, 2-naphthoate, and dodecylsulfate ions were examined as interlayer inorganic and organic anions (X). As anticipated, the exchange reaction of X = NO_3^- member, $Gd_{1.80}RE_{0.20}(OH)_5NO_3{\cdot}nH_2O$, with other X anions was accompanied by a significant change in PL behavior. Furthermore, despite the identical interlayer anion, the luminescence efficiency varied considerably with a dependence on the activator ion (RE^{3+}). Herein, we show that the same interlayer anion can play a role as both a filter and a sensitizer in the photoluminescence of LRHs by shielding or harvesting the UV energy for the excitation of RE^{3+}-doped LRHs and whether to filter or sensitize is dictated by the nature of activators.

Experimental

Synthesis of RE^{3+} doped-layered gadolinium hydroxynitrates.

Rare earth doped-layered gadolinium hydroxides with interlayer NO_3^- anion, $Gd_{1.80}RE_{0.20}(OH)_5NO_3{\cdot}nH_2O$ where RE = Eu, Tb, or Ce, were prepared using a precipitation method.[1b] Typically, $Gd(NO_3)_3{\cdot}6H_2O$ (18.0 mmol), $NaNO_3$ (260 mmol), hexamethylenetetramine (HMT; 20 mmol), and corresponding $RE(NO_3)_3{\cdot}xH_2O$ (2.0 mmol) were dissolved in 200 mL deionized water. Resulting aqueous solutions were heated at 90°C with mild stirring (350 rpm) for 14 h and then cooled to room temperature. The precipitates were filtered, washed with distilled water several times, and dried at 60°C.

Synthesis of $Gd_{1.80}RE_{0.20}(OH)_5X{\cdot}nH_2O$.

All other RE^{3+} doped-layered gadolinium hydroxides, $Gd_{1.80}RE_{0.20}(OH)_5X{\cdot}nH_2O$ except X = NO_3^-, were prepared by exchange reactions of NO_3^- with X anions.

For the exchange of inorganic anions, $Gd_{1.80}RE_{0.20}(OH)_5NO_3{\cdot}nH_2O$ (300 mg) was added to 30 mL of 1.0 M aqueous NaF, NaCl, KI, NaOH, and $KClO_3$ solutions and 0.5 M aqueous Na_2S, Na_2CO_3, and Na_2SO_4 solutions, respectively. These mixtures were maintained at room temperature with stirring (850 rpm) for 24 h. The final products were filtered, washed with distilled water several times, and dried at 60°C.

A 0.05 M aqueous terephthalate solution was prepared by dissolving terephthalic acid ($C_6H_4(COOH)_2$) and NaOH in deionized water. The 0.1 M aqueous 2-naphthoate solution was prepared by dissolving 2-naphthoic acid ($C_{10}H_7COOH$), NaOH, and tetrahydrofuran in deionized water (THF:water = 1:1). 0.1 M aqueous dodecylsulfate solution was prepared by dissolving sodium dodecylsulfate ($CH_3(CH_2)_{11}OSO_3Na$) in deionized water. For exchange with organic anions, $Gd_{1.80}RE_{0.20}(OH)_5NO_3{\cdot}nH_2O$ (300 mg) was added to 30 mL of 0.05 M terephthalate solution and 0.1 M 2-naphthoate and dodecylsulfate solutions, respectively. After stirring (850 rpm) these mixtures for 24 h at 100°C, they were cooled to room temperature, and solid products were recovered by filtration and washed several times with copious water, a small amount of ethanol and acetone, and dried at 60°C.

Characterizations.

Powder X-ray diffraction (XRD) patterns of $Gd_{1.80}RE_{0.20}(OH)_5X{\cdot}nH_2O$ were recorded with a Bruker D8 Advance diffractometer. Thermogravimetric (TG) analysis was performed in air at a heating rate of 5°C/min using a Seiko Instruments TG/DTA320. The absorption spectra were obtained on a Shimadzu Multispec-1501 and a LAMBDA 35 UV–vis spectrophotometer. The excitation and emission spectra were recorded on a FP-6600 spectrophotometer (JASCO) with a Xenon flash lamp. X-ray photoelectron spectra were acquired at room temperature using a K-Alpha (Thermo Electron) and Al K_α ($h\nu$ = 1350 eV) X-ray radiation operated at 12 kV. High-resolution spectra of Ce 3d were accumulated 20 – 40 times at 50-eV pass energy.

Results and discussion

Synthesis and exchange reaction of LGdH:RE.

Because the layered gadolinium hydroxide (LGdH) and layered yttrium hydroxide (LYH) matrices showed the highest efficiency and stability for inducing photoluminescence during our preliminary study, LGdH was selected as a representative host matrix for red, green, and blue luminescence dopants. In an attempt to investigate the variation of PL property involved when the interlayer anion is exchanged under an identical environment, only X = NO_3^- members of $Gd_{1.80}RE_{0.20}(OH)_5X{\cdot}nH_2O$ (LGdH:RE) where RE = Eu^{3+}, Tb^{3+}, and Ce^{3+} were directly prepared. Well crystallized base materials with different activator ions were obtained by hydrolysis reactions in aqueous HMT solutions. As shown in Fig. S1, a series of strong (00*l*) reflections in XRD patterns of X = NO_3^- members corresponds to interlayer separations of 8.4 – 8.6 Å, which are close to that of the LGdH host matrix.[1a] Other members of LGdH:RE were obtained by the exchange reaction of NO_3^- with F^-, Cl^-, I^-, OH^-, ClO_3^-, S^{2-}, CO_3^{2-}, SO_4^{2-}, terephthalate, 2-naphthoate, and dodecylsulfate. As observed in XRD patterns measured after the reactions proceeded for 24 h at room temperature, a systematic shift of (002) and (004) reflections with a dependence on the size of inorganic anions verified complete anion replacements in the interlayer gallery of LGdH:Eu (Fig. S1). The completion of the exchange reaction between NO_3^- and organic anions was also confirmed by the absence of (002) and (004) reflections for X = NO_3^- lattices in corresponding XRD patterns, as compared in Fig. S2. Several well developed (00*l*) reflections in XRD patterns of X = terephthalate, 2-naphthoate, and dodecylsulfate members were in agreement with the large expansion of the interlayer space by the intercalation of long organic molecules. The disappearance of the band at ~1385 cm^{-1} in FT-IR spectra of products obtained after exchange reaction, which is characteristic of NO_3^-, supported the essentially complete exchange reaction (Fig. S3). Based on thermogravimetric (TG) analysis from room temperature to 1200°C, the measured interlayer water content (*n*) was variable in the range of 0.85 – 2.0 depending on the interlayer anion.

UV-Vis spectra of aqueous solutions containing various inorganic and organic anions.

Many organic and inorganic anions absorb light in the UV region. Thus, if its absorption wavelength range overlaps with the excitation bands of luminescence centers, the interlayer anion could act as a filter and then shield the excitation light for LGdH:RE to reduce its PL efficiency. In contrast, if the absorption energy is close to the resonance level of the activator ions in the layer, the interlayer anion would be a sensitizer and the absorbed energy could be transferred to the matrix such that the PL intensity of LGdH:RE is significantly enhanced. This consideration suggests that the extent of improvement in the PL property of LGdH:RE after the exchange reaction will vary depending on the nature of interlayer anions before replacement. For these reasons, careful examination of the UV absorption behavior of interlayer anions will be helpful for the optimal design of LGdH:RE with specific applications in mind.

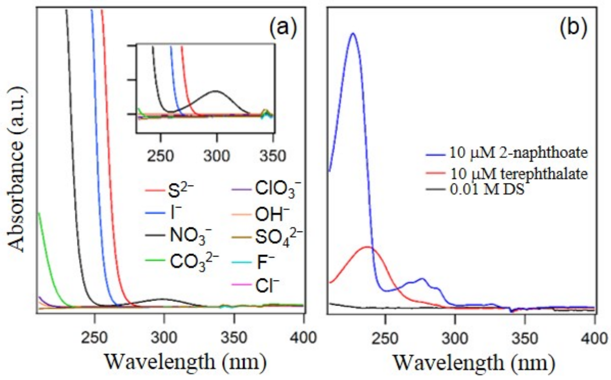

Fig. 1 UV-Vis absorption spectra of (a) 0.01 M aqueous NO_3^-, F^-, Cl^-, I^-, OH^-, ClO_3^-, S^{2-}, CO_3^{2-} and SO_4^{2-} solutions (inset: enlarged spectra) and (b) 0.01 M dodecylsulfate (DS), 10 µM terephthalate, and 10 µM 2-naphthoate solutions.

To evaluate the effect of the interlayer anion on the excitation spectra of LGdH:RE, we measured UV-Vis absorption spectra of 0.01 M aqueous NO_3^-, F^-, Cl^-, I^-, OH^-, ClO_3^-, S^{2-}, CO_3^{2-}, SO_4^{2-}, and dodecylsulfate solutions and 10 µM aqueous terephthalate and 2-naphthoate solutions. As shown in Fig. 1a, aqueous NO_3^-, I^-, and S^{2-} solutions display intense absorptions for the wavelength region less than 280 nm. In particular, a broad absorption band centered at approximately 300 nm is also observed in the UV-Vis spectrum of the NO_3^- solution. In contrast, aqueous solutions containing F^-, Cl^-, OH^-, ClO_3^-, and SO_4^{2-} anions exhibit no noticeable absorption for the 200 – 400-nm wavelength range and the CO_3^{2-} solution shows some absorbance only for wavelengths shorter than 220 nm. Fig. 1b compares the UV-Vis absorption spectra of aqueous organic anion solutions. Terephthalate and 2-naphthoate solutions show strong absorption bands in the wavelength range shorter than 300 nm, whereas the dodecylsulfate solution, despite a much higher concentration, shows no absorption at the 200 – 400 nm range. When measured at an equivalent concentration, the 2-naphthoate solution exhibits much higher absorbance than the terephthalate solution. UV absorption characteristics were also observed after insertion of these anions into the interlayer gallery of LGdH host without any activator ion. As displayed in Fig. S4, absorption spectra of aqueous suspensions containing LGdH hosts with different interlayer anions showed that UV wavelength ranges absorbed by organic and inorganic anions in the interlayer space of LGdH are similar to those in water (Fig. 1). Therefore, significant differences in the PL behavior of LGdH:RE, which was induced by replacing the interlayer anions, could be explained through consideration of the corresponding UV-Vis spectra.

Photoluminescence spectra of LGdH:Eu as a function of interlayer anions.

In general, Eu^{3+}-doped Gd compounds are recognized as a family of excellent red phosphors due to efficient internal conversion of energy absorbed by the Gd^{3+} to the excited state of Eu^{3+}.[22] Unfortunately, the LGdH matrix doped with Eu^{3+} does not yield high quantum efficiency because the many hydroxyl groups in the layer greatly increases the probability of non-radiative transitions.[23] For this reason, initial research regarding the PL property of LEuH or Eu^{3+}-doped LRHs, the $^7F_0 \rightarrow {}^5L_6$ intra $4f^6$ excitation of Eu^{3+} at ~396 nm has been mainly used for red emission.[5c,11b,13b] During the study to evaluate the emission intensity from the Eu^{3+} doped into the LRH hydroxocation layer, we observed that the UV absorption of the interlayer anions is of critical importance in the PL property. The influence of interlayer anions on the energy transfer through the LGdH matrix to Eu^{3+} is introduced in the present section. Fig. 2 compares the excitation and emission spectra of LGdH:Eu as a function of inorganic anions (X) exchanged into the interlayer space. When monitored at λ_{em} = 615 nm, the excitation spectra of LGdH:Eu mainly consist of a series of sharp peaks in the 350

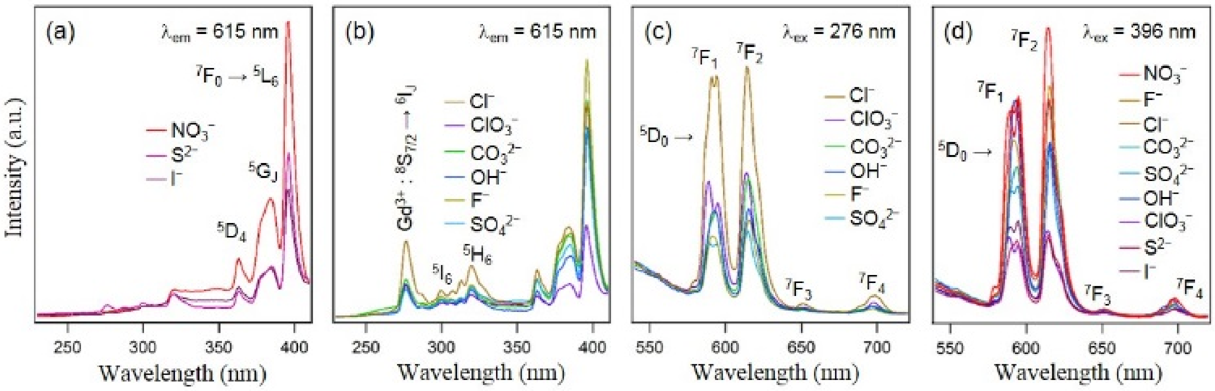

Fig. 2 (a, b) Excitation spectra monitored at 615 nm and emission spectra under (c) 276-nm and (d) 396-nm excitation of $Gd_{1.80}Eu_{0.20}(OH)_5X{\cdot}nH_2O$ (LGdH:Eu) where X = NO_3^-, F^-, Cl^-, I^-, OH^-, ClO_3^-, S^{2-}, CO_3^{2-}, and SO_4^{2-}.

– 400-nm range. These bands are assigned to the intra-$4f^6$ transitions from $^7F_0$ to $^5D_4$, ^5G_J, and $^5L_6$ states of Eu^{3+}, where the $^7F_0 \rightarrow {}^5L_6$ excitation at ~396 nm appears to be predominant.[24] It is of interest that no distinct band was observed in the range $\lambda < 300$ nm in the excitation spectra of X = NO_3^-, I^-, and S^{2-} members (Fig. 2a), whereas excitation at ~276 nm is distinguished in those of X = F^-, Cl^-, OH^-, ClO_3^-, CO_3^{2-}, and SO_4^{2-} members (Fig. 2b). This additional band is ascribed to the $^8S_{7/2} \rightarrow {}^6I_J$ transition of Gd^{3+},[25] the relative intensity of which depends on the interlayer anion. When monitored at λ_{ex} = 276 nm, characteristic $^5D_0 \rightarrow {}^7F_J$ (J = 0 – 4) transitions of Eu^{3+} are exhibited in the emission spectra of LGdH:Eu except for X = NO_3^-, I^-, and S^{2-} (Fig. 2c). Although the detection of Eu^{3+} emissions on the excitation of Gd^{3+} can be evidence for a Gd^{3+}-to-Eu^{3+} energy transfer, relatively weak intensities would indicate that the interaction between Gd^{3+} and Eu^{3+} through O^{2-} ions is not very efficient in the LGdH host hydroxide layer. Under 396-nm excitation, all examined LGdH:Eu compounds display typical $^5D_0 \rightarrow {}^7F_J$ emissions from Eu^{3+} (Fig. 2d), where the intensities of two prominent $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions are also significantly variable depending on the X anion.

One important feature that should be noted is the absence of Gd^{3+} $^8S_{7/2} \rightarrow {}^6I_J$ transition in the excitation spectra of X = NO_3^-, I^-, and S^{2-} members. Considering the strong absorption of UV light shorter than 300 nm by NO_3^-, I^-, and S^{2-} anions (Fig. 1a), it can be inferred that these interlayer anions shield the excitation light for $^8S_{7/2} \rightarrow {}^6I_J$ transition of Gd^{3+} to turn off the related emission from LGdH:Eu. Furthermore, a charge transfer related band is not observed below 300 nm, suggesting that the energy absorbed by interlayer anions such as NO_3^-, I^-, and S^{2-} is not transferred to the Eu^{3+} in the LGdH layer. Thus, the excitation quenching of Gd^{3+} conceptually corresponds to the filter effect by the interlayer anions. When we replaced NO_3^- with Cl^- or dodecylsulfate showing no absorbance at 200 – 400 nm (Fig. 1), the elimination of this anion filter led to the apparent increase of Gd^{3+} $^8S_{7/2} \rightarrow {}^6I_J$ transition, as observed in Fig. 3b. In contrast to the filter effect of inorganic anions, the organic anions absorbing UV significantly enhanced the PL efficiency of LGdH:Eu when they were intercalated into the interlayer gallery. Fig. 3a compares the excitation spectra of LGdH:Eu before and after the exchange reaction of the X anion from NO_3^- to terephthalate and 2-naphthoate. Although all three anions largely absorb UV light (Fig. 1), a strong broad charge transfer (CT) band is revealed in the excitation spectra of LGdH:Eu only with X = terephthalate and 2-naphthoate and its intensity is proportional to the absorbance of the X anion in aqueous solution. The guest anion in the interlayer may affect the coordination environment of Eu^{3+} in the layer. However, such a strong change in excitation intensity after the exchange reaction is often explained mainly by the sensitization effect of organic anion[20] when their transition from the S_0 ground state to S_1 (π, π*) excited state is induced by the absorption of UV light.[26] Coupled with a higher absorbance than the terephthalate, the excited state energy of 2-naphthoate would be closer to the $^5D_0$ level of Eu^{3+} in the LGdH matrix to cause a more efficient energy transfer.

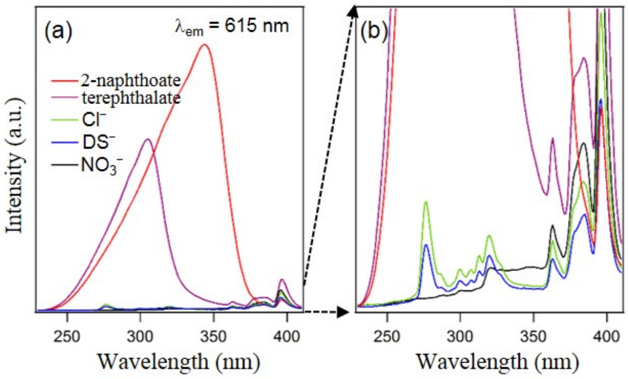

Fig. 3 (a) Excitation spectra monitored at 615 nm of $Gd_{1.80}Eu_{0.20}(OH)_5X{\cdot}nH_2O$ (LGdH:Eu) where X = NO_3^-, Cl^-, terephthalate, 2-naphthoate, and dodecylsulfate (DS^-). (b) Enlarged spectra of (a).

Photoluminescence spectra of LGdH:Tb as a function of interlayer anions.

Despite the non-radiative transitions by hydroxyl groups and intrinsically low extinction coefficient of Tb^{3+} comparable with Eu^{3+},[27] the PL intensity of Tb^{3+} in the LGdH layers was much stronger and more dependent on the nature of interlayer anions in comparison with those of Eu^{3+}. Figs. 4a and 4b show the excitation spectra of LGdH:Tb monitored at λ_{em} = 545 nm as a function of inorganic X anions. The peaks attributed to the intra-$4f^8$ transitions from $^7F_6$ to $^5L_{10-7}$, $^5G_{6-2}$, and $^5D_{2,3}$ states of Tb^{3+} are observed in common for all X members at 320 – 400

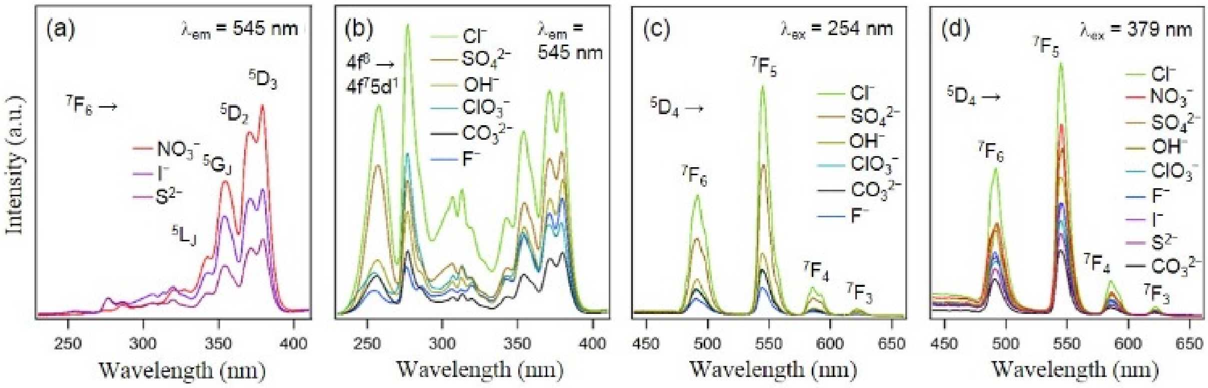

Fig. 4 (a, b) Excitation spectra monitored at 545 nm and emission spectra under (c) 254-nm and (d) 379-nm excitation of $Gd_{1.80}Tb_{0.20}(OH)_5X \cdot nH_2O$ (LGdH:Tb) where X = NO_3^-, F^-, Cl^-, I^-, OH^-, ClO_3^-, S^{2-}, CO_3^{2-}, and SO_4^{2-}.

nm. However, similar to the excitation spectra of LGdH:Eu (Fig. 2a), no distinct band is displayed at λ < ~320 nm in the excitation spectra of X = NO_3^-, I^-, and S^{2-} members whereas the sharp and strong bands arising from the 4f → 5d interconfigurational transition[25,28] of Tb^{3+} and $^8S_{7/2} \rightarrow {}^6I_J$ f–f transition of Gd^{3+} are observed at ~254 nm and ~276 nm, respectively, in the excitation spectra of X = F^-, Cl^-, OH^-, ClO_3^-, CO_3^{2-}, and SO_4^{2-} members. No excitation at λ < 320 nm indicates that the UV light for both transitions is filtered by NO_3^-, I^-, and S^{2-} interlayer anions and the energy absorbed by anions is not transferred to the excited energy level of Tb^{3+} in the LGdH layer. As a result, when X = NO_3^-, I^-, and S^{2-}, the characteristic green emission from Tb^{3+} is not achieved under the 4f–5d (254 nm) excitation (Fig. 4c). When monitored under the $^7F_6 \rightarrow {}^5D_3$ (379 nm) excitation, all members raise typical $^5D_4 \rightarrow {}^7F_J$ (J = 3 – 6) transitions[29] of Tb^{3+} ions with considerable intensities in their emission spectra (Fig. 4d).

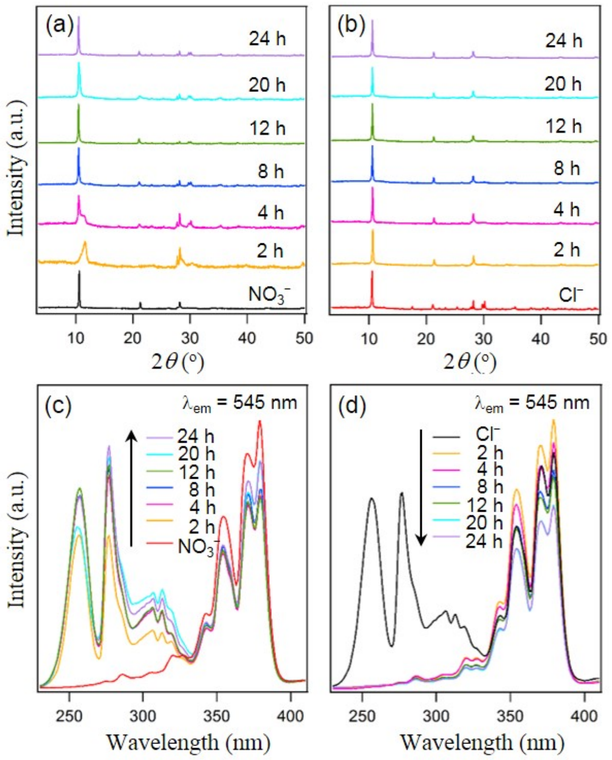

Fig. 5 XRD patterns and excitation spectra measured as a function of reaction time during the exchange reaction of $Gd_{1.80}Tb_{0.20}(OH)_5NO_3 \cdot nH_2O$ with Cl^- (a, c) and inversely $Gd_{1.80}Tb_{0.20}(OH)_5Cl \cdot nH_2O$ with NO_3^- (b, d), respectively.

To better understand the influence of the filter anion on the PL of LGdH:Tb, the excitation spectra were compared as a function of reaction time during the exchange reaction of X = NO_3^- (showing high absorbance at λ < ~320 nm) with Cl^- (showing no absorbance at 200 – 400 nm) and vice versa. As shown in Figs. 5a and 5b, while the replacement of NO_3^- by Cl^- was relatively slow and complete after a reaction longer than 8 h, the reverse reaction was rapid and complete within 2 h at room temperature. The excitation spectra of Fig. 5c show that the intercalation of Cl^- and the concomitant release of NO_3^- ions from the interlayer space of LGdH:Tb highly enhance both the 4f → 5d transition of Tb^{3+} and the $^8S_{7/2} \rightarrow {}^6I_J$ transition of Gd^{3+} with reaction time and their intensities remain almost constant after 8 h. This variation is consistent with the removal of all NO_3^- ions after exchange reaction for 8 h, as confirmed by the XRD patterns (Fig. 5a). Inversely, when the interlayer anion was replaced from Cl^- to NO_3^-, the shielding effect of UV light was recovered again to effectively quench the excitations of LGdH:Tb at both ~254 nm and ~276 nm even after reaction for 2 h (Fig. 5d), in agreement with the XRD patterns (Fig. 5b). The PL efficiency of Tb^{3+} in LGdH matrix appeared to be quite sensitive to the type of interlayer anion.

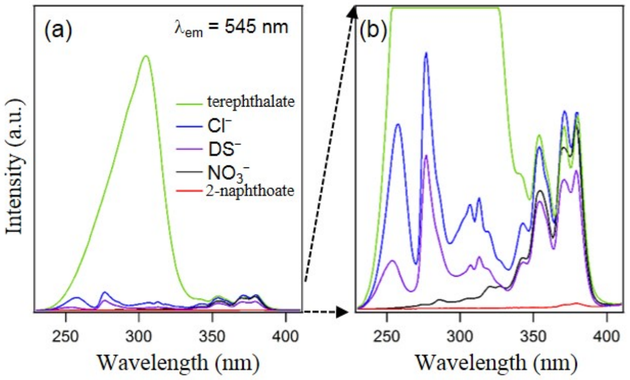

Fig. 6 (a) Excitation spectra monitored at 545 nm of $Gd_{1.80}Tb_{0.20}(OH)_5X \cdot nH_2O$ (LGdH:Tb) where X = NO_3^-, terephthalate, 2-naphthoate, and dodecylsulfate. (b) Enlarged spectra of (a).

Additional information for the relationship between the PL of Tb^{3+} in the layer and X anions in the interlayer of LGdH was obtained by comparing the excitation spectra after exchange reactions of NO_3^- and Cl^- with terephthalate, 2-naphthoate, and dodecylsulfate. As shown in Fig. 6, the energy absorbed by terephthalate was successfully converted to the photoexcitation of LGdH:Tb, which is similar to the phenomenon in LGdH:Eu and ensures that energy transfer to both Eu^{3+} and Tb^{3+} occurs in a highly efficient way in the LGdH matrix. On the contrary, when X = 2-naphthoate, all bands originated from $^8S_{7/2} \rightarrow {}^6I_J$ transition of Gd^{3+} and $4f^8 \rightarrow 4f^75d^1$ and even intra-$4f^8$ transitions of Tb^{3+} completely disappeared at the 200 – 400-nm UV region in the excitation spectra of LGdH:Tb. This behavior is in contrast to the much greater enhancement of the CT band by the sensitization of 2-naphthoate than terephthalate in the excitation spectra of LGdH:Eu (Fig. 3a). It is also noted that the role of X anions (as a filter, a sensitizer, or just a spacer) could be interpreted differently if the nature of interlayer anions constituting the LGdH structure before the exchange reaction is not carefully considered. For instance, whereas the dodecylsulfate attenuated the excitations at ~254 nm and ~276 nm when substituted for Cl^-, it significantly enhanced both excitations when substituted for NO_3^- (Fig. 6b). Thus, it is evidently demonstrated that whether to shield or harvest the excitation light is dictated by the interlayer anion–activator combinations and their effect can be in the opposite way to substantially decrease or increase the PL efficiency even in the same LGdH matrix.

Photoluminescence spectra of LGdH:Ce as a function of interlayer anions.

The Ce^{3+} has the $[Xe]4f^1$ electronic configuration where an optically active 4f electron is relatively insensitive to variations in the structural environment due to effective shielding by the filled 5s and 5p shells of the [Xe] core. In contrast, the excited $[Xe]5d^1$ configuration is not shielded by such filled shells so that the 5d electron is significantly influenced by the crystal structure, local site symmetry, and bond polarity. Consequently, the ligand field splitting of the d-levels as well as the 4f–5d separation can change the excitation and emission energies of Ce^{3+}.[30] As the environment around Ce^{3+} in the LGdH matrix is flexible depending on the interlayer anion, we investigated the influence of various inorganic and organic X anions on the excitation and emission behaviors of Ce^{3+} activator, similar to LGdH:Eu and LGdH:Tb systems. The results have contributed to a better understanding of blue emission from LGdH:Ce, which is considerably affected by the interlayer exchange reaction.

Fig. 7 displays the excitation and emission spectra of LGdH:Ce as a function of interlayer inorganic anions (X). Compared with Eu^{3+} and Tb^{3+}, the luminescence quenching of Ce^{3+} in the LGdH lattice is more serious and no excitation is detected between 200 – 400 nm when X = NO_3^-, I^-, and S^{2-} as well as even OH^-. On the other hand, two types of 4f → 5d transitions were exhibited in the excitation spectra of other X anion members (Fig. 7b), where their intensities, relative intensity ratios, and wavelengths are different depending on X (Fig. 7c). If we suppose that the 4f–5d separation is approximately constant within the same LGdH matrix, the ligand field effect is expected to dominate the PL spectra of LGdH:Ce. Thus, the extent of variation in symmetry of the site occupied by the Ce^{3+}, which is established by the change of interlayer anions, affects the energy of the Ce^{3+} excitation in the LGdH matrix. It is also noted that the intensity of these excitations observed when X = Cl^- are incomparably superior to those of any other members. Strong bands at approximately 286 and 367 nm in the excitation spectra are similar to those observed in corresponding spectra of Ce^{3+}-doped oxide $Ca_2Al_2SiO_7$ [31] but blue-shifted slightly in comparison with Ce^{3+}-doped fluoride Rb_2NaYF_6.[32] It would be pertinent here to consider that the layer structure of LGdH provides two kinds of sites for the Ce^{3+}, eight- and nine-coordinated polyhedra.[2] A different coordination number should result in a difference in size and symmetry of the Ce^{3+} site and ultimately a difference in the ligand field strength at two sites. The accompanied shift of the excited state d-energy level[33] would cause variation in the absorption energy of the Ce^{3+}. Under excitation at both 286- and 367-nm excitations, a broad band centered at ~422 nm is revealed in the emission spectra of X = Cl^- member (Fig. 7d). This blue emission is attributed to the allowed transitions from the lowest energy level of the $5d^1$ excited state to the $^2F_{5/2}$ and $^2F_{7/2}$ levels of the $4f^1$ ground state. As observed in many Ce^{3+}-doped materials, the ground state spin-orbit splitting of Ce^{3+} was not

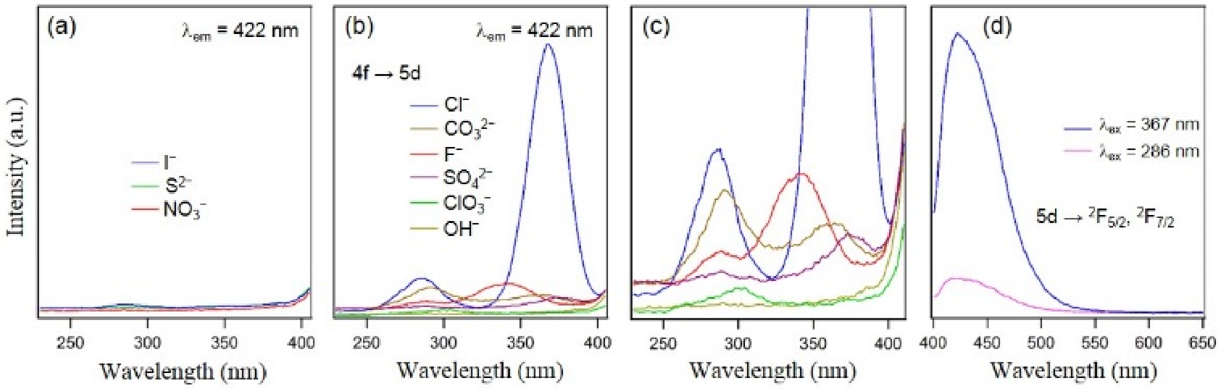

Fig. 7 (a, b) Excitation spectra monitored at 422 nm of $Gd_{1.80}Ce_{0.20}(OH)_5X{\cdot}nH_2O$ (LGdH:Ce) where X = NO_3^-, F^-, Cl^-, I^-, OH^-, ClO_3^-, S^{2-}, CO_3^{2-}, and SO_4^{2-}. (c) Enlarged spectra of (b). (d) Emission spectra of X = Cl^- member under 286- and 367-nm excitation.

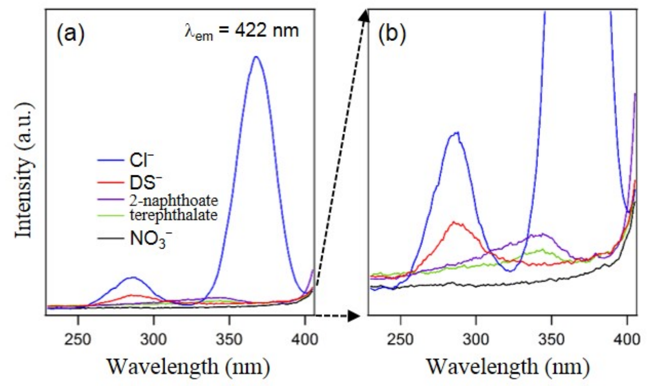

Fig. 8 (a) Excitation spectra monitored at 422 nm of $Gd_{1.80}Ce_{0.20}(OH)_5X\cdot nH_2O$ (LGdH:Ce) where X = NO_3^-, terephthalate, 2-naphthoate, and dodecylsulfate. (b) Enlarged spectra of (a).

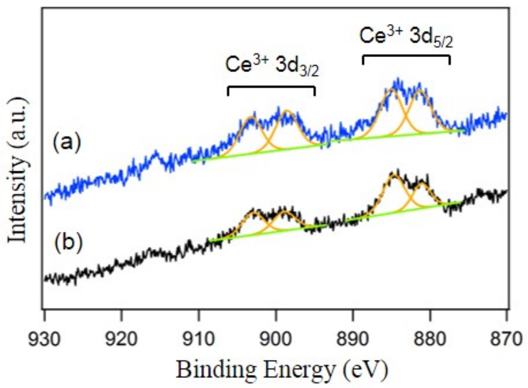

Fig. 10 XPS spectra of (a) $Gd_{1.80}Ce_{0.20}(OH)_5NO_3\cdot nH_2O$ and (b) $Gd_{1.80}Ce_{0.20}(OH)_5Cl\cdot nH_2O$ obtained after exchange reaction between NO_3^- and Cl^-.

clearly resolved in the emission spectra of LGdH:Ce, resulting in a single asymmetric emission band.

Another interesting result was the unexpectedly small influence of organic anions on the excitation behavior of LGdH:Ce, regardless of the existence of π-conjugate system, indicating that the absorbed energy by the conjugate system was not efficiently transferred to the Ce^{3+} in the LGdH matrix. As shown in Fig. 8, when Cl^- was exchanged by organic anions, excitation at both 286 and 367 nm was significantly suppressed. Furthermore, the intensity of the excitation bands when X = terephthalate and 2-naphthoate was lower than when X = dodecylsulfate with no π-conjugate system. Such a variation contrasts with the remarkable enhancement of the CT band by the sensitization of the π-system in the excitation spectra of LGdH:Eu (Fig. 3a) and LGdH:Tb (Fig. 6a). Interestingly, the dodecylsulfate replaced for NO_3^- slightly enhances the excitation at only ~286 nm, whereas a slight increase in excitation was only observed at ~345 nm when the terephthalate and 2-naphthoate were replaced for NO_3^-. Hence, it is deduced that, compared to the linear alkyl chain, the larger angular volume of terephthalate and 2-naphthoate containing aromatic rings would be reflected in a different site preference. This observation supports the hypothesis that the interlayer anion affects the polyhedral sites for the Ce^{3+} in the LGdH layer and the accompanied change in the ligand field results in a modification of 4f → 5d transitions.

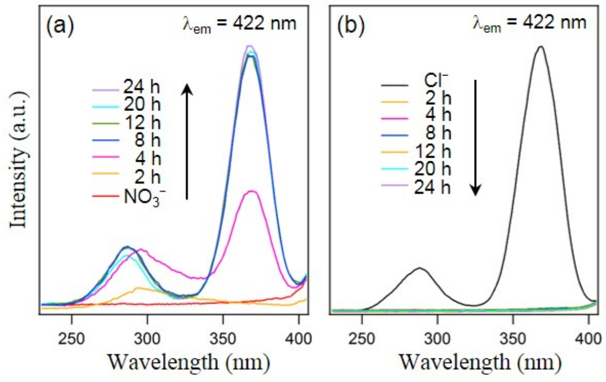

Fig. 9 Excitation spectra measured as a function of reaction time during the exchange reaction of $Gd_{1.80}Ce_{0.20}(OH)_5NO_3\cdot nH_2O$ with Cl^- (a) and inversely $Gd_{1.80}Ce_{0.20}(OH)_5Cl\cdot nH_2O$ with NO_3^- (b).

It is intriguing that the 4f → 5d excitation intensities of LGdH:Ce are exceptionally high when X = Cl^-, compared with when X = other inorganic and organic anions. In order to estimate the enhancement of these transitions by Cl^-, we measured the excitation spectra of LGdH:Ce as a function of reaction time during the exchange reaction of X = NO_3^- with Cl^- and vice versa. XRD patterns were analogous to LGdH:Tb system; the replacement of NO_3^- by Cl^- required a reaction longer than 8 h while the reverse reaction was complete within 2 h at room temperature (Fig. S5). The variation of excitation spectra was consistent with that of the XRD patterns. As displayed in Fig. 9a, when the NO_3^- is replaced by the Cl^-, the 4f → 5d transitions of LGdH:Ce are enhanced with reaction time and their intensities were constant after an 8-h reaction. The intensity of the excitation at approximately 296 nm only increases at the beginning of the exchange reaction and subsequently the 367-nm excitation is rapidly enhanced to increase its intensity higher than that at ~296 nm after reaction for 4 h. Whereas the 367-nm band position is constant, the 296-nm band is blue-shifted by approximately 10 nm after complete replacement of NO_3^- by Cl^-. Although the origin of this behavior is not straightforward, it might be associated with the kinetics of the exchange reaction and the replacement between anions seems to proceed not randomly but stage by stage in the interlayer space of LGdH. Meanwhile, during the reverse reaction from X = Cl^- to NO_3^-, both 4f → 5d transitions of LGdH:Ce were completely quenched even after reaction for 2 h. Accordingly, it was demonstrated that the PL efficiency of Ce^{3+} in the LGdH matrix was drastically improved by the intercalation of Cl^- ions into its interlayer galleries.

XPS spectra of LGdH:Ce with NO_3^- and Cl^- as interlayer anions.

Since the Ce^{3+} was inclined to be readily oxidized into the Ce^{4+} with no optically active 4f electron in general conditions, the maintenance of the 3+ oxidation state of Ce in LGdH:Ce was confirmed before and after the exchange reaction of Cl^- with NO_3^- as a representative example using X-ray photoelectron spectroscopy (XPS). In Fig. 10, the Ce 3d XPS core-level spectra of LGdH:Ce with X = NO_3^- and Cl^- exhibited two prominent $3d_{5/2}$ and $3d_{3/2}$ spin-orbit split doublets centered at approximately 883 and 902 nm, respectively. In general, the 3d spectrum of Ce^{3+} was resolved to mainly four components but the Ce^{4+} 3d electron reveals the characteristic six-line spectrum.[34] When we fit the obtained XPS curves, assuming four line contributions, all four binding energies listed in Table 1 were very close to those reported for Ce_2O_3, supporting the 3+ valence state of Ce in LGdH:Ce before and after the exchange reaction. The peaks at ~885 eV and ~903 eV correspond to the principal components of $3d_{5/2}$ and $3d_{3/2}$ contributions of the Ce^{3+}, respectively. As the localization of the valence band electron of O2p near the more electronegative oxygen ion can reconfigure the energy levels of Ce when the Ce–O bond was formed, additional peaks (~881 and ~899 eV, respectively) were observed on the lower binding energy side of corresponding principal components.[35,36] Nevertheless, a weak signature was detected at approximately 916.5 eV, which was not related to the Ce^{3+}. This peak, usually assigned to $4f^0$ orbital transitions, was adopted as the spectroscopic evidence for the existence of Ce^{4+}.[37] As a consequence, a slight contribution from Ce^{4+} in LGdH:Ce could not be ruled out.

Table 1 Binding energies of Ce (3d) obtained by the deconvolution of XPS spectra of $Gd_{1.80}Ce_{0.20}(OH)_5X\cdot nH_2O$ (LGdH:Ce) where X = NO_3^- and Cl^-. Binding energies of Ce_2O_3 are also listed for comparison.

compound	Ce^{3+} $3d_{5/2}$ (eV)		Ce^{3+} $3d_{3/2}$ (eV)		Ref.
	principal	Ce–O	principal	Ce–O	
LGdH:Ce(NO_3)	885.1	881.3	903.3	898.6	
LGdH:Ce(Cl)	884.7	881.1	903.0	898.9	
Ce_2O_3	884.4	880.6	903.9	899.3	35
Ce_2O_3(foil)	884.8	880.6	903.4	899.2	34b

Conclusions

We demonstrated that the optical properties of RE^{3+}-doped LGdHs can be largely improved by the proper combination of host matrix–interlayer anion–activator ion in the matrix. In particular, we propose that the identical interlayer anion in a gallery of LRHs can shield or harvest the UV energy for excitation of RE^{3+}-doped LRHs, and that whether to filter or sensitize is decided by the nature of the activator ions. Because of the intrinsically forbidden f – f transition and non-radiative transition by hydroxyl groups in the layer of LRHs, an in-depth understanding of whether the interlayer anions in the galleries enhance or suppress the excitation of LRHs provides the best route for designing the LRH systems with the maximum luminescence efficiency for applications in various fields. The present results, obtained from a comparative study using various inorganic and organic anions, should assist in the optimization of PL in LRH matrices.

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Notes and references

1 (a) K.-H. Lee and S.-H. Byeon, *Eur. J. Inorg. Chem.*, 2009, 929–936; (b) F. Geng, Y. Matsushita, R. Ma, H. Xin, M. Tanaka, F. Izumi, N. Iyi and T. Sasaki, *J. Am. Chem. Soc.*, 2008, **130**, 16344–16350; (c) L. J. McIntyre, L. K. Jackson and A. M. Fogg, *Chem. Mater.*, 2008, **20**, 335–340.

2 F. Geng, R. Ma and T. Sasaki, *Acc. Chem. Res.*, 2010, **43**, 1177–1185.

3 (a) K.-H. Lee and S.-H. Byeon, *Eur. J. Inorg. Chem.*, 2009, 4727–4732; (b) L. Poudret, T. J. Prior, L. J. McIntyre and A. M. Fogg, *Chem. Mater.*, 2008, **20**, 7447–7453; (c) F. Geng, H. Xin, Y. Matsushita, R. Ma, M. Tanaka, F. Izumi, N. Iyi and T. Sasaki, *Chem. Eur. J.*, 2008**, 14**, 9255–9260.

4 (a) S.Takagi, D. A. Tryk and H. Inoue, *J. Phys. Chem. B*, 2002, **106**, 5455–5460; (b) B. Sels, D. De Vos, M. Buntinx, F. Pierard, A. K. Mesmaeker and P. Jacobs, *Nature*, 1999, **400**, 855–857.

5 (a) H. Jeong, B.-I. Lee and S.-H. Byeon, *Dalton Trans.*, 2012, **41**, 14055–14058; (b) B.-I. Lee, S.-Y. Lee S.-H. Byeon, *J. Mater. Chem.*, 2011, **21**, 2916–2923; (c) B.-I. Lee and S.-H. Byeon, *Chem. Commun.*, 2011, **47**, 4093–4095.

6 F. Gandara, J. Perles, N. Snejko, M. Iglesias, B. Gomez-Lor, E. Gutierrez-Puebla and M. A. Monge, *Angew. Chem. Int. Ed.*, 2006, **45**, 7998–8001.

7 (a) W. Li, Q. Gu, F. Su, Y. Sun, G. Sun, S. Ma and X. Yang, *Inorg. Chem.*, 2013, **52**, 14010−14017; (b) Q. Gu, Y. Sun, N. Chu, S. Ma, Z. Jia and X. Yang, *Eur. J. Inorg. Chem.*, 2012, 4407–4412.

8 (a) H. Kim, B.-I. Lee and S.-H. Byeon, *Chem. Commun.*, 2015, **51**, 725–728; (b) K. Lee, B.-I. Lee and S.-H. Byeon, *Chem. Commun.*, 2013, **49**, 7165–7167; (c) V. Parashar and A. C. Pandey, *Anal. Methods*, 2010, **2**, 1227–1229.

9 (a) Y. S. Yoon, B.-I. Lee, K. S. Lee, G. H. Im, S. H. Byeon, J. H. Lee and I. S. Lee, *Adv. Funct. Mater.*, 2009, **19**, 3375–3380; (b) B.-I. Lee, K. S. Lee, J. H. Lee, I. S. Lee and S.-H. Byeon, *Dalton Trans.*, 2009, 2490–2495.

10 Y.-S. Yoon, B.-I. Lee, K. S. Lee, H. Heo, J. H. Lee, S.-H. Byeon and I. S. Lee, *Chem. Commun.*, 2010, **46**, 3654–3656.

11 (a) Q. Zhu, J.-G. Li, C. Zhi, X. Li, X. Sun, Y. Sakka, D. Golberg, Y. Bando, *Chem. Mater.*, 2010, **22**, 4204–4213; (b) F. Geng,; Y. Matsushita, R. Ma, H. Xin, M. Tanaka, N. Iyi and T. Sasaki, *Inorg. Chem.*, 2009, **48**, 6724–6730.

12 Y. Xiang, X.-F. Yu, D.-F. He, Z. Sun, Z. Cao and Q.-Q. Wang, *Adv. Funct. Mater.*, 2011, **21**, 4388–4396.

13 (a) B.-I. Lee, H. Jeong and S.-H. Byeon, *Chem. Commun.*, 2013, **49**, 11397–11399; (b) L. Wang, D. Yan, S. Qin, S. Li, J. Lu, D. G. Evans and X. Duan, *Dalton Trans.*, 2011, **40**, 11781–11787.

14 (a) X. Wu, J.-G. Li, D.-H. Ping, J. Li, Q. Zhu, X. Li, X. Sun and Y. Sakka, *J. Alloys Comp.*, 2013, **559**, 188–195; (b) L. Hu, R. Ma, T. C. Ozawa and T. Sasaki, *Inorg. Chem.*, 2010, **49**, 2960–2968.

15 B. Shao, Q. Zhao, Y. Jia, W. Lu, M. Jiao, W. Lu and H. You, *Chem. Commun.*, 2014, **50**, 12706–12709.

16 L. Hu, R. Z. Ma, T. C. Ozawa and Sasaki, *Angew Chem. Int. Ed.*, 2009, **48**, 3846 –3849.

17 Y. Zhao, J.-G. Li, M. Guo and X. Yang, *J. Mater. Chem. C*, 2013, **1**, 3584–3592.

18 (a) Y.-S. Yoon, S.-H. Byeon and I. S. Lee, *Adv. Mater.,* 2010, **22**, 3272–3276; (b) L. Hu, R. Ma, T. C. Ozawa, F. Geng, N. Iyi and T. Sasaki, *Chem. Commun.*, 2008, 4897–4899; (c) Q. Zhu, J.-G. Li, C. Zhi, R. Ma, T. Sasaki, J. X. Xu, C. H. Liu, X. D. Li, X. D. Sun and Y. Sakka, *J. Mater. Chem.*, 2011, **21**, 6903–6908.

19 S. Ida, Y. Sonoda, K. Ikeue and Matsumoto, *Chem. Commun.*, 2010, **46**, 877–879.

20 (a) Y. Sun, N. Chu, Q. Gu, G. Pan, G. Sun, S. Ma and X. Yang, *Eur. J. Inorg. Chem.*, 2013, 32−38; (b) N. Chu, Y. Sun, Y. Zhao, X. Li, G. Sun, S. Ma and X. Yang, *Dalton Trans.*, 2012, **41**, 7409−7414.
21 L. Liu, Q. Wang, C. Gao, H. Chen, W. Liu and Y. Tang, *J. Phys. Chem. C*, 2014, **118**, 14511−14520.
22 J. G. Li, X. Li, X. Sun and T. Ishigaki, *J. Phys. Chem. C*, 2008, **112**, 11707–11716.
23 A. Bahtat, M. C. Marco de DeLucas, B. Jacquier, B. Varrel, M. Bouazaoui and J. Mugnier, *Opt. Mater.*, 1997, **7**, 173–179.
24 (a) W. Di, R. A. S. Ferreira, M.-G. Willinger, X. Ren and N. Pinna, *J. Phys. Chem. C*, 2010, **114**, 6290–6297; (b) S. Quici, G. Marzanni, M. Cavazzini, P. L. Anelli, M. Botta, E. Gianolio, G. Accorsi, N. Armaroli and F. Barigelletti, *Inorg. Chem.*, 2002, **41**, 2777–2784.
25 Y.-C. Li, Y.-H. Chang, Y.-S. Chang, Y.-J. Lin and C.-H. Laing, *J. Phys. Chem. C*, 2007, **111**, 10682–10688.
26 Z. Chang, D. Evans, X. Duan, P. Boutinaud, M. D. Roy and C. Forano, *J. Phys. Chem. Solids*, 2006, **67**, 1054–1057.
27 R. Lakowicz, *Principles of Fluorescence Spectroscopy*, 3rd ed. Springer: Singapore, 2006.
28 L. van Pieterson, M. F. Reid, G. W. Burdick and A. Meijerink, *Phys. Rev. B*, 2002, **65**, 045114.
29 (a) M. H. V. Werts, R. T. F. Jukes and J. W. Verhoeven, *Phys. Chem. Chem. Phys.*, 2002, **4**, 1542–1548; (b) Q. Li, T. Li and J. Wu, *J. Phys. Chem. B*, 2001, **105**, 12293–12296.
30 P. Dorenbos, *J. Lumin.*, 2000, **91**, 155–176.
31 N. Kodama, T. Takahashi, M. Yamaga, Y. Tanii, J. Qiu and K. Hirao, *Appl. Phys. Lett.*, 1999, **75**, 1715–1717.
32 B. F. Aull and H. P. Jenssen, *Phys. Rev. B*, 1986, **34**, 6647–6655.
33 B. F. Aull and H. P. Jenssen, *Phys. Rev. B*, 1986, **34**, 6640–6646.
34 (a) D. R. Mullins, S. H. Overbury and D. R. Huntley, *Surf. Sci.*, 1998, **409**, 307–319; (b) T. L. Barr, C. G. Fries, F. Cariati, J. C. J. Bart and N. Giordano, *J. Chem. Soc. Dalton Trans.*, 1983, 1825–1829; (c) G. Praline, B. E. Koel, R. L. Hance, H.-I. Leeand J. M. White, *J. Electron Spectrosc. Relat. Phenom.*, 1980, **21**, 17–30.
35 M. L. Trudeau, A. Tschope and J. Y. Ying, *Surf. Interf. Anal.*, 1995, **23**, 219–226.
36 R. Vercaemst, D. Poelman, R. L. Van Meirhaeghe, L. Fiermans, W. H. Laflere and F. Cardon, *J. Lumin.*, 1995, **63**, 19–30.
37 (a) K. Bak and L. Hilaire, *Appl. Surf. Sci.*, 1993, **70/71**, 191–195; (b) A. Kotani, T. Jo and J. C. Parlebas, *Adv. Phys.*, 1988, **37**, 37–85.

Graphical Abstract

“Relationship between interlayer anions and photoluminescence of layered rare earth hydroxides”

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The effects of interlayer anions on the photoluminescence of layered rare earth hydroxides was investigated with Eu^{3+}, Tb^{3+}, and Ce^{3+}-doped layered gadolinium hydroxynitrate as a representative base matrix for efficient and stable anion-exchange reactions.