Development of Ion-Conductive and Vapoluminescent Porous Coordination Polymers Composed of Ruthenium(II) Metalloligand

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Supporting Information

ABSTRACT: We synthesized two new porous coordination polymers (PCPs) \(\{\text{Ln}-(\text{OH})_2\}[\text{Ru}(\text{dcbbpy})_3]_{\text{n}}\cdot4\text{nH}_2\text{O}\} (\text{Ln}=(\text{Ce, Nd}))\) composed of the luminescent ruthenium(II) metalloligand \([\text{Ru}(4,4'\text{-dicarboxy-2,2'\text{-bipyridine})}]^{4+}\) and lanthanide ions \(\text{Ln}^{3+}\) \((\text{Ln}=(\text{Ce, Nd}))\). These two PCPs \(\text{Ln}_7\text{-Ru}_4\) are isomorphous with the previously reported PCP \(\text{La}_7\text{-Ru}_4\), and the lattice constants \((a, c,\text{ and unit cell volume} V)\) changed systematically according to the lanthanide contraction. All three \(\text{Ln}_7\text{-Ru}_4\) compounds have \(\text{OH}^-\) anion containing porous structures and a large number of hydrate water molecules within the pores, resulting in moderate ion conductivities \((10^{-6}–10^{-7} \text{ S cm}^{-1})\) at 90% relative humidity (RH) and 298 K. In contrast, the structural transformation of \(\text{Ln}_7\text{-Ru}_4\) associated with water-vapor adsorption/desorption strongly depends on the lanthanide ion; the \(\text{Ln}_7\text{-Ru}_4\) compounds with larger \(\text{Ln}^{3+}\) ions recover the original porous structure at lower relative humidities (RH). A similar trend was observed for the ion conduction activation energy, suggesting that the bridging \(\text{Ln}^{3+}\) ion plays an important role in the formation of the ion-conductive pathways. \(\text{La}_7\text{-Ru}_4\) and \(\text{Ce}_7\text{-Ru}_4\) exhibit vapochromic luminescence associated with water vapor adsorption/desorption, arising from the 3MLCT emission of \([\text{4Ru}])\). This vapochromic behavior is also affected by the replacement of the \(\text{La}^{3+}\) ion; the vapochromic shift of \(\text{Ce}_7\text{-Ru}_4\) was observed at RH values (near 100% RH) higher than that of \(\text{La}_7\text{-Ru}_4\). MLCT emissions of \([\text{4Ru}])\) metallogand in \(\text{Nd}_7\text{-Ru}_4\) were barely observable in the visible region, but sharp emission bands characteristic of 4f–4f transitions of the \(\text{Nd}^{3+}\) ion were observed in the near-infrared (NIR) region (arising from the 3MLCT transition of \([\text{4Ru}])\), suggesting the transfer of energy from the \(\text{[4Ru]}\) 3MLCT excited state to the 4f–4f transition state of the \(\text{Nd}^{3+}\) ions.

INTRODUCTION

Porous coordination polymers (PCPs) and metal–organic frameworks (MOFs) have attracted much attention because of their porosity can be controlled by design, enabling the fabrication of various porous and functional materials for use as gas/vapor absorbents and chemical sensors. One of the advantages of PCP/MOF systems in comparison with other known porous materials is their easier functionalization, which is possible because of the wide variety of possible linkers, including organic compounds and metal complexes with coordination sites. For example, several proton-conducting porous materials with conductivities comparable to that of the well-known proton conductor Nafion \((<10^{-2} \text{ S cm}^{-1})\) have been prepared by the introduction of acidic groups to the porous frameworks of a PCP/MOF system. Although the investigation of PCP/MOF-based proton conductors has mainly focused on increasing the proton conductivity, several investigators have focused on the preparation of multifunctionalized proton conductive PCPs. For example, Ohkoshi et al. reported an interesting interference effect between the magnetic ordering and proton conduction of the Prussian blue analogue \(\text{V}[\text{Cr(CN)}_6\text{]_2/3\cdotnH}_2\text{O}\). Such reports suggest that ion conduction (including proton conduction) can be correlated with the other functions by modifying the crystal structure.

Concerning the evaluation of ion conductivity, the interplay between ion conduction and photophysical properties is a promising approach. Proton conductivity is normally evaluated by the alternating current (ac) impedance method, which...
requires at least two electrodes to be attached to the solid
surfaces of the material. If ion conductivity could be evaluated
by UV–vis absorption/emission measurements, the attach-
ments of electrodes could be omitted, which might make it
possible to evaluate the conductivity of complicated systems
such as fuel cells. Thus, we have recently focused on the
development of luminescent and ion-conductive PCP/MOF
systems. We previously reported a new luminescent PCP,
\(\text{La}_7(\text{OH})_5[\text{Ru}(4,4′\text{-dcdbpy})_3]_2\cdot4\text{H}_2\text{O} (\text{La}_7\text{-Ru}_4)\), which is
composed of a luminescent ruthenium(II) metallogand,
\([\text{Ru}(4,4′\text{-dcdbpy})_3]^2−\) ([4Ru]; 4,4′-dicarboxy-
2,2′-bipyrilene), and La\(^{3+}\) cations.\(^{23}\) We found that this OH−-
incorporating PCP adsorbs a large amount of water, and both
the ion conductivity and 3MLCT emission energy are
dependent on the relative humidity.\(^{23}\) However, the roles of
the bridging La\(^{3+}\) ion on both the ion conductivity and 3MLCT
emission energy were unclear. Thus, we have focused on the
development of La\(^{3+}\) cation substituted analogues (Ln\(_n\)-Ru\(_4\)),
allowing us to clarify the role of the bridging lanthanide ions on
the correlated functions, such as ion conductivity and
luminescence. Furthermore, by using the lanthanide contrac-
tion, we can achieve precise control over the crystal structure.\(^{24}\)
In addition, further functionalization allows us to take
advantages of the unique properties of lanthanide cations. For
example, lattice defects in the porous framework can be
introduced by substitution of La\(^{3+}\) with Ce\(^{3+}\), because cerium
can exist in both trivalent and tetravalent oxidation states. Nd\(^{3+}\)
cations are well-known to exhibit near-infrared (NIR) emission
due to the 4f→4f transitions. Ever since Veggel et al. demon-
strated the energy transfer from the 3MLCT excited
state of the \([\text{Ru}(\text{bpy})_2]^2−\) moity to the 4f→4f transition state of the
Nd\(^{3+}\) ion,\(^{25}\) significant investigation into the development of
energy transfer systems based on Ru(II), Os(II), and Pt(II)
complexes for use as light harvesting antennas has been
conducted.\(^{26,27}\) Similarly, in the La\(_n\)-Ru\(_4\) porous framework, the
[4Ru] metallogand is surrounded by more than six
coordinated La\(^{3+}\) cations; consequently, the efficient transfer
of energy from [4Ru] to the Nd\(^{3+}\) ion can be expected. Herein,
we report the crystal structures, ion conductivities, and
luminescence properties of these new PCPs, Ln\(_n\)-Ru\(_4\) (Ln = Ce, Nd),
composed of the luminescent ruthenium(II) metal-
logand [4Ru] and Ln\(^{3+}\) ions, and we discuss the effect of
substitution of the La\(^{3+}\) cations of the previously reported PCP
La\(_7\)-Ru\(_4\) with Ce\(^{3+}\) or Nd\(^{3+}\) cations.

### EXPERIMENTAL SECTION

**General Procedures.** The starting materials (RuCl\(_3\)-3H\(_2\)O, LaCl\(_3\)-
7H\(_2\)O, CeCl\(_3\)-7H\(_2\)O, and NdCl\(_3\)-6H\(_2\)O) were used as received from
commercial sources. Solvents were used without any further
purification. Unless otherwise stated, all reactions were performed in
air. The Ru(II) metallogand \([\text{Ru}(\text{H}_2\text{dbcpy})_2](\text{dbcpy})]^{-}\) was prepared
according to a previously published method.\(^{28}\) Elemental analysis
was performed at the analysis center of Hokkaido University.

**Synthesis of \([\text{Ln}_2(\text{OH})_3][\text{Ru}(\text{dbcpy})_3]_2\cdot4\text{H}_2\text{O} (\text{Ln}_2\text{-Ru}_{2})\) \(\text{Ln} = \text{Ce, Nd}\).** These complexes were synthesized by our previously
reported method.\(^{29}\) A solution of LnCl\(_3\)-nH\(_2\)O (3.96 × 10\(^{-2}\) mmol) in
EtOH (2 mL) was carefully layered on top of a solution of
\([\text{Ru}(\text{H}_2\text{dbcpy})_2](\text{dbcpy})]^{-}\cdot6\text{H}_2\text{O} (187.6 \text{ mg}, 2.23 \times 10^{-2} \text{ mmol})
in aqueous ammonia (2 mL, pH 11.7) with an ethyl acetate buffer (1
mL). Red platelet crystals began to form after standing at 233 K
for several days. After 2 weeks, these crystals were collected by
filtration, washed with water, and dried in air.

**Ce\(_7\)-Ru\(_4\).** Yield: 24.0 mg, 1.75 × 10\(^{-2}\) mmol, 78.4% based on
\([\text{Ru}(\text{H}_2\text{dbcpy})_2](\text{dbcpy})]^{-}\cdot6\text{H}_2\text{O}. \text{ Anal. Calcd for}
\(\text{Ce}_7\text{H}_4\text{Ru}_7\text{N}_2\text{O}_{11}\text{C}_{17.5}(\text{OH})_{12.5}\cdot16\text{H}_2\text{O}: \text{C}, 31.24; \text{H}, 3.64; \text{N}, 6.07.
Found: C, 30.96; H, 3.74; N, 6.10.

**Nd\(_7\)-Ru\(_4\).** Yield: 25.5 mg, 1.85 × 10\(^{-2}\) mmol, 82.9% based on
\([\text{Ru}(\text{H}_2\text{dcdbpy})_2](\text{dbcpy})]^{-}\cdot6\text{H}_2\text{O}. \text{ Anal. Calcd for}
\(\text{Nd}_7\text{H}_4\text{Ru}_7\text{N}_2\text{O}_{11}\text{C}_{17.5}(\text{OH})_{12.5}\cdot14.5\text{H}_2\text{O}: \text{C}, 31.75; \text{H}, 3.52; \text{N},
6.15. Found: C, 30.9; H, 3.65; N, 6.09.

**Powder X-ray Diffraction.** Powder X-ray diffraction measure-
ments were conducted using a Rigaku SPD diffractometer at beamline
BL-8B at the Photon Factory, KEK, Japan, or a Bruker D8 Advance
diffractometer equipped with a graphite monochromator using Cu Kα
radiation and a one-dimensional LynxEye detector. The wavelength of
the synchrotron X-rays was 1.126 Å. The PXRD patterns were
analyzed by using the whole powder pattern decomposition (WPPD)
method using the TOPAS 4.2 software.\(^{27}\)

**Luminescence Properties.** The luminescence spectrum of each
complex was measured using a JASCO FP-6600 spectrofluorometer at
room temperature. The typical slit widths of the excitation and
emission light were 5 and 6 nm, respectively. The relative humidity
was controlled by using the saturated aqueous solutions of various
metal salts. The wavelength of the emission maximum \(\ell_\text{max}\) of each
observed spectrum was simply determined by reading the maximum
value of the emission band. The luminescence quantum yield was
recorded on a Hamamatsu Photonics C9290-02 absolute photo-
luminescence quantum yield measurement system equipped with an
integrating sphere apparatus and 150 W CW xenon light source.
Excitation and emission spectra in the near-infrared (NIR) region were
measured using a Horiba FluoroLog spectrometer.

**UV–Vis Absorption Measurements.** The UV–vis absorption
spectra were recorded on a Shimadzu UV-2400PC spectrophotometer.
The diffuse reflectance spectra were recorded on the same
spectrophotometer equipped with an integrating sphere apparatus.
The obtained reflectance spectra were converted to absorption spectra
using the Kubelka–Munk function \(F(R_\infty)\).

**Ionic Conductivity Measurements.** Impedance measurements
were performed at relative humidities (RH) of 40–90% at 298 K using
a Solartron 1260 impedance/gain-phase analyzer and a Solartron 1296
dielectric interface (Solartron Co., Ltd.) equipped with an SH-221
temperature–humidity controller (ESPEC Corp.). The temperature
dependence of the ionic conductivity was investigated in the
temperature range of 293–333 K. The sample was processed into
pellets of 2.5 mm diameter, and SILBEST No. 8560 porous gold paint
(Tokuriki Chemical Research Co., Ltd.) was used for the electrodes.

**Vapor Adsorption Isotherms.** The vapor adsorption isotherms
of each complex were measured using BELSORP-max vapor
adsorption isotherm measurement equipment at 298 K. All samples
were dried by heating at 120 °C under vacuum for 12 h to remove all
hydrated water molecules before each measurement.

**Thermogravimetric Analysis.** Thermogravimetric analysis (TG)
and differential thermal analysis (DTA) were performed using a
Rigaku ThermoEvo TG8120 analyzer.

**Computational Methods.** All ground state structure optimizations
were performed with the M06L\(^{30}\) functional as implemented in
the Gaussian09 program package.\(^{31}\) The SDD basis sets and the
associated effective core potentials were employed for Ru and La,
and the 6-31G(d) basis sets were used for the other atoms.\(^{32}\) The
model structures were generated starting from the X-ray structure of
La\(_7\)-Ru\(_4\). In order to avoid structural deformations of the model
complexes upon optimizations, coordinates of the La\(^{3+}\) ions were
frozen at their position in the X-ray structure. Vibrational frequency
calculations were performed to verify the optimized structures (i.e., no
imaginary frequencies). The lowest triplet excited states of the model
complexes were optimized by time-dependent density functional
theory (TDDFT). The PBE1PBE\(^{33}\) functional and the above basis sets
were employed for excited state calculations.

### RESULTS AND DISCUSSION

**Syntheses and Crystal Structures.** To investigate the effect of
replacement of the lanthanide ion of the La\(_7\)-Ru\(_4\) structure, powder X-ray diffraction (PXRD) patterns of all three
Ln₇-Ru₄ compounds were measured at room temperature (Figure 1). The observed PXRD patterns of all three Ln₇-Ru₄ compounds were almost identical with each other and qualitatively agreed with the PXRD simulation of the Ln₇-Ru₄ crystal structure, indicating that Ce₇-Ru₄ and Nd₇-Ru₄ are isomorphs of La₇-Ru₄. The refinement of the lattice constants for Ce₇-Ru₄ and Nd₇-Ru₄ based on the crystal structure of La₇-Ru₄ revealed that the lattice constants (a, c, and unit cell volume V) of these two Ln₇-Ru₄ structures were smaller than those of the La₇-Ru₄ compound, as expected from the contraction of the ionic radius of the lanthanide ion (see Table 1 and Figure S1 in the Supporting Information).

Water Vapor Adsorption Behavior. Because the Ln₇-Ru₄ PCPs (Ln = La, Ce, Nd) have similar porous structures containing a large number of water molecules and several OH⁻ anions, we measured the water vapor adsorption isotherms and PXRD patterns of Ce₇-Ru₄ and Nd₇-Ru₄ at various RH values to clarify the changes to the crystal structures induced by water vapor adsorption and desorption. Before the measurements, all three Ln₇-Ru₄ compounds were dried by heating at 120 °C under vacuum for 12 h to remove all hydrated water. As mentioned above, this drying temperature is high enough to remove all water molecules (see Figure S2 in the Supporting Information), and the chemical formulas of Ln₇-Ru₄ are C₃₆H₁₈Ru₁N₆O₁₂Ln₁.₇₅(OH)₁.₂₅ at the beginning of these measurements. Figure 2 shows the water-vapor adsorption isotherms at 298 K. All three Ln₇-Ru₄ compounds show similar adsorption behaviors. The isotherms of Ce₇-Ru₄ and Nd₇-Ru₄ are very similar to the previously reported isotherm of La₇-Ru₄, but the degree of water-vapor adsorption increased sharply up to 4 mol mol⁻¹ per [4Ru] at relative pressures lower than P/P₀ = 0.1 and increased monotonically at higher pressures. This rapid adsorption at low pressures could be due to chemisorption derived from the coordinatively unsaturated Ln³⁺ cations in the anhydrous state. In fact, the number of the coordinated water molecules in the La₇-Ru₄ structure (4.5 per [4Ru], as estimated from the crystal structure) corresponds to the observed amount of vapor uptake at P/P₀ = 0.1. This result suggests that the number of coordinatively unsaturated sites of Ln₇-Ru₄ is independent of the Ln³⁺ ion. All three Ln₇-Ru₄ PCPs adsorbed about 15–16 water molecules at a saturated vapor pressure, which agrees with hydration numbers estimated from elemental and TG-DTA analyses. In the desorption process, the adsorbed water molecules were gradually released in a hysteresis, suggesting that there are relatively strong agreements with those derived from the elemental analysis; the hydration numbers for La₇-Ru₄, Ce₇-Ru₄, and Nd₇-Ru₄ are 15.5, 16.0, and 14.5, respectively (see the Experimental Section). These results indicate that the porous Ln₇-Ru₄ structures contain OH⁻ anions and a large number of hydrate water molecules; therefore, Ce₇-Ru₄ and Nd₇-Ru₄ may exhibit ion-conducting (H⁺ or OH⁻) behavior similar to that of the La₇-Ru₄ structure.

Table 1. Lattice Constants Estimated by the WPPD Method of the PXRD Patterns of La₇-Ru₄, Ce₇-Ru₄, and Nd₇-Ru₄

<table>
<thead>
<tr>
<th></th>
<th>La₇-Ru₄</th>
<th>Ce₇-Ru₄</th>
<th>Nd₇-Ru₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>cryst syst</td>
<td>trigonal</td>
<td>trigonal</td>
<td>trigonal</td>
</tr>
<tr>
<td>space group</td>
<td>P3m1</td>
<td>P3m1</td>
<td>P3m1</td>
</tr>
<tr>
<td>a/Å</td>
<td>13.9916(8)</td>
<td>13.9343(7)</td>
<td>13.8805(5)</td>
</tr>
<tr>
<td>c/Å</td>
<td>30.685(2)</td>
<td>30.516(2)</td>
<td>30.364(1)</td>
</tr>
<tr>
<td>V/Å³</td>
<td>5202.4(7)</td>
<td>5131.4(6)</td>
<td>5066.6(4)</td>
</tr>
<tr>
<td>Rwp (%)</td>
<td>7.75</td>
<td>7.55</td>
<td>7.68</td>
</tr>
</tbody>
</table>

estimations also suggest that the pore sizes and void fractions of Ln₇-Ru₄ (Ln = Ce, Nd) are smaller than that of La₇-Ru₄ (3 × 5 Å and 25.5%, respectively). As reported previously, the trivalent La³⁺ ion and tetravalent anionic metalloligand [4Ru]⁴⁻ crystallized in a molar ratio of 7:4 in the La₇-Ru₄ structure, suggesting the presence of OH⁻ ions to maintain charge neutrality.²³ We also conducted elemental analysis for the Ce₇-Ru₄ and Nd₇-Ru₄ samples to determine if Ln₇-Ru₄ contained OH⁻ anions in the same way as La₇-Ru₄ (see the Experimental Section), and we found that the structures do not contain Cl⁻ anions. Thus, we concluded that Ce₇-Ru₄ and Nd₇-Ru₄ crystallized with OH⁻ counteranions, as in La₇-Ru₄. TG-DTA analysis was conducted to estimate the number of hydrate waters in Ln₇-Ru₄. The observed weight losses (La₇-Ru₄, 18.9%; Ce₇-Ru₄, 19.0%; Nd₇-Ru₄, 19.0%) up to 200 °C, where most of the water molecules were removed from the crystal structure, were almost same for the three complexes (see Figure S2 in the Supporting Information). These weight losses suggest that Ln₇-Ru₄ contained about 15 water molecules per [4Ru] metalloligand (calculated values: La₇-Ru₄, 19.7%; Ce₇-Ru₄, 19.7%; Nd₇-Ru₄, 19.6%). These estimates also quantitatively agree with those derived from the elemental analysis; the hydration numbers for La₇-Ru₄, Ce₇-Ru₄, and Nd₇-Ru₄ are 15.5, 16.0, and 14.5, respectively (see the Experimental Section). These results indicate that the porous Ln₇-Ru₄ structures contain OH⁻ anions and a large number of hydrate water molecules; therefore, Ce₇-Ru₄ and Nd₇-Ru₄ may exhibit ion-conducting (H⁺ or OH⁻) behavior similar to that of the La₇-Ru₄ structure.
hydrogen bonds between the adsorbed water molecules and the porous $\text{Ln}_7\text{-Ru}_4$ framework.

Powder X-ray diffraction patterns of the three $\text{Ln}_7\text{-Ru}_4$ (Ln = La, Ce, Nd) PCPs at various RHs are shown in Figure 3. We have previously reported the reversible structural transformation of the $\text{La}_7\text{-Ru}_4$. The porous structure determined by X-ray analysis was found to collapse on the removal of water by heating, but the porosity was regenerated on water readsorption at relative humidities greater than 85% RH. During readsorption, the structure passes through an intermediate phase, as shown in Figure 3, and the original porous phase is recovered at 85% RH. Interesting differences were observed on the change of the Ln$^{3+}$ cation from La$^{3+}$ to Ce$^{3+}$ or Nd$^{3+}$. Although the shape of the strongest diffraction peak arising from Ce$_7$-Ru$_4$ (at around 13°) changed when the RH rose above 43%, the observed pattern at 85% RH, where the porous La$_7$-Ru$_4$ structure was recovered, was different from the simulated pattern. In addition, the relative humidity dependence of the PXRD pattern of the Nd$_7$-Ru$_4$ was not as clear as that of the other two. Aside from the pattern at 100% RH, only a low-intensity diffraction peak observed at 13.8° shifted as the relative humidity changed. At 100% RH, the La$_7$-Ru$_4$ and Ce$_7$-Ru$_4$ PXRD patterns agreed qualitatively with the simulated patterns, indicating that the original porous structures were recovered on readsorption of water vapor.

In contrast, the Nd$_7$-Ru$_4$ pattern at 100% RH was similar to that of the simulated pattern, but several different peaks (e.g., the peak at 13°) were observed, suggesting that the original porous structure may be incompletely recovered even at 100% RH. These PXRD results clearly indicate the role of the Ln$^{3+}$ cation on the water-vapor-induced structural transformation of Ln$_7$-Ru$_4$; that is, the threshold RH to recover the porous structure of Ln$_7$-Ru$_4$ increased with decreasing ionic radius ($i$) of the Ln$^{3+}$ cation. This could be due to the presence of a 12-coordinate Ln$^{3+}$ site in the La$_7$-Ru$_4$ crystal structure. As previously reported (see Figure S3 in the Supporting Information), the La1 site, one of the cross-linking sites forming the porous coordination framework, has a 12-coordinate geometry that connects six [4Ru] metalloligands. Generally, the stability of 12-coordinate structures decreases with a decrease in the ion radius. Because the ionic radius of Ln$^{3+}$ cations decreases in the order La$^{3+} >$ Ce$^{3+} >$ Nd$^{3+}$, the stability of the porous structure supported by the 12-coordinated Ln$^{3+}$ cations should also decrease in this order.

**Ion Conductivity.** As shown in the previous section, three Ln$_7$-Ru$_4$ PCPs (Ln = La, Ce, Nd) adsorbed a large quantity of water vapor, and the water-vapor-induced structural transformation strongly depends on the cross-linking Ln$^{3+}$ ion. These results motivated us to investigate the influence of Ln$^{3+}$ cation exchange on the ion conductivity. Thus, we measured the ion conductivity at various RHs, as shown in Figure 4.

Although the conductivities of Ln$_7$-Ru$_4$ were found to be low at low RHs (ca. 10$^{-9}$ S cm$^{-1}$ at 40% RH), they increased by 2–3 orders of magnitude with increasing RH and finally reached values in the range of 10$^{-6}$–10$^{-7}$ S cm$^{-1}$ at 90% RH. Hydrogen-bonding networks, including carboxy groups and H$_2$O molecules coordinated to La$^{3+}$ ions (or OH$^-$ anions), are clearly formed in the porous channels of La$_7$-Ru$_4$ (see Figure S4 in the Supporting Information). These porous channels could be effective ion-conductive pathways. Ce$_7$-Ru$_4$ showed conductivity slightly higher than that of the other Ln$_7$-Ru$_4$ compounds. Although there is no direct evidence, this marginally higher conductivity of Ce$_7$-Ru$_4$ might be due to
the slightly higher H⁺ or OH⁻ concentration originating from the lattice defect of the tetravalent Ce⁴⁺−OH⁻ sites instead of the water-coordinated trivalent Ce³⁺−OH₂ site.

Figure 5 shows the Arrhenius plots of the ion conductivities at 40, 75, and 85% RH. All Ln₇-Ru₄ structures had relatively high activation energies at 40% RH, and the values seem to be independent of the bridging Ln³⁺ ion (La₇-Ru₄, 0.69 eV; Ce₇-Ru₄, 0.68 eV; Nd₇-Ru₄, 0.70 eV). As mentioned in the previous section, the porous structures of all three Ln₇-Ru₄ compounds collapsed at 40% RH (see Figure 3), and the hydration numbers are thought to be less than eight per [4Ru]. Thus, the high activation energies of Ln₇-Ru₄ at 40% RH result from the lack of an ion conduction pathway. Furthermore, the activation energy decreased drastically with increasing RH (see Figure S5 in the Supporting Information), and several noteworthy differences among the three Ln₇-Ru₄ structures were observed. The activation energies of the La₇-Ru₄ structure at 75 and 85% RH were almost constant (0.29 and 0.27 eV, respectively). In contrast, the activation energy of Ce₇-Ru₄ at this region decreased by ca. 20% from 0.35 eV at 75% RH to 0.28 eV at 85% RH. For Nd₇-Ru₄, at both 75 and 85% RH, an almost constant activation energy (0.40 eV) was determined, and this activation energy is larger than those of the other two PCPs. Considering that the number of hydrate water molecules in the Ln₇-Ru₄ structures are very similar at each RH (see Figure 2), a plausible reason for the different activation energies of the three Ln₇-Ru₄ could be the water-vapor-induced structural transformation, as mentioned in the previous section. Taking account of the fact that the original porous framework of La₇-Ru₄ gradually recovered at RHs greater than 54% and completely recovered above 85% RH (see Figure 3), the negligible difference in the activation energy of La₇-Ru₄ between 75 and 85% RH suggests that ion-conductive pathways are formed in the water-filled channels at 75% RH. In contrast, the smaller activation energy of Ce₇-Ru₄ at 85% RH in comparison to that at 75% RH suggests the gradual formation of ion conduction pathways in the porous coordination framework in this RH region. The same activation energy was observed for Nd₇-Ru₄ at both 75 and 85% RH, which is consistent with the negligible changes in the crystal structure, as observed in the PXRD measurements. The results concerning the activation energy of ion conduction clearly indicate that the
bridging Ln³⁺ ion plays an important role in the formation of ion-conductive pathways.

**Emission Properties.** As mentioned in the Introduction, we have previously reported the interesting ion-conduction-correlated vapochromic luminescence of La₇-Ru₄, which is triggered by the adsorption/desorption of water vapor. To investigate the influence of the replacement of the lanthanide ion on the vapochromic luminescence, the emission spectra of Ce₇-Ru₄ at different RHs at room temperature were measured. As shown in Figure 6a, as-synthesized Ce₇-Ru₄ exhibits a broad dark red emission with an emission maximum at 684 nm without any vibronic progression. In contrast, the dried sample exhibits the red-shifted emission centered at 705 nm. When the relative humidity was increased from 11 to 100%, the wavelength of the emission maximum remained almost unchanged up to 85% RH (Figure 6b). At 100% RH, an emission spectrum very similar to that of the as-synthesized compound was observed. This result is consistent with the water-vapor-induced structural transformation discussed in Water-Vapor Adsorption Behavior. That is, as discussed in our previous paper concerning La₇-Ru₄, the porous structure collapsed on the removal of hydrate water molecules, resulting in a higher density of Ln³⁺ cations around the [4Ru] metalloligands. This dense packing around the [4Ru] metallobands by the positively charged Ln³⁺ ions may electrostatically affect the energy of the π° orbital of the 4,4'-dcbpy ligand or the vibronic states of the photoexcited state, resulting in a lower emission energy in the dried state. Unfortunately, the emission intensity of the 4f−4f transitions of the Nd³⁺ ion may originate from energy transfer from the 1MLCT excited state of [4Ru] to the 4f−4f transition state of the Nd³⁺ ions. Our preliminary results on the La₇³⁺ and Nd³⁺ mixed PCP La₃Nd₄-Ru₄ (equimolar amounts of LaCl₃·7H₂O and NdCl₃·6H₂O were used in the synthesis), which exhibited both 1MLCT emission of [4Ru] and 4f−4f emission of Nd³⁺ (see Figure S7 in the Supporting Information), suggests that the energy transfer efficiency is not so high. Unfortunately, the emission intensity of the 4f−4f emission of the Nd³⁺ center of Nd₇-Ru₄ in the NIR region was weak, preventing further investigation of its RH dependence. The reason for this may be the presence of a large number of hydrate water molecules in the porous channels and OH⁻ anions in the porous frameworks that deactivate the 4f−4f transition states via O−H vibrations.

### CONCLUSION

We synthesized two luminescent PCPs, {Ln₃(OH)₃[Ru(dcbpy)₃]₄·4nH₂O} (Ln₆-Ru₄; Ln = Ce, Nd), that are the Ln³⁺-cation substituted analogues of our previously reported PCP La₇-Ru₄. All three Ln₆-Ru₄ compounds have almost identical porous structures and adsorb about 15–16 water molecules per [4Ru] metallogand at 100% RH. The porous structure of all three Ln₆-Ru₄ compounds collapsed on the removal of hydrate water molecules, but this could be regenerated on readsoption of water. Interestingly, the threshold RH to regenerate the original porous structure strongly depends on the bridging metal ions, suggesting the importance of the stability of the 12-coordinate structure of the Ln³⁺ ion. This Ln³⁺ ion dependent behavior was also observed in the ion conduction and luminescence properties; all three Ln₆-Ru₄ compounds have ion conductivities of around 10⁻⁶−⁻⁷ S cm⁻¹ at 90% RH, but the activation energy was reduced on the regeneration of the porous framework. These results clearly indicate that the bridging Ln³⁺ ion plays an important role in the formation of the ion-conductive pathway. Similarly, the vapochromic luminescence behavior of Ce₇-Ru₄ was observed at an RH region higher than that of La₇-Ru₄. In addition, our computational results suggest that the number of

**Figure 7.** (a) NIR luminescence spectra (λₑ = 420 nm) of Nd₇-Ru₄ in the solid state at room temperature. (b) Excitation spectra (λₑ = 1054 nm, blue) and diffuse reflectance spectra (black) of Nd₇-Ru₄ in the solid state at room temperature.
H$_2$O molecules in the La$^{3+}$ coordination sphere affect the emission that originates from the MLCT of $[4Ru]$. In contrast, Nd$^{3+}$-Ru$_4$ barely exhibited the $[4Ru]$ MLCT emission. Instead, the sharp emission bands characteristic of 4f$\rightarrow$4f transitions were clearly detected in the NIR region, suggesting energy transfer from the $[4Ru]$ MLCT excited state to the 4f$\rightarrow$4f transition states of the Nd$^{3+}$ ions. Our work on this system interferes with the emission properties of the luminophore.

### REFERENCES


