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Lanthanide-Containing Polyoxometalate Crystallized with Bolaamphiphile Surfactants as Inorganic–Organic Hybrid Phosphors

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Abstract: Lanthanide elements such as europium exhibit distinctive emissions due to the transitions of inner-shell 4f electrons. Inorganic materials containing lanthanide elements have been widely used as phosphors in conventional displays. The hybridization of lanthanide ions with organic components enables to control of the material’s shapes and properties and broadens the possibility of lanthanide compounds as inorganic–organic materials. Lanthanide ion-containing polyoxometalate anions (Ln-POM) are a promising category as an inorganic component to design and synthesize inorganic–organic hybrids. Several inorganic–organic Ln-POM systems have been reported by hybridizing with cationic surfactants as luminescent materials. However, single-crystalline ordering has not been achieved in most cases. Here, we report syntheses and structures of inorganic–organic hybrid crystals of lanthanide-based POM and bolaamphiphile surfactants with two hydrophilic heads in one molecule. An emissive decatungstoeuropate ([EuW10O36]9−, EuW10) anion was employed as a lanthanide source. The bolaamphiphile counterparts are 1,8-octamethylenediammonium ([H3N(CH2)8NH3]+, C8N2) and 1,10-decamethylenediammonium ([H3N(CH2)10NH3]+, C10N2). Both hybrid crystals of C8N2-EuW10 and C10N2-EuW10 were successfully obtained as single crystals, and their crystal structures were unambiguously determined using X-ray diffraction measurements. The photoluminescence properties of C8N2-EuW10 and C10N2-EuW10 were investigated by means of steady-state and time-resolved spectroscopy. The characteristic emission derived from the EuW10 anion was retained after the hybridization process.

Keywords: polyoxometalate; surfactant; single crystal; inorganic–organic hybrid; photoluminescence

1. Introduction

Lanthanide elements can attribute several functions to materials, which have been applied to ionic conductors [1], magnetic materials [2], and biological reagents [3]. One of the most distinctive characteristics are emission properties [4]. Some lanthanides such as europium and terbium exhibit distinctive emission due to the transitions of inner-shell 4f electrons. Inorganic lanthanide compounds have been widely employed as phosphors in conventional displays and imaging technologies. The combination of lanthanide ions with organic moiety enables to control of the material’s shapes and properties and broadens the application areas of lanthanide compounds as inorganic–organic hybrid luminescent materials [5–9].

As for the lanthanide source, lanthanide-containing polyoxometalate (Ln-POM) anions are promising inorganic components [10–13]. Various types of Ln-POM anions have been
synthesized as single crystals under ambient and/or hydrothermal conditions [14–17]. Hybridizing Ln-POM with organic moieties achieves controllable inorganic—organic hybrid materials in their luminescent properties and material shapes [18–21]. Decatungstoeuropate ([EuW\textsubscript{10}O\textsubscript{36}]\textsuperscript{9−}, EuW\textsubscript{10}, Figure 1a) anion exhibits strong emission at room temperature with a decay time of millisecond order [22–25], and is often utilized to build up luminescent hybrid materials [18,19]. The EuW\textsubscript{10} anion has two W\textsubscript{5}O\textsubscript{18}\textsuperscript{6−} ligands that absorb ultraviolet (UV) light by O → W ligand-to-metal charge-transfer (LMCT). The intramolecular energy transfer from the LMCT state of W\textsubscript{5}O\textsubscript{18}\textsuperscript{6−} ligands to the \(5D_0\) state of Eu\textsuperscript{3+} causes distinct orange-red light emission.

![Figure 1](image)

**Figure 1.** (a) Molecular structure of decatungstoeuropate anion, \([\text{EuW}_{10}\text{O}_{36}]^{9−}\) (EuW\textsubscript{10}). Each polyhedron represents a WO\textsubscript{6} unit, and the red sphere represents a Eu\textsuperscript{3+} ion. (b) Molecular structure of bolaamphiphiles utilized in this work. Upper: 1,8-octamethylene diammonium, [H\textsubscript{3}N(CH\textsubscript{2})\textsubscript{8}NH\textsubscript{3}]\textsuperscript{2+} (C\textsubscript{8}N\textsubscript{2}); bottom: 1,10-decamethylene diammonium, [H\textsubscript{3}N(CH\textsubscript{2})\textsubscript{10}NH\textsubscript{3}]\textsuperscript{2+} (C\textsubscript{10}N\textsubscript{2}).

Cationic surfactants and polymer matrices as well as neutral block copolymers effectively hybridized with the EuW\textsubscript{10} anion to obtain luminescent nanocomposites [26–29], thin films [30–37], and sensors [38–41]. These systems are functional as soft matter and compatible with living organisms. However, single-crystalline ordering has not been achieved in most cases, which can be a drawback with the use as solid-state materials. The surfactant molecules are also effective as structure-directing reagents to construct one-dimensional tunnel and two-dimensional layer structures. Additionally, the EuW\textsubscript{10} anion has rarely been crystallized with organic cations [42] and organic moieties [43,44].

Here, we report syntheses and structures of inorganic–organic hybrid crystals of the luminescent EuW\textsubscript{10} anion and cationic bolaamphiphile surfactants, which have two hydrophilic heads in one molecule. The bolaamphiphile counterparts employed are 1,8-octamethylene diammonium ([H\textsubscript{3}N(CH\textsubscript{2})\textsubscript{8}NH\textsubscript{3}]\textsuperscript{2+}, C\textsubscript{8}N\textsubscript{2}) and 1,10-decamethylene diammonium ([H\textsubscript{3}N(CH\textsubscript{2})\textsubscript{10}NH\textsubscript{3}]\textsuperscript{2+}, C\textsubscript{10}N\textsubscript{2}), as shown in Figure 1b. Both hybrid crystals of C\textsubscript{8}N\textsubscript{2}-EuW\textsubscript{10} and C\textsubscript{10}N\textsubscript{2}-EuW\textsubscript{10} were successfully obtained as single crystals, and their crystal structures were unambiguously determined using X-ray diffraction measurements. The photoluminescence properties were evaluated by means of steady-state and time-resolved spectroscopy.

2. Results

2.1. Synthesis of EuW\textsubscript{10}-Bolaamphiphile Hybrid Crystals

C\textsubscript{8}N\textsubscript{2}-EuW\textsubscript{10} and C\textsubscript{10}N\textsubscript{2}-EuW\textsubscript{10} hybrid crystals were synthesized via ion-exchange reactions using sodium salt of EuW\textsubscript{10} (Na-EuW\textsubscript{10}) and bolaamphiphile cations. The as-prepared precipitate of C\textsubscript{8}N\textsubscript{2}-EuW\textsubscript{10} was obtained in 15–20% yield, and the as-prepared precipitate of C\textsubscript{10}N\textsubscript{2}-EuW\textsubscript{10} was obtained in 40–50% yield. In each case, single crystals were successfully isolated from the synthetic filtrate after the removal of the as-prepared precipitate of C\textsubscript{8}N\textsubscript{2}-EuW\textsubscript{10} or C\textsubscript{10}N\textsubscript{2}-EuW\textsubscript{10}. The yields of isolated single crystals were ca. 50% for C\textsubscript{8}N\textsubscript{2}-EuW\textsubscript{10}, and ca. 30% for C\textsubscript{10}N\textsubscript{2}-EuW\textsubscript{10}. Figure 2 shows IR spectra of the as-prepared precipitates and single crystals of C\textsubscript{8}N\textsubscript{2}-EuW\textsubscript{10} and C\textsubscript{10}N\textsubscript{2}-EuW\textsubscript{10}. The spectra
of $\text{C}_8\text{N}_2\text{-EuW}_{10}$ (Figure 2b,c) showed characteristic peaks of the EuW$_{10}$ anion in the range of 400–1000 cm$^{-1}$ ($\nu_{as}(W=O_t)$), 820–850 cm$^{-1}$ [$\nu_{as}(W-O_b-W)$], 700–710 cm$^{-1}$ [$\nu_{as}(W-O_c-W)$] [45]. The peaks in the range of 2800–3000 cm$^{-1}$ were derived from the $\text{C}_8\text{N}_2$ cation (2920 cm$^{-1}$ [$\nu_{as}(-\text{CH}_2-)$], 2850 cm$^{-1}$ [$\nu_s(-\text{CH}_2-)$]), which indicates the successful hybridization of the EuW$_{10}$ anion and $\text{C}_8\text{N}_2$ cation. The IR spectra of the $\text{C}_8\text{N}_2\text{-EuW}_{10}$ as-prepared precipitate (Figure 3a) and single crystal (Figure 3e) were both similar to the calculated pattern.

**Figure 2.** IR spectra of EuW$_{10}$ and bolaamphiphile hybrid crystals: (a) starting material of Na-EuW$_{10}$; (b) as-prepared precipitate of $\text{C}_8\text{N}_2\text{-EuW}_{10}$; (c) single crystal of $\text{C}_8\text{N}_2\text{-EuW}_{10}$; (d) as-prepared precipitate of $\text{C}_{10}\text{N}_2\text{-EuW}_{10}$; and (e) single crystal of $\text{C}_{10}\text{N}_2\text{-EuW}_{10}$.

Figure 3 demonstrates powder XRD patterns of the $\text{C}_8\text{N}_2\text{-EuW}_{10}$ and $\text{C}_{10}\text{N}_2\text{-EuW}_{10}$ hybrid crystals. The XRD patterns of the $\text{C}_8\text{N}_2\text{-EuW}_{10}$ as-prepared precipitate (Figure 3a) were crystalline, but slightly different from those of the $\text{C}_8\text{N}_2\text{-EuW}_{10}$ single crystal (Figure 3b), and calculated from the results using single-crystal X-ray diffraction (Figure 3c). Slight differences in the peak position and intensity of the patterns may be derived from the desolvation of water molecules of crystallization (see below). The XRD pattern of the $\text{C}_8\text{N}_2\text{-EuW}_{10}$ single crystal was similar to that calculated from results using single-crystal X-ray diffraction (Figure 3c). The XRD patterns of the $\text{C}_{10}\text{N}_2\text{-EuW}_{10}$ as-prepared precipitate (Figure 3d) and single crystals (Figure 3e) were both similar to the calculated pattern from the results using single-crystal X-ray diffraction (Figure 3f). The results of IR spectra and powder XRD patterns indicate that both $\text{C}_8\text{N}_2\text{-EuW}_{10}$ and $\text{C}_{10}\text{N}_2\text{-EuW}_{10}$ hybrid crystals were obtained in a single phase and that the as-prepared precipitate and single crystal were essentially the same in their molecular and crystal structures.
The crystal packing of C₈N₂-EuW₁₀ was a layer structure viewed along the b-axis (Figure 4a, left). The layer structure consisted of EuW₁₀ inorganic layers and C₈N₂ organic layers parallel to the ab plane with a periodicity of 15.5 Å. The crystal packing viewed along the a-axis exhibited a honeycomb-like feature (Figure 4a, right). The EuW₁₀ anions interacted with each other to form a one-dimensional chain structure (Figure 4b). The O···O distances were 2.73 Å (O12···O21) and 2.92 Å (O26···O28). As the BVS calculation suggested, the associated H⁺ was located onto O21, and the short contact of O12···O21 (2.73 Å) was due to O–H···O hydrogen bonding [47]. Some water molecules (O37, O40, O43, and O44) were located inside the inorganic EuW₁₀ layer. These water molecules and EuW₁₀ anions formed a two-dimensional network (EuW₁₀-H₂O layer) through O–H···O hydrogen bonding with O···O distance ranging from 2.67 to 2.94 Å (mean value: 2.81 Å).
Some hydrophilic heads of C₈N₂ penetrated the EuW₁₀-H₂O layers with the N–H···O hydrogen bonding with distances of 2.71–3.04 Å (mean value: 2.85 Å) [47].

Table 1. Crystallographic data.

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Figure 4. Crystal structure of C₈N₂-EuW₁₀ (Eu: pink; C: gray; N: blue; O: red). WO₆ units in EuW₁₀ are depicted in the polyhedral model. H atoms are omitted for clarity. (a) Packing diagram along b-axis (left) and a-axis (right). Solvent atoms are omitted for clarity. (b) One-dimensional arrangement
of EuW\textsubscript{10} anions. Broken lines represent short contacts between EuW\textsubscript{10} anions. Symmetry codes: (i) 2 – \(x\), –0.5 + \(y\), 0.5 – \(z\); (ii) 2 – \(x\), 0.5 + \(y\), 0.5 – \(z\). (c) Molecular arrangement of the inorganic monolayer (ab plane). Broken lines represent short contacts between EuW\textsubscript{10} anions and solvents.

The chemical formula of C\textsubscript{10}N\textsubscript{2}-EuW\textsubscript{10} was determined to be [H\textsubscript{3}N(CH\textsubscript{2})\textsubscript{10}NH\textsubscript{3}]\textsubscript{3.5}H\textsubscript{2} [EuW\textsubscript{10}O\textsubscript{36}].6.5H\textsubscript{2}O. Three and a half C\textsubscript{10}N\textsubscript{2} cations (2+ charge) and two H\textsuperscript{+} (1+ charge) were connected to one EuW\textsubscript{10} anion (9− charge) with four water molecules of crystallization (Figure 5). No residual Na\textsuperscript{+} was observed using EDS analysis. As shown in the asymmetric unit (Figure S2), a half C\textsubscript{10}N\textsubscript{2} cation (containing N7) was onto the inversion center with anti-conformation. Other C\textsubscript{10}N\textsubscript{2} cations were bent with gauche conformation, and two C\textsubscript{10}N\textsubscript{2} cations (with N3 and N4A, N4B; with N5 and N6A, N6B) were disordered with site occupancies of 0.558 and 0.442. Four water molecules were crystallographically assigned (Figure S2), while the presence of six and a half molecules per EuW\textsubscript{10} anion was suggested by the thermal gravimetric (TG) analyses (Figure S3). The associated H\textsuperscript{+} was not detected using X-ray diffraction. The BVS value of O22 was 1.04 and seemed to be protonated (the BVS values of other O atoms: 1.59–1.96). The second H\textsuperscript{+} was not revealed in its position but may be located in the vicinity of O18 (BVS value: 1.60) or O19 (BVS value: 1.59). The coordination environment was similar to those of C\textsubscript{8}N\textsubscript{2}-EuW\textsubscript{10} and Na-W\textsubscript{10} [25]: Eu–O distances of 2.43–2.47 Å (mean value: 2.45 Å) and the shortest Eu⋯Eu distance of 10.50 Å.

Figure 5. Crystal structure of C\textsubscript{10}N\textsubscript{2}-EuW\textsubscript{10} (Eu: pink; C: gray; N: blue; O: red). WO\textsubscript{6} units in EuW\textsubscript{10} are depicted in the polyhedral model. H atoms and disordered parts are omitted for clarity. (a) Packing diagram along the b-axis (left) and a-axis (right). Solvent atoms are omitted for clarity. (b) One-dimensional arrangement of EuW\textsubscript{10} anions. Broken lines represent short contacts between EuW\textsubscript{10} anions. Symmetry codes: (i) 1 – \(x\), –0.5 + \(y\), 1.5 – \(z\); (ii) 1 – \(x\), 0.5 + \(y\), 1.5 – \(z\). (c) Molecular arrangement of the inorganic monolayer (ab plane). Broken lines represent short contacts between EuW\textsubscript{10} anions and solvents.

The crystal packing of C\textsubscript{10}N\textsubscript{2}-EuW\textsubscript{10} viewed along the b-axis was a layer structure composed of EuW\textsubscript{10} inorganic layers and C\textsubscript{10}N\textsubscript{2} organic layers parallel to the ab
plane (Figure 5a, left). The layered distance was 15.8 Å. As viewed along the a-axis (Figure 5a, right), the crystal packing was a honeycomb-like structure. The EuW$_{10}$ anions formed a one-dimensional infinite chain (Figure 5b) by short contacts between O6 and O22 with an O···O distance of 2.71 Å. This short contact will be due to the O–H···O hydrogen bonding [47], since O22 is the plausibly protonated O atom by the BVS calculation. The crystallographically assigned water molecules were located inside the inorganic EuW$_{10}$ layer to form a two-dimensional network with the EuW$_{10}$ anions (EuW$_{10}$-H$_2$O layer) through the O–H···O hydrogen bonds (O···O distance: 2.72–3.04 Å; mean value: 2.88 Å) (Figure 5c). Some hydrophilic heads of C$_{10}$N$_2$ were located in the EuW$_{10}$-H$_2$O layers with N–H···O hydrogen bonds (N···O distance: 2.66–3.04 Å; mean value: 2.83 Å) [47].

2.3. Photoluminescent Properties of EuW$_{10}$-Bolaamphiphile Hybrid Crystals

The hybrid crystals of C$_8$N$_2$-EuW$_{10}$ and C$_{10}$N$_2$-EuW$_{10}$ exhibited distinct photoluminescence derived from the EuW$_{10}$ anion. Figure 6 shows steady-state spectra of C$_8$N$_2$-EuW$_{10}$ and C$_{10}$N$_2$-EuW$_{10}$. Diffuse reflectance spectra (Figure 6a) showed absorptions around 395 nm and 465 nm, which were assigned as f-f transitions of Eu$^{3+}$: 395 nm for $^7$F$_0$ → $^5$L$_{6}$ transition, and 465 nm for $^7$F$_0$ → $^5$D$_2$ transition [14,15]. Each excitation spectrum (Figure 6b) exhibited a broad peak around 200–340 nm owing to the excitation into the O → W LMCT band in the W$_8$O$_{18}$ $^{6-}$ ligands. The f-f transitions mentioned above were also observed in the excitation spectra. In the emission spectra, distinct peaks due to $^5$D$_0$ → $^7$F$_j$ ($j = 0, 1, 2, 3, 4$) transition of Eu$^{3+}$ were observed around 580–710 nm (Figure 5c) [22–25].

![Figure 6](image_url)

**Figure 6.** Steady-state spectra of C$_8$N$_2$-EuW$_{10}$ and C$_{10}$N$_2$-EuW$_{10}$. The measurement temperature was 300 K: (a) diffuse reflectance spectra; (b) excitation spectra monitored on the emission at 595 nm; (c) emission spectra were measured with an excitation wavelength of 265 nm.

The photoluminescent properties of the C$_8$N$_2$-EuW$_{10}$ and C$_{10}$N$_2$-EuW$_{10}$ hybrid crystals were evaluated by means of time-resolved spectroscopy. The emission spectra acquired using a single pulse excitation (Figure 7a,b) exhibited characteristic emission derived from the EuW$_{10}$ [22–25]. Emission peaks at 575 nm are assigned to $^5$D$_0$ → $^7$F$_3$ transition, and peaks at 611 and 618 nm to $^5$D$_0$ → $^7$D$_2$ transition. The peaks around 650 nm are assignable to $^5$D$_0$ → $^7$F$_3$ transition, and peaks at 691 and 700 nm to $^5$D$_0$ → $^7$F$_4$ transition. The spectrum profiles of C$_8$N$_2$-EuW$_{10}$ and C$_{10}$N$_2$-EuW$_{10}$ were almost the same irrespective of the measurement temperatures. However, the emission decay
profiles of C_{8}N_{2}-EuW_{10} and C_{10}N_{2}-EuW_{10} were different. The emission decay profiles of C_{8}N_{2}-EuW_{10} were approximated with two exponential functions (red plots in Figure 7c,d). The emission lifetimes at 28.5 ± 0.1 ms at 15 K and 31.0 ± 0.1 ms at 300 K (Table 2). In the case of C_{10}N_{2}-EuW_{10}, the emission decay profiles were approximated with two exponential functions (red plots in Figure 7c,d). The emission lifetimes at 15 K were estimated to be 1.1 ± 0.1 ms for a slower decay component and 3.1 ± 0.1 ms for a faster decay component (Table 2). The emission lifetimes at 300 K were 1.1 ± 0.1 ms and 1.8 ± 0.1 for a faster and slower component, respectively. The emission decay lifetimes of C_{8}N_{2}-EuW_{10} and C_{10}N_{2}-EuW_{10} at 15 K were comparable to that of Na-EuW_{10} [25,33] but became shorter at 300 K. The increase in the number of carbon atoms in the bolaamphiphile cation resulted in a shorter emission lifetime at 300 K of C_{10}N_{2}-EuW_{10} [33].

Figure 7. Photoluminescence properties of C_{8}N_{2}-EuW_{10} and C_{10}N_{2}-EuW_{10} investigated using time-resolved spectroscopy. Each spectrum or decay profile was obtained by a single pulse excitation with a wavelength of 266 nm. Emission spectra were acquired 50–100 μs after the excitation. Emission decays were monitored at the emission at 593 nm: (a) emission spectra measured at 15 K; (b) emission spectra measured at 300 K; (c) emission decay profiles measured at 15 K; (d) emission decay profiles measured at 300 K.

Table 2. Emission lifetimes (τ/ms) of C_{8}N_{2}-EuW_{10} and C_{10}N_{2}-EuW_{10}.

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<th>Compound</th>
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<td>C_{8}N_{2}-EuW_{10}</td>
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<tr>
<td>C_{10}N_{2}-EuW_{10}</td>
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<td>Na-EuW_{10}</td>
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1 Two exponential decays were applied. 2 The decay time at 4.2 K. Taken from Ref. [25] as a comparison. 3 The value at r.t. taken from Ref. [33].

As for the preparation of inorganic–organic luminescent materials, the lasing property is a promising character to be tackled in several applications. As shown in Figure 8, the emission intensity of C_{8}N_{2}-EuW_{10} and C_{10}N_{2}-EuW_{10} depended on the excitation laser power. After the threshold value of the excitation laser power, the emission intensity increased linearly, indicating the emergence of the lasing property [48]. The threshold values at 15 K were 28.5 and 25.4 mJ cm^{-2} for C_{8}N_{2}-EuW_{10} and C_{10}N_{2}-EuW_{10}, respectively. The threshold values at 300 K were 26.0 and 25.2 mJ cm^{-2} for C_{8}N_{2}-EuW_{10} and C_{10}N_{2}-EuW_{10}, respectively. These threshold values will be essentially in the same order.
Figure 8. Emission intensity–excitation laser power dependency of C8N2-EuW10 and C10N2-EuW10 at (a) 15 K and (b) 300 K. Each data point was obtained by a single pulse excitation with a wavelength of 266 nm on the emission at 593 nm. Data acquisition time: 50–100 μs after the excitation.

3. Discussion

Lanthanide-containing polyoxometalate (Ln-POM) single crystals hybridized with surfactant molecules were first obtained in this work. Using bolaamphiphile surfactants was critical for the crystallization of the Ln-POM hybrid crystals. Bolaamphiphiles have two hydrophilic heads [49,50]. Hybrid crystals of POM with bolaamphiphiles have higher solubility in conventional solvents, and it is rather easier to isolate single crystals [51,52]. The size of the hydrophilic heads of C8N2 and C10N2 are smaller than those of quaternary alkylammonium cations, which may be another reason for the successful isolation of single crystals of C8N2-EuW10 and C10N2-EuW10. The effect of surfactant length on luminescent properties will be an interesting topic; however, preparing single crystals with longer surfactants may be difficult.

The powder XRD patterns of the as-prepared precipitate (Figure 3a) and single crystal (Figure 3b) of the C8N2-EuW10 hybrid crystal were slightly different. On the other hand, the essential feature of the XRD patterns of as-prepared precipitate (Figure 3a) is similar to that calculated from the single-crystal structure of C8N2-EuW10 (Figure 3c). The as-prepared precipitate and single crystal of C8N2-EuW10 is considered to be the same phase. The differences in the peak position and intensity of the patterns will be derived from the desolvation of water molecules of crystallization, the different measurement temperatures (powder: room temperature; single crystal: 93 K), and the preferred orientation derived from the layered structure of C8N2-EuW10. In the case of C10N2-EuW10, the XRD patterns of the as-prepared precipitate (Figure 3d) and single crystal (Figure 3e) were quite similar. The water molecules in the C10N2-EuW10 hybrid crystal were located inside the inorganic layers of EuW10 with short-contact interaction, and plausibly less easily desorbed from the crystal lattice. TG analyses indicated the stability of C8N2-EuW10 and C10N2-EuW10 until 180–200 °C (Figure S3).

The structures of C8N2-EuW10 and C10N2-EuW10 hybrid crystals were unambiguously revealed by means of single-crystal X-ray diffraction measurements. In summary, the crystal structures were similar concerning the cell parameters (Table 1) and packing features (Figures 4 and 5). The crystal structures of C8N2-EuW10 and C10N2-EuW10 were layer structures viewed along the b-axis, and a honeycomb-like feature viewed along the a-axis. Such structural features are observed for some POM-surfactant crystals [52,53]. The packing features of EuW10 in C8N2-EuW10 and C10N2-EuW10 were almost the same, while the number of bolaamphiphile cations and their conformations were different. In both hybrid crystals, the EuW10 anions formed one-dimensional chain structures. The residual H⁺ was relevant to the formation of the one-dimensional chain structure. These one-dimensional chains of EuW10 together with water molecules formed two-dimensional networks of EuW10-H2O parallel to the ab plane (Figures 4c and 5c).
The photoluminescence spectroscopy of C$_8$N$_2$-EuW$_{10}$ and C$_{10}$N$_2$-EuW$_{10}$ revealed the emission properties of C$_8$N$_2$-EuW$_{10}$ and C$_{10}$N$_2$-EuW$_{10}$. The photoluminescence of the EuW$_{10}$ anion was essentially retained: characteristic emission derived from Eu$^{3+}$ (Figures 6 and 7) and an emission lifetime of millisecond order (Table 2). The hybridization of EuW$_{10}$ with organic moieties sometimes shortens the emission lifetime (<1 ms) [33,54]; however, primary ammonium cation can retain the emission lifetime of millisecond order [31]. The primary ammonium cation can form N–H···O hydrogen bonds between the EuW$_{10}$ anion to prevent water molecules from approaching near Eu$^{3+}$. The excitation energy owing to O → W LMCT can transfer to Eu$^{3+}$ without nonradiative deactivation through the vibration states of the high-frequency O–H oscillators of water molecules [55,56]. The EuW$_{10}$ anion has no coordinated water and therefore a long emission decay time (3.5 ms at 4.2 K) and high quantum yield (0.99) for Na-EuW$_{10}$ at 4.2 K [25]. As shown in Table 2, the emission decay time of C$_8$N$_2$-EuW$_{10}$ (3.0 ± 0.1 ms) and C$_{10}$N$_2$-EuW$_{10}$ (3.1 ± 0.1 ms for a slower component) at 15 K were comparable to that of Na-EuW$_{10}$ (3.5 ms) at 4.2 K. This implies that the emission behavior of C$_8$N$_2$-EuW$_{10}$ and C$_{10}$N$_2$-EuW$_{10}$ was almost identical to that of Na-EuW$_{10}$ derived from the suppression of the thermal deactivation of the excitation energy at the low temperature. At the high temperature (300 K), the emission decay time of C$_8$N$_2$-EuW$_{10}$ (2.5 ± 0.1 ms) was similar to that of Na-EuW$_{10}$ (2.6 ms), but C$_{10}$N$_2$-EuW$_{10}$ exhibited the faster decay time of 1.8 ± 0.1 ms. This will be due to more carbon atoms in the crystal lattice [33] and fewer N–H···O hydrogen bonds between EuW$_{10}$ and surfactant cations. The kinetic constants of energy transfer can be estimated using the magnetic-dipole $^5$D$_0$ → $^7$F$_1$ transition as a standard [56], since the rate of $^5$D$_0$ → $^7$F$_1$ (1.35 × 10$^{22}$ s$^{-1}$) is almost independent of the geometry of Eu$^{3+}$. The relative intensity of $^5$D$_0$ → $^7$F$_1$ emission to the total emission ($^5$D$_0$ → $^7$F$_n$, n = 0–4) at 300 K was 0.38 for C$_8$N$_2$-EuW$_{10}$ and 0.41 for C$_{10}$N$_2$-EuW$_{10}$, respectively. Therefore, for C$_8$N$_2$-EuW$_{10}$, the radiative rate ($k_{\text{rad}}$) was 3.6 × 10$^2$ (=1.35 × 10$^{22}$/0.36) s$^{-1}$ and the experimental decay rate was (4.0 ± 0.2) × 10$^2$ (=1/((2.5 ± 0.1) × 10$^{-3}$)) s$^{-1}$, and then the estimated nonradiative rate ($k_{\text{nr}}$) was (0.4 ± 0.2) × 10$^2$ (=4.0 ± 0.2 × 10$^{-2}$ – 3.6 × 10$^2$) s$^{-1}$. For C$_{10}$N$_2$-EuW$_{10}$, the respective values of radiative rate ($k_{\text{rad}}$) and experimental decay rate were 3.3 × 10$^2$ (=1.35 × 10$^{22}$/0.41) s$^{-1}$ and (5.6 ± 0.3) × 10$^2$ (=1/((1.9 ± 0.1) × 10$^{-3}$)) s$^{-1}$, and the estimated nonradiative rate ($k_{\text{nr}}$) was (2.3 ± 0.3) × 10$^2$ (=5.6 ± 0.3 × 10$^{-2}$ – 3.3 × 10$^2$) s$^{-1}$. The reason for the presence of fast decay components in the C$_{10}$N$_2$-EuW$_{10}$ emission (Table 2) was unclear but may be derived from the presence of more H$^+$ in the crystal lattice. In addition, both C$_8$N$_2$-EuW$_{10}$ and C$_{10}$N$_2$-EuW$_{10}$ hybrid crystals exhibited lasing properties (Figure 8). The threshold values (25–28 mJ cm$^{-2}$) were larger than those of recent organic lasers [57,58]. Although further improvement in materials processing will be necessary, the photoluminescence properties of C$_8$N$_2$-EuW$_{10}$ and C$_{10}$N$_2$-EuW$_{10}$ mentioned above show the possibility of a new series of inorganic–organic hybrid phosphors.

4. Materials and Methods

4.1. Materials

Chemical reagents purchased from commercial sources (FUJIFILM Wako Pure Chemical Corporation, Osaka, Japan, Tokyo; and Kanto Chemical Co., Inc., Tokyo, Japan) were utilized without further purification. Solid 1,8-octamethylenediammonium chloride ([H$_3$N(CH$_2$)$_8$NH$_3$]Cl$_2$, C$_8$N$_2$-Cl) and 1,10-decamethylenediammonium chloride ([H$_3$N(CH$_2$)$_{10}$NH$_3$]Cl$_2$, C$_{10}$N$_2$-Cl) were prepared by adding equimolar hydrochloric acid to 1,8-octanediamine and 1,10-decanediamine, respectively. The sodium salt of EuW$_{10}$ (Na$_6$[EuW$_{10}$O$_{36}$]·32H$_2$O, Na-EuW$_{10}$) was prepared according to the literature [25].

4.2. Measurements

Infrared (IR) spectra were recorded with an FT/IR-4200ST spectrometer (Jasco Corporation, Tokyo, Japan, KBr pellet method). Powder X-ray diffraction (XRD) patterns were measured on a MiniFlex300 diffractometer (Rigaku Corporation, Tokyo, Japan, Cu K$_\alpha$
radiation, $\lambda = 1.54056 \text{ Å}$. CHN (carbon, hydrogen, and nitrogen) elemental analyses were performed with a 240II elemental analyzer (PerkinElmer, Inc., Waltham, MA, USA). Energy dispersive X-ray (EDS) spectroscopy was performed on a JSM-6000Plus (JEOL, Tokyo, Japan). Thermal gravimetric (TG) analyses were measured with a TG/DTA-6200 (Seiko Instruments, Chiba, Japan) at a heating rate of 10 °C min$^{-1}$ under a nitrogen atmosphere.

Steady-state spectra (diffuse-reflectance, excitation, and emission) were obtained at 300 K on an FP-6500 fluorescence spectrometer (Jasco Corporation, Tokyo, Japan) using Xe lamp excitation. Time-resolved emission spectra were acquired at 15 and 300 K, using an Ultra CFR 400 YAG:Nd$^{3+}$ laser (Big Sky Laser Technologies, Inc., Bozeman, MT, USA, 266 nm fourth harmonics, pulse duration 10 ns with a repetition rate of 10 Hz) as an excitation source. A Spectra Pro 2300i and PI-Max intensified CCD camera (Princeton Instruments, Inc., Trenton, NJ, USA) were employed as a spectrometer and a detector, respectively. Pelletized samples of the as-prepared precipitate of C$_8$N$_2$-EuW$_{10}$ and C$_{10}$N$_2$-EuW$_{10}$ were utilized for the photoluminescence measurements.

4.3. Synthesis of C$_8$N$_2$-EuW$_{10}$ Hybrid Crystal

A water/ethanol (20 mL, 1:1 (v/v)) solution of C$_8$N$_2$-Cl (0.11 g, 0.50 mmol) was added to an aqueous solution (20 mL) of Na-EuW$_{10}$ (0.47 g, 0.14 mmol), and stirred for 10 min. The resultant suspension was heated until 60 °C with stirring (for 5–10 min) and quickly filtered to obtain a colorless as-prepared precipitate of C$_8$N$_2$-EuW$_{10}$ (0.078 g, yield 17%). Colorless plates of C$_8$N$_2$-EuW$_{10}$ single crystal were isolated from the hot synthetic filtrate kept at 25–42 °C (0.25 g, yield 51%). No presence of Na$^+$ in the C$_8$N$_2$-EuW$_{10}$ single crystals was confirmed using EDS spectroscopy. Anal. Calcld for C$_{32}$H$_{105}$N$_8$EuW$_{10}$O$_{44}$: C, 11.66; H, 3.21; N, 3.40%. Found: C, 11.45; H, 2.98; N, 3.29%. IR (KBr disk): 936 (m), 840 (s), 775 (s), 704 (s), 537 (w), 489 (w), 440 (w), 423 (m) cm$^{-1}$.

4.4. Synthesis of C$_{10}$N$_2$-EuW$_{10}$ Hybrid Crystal

The synthesis of C$_{10}$N$_2$-EuW$_{10}$ was carried out using a similar procedure as for C$_8$N$_2$-EuW$_{10}$. A colorless as-prepared precipitate of C$_{10}$N$_2$-EuW$_{10}$ was obtained from the combined suspension of Na-EuW$_{10}$ and C$_{10}$N$_2$-Cl (0.22 g, yield 49%). Colorless plate single crystals of C$_{10}$N$_2$-EuW$_{10}$ were isolated from the hot synthetic filtrate (0.11 g, yield 34%). No presence of Na$^+$ in the C$_{10}$N$_2$-EuW$_{10}$ single crystals was confirmed using EDS spectroscopy. Anal. Calcld for C$_{37}$H$_{105}$N$_8$EuW$_{10}$O$_{47}$: C, 13.65; H, 3.06; N, 3.01%. Found: C, 13.79; H, 3.15; N, 3.14%. IR (KBr disk): 946 (m), 848 (s), 824 (m), 773 (s), 703 (s), 531 (w), 494 (w), 459 (w), 418 (m) cm$^{-1}$.

4.5. X-ray Crystallography

Single-crystal X-ray diffraction measurements were performed with a Rigaku XtaLAB PRO P200 diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) or Cu Kα radiation (λ = 1.54184 Å). The data collection and processing including absorption correction were performed by CrystalsPro (Version 1.171.39.46) [59]. Crystal structures were solved by SHELXT (Version 2018/2) [60], and refined through the full-matrix least-squares using SHELXL (Version 2018/3) [61]. The diffraction data recorded at the 2D beamline in the Pohang Accelerator Laboratory (PAL) confirmed the same crystal structure. CCDC 2352151-2352152.

5. Conclusions

Lanthanide-containing polyoxometalate-surfactant hybrid crystals were first obtained as single crystals. A highly luminous decatungstoeuropate (EuW$_{10}$) anion was successfully crystallized with bolaamphiphile surfactant cations (C$_8$N$_2$ and C$_{10}$N$_2$). Both C$_8$N$_2$-EuW$_{10}$ and C$_{10}$N$_2$-EuW$_{10}$ hybrid crystals had a similar packing of the EuW$_{10}$ anion: a layer structure viewed along the b-axis and a honeycomb-like structure viewed along the a-axis. The EuW$_{10}$ anions formed a two-dimensional network parallel to the ab plane by O–H···O hydrogen bonding with water molecules. The luminescent properties of C$_8$N$_2$-
EuW\textsubscript{10} and C\textsubscript{10}N\textsubscript{2}-EuW\textsubscript{10} were investigated by means of steady-state and time-resolved spectroscopy. The characteristic emission owing to EuW\textsubscript{10} was essentially retained after the hybrid crystals. The emission decay time of C\textsubscript{10}N\textsubscript{2}-EuW\textsubscript{10} became shorter than that of C\textsubscript{10}N\textsubscript{2}-EuW\textsubscript{10}, especially at a high temperature (300 K), suggesting the thermal deactivation of the excitation energy derived from the longer organic surfactant of C\textsubscript{10}N\textsubscript{2}. The C\textsubscript{8}N\textsubscript{2}-EuW\textsubscript{10} and C\textsubscript{10}N\textsubscript{2}-EuW\textsubscript{10} hybrid crystals exhibited preliminary lasing properties, which is promising as a new category of inorganic–organic phosphors.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/inorganics12060146/s1, Figure S1: Asymmetric unit of C\textsubscript{8}N\textsubscript{2}-EuW\textsubscript{10}; Figure S2: Asymmetric unit of C\textsubscript{10}N\textsubscript{2}-EuW\textsubscript{10}; Figure S3: TG profiles of C\textsubscript{8}N\textsubscript{2}-EuW\textsubscript{10} and C\textsubscript{10}N\textsubscript{2}-EuW\textsubscript{10}.

**Author Contributions:** Conceptualization, T.I.; methodology, R.I. and T.S.; validation, Y.S., T.K. and T.I.; formal analysis, T.I., Y.S., T.K., T.M. and Y.O.; investigation, R.I., R.K., Y.S., T.S. and K.K.; resources, Y.S. and Y.O.; writing—original draft preparation, T.I.; writing—review and editing, T.I. and Y.S.; visualization, T.I., Y.S., R.I. and T.M.; funding acquisition, T.I. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded in part by JSPS KAKENHI (grant number JP21K05232), and the Research and Study Project of Tokai University Research Organization.

**Data Availability Statement:** Further details of the crystal structure investigation (CCDC 2352151-2352152) can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif (accessed on 30 April 2024), or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033.

**Acknowledgments:** This work is partially supported by the Tokai University Imaging Center for Advanced Research. X-ray diffraction measurements with synchrotron radiation were performed at the Pohang Accelerator Laboratory (Beamline 2D, proposal No. 2019-1st-2D-015), a synchrotron radiation facility in Pohang, Republic of Korea, supported by Pohang University of Science and Technology (POSTECH).

**Conflicts of Interest:** The authors declare no conflicts of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

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