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Novel Polyoxometalate-Templated, 3-D Supramolecular Networks Based on Lanthanide Dimers: Synthesis, Structure, and Fluorescent Properties of $[Ln_2(DNBA)_4(DMF)_8][Mo_6O_{19}]$ (DNBA = 3,5-Dinitrobenzoate)

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The spherical Lindquist type polyoxometalate, $Mo_6O_{19}^{2-}$, has been used as a noncoordinating anionic template for the construction of novel three-dimensional lanthanide–aromatic monocarboxylate dimer supramolecular networks $[Ln_2(DNBA)_4(DMF)_8][Mo_6O_{19}]$ (Ln = La **1**, Ce **2**, and Eu **3**, DNBA = 3,5-dinitrobenzoate, DMF = dimethylformamide). The title compounds are characterized by elemental analyses, IR, and single-crystal X-ray diffractions. X-ray diffraction experiments reveal that two Ln(III) ions are bridged by four 3,5-dinitrobenzoate anions as asymmetrically bridging ligands, leading to dimeric cores, $[Ln_2(DNBA)_4(DMF)_8]^{2+}$; $[Ln_2(DNBA)_4(DMF)_8]^{2+}$ groups are joined together by π–π stacking interactions between the aromatic groups to form a two-dimensional grid-like network; the 2-D supramolecular layers are further extended into 3-D supramolecular networks with 1-D box-like channels by hydrogen-bonding interactions, in which hexamolybdate polyanions reside. The compounds represent the first examples of 3-D carboxylate-bridged lanthanide dimer supramolecular "host" networks formed by π–π stacking and hydrogen-bonding interactions encapsulating noncoordinating "guest" polyoxoanion species. The fluorescent activity of compound **3** is reported.

Polyoxometalates (POMs), in addition to their importance in catalysis, biochemical separation, and medicinal chemistry, play an important role for the design of new materials with novel electronic, magnetic, and topological properties.[1−3] A new area of interest is the construction of supramolecular arrays based on POM building blocks and various organic ligands (such as N-containing ligands, amino acids, polypeptides, tetrathiafulvalenes, organometallics, and cyclopentadienyl derivatives).[2,4−8] These assemblies possess interesting one- (1-D), two- (2-D), and three-dimensional (3-D) structures and exhibit potential applications in catalysis, medicine, and electrical-conductive and magnetic materials.[9−11] Several successful strategies have been developed to integrate POMs

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into hybrid solid-state materials,[11] which are mainly based on simple materials, by hydrothermal methods. Most recently, POM-templated transition metal coordination polymers have been synthesized.[12] However, no high-dimensional rare-earth complex network encapsulating polyoxoanions has been reported yet. The motivation of such studies lies not only in the combinations of "value-adding properties" and introducing possible synergistic effects[2g,10b] but also in creating opportunities to use the redox properties of the POMs to carry out chemical reactions within the intercrystalline voids, avoiding disruption of the framework topology and crystallinity.[12]

Supramolecular assemblies constructed from organic and/or inorganic molecular building blocks have attracted extensive interest owing to their novel and diverse topologies and potential applications in host−guest chemistry, shape-selective catalysis, absorption, and electrical-conductive, magnetic, and photosensitive materials in recent years.[6a,13−16] Hydrogen-bonding and $\pi-\pi$ stacking interactions play a crucial role in assembling complicated supramolecular architectures.

Lanthanide complexes have attracted much attention in recent years owing to their special spectroscopic and magnetic properties, as well as their potential use as luminescent probes, NMR shift agents, magnetic resonance imaging agents, and radiotherapeutic agents.[17,18] A large number of lanthanide complex containing carboxylate ligands have been prepared, which are either in polymeric forms[19,20] or in dimeric complexs forms.[21] To our knowledge, no extended 3-D lanthanide dimer supramolecular networks using polyoxoanions as templates have been reported.

In the hope that the combination of lanthanide complexes with POMs not only shows value-adding properties and possible synergistic effects but also allows the creation of new networks with unique physical properties, here we report three novel POM-templated supramolecular assemblies based on lanthanide dimer building blocks, $[La_2(DNBA)_4(DMF)_8][Mo_6O_{19}]$ (DNBA = 3,5-dinitrobenzoate, DMF = dimethylformamide) **1**, $[Ce_2(DNBA)_4(DMF)_8][Mo_6O_{19}]$ **2**, and $[Eu_2(DNBA)_4(DMF)_8][Mo_6O_{19}]$ **3**. The title compounds exhibit an interesting 3-D box-like "host" network constructed from lanthanide dimers by $\pi-\pi$ stacking and hydrogen-bonding interactions, in which polyoxoanion "guests" reside. To our knowledge, **1**, **2**, and **3** represent the first examples of POM-templated 3-D rare-earth−carboxylate supramolecular networks.

Experimental Section

General Considerations. All chemicals purchased were of reagent grade and used without further purification. $[(n\text{-}C_4H_9)_4N]_2Mo_6O_{19}$ was synthesized by the improved methods of the literature[22] and characterized by IR spectra and TG analyses. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. Mo, La, Ce, and Eu were determined by a Leaman inductively coupled plasma (ICP) spectrometer. The FTIR spectra were recorded in the range 400−4000 cm^{-1} on an Alpha Centauri FT/IR spectrophotometer with pressed KBr pellets. Photoluminescence spectra were measured using a FL-2T2 instrument (SPEX, USA) with 450 W Xenon lamp monochromatized by double grating (1200).

Synthesis of $[La_2(DNBA)_4(DMF)_8][Mo_6O_{19}]$ 1. Eight milliliters of a DMF solution of $[Bu_4N]_2Mo_6O_{19}$ (0.2 mmol, 0.221 g) and 5 mL of a glacial acetic acid (HOAc) solution of 3,5-dinitrobenzoic acid (1 mmol, 0.212 g) were added dropwise to a stirred 5 mL

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Table 1. Crystal Data and Structure Refinement for Compounds **1**, **2** and **3**

	1	**2**	**3**
empirical formula	$C_{52}H_{68}La_2Mo_6N_{16}O_{51}$	$C_{52}H_{68}Ce_2Mo_6N_{16}O_{51}$	$C_{52}H_{68}Eu_2Mo_6N_{16}O_{51}$
fw	2586.68	2589.10	2612.78
cryst syst	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	13.288 (3)	13.2731 (9)	12.7551 (12)
b/Å	13.872 (3)	13.8730 (7)	13.3435 (12)
c/Å	14.186 (3)	14.2067 (6)	14.1947 (15)
α/deg	102.21 (3)	102.652 (2)	114.776 (6)
β/deg	100.95(3)	101.030 (2)	105.257 (4)
γ/deg	116.24 (3)	115.683 (2)	95.240 (3)
V/Å^3, Z	2169.1 (8), 1	2175.0 (2), 1	2059.4 (3), 1
F(000)	1266	1268	1278
μ/mm^{-1}	1.909	1.968	2.496
refln collected	13695	16053	10960
indep reflns	9153 ($R_{int} = 0.0532$)	9888 ($R_{int} = 0.0301$)	8221 ($R_{int} = 0.0644$)
GOF on F^2	0.977	0.980	1.012
R1[a] [$I > 2\sigma(I)$]	0.0468	0.0342	0.0468
wR2[b] [$I > 2\sigma(I)$]	0.1200	0.0822	0.1315

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}$.

ethanol (EtOH) solution of $LaCl_3 \cdot 7H_2O$ (1 mmol, 0.371 g) in succession. The light yellow solution was stirred at 60 °C for 2 h. The resulting solution was filtrated and then allowed to evaporate in air at room temperature. Slow evaporation afforded light yellow crystal of **1**. Yield: 104 mg (20% yield based on Mo). Elemental anal. Calcd for $C_{52}H_{68}La_2Mo_6N_{16}O_{51}$: C, 24.15; H, 2.65; N, 8.66; Mo, 22.25; La, 10.74. Found: C, 24.18; H, 2.42; N, 8.67; Mo, 22.35; La, 10.74. FTIR data (cm^{-1}): 3102 (w), 2934 (w), 1651 (s), 1583 (w), 1542 (s), 1496 (w), 1461 (w), 1437 (w), 1399 (m), 1348 (s), 1252 (w), 1109 (w), 959 (s), 802 (s), 723 (s), 673 (m).

$[Ce_2(DNBA)_4(DMF)_8][Mo_6O_{19}]$ 2. The preparation of **2** was similar to that of **1** except that $Ce(NO_3)_3 \cdot 6H_2O$ was used. Yield: 109 mg (21% yield based on Mo). Elemental anal. Calcd for $C_{52}H_{68}Ce_2Mo_6N_{16}O_{51}$: C, 24.12; H, 2.65; N, 8.66; Mo, 22.23; Ce, 10.82. Found: C, 24.23; H, 2.30; N, 8.63; Mo, 22.27; Ce, 10.85. FTIR data (cm^{-1}): 3104 (w), 2933 (w), 1652 (s), 1628 (s, sh), 1589 (w), 1541 (s), 1497 (w), 1459 (w), 1437 (w, sh), 1380 (m), 1348 (s), 1251 (w), 1109 (w), 961 (s), 800 (s), 722 (s), 710 (sh), 673 (m).

$[Eu_2(DNBA)_4(DMF)_8][Mo_6O_{19}]$ 3. The preparation of **3** was similar to that of **1** except that $EuCl_3$ was used. Yield: 85 mg (16% yield based on Mo). Elemental anal. Calcd for $C_{52}H_{68}Eu_2Mo_6N_{16}O_{51}$: C, 23.90; H, 2.62; N, 8.58; Mo, 22.03; Eu, 11.63. Found: C, 23.88; H, 2.63; N, 8.59; Mo, 22.10; Eu, 11.62. FTIR data (cm^{-1}): 3102 (w), 2935 (w), 1649 (s), 1589 (w), 1540 (s), 1498 (w), 1458 (w), 1438 (w), 1403 (m), 1377 (m), 1348 (s), 1251 (w), 1112 (w), 958 (s), 801 (s), 722 (s), 712 (sh), 677 (m).

X-ray Crystallography. A yellow single crystal of **1** with dimensions of 0.34 × 0.29 × 0.10 mm^3 was mounted on the tip of a glass fiber in air. Data were collected on a Rigaku R-AXIS RAPID IP diffractometer with Mo Kα ($\lambda = 0.71073$ Å) at 293 K in the range $1.96° < \theta < 27.48°$. An empirical absorption correction was applied (1.909 mm^{-1}).[23] A total of 13695 (9153 unique, $R_{int} = 0.0532$) reflections were measured ($-17 \leq h \leq 17$, $-17 \leq k \leq 17$, $-18 \leq l \leq 18$).

A yellow single crystal of **2** with dimensions 0.28 × 0.24 × 0.14 mm^3 was mounted on the tip of a glass fiber in air. Data were collected on a Rigaku R-AXIS RAPID IP diffractometer with Mo Kα ($\lambda = 0.71073$ Å) at 293 K in the range $2.36° < \theta < 27.48°$. An empirical absorption correction was applied (1.968 mm^{-1}).[23] A total of 16053 (9888 unique, $R_{int} = 0.0301$) reflections were measured ($-17 \leq h \leq 17$, $-18 \leq k \leq 18$, $-18 \leq l \leq 17$).

A yellow single crystal of **3** with dimensions 0.33 × 0.30 × 0.29 mm^3 was mounted on the tip of a glass fiber in air. Data were collected on a Rigaku R-AXIS RAPID IP diffractometer with Mo Kα ($\lambda = 0.71073$ Å) at 293 K in the range $1.95° < \theta < 27.45°$. An empirical absorption correction was applied (2.496 mm^{-1}).[23] A total of 10960 (8221 unique, $R_{int} = 0.0644$) reflections were measured ($-15 \leq h \leq 16$, $-17 \leq k \leq 17$, $-18 \leq l \leq 18$).

All structures were solved by the direct method and refined by the full-matrix least-squares on F^2 using the SHELXL-97 software.[24] All of the non-hydrogen atoms were refined anisotropically. All of the hydrogen atoms were located in Fourier difference maps. A summary of the crystallographic data and structural determination for **1**, **2**, and **3** is provided in Table 1.

Results and Discussion

Preparations of Complexes. The self-assembly reaction of $LnCl_3$ or $Ln(NO_3)_3$ (Ln = La, Ce, Eu) with 3,5-dinitrobenzoic acid and hexamolybdate in DMF−HOAc−EtOH mixed solution is an effective route for preparation of novel rare-earth supramolecular networks containing POMs. The isolation of the title compounds depends on the choice of ligands containing carboxylic acid, solvent system, and temperature. If the 3,5-dinitrobenzoic acid was replaced by 4-aminobenzoic acid or sodium of terephthalic acid under the same conditions, we could not obtain the expected single crystal but only precipitate. If the reaction was performed in a CH_3CN−HOAc−$CHCl_3$−DMSO mixed solvent system, only a kind of unstable yellow crystal was obtained. If HOAc was not added into the reaction system, a lot of white precipitate was obtained probably due to the decomposition of polyoxoanion at neutral or basic solution. If the reaction temperature is higher than 80 °C,we can only obtain colorless crystal $[(n\text{-}C_4H_9)_4N]_4[\beta\text{-}Mo_8O_{26}]$.

Most reported lanthanide (III) carboxylates show either polymeric structures[19,20] or dimeric structrues.[21] We obtained three novel 3-D supramolecular networks constructed from lanthanide dimers; this can be attributed to the template effect

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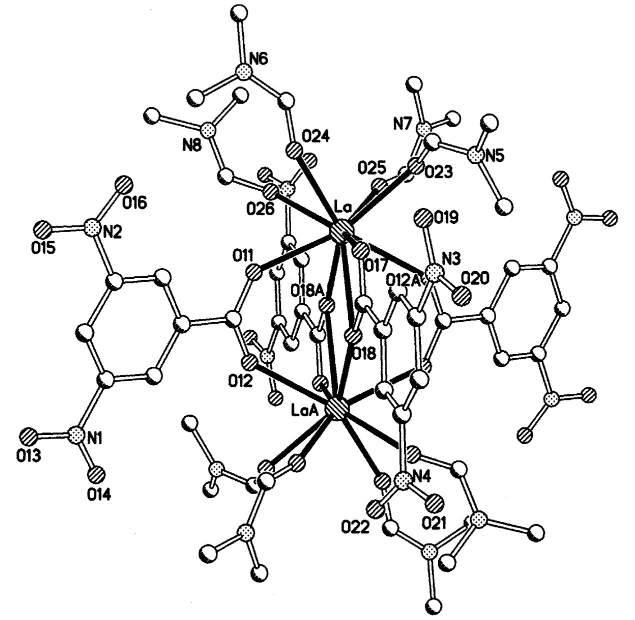


Figure 1. View of the structure of the $[La_2(DNBA)_4(DMF)_8]^{2+}$ dimer cation with the atom-labeling scheme, showing the two-coordination fashion of 3,5-dinitrobenzoic acid. The hydrogen atoms are omitted for clarity.

of hexamolybdate, which is similar to Keller's report.[12] The size, shape, and charge of the POM template may play an important role in such a 3-D supramolecular framework.

Crystal Structures of Complexes. X-ray crystallography shows that compound **1** consists of a lanthanum−3,5-dinitrobenzoate−dimethylformamide dimer cation $[La_2(DNBA)_4(DMF)_8]^{2+}$ and a polyoxoanion $Mo_6O_{19}^{2-}$. The polyoxoanion $Mo_6O_{19}^{2-}$ is the well-known Lindquist structure and consists of a central oxygen atom about which are arrayed six metal atoms in an octahedral geometry. Three kinds of oxygen atoms exist in the cluster, that is, the terminal oxygen O_a, double-bridging oxygen O_b, and central oxygen O_c. Thus, the Mo−O bond lengths can be grouped into three sets: $Mo-O_a$ 1.671(4)−1.688(4) Å, $Mo-O_b$ 1.883(4)−1.965(4) Å, and $Mo-O_c$ 2.3126(10)−2.3209(8) Å.

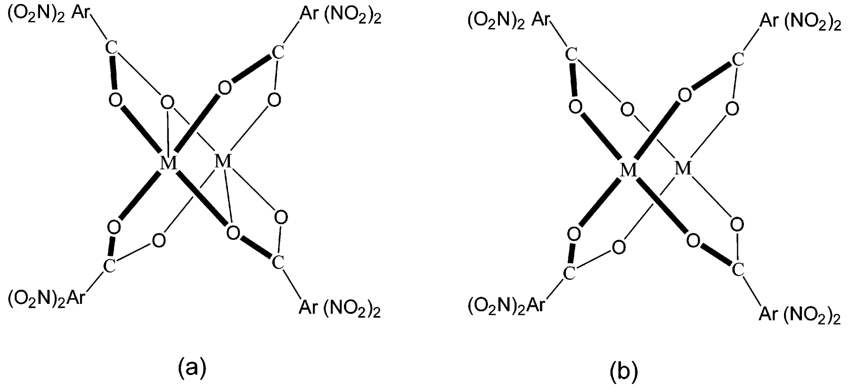
The lanthanum complex cation contains two La(III) centers bridged by four 3,5-dinitrobenzoate anions, leading to a dimeric $[La_2(DNBA)_4(DMF)_8]^{2+}$ core. The perspective view of the dimer cation together with the atomic numbering scheme is illustrated in Figure 1. Each La ion is nine-coordinate bonding to four bridging oxygen atoms and one oxygen atom of four 3,5-dinitrobenzoate units and four oxygen atoms from four DMF units. The La−O distances range from 2.472 to 2.970 Å, and the average La−O distance is 2.558 Å. It should be noted that four 3,5-dinitrobenzoate ligands can be described as two groups (I and II). Group I contains two 3,5-dinitrobenzoate ligands acting in tridentate fashion. O18 (or O18A) bridges two metal atoms (La and LaA), and O17 (or O17A) only coordinates to one metal atom La (or LaA). The distance between the bridging oxygen atom O18 and La is 2.970(4) Å, which is the longest distance around the La ion. The angles O18−La−O18A and La−O18−LaA are 74.72(13)° and 105.28(12)°, respectively. Hence, it is noted that the four-membered ring La−O18−LaA−O18A is obviously perfectly planar and correspondingly the two 3,5-dinitrobenzoate ligands are also in the same plane. The other two 3,5-dinitrobenzoate ligands act in bidentate fashion. O11 and O12 coordinate to La and LaA, respectively. These two ligand molecules are parallel to each other. Such a coordination mode is similar to those of early reported binuclear lanthanide complexes containing carboxylate in which carboxylates act in both bidentate fashion and tridentate fashion.[21e] A schematic illustration of the coordination fashion of the dimer cation of **1** is shown in Scheme 1a.

The structure of the dimeric $[Ce_2(DNBA)_4(DMF)_8]^{2+}$ cation in **2** is a little different from that of the dimeric $[La_2(DNBA)_4(DMF)_8]^{2+}$ cation in **1**, as shown in Figure 2. Each Ce(III) ion is eight-coordinate bonding to four bridging oxygen atoms of four 3,5-dinitrobenzoate units and four oxygen atoms from four DMF units. The Ce−O distances range from 2.444 to 2.550 Å, and the average Ce−O distance is 2.486 Å, which is a little shorter than that of La−O. Four 3,5-dinitrobenzoate ligands all act in bidentate fashion. It is noted the eight-membered ring Ce−O17−C14−O18−CeA−O17A−C14A−O18A is also perfectly planar and correspondingly the two 3,5-dinitrobenzoate ligands are also in the same plane. The other two 3,5-dinitrobenzoate ligands are parallel each other. The structure of the dimeric $[Eu_2(DNBA)_4(DMF)_8]^{2+}$ cation in **3** is the same as that of $[Ce_2(DNBA)_4(DMF)_8]^{2+}$, and no more description of it will be given. A schematic illustration of the coordination fashion of the dimer cations of **2** and **3** is shown in Scheme 1b.

It is very interesting that compounds **1** and **2** are isomorphous, though the structure of the dimeric cations in **1** and **2** is a little different. From inspection of CIF data it is clear that in **1** the polyoxomolybdate is positioned about the inversion center at (1.5, 0.5, 0.5) and the La(III) dimer cation lies about an inversion center at (0.5, 0, 0). In the isomorphous compound **2**, the polyoxomolybdate is positioned about the inversion center at (0, 0, 0) and the Ce(III) dimer cation lies about an inversion center at (0, 0.5, 0.5).

The most unusual structural feature of compounds **1**, **2**, and **3** is that dimeric cation $[Ln_2(DNBA)_4(DMF)_8]^{2+}$ groups are joined together by offset $\pi-\pi$ stacking interactions between aromatic rings along the *b*- and *c*-axes to form a two-dimensional grid-like network, as shown in Figure 3. The close contact distance between adjacent aromatic rings is ca. 3.5 Å along the *b*-axis and 3.4 Å along the *c*-axis. As is described above, each lanthanide dimer possesses four DMF molecules and four 3,5-dinitrobenzoate units, and the oxygen atoms from the nitro group of 3,5-dinitrobenzoate in one 2-D layer are linked to carbon atoms from the methyl group of DMF molecules in another 2-D layer through a hydrogen-bonding interaction (see Supporting Information Figure S8 and Scheme S1). Therefore, the 2-D supramolecular layers are further extended into a 3-D supramolecular network with 1-D box-like channels, as shown in Figure 4. The size of the box is 7.2 × 7.4 Å. The polyoxoanion was encapsulated inside as a "guest" cluster anion and well surrounded by these "host" box-like units. Although Chen et al. and other groups have reported related work on monomeric metal complexes that extended into a 3-D network via supramolecular interactions such as H-bonds and

Scheme 1 [a]



[a] (a) Schematic illustration of the coordination fashion of the dimer cation of **1**. (b) Schematic illustration of the coordination fashion of the dimer cations of **2** and **3**. The DMF molecules have been omitted for clarity.

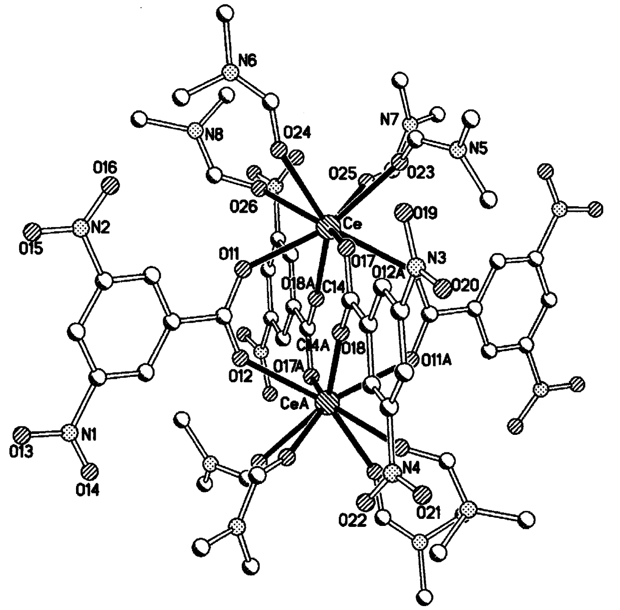


Figure 2. View of the structure of the $[Ce_2(DNBA)_4(DMF)_8]^{2+}$ dimer cation with the atom-labeling scheme, showing the one-coordination fashion of 3,5-dinitrobenzoic acid. The hydrogen atoms are omitted for clarity.

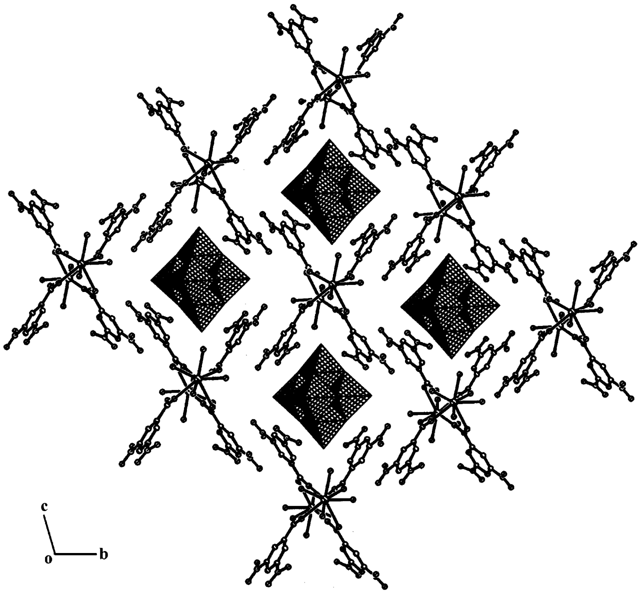


Figure 3. Ball-and-stick representation of the grid-like cavity based on lanthanide dimers encircling POM anions shown in a polyhedral representation along the *a*-axis. The DMF molecules have been omitted for clarity.

$\pi-\pi$ stacking interactions with small anions as guests,[14e,f] Zubieta et al. have reported composite solid constructed from 1-D or 3-D coordination polymer matrices and molybdenum oxide subunits by a hydrothermal method, in which polyoxoanions were encapsulated,[11b,f] and Keller et al. have reported POM-templated coordination polymer.[12] There is no report on rare-earth−carboxylate high-dimensional "host" network encapsulating polyoxoanion. Compared with previous reported lanthanide−carboxylate complexes[19−21] and 3-D supramolecular monomeric metal complexes with small anions as guests,[14e,f] compounds **1**, **2**, and **3** represent the first 3-D extended lanthanide−carboxylate supramolecular "host" networks with 1-D box-like channels encapsulating large polyoxoanion "guests".

FT-IR Spectroscopy. In the IR spectrum of **1**, the characteristic peaks at 802 and 959 cm^{-1} are attributed to the $\nu(Mo-O-Mo)$ and $\nu(Mo{=}O)$ of the $Mo_6O_{19}^{2-}$ polyanions, respectively. The feature band at 1651 cm^{-1} can be ascribed to $\nu(C{=}O)$ of DMF. Bands in the range 1460−1583 cm^{-1} are characteristic of the phenyl ring of 3,5-dinitrobenzoate. The characteristic peaks at 1542 and 1437 cm^{-1} are attributed to the O−C−O group of 3,5-dinitrobenzoate. The IR spectra of **2** and **3** are very similar to that of **1**. (See Supporting Information Figures S5−S7.)

Photoluminescence Properties. Since an intramolecular energy transfer from the oxygen-to-metal (O→M) ligand−metal charge transfer (LMCT) to a lanthanide cation can occur in the POM lattice, the photoluminescence behavior of some polyoxometalates containing lanthanide cations has been investigated by Yamase and other groups.[2d,25−26] Here we found that compound **3** showed red photoluminescence. Figure 5 shows the excitation and emission spectra of **3** at room temperature. We can see that the excitation spectrum of **3** shows characteristic peaks of Eu^{3+} at 394 nm ($^7F_0 \rightarrow {}^5L_6$), 418 nm ($^7F_0 \rightarrow {}^5D_3$), and 466 nm ($^7F_0 \rightarrow {}^5D_2$). The broad band ranging from 310 to 370 nm corresponding to

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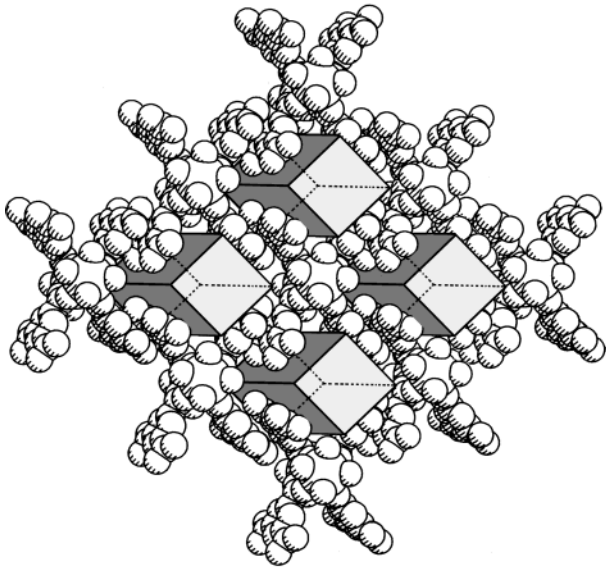

Figure 4. Space-filling diagram of the 3-D "host" network and the box-like cavities of the title compounds constructed from lanthanide dimers by $\pi-\pi$ stacking interactions between benzene rings and hydrogen-bonding interactions (along the *a*-axis).

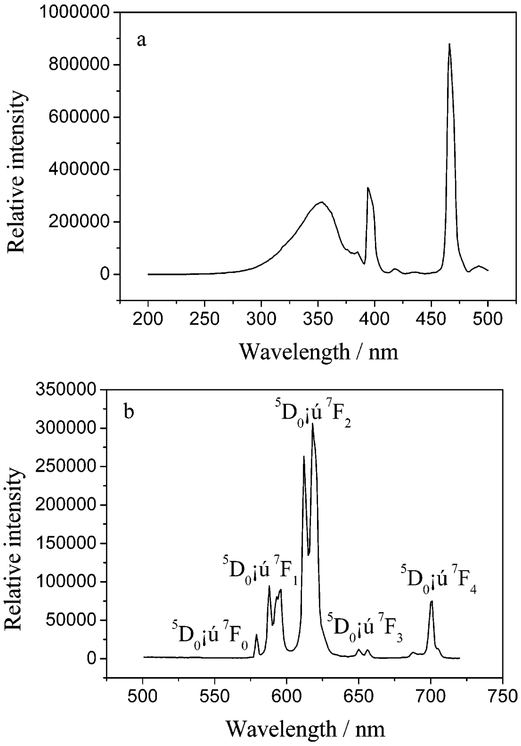

Figure 5. (a) Excitation spectrum of solid **3** ($\lambda_{em} = 618$ nm). (b) Emission spectrum of solid **3** ($\lambda_{ex} = 352$ nm).

the O→Mo LMCT transition plays an important role in the luminescence of **3**. Photoexcitation of the LMCT band leads to energy transfer from polyoxoanion to Eu^{3+} followed by a characteristic luminescence of Eu^{3+}.[27,28a] Compared with the O→W LMCT band of polyoxometalloeuropates,[27] the O→Mo LMCT band red-shifts, which is consistent with our earlier report.[28b]

The corresponding emission spectrum of **3** exhibits the characteristic transition of the Eu^{3+} ion. The peaks are attributed to $^5D_0 \rightarrow {}^7F_J$ ($J = 0, 1, 2, 3, 4$) transitions. The symmetric forbidden emission $^5D_0 \rightarrow {}^7F_0$ at 580 nm can be found in solid **3**. It is well-known that the $^5D_0 \rightarrow {}^7F_0$ transition is strictly forbidden in a field of symmetry. Hence, the above result reveals that Eu^{3+} in **3** occupy sites with low symmetry and without an inversion center. The $^5D_0 \rightarrow {}^7F_1$ transition is a magnetic dipole transition, and its intensity varies with the crystal field strength acting on Eu^{3+}. On the other hand, the $^5D_0 \rightarrow {}^7F_2$ transition is an electric dipole transition and is extremely sensitive to chemical bonds in the vicinity of Eu^{3+}. The intensity of the $^5D_0 \rightarrow {}^7F_2$ transition increases as the site symmetry of Eu^{3+} decreases. Therefore, the intensity ratio of the $^5D_0 \rightarrow {}^7F_2$ transition to the $^5D_0 \rightarrow {}^7F_1$ transition is widely used as a measure of the coordination state and the site symmetry of the rare earth.[29] For compound **3**, the strongest emission is in the $^5D_0 \rightarrow {}^7F_2$ transition region and the $^5D_0 \rightarrow {}^7F_2$ peak was split into two levels at 612 and 618 nm. The $^5D_0 \rightarrow {}^7F_1$ transition was the next, and the emission peak was also split into two levels at 588 and 596 nm. The intensity ratio $I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$ is equal to ca. 3.2, which also suggests the low site symmetry of the Eu^{3+} ion in **3**.

Conclusions

In this paper, three novel supramolecular architectures based on POMs and lanthanide dimer building blocks $[Ln_2(DNBA)_4(DMF)_8][Mo_6O_{19}]$ (Ln = La **1**, Ce **2**, and Eu **3**, DNBA = 3,5-dinitrobenzoate, DMF = dimethylformamide) have been synthesized and structurally characterized. Here a polyoxoanion acts as a noncoordination template around which a 2-D grid-like network is constructed by $\pi-\pi$ stacking interactions of the benzene ring of the adjacent lanthanide complex; the 2-D framework is further extended into a 3-D box-like network by hydrogen-bonding interactions of the adjacent lanthanide complex. The compounds represent a novel host−guest supramolecular assembly, in which the polyoxoanions act as "guests" to reside in the 3-D "box-like" lanthanide dimer supramolecular "host" network, the size of which is 7.2 × 7.4 Å. Compound **3** exhibits obvious photoluminescence at room temperature.

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Supporting Information Available: Crystallographic data in CIF format. View of the structure of the Lindquist polyoxoanion $Mo_6O_{19}^{2-}$, ORTEP drawings and IR spectra of **1**−**3**, view of the 3-D H-bonding network, and schematic illustration of the interlayer H-bonding interactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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