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Synthesis, Crystal Structure, and Photochromism of Novel Two-Dimensional Supramolecular Networks Based on Keggin-Type Polyoxoanion and Lanthanide Coordination Cations

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Three new compounds $[Ln(NMP)_4(H_2O)_4][H_xGeMo_{12}O_{40}]\cdot 2NMP\cdot 3H_2O$ (Ln = Ce^{IV} (**1**), Pr^{IV} (**2**), $x = 0$; Ln = Nd^{III} (**3**), $x = 1$; NMP = *N*-methyl-2-pyrrolidone) have been prepared in aqueous solution and characterized by elemental analyses, IR, UV–vis, and TG analyses. The single crystal X-ray diffraction shows that all three compounds are isostructural. In their structures, an interesting two-dimensional supramolecular network is constructed by the $[GeMo_{12}O_{40}]^{4-}$ anion and $[Ln(NMP)_4(H_2O)_4]^{3+/4+}$ cation building blocks via hydrogen-bonding interactions, exhibiting the porous structure. Upon irradiation with UV light, the crystals of **1**–**3** show photochromic behavior.

Polyoxometalates (POMs), one type of well-known polynuclear metal−oxo cluster, have attracted great attention in recent years because of their potential applications in catalysis, medicine, and material science.[1−4] They can be tuned at the molecular level and exhibit fascinating structures and properties.[5,6] One part of the challenging work in this field is the preparation of novel compounds containing polyoxoanions and lanthanide cations.[7−14] Such compounds are good candidates for various electronic, magnetic, and photosensitive materials.[3b] Some crystal structures of rare-earth-containing isopolyanions have been reported thus far.[7−9] Furthermore, a series of compounds combined with rare earth and unsaturated heteropolyanions have been isolated.[10−14] However, the structures composed of rare earth elements and saturated heteropolyanions (such as α-Keggin type) are still

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scare.[15,16] In most cases, it appears that the oxygen atoms on the surface of POMs are rather reactive and are easily combined with the highly oxophilic rare earth ions to form precipitation instead of crystallization.[15] The introduction of protecting organic ligands may be one of the effective methods to inhibit precipitation by coordinating rare earth ions and decreasing their highly oxophilic properties.

In this paper, we choose *N*-methyl-2-pyrrolidone (NMP) as a protecting ligand and isolate single crystals of three novel lanthanide-containing polyoxometalate compounds, $[Ce(NMP)_4(H_2O)_4][GeMo_{12}O_{40}]\cdot 2NMP\cdot 3H_2O$ (**1**), $[Pr(NMP)_4(H_2O)_4][GeMo_{12}O_{40}]\cdot 2NMP\cdot 3H_2O$ (**2**), and $[Nd(NMP)_4(H_2O)_4][HGeMo_{12}O_{40}]\cdot 2NMP\cdot 3H_2O$ (**3**). All the compounds are isostructural, in which the α-Keggin-type polyoxoanions $[GeMo_{12}O_{40}]^{4-}$ are linked by $[M(NMP)_4(H_2O)_4]$ complex cations through the hydrogen-bonding interactions. The whole crystal structure of these compounds displays a novel two-dimensional (2-D) supramolecular network with porous structures. To the best of our knowledge, the combination of rare-earth-organic complex moieties with saturated heteropolyoxoanions has not been reported to date.

Experimental Section

Physical Measurements and Analyses. Elemental analyses were determined by means of POEMS (TJA). TG measurements were carried out on a Perkin-Elmer TG-7 thermal analysis system in flowing N_2 with a heating rate of 10 °C min^{-1}. The IR spectra (KBr pellets) were recorded on an Alpha Centauri FTIR spectrometer (400−2000 cm^{-1} range). Diffuse reflectance UV−vis spectra ($BaSO_4$ pellets) were obtained with a Varian Cary 500 UV−vis−NIR spectrometer. The EPR spectrum was recorded on a Japanese JES-FE3AX spectrometer at 293 K. Photochromic experiments were carried out using a 500 W high-pressure mercury lamp as the light source.

Syntheses of Compounds 1−3. $[Ce(NMP)_4(H_2O)_4][GeMo_{12}O_{40}]\cdot 2NMP\cdot 3H_2O$. All chemicals were of reagent grade and used without further purification. $H_4GeMo_{12}O_{40}\cdot nH_2O$ was prepared according to the literature[17] and recrystallized twice from hot water. Compound **1** was prepared as follows. $CeCl_4$ powder (0.3089 g, 1.10 mmol) was added to a solution of $H_4GeMo_{12}O_{40}\cdot nH_2O$ (2 g, 1.10 mmol) in 5 mL of deionized water at room temperature with stirring. After the mixed solution was stirred at 90−95 °C for 30 min, *N*-methyl-2-pyrrolidone (1 mL) was added with stirring. The yellow precipitate was formed, collected by filtration, and dried in a vacuum overnight to yield 2.15 g of crude product. Crude product was recrystallized from the mixed solution of water (4 mL) and acetonitrile (6 mL) at 70−75 °C, and yellow-green block crystals were collected (yield: 63.5%). Anal. Calcd for compound **1**: C, 13.22; H, 2.52; N, 3.08; Ce, 5.14; Ge, 2.66; Mo, 42.25%. Found: C, 13.28; H, 2.49; N, 3.12; Ce, 5.20; Ge, 2.64; Mo, 42.34%. IR spectrum (cm^{-1}): 3420 (vs), 2931 (w), 1637(vs), 1510 (s), 1474 (w), 1456 (m), 1408 (s), 1309 (m), 1259 (m), 1115 (m), 949 (s), 878 (s), 807 (s), 774 (s), 669 (w), 609 (w), and 502(m).

Table 1. Crystal Data and Structure Refinement for **1−3**

	1	**2**	**3**
formula	$C_{30}H_{68}CeGeMo_{12}N_6O_{53}$	$C_{30}H_{68}GePrMo_{12}N_6O_{53}$	$C_{30}H_{69}GeNdMo_{12}N_6O_{53}$
fw	2724.89	2726.69	2730.02
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	17.313(4)	17.3469(5)	17.337(4)
b/Å	18.316(4)	18.2955(5)	18.283(4)
c/Å	23.039(5)	23.0726(7)	23.015(4)
β/deg	107.19(3)	106.9990(10)	107.00(1)
V/Å^3, Z	6979(2), 4	7002.6(4), 4	6976.6(3), 4
D_c/g cm^{-3}	2.593	2.586	2.599
μ /cm^{-1}	3.250	3.285	3.343
reflns collected	27476	28629	29883
indep reflns	15049 ($R_{int} = 0.0185$)	15641 ($R_{int} = 0.0464$)	15786 ($R_{int} = 0.0200$)
params	913	895	895
GOF on F^2	1.226	1.054	1.080
R1,[a] wR2[b] $[I > 2\sigma(I)]$	0.0461, 0.1323	0.0629, 0.1188	0.0378, 0.0972
all data	0.0567, 0.1449	0.0375, 0.0984	0.0283, 0.0848

Table 2. Selected Bond Distances (Å) and Angles (deg) of **1**

Ce−O(41)	2.370(8)	Mo(1)−O(25)	1.686(6)
Ce−O(43)	2.406(7)	Mo(1)−O(26)	1.812(6)
Ce−O(42)	2.409(7)	Mo(1)-O(16)	1.834(6)
Ce−O(44)	2.417(7)	Mo(1)−O(3)	2.045(6)
Ce−OW(2)	2.529(9)	Mo(1)−O(29)	2.057(6)
Ce−OW(4)	2.549(7)	Mo(1)−O(39)	2.288(5)
Ce−OW(3)	2.566(8)	Ge−O(39)	1.724(5)
Ce−OW(1)	2.597(9)	Ge−O(32)	1.728(5)
Ge−O(30)	1.733(5)	Ge−O(8)	1.732(5)
O(41)−Ce−O(43)	144.9(3)	O(25)−Mo(1)−O(26)	104.5(3)
O(41)−Ce−O(42)	136.8(3)	O(25)−Mo(1)−O(16)	103.6(3)
O(41)−Ce−O(44)	80.4(3)	O(25)−Mo(1)−O(3)	94.9(3)
O(41)−Ce−OW(2)	75.2(4)	O(25)−Mo(1)−O(29)	97.1(3)
O(41)−Ce−OW(4)	68.8(3)	O(25)−Mo(1)−O(39)	166.4(3)
O(41)−Ce−OW(3)	76.8(4)	O(39)−Ge−O(32)	109.4(3)
O(41)−Ce−OW(1)	108.5(3)	O(39)−Ge−O(8)	109.1(3)
O(39)−Ge−O(30)	109.0(3)	O(30)−Ge−O(8)	109.8(3)

Table 3. Selected Bond Distances (Å) and Angles (deg) of **2**

Pr−O (41)	2.353(6)	Mo(1)−O(6)	1.692(5)
Pr−O(42)	2.389(6)	Mo(1)−O(30)	1.814(5)
Pr−O(44)	2.396(6)	Mo(1)−O(14)	1.832(5)
Pr−O(43)	2.400(5)	Mo(1)−O(32)	2.032(5)
Pr−OW(1)	2.513(8)	Mo(1)−O(23)	2.042(5)
Pr−OW(2)	2.541(6)	Mo(1)−O(4)	2.279(5)
Pr−OW(3)	2.551(6)	Ge−O(1)	1.736(5)
Pr−OW(4)	2.554(7)	Ge−O(2)	1.726(5)
Ge−O(4)	1.734(4)	Ge−O(3)	1.727(4)
O(41)−Pr−O(43)	136.9(2)	O(30)−Mo(1)−O(6)	103.1(3)
O(41)−Pr−O(42)	145.4(2)	O(30)−Mo(1)−O(14)	99.3(2)
O(41)−Pr−O(44)	80.3(2)	O(30)−Mo(1)−O(23)	157.3(2)
O(41)−Pr−OW(2)	68.4(2)	O(30)−Mo(1)−O(4)	88.57(2)
O(41)−Pr−OW(4)	108.5(3)	O(30)−Mo(1)−O(32)	85.0(2)
O(41)−Pr−OW(3)	76.8(3)	O(2)−Ge−O(3)	109.1(2)
O(41)−Pr−OW(1)	75.5(3)	O(2)−Ge−O(1)	109.4(2)
O(3)−Ge−O(1)	109.5(2)	O(4)−Ge−O(1)	109.8(2)

$[Pr(NMP)_4(H_2O)_4][GeMo_{12}O_{40}]\cdot 2NMP\cdot 3H_2O$. The preparation procedure was similar to that already described. $PrCl_4$ (0.3098 g) was used. Anal. Calcd for compound **2**: C, 13.21; H, 2.51; N, 3.08; Ge, 2.66; Pr, 5.17; Mo, 42.2%. Found: C, 13.29; H, 2.43; N, 3.16; Ge, 2.46; Pr, 5.07; Mo, 42.6%. IR spectrum (cm^{-1}): 3426 (vs), 2925 (w), 1636 (s), 1510 (m), 1450 (w), 1405 (m), 1310 (w), 1257 (w), 1115 (w), 947 (s), 878 (s), 806 (w), 772 (s), and 606 (w).

$[Nd(NMP)_4(H_2O)_4][HGeMo_{12}O_{40}]\cdot 2NMP\cdot 3H_2O$. This compound was prepared by means of the described procedure. $NdCl_3$ (0.3112 g) was used. Anal. Calcd for compound **3**: C, 13.20; H, 2.55; N, 3.08; Ge, 2.66; Nd, 5.76; Mo, 42.2%. Found: C, 13.31; H, 2.49; N, 3.16; Ge, 2.46; Nd, 5.73; Mo, 42.6%. IR spectrum (cm^{-1}): 3386 (s), 2927 (w), 1636 (vs), 1510 (m), 1405 (m), 1311

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Table 4. Selected Bond Distances (Å) and Angles (deg) of **3**

Nd−O(41)	2.351(4)	Mo(1)−O(6)	1.694(4)
Nd−O(42)	2.372(4)	Mo(1)−O(30)	1.812(3)
Nd−O(44)	2.385(4)	Mo(1)−O(14)	1.832(3)
Nd−O(43)	2.391(4)	Mo(1)−O(32)	2.038(3)
Nd−OW(1)	2.501(5)	Mo(1)−O(23)	2.048(4)
Nd−OW(2)	2.527(4)	Mo(1)−O(4)	2.276(3)
Nd−OW(3)	2.535(4)	Ge−O(1)	1.738(3)
Nd−OW(4)	2.525(5)	Ge−O(2)	1.732(3)
Ge−O(4)	1.731(3)	Ge−O(3)	1.727(3)
O(41)−Nd−O(43)	137.98(16)	O(30)−Mo(1)−O(6)	103.2(2)
O(41)−Nd−O(42)	144.47(16)	O(30)−Mo(1)−O(14)	99.2(2)
O(41)−Nd−O(44)	80.67(16)	O(30)−Mo(1)−O(23)	157.4(1)
O(41)−Nd−OW(2)	68.70(14)	O(30)−Mo(1)−O(4)	88.4(1)
O(41)−Nd−OW(4)	107.40(19)	O(30)−Mo(1)−O(32)	85.2(1)
O(41)−Nd−OW(3)	77.51(19)	O(2)−Ge−O(3)	109.1(2)
O(41)−Nd−OW(1)	74.39(19)	O(2)−Ge−O(1)	109.8(1)
O(3)−Ge−O(1)	109.4(2)	O(4)−Ge−O(1)	109.6(2)

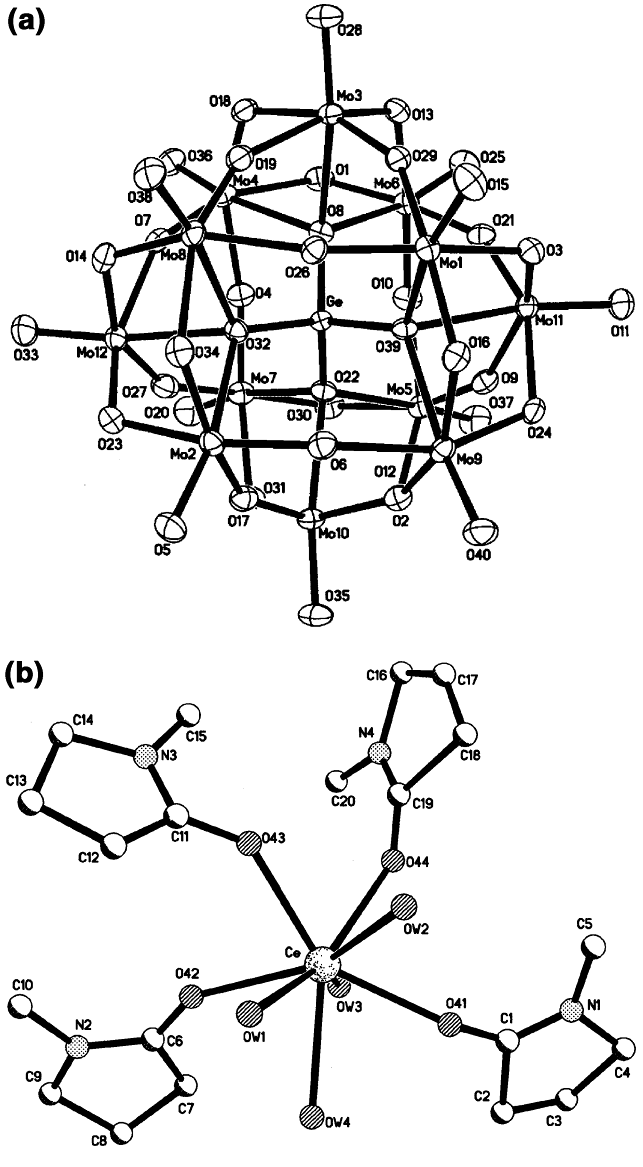


Figure 1. (a) ORTEP drawing of the polyoxoanion of **1** with thermal ellipsoids at 50% probability. (b) The structure of the $[Ce(NMP)_4(H_2O)_4]^{4+}$ cations of **1**. The hydrogen atoms are omitted for clarity.

(w), 1257 (w), 1115 (w), 947 (s), 878 (s), 805 (w), 772 (s), 606 (w), and 500 (m).

Table 5. Hydrogen Bond Distance (Å) of Compound **1**

hydrogen bond	bond distance (Å)
OW(3)···O(38)	2.873
OW(3)···O(40C)	2.998
OW(4)···O(36B)	2.800
OW(4)···O(37A)	2.749
OW(1)···OW(7)	2.744
OW(2)···OW(6A)	2.818
OW(2)···OW(6B)	2.945
OW(5)···O(18)	2.873
OW(5)···O(22B)	2.988

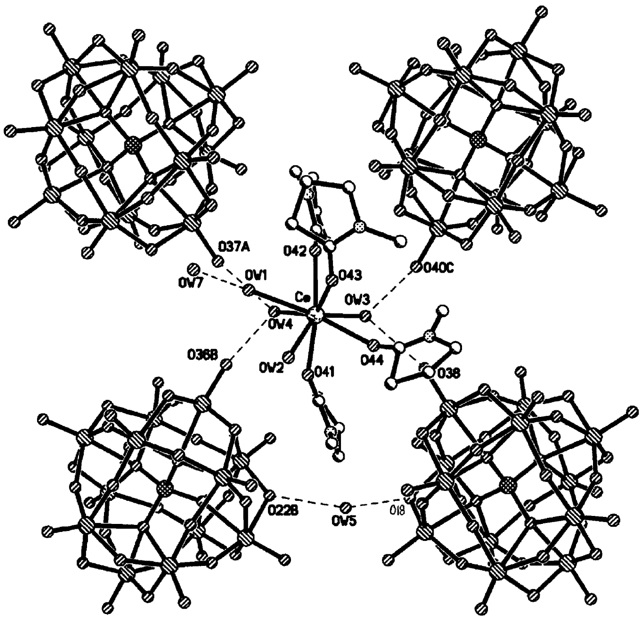


Figure 2. Hydrogen-bonding interactions between the $[GeMo_{12}O_{40}]^{4-}$ anions and $[Ce(NMP)_4(H_2O)_4]^{4+}$ cations.

X-ray Crystallography. The structures of compounds **1**−**3** were determined by single crystal X-ray diffraction. Preliminary examination and data collection of compounds **1** and **2** were performed on a SMART platform diffractometer equipped with a Siemens CCD area detector using graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at room temperature. Data of compound **3** were collected on a Rigaku R-Axis IP diffractometer with empirical absorptions. All the structures were solved by the direct method and refined by the full-matrix least-squares method on F^2. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from difference Fourier maps. The crystal data and refinement parameters of the compounds are listed in Table 1, and selected bonds and angles of **1**, **2,** and **3** are listed in Tables 2, 3, and 4, respectively. CCDC numbers are 190474 for **1**, 195764 for **2**, and 195765 for **3**.

Results and Discussion

Structure of Compound 1. X-ray analysis shows that all the three compounds are isostructural. As an example, compound **1** was described here, which consists of one $[GeMo_{12}O_{40}]^{4-}$ anion, one $[Ce(NMP)_4(H_2O)_4]^{4+}$ cation, two dissociated NMP, and three water molecules. The polyoxoanion structure of **1** is displayed in Figure 1a. The polyoxoanion of **1** exhibits a classical α-Keggin-type structure. In the polyoxoanion, the central Ge atom is surrounded by a tetrahedron in which all oxygen (O_a) vertices are linked to four Mo_3O_{10} groups, respectively. Each Mo_3O_{10} triplet

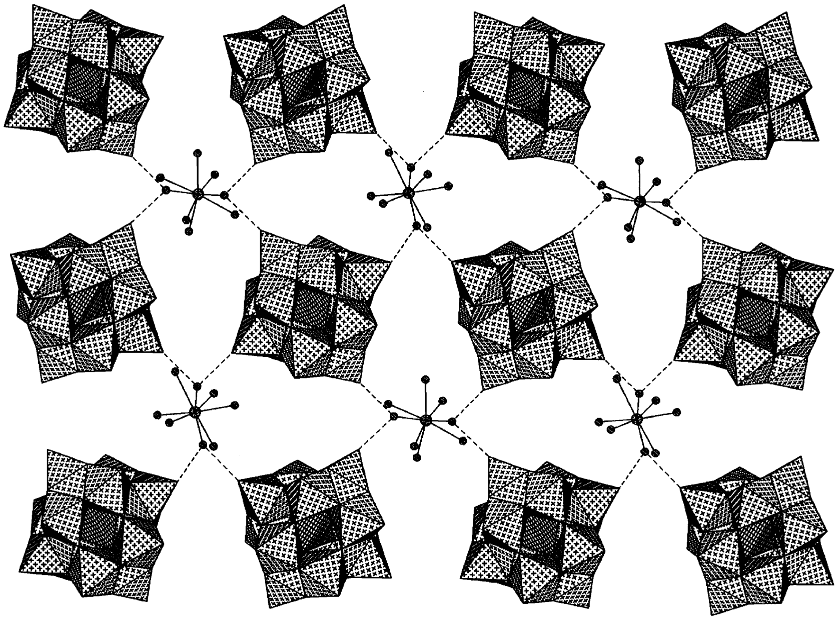


Figure 3. Projection of the structure of compound **1** viewed down the *ab* planes. Organic groups and dissociated molecules are omitted for clarity.

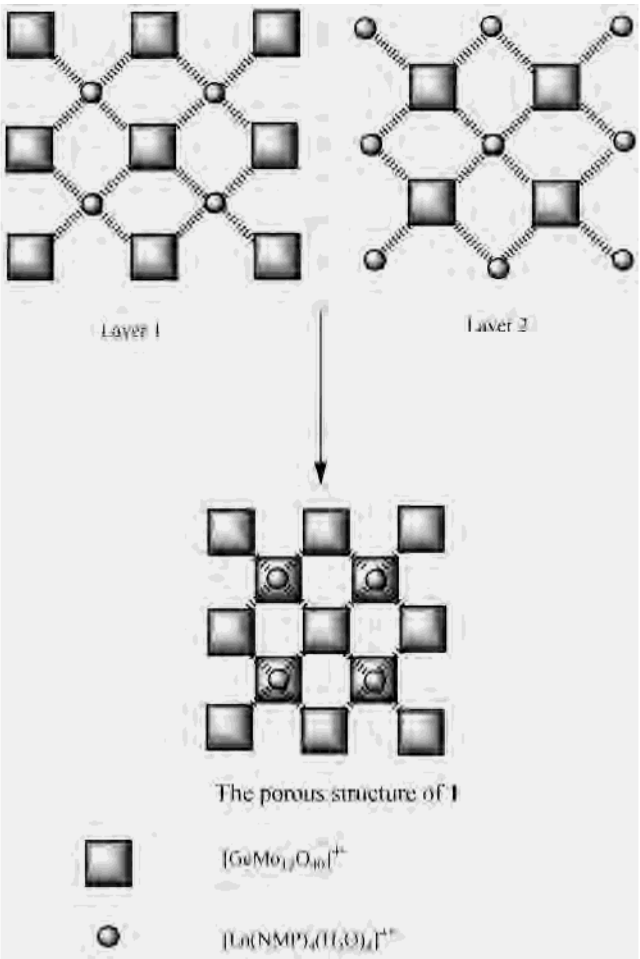
consists of three MoO_6 octahedra linked in a triangular arrangement by sharing edges (O_c), and four Mo_3O_{10} moieties are linked together by sharing corners (O_b). There is a terminal oxygen atom (O_d) in every MoO_6 octahedron. The bond lengths are as follows: the Ge—O_a bond lengths are in the range 1.724(5)−1.733(5) Å, and the Mo═O_d bond lengths are in the range 1.670(6)−1.705(6) Å. The Mo—$O_{b,c}$ bonds in each MoO_6 unit range from 1.796(6) to 2.068(6) Å. The O—Ge—O bond angles are in the range 109.0(3)−109.8(3)°.

Figure 1b gives the structure of Ce^{4+} coordination cations. The Ce^{4+} center exhibits a dodecahedral environment and coordinates to eight oxygen atoms, among which four are from the C═O groups of *N*-methyl-2-pyrrolidone and the remaining four come from coordinated water molecules. The average Ce—OW distance is 2.559 Å, which is longer than the average Ce—O(NMP) distance of 2.400 Å. Among the four coordinated water molecules, only OW(3) and OW(4) exhibit weak hydrogen bonds to the terminal oxygen atoms of two $[GeMo_{12}O_{40}]^{4-}$ anions. Furthermore, there are hydrogen-bonding interactions between the remaining nomadic water molecules, and two bridge oxygen atoms of two $[GeMo_{12}O_{40}]^{4-}$ anions [OW(5)···O(18), OW(5)···O(22B)]. The hydrogen bonding interactions of **1** are shown in Figure 2. The hydrogen bonds of **1** are listed in Table 5.

The most interesting structural feature of **1** is that all the $[GeMo_{12}O_{40}]^{4-}$ anions are linked together by $[Ce(NMP)_4(H_2O)_4]^{4+}$ via the hydrogen-bonding interaction and form an interesting 2-D supramolecular network on the *ab* plane (see Figure 3). Furthermore, the networks in different layers are interlaced; thus, a porous structure is formed along the *c* axis. Scheme 1 illustrates this structural feature. The porous structure is shown in Figure 4, which is occupied by NMP and the dissociated solvent molecules.

Compounds **2** and **3** have the similar structural feature to compound **1**, and no more discussion is given.

Scheme 1. Schematic Illustration of the Packing Arrangement of Compound **1**



IR Spectra of Compounds 1−3. In the IR spectrum of compound **1** (Figure 5), bands in the 1000−700 cm^{-1} region are similar to those of $H_4GeMo_{12}O_{40}$. The characteristic peaks at 949, 878, 807, 774 cm^{-1} are attributed to ν_{as}(Ge—Oa),

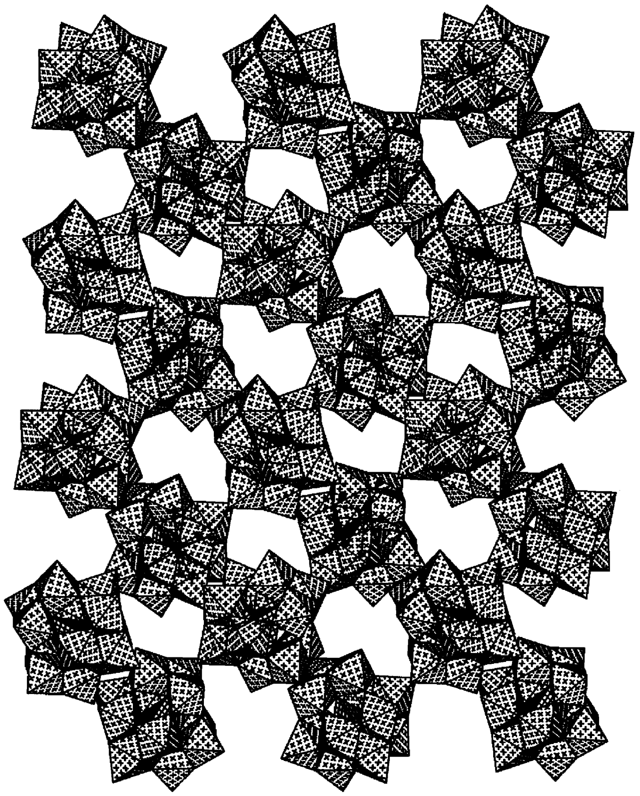


Figure 4. The packing arrangement with porous structure of **1** along the *c* axis.

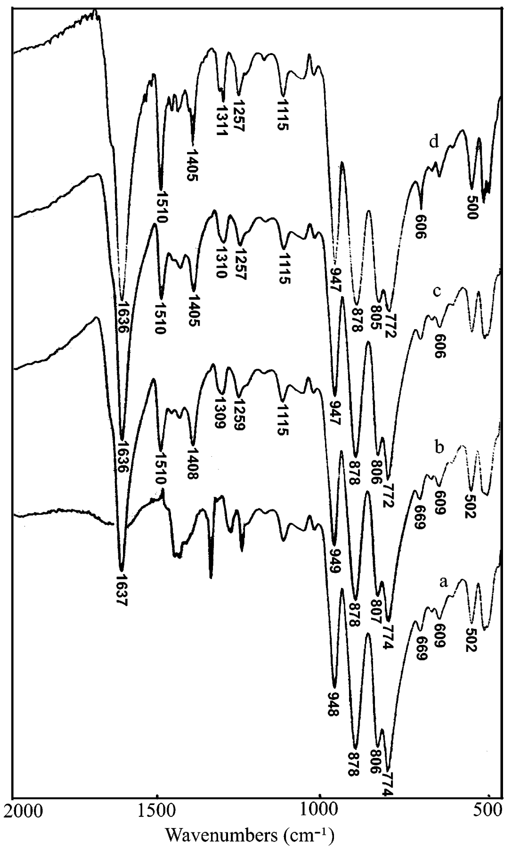


Figure 5. The IR spectra of $H_4GeMo_{12}O_{40}\cdot nH_2O$ (a), compound **1** (b), compound **2** (c), and **3** (d).

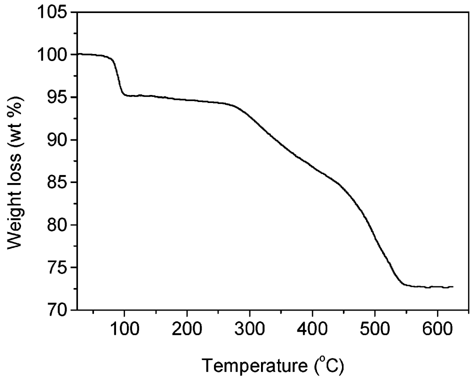


Figure 6. The TG curve of compound **1**.

ν_{as}(Mo═Ot), ν_{as}(Mo—Ob—Mo), and ν_{as}(Mo—Oc—Mo), respectively, showing that the polyoxoanion has an α-Keggin structure. Bands at 1637, 1510, 1474, 1259, 1115 cm^{-1} are characteristic of the NMP molecule. In comparison with the free NMP molecules, the frequency attributed to the ν(C—N) of NMP in compound **1** is shifted from 1270 to 1259 cm^{-1}, which demonstrates that the NMP molecules are coordinated to the metal ions. The strong peak at 1637 cm^{-1} is assigned to the ν(C═O) vibration of NMP molecules. The broad peak at 3420 cm^{-1} and absorptions in the range 1456—1309 cm^{-1} are characteristics of water molecules.

Similar IR characteristics have been observed for compounds **2** and **3**.

TG Analyses of Compounds 1—3. The TG curve of compound **1** (shown in Figure 6) is divided into three stages. The first weight loss is 4.95% in the temperature range 80—105 °C, corresponding to the release of water molecules. The second weight loss of 7.24% from 275 to 365 °C and the third weight loss of 14.31% in 370—540 °C are ascribed to the release of the two dissociated and four coordinated NMP molecules, respectively. The whole weight loss (26.50%) is in good agreement with the calculated value (26.43%). The sample does not lose weight at temperatures higher than 570 °C.

Compounds **2** and **3** exhibit similar weight loss stages. The whole weight losses of compound **2** and **3** are 26.49% and 26.44%, which are in good agreement with the calculated values 26.42% and 26.39%, respectively.

Solid-State Electronic Spectrum. Figure 7 illustrates the reflectance electronic spectra of compound **1** (before and after irradiation) compared with $H_4GeMo_{12}O_{40}\cdot nH_2O$. It is shown that the absorption bands of compound **1** in the region 200—400 nm undergo a small red shift compared to those of $H_4GeMo_{12}O_{40}\cdot nH_2O$, which are similar to those found for $(Hgly\text{-}Gly)_3PMo_{12}O_{40}\cdot 4H_2O$,[4d] and therefore indicate that the interactions between organic moieties and $GeMo_{12}O_{40}{}^{4-}$ are weak in the solid state.

Photochromism. Irradiation of pure crystals of **1**—**3** by a mercury lamp for 3 h in ambient environment induces obvious photochromism in the solid state. The color of crystal changes from yellow-green to deep brown. After stopping irradiation for 40 h, the color can slowly return to the original green. As shown in Figure 7, the solid reflectance electronic spectra of the irradiated sample showed no obvious changes in the region 200—400 nm after irradiation. However, a new

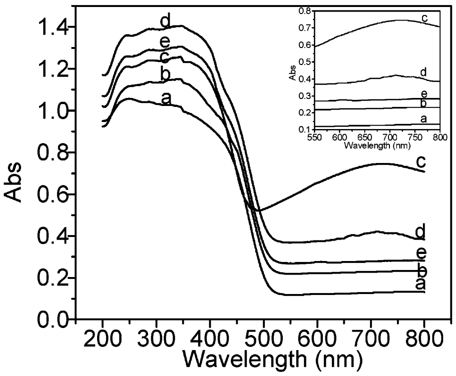


Figure 7. UV−vis spectra of $H_4GeMo_{12}O_{40}{\cdot}nH_2O$ (a) and compound **1** before irradiation (b), after irradiation (c), stopping irradiation for 25 h (d), and stopping irradiation for 40 h (e).

absorption band appears in the visible region, which is assigned to the intervalence charge transfer ($Mo^{5+} \rightarrow Mo^{6+}$) bands of heteropoly anions and is characteristic of heteropoly blues.[18] This indicates that electron transfer occurs between the organic moieties and the heteropoly anions, which results in the reduction of heteropoly anions to heteropoly blues.[1,19] This conclusion has further been confirmed by means of EPR analysis. No EPR signal at 77 K was observed for the unirradiated sample, but after UV irradiation for 3 h, compound **1** showed a significant paramagnetic signal, Figure 8. This signal is attributed to Mo^{5+} with $g = 1.9464$, in agreement with the value reported in the literature.[19] After stopping irradiation, the absorption band of compound **1** in the visible region gradually disappeared as shown in Figure 7. The EPR signal of compound **1** disappeared also.

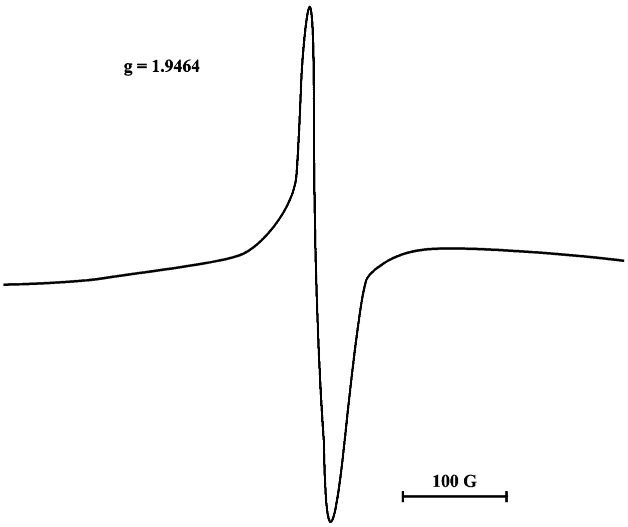


Figure 8. The EPR spectrum of compound **1** at 77 K.

The photochromic mechanism of compounds **1**−**3** may be similar to the one proposed by Professor Hill's group for a solvated polyoxometalate complex $H_3PMo_{12}O_{40}{\cdot}6DMA{\cdot}CH_3CN{\cdot}0.5H_2O$.[20] The weak intermolecular interactions between the DMA molecules and the polyoxometalate moieties result in the photosensitive behavior of this complex. In compounds **1**−**3**, the organic substrate−polyoxometalate electronic interactions may result from both secondary Coulombic and induced-dipole effects.[20] Studies on the detailed and complete mechanism are currently underway.

Conclusion

The introduction of protecting organic ligand NMP led to the successful preparation of three new compounds $[M(NMP)_4(H_2O)_4][GeMo_{12}O_{40}]{\cdot}2NMP{\cdot}3H_2O$ (M = Ce, **1**; Pr, **2**) and $[Nd(NMP)_4(H_2O)_4][HGeMo_{12}O_{40}]{\cdot}2NMP{\cdot}3H_2O$ (**3**). An interesting 2-D supramolecular network with porous structures is formed via the extensive hydrogen-bonding interactions between $[M(NMP)_4(H_2O)_4]^{3+/4+}$ and $[GeMo_{12}O_{40}]^{4-}$ units. All the compounds exhibit the attractive photochromism phenomena, and these can be potential candidates for photosensing materials.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determination of compounds **1**−**3**. Additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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