A series of 3D Porous Lanthanide-Substituted Polyoxometalate Frameworks Based on Rare Hexadecahedral {Ln₆W₈O₂₈} Heterometallic Cageshaped Clusters

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Section 1: Experimental Section

Materials and General methods: $Na_{10}[\alpha-SiW_9O_{34}] \cdot 16H_2O$ was synthesized on the basis of literature method and proved by IR spectroscopy.¹ Other reactants and solvents were obtained from commercial sources and used for reactions without further purification. Powder X-ray diffraction (PXRD) analyses were recorded on a Rigaku Ultima IV diffractometer with Cu K α radiation ($\lambda = 1.54178$ Å). Thermogravimetric analysis (TGA) were performed on a Mettler Toledo TGA/SDTA 851e analyzer under an air-flow atmosphere with a heating rate of 10 °C/min in the temperature of 30-800 °C. The infra-red (IR) spectra were recorded on a Nicolet iS50 at room temperature. Energydispersive spectrometry (EDS) analyses were performed using a Hirox SH-4000 M type desktop scanning electron microscope. UV-vis adsorption spectra were collected using a PerkinElmer Lambda 35 spectrophotometer to monitor the release process. Fluorescence spectra were measured on an Edinburgh Instrument FS980 TCSPC luminescence spectrometer by using crystalline samples. Variable-temperature susceptibility measurement was performed in the temperature range of 2 - 300 K at a magnetic field of 1 KOe on crystalline samples with a Quantum Design PPMS-9T magnetometer. The experimental susceptibilities were corrected for the Pascal's constants.

Adsorption Analysis: Single-component gas measurements were performed with an Accelerated Surface Area and Porosimetry 2020 (ASAP 2020) surface area analyzer. All gases were used in the adsorption experiment of 99.999% purity or higher.

Ionic conductivity experiments: Ac impedance measurements were carried out with a zennium/IM6 impedance analyzer over the frequency range from 0.1 Hz to 5 MHz with an applied voltage of 50mV. The relative humidity was controlled by a STIK Corp. CIHI-150B incubator. The sample was pressed to form a cylindrical pellet of crystalline powder sample (~1.0 mm thickness ×5 mm ϕ) coated with C-pressed electrodes. Two silver electrodes were attached to both sides of pellet to form four end S3 terminals (quasi-four-probe method). The bulk conductivity was estimated by semicircle fittings of Nyquist plots.

Synthesis of Na₂[Gd₂(H₂O)₁₁]₂[Gd₃(H₂O)₂(α -SiW₁₁O₃₉)₂]₂·69H₂O (1-Gd): Gd(NO₃)₃·6H₂O (0.22 mmol, 100 mg), Na₁₀[α -SiW₉O₃₄]·16H₂O (0.15 mmol, 400 mg), In(NO₃)₃·4.5H₂O (0.26 mmol, 100 mg), dodecanoic acid (0.25 mmol, 50 mg) and NaClO₄ (0.70 mmol, 100 mg) were dissolved in 4 mL H₂O in a 20 mL vial, and then the mixture was heated to 100 °C for 4 days and cooled to room temperature. The pH values before and after the reaction were 4.3 and 2.5 respectively. White prism crystals of **1-Gd** suitable for X-ray diffraction experiments were obtained by filtration, washed with H₂O and air-dried. Yield: about 52.6 % (based on Gd(NO₃)₃·6H₂O). IR (KBr pellet, *v*/cm⁻¹): 3254(vs), 1599(s), 1432(w), 1306(w), 1260(w), 993(w), 948(m), 832(m), 625(w).

Synthesis of $Na_2[Eu_2(H_2O)_{11}]_2[Eu_3(H_2O)_2(\alpha-SiW_{11}O_{39})_2]_2$: 69H₂O (1-Eu): The reaction process of 1-Eu is similar

to **1-Gd** except that Eu(NO₃)₃·6H₂O (0.22 mmol, 100 mg) was used to replace Gd(NO₃)₃·6H₂O (0.22 mmol, 100 mg). Yield: 48.3 % (based on Eu(NO₃)₃·6H₂O). IR: 3248(vs), 1623(vs), 993(w), 948(w), 826(w), 619(w).

Synthesis of Na₂[**Tb**₂(**H**₂**O**)₁₁]₂[**Tb**₃(**H**₂**O**)₂(α -SiW₁₁O₃₉)₂]₂·69H₂O (1-**Tb**): The reaction process of 1-**Tb** is similar to 1-Gd except that Tb(NO₃)₃·6H₂O (0.55 mmol, 250 mg) was used to replace Gd(NO₃)₃·6H₂O (0.22 mmol, 100 mg). Yield: 50.4% (based on Tb(NO₃)₃·6H₂O). IR: 3243(vs), 1618(vs),1416(w), 1008(w), 948(m), 832(w), 614(w). **Synthesis of Na**₂[**Dy**₂(**H**₂**O**)₁₁]₂[**Dy**₃(**H**₂**O**)₂(α -SiW₁₁O₃₉)₂]₂·69H₂O (1-**Dy**): The reaction process of 1-**Dy** is similar to 1-Gd except that Dy(NO₃)₃·6H₂O (0.65 mmol, 300 mg) was used to replace Gd(NO₃)₃·6H₂O (0.22 mmol, 100 mg). Yield: 58.5 % (based on Dy(NO₃)₃·6H₂O). IR: 3239(vs), 1618(vs),1397(w), 993(w), 924(w), 836(w), 700(w), 619(w).

Synthesis of Na₂[Sm₂(H₂O)₁₁]₂[Sm₃(H₂O)₂(α -SiW₁₁O₃₉)₂]₂·69H₂O (1-Sm): The reaction process of 1-Sm is similar to 1-Gd except that Sm(NO₃)₃·6H₂O (0.45 mmol, 200 mg) was used to replace Gd(NO₃)₃·6H₂O (0.22 mmol, 100 mg). Yield: 38.6 % (based on Sm(NO₃)₃·6H₂O). IR: 3233(vs), 1614(vs), 1427(w), 1255(w), 1144(w), 998(w), 924(m), 836(m), 640(w).

Synthesis discussion: The compounds **1-Ln** (Ln= Sm, Eu, Gd, Tb and Dy) were obtained from the reaction of Ln(NO₃)₃·6H₂O (Ln= Sm, Eu, Gd, Tb and Dy), Na₁₀[α -SiW₉O₃₄]·16H₂O, In(NO₃)₃·4.5H₂O and dodecanoic acid. We have tried to synthesize isostructural **1-Ln** (Ln = Y³⁺, La³⁺, Yb³⁺, Er³⁺) using light lanthanide Y³⁺, La³⁺ salts and heavy lanthanide Yb³⁺, Er³⁺ salts, but no analogous products were obtained. The acid environment (pH=2.5) provided by organic dodecanoic acid is one of the important factors for the syntheses of **1-Ln**. During the preparation of **1-Gd**, the pH value of the reaction solution is 3.5 without the presence of dodecanoic acid. But the pH can be lowered to 2.5 after the addition of tiny amounts of dodecanoic acid. So dodecanoic acid such as pyridin-4-bronic acid, toluene-4-sulfonic acid, and 1,3,5-benzenetricarboxylic acid as pH adjustor under the same conditions, unfortunately a large amount of unknown white powder were generated. The In(NO₃)₃·4.5H₂O also plays an important role in the formation **1-Gd**, though it is not found in the final product. Such metal salt may act as a mineralizer during the reaction. So we come to the conclusion that the dodecanoic acid and In(NO₃)₃·4.5H₂O are necessary for the self-assembly of **1-Ln**

Single-crystal structure analysis: Single-crystal X-ray diffraction data of **1-Gd** were collected on Bruker Apex Duo CCD diffractometer with a graphite-monochromatized Mo K α radiation ($\lambda = 0.71073$ Å) operating at 298 K. The structure of **1-Gd** was solved through direct methods and refined by full-matrix least-squares refinements based on F^2 adopting the SHELX-2014 program package.² The disordered solvent molecules in **1-Gd** were removed by the SQUEEZE program in PLATON.³ All non-H atoms were located with successive difference Fourier syntheses and refined anisotropically. The H atoms of the free water molecules and coordinated water molecule have not been included in the final refinement. Crystallographic data and structure refinements for **1-Gd** are summarized in Table S1. CCDC 1938608 contains supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <u>www.ccdc.cam.ac.uk/data_request/cif</u>.

Section 2: Additional table

Table S1 Crystal Data and Structure Refinement for 1-Gd.

	1-Gd	
Empirical formula	$Gd_{10}Na_2O_{263}Si_4W_{44}H_{69}$	
Formula weight	14097.17	
Crystal system	Monoclinic	
Space group	$P2_{1}/n$	
<i>a</i> (Å)	13.7404(18)	
<i>b</i> (Å)	26.426(3)	
<i>c</i> (Å)	29.898(4)	
α (°)	90	
β (°)	93.635(2)	
γ (°)	90	
$V(\text{\AA}^3)$	10834(2)	
Ζ	2	
<i>F</i> (000)	11052	
Crystal size / mm ³	0.22 ×0.19 ×0.14	
heta range / °	1.541 to 25.127	
Limiting indices	-16<=h<=16	
	-31<=k<=31	
	-32<=l<=35	
$\rho_{calcd}(g \text{ cm}^{-3})$	3.962	
Temperature (K)	298(2)	
$\mu(mm^{-1})$	26.383	
Refl. Collected	72640	
Independent relf.	19226	
Parameters	1154	

$R_{\rm int}$	0.0737
GOF on F ²	1.041
Final <i>R</i> indices $(I = 2\sigma(I))$	R_1 =0.0865, wR_2 =0.1978
R indices (all data)	$R_1 = 0.1277, wR_2 = 0.2291$

$$\begin{split} R_1 &= \sum ||F_o| - |F_c|| / \sum |F_o|. \ w R_2 = [\sum w (F_o^2 - F_c^2)^2 / \sum w (F_o^2)^2]^{1/2}; \ w = 1 / [\sigma^2 (F_o^2) + (xP)^2 + yP], \ P = (F_o^2 + 2F_c^2) / 3, \ where \ x = 0.132300, \ y = 0 \ \text{for 1-Gd}. \end{split}$$

Table S2 Unit cell parameters of 1-Eu, 1-Tb, 1-Dy a	and 1-Sm with isomorphic structures of 1-Gd
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1-Gd	$a = 13.7404(18)$ Å, $b = 26.426(3)$ Å, $c = 29.898(4)$ Å, $a = 90^{\circ}$, $\beta = 93.6^{\circ}$, $\gamma = 90^{\circ}$, $V = 10834(2)$ Å ³
1-Sm	$a = 14.69$ Å, $b = 26.10$ Å, $c = 29.67$ Å, $\alpha = 90$ °, $\beta = 95.60$ °, $\gamma = 90$ °, $V = 11324$ Å ³
1-Eu	$a = 14.70$ Å, $b = 26.21$ Å, $c = 29.92$ Å, $\alpha = 90^{\circ}$, $\beta = 95.49^{\circ}$, $\gamma = 90^{\circ}$, $V = 11476$ Å ³
1-Tb	$a = 13.90$ Å, $b = 26.51$ Å, $c = 30.01$ Å, $\alpha = 90^{\circ}$, $\beta = 93.83^{\circ}$, $\gamma = 90^{\circ}$, $V = 11034$ Å ³
1-Dy	$a = 14.54$ Å, $b = 26.28$ Å, $c = 30.05$ Å, $\alpha = 90^{\circ}$, $\beta = 95.12^{\circ}$, $\gamma = 90^{\circ}$, $V = 11434$ Å ³

Table S3 Comparison of the conductivity of **1-Gd** with those of some representative heteropolyoxometalates conducting materials.

Compounds	Conductivit	Condition	Reference
	y (S cm ⁻¹)	(Temp., RH)	
1-Gd	3.54×10^{-3}	85 °C, 98% RH	This work
$ \{ [W_{14}Ce^{IV}_{6}O_{61}] ([W_{3}Bi_{6}Ce^{III}_{3}(H_{2}O)_{3}O_{14}] [B-\alpha-BiW_{9}O_{33}]_{3})_{2} \}^{34-1} $	2.4×10^{-3}	25 °C, 90% RH	S4
$[Cu_3(\mu_3-OH)(H_2O)_3(atz)_3]_3 [P_2W_{18}O_{62}] \cdot 14H_2O$	4.4×10^{-6}	25 °C, 97% RH	S5
$[Co(bpz)(Hbpz)][Co(SO_4)_{0.5}(H_2O)_2(bpz)]_4[PMo^{VI}_8Mo^V_4V^{IV}_4$	1.5×10^{-3}	75 °C, 98% RH	S6
O ₄₂]·13H ₂ O			
$[Ce^{III}(H_2O)_6]\{[Ce^{IV}_7Ce^{III}_3O_6(OH)_6(CO_3)(H_2O)_{11}][(P_2W_{16}O_{59})]$	2.65×10^{-4}	100 °C, 75% RH	S7
3}16			
$Cu_6 (Trz)_{10}(H_2O)_4 [H_2SiW_{12}O_{40}] \cdot 8H_2O$	$1.84 imes 10^{-6}$	95 °C, 95% RH	S8
[H ₃ (3-PyBim) ₂][PMo ₁₂ O ₄₀]·3.5H ₂ O·CH ₃ CN·CH ₃ OH	3.34×10^{-3}	100 °C, 95% RH	S9
[H ₃ (3-PyBim) ₂][PMo ₁₂ O ₄₀]·4H ₂ O·CH ₃ CN	1.36×10^{-3}	100 °C, 95% RH	S10
${H[Ni(Hbpdc)(H_2O)_2]_2[PW_{12}O_{40}] \cdot 8H_2O}_n$	1.35×10^{-3}	100 °C, 95% RH	S11
$[M(H_2O)_8][H(H_2O)_{2.3}](HINO)_4[PXO_{40}]$ (M=Zn, Mn, Cu;	1.30×10^{-3}	100 °C, 95% RH	S12
X=W, Mo)			

Hatz = 3-amino-1, 2, 4-triazolate; H₂bpz = 3, 3', 5, 5'-tetramethyl-4, 4'-bipyrazole; Trz =1, 2, 4-triazole; 3-PyBim = 2-(3-pyridyl) benzimidazole; H₂bpdc = 2, 2'-bipyridyl-3,3'-dicarboxylic acid; HINO = *N*-oxide



Section 3: Additional structural figures and characterizations

Figure S1 View of the coordination environments of Gd³⁺ ions in 1-Gd.



Figure S2 Hexadecahedral cage-shaped heterometallic cluster {Gd₆W₈O₂₈} with a dimension of $7.0 \times 7.0 \times 6.0$ Å³.



Figure S3 View of a size of ${[Ln_3(H_2O)_3(\alpha-SiW_{11}O_{39})_2]_2}^{14-}$ polyanion along the *a* direction.



Figure S4 View of a size of $\{[Ln_3(H_2O)_3(\alpha-SiW_{11}O_{39})_2]_2\}^{14}$ polyanion along the *c* direction.



Figure S5 The assembly of tetrameric $\{[Ln_3(H_2O)_3(\alpha-SiW_{11}O_{39})_2]_2\}^{14}$ cluster.



Figure S6 (a) View of $\{[Ln_3(H_2O)_3(\alpha-SiW_{11}O_{39})_2]_2\}^{14}$ cluster linked by eight Gd^{3+} ions. (b and c) View of the onedimensional "H"-shaped channel running along *a* axis. (d) View of the 3D structure *via* alternately connection of the centrosymmetric 2D layers in …ABAB… mode.



Figure S7 View of the topology of the 3D framework for 1-Gd. Each $\{[Ln_3(H_2O)_3(\alpha-SiW_{11}O_{39})_2]_2\}^{14-}$ cluster function as eight-connected node.



Figure S8 SEM and EDS images of 1-Ln



Figure S9 The simulated and experimental PXRD patterns of 1-Ln.



Figure S10 IR spectra of 1-Ln.

In the IR spectra, the strong and wide broad bands in 3338.5-3182.6 cm⁻¹ can be attributed to the stretching vibrations of -OH of the coordination water, the sharp broad band in 1617.9 cm⁻¹ stems from the bending vibration of -OH of the coordination water, the bands at 942, 835 and 704 cm⁻¹ are attributed to the asymmetrical stretching vibrations of terminal W-O_t, corner-sharing W-O_b and edge-sharing W-O_c bands, respectively. (O_t: terminal O atom; O_b: μ_2 -O atom; O_c: μ_4 -O atom).



Figure S11 TGA curves of 1-Ln.



Figure S12 The simulated and variable-temperature experimental PXRD patterns of 1-Gd.



Figure S13 PXRD patterns of 1-Gd after being soaked in different concentrated HCl and NaOH aqueous for 24 hours.



Figure S14 PXRD patterns of 1-Gd after being soaked in different organic solvent for 24 hours. "EtOH = ethanol, DMF = N, N'-dimethylformamide, CH_2Cl_2 = dichloromethane, DMA= N, N'-dimethylacetamide, CH_3OH = methanol, CH_3CN = acetonitrile, CH_3COCH_3 = acetone"



Figure S15 (a) Plots of UV-vis absorption spectra of 1-Ln. (b)-(f) Plots of Kubelka-Munk function of 1-Ln band gaps.



Figure S16 N₂ and CO₂ sorption isotherms of 1-Gd at 77 and 298 K, respectively.



Figure S17 PXRD patters after water vapor adsorption and proton conduction for 1-Gd.



Figure S18 Arrhenius plot of the conductivity of 1-Gd.



Figure S19 The excitation spectra of 1-Ln: a) 1-Eu, b) 1-Tb, c) 1-Dy and d) 1-Sm.



Figure S20 The luminescence decay curves of (a) 1-Eu and (b) 1-Tb.



Figure S21 Frequency-dependent behavior of χ'_m and χ''_m for 1-Tb (a and b) and 1-Dy (c and d) in zero static field at 2-

20 K.

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