Inorganic Chemistry

Sandwich-Type Uranyl Phosphate–Polyoxometalate Cluster Exhibiting Strong Luminescence

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Cite This: Ino	rg. Chem. 2021, 60, 6790–6795	 Read Online	
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ABSTRACT: A pure inorganic uranyl phosphate-polyoxometalate of $Na_{17}{Na@[(SbW_9O_{33})_2(UO_2)_6(PO_3OH)_6]} \cdot xH_2O$ (abbreviated as $Na@U_6P_6$, with $x \approx 46$) featuring a sandwich-type structure was prepared using Keggin-type trilacunary [α -B-SbW_9O_{33}]⁹⁻ units as building blocks, which were formed in situ by SbCl₃ and Na_2WO_4 · $2H_2O$. Crystal structural analysis showed that six UO_2^{2+} cations and six PO_3OH²⁻ anions generated a wheel-like cluster unit with a Na⁺ center ($[Na@(UO_2)_6(PO_3OH)_6]^+$) that is stabilized by two [α -B-SbW_9O_{33}]⁹⁻ units. $Na@U_6P_6$ displayed a solid-state photo-luminescence quantum yield of 33% at 300 K. The temperature-dependent fluorescence emission spectra showed that $Na@U_6P_6$ has temperature increased from 200 to 300 K. These results suggest that such uranyl phosphate-polyoxometalate clusters could serve as potential temperature-sensitive molecular materials.



1. INTRODUCTION

The study of actinide complexes has received extensive attention in the past decade because of their potential applications in the nuclear fuel cycle.¹ Among the actinides, the contribution of U and its waste to environmental pollution are of great concern to scientists.² UO₂²⁺ is the most stable form of U and can coordinate with a variety of O/N/Scontaining ligands to form complexes with different properties; this propensity can be used in the storage and separation of radioactive waste. Polyoxometalates (POMs), defined as earlytransition-metal clusters (e.g., M = V, Nb, Ta, Mo, W) with their highest oxidation states, are a class of oxygen-rich multidentate inorganic ligands that have been widely used in various research fields.³ Previous investigations have found that linear UO2²⁺ combines easily with lacunary POMs containing polyoxo groups to form uranyl polyoxometalate clusters.² Trilacunary POMs are particularly suitable for chelating UO2²⁺ ions⁵ because the linear uranyl structure ($O=U=O^{2+}$) can easily coordinate with them by occupying their vacancy sites, thus making this an effective strategy for coordinating UO₂²⁺ ions.

Compared with the frequent reports on trilacunary POMbased 3d,⁶ 3d–4f,⁷ or 4f clusters,⁸ the synthesis of POM-based actinide clusters still remains a challenge,^{9,10} and the understanding of their structure–function relationship is limited. Since Pope and co-workers reported the first sandwich-type uranyl polyoxometalate $\{(UO_2)_2(PW_9O_{34})_2\}$ cluster in 1999,^{5a} only a few sandwich-type uranyl polyoxometalate clusters have been studied,^{5,11} and exploration of the potential applications of such complexes is especially scant. The uranyl ion has very good stability and attractive optical properties; ¹² its emission is derived from the highest occupied molecular orbital (HOMO) \rightarrow lowest unoccupied molecular orbital (LUMO) ($O_{2p} \rightarrow U_{5f}$) electron transition, ¹³ which exhibits no transition resistance. Therefore, uranyl ions possess strong, intrinsic luminescence. Unfortunately, in-depth studies on the luminescence properties of most reported uranyl polyoxometalate clusters have not been conducted; such studies could further reveal the versatility of these complexes.

Herein, a uranyl phosphate–polyoxometalate cluster with the formula $Na_{17}\{Na@[(SbW_9O_{33})_2(UO_2)_6(PO_3OH)_6]\}$. xH_2O (abbreviated as $Na@U_6P_6$, with $x \approx 46$) was obtained using in situ formed Keggin-type trilacunary POMs of $[\alpha$ -B- $SbW_9O_{33}]^{9-}$ as inorganic ligands. Structural analysis showed that $Na@U_6P_6$ is a pure sandwich-type inorganic metal cluster with a wheel-like $[Na@(UO_2)_6(PO_3OH)_6]^+$ unit as the sandwich linker. Fluorescence measurements revealed that $Na@U_6P_6$ has a solid-state photoluminescence quantum yield (PLQY) of 33%. In addition, the temperature-dependent fluorescence emission spectra showed that the emission intensity of $Na@U_6P_6$ decreased by 77% as the temperature increased from 200 to 300 K. This indicates that $Na@U_6P_6$ has temperature-sensitive fluorescence properties over the measured experimental conditions and that these uranyl polyox-

 Received:
 March 1, 2021

 Published:
 April 22, 2021





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ometalate clusters could be used as a potential temperaturesensitive material.

2. EXPERIMENTAL SECTION

Materials and Physical Measurements. All materials, reagents, and solvents were of commercial origin and were used as received. Caution!Although isotopically depleted uranium was used for all experiments described here, appropriate precautions are essential for handling all radioactive materials. IR spectra were recorded on a Nicolet iS50 spectrophotometer with pressed KBr pellets in the range of 4000–400 cm^{-1} . Powder X-ray diffraction data were recorded on a X'pert PRO powder X-ray diffractometer (Cu K α , λ = 1.54184 Å) at room temperature. Thermogravimetric analysis (TGA) was performed on a SDT-Q600 thermal analyzer with a heating rate of 10 °C· min⁻¹. Inductively coupled plasma emission spectroscopy (ICP-OES) data were obtained with a Thermo Fisher iCAP7000 spectrometer. Emission spectra were acquired at room temperature by a steady-state spectrometer (FLS-980, Edinburgh) with a 450 W xenon lamp. Timeresolved photoluminescence decay curves were obtained on the same spectrometer but with a μF^2 xenon lamp. The luminescence overall absolute quantum yield for a sample powder was collected by the same spectrometer using a 450 W xenon lamp and an integrating sphere (coating with a polytetrafluoroethylene-like material with a reflectance of >99% over the spectral range of 400-1500 nm). The temperature-dependent emission spectra were acquired by a steadystate spectrometer (FLS-980, Edinburgh).

Preparation of the Mixed Aqueous Solution of NaOAc·3H₂O (0.2 mol·L⁻¹) and Na₂WO₄·2H₂O (1.0 mol·L⁻¹). NaOAc·3H₂O (0.02 mol, 2.72 g) and Na₂WO₄·2H₂O (0.1 mol, 32.98 g) were dissolved in 100 mL of deionized water. The mixed aqueous solution of NaOAc·3H₂O (0.2 mol·L⁻¹) and Na₂WO₄·2H₂O (1.0 mol·L⁻¹) was obtained.

Preparation of an Aqueous Solution of SbCl₃ (2.0 mol·L⁻¹). The aqueous solution of SbCl₃ (2.0 mol·L⁻¹) was prepared by dissolving Sb₂O₃ (0.01 mol, 2.92 g) in 10 mL of HCl (37% aqueous solution).

Synthesis of Na17{Na@[(SbW9O33)2(UO2)6(PO3OH)6]}·xH2O (Na@U₆P₆, with $x \approx 46$). A total of 200 μ L of SbCl₃ (1.0 mol- L^{-1}) was added to the mixed aqueous solution (4.0 mL) of NaOAc· $3H_2O$ (0.2 mol·L⁻¹) and Na₂WO₄·2H₂O (1.0 mol·L⁻¹). The reaction solution was stirred for 1–2 min until clarified. A total of 200 μ L of $H_{2}PO_{4}$ (2.0 mol·L⁻¹) was added and stirred for 1–2 min. Then, the aqueous solution of 200 μ L of UO₂(NO₃)₂·6H₂O (2.0 mol·L⁻¹) was added to the above mixed solution and stirred for 10 min. The mixed solution was further heated in a water bath at 95 °C for 5 h. The resulting solution was filtered and left to slowly evaporate at room temperature, and then yellow-green crystals were obtained after 1 day. Yield: 29%, based on UO₂(NO₃)₂ 6H₂O. Anal. Calcd: Na, 5.14; Sb, 3.03; P, 2.31; W, 41.12; U, 17.75. Found: Na, 5.35; Sb, 2.99; P, 2.48; W, 41.50; U, 17.73. IR (KBr, cm⁻¹): 3436 (s), 2924 (s), 2854 (m), 1630 (s), 1466 (w), 1457 (w), 1383 (m), 1121 (w), 1051 (s), 1009 (m), 973 (m), 938 (m), 890 (s), 842 (s), 795 (w), 761 (w), 686 (w), 607 (w), 558 (w), 507 (m), 485 (w).

X-ray Crystallography. Data for compound Na@U₆P₆ were collected on an Agilent Technologies SuperNova Microfocus single diffractometer using Mo K α radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods, and non-H atoms were refined anisotropically by a least-squares method on F^2 using the OLEX2 program.¹⁴ Crystal data as well as details of the data collection and refinement for Na@U₆P₆ are summarized in Table S1. According to the charge balance, ICP-OES, and TGA, there were about 46 guest water molecules in compound Na@U₆P₆. Because of disorder, these guest water molecules were removed using SQUEEZE.¹⁵ CCDC 2059822 contains the supplementary crystallographic data for Na@U₆P₆ for this paper.

3. RESULTS AND DISCUSSION

Synthesis Strategy and Crystal Structure Analysis. Trilacunary POMs are particularly suitable for chelating UO₂²⁺ ions⁵ because the linear uranyl structure $(O=U=O^{2+})$ can easily coordinate with them by occupying their vacancy sites, thus making this an effective strategy for coordinating UO_2^{2+} ions. Compound Na@U₆P₆ was synthesized from the reaction of SbCl₃, NaOAc·3H₂O, Na₂WO₄·2H₂O, H₃PO₄, and $UO_2(NO_3)_2$ ·6H₂O in aqueous solution. During the reaction, the trilacunary $[\alpha$ -B-SbW₉O₃₃]⁹⁻ was formed in situ by SbCl₃ and Na₂WO₄·2H₂O. H₃PO₄ was involved in the coordination of compound Na@U₆P₆ in the form of monoprotonation in this acidic reaction system.

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Single-crystal analysis showed that $Na@U_6P_6$ crystallizes in the triclinic $P\overline{1}$ space group and displays a sandwich structure, with the largest diameter being 1.9 nm (Figure 1). The cluster



Figure 1. Polyhedral (a) and ball-and-stick (b) views of the uranyl phosphate – polyoxometalate cluster { $Na@[(Sb-W_9O_{33})_2(UO_2)_6(PO_3OH)_6]$ }¹⁷⁻. Colo code: Sb, gray; W, green; P, pink; U, yellow; O, red; Na, blue.

of $\{Na@[(SbW_9O_{33})_2(UO_2)_6(PO_3OH)_6]\}^{17-}$ can be viewed as a wheel-like uranyl phosphate cluster unit of $[Na@(UO_2)_6(PO_3OH)_6]^+$, which is sandwiched between two trilacunary $[\alpha$ -B-SbW_9O_{33}]^{9-} units (Figure 2). Six UO_2^{2+} cations and six PO_3OH^{2-} anions are alternately arranged around a Na^+ ion, forming the wheel-like $[Na@(UO_2)_6(PO_3OH)_6]^+$ cluster unit (Figure 2b). The two trilacunary $[\alpha$ -B-SbW_9O_{33}]^{9-} units cover the upper and lower faces of the wheel-like cluster unit in a centrally symmetric manner (Figure 2a,c) to form the sandwich-type anionic core



Figure 2. (a and c) Two centrally symmetric trilacunary $[\alpha$ -B-SbW₉O₃₃]⁹⁻ units. (b) Wheel-like cluster unit of $[Na@(UO_2)_6(PO_3OH)_6]^+$. (d) Sandwich-type $\{Na@[(Sb-W_9O_{33})_2(UO_2)_6(PO_3OH)_6]\}^{17-}$. (e) Na⁺ ion in the same plane as the six P atoms. (f) Alternating arrangement of six U and six P atoms. Colo code: Sb, gray; W, green; P, pink; U, yellow; O, red; Na, blue.

of ${Na@[(SbW_9O_{33})_2(UO_2)_6(PO_3OH)_6]}^{17-}$ (Figure 2d). The trilacunary $[\alpha$ -B-SbW_9O_{33}]^{9-} unit is a common inorganic building block that can coordinate with metal ions, such as UO_2^{2+} (Figure S1), through three lacunary sites to form POMbased metal complexes.¹⁶ Alternatively, the sandwich-type anionic core of $\{Na@[(SbW_9O_{33})_2(UO_2)_6(PO_3OH)_6]\}^{17-}$ can be viewed as two $[(\alpha$ -B-SbW₉O₃₃)(UO₂)₃]³⁻ units (Figure S1c) that are connected by six PO₃OH²⁻ units and a central Na⁺ ion. Interestingly, the templated Na⁺ ion is located in the center of the sandwich-type Na@U₆P₆ complex because it coordinates with the acyl O atom of UO_2^{2+} in the axial direction, which is in the same plane as the six P atoms (Figure 2f). The resulting uranyl phosphate polyoxometalate sandwich structure is significantly different from previously reported sandwich-type uranyl polyoxometalate clusters that comprise two lacunary POM units directly connected through UO₂²⁺ linkers.⁵ In addition, the anionic cluster core of {Na@[(Sb- $W_9O_{33}_2(UO_2)_6(PO_3OH)_6]^{17-}$ as a node can be extended into a purely inorganic three-dimensional metal frame if the peripheral Na⁺ ions act as linkers (Figure 3). All of the U



Figure 3. Pure inorganic three-dimensional metal frame of compound $Na@U_6P_6.$

atoms in this complex show a distorted pentagonal-bipyramidal configuration. Except for the two acyl O atoms in the axial direction, the other five-coordinated O atoms are in the same plane. Two are connected to $[\alpha$ -B-SbW₉O₃₃]⁹⁻ units by W–O–U bridges, and the other three are connected to P atoms by U–O–P bridges (Figure S2b). Notably, $[\alpha$ -B-SbW₉O₃₃]⁹⁻ was generated in situ by SbCl₃ and Na₂WO₄·2H₂O. The $[\alpha$ -B-SbW₉O₃₃]⁹⁻ unit was confirmed to have been formed in situ instead of $[PW_9O_{34}]^{9-}$ based on the following points: (a) the coordination mode of {SbO₃} (Figure S3a), and not that of {PO₄} (Figure S3b), was observed; (b) the bond lengths of 1.978(8)–2.002(8) and 1.494(8)–1.566(9) Å for Sb···O and P···O, respectively, are representative of those of $[\alpha$ -B-SbW₉O₃₃]⁹⁻ (Table S2); (c) the characteristic peaks of $[\alpha$ -B-SbW₉O₃₃]⁹⁻ appeared in the IR spectra of Na@U₆P₆ (Figure S4).

The results of bond-valence-sum (BVS) calculations for $Na@U_6P_6$ show that all of the W, Sb, P, and U atoms are in the 6+, 3+, 5+, and 6+ oxidation states, respectively (Table S3). Terminal atoms O54, O49, and O58 on the P1, P2, and P3 atoms, respectively, demonstrated BVS results of 1.38, 1.41, and 1.34, respectively, suggesting that they are all monoprotonated.

Luminescence Properties. The results of the solid-state luminescence measurements show that $Na@U_6P_6$ exhibits intense photoluminescence emissions with 441 nm excitation at 300 K. The luminescence spectrum (Figure 4a) is



Figure 4. (a) Solid-state fluorescence emission spectra of $Na@U_6P_6$ and $UO_2(NO_3)_2$ ·6H₂O under excitation at 441 nm. (b) Photoluminescence decay curve of $Na@U_6P_6$. (c) Emission map of spectra recorded from 100 to 300 K. (d) Variation trend of each emission peak of $Na@U_6P_6$.

characterized by five broad emission peaks from 450 to 650 nm with a maximum emission peak at 517 nm, which is attributable to uranyl ion emission from the triplet to singlet state.¹⁷ Additionally, four shoulders were noted at 496, 540, 565, and 590 nm. The spectrum shows a typical vibronic structure, resulting from the symmetrical vibration of the O= U=O bonds, corresponding to the electronic transitions of S₁₁ \rightarrow S₀₀ and S₁₀ \rightarrow S_{0 ν} ($\nu = 0-3$).¹⁸ In comparison with the emission peaks in the spectrum of UO₂(NO₃)₂·6H₂O, the five emission peaks of Na@U₆P₆ were red-shifted by varying degrees, which is probably because of the changes in the number of donor atoms in the equatorial plane of the U coordination sphere.^{19,20} Specifically, U⁶⁺ exhibits a hexagonal-bipyramidal geometry in the Na@U₆P₆ cluster.

The luminescence decay time of $Na@U_6P_6$ was measured at room temperature with excitation and emission bands at 441 and 517 nm, respectively. As shown in Figure 4b, the photoluminescence lifetime (τ) of Na@U₆P₆ was determined to be 121.90 μ s using the exponential decay functional equation $I = A \exp(-t/\tau)$, with a preexponential factor (A) of 4898. The emission colors of $Na@U_6P_6$ and $UO_2(NO_3)_2$. $6H_2O$ are both green, like that of UO_2^{2+} , under 365 nm UV irradiation (Figure S6a) and correspond to the $CIE_{x,y}$ coordinate values of (0.20, 0.66) and (0.20, 0.60), respectively. Compared with $UO_2(NO_3)_2 \cdot 6H_2O_1$, the values of Na@U₆P₆ significantly shifted toward the y coordinate (Figure S6b). Furthermore, the PLQY of solid-state Na@U₆P₆ was collected at room temperature with an excitation band at 441 nm. The PLQY of $Na@U_6P_6$ was 33%, which is higher than that of $UO_2(NO_3)_2 \cdot 6H_2O$ (27%). The luminescence of the uranyl ion is related to the type of complex that it is a part of, the presence of water molecules around the U⁶⁺ atom, counterbalance ions, and the solvent type because all of these affect the

vibration of the O=U=O double bonds.²¹ The greater the vibration of the O=U=O bonds, the greater the energy loss during the transition process, which negatively impacts the luminescence. In Na@U₆P₆, the central Na⁺ ion is coordinated with six acyl O atoms of six UO₂²⁺ ions in the axial direction, further stabilizing the O=U=O double bonds and enhancing the luminescence effects of Na@U₆P₆.

To evaluate the potential of $Na@U_6P_6$ in temperature sensing, the temperature-dependent emission spectra of Na@ U_6P_6 were obtained (Figure 4c,d) between 100 and 300 K. The temperature-dependent luminescent behavior of Na@ U_6P_6 is significantly different from that of $UO_2(NO_3)_2 \cdot 6H_2O_3$ (Figure S7). As presented in Figure 4c, the emission intensity of $Na@U_6P_6$ shows a small change over the temperature range 100–200 K, suggesting that $Na@U_6P_6$ has a weak temperature sensitivity in this temperature range. As the temperature rose to 300 K, the emission intensity of $Na@U_6P_6$ dropped sharply by 77% and showed a thermal sensitivity of $0.79\% \cdot K^{-1}$. This indicated that $Na@U_6P_6$ has a strong temperature sensitivity in the range 200-300 K. Normally, the fluorescence intensity decreases with an increase in the temperature because more nonradiative transitions occur. For Na@U₆P₆, the rapid decrease in the fluorescence intensity from 200 to 300 K may be attributed to the quenching effect of heavy metals on uranyl fluorescence.

4. CONCLUSION

In summary, a uranyl phosphate polyoxometalate cluster, Na@ U_6P_6 , was obtained, stabilized by two Keggin-type trilacunary $[\alpha$ -B-SbW₉O₃₃]⁹⁻ units formed in situ. Structural analysis showed that Na@U₆P₆ displayed a sandwich-type structure, in which six UO₂²⁺ ions and six PO₃OH²⁻ ions are templated by a Na⁺ ion to form a wheel-like cluster unit that is further sandwiched by two $[\alpha$ -B-SbW₉O₃₃]⁹⁻ units. Interestingly, Na@U₆P₆ exhibited a PLQY of 33% at room temperature, and its emission intensity decreased significantly when the temperature was increased from 200 to 300 K, indicating that Na@U₆P₆ has temperature-sensitive characteristics over the measured experimental conditions. This work suggests that uranyl phosphate polyoxometalate complexes could serve as luminescent materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c00622.

Tables and additional figures (PDF)

Accession Codes

CCDC 2059822 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, 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.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Grants 21871224, 21673184, 21721001, and 21901002) and the Open Project of the State Key Laboratory of Physical Chemistry of the Solid Surface of Xiamen University (Grant 201822).

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