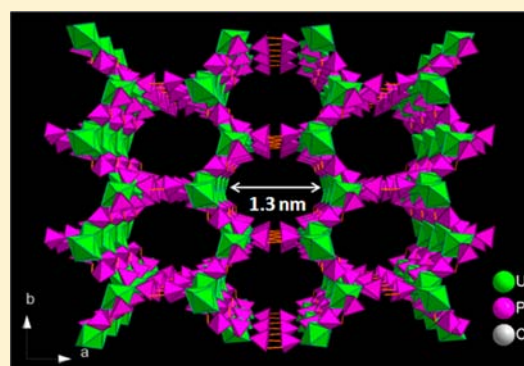


Syntheses and Structures of Uranyl Ethylenediphosphonates: From Layers to Elliptical Nanochannels

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Supporting Information

ABSTRACT: A family of uranium diphosphonates have been hydrothermally synthesized through the reaction of ethylenediphosphonic acid (EDP, H₄L) and uranyl nitrate/zinc uranyl acetate in the presence of organic templates, such as tetraethyl ammonium (NEt₄⁺), 4,4'-bipyridine (bipy), and 1,10-phenanthroline (phen). The UO₂²⁺ in UO₂(H₂O)(H₂L)- (EDP-U1) is equatorially five-coordinated by four phosphonate groups and one aqua ligand, forming a pentagonal bipyramid. Each EDP ligand is doubly protonated and chelates three UO₂²⁺, resulting in a layered structure. Compounds (NEt₄)₂(UO₂)₃(HL)₂(H₂L)·4H₂O (EDP-U2) and (H₂bipy)UO₂L (EDP-U3) have the same layered structure in which NEt₄⁺ and protonated bipy fill in the uranyl–phosphonate interlayers, respectively, and play a role to balance the negative charges. Different from that in EDP-U1, the UO₂²⁺ exists in the form of a UO₆ tetragonal bipyramid and is surrounded by four different EDP ligands in EDP-U2 and EDP-U3. (Hphen)₂(UO₂)₂(H₂L)₃ (EDP-U4) features a three-dimensional framework structure with large elliptical channels along the *c* axis (1.3 × 1.1 nm²). Monoprotonated phen molecules fill in these channels and hold together through strong π···π interactions. All of the four compounds have been characterized by IR and photoluminescent spectroscopy. Their characteristic emissions have been attributed as transition properties of uranyl cations. The ion-exchange study indicates that [Co(en)₃]³⁺ could partially replace the protonated phen molecules.



INTRODUCTION

Metal phosphonates have received great attention in coordination chemistry and material science due to their fantastic structural diversities and excellent physicochemical properties.¹ Uranyl phosphonates have shown potential applications in ion-exchange,² proton conductivity,³ chiral materials,⁴ and biomaterials.^{5,6} The linear UO₂²⁺ species, as the existing form of uranium(VI), is equatorially coordinated by 4–6 ligands, in the most cases, to form tetragonal-, pentagonal-, and hexagonal-bipyramidal geometries.^{7–11} It is precisely because of the generally inert nature of the two “yl” oxo atoms, 1-dimensional (1-D) and 2-dimensional (2-D) uranyl coordination assemblies are favored. However, by modulation and modification of the organic residues of phosphonate ligands, various uranyl phosphonate structures, including 1-D chains, ribbons,^{4,12–14} tubules,^{3,15–17} 2-D layers,^{18–22} and 3-dimensional (3-D) frameworks,^{22–26} have been isolated. It has been proved that the synthesis of 3-D uranium phosphonates is less successful compared with the low dimensional compounds.^{7,11} Various strategies have been adopted to isolate 3-D uranyl framework structures, including by introducing a second functional group, such as pyridine or a carboxylate-containing moiety, into the

ligands or incorporating transition-metal ions, thus leaving potentials as additional coordination sites. So far, the 3-D porous open-framework uranyl phosphonates have been rarely reported.^{4,27} Albrecht-Schmitt and co-workers recently described the synthesis of a heterobimetallic U^{VI}/Cd^{II} carboxyphosphonate, [Cd₃(UO₂)₆(PO₃CH₂CO₂)₆(H₂O)₁₃]·6H₂O, which features a rhombohedral channel structure with hydrated Cd(II) in a flower shape filled in the channels.²⁷ Two porous uranyl methylenediphosphonates have been synthesized and display channel structures of 1 × 1 nm² that are large enough to fill [Co(en)₃]³⁺ through an ion-exchange approach.⁴

It is worthy to note here that the templates with various sizes, shapes, and charges also play key roles in the construction of uranium phosphonates. In our recent work, N-containing ligands, such as pyridine or imidazole derivatives, have been widely utilized as either templates or coligands to guide the formation of uranyl phosphonates with chains, layers, as well as framework structures.^{21,22} Those results indicate the outstanding directing ability of the templates and encourage us

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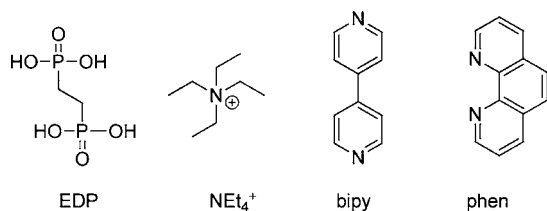
to further investigate the syntheses of uranyl hybrids by expanding the sorts of templates and phosphonic ligands. As an ongoing study, we choose ethylenediphosphonic acid (EDP, H_4L) as a new construction agent, which has never been used before in the synthesis of uranium phosphonates. Some templates were also adopted as structure-directing agents. The reason why we select EDP as a ligand is based on the following consideration: so far, the diphosphonic acids utilized in the synthesis of uranium compounds mainly consist of methylenediphosphonic acid (MDP), 1-hydroxy ethylidene-1,1-diphosphonic acid (HEDP), benzenedisphosphonic acids, and 4,4'-biphenylenbisphosphonic acid. A common feature of these ligands is their rigidity. The EDP ligand, however, with the $-CH_2CH_2-$ moiety as its backbone, is pretty flexible and has versatile coordination modes, which thus may result into new architectures. Herein, we report a family of uranyl ethylenediphosphonates, namely, $UO_2(H_2O)(H_2L)$ (EDP-U1), $(NEt_4)_2(UO_2)_3(HL)_2(H_2L)\cdot 4H_2O$ (EDP-U2), $(H_2bipy)UO_2L$ (EDP-U3), and $(Hphen)_2(UO_2)_2(H_2L)_3$ (EDP-U4) (NEt_4^+ = tetraethyl ammonium, bipy = 4,4'-bipyridine, and phen = 1,10-phenanthroline). Their crystal structures, correlations, discrepancies, as well as infrared spectroscopy, photoluminescence, and ion-exchange properties are studied.

EXPERIMENTAL SECTION

Caution! Standard procedures for handling radioactive material should be followed, although the uranyl compounds used in the lab contained depleted uranium.

Materials, Syntheses, and Characterization. All chemicals were purchased commercially and used without further purification. Ethylenediphosphonic acid was synthesized according to a previously reported procedure.²⁸ The ligand and organic templates are listed in Scheme 1. X-ray powder diffraction (XRD) data were collected on a

Scheme 1. Schematic Representation of the Ligands



D8 Focus (Bruker) diffractometer at 40 kV and 30 mA with monochromated $Cu K\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$) with a scan speed of $5^\circ/\text{min}$ and a step size of 0.02° in 2θ . Inductively coupled plasma (ICP) analyses and elemental analyses of C, H, and N were conducted on a Perkin-Elmer Optima 3300DV spectrometer and a Perkin-Elmer 2400 elemental analyzer, respectively. Energy-disperse spectroscopy (EDS) spectra were obtained by using a scanning electron microscope (Hitachi S-4800) equipped with a Bruker AXS XFlash detector 4010. All IR measurements were obtained using a Bruker TENSOR 27 Fourier transform infrared spectrometer. Samples were diluted with spectroscopic KBr and pressed into a pellet. Scans were run over the range of $400\text{--}4000 \text{ cm}^{-1}$. The fluorescence spectra were performed on a Horiba Jobin Yvon Fluorolog-3 fluorescence spectrophotometer, equipped with a 450 W Xe lamp as the excitation source and an iHR320 monochromator equipped with a liquid-nitrogen-cooled R5509-72 PMT as the detector.

Synthesis of EDP-U1. A mixture of $UO_2(NO_3)_2\cdot 6H_2O$ (40 mg, 0.1 mmol), ethylenediphosphonic acid (40 mg, 0.21 mmol), HNO_3 (65%, 1 drop), and deionized water (1.0 mL) was loaded into a 20 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and heated at 160°C for 2 days, and then cooled to room temperature. Yellow rodlike crystals were isolated. Yield 23 mg (48% based on

uranium); initial pH 0.5; final pH 1.5. Anal. Calcd (wt %) for $C_2H_8O_9P_2U$: C, 5.05; H, 1.69. Found: C, 5.34; H, 1.75.

Synthesis of EDP-U2. A mixture of $UO_2(NO_3)_2\cdot 6H_2O$ (40 mg, 0.1 mmol), ethylenediphosphonic acid (40 mg, 0.21 mmol), NEt_4OH (100 μL , 25% in water, 0.17 mmol), and deionized water (1.0 mL) was loaded into a 20 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and heated at 160°C for 2 days, and then cooled to room temperature. Yellow block-like crystals were isolated. Yield 19 mg (33% based on uranium); initial pH 1.0; final pH 1.5. Anal. Calcd (wt %) for $C_{22}H_{68}N_2O_{28}P_6U_3$: C, 15.46; H, 4.01; N, 1.64. Found: C, 15.64; H, 4.08; N, 1.71.

Synthesis of EDP-U3. A mixture of $Zn(UO_2)(OAc)_4\cdot 7H_2O$ (40 mg, 0.04 mmol), ethylenediphosphonic acid (20 mg, 0.1 mmol), 4,4'-bipyridine (20 mg, 0.13 mmol), and deionized water (1.0 mL) was loaded into a 20 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and heated at 160°C for 2 days, and then cooled to room temperature. Yellow rodlike crystals were isolated. Yield 15 mg (50% based on uranium); initial pH 2.5; final pH 2.5. Anal. Calcd (wt %) for $C_{12}H_{14}N_2O_8P_2U$: C, 23.47; H, 2.30; N, 4.56. Found: C, 23.58; H, 2.41; N, 4.72.

Synthesis of EDP-U4. A mixture of $Zn(UO_2)(OAc)_4\cdot 7H_2O$ (40 mg, 0.04 mmol), ethylenediphosphonic acid (40 mg, 0.21 mmol), phen (20 mg, 0.11 mmol), and deionized water (1.0 mL) was loaded into a 20 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and heated at 180°C for 2 days, and then cooled to room temperature. Yellow block-like crystals were isolated. Yield 18 mg (61% based on uranium); initial pH 2.0; final pH 1.5. Anal. Calcd (wt %) for $C_{15}H_{18}N_2O_{11}P_3U$: C, 24.57; H, 2.47; N, 3.82. Found: C, 24.73; H, 2.56; N, 3.98.

Other Experiments. Many attempts were made to synthesize new uranyl ethylenediphosphonates using other templates, but failed, such as 2,2'-bipyridine, 1,3,5-tri(1*H*-imidazol-1-yl)benzene, 1-phenyl-1*H*-imidazole, 1,4-di(1*H*-imidazol-1-yl)benzene, triethylamine, etc. Maybe the reaction conditions still needed to be optimized, including temperature, pH values, and starting material loading ratios.

X-ray Crystal Structure Determination. Suitable single crystals for title compounds were selected for single-crystal X-ray diffraction analyses. Crystallographic data were collected at 293 K on a Bruker Apex II CCD diffractometer with graphite monochromated $Mo-K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Data processing was accomplished with the SAINT program.²⁹ The structures were solved by direct methods and refined on F^2 by full-matrix least-squares using SHELXTL-97.³⁰ Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. All hydrogen atoms were placed by geometrical considerations and were added to the structure factor calculation. A summary of the crystallographic data for these title complexes is listed in Table 1. Selected bond distances and angles are given in Tables S1–S4 (Supporting Information).

RESULT AND DISCUSSION

Structure of EDP-U1. The asymmetric unit of EDP-U1 consists of one crystallographically unique uranyl cation, one ethylenediphosphonate ligand, and one aqua ligand (Figure 1). The UO_2^{2+} cation is equatorially coordinated by one aqua ligand and four $\mu\text{-O}$ atoms from four different phosphonate groups, thus forming a pentagonal-bipyramidal geometry, in which the $U(1)=O_{yl}$ distances are 1.771(6) and 1.778(6) \AA . Within the equatorial plane, the $U(1)-O(1w)$ bond length of 2.479(6) \AA is slightly longer than other four bonds ranging from 2.280(6) to 2.314(6) \AA . The bond angle of $O(1)=U(1)=O(2)$ is $178.6(3)^\circ$. The calculated bond-valence sum for $U(1)$ is 6.05, which is consistent with the formal valence of $U(VI)$.³¹ The diphosphonic acid serves as a tetradentate ligand but bridges three uranyl cations, in which P(1) and P(2) phosphonate groups coordinate to one uranium atom through O(3) and O(6) atoms. On the basis of the analyses of charge balance and P–O distances, O(5) and O(7) are protonated.

Table 1. Crystal Data and Structure Refinement for Title Uranyl Ethylenediphosphonates

compound	EDP-U1	EDP-U2	EDP-U3	EDP-U4
empirical formula	C ₂ H ₈ O ₉ P ₂ U	C ₂₂ H ₆₈ N ₂ O ₂₈ P ₆ U ₃	C ₁₂ H ₁₄ N ₂ O ₈ P ₂ U	C ₁₅ H ₁₈ N ₂ O ₁₁ P ₃ U
fw	476.05	1708.69	614.22	733.25
crystal system	monoclinic	triclinic	triclinic	monoclinic
space group	P2 ₁ /n	P $\bar{1}$	P $\bar{1}$	C2/c
a/Å	8.2346(7)	8.4769(8)	8.6012(12)	25.4936(10)
b/Å	5.6216(5)	9.7317(9)	9.7918(13)	11.6771(5)
c/Å	19.6698(16)	14.7070(15)	19.392(3)	13.4533(5)
α /deg	90	83.8480(10)	86.421(2)	90
β /deg	92.7100(10)	85.1580(10)	87.197(2)	93.6380(10)
γ /deg	90	89.3040(10)	84.558(2)	90
V/Å ³	909.53(13)	1202.0(2)	1621.2(4)	3996.9(3)
Z	4	1	4	8
T/K	293(2)	293(2)	293(2)	293(2)
λ (Mo K α)/Å	0.71073	0.71073	0.71073	0.71073
F(000)	856	804	1144	2776
ρ_{calcd} (Mg/m ³)	3.477	2.361	2.517	2.437
μ (Mo K α)/mm ⁻¹	18.225	10.367	10.256	8.429
R ₁ /wR ₂ (I > 2 σ (I)) ^a	0.0303/0.0757	0.0354/0.0903	0.0472/0.1051	0.0247/0.0600
R ₁ /wR ₂ (all data)	0.0325/0.0766	0.0387/0.0921	0.0713/0.1165	0.0315/0.0753

$$^a R_1 = \sum(\Delta F / \sum(F_o)); wR_2 = (\sum[w(F_o^2 - F_c^2)] / \sum[w(F_o^2)]^{1/2}, w = 1/\sigma^2(F_o^2).$$

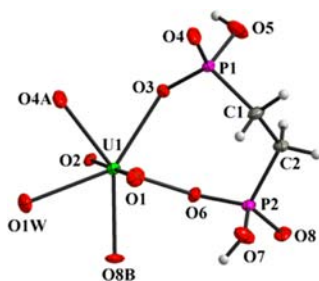


Figure 1. ORTEP representation of the asymmetric unit in **EDP-U1**. Thermal ellipsoids are drawn at the 50% probability level. Symmetry code A: $2 - x, -y, 1 - z$; B: $1.5 - x, -0.5 + y, 0.5 - z$.

The connections of pentagonal bipyramids and phosphonate groups result in a 2-D layered structure (Figure 2a). Within such a layer, two different types of uranyl pentagonal arrays can be observed along the *c* axis (A and B). These layers are stacked

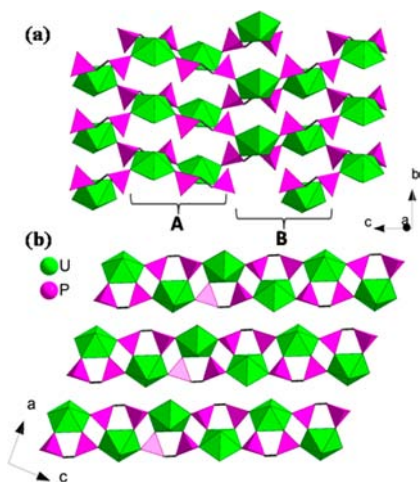


Figure 2. (a) The layered structure of **EDP-U1**, in which the chains of two different arrays A and B are highlighted. (b) The layers are stacked together along the *b* axis. Hydrogen atoms are omitted for clarity.

together along the *a* axis with a close interlayer distance of ~ 2.7 Å (Figure 2b).

Structures of EDP-U2 and EDP-U3. Both compounds crystallize in a triclinic space group $P\bar{1}$ and feature a layered structure in which the interlayers of uranyl phosphonates are filled by organic templates. As shown in Figure 3a, there are two crystallographically distinct uranium sites in **EDP-U2** and one and a half distinct ethylenediphosphonate groups in the asymmetric unit. U(1) locates in the inversion center and is in a tetragonal-bipyramidal environment defined by four μ -O atoms from four unique phosphonate groups in the equatorial plane (U–O: 2.282(5) and 2.291(5) Å), and two symmetrical “yl” oxo atoms (U=O(1): 1.790(5) Å). U(2) locates in a general position, and is also four-coordinated by μ -O atoms from different phosphonates in the equatorial plane (U–O: 2.265(5)–2.310(5) Å), leaving two axial atoms with an identical U=O bonding of 1.781(5) Å. The calculated bond-valence sum for the uranium atoms indicates 5.84 for U(1) and 5.89 for U(2). To keep the charge balance, O(5) and O(12) atoms are protonated, which are also reflected on the corresponding long bond distances of P(1)–O(5) (1.548(5) Å) and P(3)–O(12) (1.540(5) Å). Different from **EDP-U2**, the asymmetric unit in **EDP-U3** contains two crystallographically uranyl centers and two EDP ligands (Figure 3b). Both uranium ions are in a tetragonal-bipyramidal environment; within the equatorial plane, the average U–O bond length is 2.283(8) Å, which is very close to that in **EDP-U2** (2.286(9) Å), but slightly shorter than **EDP-U1** (2.380(6) Å). The U=O_{yl} distances are ranging from 1.776(7) to 1.792(7) Å with bond angles of 179.0(3)° and 179.5(3)°, respectively. The calculated bond-valence sum for the uranium atoms indicates 5.93 for U(1) and 5.89 for U(2). None of the oxygen atoms in the phosphonate groups are protonated; such character is largely different from **EDP-U2**.

EDP-U2 and **EDP-U3** structurally have a similar uranyl phosphonate layer (Figure 4). The ratio of the uranium center and the EDP ligand is 1:1. Two neighboring UO₆ tetragonal bipyramids are connected by two PO₃ moieties, resulting into a linear chain along the *b* axis, which is further bridged by the

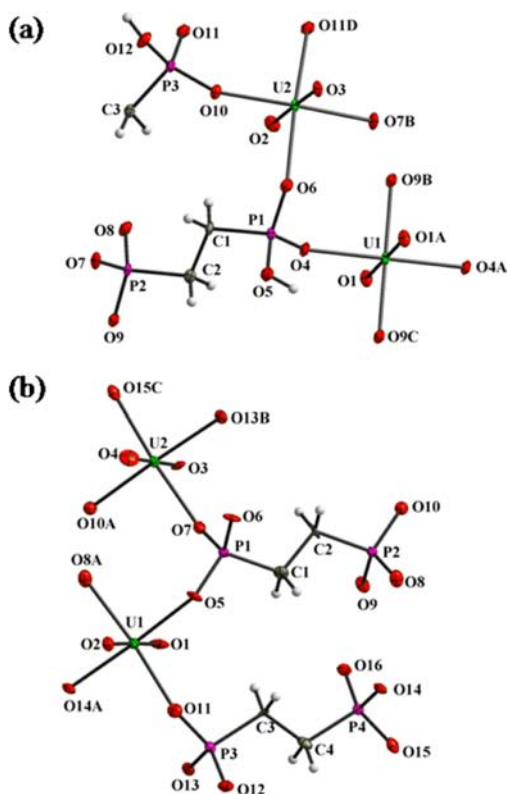


Figure 3. (a) ORTEP representation of the asymmetric unit in EDP-U2. Symmetry code A: $-x, 1 - y, 1 - z$; B: $-1 + x, y, z$; C: $1 - x, 1 - y, 1 - z$; D: $-x, 1 - y, 2 - z$. (b) ORTEP representation of the asymmetric unit in EDP-U3. Symmetry code A: $-1 + x, y, z$; B: $x, 1 + y, z$; C: $-1 + x, 1 + y, z$. All thermal ellipsoids are drawn at the 50% probability level.

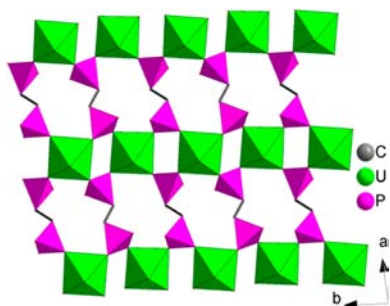


Figure 4. The common layer in EDP-U2 and EDP-U3. Hydrogen atoms are omitted for clarity.

flexible CH_2CH_2 groups along the a axis to form a 2-D layer perpendicular to the c axis. It is worthy to note here that the uranyl phosphonate layer in EDP-U2 is protonated and carries fewer charges in comparison with that in EDP-U3. This means that the $[\text{UO}_2\text{L}]$ anionic layer can hold its structure unchanged while adsorbing protons.

The uranyl phosphonate layers in EDP-U2 and EDP-U3 stack together with NEt_4^+ cations and protonated 4,4-bipyridine molecules filling in the interlayer spaces, respectively (Figures 5 and 6). The H_2bipy molecules spread in the ab plane and are held together by strong $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonding (2.768(6) Å) and $\pi\cdots\pi$ interactions (3.691 Å, Figure 7).

Structure of EDP-U4. Compound EDP-U4 crystallizes in the monoclinic space group $C2/c$ and features an interesting 3-D open-framework structure with nanosized channels projected

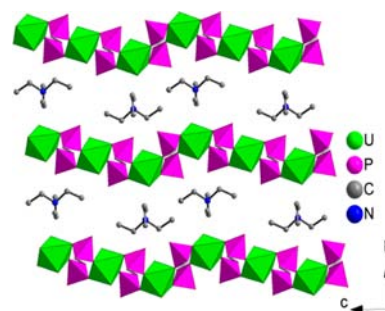


Figure 5. Structural view of EDP-U2 down the a axis. Hydrogen atoms are omitted for clarity.

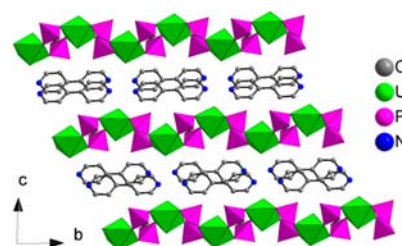


Figure 6. Structural view of EDP-U3 down the a axis. Hydrogen atoms are omitted for clarity.

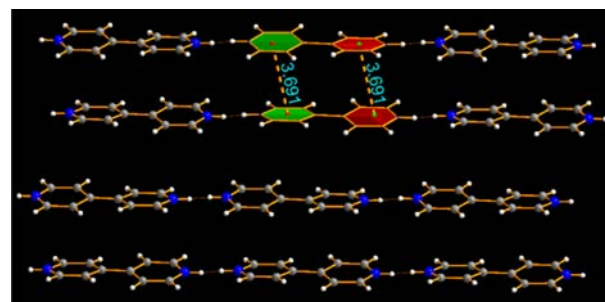


Figure 7. The orientation of the 4,4-bipy layer in EDP-U3. The organic templates are held together by strong hydrogen bonding and $\pi\cdots\pi$ interactions. Color code: C, grey; N, blue; H, white.

along the c axis. There are one crystallographically distinct uranyl center and one and a half crystallographically independent EDP ligands in its asymmetric unit (Figure 8). The diphosphonate ligand has two types of coordination mode: the one containing P(1) and P(2) groups is in a *cis*-mode and chelates three uranyl cations; the other one containing two P(3) groups is in a *trans*-mode and directly bridges two uranyl

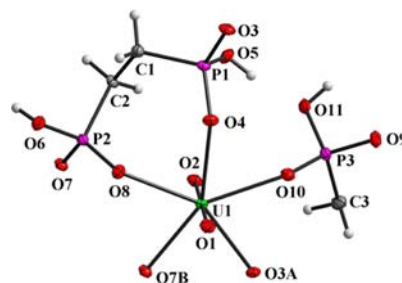


Figure 8. ORTEP representation of the asymmetric unit in EDP-U4. Thermal ellipsoids are drawn at the 50% probability level. Symmetry code A: $x, -y, -0.5 + z$; B: $0.5 - x, 0.5 - y, -z$.

cations. O(5), O(6), and O(11) are protonated based on the analysis of their P–O distances: P(1)–O(5) 1.577(4) Å, P(2)–O(6) 1.585(4) Å, and P(3)–O(11) 1.552(4) Å. The uranyl cation is coordinated by five oxygen atoms from four EDP ligands, forming a pentagonal-bipyramidal geometry. The bond distances in the uranyl unit are 1.775(4) and 1.778(4) Å for O(1) and O(2), respectively. The bond distances in the equatorial plane range from 2.337(4) to 2.404(4) Å. The average length of 2.377(6) Å is very close to that in EDP-U1 (2.380(6) Å). The valence of U(1) is 6.08 on the basis of the calculated bond-valence sum. The synergetic connection of UO_7 polyhedra by *cis*- and *trans*-EDP ligands results into a 3-D open-framework structure with nanosized channels in the [001] direction (Figure 9).

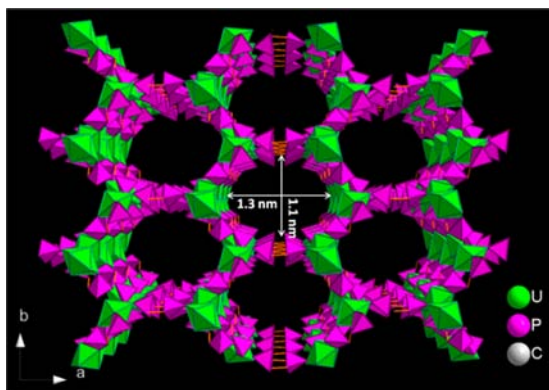


Figure 9. View of EDP-U4 projected along the *c* axis. Hydrogen atoms and protonated phen molecules are omitted for clarity.

The measured opening size is $1.3 \times 1.1 \text{ nm}^2$ (O...O distance) along the *c* axis, and the phen molecules reside in the channels. The channel size is slightly larger than those reported in UC1P2N-1 ($1.0 \times 1.0 \text{ nm}^2$ viewed along the *c* axis) and KUC1P2-1 ($1.0 \times 1.08 \text{ nm}^2$ viewed along the *c* axis).⁴ The overall uranyl phosphonate framework is anionic, so the N(1) site is protonated to balance the charge and form a strong hydrogen bonding interaction with O(9) of 2.731 Å. An orientation view of the phen molecules in the crystal is depicted in Figure 10a. The templates are stacked together along the [001] direction and held together by strong $\pi \cdots \pi$ interactions (3.570 and 3.656 Å, panels b and c in Figure 10).

Structure Discussion. As far as we know, methylenediphosphonic acid (MDP) is a dominant ligand for construction of uranyl phosphonates, which include layered and framework structures.^{4,32} In the known uranyl methylenediphosphonates, the phosphonate ligand appears in five coordination ways with PO_3 , adopting η_2 and η_3 coordination modes listed in Scheme 2 (labeled as black). Three of the manners take a closed circle fashion with 0, 1, and 2 uranium atoms appending. The other two assume an open circle mode, one of which is diprotonated, the other connects to two uranium atoms. No matter what kind of mode it adopted, the core is in an open or closed eight-membered ring and its shape remains unchanged. In contrast, the ethylenediphosphonate ligand is more flexible as a result of the soft P–CH₂CH₂–P moiety. On the basis of the analysis of the four uranyl complexes presented in this work, the EDP ligand has *cis*- and *trans*-coordination fashions (two of which are in *cis*-mode and four are in *trans*-mode). It is noted that only one η_2 coordination mode of the PO_3 group has been observed. The phosphonate groups prefer to be more likely

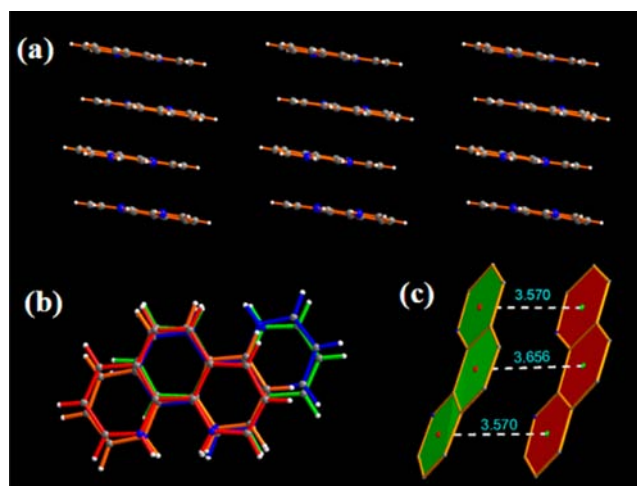
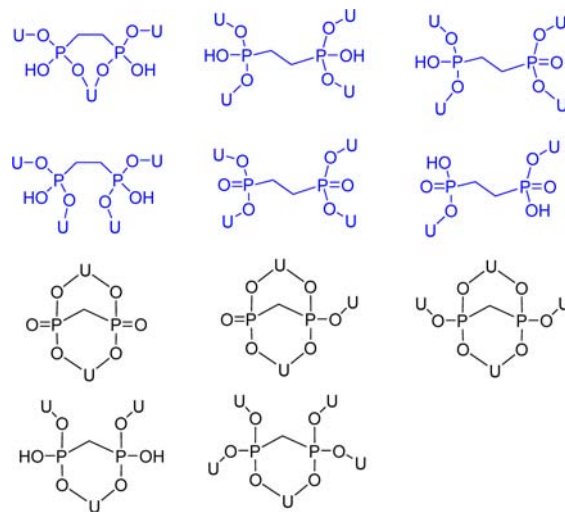


Figure 10. (a) A distribution view of the phen molecules in the crystal (down the *ac* plane). (b) A view of the phen molecules within a single channel (along the *c* axis). (c) A view of $\pi \cdots \pi$ stacking interactions of the phen molecules. Color code: C, grey; N, blue; H, white.

Scheme 2. Summary of Coordination Modes in Uranyl Ethylenediphosphonate (Labeled as Blue, This Work) and Uranyl Methylenediphosphonate (Labeled as Black, Checked from CCDC)



protonated either in one side or in both sides, whereas it hardly happens to MDP. Future work will be focused on modulation of synthetic conditions to enrich the structures of uranyl ethylenediphosphonates.

Ion-Exchange Study. The large channels and the protonated phen molecules suggest EDP-U4 to be a potential candidate for cation exchange. Thus, the ion-exchange capacity of EDP-U4 has been investigated. Typical ion-exchange experiments were performed as follows: synthesized single crystals were placed in 1 mL of 0.1 M solutions of $\text{Co}(\text{en})_3\text{Cl}_3$ with a pH of 2.0 adjusted by hydrochloric acid. The mixture was placed at room temperature without disturbing for 24 h. The exchanged products were then isolated in air by filtration and washed with deionized water. As seen from SEM images (Figure S1, Supporting Information), the morphology of single crystals of EDP-U4 could be basically maintained after $\text{Co}(\text{en})_3^{3+}$ exchanging for 6 h. The crystallinity was then destroyed when standing for 24 h. This can be further

confirmed by the powder X-ray diffraction (PXRD) patterns (Figure S3, Supporting Information), which show primary diffraction peaks after ion exchanging for 6 h, and the loss of all peaks, which continued for 24 h. The exchanging amount of protonated phen by $\text{Co}(\text{en})_3^{3+}$ was about 60% given by EDX (Figure S2, Supporting Information) and ICP analyses. The reason why the framework collapsed may lie in the fact that larger channels are less stable compared with small ones (such as UC1P2N-1, channel size of $1.0 \times 1.0 \text{ nm}^2$).

IR Spectroscopy. The synthesized uranyl ethylenediphosphonates were characterized by IR spectra (Figure 11).

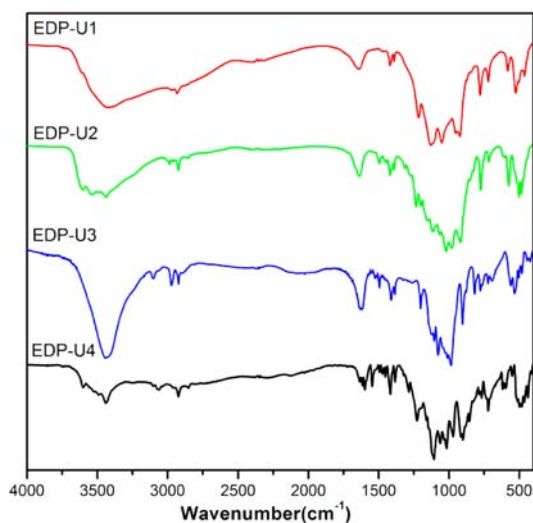


Figure 11. Infrared spectra for EDP-U1, -U2, -U3, and -U4.

The stretching and bending vibrations of H_2O are indicated around 3600 and 1640 cm^{-1} , respectively. The peaks around 2970 , 2880 , and 1420 cm^{-1} are attributed to the CH_2 stretching modes. The asymmetric and symmetric stretching modes of $\text{U}=\text{O}$ are observed from about 780 to 920 cm^{-1} . The bands locating about 970 cm^{-1} and in the low wavenumber region from 770 to 550 cm^{-1} are dominated by the $\text{O}-\text{P}-\text{O}$ bending and $\text{P}-\text{C}$ stretching vibrations. It is clear that the spectra of EDP-U2, EDP-U3, and EDP-U4 exhibit an additional vibration peak around 1500 cm^{-1} compared to EDP-U1, which is due to the stretching vibrations of the organic templates.

Photoluminescent Properties. The photoluminescent properties of these compounds were studied, and the spectra are illustrated in Figure 12. They all exhibit characterized emission from UO_2^{2+} , which usually consists of several emission peaks. Five peaks are observed in the spectra for all the title complexes: 484 , 501 , 523 , 546 , and 572 nm for EDP-U1; 474 , 491 , 512 , 535 , and 560 nm for EDP-U2; 493 , 504 , 526 , 548 , and 574 nm for EDP-U3; and 481 , 497 , 519 , 541 , and 566 nm for EDP-U4. These emission peaks correspond to the electronic and vibronic transitions of $S_{11}-S_{00}$ and $S_{10}-S_{0v}$ ($v = 0-4$), which are related to the symmetric and antisymmetric vibrational modes of the uranyl cation. Compared to the benchmark compound $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$,²² these compounds are red shifted by a value of 13 nm (EDP-U1), 2 nm (EDP-U2), 16 nm (EDP-U3), and 9 nm (EDP-U4). The spectral shift may originate from the influence of equatorial ethylenediphosphonate and organic templates.

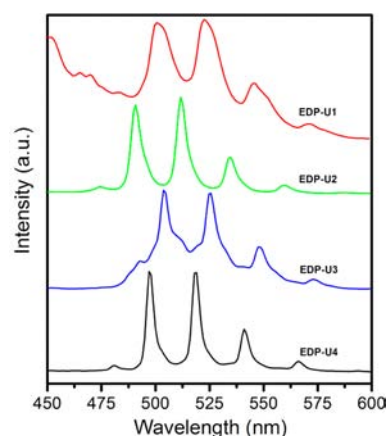


Figure 12. Emission spectra of EDP-U1, -U2, -U3, and -U4.

CONCLUSION

In summary, we have synthesized a series of uranyl phosphonates by using ethylenediphosphonic acid as the ligand for the first time. EDP-U1 is a template-free assembly with a layered structure formed by UO_7 pentagonal bipyramids and ethylenediphosphonate groups. EDP-U2 and EDP-U3 are also present as layered structures, but with the U atom in a UO_6 tetragonal-bipyramidal geometry. NET_4^+ and protonated bipy exist between the interlayers of EDP-U2 and EDP-U3 as the counterions, respectively. The 3-D framework of EDP-U4 is featured by one-dimensional large elliptical channels with the opening of $1.3 \times 1.1 \text{ nm}^2$, in which protonated phen can be partially exchanged by $\text{Co}(\text{en})_3^{3+}$. Photoluminescent studies reveal that all of the uranyl ethylenediphosphonates exhibit a characteristic green light emission of uranyl centers. This work demonstrates the success of construction of new uranyl phosphonates by the flexible alkyl diphosphonate ligand and encourages us to further expand the kinds of flexible organic ligands to enrich structural diversities of uranyl complexes in the near future.

ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic CIF files, selected bond lengths and angles, EDX, SEM, and PXRD patterns. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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