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Syntheses and Structures of a Series of Uranyl Phosphonates and Sulfonates: An Insight into Their Correlations and Discrepancies

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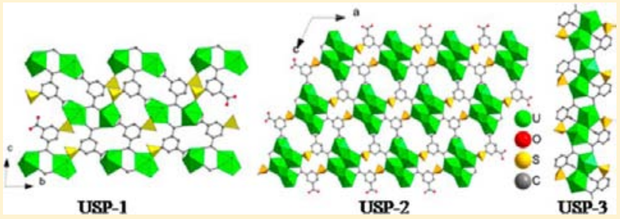
S *Supporting Information*



ABSTRACT: Six uranyl phosphonates and sulfonates have been hydrothermally synthesized, namely, $(H_2tib)[(UO_2)_3(PO_3C_6H_5)_4]\cdot 2H_2O$ (**UPhP-1**), $Zn(pi)_2(UO_2)(PO_3C_6H_5)_2$ (**UPhP-2**), $Zn(dib)(UO_2)(PO_3C_6H_5)_2\cdot 2H_2O$ (**UPhP-3**), $(HTEA)[(UO_2)(5\text{-}SP)]$ (**USP-1**), $(Hdib)_2[(UO_2)_2(OH)(O)(5\text{-}SP)]$ (**USP-2**), and $Zn(phen)_3(UO_2)_2(3\text{-}SP)_2$ (**USP-3**) (tib = 1,3,5-tri(1H-imidazol-1-yl)benzene, pi = 1-phenyl-1H-imidazole, dib = 1,4-di(1H-imidazol-1-yl)benzene, TEA = triethylamine, phen = 1,10-phenanthroline, 5-SP = 5-sulfoisophthalic acid, and 3-SP = 3-sulfoisophthalic acid). **UPhP-1** has been determined to be a layered structure constructed by UO_7 pentagonal bipyramids, UO_6 octahedra, and phenylphosphonates. Protonated tib plays a role in balancing the negative charge and holding its structure together. **UPhP-2** is made up of UO_6 octahedra, ZnO_2N_2 tetrahedra and PO_3C tetrahedra in phenylphosphonates, forming a 1D assembly, which is stabilized by chelate phen ligand. Further connection of such chainlike structure via dib yields a 2D layered architecture of **UPhP-3**. Although sulfonate group possesses similar tetrahedral structure as the phosphonate group, a unidentated coordination mode is only found in this work. UO_7 pentagonal bipyramids are linked by 5-SP to form the layered assembly of **USP-1**. **USP-2** also consists of the same sulfonate ligand, but features tetranulear uranyl clusters. Similarly, protonated TEA and dib molecules enable stabilization of their structures, respectively. Formed by dinuclear uranyl cluster and 3-SP ligand, **USP-3** appears as a 1D arrangement, in which $Zn(phen)_3$ acts as the counterion to compensate the negative charge. All of these compounds have been characterized by IR and photoluminescent spectroscopy. Their characteristic emissions have been attributed as transition properties of uranyl cations.

INTRODUCTION

In recent years, the class of uranyl phosphonates has been developed into an important member of uranium organic coordination polymer family due to their fantastic structural diversities and excellent physicochemical properties. Uranyl phosphonates have shown potential applications in ion-exchange,[1,2] proton conductivity,[3] chiral materials,[4] and biomaterials.[5,6] The UO_2^{2+} species, as the dominating state of uranium, 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, 1D and 2D uranyl coordination assemblies are favored. However, by modulation and modification of the organic residues of phosphonate ligands, various uranyl phosphonate structures including 1D chains, ribbons[4,12−14] or tubules,[3,15−17] 2D layers,[18−22] and even 3D frameworks[22−26] have been isolated. In contrast with phosphonate, sulfonate group displays a similar geometry but with lower charge and weaker coordination ability, therefore usually adopts η^1 and η^2 coordination modes.[27] Such character is different from phosphonates functionalizing in uranyl networks, which generally adopt η^2 and/or η^3 coordination modes. Compared with metal phosphonates, studies of sulfonate coordination polymers are considerably less, not to mention the actinide sulfonates. To increase the coordination ability of sulfonate ligands in construction of new uranyl hybrid materials, a synergistic functional group such as hydroxyl or carboxylate group is usually attached to the ligand.[28−35] For example, Thuéry synthesized a family of uranyl and heterometallic complexes using 2-, 3-, and 4-sulfobenzoic, and 4,5-dihydroxy-1,3-benzenedisulfonic acids.[33−35] Accordingly, 3- and 5-sulfoisophthalic acids with two carboxylate groups, that would construct more possible structures and further extend the structural diversities of uranyl sulfonates, arise our interest. In addition, apart from the important roles played by cooperative functional groups, structural directing agents or templates also play a key role in construction of uranyl compounds. In our recent work, imidazole-based complexes were utilized either as templates or coligands to guide the formation of a series of uranyl diphosphonates, with chains, layers, as well as framework

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structures.[21,22] Those results exhibit the outstanding directing ability of imidazole-based species, and encourage us to further investigate the syntheses of uranyl hybrids by expanding the sorts of imidazole-based template complexes and modulating the organic ligands.

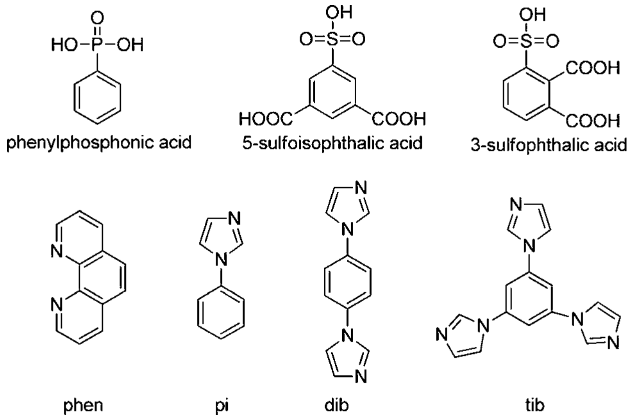
In this article, six uranyl phosphonates and sulfonates, $(H_2tib)[(UO_2)_3(PO_3C_6H_5)_4]\cdot 2H_2O$ (**UPhP-1**), $Zn(pi)_2(UO_2)(PO_3C_6H_5)_2$, (**UPhP-2**) $Zn(dib)(UO_2)(PO_3C_6H_5)_2\cdot 2H_2O$ (**UPhP-3**), $(HTEA)[(UO_2)(5\text{-}SP)]$ (**USP-1**), $(Hdib)_2[(UO_2)_2(OH)(O)(5\text{-}SP)]$ (**USP-2**), and $Zn(phen)_3(UO_2)_2(3\text{-}SP)_2$ (**USP-3**) (tib =1,3,5-tri(1H-imidazol-1-yl)benzene, pi =1-phenyl-1H-imidazole, dib =1,4-di(1H-imidazol-1-yl)benzene, TEA = triethylamine, phen =1,10-phenanthroline, 5-SP = 5-sulfoisophthalic acid, 3-SP = 3-sulfoisophthalic acid) have been prepared based on phenylphosphonate, and sulfoisophthalate ligands. Their crystal structures, correlations, discrepancies, as well as infrared spectroscopy and photoluminescence 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 and Syntheses. All chemicals were purchased commercially and used without further purification. Template tib was synthesized according to the documented procedures.[36] The phenylphosphonate and sulfonate ligands, as well as the corresponding templates are listed in Scheme 1. Elemental analyses of C, H, N, and S in the solid samples were performed with a VarioEL analyzer. 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 400−4000 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 a monochromator iHR320 equipped with a liquid-nitrogen-cooled R5509−72 PMT as detector.

Scheme 1. Schematic Representation of the Ligands



Synthesis of UPhP-1. A mixture of $(UO_2)(OAc)_2\cdot 2H_2O$ (40 mg, 0.1 mmol), phenylphosphonic acid (20 mg, 0.13 mmol), tib (20 mg, 0.07 mmol), and deionized water (1.0 mL) was loaded into a 20 mL Teflon-lined stainless steel autoclave (pH 3.0). 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 (26% based on uranium). Anal. Calcd (wt %) for $C_{39}H_{32}N_6O_{20}P_4U_3$: C, 26.86; H, 1.84; N, 4.82. Found: C, 27.08; H, 1.98; N, 4.58.

Syntheses of UPhP-2 and UPhP-3. A mixture of $Zn(UO_2)(OAc)_4\cdot 7H_2O$ (40 mg, 0.04 mmol), phenylphosphonic acid (20 mg, 0.13 mmol), pi (20 mg, 0.17 mmol for **UPhP-2**), or dib (20 mg, 0.1 mmol for **UPhP-3**), and deionized water (1.0 mL) was loaded into a 20 mL Teflon-lined stainless steel autoclave (pH 2.0 and 2.5, respectively). The mixture was heated at 160 °C for 2 days, and then cooled to room temperature. Yellow rodlike crystals were isolated, yield 17 mg and 14 mg, respectively (46% and 40% based on uranium). Anal. Calcd (wt %) for $C_{30}H_{26}N_4O_8P_2UZn$ (**UPhP-2**): C, 38.47; H, 2.78; N, 5.98. Found: C, 39.03; H, 2.81; N, 6.11. For $C_{24}H_{20}N_4O_{10}P_2UZn$ (**UPhP-3**): C, 32.37; H, 2.25; N, 6.29. Found: C, 33.24; H, 2.36; N, 6.15.

Synthesis of USP-1. A mixture of $(UO_2)(OAc)_2\cdot 2H_2O$ (40 mg, 0.1 mmol), sodium 3,5-dicarboxybenzenesulfonate (54 mg, 0.2 mmol), TEA (20 μL, 0.14 mmol) and deionized water (3.0 mL) was loaded into a 20 mL Teflon-lined stainless steel autoclave (pH 3.5). The autoclave was sealed and heated at 160 °C for 2 days, and then cooled to room temperature. Yellow rhombic plate crystals were isolated, yield 20 mg (32% based on uranium). Anal. Calcd (wt %) for $C_{14}H_{19}NO_{19}SU$: C, 27.30; H, 3.09; N, 2.27; S, 5.20. Found: C, 27.78; H, 3.15; N, 2.14; S, 5.12.

Synthesis of USP-2. A mixture of $Zn(UO_2)(OAc)_4\cdot 7H_2O$ (40 mg, 0.04 mmol), sodium 3,5-dicarboxybenzenesulfonate (27 mg, 0.1 mmol), dib (20 mg, 0.1 mmol) and deionized water (1.0 mL) was loaded into a 20 mL Teflon-lined stainless steel autoclave (pH 3.5). The autoclave was sealed and heated at 160 °C for 2 days, and then cooled to room temperature. Yellow rodlike crystals were isolated, yield 11 mg (45% based on uranium). Anal. Calcd (wt %) for $C_{32}H_{28}N_8O_{14}SU_2$: C, 30.55; H, 2.23; N, 8.92; S, 2.55. Found: C, 31.26; H, 2.31; N, 8.79; S, 2.46.

Synthesis of USP-3. A mixture of $Zn(UO_2)(OAc)_4\cdot 7H_2O$ (40 mg, 0.04 mmol), 3-SP (100 μL, 0.2 mmol), phen (20 mg, 0.11 mmol) and deionized water (3.0 mL) was loaded into a 20-mL Teflon-lined stainless steel autoclave (pH 1.5). The autoclave was sealed and heated at 160 °C for 2 days, and then cooled to room temperature. Yellow rodlike crystals were isolated, yield 12 mg (39% based on uranium). Anal. Calcd (wt %) for $C_{52}H_{32}N_6O_{19}S_2U_2Zn$: C, 37.81; H, 1.94; N, 5.09; S, 3.88. Found: C, 38.05; H, 2.03; N, 5.14; S, 3.64.

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*α* radiation (λ = 0.71073 Å). Data processing was accomplished with the *SAINT* program.[37] The structures were solved by direct methods and refined on F^2 by full-matrix least-squares using *SHELXTL-97*.[38] 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 Table S1 of the Supporting Information.

■ RESULT AND DISCUSSION

Structure of UPhP-1. **UPhP-1** comprises a 2D layered structure. There are three crystallographically distinct uranium atoms and four distinct phenylphosphonate groups in the asymmetric unit (Figure 1a). U(1) is in the octahedral environment defined by four bridging oxygen (μ-O) atoms (O(7), O(16), O(17), and O(18)) from four unique phenylphosphonate groups in the equatorial plane (U−O: 2.221(12)−2.287(12) Å), and two *yl* oxo atoms (U═O: 1.758(12) and 1.775(12) Å). U(2) and U(3) are five-coordinated by three μ-O atoms and two tribridging oxygen (μ_3-O) atoms from four distinct phenylphosphonates in the equatorial plane (U−O: 2.254(12) − 2.559(12) Å), leaving two axial atoms (U═O: 1.745(13) − 1.765(12) Å), resulting in pentagonal bipyramidal geometry. Such U(2)- and U(3)-centered pentagonal bipyramids connect each other into a dimer via edge-sharing. The calculated bond-valence sum for the uranium atoms indicates 6.13 for U(1), 6.14 for U(2) and

Table 1. Crystal Data and Structure Refinement for Synthesized Uranyl Phosphonates and Sulfonates

compound	UPhP-1	UPhP-2	UPhP-3	USP-1	USP-2	USP-3
CCDC	916 425	916 426	916 427	916 428	916 429	916 430
empirical formula	$C_{39}H_{32}N_6O_{20}P_4U_3$	$C_{30}H_{26}N_4O_8P_2UZn$	$C_{24}H_{20}N_4O_{10}P_2UZn$	$C_{14}H_{19}NO_9SU$	$C_{32}H_{28}N_8O_{14}SU_2$	$C_{52}H_{32}N_6O_{19}S_2U_2Zn$
F_w	1742.68	935.89	889.78	1230.78	1256.74	1650.39
cryst syst	triclinic	triclinic	monoclinic	triclinic	monoclinic	triclinic
space group	$P\overline{1}$	$P\overline{1}$	$P2_1/n$	$P\overline{1}$	$P2_1/n$	$P\overline{1}$
a/Å	9.7096(12)	10.4332(6)	13.1880(11)	9.2047(7)	13.6408(9)	12.8625(12)
b/Å	10.6095(14)	16.2774(10)	10.4948(9)	13.1351(9)	20.8488(13)	13.1683(13)
c/Å	14.018(3)	20.1860(12)	21.5361(18)	16.0557(11)	13.9140(8)	17.2155(17)
α/°	101.815(3)	71.3210(10)	90	84.2900(10)	90	72.216(2)
β/°	93.434(3)	82.4270(10)	95.9990(10)	83.1800(10)	115.9900(10)	71.658(2)
γ/°	117.157(2)	79.9300(10)	90	86.8280(10)	90	71.0660(10)
V/Å^3	1238.0(3)	3186.9(3)	2964.4(4)	1916.0(2)	3556.9(4)	2550.0(4)
Z	1	4	4	4	4	2
T/K	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
λ (Mo Kα), Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
F(000)	804	1800	1696	1160	2352	1568
ρ_{calcd} (Mg/m^3)	2.337	1.951	1.994	2.133	2.347	2.149
μ (Mo Kα), mm^{-1}	9.998	5.984	6.433	8.625	9.236	6.971
R_1/wR_2 ($I > 2\sigma(I)$)[a]	0.0418/0.0980	0.0444/0.0998	0.0308/0.0681	0.0496/0.1092	0.0400/0.0637	0.0311/0.0622
R_1/wR_2 (all data)	0.0445/0.1000	0.0662/0.1154	0.0468/0.0752	0.0759/0.1227	0.0744/0.0738	0.0456/0.0685

U(3). These values are consistent with the formal valence of U(VI).[39] All of the four phenylphosphonate groups are bridged to three unique uranyl cations. Two of the phenylphosphonate groups link the uranyl dimer through edge-sharing. The connection between the dimer pentagonal bipyramids and phenylphosphonates produces a chain, which is joined by U(1)-centered octahedra to form the layered structure of **UPhP-1** (Figure 1b). Such layers are stacked directly on top of each other (AA stacking) to give rise to a 3D supramolecular architecture (Figure 1c). Protonated tib molecules lie between the layers to hold the structure and compensate the negative charge.

Structure of UPhP-2. Single crystal X-ray diffraction study reveals that **UPhP-2** crystallizes in the triclinic space group $P\overline{1}$. The asymmetric unit consists of two zinc atoms, four phenylphosphonate groups and four pi molecules (Figure 2a). Both of the uranium atoms are octahedrally coordinated by two *yl* oxo atoms and four equatorial μ-O atoms from four distinct phenylphosphonates. The valence of uranium atoms is 5.94 for U(1) and 5.98 for U(2) based on calculated bond-valence sum. This is in agreement with the formal valence of U(VI).[39] Two zinc atoms are in tetrahedral coordination defined by two μ-O atoms and two N atoms, which are from two phenylphosphonates and two pi molecules, respectively. All of the phenylphosphonate groups coordinate to two uranyl centers and one zinc atoms through sharing oxygens. As shown in Figure 2b, the connection of UO_6 octahedra, ZnO_2N_2, and PO_3C tetrehedra leads to 1D chainlike structure, in which pi molecules coordinate to zinc atoms to stabilize the whole structure (Figure 2c).

Structure of UPhP-3. **UPhP-3** crystallizes in the monoclinic space group $P2_1/n$ and contains one crystallographically unique uranium atom, one crystallographically unique zinc atoms, two crystallographically unique phenylphosphonate groups and one dib ligand (Figure 3a). Similar to **UPhP-2**, the uranium atom is in octahedral environment and chelated by four P-centered tetrahedra of the phenylphosphonates, and the phenylphosphonate joins two UO_6 octahedra and one ZnO_2N_2 tetrahedron. Bond-valence sum at the uranium site is 5.96, in agreement with the formal valence of U(VI).[39] A same chain as in **UPhP-2** is formed by UO_6, ZnO_2N_2, and PO_3C polyhedra (Figure 3b). Such chains are linked by dib via sharing N atoms together with Zn-centered tetrahedra to create a layered structure of **UPhP-3**. The layers stagger each other to make the supramolecular structure (Figure 3c).

Structure of USP-1. The layered structure of **USP-1** comprises two crystallographically distinct uranyl centers in form of pentagonal bipyramids, which is defined by two *yl* oxo atoms and five equatorial μ-O atoms from three carboxylates in three 5-SP and one sulfonate in the fourth 5-SP (Figure 4a). The U=O distances are from 1.747(8) to 1.752(7) Å, and the O=U=O angles are 178.3(3) and 179.1(3)°. The valence of uranium atoms is 6.15 for U(1) and 6.19 for U(2) based on calculated bond-valence sum. The carboxylates and sulfonates in the 5-SP ligand possess different coordination modes. One carboxylate is bidentately coordinated to two distinct uranyl centers with U−O distances from 2.337(6) to 2.374(6) Å. The other carboxylate is also bidentate, but links to one uranyl center. The sulfonate is unidentately bridged to a uranyl group through corner sharing (average U−O: 2.454(7) Å). The UO_7 pentagonal bipyramids are connected by bridging 5-SP to form the 2D layered structure of **USP-1** (Figure 4b). Such layers stack parallel to (101) plane with protonated TEA cations locating between them to compensate the molecular charge and stabilize the supramolecule (Figure 4c).

Structure of USP-2. **USP-2** also represents a layered structure, which features a well-known tetranuclear uranyl structural building cluster. All of the uranyl centers are in the pentagonal bipyramidal geometry (Figure 5a). The average uranyl U=O bonds is 1.776(5) Å, while the distances for the equatorial U−O bonds are in the range of 2.194(4) to 2.525(5) Å. The valences of uranium atoms are 6.07 for U(1) and 6.08 for U(2) based on calculated bond-valence sum. The uranium-centered bipyramids condense into clusters through sharing three common edges. In addition, two μ_3-oxygen donors and two hydroxy groups serve as common corners for each cluster. The connection mode of 5-SP is similar to that in **USP-1**. One

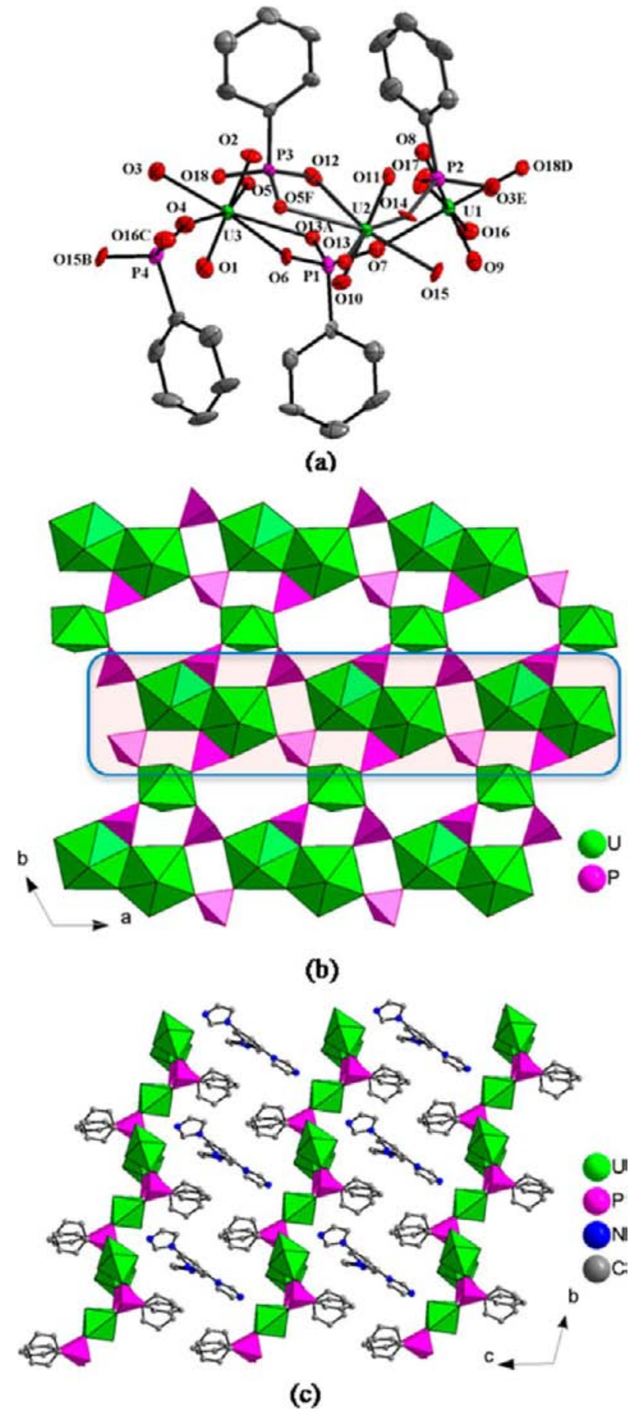


Figure 1. (a) ORTEP representation of the coordination environment in **UPhP-1**. Thermal ellipsoids are drawn at the 50% probability level. Symmetry code: A, *x*, −1 + *y*, *z*; B, −1 + *x*, −1 + *y*, *z*; C, −1 + *x*, *y*, *z*; D, 1 + *x*, *y*, *z*; E, 1 + *x*, 1 + *y*, *z*; F, *x*, 1 + *y*, *z*. (b) The layer of **UPhP-1** contains the chain in highlight. (c) The layers stack along the [100] direction.

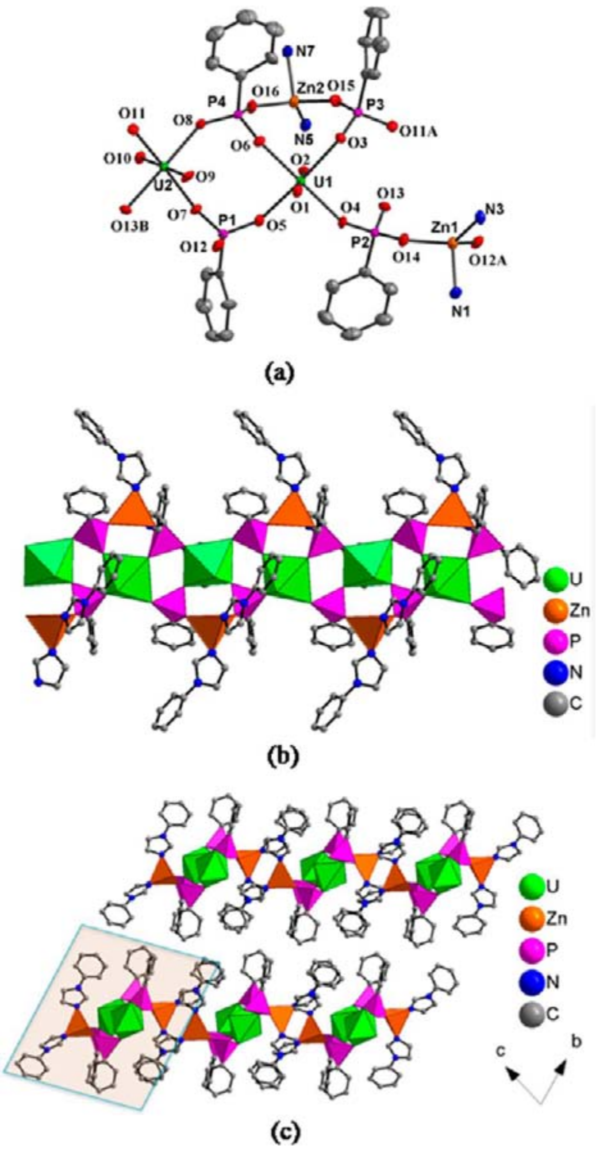


Figure 2. (a) ORTEP representation of the coordination environment in **UPhP-2**. Thermal ellipsoids are drawn at the 50% probability level. pi molecules were deleted for clarity. Symmetry code: A, 1 + *x*, *y*, *z*; B, −1 + *x*, *y*, *z*. (b) 1D structure of **UPhP-2**. (c) View of whole supramolecule of **UPhP-2** along the [100] direction showing one single chain in highlight.

bidentate carboxylate coordinates to two pentagonal bipyramids of one tetranuclear cluster, and the other bidentate carboxylate is linked to another cluster via one uranyl center. The unidentate sulfonate also is connected to one uranyl group of a cluster through corner-sharing. Thus, one 5-SP is linked to three clusters, and one cluster is connected by six 5-SP ligands. Such connection produces the 2D arrangement of **USP-2** (Figure 5b). The layers of **USP-2** stack parallel (011) plane forming the 3D supramolecular structure (Figure 5c). Protonated dib molecules fill in the interlayers to compensate the negative charge of the structure and hold it.

Structure of USP-3. The structure of **USP-3** comprises a 1D chainlike architecture. There are two crystallographically distinct uranyl centers, two 3-SP and one Zn(phen)$_3$ in its asymmetric unit (Figure 6a). Both of the uranium atoms are in the pentagonal bipyramidal environment. Two UO$_7$ pentagonal bipyramids polymerize into a dinuclear cluster by edge-sharing. The valences of uranium atoms are 6.12 for U(1) and 6.13 for U(2) based on calculated bond-valence sum. The sulfonate of 3-SP is unidentate, and shares a common corner with a uranyl center (U−O(sulfonate): 2.361(4) and 2.383(4) Å). One unidentate carboxylate of 3-SP is joined to a dimer via μ_3-oxygen. The other carboxylate of 3-SP is bidentate, and links two dimers, leading to a chainlike structure of **USP-3** (Figure

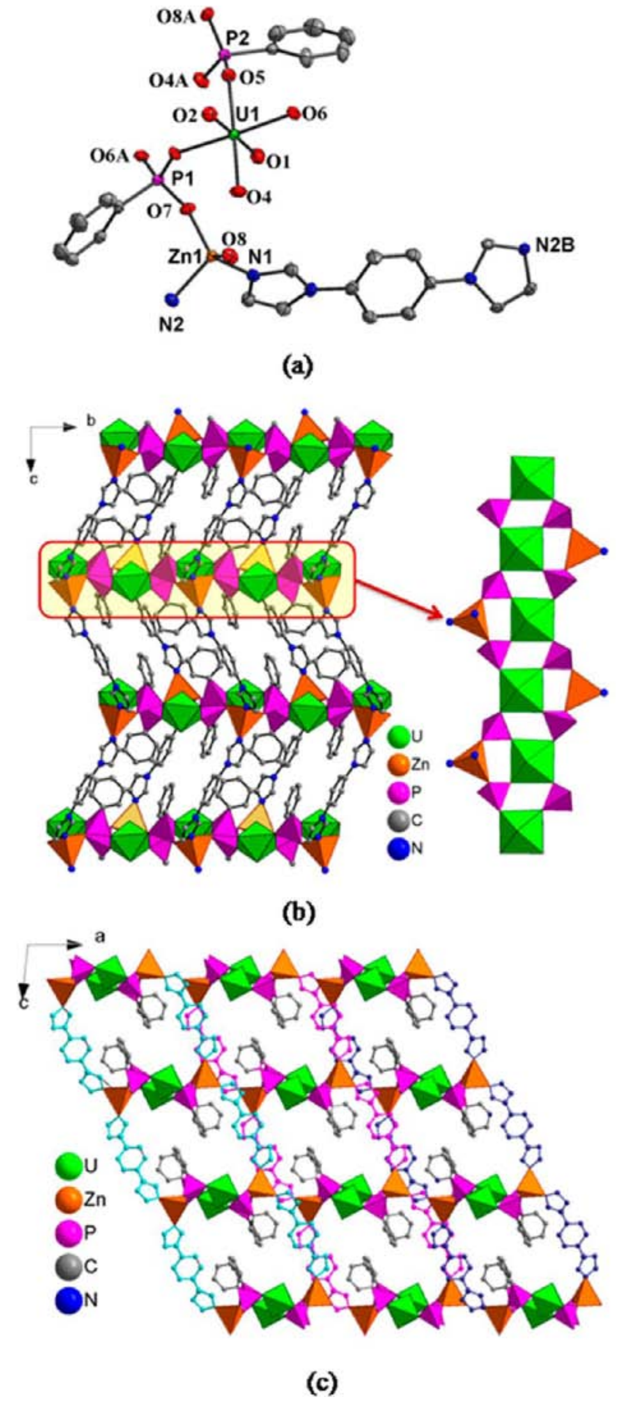


Figure 3. (a) ORTEP representation of the coordination environment in **UPhP-3**. Thermal ellipsoids are drawn at the 50% probability level. Symmetry code: A, 1.5 − *x*, −0.5 + *y*, 0.5 − *z*; B, 0.5 + *x*, 0.5 − *y*, 0.5 + *z*. (b) Chains (in highlight) are connected by dib to form the layered structure of **UPhP-3**. (c) View along the [010] direction showing the stacking of layers, purple, light, and dark blue represent different dib in different layers.

6b). Among these chains, airscrew-like Zn(phen)$_3$ fills in and balances the charge.

Structure Discussion. As far as we known, only 1D linear or tubular structures of uranyl phenylphosphonates have been isolates.[15−17] The syntheses of **UPhP-1**, **-2**, and **-3** enrich the structural diversities of uranyl phosphonates. Insight into these synthesized uranyl phenylphosphonate compounds, fully deprotonated phosphonates and imidazole-based complexes play key roles in construction of structures. In **UPhP-1**, protonated tib, serves as template to stabilize the structure, as well as the charge compensator. For **UPhP-2** and **UPhP-3**, which contain second metal Zn inside, the same chain can be clearly separated from their structures (Figure 2b and Figure 3b). This chain is constructed by UO$_6$ octahedra, PO$_3$C, and ZnO$_2$N$_2$ tetrahedra. In **UPhP-2**, only one N donor of pi molecule can be utilized to connect Zn atom. Thus, 1D chain is finally produced. Whereas in **UPhP-3**, every dib is linked to two such chains leading to a 2D structure. For most known organo-templated uranyl phosphonates, amines, pyridines, piperazines, and encapsulated cations serve as structure-directing agents.[1,18a,20,23] Until recently, our group used imidazole-based complexes to successfully generate a series of uranyl diphosphonates.[21] On the basis of these structural features of our previous and present work, some conclusions can be drawn. First, the imidazole-based complexes are good templates for the syntheses of uranyl phosphonates; meanwhile, they could be easily protonated to compensate the negative charge of the structures. Second, imidazole-based complexes are hard to coordinate with uranyl center. At last, the zinc atom is important in construction of novel heterobimetallic uranyl

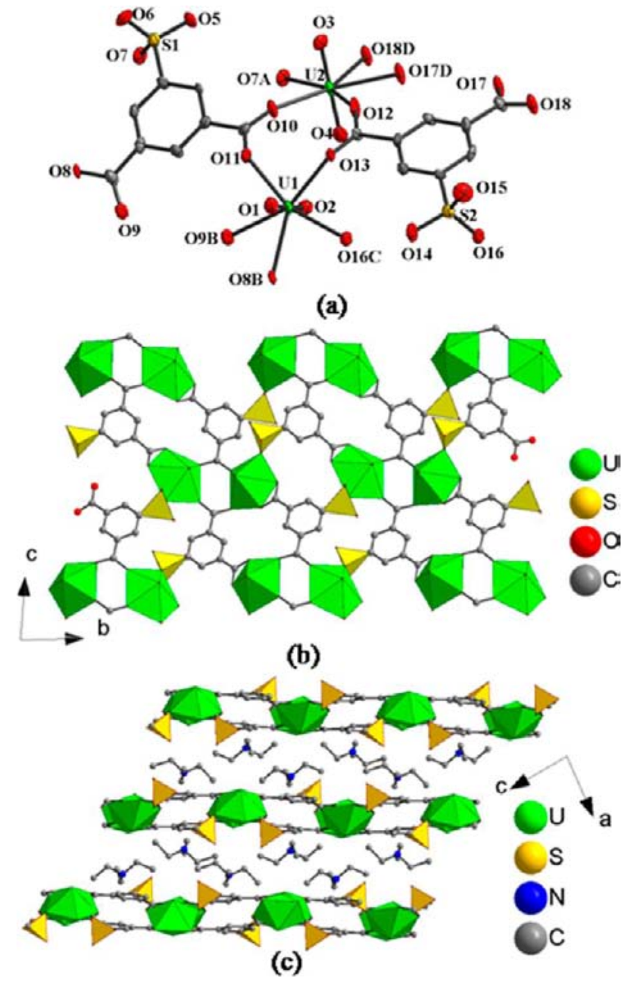


Figure 4. (a) ORTEP representation of the coordination environment in **USP-1**. Thermal ellipsoids are drawn at the 50% probability level. Symmetry code: A, −*x*, 1 − *y*, 1 − *z*; B, −*x*, −*y*, 1 − *z*; C, 1 − *x*, −*y*, −*z*; D, 1 − *x*, 1 − *y*, −*z*. (b) Layer of **USP-1**. (c) TEA cations exit between the layers.

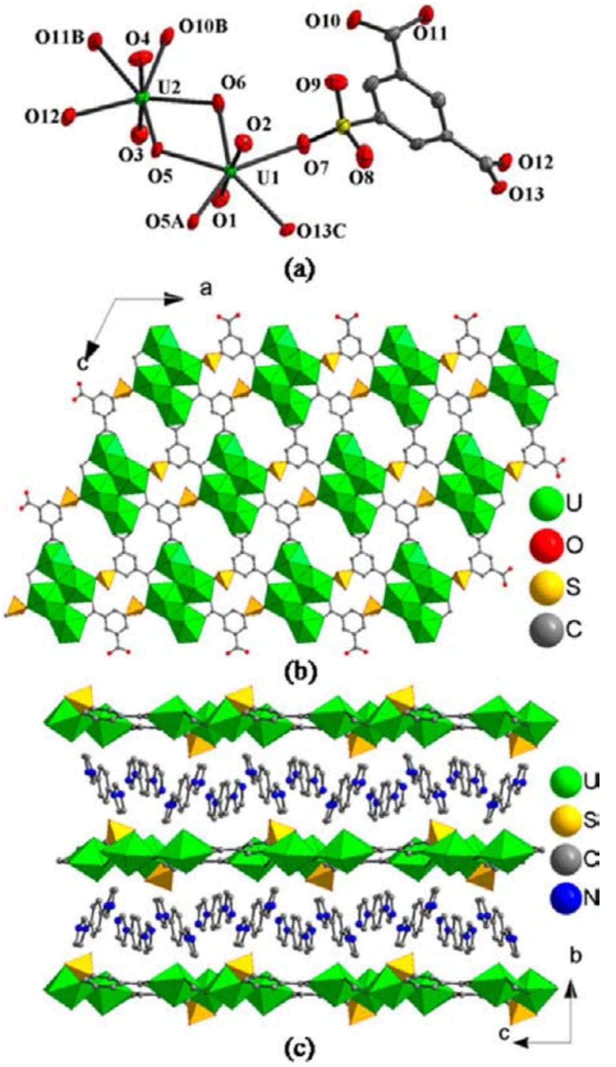


Figure 5. (a) ORTEP representation of the coordination environment in **USP-2**. Thermal ellipsoids are drawn at the 50% probability level. Symmetry code: A, 2 − *x*, −*y*, −*z*; B, 2 − *x*, −*y*, 1 − *z*; C, 1 − *x*, −*y*, −*z*. (b) Layer of **USP-2** comprises the tetranuclear cluster. (c) View of the 2D assembly along the [100] direction.

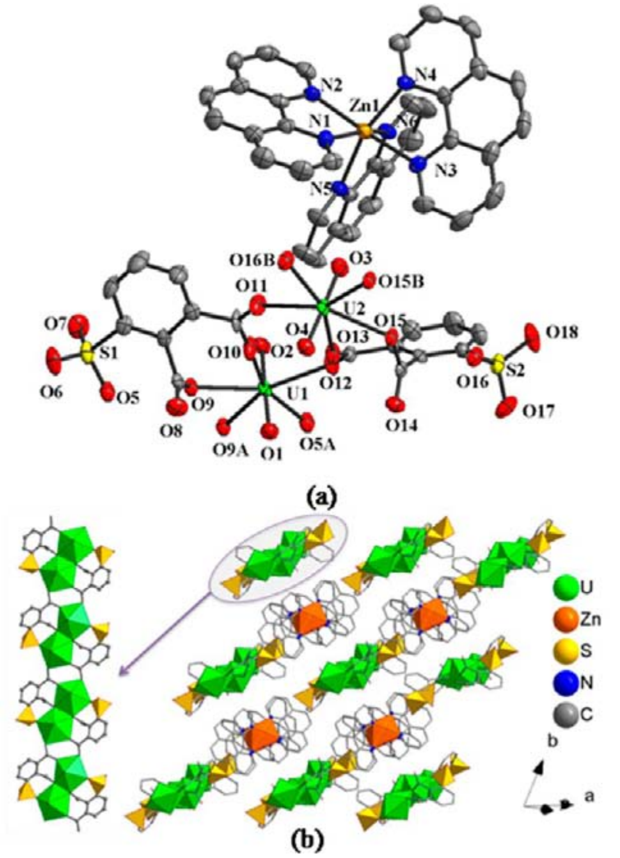
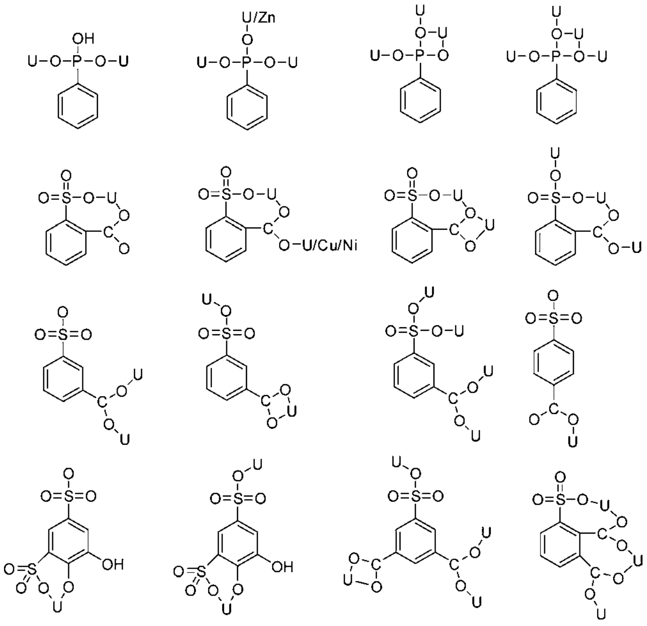


Figure 6. (a) ORTEP representation of the coordination environment in **USP-3**. Thermal ellipsoids are drawn at the 50% probability level. Symmetry code: A, −*x*, 2 − *y*, 1 − *z*; B, 1 − *x*, 2 − *y*, −*z*. (b) Chainlike structures of **USP-3** stack with Zn(phen)$_3$ locating in the void space. The single chain is in highlight.

Scheme 2. Summary of Coordination Modes of Phenylphosphonate and Arylsulfonates in Uranyl Complexes



architectures, where they can link phosphonate groups, uranium-centered polyhedra and N-donor organic complexes resulting in rich structural diversities.

As for the synthesized sulfonates, a common feature is the unidentate sulfonate group (η^1 bonding mode) of the ligand. The S, in distorted tetrahedral coordination defined by one C and three O atoms, is connected to UO_7 pentagonal bipyramid through corner sharing. The S−O distances range from 1.418(8) to 1.493(4) Å, slightly shorter than that of P−O bond lengths. This coordination mode is common for sulfonates, and different from that in phenylphosphonates, which are usually bidentate or tridentate in coordination with uranyl center (Scheme 2). The pK_a value of phenylsulfonic acid is 0.7, much lower than that of phenylphosphonic acid (1.86 and 7.51). This means that the phenylphosphonate ligand is more likely to be partially protonated in synthesized structures. The low pH values are curial for crystallization of title compounds (2.0−3.0 for uranyl phosphonates, and 1.5−3.5 for uranyl sulfonates). We summarize the coordination modes of phenylphosphonate and arylsulfonate ligands-based uranyl complexes including this work (Scheme 2). It is noteworthy that for known uranyl or mixed uranyl−transition metal arylsulfonates,[33−35] the bidentate (η^2) coordination of sulfonate groups are less happened compared to unidentate one, and the tridentate (η^3) mode never occurs. Moreover, additional functional groups especially carboxylate extend the coordination sites and manners leading to more diverse architectures. Interestingly, although the carboxylate groups of 5-SP possess same coordination manner, mononuclear and tetranuclear uranyl units take place in **USP-1** and **USP-2**, respectively, resulting in totally different layered arrangement. Whereas in **USP-3**, binuclear uranyl units are connected by 3-SP ligand. It seems that the position of sulfonate and carboxylate groups of 3-SP prefers to form a 1D assembly. In our work, an additional carboxylate group is introduced into the sulfonate ligand compared to previously reported examples,[33−35] and new structures are produced.

IR Spectroscopy. The IR spectra of these synthesized uranyl phosphonates and sulfonates are shown in Figure S1 of the Supporting Information. The asymmetric and symmetric stretching modes of U═O are observed from about 840 to 925 cm^{-1}.[15] The bands between 1400−1650 cm^{-1} are attributed to the skeletal vibrations of the aromatic rings. The bands in the low wavenumber region from 680 to 760 cm^{-1} are dominated by the out-of-plane vibrations of the phenyl rings. The stretching vibrations of H_2O and OH are determined at around 3450 cm^{-1}. For phosphonates, **UPhP-1** to **UPhP-3**, the group of peaks around 1000−1150 cm^{-1} is assigned to the vibrations of PO_3 group. For sulfonates, **USP-1** to **USP-3**, the adsorption in the region of 1000 − 1260 cm^{-1} is related to sulfonate groups. The intensive peak at 624 cm^{-1} is attributed to the S−O stretching vibrations.[27c]

Photoluminescent Properties. All of the photoluminescent spectra of the title compounds are illustrated in Figure 7. They all exhibit characterized emission from uranyl cations, which usually consists of several emission peaks. This charge-transfer based emission centered near 520 nm is always related to the symmetric and antisymmetric vibrational modes of the uranyl cation. Five peaks are observed in the spectra for **UPhP-1** (472, 504, 525, 549, and 575 nm), **UPhP-2** (469, 506, 526, 555, and 579 nm), **UPhP-3** (470, 508, 530, 553, and 577 nm), **USP-1** (475, 491, 512, 535, and 562 nm), and **USP-3** (486, 502, 524, 548, and 574 nm) that correspond to the electronic and vibronic transitions S_{11}−S_{00} and S_{10}−$S_{0\nu}$ (ν = 0−4). Compared to the benchmark compound $UO_2(NO_3)_2{\cdot}6H_2O$,[22] these compounds are red-shifted by a value of 15 nm (**UPhP-1**), 16 nm (**UPhP-2**), 20 nm (**UPhP-3**), 2 nm (**USP-1**), and 14 nm (**USP-3**). The spectral shift may originate from the influence of equatorial phenylphosphonate and sulfonate groups. Although no fine-structured spectrum is obtained for **USP-2**, the main broad peak centered at 524 nm is unambiguously attributed to the charge transfer of uranyl cations.[40] In principle, not all uranyl complexes can exhibit fluorescence. Their luminescence and specially fine−structure ones are related to many factors, such as size and quality of the crystal, disorder within the equatorial plane of the uranyl group, and so on.[24]

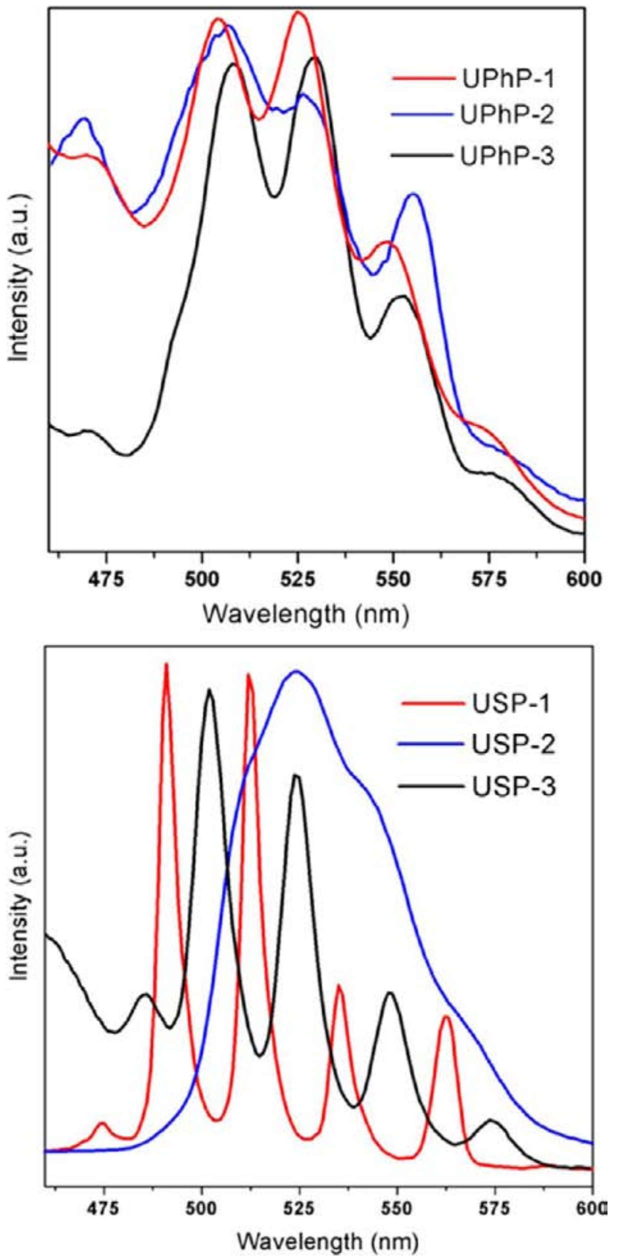


Figure 7. Emission spectra of **UPhP-1** (λ_{ex} = 420 nm), **UPhP-2** (λ_{ex} = 274 nm), **UPhP-3** (λ_{ex} = 277 nm), **USP-1** (λ_{ex} = 280 nm), **USP-2** (λ_{ex} = 362 nm), and **USP-3** (λ_{ex} = 350 nm).

■ CONCLUSIONS

In this work, by combining with N-based structure directing agents, ligands of phenylphosphonic acid, and two arylsulfonic acid have been chosen to construct novel uranyl hybrids. Their correlations and discrepancies have also been investigated. Three uranyl phosphonates and three uranyl sulfonates have been successfully synthesized and structurally characterized. Some important phenomena and conclusions are yielded as follows. First of all, the addition of imidazole-based species remarkably enriches the structural diversities of uranyl phenylphosphonates. Among these synthesized compounds, **UPhP-1** comprises 2D layered assemblies with tib as the template. **UPhP-2** is a chain-like structure composed of U-, Zn-, and P-centered polyhedra. Such chains are further connected by dib to form the layered **UPhP-3**. Second, although the sulfonate group possesses the similar geometry to phosphonate with potential unidentate, bidentate and tridentate coordination sites, only unidentate sulfonates are observed in this study. For previously reported uranyl arylsulfonates, such coordination manner of sulfonte group is very common; however, bidentate mode are less happened, and tridentate fashion never occurs. Third, additional carboxylate groups play a key role in constructing new uranyl sulfonates. Despite the 5-SP ligands display the same coordination manner, **USP-1** and **USP-2** wholly differ in layered arrangements corresponding to mononuclear and tetranuclear uranyl clusters, respectively. Upon changing the substituted sites of carboxylate groups, linear assembly of **USP-3** is formed with $Zn(phen)_3$ as the template. These interesting observations encourage us to further expand applicability of phosphonate and sulfonate ligands, as well as the imidazole-based structural directing agents, to construct novel structural architectures, and investigate their potential applications in the future.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic cif files, selected bond lengths and angles, and the IR spetra. 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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