Inorganic Chemistry
Article
pubs.acs.org/IC

# Synthesis, Structures, and Properties of Uranyl Hybrids Constructed by a Variety of Mono- and Polycarboxylic Acids

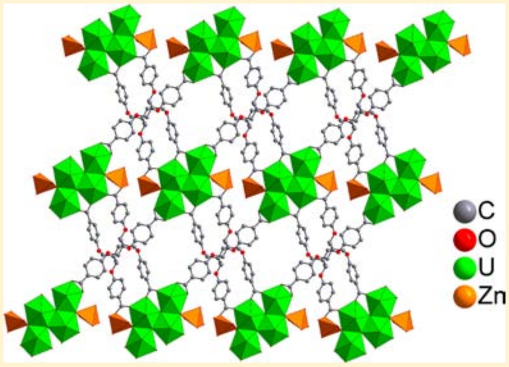
Weiting Yang,[†,∥] Song Dang,[†,∥] Hao Wang,[†,‡] Tao Tian,[†] Qing-Jiang Pan,[§] and Zhong-Ming Sun*[,†]

[†]State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun, Jilin 130022, China

[‡]School of Chemistry and Environmental Engineering, Changchun University of Science & Technology, Changchun 130022, China

[§]Key Laboratory of Functional Inorganic Material Chemistry of Education Ministry, School of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, China

*Supporting Information*



**ABSTRACT:** A series of uranyl−organic coordination polymers have been hydrothermally synthesized by using a variety of carboxylic ligands, 3,3′-((2-((3-carboxyphenoxy)methyl)-2-methylpropane-1,3-diyl)bis(oxy))dibenzoic acid ($H_3L^1$), 4,4′-(3-(4-carboxyphenethyl)-3-hydroxypentane-1,5-diyl)-dibenzoic acid ($H_3L^2$), chelidamic acid ($H_2L^3$), and benzoic acid ($HL^4$) in the presence of N-bearing coligands, including 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen), 1-([1,1′-biphenyl]-4-yl)-1*H*-imidazole (bpi), and 1,4-di(1*H*-imidazol-1-yl)benzene (dib). Compounds $(UO_2)(HL^1)$ (**1**) and $Zn(H_2O)_3(UO_2)_2(O)(OH)(L^2)\cdot H_2O$ (**2**) are constructed by semirigid ligands. The former is a one-dimensional ribbon-like structure with $UO_7$ pentagonal bipyramids as the building unit, while the latter adopts a tetramer of $UO_7$ pentagonal bipyramids to build a layered structure. Mononuclear $UO_7$ pentagonal bipyramids are connected by $L^3$ groups to generate a two-dimensional arrangement of $UO_2(L^3)(H_2dib)_{0.5}$ (**3**), in which the protonated dib molecules provide space filling and form $\pi\cdots\pi$ interactions with the layers. Compounds $UO_2(L^3)(phen)$ (**4**), $UO_2(L^3)_2(Hbpi)_2$ (**5**), and $UO_2(L^4)_2(bipy)$ (**6**) are molecular complexes, in which **4** and **6** are neutral, and **5** comprises protonated bpi as the counterion. The uranyl center in compound **4** is chelated by one phen and one $L^3$ group to form a $UO_5N_2$ pentagonal bipyramid, while in compound **5**, two $L^3$ groups are coordinated to an uranyl center, producing a $UO_8$ polyhedron. Compound **6** consists of a $UO_6N_2$ polyhedron of uranyl unit coordinated by one bipy and two benzoate groups. Compounds $Zn(phen)_3[(UO_2)(C_2O_4)(L^4)]_2$ (**7**) and $Zn(bpi)_2(UO_2)(O)(C_2O_4)_{0.5}(L^4)\cdot H_2O$ (**8**) feature one-dimensional structures. In **7**, $UO_7$ pentagonal bipyramids are alternatively connected by oxalate groups to form the chain, in which unidentate benzoate groups are coordinated to the uranium atoms. $Zn(phen)_3$ cations fill the void space of the chains to compensate the negative charge. Differently, the chain of **8** can be seen as the heterometallic tetramer of $UO_7$ and $ZnO_2N_2$ polyhedra connected by oxalate groups, and then bpi and benzoate groups are coordinated to the chain. All of the compounds have been characterized by IR and photoluminescent spectroscopy, and compounds **2**, **3**, **5**, **6**, and **8** exhibit characteristic emissions of uranyl cations.

## ■ INTRODUCTION

Over the past few decades, actinide-based complexes have attracted increasing attention in their syntheses and characterization.[1] Uranium, as the most represented element of actinides, has been mostly investigated in comparison with other actinide elements. In addition, the contributions involving the elaboration of uranium-containing solids also are due to the particular 5f element, which can be used as a fuel in nuclear power.[2] Apart from the nuclear physics, uranium also exhibits rich coordination chemistry and structure chemistry in forming a variety of compounds with other elements. Among the uranium-bearing materials, those comprising U(VI) are most common by far, which generally exists in the form of linear uranyl species ($UO_2^{2+}$). Outside of constructing inorganic uranyl solids, such as phosphates,[3] sulphates,[4] borates,[5] and silicates,[6] the uranyl moiety can also bond to organic molecules, resulting in uranyl−organic hybrid materials or uranyl−organic coordination polymers.[7] Growing interest on research on uranyl−organic compounds has been aroused not only due to their rich structural chemistry, but also the potential applications in nuclear waste disposal and separation processes.[8]

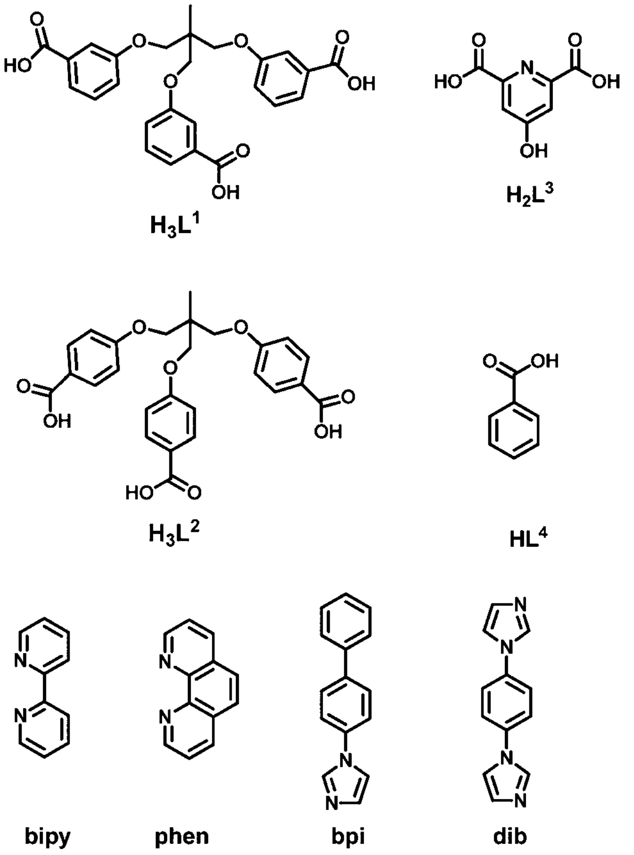
Following the strategy of construction of transition metal coordination polymers, various organic ligands have been utilized to isolate uranyl hybrid materials,[9−14] especially carboxylic acids. These uranium-bearing complexes exhibit various structures including clusters,[15] chains,[16] layers,[17] and frameworks,[18] along with versatile physiochemical properties, for example, luminescence,[19] photocatalytic performance,[20] and

**Received:** May 17, 2013
**Published:** October 16, 2013

ACS Publications © 2013 American Chemical Society

photoelectric conversion.[7a,15] Most of the reported uranyl−carboxylate coordination polymers are constructed of rigid or flexible carboxylate ligands.[1a] Recently, our group reported the first examples of 3-fold interpenetrated uranyl−organic frameworks by using semirigid carboxylic acids,[21] which are beneficial for the construction of novel uranyl organic materials. As an ongoing study, we choose two isomeric ligands with semirigidity, 3,3′-((2-((3-carboxyphenoxy)methyl)-2-methylpropane-1,3-diyl)bis(oxy))dibenzoic acid ($H_3L^1$) and 4,4′-((2-((4-carboxyphenoxy)methyl)-2-methylpropane-1,3-diyl)bis(oxy))dibenzoic acid ($H_3L^2$), as the construction agents, and two new uranyl organic coordination polymers $(UO_2)(HL^1)$ (**1**) and $Zn(H_2O)_3(UO_2)_2(O)(OH)(L^2)\cdot H_2O$ (**2**) have been obtained. For further investigating and comparing the coordination modes of carboxylate ligands, dicarboxylic acid (chelidamic acid, $H_2L^3$) and monocarboxylic acid (benzoic acid, $HL^4$) have also been used to synthesize uranyl materials. On the other hand, our precise works demonstrated that the N-donor organic species could supply coligands, templates, charge compensators, or space filling in the construction of uranyl hybrids.[9,10a] Thus, various N-contained organic species (bipy, phen, bpi, and dib) were also introduced into the reaction system. Six uranyl complexes $UO_2(L^3)(H_2dib)_{0.5}$ (**3**) with two-dimensional (2-D) layered structures, $UO_2(L^3)(phen)$ (**4**), $UO_2(L^3)_2(Hbpi)_2$ (**5**), and $UO_2(L^4)_2(bipy)$ (**6**) with molecular assemblies, and $Zn(phen)_3[(UO_2)(C_2O_4)(L^4)]_2$ (**7**) and $Zn(bpi)_2(UO_2)(O)(C_2O_4)_{0.5}(L^4)\cdot H_2O$ (**8**) with one-dimensional (1-D) chains were isolated. Their syntheses and structures have been studied in detail. Most of these uranium carboxylates exhibit typical emissions of green light, which is an interesting phenomenon and motivates us to make further investigation.

**Scheme 1. Structure of the Ligands**



## ■ EXPERIMENTAL SECTION

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

**Materials, Syntheses, and Characterization.** All chemicals were purchased commercially and used without further purification, uranyl nitrate, uranyl acetate, and zinc uranyl acetate (99.8%, Sinpharm Chemical Reagent Co. Ltd.). $H_3L^1$ and $H_3L^2$ are synthesized according to the reported procedure.[21,22] The carboxylate and N-donor ligands are listed in Scheme 1. The reaction mixtures were loaded into a 20 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and heated at 160 °C for 2−4 days, and then cooled to room temperature naturally. Yellow single crystals were isolated for all of the title compounds. Powder X-ray diffraction (PXRD) patterns were performed on a D8 Focus (Bruker) diffractometer with Cu K$\alpha$ radiation ($\lambda$ = 0.15405 nm, continuous, 40 kV, 40 mA, increment = 0.02°). Elemental analyses of C, H, and N were conducted on a Perkin-Elmer Optima 3300DV spectrometer and a Perkin−Elmer 2400 elemental 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. The photomultiplier tube voltage was 700 V, the scan speed was 1200 nm $min^{-1}$, and the excitation and the emission slit width were 5.0 and 5.0 nm, respectively.

*Synthesis of* $(UO_2)(HL^1)$ *(**1**).* The reaction mixture is formed by $UO_2(NO_3)_2\cdot 6H_2O$ (25 mg, 0.05 mmol), $H_3L^1$ (50 mg, 0.1 mmol), sodium phenylsulfonate (26.8 mg, 0.1 mmol), $H_2O_2$ (30%, 1 mL), and deionized water (1.5 mL). The solution pH was 3.0 before the reaction and 2.5 at the end. Yield: 19 mg (51% based on uranium). Anal. Calcd (wt %) for $C_{26}H_{22}O_{11}U$: C, 41.72; H, 2.96. Found: C, 41.96; H, 3.01.

*Synthesis of* $Zn(H_2O)_3(UO_2)_2(O)(OH)(L^2)\cdot H_2O$ *(**2**).* The reaction mixture is formed by $ZnUO_2(OAc)_4\cdot 7H_2O$ (130 mg, 0.12 mmol), $H_3L^2$ (24.7 mg, 0.05 mmol), sodium phenylsulfonate (52 mg, 0.2 mmol), $H_2O_2$ (30%, 3 mL), and deionized water (2.0 mL). The solution pH was 3.5 before the reaction and 3.0 at the end. Yield: 22.7 mg (38% based on $H_3L^2$). Anal. Calcd (wt %) for $C_{26}H_{33}O_{20}U_2Zn$: C, 26.49; H, 1.8. Found: C, 26.88; H, 1.82.

*Syntheses of* $UO_2(C_7H_2O_6)(dib)_{0.5}$ *(**3**) and* $UO_2(C_7H_2O_6)_2(Hbpi)_2$ *(**5**).* The reaction mixture consists of $UO_2(OAc)_2\cdot 2H_2O$ (40 mg, 0.1 mmol), chelidamic acid (9.2 mg, 0.05 mmol), dib (3 mg, 0.01 mmol for **3**) or bpi (15 mg, 0.05 mmol for **5**), and deionized water (1.0 mL). The solution pH values before and after the reaction are 3.0 and 2.5 for **3**, and 4.0 and 2.5 for **5**. Yield: 5.4 mg for **3** (48% based on dib) and 11 mg for **5** (41% based on bpi). Anal. Calcd (wt %) for $C_{13}H_7N_2O_8U$: C, 28.07; H, 1.45; N, 5.03. Found: C, 28.43; H, 1.36; N, 4.97. Anal. Calcd (wt %) for $C_{44}H_{30}N_4O_{14}U$: C, 49.17; H, 3.0; N, 7.82. Found: C, 49.03; H, 2.88; N, 7.58.

*Synthesis of* $UO_2(C_7H_2O_6)(phen)$ *(**4**).* The mixture is comprised of $UO_2(OAc)_2\cdot 2H_2O$ (40 mg, 0.1 mmol), chelidamic acid (18.4 mg, 0.1 mmol), phen (19.6 mg, 0.1 mmol), and deionized water (1.0 mL). The solution pH was 4.0 before the reaction and 3.0 at the end. Yield: 25 mg (39% based on uranium). Anal. Calcd (wt %) for $C_{19}H_{10}N_2O_9U$: C, 35.25; H, 1.71; N, 6.49. Found: C, 35.34; H, 1.75; N, 6.12.

*Synthesis of* $UO_2(C_7H_5O_2)_2(bipy)$ *(**6**).* The mixture contains $UO_2(OAc)_2\cdot 2H_2O$ (40 mg, 0.1 mmol), chelidamic acid (12 mg, 0.1 mmol), bipy (2 mg, 0.01 mmol), and deionized water (1.0 mL). The solution pH was 3.0 before the reaction and 2.0 at the end. Yield: 4 mg (61% based on bipy). Anal. Calcd (wt %) for $C_{24}H_{18}N_2O_6U$: C, 43.12; H, 2.71; N, 4.19. Found: C, 43.14; H, 2.75; N, 4.06.

*Synthesis of* $Zn(phen)_3[(UO_2)(C_2O_4)(C_7H_5O_2)]_2$ *(**7**).* The mixture is made up of $ZnUO_2(OAc)_4\cdot 7H_2O$ (52 mg, 0.05 mmol), oxalic acid (6.3 mg, 0.05 mmol), benzoic acid (12 mg, 0.1 mmol), phen (19.6 mg, 0.1 mmol), and deionized water (1.0 mL). The solution pH was 3.0 before

Table 1. Crystal Data and Structure Refinement for Compounds 1−8

| | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| empirical formula | $C_{26}H_{22}O_{11}U$ | $C_{26}H_{21}O_{19}U_2Zn$ | $C_{13}H_8N_3O_7U$ | $C_{19}H_{11}N_3O_8U$ |
| fw | 748.47 | 1178.86 | 556.25 | 647.34 |
| $T$ (K) | 173(2) | 173(2) | 173(2) | 173(2) |
| $\lambda$ (Å) | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| space group | $P\bar{1}$ | $P\bar{1}$ | $P2_1/n$ | $P2_1/n$ |
| $a$ (Å) | 10.6455(5) | 9.435(2) | 9.2754(9) | 7.5465(10) |
| $b$ (Å) | 11.1830(6) | 9.543(2) | 12.4668(12) | 19.876(3) |
| $c$ (Å) | 11.4638(6) | 18.302(4) | 12.7002(12) | 12.9350(17) |
| $\alpha$ (deg) | 79.0370(10) | 83.054(4) | 90 | 90 |
| $\beta$ (deg) | 84.6470(10) | 80.725(4) | 91.790(2) | 100.948(2) |
| $\gamma$ (deg) | 71.8160(10) | 80.128(4) | 90 | 90 |
| $V$ ($Å^3$) | 1272.09(11) | 1595.0(6) | 1467.9(2) | 1904.9(4) |
| $Z$, $\rho_{calcd}$ ($Mg/m^3$) | 2, 1.954 | 2, 2.455 | 4, 2.517 | 4, 2.257 |
| $\mu$(Mo K$\alpha$) ($mm^{-1}$) | 6.441 | 10.958 | 11.102 | 8.577 |
| GOF | 1.057 | 1.028 | 0.997 | 0.993 |
| $R_1/wR_2$ ($I > 2\sigma(I)$)$^a$ | 0.0287/0.0677 | 0.0453/0.1051 | 0.0375/0.0665 | 0.0321/0.0778 |
| $R_1/wR_2$ (all data) | 0.0334/0.0697 | 0.0666/0.1240 | 0.0623/0.0756 | 0.0442/0.0828 |

| | 5 | 6 | 7 | 8 |
|---|---|---|---|---|
| empirical formula | $C_{44}H_{32}N_6O_{12}U$ | $C_{24}H_{18}N_2O_6U$ | $C_{54}H_{34}N_6O_{16}U_2Zn$ | $C_{38}H_{29}N_4O_8UZn$ |
| fw | 1074.79 | 668.43 | 1564.3 | 973.05 |
| $T$ (K) | 173(2) | 173(2) | 173(2) | 173(2) |
| $\lambda$ (Å) | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| space group | $C2/c$ | $P\bar{1}$ | $C2/c$ | $P\bar{1}$ |
| $a$ (Å) | 24.0648(14) | 8.8559(14) | 25.0976(9) | 9.4854(5) |
| $b$ (Å) | 10.8935(6) | 9.0269(14) | 11.7435(4) | 13.3798(7) |
| $c$ (Å) | 15.1810(9) | 14.430(2) | 20.7722(8) | 15.5233(8) |
| $\alpha$ (deg) | 90 | 88.123(3) | 90 | 102.2910(10) |
| $\beta$ (deg) | 97.9250(10) | 80.122(3) | 123.5640(10) | 102.2850(10) |
| $\gamma$ (deg) | 90 | 74.356(3) | 90 | 110.3550(10) |
| $V$ ($Å^3$) | 3941.7(4) | 1094.3(3) | 5101.5(3) | 1714.00(15) |
| $Z$, $\rho_{calcd}$ ($Mg/m^3$) | 4, 1.811 | 2, 2.029 | 4, 2.037 | 2, 1.885 |
| $\mu$(Mo K$\alpha$) ($mm^{-1}$) | 4.195 | 7.461 | 6.880 | 5.479 |
| GOF | 1.039 | 1.016 | 1.007 | 1.004 |
| $R_1/wR_2$ ($I > 2\sigma(I)$)$^a$ | 0.0224/0.0500 | 0.0431/0.0875 | 0.0234/0.0491 | 0.0305/0.0686 |
| $R_1/wR_2$ (all data) | 0.0278/0.0520 | 0.0569/0.0989 | 0.0299/0.0513 | 0.0368/0.0712 |

$^aR_1 = \sum(\Delta F/\sum(F_o))$; $wR_2 = (\sum[w(F_o^2 - F_c^2)])/\sum[w(F_o^2)^2]^{1/2}$, $w = 1/\sigma^2(F_o^2)$.

the reaction and 2.0 at the end. Yield: 17.6 mg (45% based on uranium). Anal. Calcd (wt %) for $C_{54}H_{34}N_6O_{16}U_2Zn$: C, 41.46; H, 2.19; N, 5.37. Found: C, 41.80; H, 2.21; N, 5.27.

*Synthesis of* $Zn(bpi)_2(UO_2)(O)(C_2O_4)_{0.5}(C_7H_5O_2)\cdot H_2O$ (**8**). The procedure is similar to **7**, except for the addition of bpi (15 mg, 0.05 mmol). The solution pH was 3.0 before the reaction and 2.0 at the end. Yield: 9.5 mg (39% based on bpi). Anal. Calcd (wt %) for $C_{38}H_{29}N_4O_8UZn$: C, 46.90; H, 3.00; N, 5.76. Found: C, 46.98; H, 3.06; N, 5.68.

**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 Å). Data processing was accomplished with the SAINT program.[23] The structures were solved by direct methods and refined on $F^2$ by full-matrix least-squares using SHELXTL-97.[24] 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. The ISOR and DELU instructions have been used to refine the ADP of C1, C2, C3, and O9 in compound **1**, and O1w in compound **2**. A summary of the crystallographic data for these title complexes is listed in Table 1 (CCDC 939852−939859). Selected bond distances and angles are given in Supporting Information Table S1.

## RESULTS AND DISCUSSION

**Syntheses.** All of these compounds were synthesized under mild hydrothermal condition. Powder X-ray diffraction patterns of complexes **1**−**8** are basically in agreement with the simulated ones generated on the basis of single-crystal structural data (Supporting Information Figures S1−S8). However, there are still some trace amounts of impure phases in complexes **5** and **6**, as indicated by the powder XRD patterns. For complexes **1** and **2**, the addition of sodium phenylsulfonate and $H_2O_2$ is necessary, although they are not involved in the final products. In the absence of phenylsulfonate or $H_2O_2$, unknown amorphous phases instead of crystals were obtained. It is noteworthy that the pH values (3.0−4.0) are crucial for the crystallization of the title uranyl hybrids. Besides, N-bearing organic species serve as coligands or templates in the construction of these complexes (except for compounds **1** and **2**).

**Structure of Compound 1.** This compound crystallizes in the triclinic space group $P\bar{1}$. There is one crystallographically distinct uranyl center and one $L^1$ ligand in its asymmetric unit (Figure 1a). The uranyl center is equatorially coordinated by five oxygen atoms of four carboxylate groups from three $L^1$ ligands, resulting in a $UO_7$ pentagonal bipyramid. The U=O

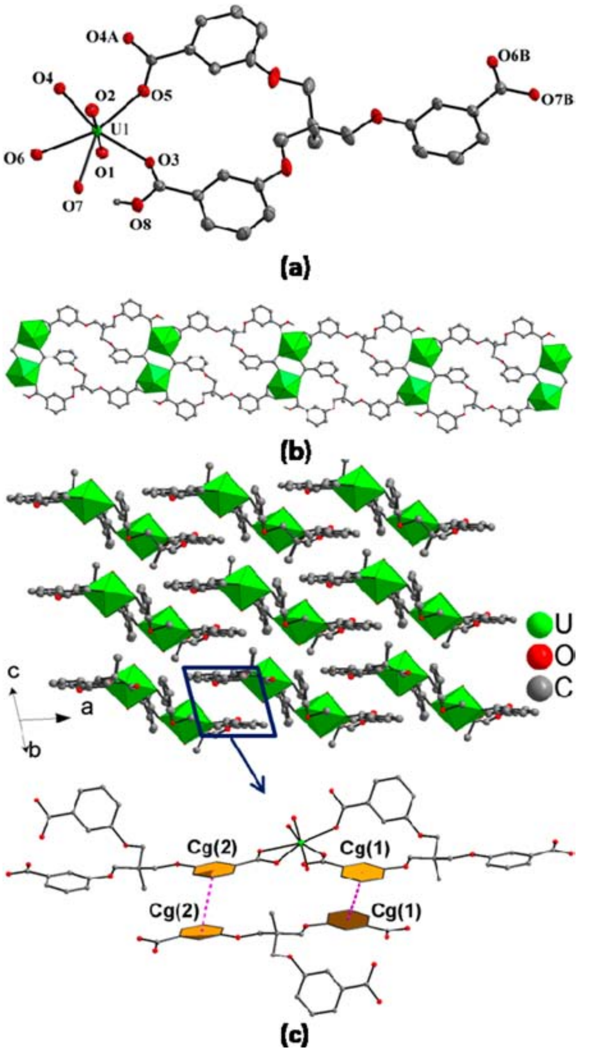


**Figure 1.** (a) ORTEP representation of the asymmetric unit of compound **1**. Thermal ellipsoids are drawn at the 30% probability level. Symmetry code: A, $2 - x$, $-y$, $1 - z$; B, $x$, $1 + y$, $1 + z$. (b) The 1-D structure constructed by $UO_7$ pentagonal bipyramids and $L^1$ ligands. (c) The 1-D ribbons are packed via $\pi-\pi$ interaction.

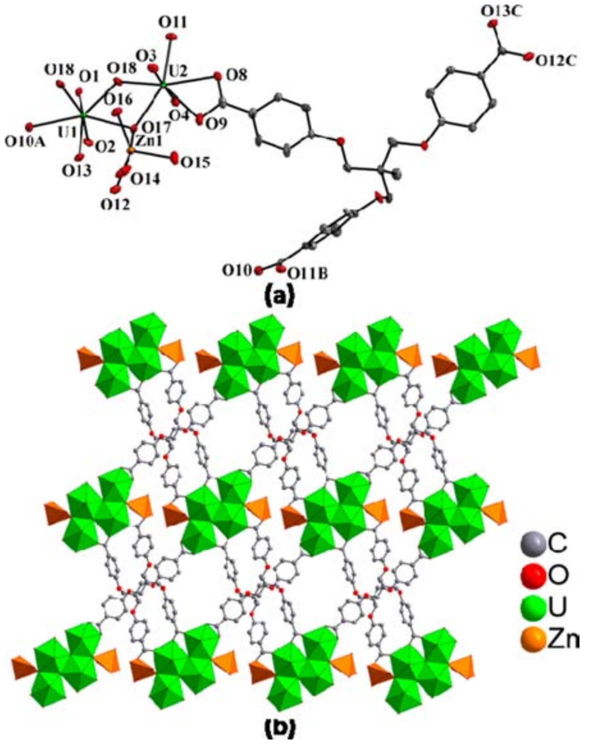


**Figure 2.** (a) ORTEP representation of the asymmetric unit of compound **2**. Thermal ellipsoids are drawn at the 30% probability level. Symmetry code: A, $1 - x$, $1 - y$, $1 - z$; B, $-1 + x$, $-1 + y$, $z$; C, $x$, $-1 + y$, $1 + z$; D, $2 - x$, $2 - y$, $1 - z$. (b) The layered structure in compound **2** formed by hexanuclear cluster of $UO_7$ and $ZnO_5$ polyhedra and $L^2$ ligands.

length is 1.765(4) Å, while the U−O distances in the equatorial plane range from 2.301(3) to 2.486(4) Å. The carboxylate moieties feature three coordination modes in the $L^1$ ligand, where the first is didentately coordinated to one uranyl center, the second also is didentate, and links two uranyl centers, and the last is unidentately bridged to one uranyl center, leaving an OH group with C−O distance of 1.305(6) Å. Thus, every $L^1$ ligand bridges three uranyl centers, and one uranyl cation links three $L^1$ ligands. Such a connection produces a 1-D ribbon-like arrangement (Figure 1b). The whole structure is hold by weak $\pi-\pi$ stacking (3.75−3.92 Å) of the ligands on the ribbons (Figure 1c).

**Structure of Compound 2.** Compound **2** also crystallizes in the space group $P\overline{1}$, but comprises a 2-D structure. The asymmetric unit contains two crystallographically unique uranium atoms, one zinc atom, and one $L^2$ ligand (Figure 2a). Both of the uranyl centers are in the pentagonal bipyramidal geometry. The average uranyl U═O bond length is 1.785(7) Å, while the distances for the equatorial U−O bonds are in the range of 2.215(7)−2.515(7) Å. The uranium-centered bipyramids condense into a well-known tetranuclear structural building cluster through sharing three common edges (Figure 2b). In addition, two $\mu_3$-oxygen donors and two hydroxy groups serve as common corners for each cluster. The zinc atom is five coordinated by oxygens, one of which is $\mu_3$-oxygen shared with two uranyl centers, one is from a carboxylate group, and three are coordinated water molecules. Two $ZnO_5$ trigonal pyramids are connected to the tetranuclear cluster to form a heterometallic hexamer. The $L^2$ ligand possesses three different didentate coordination modes in its three carboxylate moieties. The carboxylate groups are coordinated to one uranyl cation, two uranyl centers, and one uranyl and one zinc center, respectively. Every $L^2$ ligand links three hexanuclear clusters of $UO_7$ and $ZnO_5$ polyhedra, and this cluster is bridged to six $L^2$ ligands; thus a 3,6-connected 2-D layered structure with *kdg* net is generated (Figure 2b). Such layers are packed to form the whole structure of compound **2**.

**Structure of Compound 3.** It crystallizes in the space group $P2_1/n$ and exhibits a 2-D structure. As shown in Figure 3a, the uranyl center is five coordinated in the equatorial plane by four oxygen atoms and one N atom from three $L^3$ groups, resulting in a pentagonal bipyramid. Two carboxylate moieties and one nitrogen atom in the heterocycle of the $L^3$ group adopt a tridentate coordination mode to chelate one uranyl center; meanwhile, the didentate carboxylate and O atom of the $L^3$ bridge another uranyl cation, respectively. Thus, every $L^3$ also bridges three uranyl centers to produce a layered structure. The protonated dib molecules serve as templates and counterions existing between the layers, and form a strong $\pi-\pi$ interaction with $L^3$ ligands (3.45 Å) (Figure 3b). Topological analysis

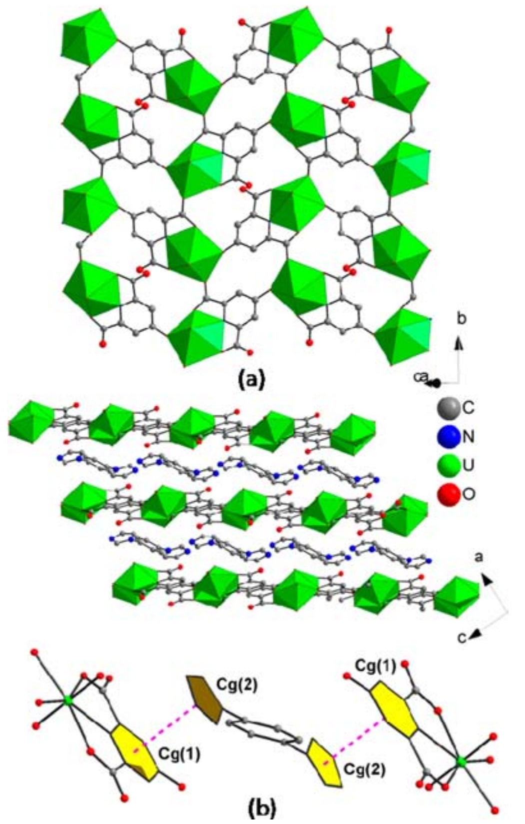


**Figure 3.** (a) The layered structure of compound **3** formed by $UO_7$ units and $L^3$ groups. (b) The dib molecules locate between the uranyl coordination layers of compound **3**.

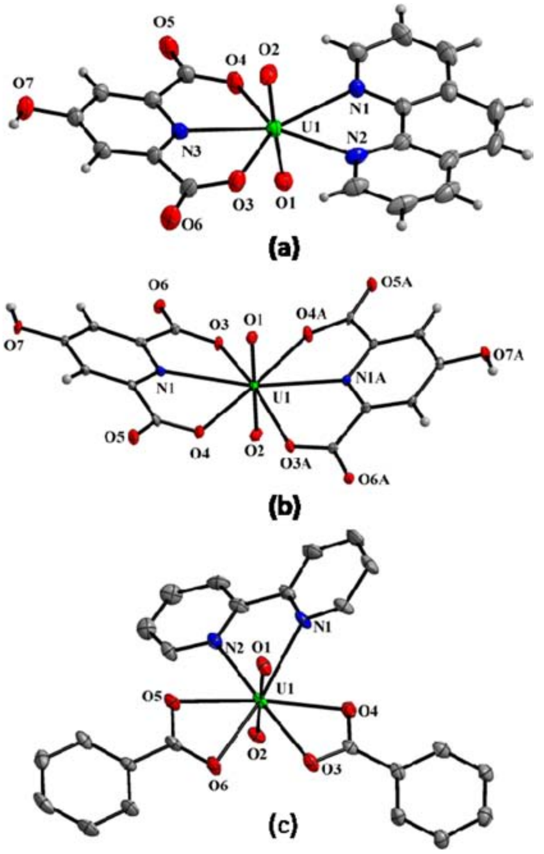


**Figure 4.** The molecular structures of compounds **4** (a), **5** (b), and **6** (c). Symmetry code in compound **5**: A, 1 − *x*, *y*, 1.5 − *z*.

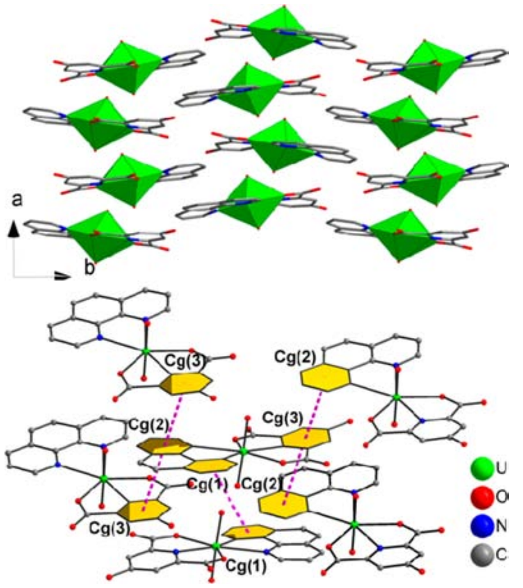


**Figure 5.** The packing mode of compound **4** with π−π stacking.

reveals a *sql* net with point symbol of $\{4^4 \cdot 6^2\}$ for this layered structure.

**Structures of Compounds 4−6.** These three compounds all feature mononuclear molecular structures (Figure 4). For compound **4**, the uranyl center is equatorially chelated by didentate phen and tridentate $L^3$ group, resulting in pentagonal bipyramidal geometry (Figure 4a). The U−N distances are 2.466(4) and 2.553(5) Å, which are typical for those reported values. It is interesting that compound **5** can be seen as the phen ligand of compound **4** is replaced by another $L^3$ group, leading to a hexagonal bipyramid (Figure 4b). In compound **6**, the uranium is also in a hexagonal bipyramidal geometry defined by two "*yl*" oxo atoms in the axis, four oxygen atoms of two benzoate groups in the equatorial plane, and two N atoms of one bipy significantly displaced from the hexagonal plane (Figure 4c).

The packing model of compound **4** along *c* axis is depicted in Figure 5. The form of extended interaction apparent in this assembly is π−π stacking. Every molecule interacts with five neighboring molecules forming two types of π−π interaction between the aromatic groups. One π−π arrangement is generated from the slipped stacking between the phen ligands with the intercentroid distance of 3.83 Å (Cg(1)−Cg(1)). The other π−π interaction is between the $L^3$ and phen ligands with the intercentroid distances of 3.72 and 3.83 Å (Cg(2)−Cg(3)). For compound **5**, two $L^3$ are coordinated to one uranyl center, generating two negative charges. Protonated bpi cations trapped in the interspace of the structure serve as template and charge compensator (Figure 6). The π−π interactions are formed between the molecular structure and bpi with the intercentroid distances from 3.55 Å (Cg(1)−Cg(3)) to 3.99 Å (Cg(1)−Cg(2)), as well as between the bpi cations (Cg(2)−Cg(3): 3.67 Å). As for compound **6**, the extended interaction is also the π−π stacking (Figure 7). Every molecule using aromatic rings of benzoate and bipy groups interacts with four neighboring ones. The strong interaction exists between the bipy molecules with an intercentroid distance of 3.57 Å and a centroid offset of 0.97 Å. Longer distances of 3.80 Å are

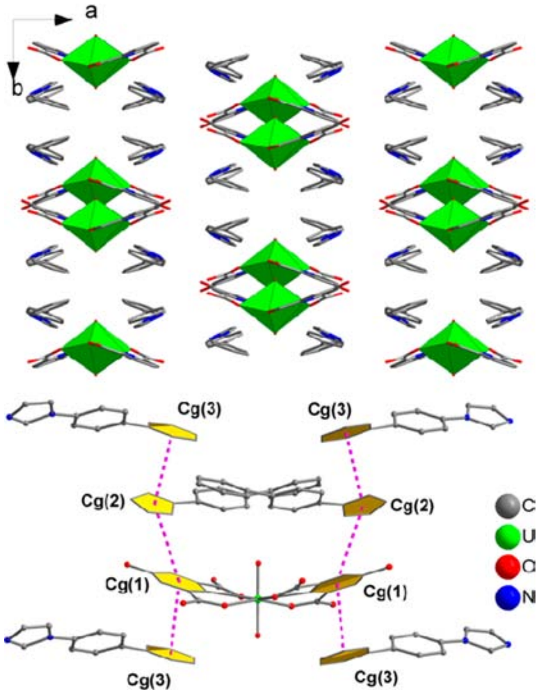


**Figure 6.** The packing mode of compound **5** with π−π stacking.

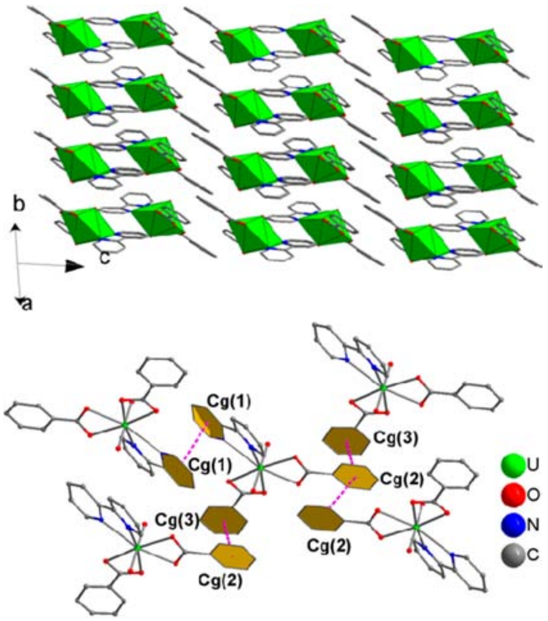


**Figure 7.** The packing mode of compound **6** stabilized by π−π interaction.

**Table 2. Summary of π−π Interactions in Synthesized Compounds**

| | | Cg−Cg (Å) | α (deg) | slippage (Å) |
|---|---|---|---|---|
| 1 | Cg(1)−Cg(1) | 3.92 | 0 | 1.46 |
| | Cg(2)−Cg(2) | 3.75 | 0 | 1.59 |
| 3 | Cg(1)−Cg(2) | 3.45 | 4.70 | |
| 4 | Cg(1)−Cg(1) | 3.83 | 0 | 1.78 |
| | Cg(2)−Cg(3) | 3.72/3.83 | 8.5 | |
| 5 | Cg(1)−Cg(2) | 3.99 | 1.30 | |
| | Cg(1)−Cg(3) | 3.55 | 3.08 | |
| | Cg(2)−Cg(3) | 3.67 | 4.09 | |
| 6 | Cg(1)−Cg(1) | 3.57 | 0 | 0.97 |
| | Cg(2)−Cg(2) | 3.80 | 0 | 1.4 |
| | Cg(2)−Cg(3) | 3.80 | 8.24 | |
| 7 | Cg(1)−Cg(2) | 3.94 | 4.54 | |
| 8 | Cg(1)−Cg(1) | 3.64 | 0 | 1.31 |

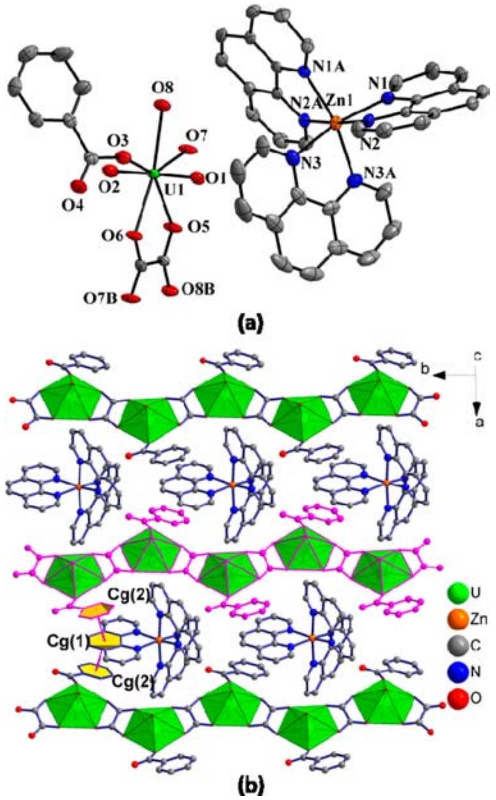


**Figure 8.** (a) ORTEP representation of the asymmetric unit of compound **7**. Thermal ellipsoids are drawn at the 50% probability level. Symmetry code: A, 2 − *x*, *y*, 0.5 − *z*; B, 0.5 − *x*, 0.5 + *y*, 0.5 − *z*. (b) The linear structures of compound **7** with $Zn(phen)_3$ as the template. The single line is highlighted in purple.

indicated between the benzoate groups (Cg(2)−Cg(2) and Cg(2)−Cg(3)). Such π−π interactions locating in complexes **4**−**6** are the extended force to hold the whole supramolecular structure. The detailed intercentroid distances, dihedral angles, and slippage are listed in Table 2.

**Structure of Compound 7.** Compound **7** crystallizes in a monoclinic space group *C*2/*c* and comprises a 1-D linear uranyl coordination polymer. There is one unique uranium atom, one benzoate, one oxalate, and one-half of a $Zn(phen)_3$ moiety in the asymmetric unit (Figure 8a). Every uranyl center in this compound is equatorially coordinated by five oxygen atoms from two oxalate groups and one unidentate benzoate unit, producing a $UO_7$ pentagonal bipyramid. Such $UO_7$ polyhedral units are connected by oxalate groups to generate a linear structure, on either side of which the benzoates are connected (Figure 8b). Propeller-like $Zn(phen)_3$ serves as the template as well as the counterion in the interspaces of the chains. The whole structure is stabilized by weak π−π interactions between the phen and benzoate groups (Cg(1)−Cg(2): 3.94 Å, Table 2).

**Structure of Compound 8.** Compound **8** also comprises a 1-D structure, but consists of a heterometallic $[Zn_2U_2O_{14}N_4]$ cluster as its building unit. As shown in Figure 9a, there is one distinct uranium atom, one zinc atom, one benzoate, one-half of

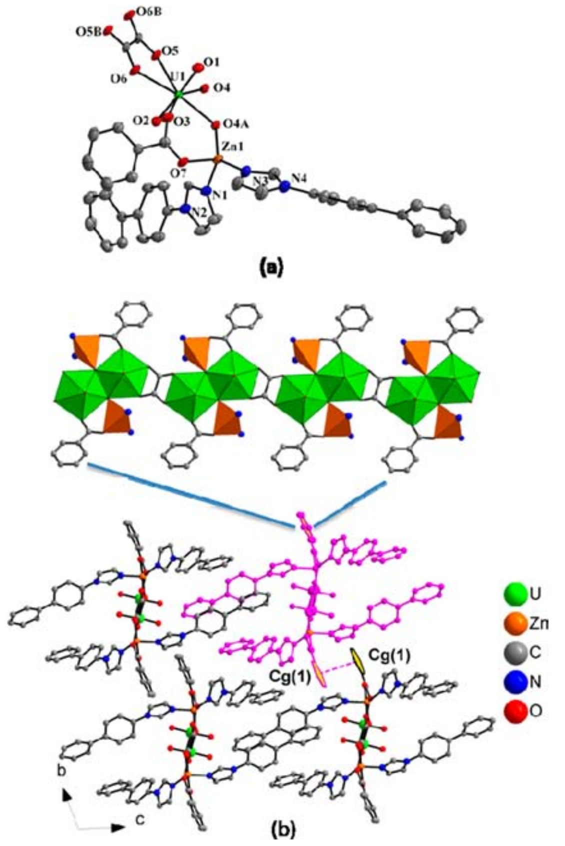


**Figure 9.** (a) ORTEP representation of the asymmetric unit of compound **8**. Thermal ellipsoids are drawn at the 50% probability level. Symmetry code: A, $1 - x$, $1 - y$, $1 - z$; B, $2 - x$, $1 - y$, $1 - z$. (b) The packing mode of compound **8** viewed along the [100] direction with the 1-D structure formed by tetranuclear $[UZnO_{14}N_4]$ units (highlighted in purple).

an oxalate, and two bpi molecules in its asymmetric unit. The uranium atom is seven coordinated by two "*yl*" oxo atoms and five equatorial oxygen atoms. Two such $UO_7$ pentagonal bipyramids connect each other via edge sharing forming a dimer. The zinc atom is tetrahedrally coordinated by two bridging oxygen atoms and two N atoms from two bpi molecules. Two $ZnO_2N_2$ polyhedra share a common corner with the uranyl dimer, resulting in the tetranuclear unit (Figure 9b). Similar to compound **7**, the units are also bridged by oxalate groups to generate the linear structure, and the benzoates and coordinated bpi molecules are connected on both sides of the chain. The chains interact with each other through $\pi-\pi$ interactions (3.64 Å, Table 2) between benzoate groups to form the whole supramolecular structure (Figure 9b).

**Structure Discussion.** Semirigid tricarboxylalic acid ($H_3L^1$) as three connected nodes bridges three $UO_7$ units forming a 1-D structure of compound **1**, while when the carboxylate groups are changed to the para-position ($H_3L^2$), a layered arrangement of compound **2** with *kdg* plane net is produced, which features tetranuclear clusters of $UO_7$ polyhedra. Although the semirigid ligands are isomer, they adopt different coordination modes in compounds **1** and **2**, where $L^1$, $\mu_5$: $\eta^2$, $\eta^2$, $\eta^1$ and $L^2$, $\mu_6$: $\eta^2$, $\eta^2$, $\eta^2$. These two structures are different from the known 3-fold-interpenetrated network,[21] whose ligand can be seen as the methyl of $H_3L^2$ is replaced by ethyl. When dicarboxylic acid was used in the synthesis, three complexes (**3**−**5**) have been isolates. In compound **3**, the $L^3$ group adopts $\mu_5$: $\eta^2$ (carborxylate), $\eta^1$ (carborxylate), $\eta^1$ (O-donor), $\eta^1$ (N-donor) coordination modes, and links three uranyl centers to generate a 2-D structure. This layer can be simplified as *sql* net. In molecular compounds **4** and **5**, the $L^3$ ligand assumes tridentate coordination mode $\mu_3$: $\eta^1$ (carborxylate), $\eta^1$ (carborxylate), $\eta^1$ (N-donor). The anionic molecular assembly of **5** is isostructural to neutral $[UO_2(dipicH)_2]\cdot 4H_2O$ (dipic = dipicolinate),[25] which is stabilized by intermolecular $\pi$-stacking. In contrast, the extended interaction apparent in **5** is formed between the uranyl arrangement and the bpi template. The monocarboxylic acid (the benzoate group) serves as didentate ligand to chelate one uranyl cation in compound **6** and bridge one uranyl center and one zinc atom in compound **8**, while in compound **7**, it takes a unidentate coordination fashion. Complex **6** is analogous to its F-substituted derivative $UO_2(O_2CC_6F_5)_2$-(bipy).[26] It is noteworthy that the significant effect on the crystal structures is caused by Zn ions. In **7**, the $Zn(phen)_3$ unit as template and counterion interacts with the uranyl anionic part via $\pi-\pi$ interactions. For two uranyl−zinc heterometallic complexes (**2** and **8**), different $UO_7$ pentagonal pyramid condensation is observed (tetranuclear $U_4(\mu_3\text{-}OH)_2$ for **2** and dinuclear $U_2$ for **8**), and then Zn species are further coordinated to the clusters, leading to two types of heterometallic hexamer and tetramer units, respectively. Another important role is played by the N-ligands in the construction of compounds **3**−**8**. In compounds **3** and **5**, protonated dib and bpi show as the template and counterion, respectively. In **4** and **6**, phen and bipy play the part of coligands coordinating to the uranyl cation. In **7** and **8**, phen and bpi are coordinated to the zinc atoms as coligands.

**IR Spectroscopy.** All of these synthesized compounds were characterized by IR spectroscopy (Supporting Information Figure S9). From 1647 to 1022 $cm^{-1}$, multiple intense bonds are displayed, which are due to the carboxylate groups and aromatic ring deformations including benzene and N-heterocyclic rings. These peaks cannot be precisely determined. The antisymmetric stretching modes of the uranyl cation are observed in the area 968−846 $cm^{-1}$, while the symmetric stretching modes are observed in the range of 834−760 $cm^{-1}$. The bands in the low wavenumber region of 600−420 $cm^{-1}$ correspond to the elongations of the U−O in equatorial positions.[27]

**Photoluminescent Properties.** The emission of green light centered near 520 nm from uranyl-containing compounds has been documented for decades. This charge-transfer-based emission is always related to the symmetric and antisymmetric vibrational modes of the uranyl cation, and generally there are several typical peaks in the spectrum. The photoluminescent properties of these compounds were studied, and the spectra are illustrated in Figure 10. Compounds **3**, **5**, and **6** exhibit several emission peaks in the range of 474−570 nm, which are typical for uranyl complexes. Compound **5** exhibits very strong uranyl emission with principal emission maxima at 474, 491, 512, 535, and 560 nm. Compounds **3** and **6** also produce characterized uranyl emissions with relatively high intensity (485, 499, 520, 544, and 569 nm for **3**, 474, 491, 512, 535, and 560 nm for **6**). These emission peaks correspond to the electronic and vibronic transitions $S_{11}-S_{00}$ and $S_{10}-S_{0v}$ ($v$ = 0−4). As compared to the benchmark compound $UO_2(NO_3)_2\cdot 6H_2O$,[10b] these compounds are red-shifted by a value of 10 nm for compound **3**, and 2 nm for compounds **5** and **6**. Such a behavior was previously observed for other uranyl compounds.[10−12] For compounds **2** and **8**, a broad band in the

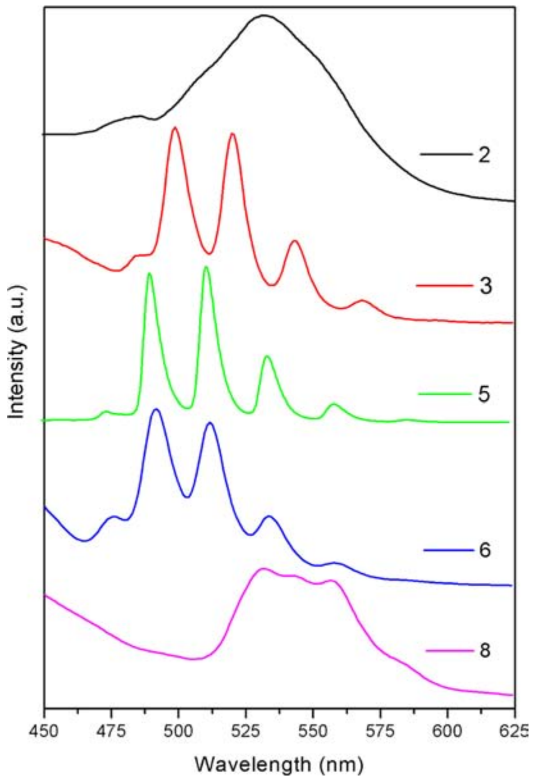


**Figure 10.** The photoluminescent spectra of compounds **2** ($\lambda_{ex}$ = 444 nm), **3** ($\lambda_{ex}$ = 363 nm), **5** ($\lambda_{ex}$ = 327 nm), **6** ($\lambda_{ex}$ = 426 nm), and **8** ($\lambda_{ex}$ = 362 nm), showing the green light emission of uranyl centers.

area of 500−580 nm with no fine structures was resolved (very weak for **2**); however, this is also originating from the charge transfer of uranyl cations.[15] For compounds **1**, **4**, and **7**, no characteristic emission of uranyl cations was observed. To the best of our knowledge, not all uranyl complexes exhibit luminescence of $UO_2^{2+}$ cations. Many factors are relevant to the luminescent property, such as size and quality of the crystal, disorder within the equatorial plane of the uranyl group, and so on.[28] It is particularly noteworthy that **3**, **5**, **6**, and **8** with strong luminescence all comprise short $\pi-\pi$ contacts with intercentroid distances of 3.45−3.67 Å (Table 2). In contrast, for **1**, **2**, **4**, and **7**, relatively remote contacts between parallel aromatic entities (>3.7 Å) are arranged, and weak emission and even lack of emission are shown. On the basis of these results, it seems plausible that $\pi$-stacking interactions contribute to the strong uranyl emission. This is consistent with the observation reported by Thuéry et al.[25]

## ■ CONCLUSION

In summary, we have synthesized a series of uranyl coordination materials by using various mono-, di-, and tricarboxylic acids. Compound **1** is a 1-D structure constructed of $UO_7$ polyhedra and semirigid $L^1$ ligand. Compound **2** features a layered arrangement containing tetranuclear of uranyl centers as the building unit connected by semirigid $L^2$ ligand. Compound **3** also features a 2-D structure, but is constructed by mononuclear uranyl centers and $L^3$ groups. Neutral molecular assemblies of compounds **4** and **6** are composed of uranyl center, carboxylate, and N-ligands, while the negative charge of molecular **5** is compensated by protonated bpi. Uranyl oxalate chain in compound **7** is coordinated by unibentate benzoate, and assured by $Zn(phen)_3$. Compound **8** is a heterometallic linear structure featuring tetramer of $UO_7$ and $ZnO_2N_2$ polyhedra. Benzoate and bpi molecules are coordinated to the chain. Photoluminescent studies reveal that compounds **2**, **3**, **5**, **6**, and **8** display characteristic emissions of uranyl centers. This work enriches the structural diversity of uranyl complexes and demonstrates the success of construction of new uranyl hybrids by organic ligands.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

X-ray crystallographic CIF files, selected bond lengths and angles, and IR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

## ■ AUTHOR INFORMATION

### Corresponding Author

*E-mail: szm@ciac.ac.cn.

### Author Contributions

‖These authors contributed equally.

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

We are thankful for the support of this work by the National Nature Science Foundation of China (21171662, 21301168, 21101148), Jilin Province Youth Foundation (20130522132JH, 20130522123JH, 201201005), SRF for ROCS (State Education Ministry), and Program for New Century Excellent Talents in University (NECT-11-0958).

## ■ REFERENCES

(1) (a) Wang, K. X.; Chen, J. S. *Acc. Chem. Res.* **2011**, *44*, 531−540. (b) Cahill, C. L.; de Lill, D. T.; Frisch, M. *CrystEngComm* **2007**, *9*, 15−26. (c) Polinski, M. J.; Wang, S. A.; Alekseev, E. V.; Depmeier, W.; Liu, G. K.; Haire, R. G.; Albrecht-Schmitt, T. E. *Angew Chem., Int. Ed.* **2012**, *51*, 1869−1872.

(2) (a) Gorden, A. E. V.; Xu, J.; Raymond, N. K.; Durbin, P. *Chem. Rev.* **2003**, *103*, 4207−4282. (b) Ewing, R. C. *Can. Mineral.* **2001**, *39*, 697−715. (c) Prapaipong, P.; Shock, E. L.; Koretsky, C. M. *Geochim. Cosmochim. Acta* **1999**, *63*, 2547.

(3) Villa, E. M.; Marr, C. J.; Jouffret, L. J.; Alekseev, E. V.; Depmeier, W.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **2012**, *51*, 6548−6558.

(4) Norquist, A. J.; Doran, M. B.; O'Hare, D. *Inorg. Chem.* **2005**, *44*, 3837−3843.

(5) Wang, S. A.; Alekseev, E. V.; Stritzinger, J. T.; Liu, G. K.; Depmeier, W.; Albrecht-Schmitt, T. E. *Chem. Mater.* **2010**, *22*, 5983−5991.

(6) Lee, C.-S.; Wang, S.-L.; Lii, K.-H. *J. Am. Chem. Soc.* **2009**, *131*, 15116−15117.

(7) (a) Chen, W.; Yuan, H. M.; Wang, J. Y.; Liu, Z. Y.; Xu, J. J.; Yang, M.; Chen, J. S. *J. Am. Chem. Soc.* **2003**, *125*, 9266−9267. (b) Poojary, D. M.; Cabeza, A.; Aranda, M. A. G.; Bruque, S.; Clearfield, A. *Inorg. Chem.* **1996**, *35*, 1468−1473. (c) Knope, K. E.; de Lill, D. T.; Rowland, C. E.; Cantos, P. M.; de Bettencourt-Dias, A.; Cahill, C. L. *Inorg. Chem.* **2012**, *51*, 201−206. (d) Andrews, M. B.; Cahill, C. L. *Angew Chem., Int. Edit.* **2012**, *51*, 6631−6634.

(8) Burns, P. C.; Ewing, R. C.; Navrotsky, A. *Science* **2012**, *335*, 1184−1188.

(9) (a) Mihalcea, I.; Henry, N.; Volkringer, C.; Loiseau, T. *Cryst. Growth Des.* **2012**, *12*, 526−535. (b) Olchowka, J.; Falaise, C.; Volkringer, C.; Henry, N.; Loiseau, T. *Chem.-Eur. J.* **2013**, *19*, 2012−2022. (c) Yu, Z. T.; Liao, Z. L.; Jiang, Y. S.; Li, G. H.; Li, G. D.; Chen, J. S. *Chem. Commun.* **2004**, 1814−1815.

(10) (a) Wu, H. Y.; Yang, W. T.; Sun, Z. M. *Cryst. Growth Des.* **2012**, *12*, 4669−4675. (b) Yang, W. T.; Wu, H. Y.; Wang, R. X.; Pan, Q. J.;

Sun, Z. M.; Zhang, H. J. *Inorg. Chem.* **2012**, *51*, 11458−11465. (c) Diwu, J.; Albrecht-Schmitt, T. E. *Chem. Commun.* **2012**, *48*, 3827−3829.

(11) (a) Yang, W. T.; Tian, T.; Wu, H. Y.; Pan, Q. J.; Dang, S.; Sun, Z. M. *Inorg. Chem.* **2013**, *52*, 2736−2743. (b) Thuery, P. *Inorg. Chem.* **2013**, *52*, 435−447. (c) Thuery, P. *CrystEngComm* **2012**, *14*, 3363−3366.

(12) (a) Tian, T.; Yang, W.; Pan, Q. J.; Sun, Z. M. *Inorg. Chem.* **2012**, *51*, 11150−11154. (b) Adelani, P. O.; Jouffret, L. J.; Szymanowski, J. E. S.; Burns, P. C. *Inorg. Chem.* **2012**, *51*, 12032−12040.

(13) (a) Mal, S. S.; Dickman, M. H.; Kortz, U. *Chem.-Eur. J.* **2008**, *14*, 9851−9855. (b) Miro, P.; Ling, J.; Qiu, J.; Burns, P. C.; Gagliardi, L.; Cramer, C. J. *Inorg. Chem.* **2012**, *51*, 8784−8790.

(14) (a) Adelani, P. O.; Albrecht-Schmitt, T. E. *Angew. Chem., Int. Ed.* **2010**, *49*, 8909−8911. (b) Adelani, P. O.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **2011**, *50*, 12184−12191. (c) Adelani, P. O.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **2009**, *48*, 2732−2734. (d) Grohol, D.; Subramanian, M. A.; Poojary, D. M.; Clearfield, A. *Inorg. Chem.* **1996**, *35*, 5264−5271.

(15) Yu, Z. T.; Li, G. H.; Jiang, Y. S.; Xu, J. J.; Chen, J. S. *Dalton Trans.* **2003**, 4219−4220.

(16) Thuery, P. *Cryst. Growth Des.* **2011**, *11*, 347−355.

(17) (a) Knope, K. E.; Cahill, C. L. *Inorg. Chem.* **2009**, *48*, 6845−6851. (b) Kerr, A. T.; Cahill, C. L. *Cryst. Growth Des.* **2011**, *11*, 5634−5641. (c) Thuery, P. *CrystEngComm* **2009**, *11*, 232−234.

(18) (a) Borkowski, L. A.; Cahill, C. L. *Inorg. Chem.* **2003**, *42*, 7041−7045. (b) Lhoste, J.; Henry, N.; Roussel, P.; Loiseau, T.; Abraham, F. *Dalton Trans.* **2011**, *40*, 2422−2424.

(19) Volkringer, C.; Henry, N.; Grandjean, S.; Loiseau, T. *J. Am. Chem. Soc.* **2012**, *134*, 1275−1283.

(20) Yu, Z. T.; Liao, Z. L.; Jiang, Y. S.; Li, G. H.; Chen, J. S. *Chem.-Eur. J.* **2005**, *11*, 2642−2650.

(21) Wu, H. Y.; Wang, R. X.; Yang, W. T.; Chen, J. L.; Sun, Z. M.; Li, J.; Zhang, H. J. *Inorg. Chem.* **2012**, *51*, 3103−3107.

(22) (a) Guo, M.; Sun, Z. M. *J. Mater. Chem.* **2012**, *22*, 15939−15946. (b) Dang, S.; Zhang, J. H.; Sun, Z. M. *J. Mater. Chem.* **2012**, *22*, 8868−8873. (c) Dang, S.; Ma, E.; Sun, Z. M.; Zhang, H. J. *J. Mater. Chem.* **2012**, *22*, 16920−16926. (d) Horvath, G.; Rusa, C.; Kontos, Z.; Gerencser, J.; Huszthy, P. *Synth. Commun.* **1999**, *29*, 3719−3731.

(23) *SMART and SAINT (software packages)*; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1996.

(24) *SHELXTL Program, version 5.1*; Siemens Industrial Automation, Inc.: Madison, WI, 1997.

(25) Harrowfield, J. M.; Lugan, N.; Shahverdizadeh, G. H.; Soudi, A. A.; Thuéry, P. *Eur. J. Inorg. Chem.* **2006**, 389−396.

(26) Deacon, G. B.; Mackinnon, P. I.; Taylor, J. C. *Polyhedron* **1985**, *4*, 103.

(27) Mer, A.; Obbade, S.; Rivenet, M.; Renard, C.; Abraham, F. *J. Solid State Chem.* **2012**, *185*, 180−186.

(28) Adelani, P. O.; Albrecht-Schmitt, T. E. *Cryst. Growth Des.* **2011**, *11*, 4227−4237.