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Extended Structures and Physicochemical Properties of Uranyl–Organic Compounds

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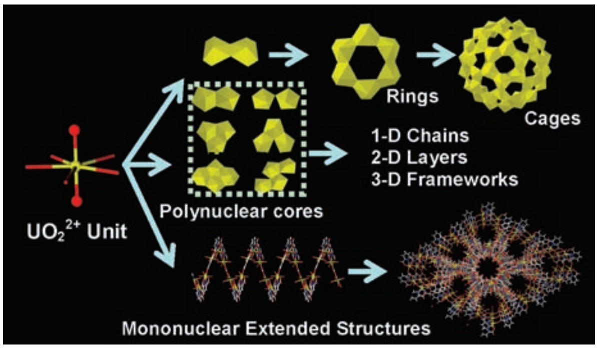
CONSPECTUS



The ability of uranium to undergo nuclear fission has been exploited primarily to manufacture nuclear weapons and to generate nuclear power. Outside of its nuclear physics, uranium also exhibits rich chemistry, and it forms various compounds with other elements. Among the uranium-bearing compounds, those with a uranium oxidation state of +6 are most common and a particular structural unit, uranyl UO_2^{2+} is usually involved in these hexavalent uranium compounds. Apart from forming solids with inorganic ions, the uranyl unit also bonds to organic molecules to generate uranyl–organic coordination materials. If appropriate reaction conditions are employed, uranyl–organic extended structures (1-D chains, 2-D layers, and 3-D frameworks) can be obtained. Research on uranyl–organic compounds with extended structures allows for the exploration of their rich structural chemistry, and such studies also point to potential applications such as in materials that could facilitate nuclear waste disposal.

In this Account, we describe the structural features of uranyl–organic compounds and efforts to synthesize uranyl–organic compounds with desired structures. We address strategies to construct 3-D uranyl–organic frameworks through rational selection of organic ligands and the incorporation of heteroatoms. The UO_2^{2+} species with inactive U═O double bonds usually form bipyramidal polyhedral structures with ligands coordinated at the equatorial positions, and these polyhedra act as primary building units (PBUs) for the construction of uranyl–organic compounds. The geometry of the uranyl ions and the steric arrangements and functionalities of organic ligands can be exploited in the the design of uranyl–organic extended structures,

We also focus on the investigation of the promising physicochemical properties of uranyl–organic compounds. Uranyl–organic materials with an extended structure may exhibit attractive properties, such as photoluminescence, photocatalysis, photocurrent, and photovoltaic responses. In particular, the intriguing, visible-light photocatalytic activities of uranyl–organic compounds are potentially applicable in decomposition of organic pollutants and in water-splitting with the irradiation of solar light. We ascribe the photochemical properties of uranyl–organic compounds to the electronic transitions within the U═O bonds, which may be affected by the presence of organic ligands.

1. Introduction

Uranium is the heaviest naturally occurring element on the earth, and it has been playing very important roles in the progression of humankind. The most impressive feature for uranium is its fissionability which can be exploited to manufacture nuclear weapons and to generate nuclear power. Elemental uranium is easily oxidizable, and the oxidation state of uranium in its oxidized form varies from +2 to +6 depending on the compound it forms or on the solution in which it is present. Nevertheless, the most stable oxidation state for this element is +6, and a corresponding species, the uranyl unit UO_2^{2+}, features a large number of uranium-bearing compounds. Uranyl may be bound to inorganic ions to form various inorganic compounds, whereas coordination linkage of organic molecules with uranyl units leads to significant diversification in structure and bonding for uranyl–organic solids. Among the uranyl–organic compounds, those with an extended structure (1-D chains, 2-D layers, or 3-D frameworks) have attracted much attention because of their intriguing architectures and potential optical, magnetic, fluorescent, and electronic applications.[1−3] The research on uranyl–organic

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compounds is also motivated by possible application for nuclear waste treatment in nuclear industry.

As for construction of metal–organic frameworks (MOFs) involving d-block and lanthanide metals,[4–8] the design of uranyl–organic extended structures can take advantage of the geometry of uranyl ions and the sterics and functionalities of the organic ligands. Through varying organic ligands, a variety of uranyl–organic extended structures with rich structural features have been prepared via various synthetic routes, including hydrothermal, solvothermal, sol–gel, and room temperature crystallization ones. The uranyl-bearing compounds composed of uranyl units and inorganic polyhedral anions,[9–12] such as silicates, phosphates, germanates, arsenates, and molybdates, may also occlude organic molecules as charge-balancing and space-filling species, but these compounds possess no metal–organic linkages, and consequently they will not be detailed in this account.

Similar to other transition metal ions, uranyl ions exhibit a strong coordination affinity to oxygen, nitrogen, and fluorine atoms, leading to uranyl bipyramids and even polynuclear uranium structural building units. These structural building units may be cross-linked by organic and/or inorganic components into various uranyl–organic coordination structures. Besides their amazing structural features, uranyl–organic extended structures also exhibit interesting physicochemical properties, such as photoluminescence, photocatalysis, and photoelectric conversion. The photoluminescence of uranyl–organic extended structures mainly arises from the excitation and relaxation of the U═O double bonds and, in some cases, from the interaction between the ligands and the uranium centers via the "antenna effect". Some uranyl–organic materials respond to visible light,[1,3] and visible-light photocatalysis of uranyl compounds has been observed.

In this Account, the rich structure chemistry and the related physicochemical properties of uranyl–organic compounds with an extended structure will be demonstrated, and strategies toward the design and preparation of uranyl–organic materials with a 3-D framework will be discussed.

2. Structural Building Units

Uranium-containing inorganic–organic coordination compounds with an extended structure are featured by involvement of the linear uranyl ion, UO_2^{2+}. The uranyl cation consists of a uranium center with a formal charge of +6 and two oxygen atoms called uranyl or terminal oxygens. The double bonds formed between the uranium and the terminal oxygen atoms in UO_2^{2+} are kinetically inactive in various chemical environments and reactions.

Isolated UO_2^{2+} cations exist in highly acidic aqueous solutions. Nevertheless, in less acidic media, the number and identity of uranyl species vary with the concentrations of both the UO_2^{2+} (aq) and the OH^- (aq) ions.[13] Increasing the pH value to over 3.0 and/or the UO_2^{2+} concentration to over 10^{-4} M, the uranyl cations tend to hydrolyze and polymerize, forming a number of polynuclear uranyl species, such as $U_2O_5^{2+}$ and $U_3O_8^{2+}$.[13] A dinuclear model of uranyl citrate was first proposed by Rajan and Martell in 1965.[14] Lately, with extended X-ray absorption fine structure (EXAFS) technique, it was revealed that in a solution with low pH values dinuclear species with uranium coordination to both hydroxyl and carboxylate groups exist.[15] Another popular species, trinuclear $(UO_2)_3(OH)_5^+$ complexes, may lose a water molecule under crystallization conditions to form an oxo-hydroxo-uranium polyhedral cation, $(UO_2)_3O(OH)_3^+$. It is rational that, under highly acidic conditions, the monomeric UO_2^{2+} cations directly take part in the crystal growth, while in solutions with relatively high pH values oligomeric uranyl species are formed and subsequently involved in the crystallization of uranyl–organic compounds. This tendency has been observed by Cahill and Rowland[16] in the formation of uranyl squarates from an aqueous solution under ambient conditions.

The uranyl species with coordination geometries such as square, pentagonal, and hexagonal bipyramids can be regarded as the primary building units (PBUs) of uranyl–organic extended structures (Figure 1). Corner- and/or edge-sharing the equatorial atoms of the monomeric uranyl units results in oligomeric uranyl cations ranging from dimers to hexamers that may act as secondary building units (SBUs) for the construction of uranyl–organic extended structures.

A large number of uranyl–organic coordination compounds, including clusters, 1-D chains, 2-D layers, and 3-D frameworks have been constructed by monomeric uranyl polyhedra. For instance, $UO_2(pdc)(H_2O)$ (pdc = pyridine-2,6-dicarboxylic acid), a chain structure of uranyl–organic coordination polymer, is formed by linkage of uranyl units with pdc molecules (Figure 2a–c).[17] Nanochannels with a diameter of about 6.4 Å are generated through the helical arrangement of the uranyl ions and the pdc molecules, and as a result the compound exhibits considerable adsorption capacity for water and methanol. Uranyl-based metallamacrocycles with three and four pentagonal bipyramid PBUs have been prepared through the binding of uranyl with (2*R*,3*R*,4*S*,5*S*)-tetrahydrofurantetracarboxylic acid in

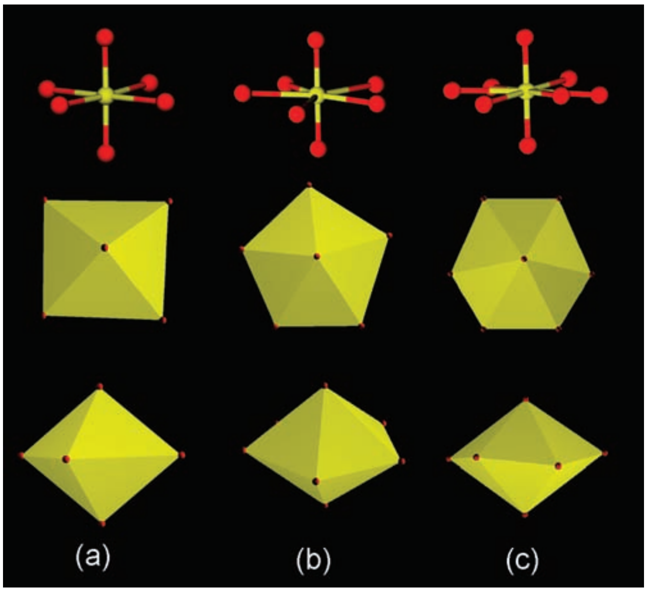


FIGURE 1. Coordination polyhedra in uranyl compounds: (a) square bipyramid, (b) pentagonal bipyramid, and (c) hexagonal bipyramid centered by uranium atom.

N-ethylpiperidine or triethylamine, respectively (Figure 2d),[18] providing an example of easy structure-tailoring in uranyl–organic assemblies through involvement of appropriate base molecules. By using 1,2,3,4-butanetetracarboxylic acid (H_4BTC) and 1,2,3,4-cyclobutanetetracarboxylic acid (H_4CBTC) as rigid linkers, various 2-D layers and 3-D frameworks were built up from monomeric uranyl building units.[19] Furthermore, under appropriate conditions, uranyl polyhedra may self-assemble into closed clusters containing 20, 24, 28, 32, 36, 40, 44, 50, and 60 uranyl polyhedra (designated U*n* by Burns and co-workers) (Figure 2e).[20–22] Some of these clusters have fullerene topologies with 12 pentagons as well as hexagons. The largest, U60, adopts the same topology as C60 with 12 isolated pentagons and 20 hexagons.

The dimeric uranyl units (Figure 3a,b), formed by the edge- and corner-sharing of two uranyl monomers are popular SBUs in uranyl–organic extended structures. For example, after reaction with pyridine-2,6-dicarboxylic acid in the presence of triethylamine, uranyl nitrate forms edge-sharing dinuclear uranyl complexes.[23] The dimeric species can be assembled through organic chelating agents and/or heteroatoms to form 1-D,[17,24] 2-D,[25] or 3-D structures.[17] We prepared a 1-D U–Zn–organic chain compound using pyridine-2,6-dicarboxylic acid as ligand.[17] This compound contains μ_2-OH corner-sharing dinuclear uranyl clusters in its structure.

Crystallographic analyses show that many uranyl–organic structures and minerals consist of trinuclear uranyl cores. The first uranyl–organic complex with a trinuclear core was crystallized with 1,3,5-triketonate ligands in the presence of triethylamine by Lintvedt and co-workers in 1982.[26] The uranium atoms in this trinuclear core are in discrete triangular arrangement, with each of these uranium atoms being bound to the other two through a μ_3-oxygen atom located at the center of the uranium triangle (Figure 3c). When one of the μ_2-oxygen atoms between two uranium atoms is replaced by a bridging organic agent or heteroatom moiety,[27] this trinuclear core will deviate from an ideal triangular shape (Figure 3d).

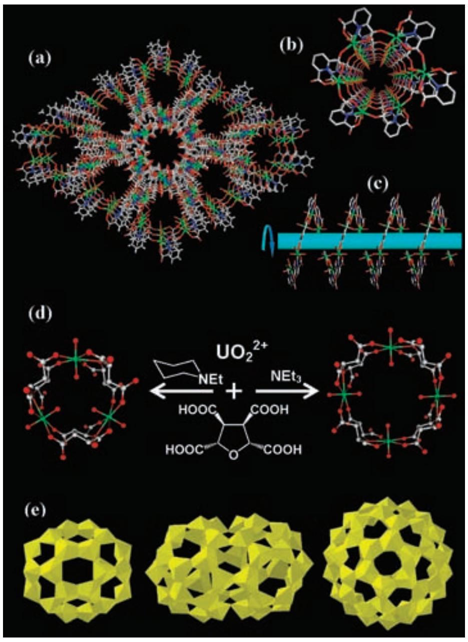


FIGURE 2. (a) 3-D structure showing 1-D channels, (b) a single channel formed by each single-stranded helix along the *c* axis, and (c) the single-stranded helix along the *a* axis for the compound $UO_2(pdc)(H_2O)$; (d) schematic reaction pathways and ball-and-stick representation of the metallamacrocycles $[UO_2L]_3^{6-}$ (left) and $[UO_2L]_4^{8-}$ (right); and (e) polyhedral representations of the uranyl peroxide components for the U36 (left), U44 (middle), and U60 (right) structures.

Four uranium atoms can be linked together by bridging μ_3-oxygen and μ_2-oxygen atoms to form the tetrameric SBU, $U_4(\mu_3\text{-}O)_2(\mu_2\text{-}O)_4$ core (Figure 3e). The replacement of the equatorial μ_2-oxygen atoms by other ligands, such as acetic acid, may lead to many interesting varieties in the configuration of this tetramer (Figure 3f–i). For example, a uranium–organic complex built up from tetrauranium clusters, namely, $[Zn_2(phen)_4U_4O_{10}(OAc)_2(NA)_2\text{–}(QA)_2]$ (phen = 1,10-phenanthroline; HOAc = acetic acid; HNA = nicotinic acid; H_2QA = quinolinic acid) has been crystallized previously.[28] The substitution of two μ_2-oxygen atoms by two carboxylate ligands leads to the formation of the tetranuclear $U_4(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2$ core (Figure 3f,g). If one or four

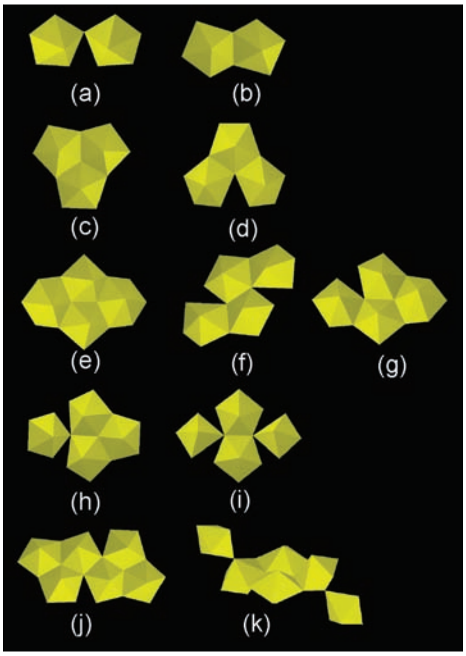


FIGURE 3. SBUs built up by corner- and edge-sharing the equatorial oxygen atoms of the uranyl units. (a,b) dimers, (c,d) trimers, (e−i) tetramers, and (j,k) hexamers.

μ_2-oxygen atoms are replaced, new tetranuclear cores, $U_4(\mu_3\text{-}O)_2(\mu_2\text{-}O)_3$ and $U_4(\mu_3\text{-}O)_2$, will be obtained (Figure 3h, i), as observed in $(UO_2)_4(O)_2(H2O)_2(C_7H_{10}O_4)_2(C_{10}H_8N_2)\cdot H_2O$ and $(UO_2)_2(O)(C_8H_{12}O_4)(C_{12}H_{12}N_2)$,[29] respectively.

Several uranyl extended structures composed of hexanuclear cores have been reported in the literature. In principle, these hexanuclear cores can be regarded as the derivatives of the above-mentioned tetranuclear $U_4(\mu_2\text{-}O)_4$ and $U_4(\mu_3\text{-}O)_2$, and trinuclear $U_3(\mu_3\text{-}O)(\mu_2\text{-}O)_3$ cores. For example, the edge-sharing of two $U_3(\mu_3\text{-}O)(\mu_2\text{-}O)_3$ cores leads to the formation of a planar hexanuclear $U_6(\mu_3\text{-}O)_4(\mu_2\text{-}O)_4$ core (Figure 3j), as observed in a 2-D uranyl-pyridinedicarboxylate compound.[30] Alternatively, oxo-bonding of two dangling uranium atoms to a nearly planar tetrameric $U_4(\mu_3\text{-}O)_2(\mu_2\text{-}O)_4$ core generates a new type of hexanuclear core (Figure 3k).[31]

3. Construction of 3-D Uranyl−Organic Frameworks

Three-dimensional frameworks usually exhibit many superior properties such as porous adsorption, ion exchange, and catalysis, and they are considered to be more stable than 1-D or 2-D structures. Therefore, the construction of 3-D uranium−organic frameworks is highly desirable. However, in contrast with uranyl−organic compounds containing 1-D chains,[3,32] 2-D layers,[3] and even cagelike structures,[21] the formation of 3-D uranium−organic frameworks has proved to be less successful. The main reason behind this phenomenon is the presence of the strong U═O bonds in the linear UO_2^{2+} ions, and the coordination geometry of the uranyl ion is considerably constrained by its linear shape.[33] The accessibility of the uranium center in the uranyl units is limited, and the incoming ligands can only bond to the center at the equatorial positions, forming a planar conformation with terminal U═O bonds almost perpendicular to the equatorial plane. As a result of lack of bonding from axial directions, uranyl−organic coordination compounds usually prefer chain/sheet arrangements to 3-D structures, especially when planar aromatic ligands are employed.[3,30]

The cross-linking ability of the metal centers and the ligands is of great importance for the design and synthesis of 3-D uranyl−organic compounds. Two strategies based on the rational selection of structure building components are usually used to construct three-dimensional uranyl−organic framework compounds. One is to employ organic molecules with multidentate coordination points and flexible backbones, such as aliphatic and alicyclic dicarboxylic acids as the ligands,[34,35] and the other is to introduce extra metal ions with high cross-linking ability to the reaction systems.[1,36−40] These extra metal ions can provide additional connecting nodes for the construction of the 3-D frameworks.

3.1. Impact of Ligand Geometry. As demonstrated previously, the geometries of organic ligands, usually carboxylic acids, exert a significant impact on the overall structures of metal−organic framework materials.[7] For the construction of 3-D uranyl−organic structures, it is essential that the chelating carboxylate groups in carboxylic acids are not within the same coordination plane. Taking carboxylate groups in aliphatic and alicyclic dicarboxylic acids, for example, there are three uranyl−carboxylate coordination geometries, that is, bidentate, bridging bidentate, and bridging tridentate.[25] Given the flexible carbon backbones, the aliphatic chain can rotate out of the equatorial plane of the UO_2^{2+} centers. Thus, in bridging bidentate and bridging tridentate connectivity modes, the aliphatic acids can assemble the uranyl building units into 3-D frameworks. For instance, employing adipic acid molecules as organic linkers, a 3-D uranyl−organic framework $UO_2(C_6H_8O_4)$ is built from $(UO_2)O_4(H_2O)_2$ dinuclear SBUs.[34] In this framework, the adipic acid molecules take two different geometries, namely "flat" and "kinked". The dinuclear uranyl building units are connected by the flat adipic acid molecules into a layer, further into a framework by the kinked acid molecules (Figure 4). The ability of the adipic acid backbone to rotate

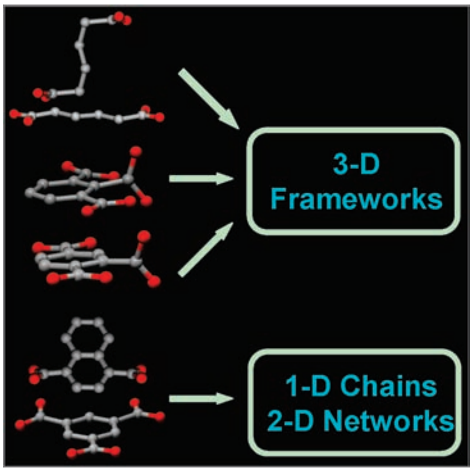


FIGURE 4. Effect of ligand conformation on formation of uranyl–organic structures.

about the single C–C bonds likely contributes to the construction of the 3-D framework. For the easy rotation of the backbones, a sufficient chain length is required in the building of 3-D frameworks. Actually, no 3-D uranyl–organic frameworks have been obtained, thus far, from dicarboxylate chains shorter than four carbons.[24]

For arylcarboxylic acids, strong steric hindrance and thus additional connectivity is critical for the generation of 3D uranyl–organic coordination architectures. Here we take 1,2,3-benzenetricarboxylate (v-BTC) and 1,2,4-benzenetricarboxylate (m-BTC) for example. Because of steric hindrance, at least one of the adjacent carboxylate groups in the v-BTC and m-BTC ligands is forced out of the ring plane and adopts a vertical conformation to avoid short contact of the O donors (Figure 4). The vertically oriented carboxylate groups increase the connectivity of the coordination structures from planar to three-dimensional. Recently, employing v-BTC and m-BTC as organic ligands, three 3-D uranyl–organic coordination frameworks $(UO_2)_3(v\text{-}BTC)_2(H_2O)_4$, $(UO_2)_6O(OH)(m\text{-}BTC)_2(m\text{-}HBTC)_2(H_2O)_2(H_3O)\cdot 6H_2O$, and $(UO_2)_2O(m\text{-}BTC)[NH_2(CH_3)_2]_2\cdot H_2O$ have been successfully prepared in our group,[41] demonstrating the importance of strong steric hindrance in arylcarboxylic acids for the formation of 3-D uranyl–organic structures. In contrast, 1,4-naphthalenedicarboxylate and 1,3,5-benzenetricarboxylate ligands, which prefer a planar conformation due to well separated carboxylate groups along the aromatic rings, tend to form 1-D or 2-D structures rather than 3-D coordination architectures (Figure 4).[3] Therefore, for successful construction of 3-D uranyl–organic coordination compounds, the rational selection of appropriate ligands is one of the key challenges.

3.2. Incorporation of Heterometal Ions. Besides the selection of proper ligands, an alternative approach to build up 3-D uranyl–organic frameworks is incorporation of heterometal ions with strong cross-linking ability to the reaction systems. Various metal ions, including alkali,[35,42,43] alkaline-earth,[33] d-block metal ions,[1,36–39] and even 4f lanthanides,[40] have been used together with uranyl species to construct uranyl-heterometal–organic structures with a 3-D framework.

We successfully prepared a novel 3-D framework uranyl-zinc compound, $(ZnO)_2(UO_2)_3(NA)_4(OAc)_2$ (HNA = nicotinic acid; HOAc = acetic acid), built-up by the assembly of $[(UO_2)_3(O)_2(CH_3CO_2)_2]_n$ chains via Zn^{2+} cations and nicotinate ligands (Figure 5a).[36] The infinite straight $[(UO_2)_3(O)_2(CH_3CO_2)_2]_n$ chains, formed by the connection of trinuclear uranyl units through bridging μ_3-O atoms, are corner-linked by octahedral Zn^{2+} cations via the terminal uranyl oxygen atoms, leading to the topology of a robust inorganic U–O–Zn double sheet. These double sheets are further interconnected via Zn^{2+} cations and tridentate nicotinate ligands to form a three-dimensional sandwich uranium–zinc–organic polymeric network. By using Zn^{2+} cations as additional connecting nodes, Lii and co-workers[37] prepared a mixed-metal uranyl–organic aquofluoride, $[(UO_2)_2F_8(H_2O)_2Zn_2(4,4'\text{-}bpy)_2]\cdot(4,4'\text{-}bpy)$, with a 3-D framework under hydrothermal conditions. By introducing Ni^{2+} cations into the reaction system containing quinolinic and acetic acids, a 3-D uranium–nickel–organic compound, namely, $[Ni_2(H_2O)_2(QA)_2(bipy)_2U_5O_{14}(H_2O)_2(OAc)_2]\cdot 2H_2O$(HOAc = acetic acid; bipy = 4,4′-bipyridine; H_2QA = quinolinic acid), was also prepared.[38] This 3-D framework is constructed from the polyoxouranium ribbons and Ni metal–organic layers through sharing QA ligands, with the polyoxouranium ribbons being composed of edge-sharing centrosymmetric pentanuclear U_5O cores (Figure 5b). In this uranium–nickel–organic compound, there exist two crystallographically different Ni atoms which are bridged by the QA ligands to form an infinite 1-D chain along the *a* axis. It is this chain that links the polyoxouranium ribbons into a 3-D framework via QA ligands. Other d-block metal ions are also efficient in the generation of 3-D uranyl-containing frameworks.

Alkali and alkaline-earth cations with high coordination numbers (for example, 6 for Na^+, 9 for K^+, 10 for Rb^+, and 8 for Ba^{2+}) are also proved to be suitable additional connecting nodes for the construction of 3-D uranyl–organic structures.[42] In addition to the high coordination numbers, alkali cations are apt to coordinate to the terminal oxygen

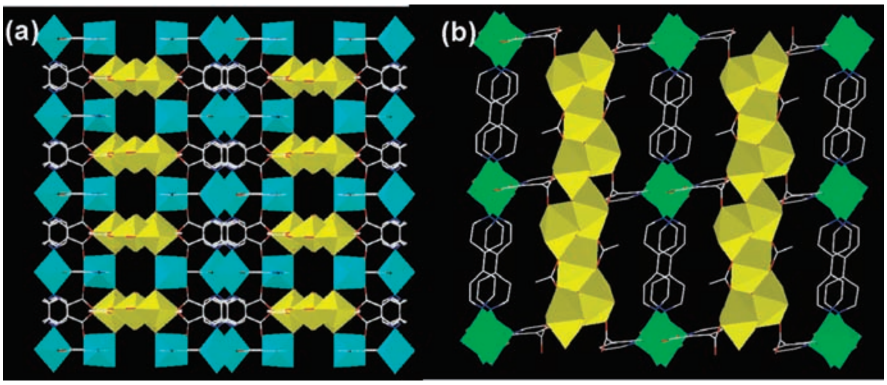


FIGURE 5. 3-D frameworks of (a) $(ZnO)_2(UO_2)_3(NA)_4(OAc)_2$ and (b) $[Ni_2(H_2O)_2(QA)_2(bipy)_2U_5O_{14}(H_2O)_2(OAc)_2]\cdot 2H_2O$ viewed along the [100] direction (U, yellow; Zn, light blue; and Ni, green).

atoms of the UO_2^{2+} moieties.[35,43] In the structure of $[(UO_2)_2(C_2O_4)_2(OH)Na(H_2O)_2]$, sheets formed by corner-sharing dimeric uranyl structural building units via bis-bidentate oxalate and bridging hydroxide groups are assembled into a 3-D framework through further bondings of Na^+ cations with the terminal oxygen groups of uranyl dimers.[35]

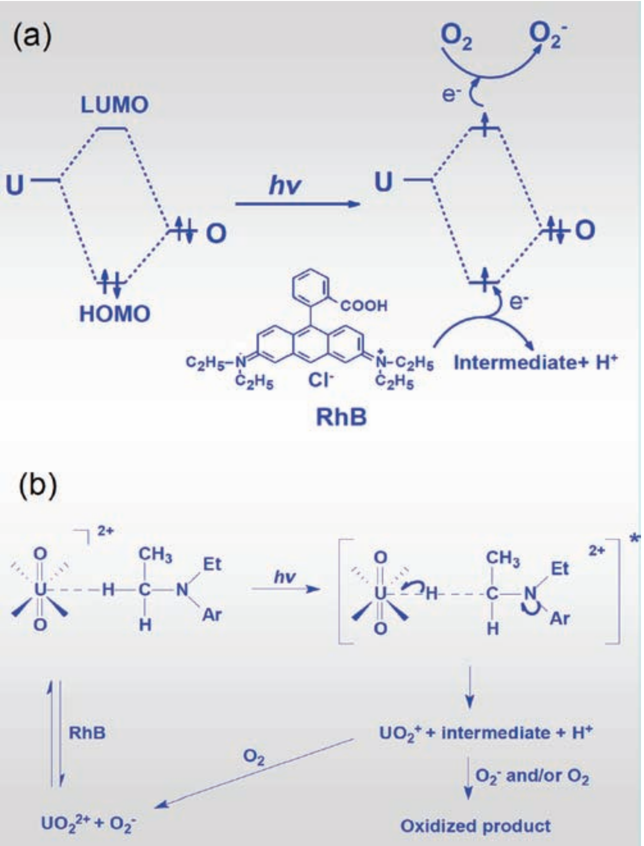
The two strategies, that is, ligand design and heteroatom incorporation, just provide the possibility for construction of 3-D uranyl−organic coordination compounds. The realization of this possibility also relies on the reaction conditions, such as the acidity of the reaction system, the concentration of uranyl ions, and reaction temperature. In addition to these two strategies, employment of suitable anions, which is frequently used in the construction of microporous materials, is also widely applied to the preparation of uranyl-bearing 3-D structures. A variety of 3-D uranyl−anionic frameworks, such as silicates, phosphates, germanates, arsenates, and molybdates, have been prepared.[9−12] However, in most of these compounds, either no organic molecules are involved or the involved molecules, such as organic amines, are not directly linked with the uranyl units; they just act as counterions or space fillers in the structures of the formed compounds.

4. Physicochemical Properties

Besides the rich structural features, uranyl−organic extended structures also exhibit attractive physicochemical properties, such as photoluminescence, photocatalysis, and photoelectronics. It has been extensively demonstrated in the literature that photoluminescence is characteristic for compounds involving uranyl units, either in solutions or in solid state. Photoexcitation of UO_2^{2+} leads to $^*UO_2^{2+}$. On the one hand, this excited uranyl species may relax to its ground state through emitting visible lights, and on the other it is also a very reactive species with high oxidation potential of approximately 2.6 eV.[44] Therefore, a uranyl compound may exhibit both photoluminescent and photocatalytic properties simultaneously. As reported previously, uranyl-containing aqueous solutions are photocatalytically active and they can lead to degradation of organic molecules efficiently under UV irradiation.[45] We found that uranyl-containing compounds with an extended structure in their solid state show remarkable photocatalytic performances as well. Water-insoluble photocatalytic solids can be easily separated from the reaction system, rendering the recycling and reuse of photocatalysts feasible. Besides photoluminescent and photocatalytic properties, photoelectric conversion behavior has also been discovered for uranyl-containing compounds.

4.1. Photoluminescence. Generally, the emission spectra of uranyl−organic extended structures show five peaks in the range of 450−600 nm, characteristic for UO_2^{2+} units.[2,39,41] These emission peaks are attributed to the transitions from the first excited electronic level to the symmetric and antisymmetric vibration levels of the uranyl ion. Recently, a solid uranyl−BETC compound, $(UO_2)_2(phen)_2(BTEC)$ (H_4BTEC = 1,2,4,5-benzenetetracarboxylic acid, phen = 1,10-phenanthroline), has been prepared hydrothermally.[2] The solid-state emission spectrum of this compound under excitation at 341 nm shows three main emission peaks at 491, 511, and 534 nm and two weak peaks at 478 and 560 nm. When monitoring the emission at 511 nm, the excitation spectrum presents a broad peak at 341 nm and several fine peaks ranging from 300 to 500 nm. Depending on compositions and structures of the uranyl−organic compounds, sometimes the fine feature of the emission peaks does not appear clearly,[30,36] and only a broad emission band in the 450−600 nm range is observed.

SCHEME 1[a]



[a](a) Photoexcitation of UO_2^{2+} species in uranyl–organic extended structures and (b) proposed photodegradation mechanism of RhB in the presence of uranyl–organic extended structures.

In some cases, the ligands on their own exhibit photoluminescence, especially when aromatic rings are involved in the ligands. In uranyl–organic compounds with photoluminescent ligands, if no emissions characteristic of free ligands are observed upon excitation at the ligand excitation wavelengths, it is possible that an efficient energy transfer from the ligand to the central metal atoms occurs. For example, after excitation of the BPM ligand in $[UO_2(NO_3)_2(bpm)]$ (bpm = 2,2′-bipyrimidine),[46] no emission from BPM appears, indicative of energy transfer from BPM to the central UO_2^{2+} ion in the photoluminescent process. Energy transfer has also been observed for the hydrothermally prepared $[(UO_2)_3O(OH)_2(3,4\text{-pydaH})(3,4\text{-pyda})_{0.5}]_n$ and $[(UO_2)_3O(OH)_2(2,4\text{-pyda})(H_2O)_2]_n \cdot nH_2O$ (3,4-pydaH_2 = 3,4-pyridinedicarboxylic acid, 2,4-pydaH_2 = 2,4-pyridinedicarboxylic acid),[30] given the fact that the excitation peaks for the two uranyl-containing structures resemble those of the free 3,4-pydaH_2 and 2,4-pydaH_2 ligands. It has been demonstrated that when the uranyl ion is excited directly, the emission intensity for the uranyl–organic materials is on the same order of magnitude as that of the spectrum resulting from direct ligand excitation,[39] indicating that there is little energy loss from radiationless decay.

4.2. Photocatalytic Performance. Since early 1800s, the photochemistry, especially the photocatalytic behavior, of uranyl compounds has attracted considerable attention.[45] As revealed by UV/vis spectroscopy, uranyl–organic extended structures respond to both UV and visible light. The absorptions in the UV and the visible regions are ascribed to the charge-transfer transitions within the uranyl group.[47,48] Two photodegradation mechanisms, namely, hydrogen abstraction and electron transfer, are generally accepted for the photocatalytic reactions involving uranyl species.[45] Upon photoexcitation, electrons may be promoted from the HOMO, the occupied 2p orbitals of oxygen, to the LUMO, the empty uranium orbitals, generating excited $^*UO_2^{2+}$ species (Scheme 1). The excited electron in the LUMO is not stable, and it may return to the HOMO instantly. However, if organic molecules (such as rhodamine B (RhB)) with an appropriate orientation are within a reasonable range, electrons from these molecules may be abstracted by the $^*UO_2^{2+}$ species, resulting in intermediates and protons. As the HOMO is occupied by the electrons from the guest molecules, the excited electrons in the uranyl unit would remain in the LUMO until they are captured by electronegative substances, such as O_2 in the solution, generating highly active peroxide anions. The peroxide anions further oxidize and decompose the organic intermediates in the solution, leading to complete degradation of the organic substances (Scheme 1).

The photocatalytic activities of uranyl–organic extended structures under UV and visible irradiation have been demonstrated previously. Through the assembly of silver and the uranium with mixed ligands, 2,2′-bipyridyl (bipy) and 1,4-benzenedicarboxylate (bdc), we prepared a metal–organic extended structure $[Ag(bipy)(UO_2)(bdc)_{1.5}]$ with a 2-D network under hydrothermal conditions.[1] This water-insoluble material exhibits superior UV- and visible-light photocatalytic activities. RhB in solution was used as a target pollutant to demonstrate the photodegradation activity of this Ag–U-organic assembly. Control experiments indicate that the RhB degradation time under UV irradiation is markedly shortened (Figure 6) in the presence of the assembly compound in comparison with in the presence of commercial TiO_2 (Degussa P25). More importantly, this Ag–U–organic material also exhibits excellent visible-light photodegradation activity for RhB degradation. It is found that the accessibility of dye molecules to the active excited

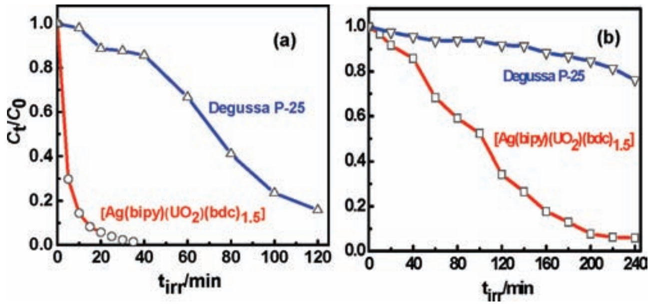


FIGURE 6. Concentration variation of RhB in the presence of [Ag(bipy)(UO_2)(bdc)$_{1.5}$] under irradiation of (a) UV light and (b) visible light.

U center of the uranyl-containing compounds affects the photocatalytic activity as well. We obtained another Ag−U−organic compound [Ag_2(phen)$_2$$UO_2$(btec)] in the presence of 1,10-phenanthroline (phen) and 1,2,4,5-benzenetetracarboxylate (btec).[1] From the structure viewpoint, the less spacious interlayer region and fully coordinated U centers in this compound are unfavorable for the access of the dye molecules. As expected, [Ag_2(phen)$_2$$UO_2$(btec)] is less efficient than the [Ag(bipy)(UO_2)(bdc)$_{1.5}$] material in degradation of RbB under both UV- and visible-light irradiations. The dependence of photocatalytic activity on structural feature has been further demonstrated by other uranyl-containing compounds, such as [$(ZnO)_2(UO_2)_3(NA)_4(OAc)_2$] (HNA = nicotinic acid)[36] and [$Ni_2(H_2O)_2(qa)_2(bipy)_2U_5O_{14}(H_2O)_2(OAc)_2$]$\cdot 2H_2O$ (HOAc = acetic acid, bipy = 4,4′-bipyridine, H_2qa = quinolinic acid).[38]

Ag^+ is sensitive to light, and it is possible for the Ag^+ ions in Ag^+-bearing compounds to contribute to photocatalytic activities directly. Recently, in the presence of 1,4-naphthalenedicarboxylate (NDC) and bipyridine (bipy), two 2-D uranyl−organic extended structures, $(UO_2)_3O[Ag(2,2'\text{-bipy})_2]_2(NDC)_3$ and $(UO_2)_8(NDC)_{12}(4,4'\text{-bipyH}_2)_3(4,4'\text{-bipyH})_3$, with and without Ag^+ have been prepared.[3] We found that these two compounds show comparable photocatalytic activities under both UV- and visible-light irradiations. Given the similar uranium content and accessibility, it is concluded that the uranyl units in these two compounds are the active centers responsible for the photocatalytic properties, whereas the Ag^+ species are of less importance.

As pointed out, molecular O_2 dissolved in solutions takes part in the photodegradation processes of dye molecules. By controlling the oxygen concentration in the bubbling gas, it is possible to elucidate the relationship between photocatalytic reaction and oxygen concentration. We found that the photocatalytic degradation rate is very sensitive to O_2 at low oxygen contents but it appears to be saturated upon increasing the oxygen content to a certain value.[3] This observation is consistent with the photodecomposition mechanism of RhB. When the concentration of O_2 in the solution is low, the photoexcited uranyl species associated with abstracted RhB molecules capture the O_2 molecules which are then transformed into excited oxygen species instantly. As a result, a sharp increase in photodegradation rate with the O_2 concentration is expectable. With further increase in O_2 concentration, the amount of RhB-associated photoexcited uranyl centers is not sufficient to excite all of the O_2 molecules and thus no further increase in the photodegradation rate with O_2 concentration is observed.

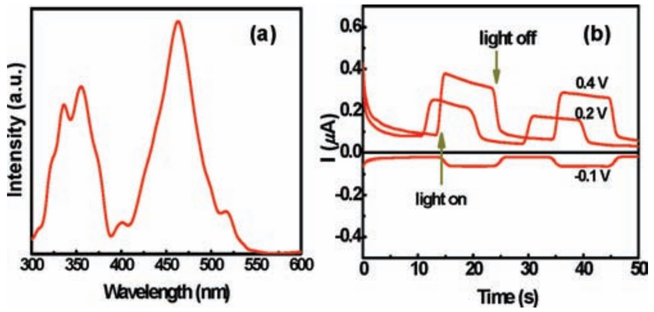


FIGURE 7. (a) SPS of $(ZnO)_2(UO_2)_3(NA)_4(OAc)_2$ and (b) transient photocurrent response of ITO−$(ZnO)_2(UO_2)_3(NA)_4(OAc)_2$ at various voltages (vs SCE).

4.3. Photoelectric Conversion. As a convenient and inexpensive characterization method, surface photovoltage technique has been widely used to study the optoelectronic properties of semiconductors and materials with semiconducting properties. Through recording the surface photovoltage spectra (SPS) and field-induced surface photovoltage spectra (FISPS), we investigated the photoelectric conversion behaviors of uranyl−organic extended structures.[28,36,41]

Under illumination without external electric field, the SPS signal for $(ZnO)_2(UO_2)_3(NA)_4(OAc)_2$ (HNA = nicotinic acid; HOAc = acetic acid), a 3-D framework,[36] shows two main response bands at approximately 350 and 463 nm (Figure 7a), in accordance with its diffuse reflectance UV−vis spectrum. Photoexcitation of the ITO−$(ZnO)_2(UO_2)_3(NA)_4(OAc)_2$ electrode in a 0.1 mol/L Na_2SO_4 solution generates an anodic photocurrent. Shuttering and unshuttering the light source leads to the variation in linear voltammograms (Figure 7b). Usually, photocurrent in an n-type semiconductor increases with anodic potential. Thus, $(ZnO)_2(UO_2)_3(NA)_4(OAc)_2$ may be regarded as a two-dimensional n-type semiconductor with its valence band consisting of the occupied O orbitals, whereas its conduction band consists of the empty metal orbitals. The low photocurrent density in combination with a low electrical conductivity (<10^{-5} S cm^{-1}) for $(ZnO)_2(UO_2)_3(NA)_4(OAc)_2$ suggests that this coordination polymer compound contains controlled carrier density.[49] This finding may help to explore new types of semiconducting materials, especially among coordination polymer compounds containing actinides.

The SPS and FISPS spectra for $(UO_2)_2O(m\text{-BTC})[NH_2(CH_3)_2]_2 \cdot H_2O$, a 3-D uranyl–organic framework, show only a single peak in the 200–600 nm wavelength range.[41] The absence of Zn^{2+} or other transition-metal ions in the compound clearly demonstrates that the uranyl species alone account for the photovoltaic response. Upon application of a positive field, the photovoltage is significantly enhanced with increasing biases, whereas if a negative field is applied, the response completely disappears. From the structure viewpoint, long-range overlap between the uranium orbitals and the delocalized π-orbitals of neighboring ligand molecules is possible in the 3-D framework of $(UO_2)_2O(m\text{-BTC})[NH_2(CH_3)_2]_2 \cdot H_2O$, and this overlap may facilitate the transfer of charge carriers along the framework and consequently enhance the photovoltaic response.

5. Concluding Remarks and Outlook

Uranyl–organic compounds constructed by the combination of uranyl ions with organic ligands have aroused great interest not only in the academic but also in the industrial sectors. In this Account, we have highlighted the recent efforts of our own group and others toward understanding the structural features, rational synthesis, and physicochemical properties of uranyl–organic materials with an extended structure. All the uranyl–organic structures are featured by the linear UO_2^{2+} unit, which can be equatorially coordinated only. The uranyl polyhedra and their oligomeric counterparts are the structural building units for the crystal structures of uranyl–organic compounds. The concentration of UO_2^{2+} and the acidity of the reaction system exert considerable impact on the oligomerization of uranyl ions and thus the uranyl–organic structures. Under highly acidic conditions, the monomeric UO_2^{2+} cations directly take part in the crystal growth of uranyl–organic compounds, whereas in solutions with a relatively high pH value, oligomeric uranyl species are formed and subsequently get involved in the crystallization of the corresponding compounds.

Because of the geometry constraint of uranyl ions, uranyl–organic coordination compounds usually prefer chain/sheet arrangements to 3-D structures. To obtain 3-D framework uranyl–organic compounds, the cross-linking ability of both the metal centers and the organic ligands should be increased. The strategies include employment of organic ligands with multidentate points and flexible backbones or strong steric hindrance and incorporation of heteroatoms in construction of uranyl–organic compounds. It is worth noting that there are a number of other factors that affect the realization of these two strategies.

Due to the electronic transitions within the U=O bonds and charge transfer from a ligand to an empty 5f orbital on the U atom upon excitation, uranyl–organic compounds exhibit attractive photoluminescent, photocatalytic, and photoelectrical properties. Under UV- and visible-light irradiation, uranyl–organic materials with an extended structure may degrade organic pollutants efficiently, and the photocatalytic activity is attributed to the presence of uranyl centers in these materials. It is believed that, with the further understanding of the nature of uranyl–organic extended structures, more physicochemical properties for uranyl–organic compounds will be revealed.

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FOOTNOTES

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