

Synthesis, Structure and Photoluminescent Studies of Two Novel Layered Uranium Coordination Polymers Constructed from UO(OH) Polyhedra and Pyridinedicarboxylates

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Two new uranium coordination polymers have been obtained from the hydrothermal reaction of $(\text{UO}_2)(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ with 3,4-pyridinedicarboxylic acid (3,4-pydaH₂) or 2,4-pyridinedicarboxylic acid (2,4-pydaH₂). $[(\text{UO}_2)_3(\mu_3\text{-O})(\mu_3\text{-OH})_2(3,4\text{-pydaH})(3,4\text{-pyda})_{0.5}]_n$ (**1**) crystallizes in the orthorhombic space group *Pccn* with $a = 18.168(2)$, $b = 12.635(1)$, $c = 16.149(1)$ Å, $V = 3707.0(5)$ Å³, and $Z = 8$. $[(\text{UO}_2)_3(\mu_3\text{-O})(\mu_3\text{-OH})(\mu_2\text{-OH})(2,4\text{-pyda})(\text{H}_2\text{O})_2]_n \cdot n\text{H}_2\text{O}$ (**2**) is in the orthorhombic space group *Pbcn* with $a = 22.788(2)$, $b = 7.1468(5)$, $c = 21.627(1)$ Å, $V = 3522.1(4)$ Å³, and $Z = 8$. Complex **1** features a wave-like 2D layer that is constructed by connecting the

1D UO(OH) ribbons by the V-shaped 3,4-pyda or 3,4-pydaH ligands. Complex **2** is a rare hexameric species amongst uranium compounds and features a (4,4) planar “open-layer”, which is constructed by the 4-connected hexameric UO(OH) polyhedra and the 2-connected 2,4-pyda ligands. The fluorescence emission (521 nm) of **2** is red-shifted by about 13 nm (emission) and about 40 nm (excitation) compared to that of **1**, and the lifetimes increase with the polymerization of UO(OH) polyhedra (145 μs for **1** compared to 24.4 μs for **2**). (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2005)

Introduction

In the area of inorganic-organic hybrid materials, metal-organic coordination polymers built from nano-sized MO(OH) clusters and multi-functional carboxylates are of current interest driven partially by their intriguing molecular topologies and crystal packing motifs as well as the fact that they may be designed with a variety of functionalities in mind, such as photoelectronics, separation, magnetism, ion exchange, gas storage, and catalysis.^[1–7] In addition to being robust and thermally stable, some possess photoluminescent properties, a feature that has contributed to the closed-shell d¹⁰ metal compounds, including 3d¹⁰ copper(I) and zinc(II), 4d¹⁰ silver(I) and cadmium(II), and 5d¹⁰ gold(I) and mercury(II) complexes, being widely investigated for new materials.^[8–11] In fact, the highest valent actinide elements have similar 5d¹⁰ electrons in spite of the shielding of the outer 6s²6p⁶ electrons, therefore they are also good candidates for luminescent materials. However, the luminescent properties of solid-state actinide compounds are relatively less studied compared to other transition metal compounds.^[12] Uranium is the most representative element of the actinides and therefore has been investigated most.^[12–15]

Several groups are endeavoring to obtain functional uranium oxide and oxyfluoride materials and have made much progress; so far, a wide range of uranyl phosphates, nitrates, perchlorates, sulfates, selenates, and iodates have been successfully synthesized and characterized.^[12a,12b,13,14] These uranium compounds can be classified as “uranium-inorganic frameworks” (UIFs), in which the frameworks are merely constructed by the inorganic UO(F) polyhedra, and the role of the organic component is just charge-balancing and/or space-filling. In contrast, the term “uranium-organic frameworks” (UOFs) means that the uranium-organic connectivity is interrupted by a bridging organic spacer.^[1c] Unlike UIFs, UOFs were hardly known before 2003, and were not rapidly developed until recently by O'Hare, Cahill, You, and Chen.^[12c,12d,15] The emergence of UOFs is meaningful because diverse organic components can be incorporated, and therefore the construction and functionalities of this kind of uranium coordination polymer are getting more intriguing.^[12c,12d,15]

The heterofunctional pyridinedicarboxylic acids are optimal ligands not only due to their “antenna effect”,^[16] which can occur through an energy transfer from the excited π orbitals of the pyridine ring to the uranium metal center,^[12c,12d,16] but also due to their ability to incorporate the MO(OH) clusters into the metal-organic frameworks.^[17] Our previous studies of 3d¹⁰ and 4d¹⁰ photoluminescent compounds revealed that the formation of MO(OH) cores can significantly increase the emission lifetime,^[11] which is important for luminescent materials. We have now extended our research to 5d¹⁰ actinides to search for new photolumi-

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nescent materials containing MO(OH) clusters, and report herein two novel layered UOFs constructed from UO(OH) polyhedra and pyridinedicarboxylates, namely $[(\text{UO}_2)_3(\mu_3\text{-O})(\mu_3\text{-OH})_2(3,4\text{-pydaH})(3,4\text{-pyda})_{0.5}]_n$ (**1**) and $[(\text{UO}_2)_3(\mu_3\text{-O})(\mu_3\text{-OH})(\mu_2\text{-OH})(2,4\text{-pyda})(\text{H}_2\text{O})_2]_n \cdot n\text{H}_2\text{O}$ (**2**).

Results and Discussion

Synthesis and Characterization

The hydrothermal method has been proved to be very effective for the synthesis of uranium coordination polymers.^[12–15] It is well known that changing the hydrothermal conditions, such as the temperature, reaction time, pH value, and molar ratio of the reactants, can significantly influence the final reaction products. In previous explorations of the synthesis of metal-cluster-based coordination polymers containing mixed organic ligands under typical hydrothermal conditions (i.e. 120–180 °C and 2–7 days), we and others have found that pH 8–9 is most suitable for the formation of metal-hydroxy(oxy) clusters,^[11,17] although uranium-hydroxy(oxy) species can be formed at a rather lower pH value of 3–4, which was used in the preparation of uranylhydroxy(oxy) clusters **1** and **2**.

Crystal Structures

X-ray structural analysis showed that compound **1** crystallizes in the orthorhombic space group *Pccn*. Each asymmetric unit in **1** contains three crystallographically unique uranyl ions, one μ_3 -oxo (O_7), two μ_3 -hydroxo groups (O_8 , O_9), and one 3,4-pydaH, all of which lie on a general position, and one 3,4-pyda which lies across a twofold axis. Selected bond lengths and angles are listed in Table 1. Bond-valence sum (BVS) calculations with U–O and U–N bond-valence parameters taken from the literature^[13a,18] confirm that the uranium centers are unambiguously U^{VI} with values of 6.10, 6.08, and 6.11 in **1**. Owing to the presence of the heavy uranium atoms, hydrogen atoms can hardly be located in the difference map, so we distinguished the μ_3 -oxo and μ_3 -hydroxo oxygen atoms by comparing the U–O bond lengths and U–O–U angles with corresponding ones of related compounds containing $(\text{UO}_2)_4(\mu_3\text{-OH})_2$ ^[13a–13c] and $(\text{UO}_2)_3(\mu_3\text{-O})$ ^[15c] cores as well as by BVS calculations on the oxygen atoms.^[13a,14c,18] Each uranium center is bound to two axial oxides to form a uranyl unit $[\text{UO}_2]^{2+}$. The U–O_{uranyl} bond lengths range between 1.75(1) and 1.79(1) Å, in good agreement with the reported average uranyl bond length of 1.758(4) Å.^[13a] Each uranyl unit is coordinated to five equatorial oxides to form a $[\text{UO}_7]$ pentagonal bipyramid (Figure 1, a) with U–O(μ_3 -oxo), U–O(μ_3 -hydroxo), and U–O(carboxylate) bonds lengths of 2.21(1)–2.264(9), 2.39(1)–2.54(1), and 2.38(1)–2.46(1) Å, respectively, which are all in the normal range of U–O distances reported in the literature.^[12–15] Interestingly, no pyridyl nitrogen atoms from the pyda and pydaH ligands are coordi-

nated to the uranyl units in **1**, therefore the polymerization of the uranyl cations extends in the [100] direction by edge-sharing the adjacent pentagonal bipyramids to form infinite $[(\text{UO}_2)_3(\mu_3\text{-O})(\mu_3\text{-OH})_2]_n^{2n+}$ ribbons. The one-dimensional ribbons are connected by 3,4-pyda and 3,4-pydaH bridges into wave-like sheets with a dihedral angle of 77.8° between the U–O ribbons (Figure 1, b). The coordination mode of the 3,4-pyda ligands in **1** is different from those found in other coordination polymers containing 3,4-pyda ligands.^[17a,17b]

Each crystallographically independent unit of **1** contains one $[(\text{UO}_2)_3(\mu_3\text{-O})(\mu_3\text{-OH})_2]^{2+}$, one $(3,4\text{-pydaH})^-$, and one half of $3,4\text{-pyda}^{2-}$. The proton on the pyridyl nitrogen could not be located from the difference map owing to the presence of the heavy uranium ion. However, the distances $[\text{N}\cdots\text{O} = 2.85(2)\text{--}3.00(2)\text{ Å}]$ between the pyridyl nitrogen and three uranyl oxygen atoms indicate the presence of a trifurcated hydrogen-bonding interaction, which means that the pyridyl nitrogen should be protonated and the net charge of the $(\text{pydaH})^-$ moiety can be assigned as -1 (Figure 1, c). Moreover, C5 can be distinguished from N1 by considering their hydrogen-bonding environment. The C \cdots O distance between C5 and O3A is 3.10(2) Å, with a C–H \cdots O angle of 173.5°, which suggests a typical C–H \cdots O interaction.^[19] However, the N2 and C11 atoms of another pyda ligand are not distinguishable because this pyda moiety lies on a twofold axis.

Compound **2** crystallizes in the orthorhombic space group *Pbcn*. Each asymmetric unit in **1** contains three crystallographically unique uranyl ions, one μ_3 -oxo (O_1), one μ_2 -hydroxo (O_2), one μ_3 -hydroxo (O_3), one 2,4-pyda, and two aqua ligands, all of which lie on a general position (Figure 2, a). Selected bond lengths and angles are listed in Table 2. BVS calculations confirm that the uranium centers are U^{VI} , with values of 6.05, 6.05, and 6.03 in **2** for U(1), U(2), and U(3), respectively.^[13a,18] There are two kinds of uranium pentagonal bipyramids in **2**, namely a $[\text{UO}_7]$ and a $[\text{UO}_6\text{N}]$ unit, with mean U=O, U–O(μ_3 -oxo), U–O(hydroxo), U–O(carboxylate), U–O(aquo), and U–N(pyridyl) bonds lengths of 1.775(7), 2.213(7), 2.397(7), 2.464(8), 2.389(8), and 2.617(9) Å, respectively. All these distances are also within the normal range of U–O or U–N bonds.^[12–15] In contrast to **1**, the pyridyl nitrogen atom and one 2-position carboxylate oxygen atom of each 2,4-pyda ligand chelate to a uranium atom, while the other carboxylate end bridges two uranyl units in a μ_2 -carboxylato-*O,O'* mode. This coordination mode has recently been found in the 3D coordination polymer $\alpha\text{-}[\text{Cd}_2(\mu_3\text{-OH})_2(2,4\text{-pyda})]$.^[17c] The pyridyl ring is efficiently driven by this chelating coordination mode to be coplanar with the uranyl pentagonal equatorial plane. Each hexameric uranyl cluster is surrounded by four 2,4-pyda ligands, which means that further polymerization of uranyl in the plane is inevitably interrupted. As shown in part b of Figure 2, the resulting open framework is a 2D (4,4) square grid by considering the hexameric uranyl clusters as the 4-connected nodes and the 2,4-pyda ligands as the connections between the 4-connected nodes. The lattice water molecules are situated be-

Table 1. Selected bond lengths [Å] and angles [°] for **1**.^[a]

Compound 1			
U(1)–O(11)	1.75(1)	U(3)–O(14)	1.76(1)
U(1)–O(10)	1.76(1)	U(3)–O(7)	2.21(1)
U(1)–O(7)	2.26(1)	U(3)–O(1)	2.38(1)
U(1)–O(2a)	2.39(1)	U(3)–O(9c)	2.44(1)
U(1)–O(5)	2.39(1)	U(3)–O(4b)	2.45(1)
U(1)–O(8)	2.49(1)	U(3)–O(8)	2.50(1)
U(1)–O(9)	2.50(1)	U(1)–U(2)	3.8498(8)
U(2)–O(13)	1.77(1)	U(1)–U(3)	3.8678(8)
U(2)–O(12)	1.79(1)	U(2)–U(3)	3.8190(9)
U(2)–O(7)	2.21(1)	U(2)–U(3a)	3.9301(8)
U(2)–O(8a)	2.39(1)	N(1)···O(15d)	2.85(2)
U(2)–O(6a)	2.41(1)	N(1)···O(12e)	3.00(2)
U(2)–O(4b)	2.46(1)	N(1)···O(10e)	2.95(2)
U(2)–O(9)	2.54(1)	C(5)···O(3d)	3.10(2)
U(3)–O(15)	1.75(1)		
O(11)–U(1)–O(10)	178.3(6)	O(4b)–U(2)–O(9)	135.9(4)
O(11)–U(1)–O(7)	90.6(5)	O(15)–U(3)–O(14)	177.5(5)
O(10)–U(1)–O(7)	90.9(5)	O(15)–U(3)–O(7)	88.6(5)
O(11)–U(1)–O(2a)	87.9(5)	O(14)–U(3)–O(7)	93.7(5)
O(10)–U(1)–O(2a)	90.5(5)	O(15)–U(3)–O(1)	91.0(5)
O(7)–U(1)–O(2a)	142.5(4)	O(14)–U(3)–O(1)	87.8(5)
O(11)–U(1)–O(5)	91.1(5)	O(7)–U(3)–O(1)	143.5(4)
O(10)–U(1)–O(5)	88.2(5)	O(15)–U(3)–O(9c)	86.3(5)
O(7)–U(1)–O(5)	139.9(4)	O(14)–U(3)–O(9c)	91.3(5)
O(2a)–U(1)–O(5)	77.6(4)	O(7)–U(3)–O(9c)	137.2(4)
O(11)–U(1)–O(8)	93.4(5)	O(1)–U(3)–O(9c)	79.1(4)
O(10)–U(1)–O(8)	87.8(5)	O(15)–U(3)–O(4b)	95.5(5)
O(7)–U(1)–O(8)	68.7(4)	O(14)–U(3)–O(4b)	86.3(5)
O(2a)–U(1)–O(8)	148.7(4)	O(7)–U(3)–O(4b)	68.7(4)
O(5)–U(1)–O(8)	71.2(4)	O(1)–U(3)–O(4b)	75.0(4)
O(11)–U(1)–O(9)	91.3(5)	O(9c)–U(3)–O(4b)	154.1(4)
O(10)–U(1)–O(9)	88.6(5)	O(15)–U(3)–O(8)	94.5(5)
O(7)–U(1)–O(9)	68.8(4)	O(14)–U(3)–O(8)	85.4(4)
O(2a)–U(1)–O(9)	73.8(4)	O(7)–U(3)–O(8)	69.3(4)
O(5)–U(1)–O(9)	151.2(4)	O(1)–U(3)–O(8)	147.0(4)
O(8)–U(1)–O(9)	137.3(3)	O(9c)–U(3)–O(8)	68.9(4)
O(13)–U(2)–O(12)	175.0(5)	O(4b)–U(3)–O(8)	136.4(4)
O(13)–U(2)–O(7)	94.5(5)	U(3b)–O(4)–U(2b)	102.2(4)
O(12)–U(2)–O(7)	89.2(5)	U(2)–O(7)–U(3)	119.3(5)
O(13)–U(2)–O(8a)	85.8(5)	U(2)–O(7)–U(1)	118.8(4)
O(12)–U(2)–O(8a)	89.2(5)	U(3)–O(7)–U(1)	119.7(5)
O(7)–U(2)–O(8a)	137.5(4)	U(2c)–O(8)–U(1)	131.7(5)
O(13)–U(2)–O(6a)	92.7(5)	U(2c)–O(8)–U(3)	107.2(4)
O(12)–U(2)–O(6a)	86.8(5)	U(1)–O(8)–U(3)	101.9(4)
O(7)–U(2)–O(6a)	138.0(4)	U(3a)–O(9)–U(1)	131.7(5)
O(8a)–U(2)–O(6a)	84.2(4)	U(3a)–O(9)–U(2)	104.4(4)
O(13)–U(2)–O(4b)	87.5(5)	U(1)–O(9)–U(2)	99.8(4)
O(12)–U(2)–O(4b)	97.0(5)	U(2)···U(3)···U(2c)	129.36(17)
O(7)–U(2)–O(4b)	68.5(4)	U(1)···U(3)···U(2c)	69.53(16)
O(8a)–U(2)–O(4b)	153.6(4)	U(3)···U(2)···U(3a)	130.45(17)
O(6a)–U(2)–O(4b)	70.6(4)	U(1)···U(2)···U(3a)	70.723(16)
O(13)–U(2)–O(9)	85.9(5)	U(2)···U(1)···U(3)	59.318(16)
O(12)–U(2)–O(9)	92.3(5)	N(1)–H(1A)···O(15d)	125.2
O(7)–U(2)–O(9)	68.7(4)	N(1)–H(1A)···O(12e)	132.7
O(8a)–U(2)–O(9)	69.0(3)	N(1)–H(1A)···O(10e)	122.1
O(6a)–U(2)–O(9)	153.2(4)	C(5)–H(5)···O(3d)	173.5

[a] Symmetry codes: a) $-x + 1, y + 1/2, -z - 1/2$; b) $-x + 3/2, -y + 3/2, z$; c) $-x + 1, y - 1/2, -z - 1/2$; d) $-x + 3/2, y, z + 1/2$; e) $x + 1/2, y - 1/2, -z$.

tween the wave-like coordination layers and form water···oxo [O···O: 2.89(1)–3.05(1) Å; O–H–O: 145(13)–174(16)°] and water···hydroxo [O···O: 2.68(1) Å; O–H–O: 164.6°] hydrogen-bonding interactions with the upper and lower layers, respectively. These may make some contributions to the bending of the hexameric U–O polyhedra,

with an angle of 142.6°, and disturb the further equatorial polymerization in **2**. It should be noted that **2** is the first hexameric species of uranium(vi) compounds, although hexameric uranium(iv) compounds have been found.^[13d,13e] As far as we know, the majority of U⁶⁺ phases prefer to adopt a structure that is based upon infinite sheets of poly-

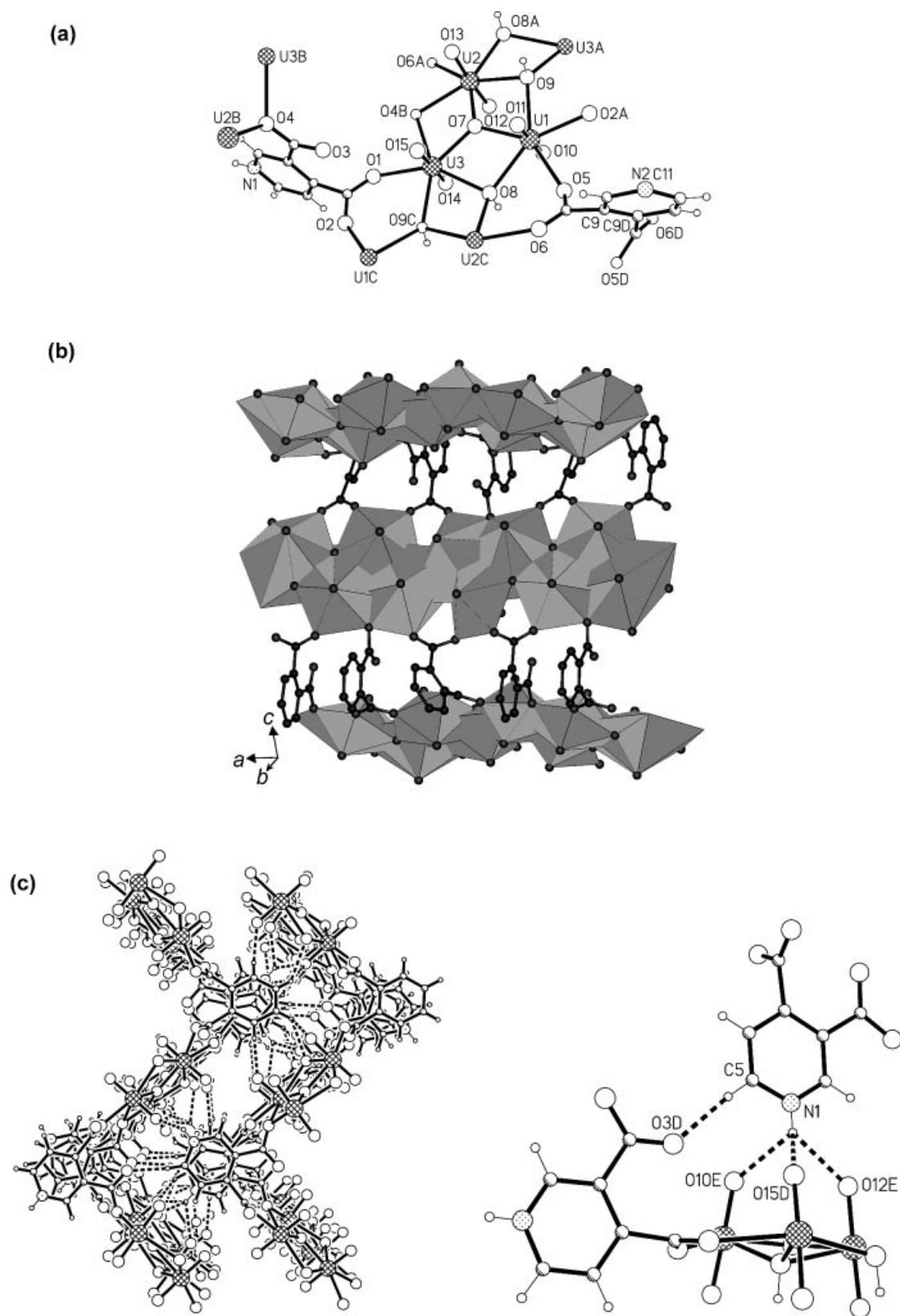


Figure 1. (a) Coordination environment in **1**. (b) A view of the 2D wave-like sheet in **1** with the UO_7 pentagonal bipyramids shown in gray. (c) Left: crystal packing between the wave-like layers in **1**; Right: an illustration of the trifurcated $\text{N-H}\cdots\text{O}$ and $\text{C-H}\cdots\text{O}$ hydrogen bonds between the adjacent layers in **1**.

hedra or a 1D chain (either trimeric, dimeric, or mononuclear).^[13–15]

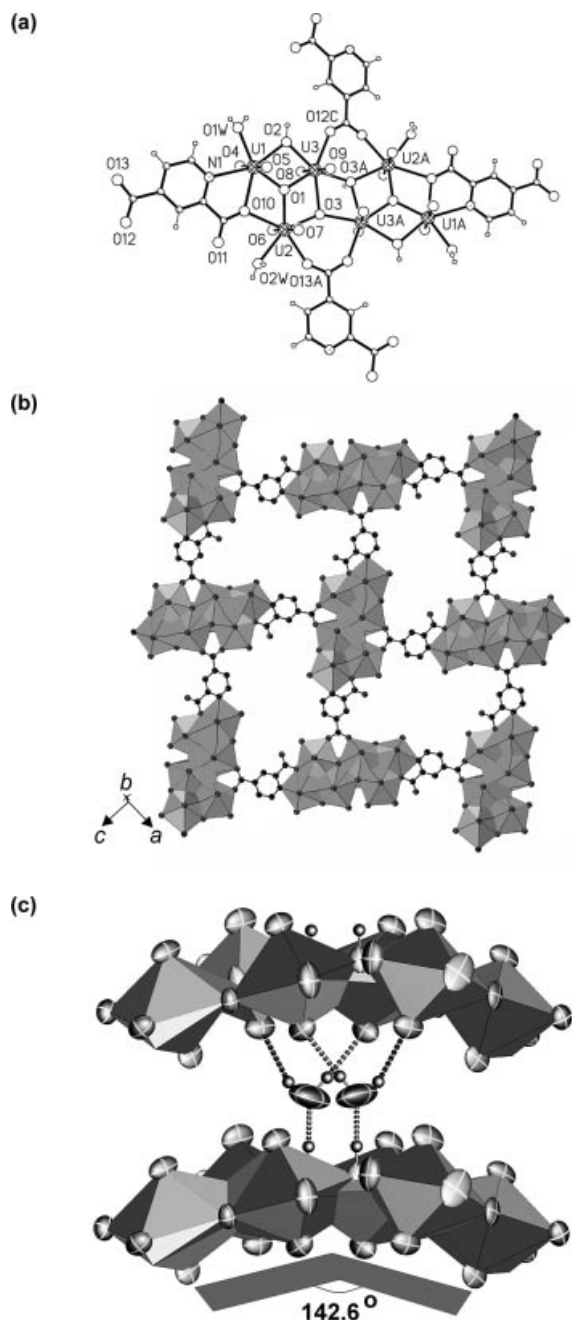


Figure 2. (a) Coordination environment in **2**. (b) A view of the 2D open-framework of **2**. (c) An illustration of the hydrogen bonding between the water molecules and the adjacent layers in **2** (atoms are shown as 50% probability displacement ellipsoids).

It is interesting to compare the dimensions and densities of compounds **1** and **2** with other recently reported UOFs and UIFs. As listed in Table 3, the representative UOFs are mainly based on uranium carboxylate coordination polymers, including the zero-dimensional metallamacrocycles constructed with (2*R*,3*R*,4*S*,5*S*)-tetrahydrofuran-tetracarboxylic acid,^[15d] the one-dimensional chains constructed

with glutaric acid,^[15a] isophthalic acid,^[15a] or adipic acid,^[15b] the two-dimensional layers constructed with 1-oxo-4-cyanopyridine,^[12c] ethyl (*S*)-lactic acid,^[12c] or 3,5-pyrazoledicarboxylic acid,^[12d] and the three-dimensional networks constructed with succinic acid,^[15a] adipic acid,^[15b] or quinolinic acid.^[15c,15e] If we sort the order as the density, **1** and **2** are the densest UOFs and are even denser than some UIFs. These results may be due to the following two facts. Firstly, these two compounds adopt a close-packing style *ABAB...* in order to fill the hollow space as much as possible, and secondly, the inorganic uranyl ions are highly polymerized with the O^{2-} or OH^- ions, which can enhance the density of the entire compounds. Although both zero-dimensional (0D) UOFs and UIFs have the lowest density, it is hard to determine the relationship between density and dimensions because there is no appropriate example (such as supramolecular isomers) in the reported UOFs and UIFs.

Luminescent Properties

The fluorescence spectra (Figure 3) of **1** and **2** were measured for crushed single-crystalline powder samples, which are pure phases, as confirmed by an XRD study (Figure S1 in the Supporting Information). Interestingly, the well-known characteristic emission fine-structure of UO_2^{2+} is observed in **1**, featuring a main peak ($\lambda = 521$ nm) and three shoulder peaks ($\lambda = 503$, 542, and 568 nm), while the emission fine-structure of **2** is inconspicuous and only a broad peak is observed ($\lambda = 534$ nm). In contrast, the highest emission peak of **2** is red-shifted by 13 nm compared to **1**, and the peaks ($\lambda = 362$, 478 nm) in the excitation spectrum of **2** are all red-shifted by 40 nm relative to **1** ($\lambda = 322$, 438 nm). It should be noted that the fluorescence spectra of free 2,4-pydaH₂ and 3,4-pydaH₂ display very weak photoluminescent properties (Supporting Information, Figure S2). Despite the weak intensity of the free ligands, the wavelengths of the excitation peaks ($\lambda = 364$ nm in 3,4-pydaH₂ and 343 nm in 2,4-pydaH₂) resemble the peaks of **1** and **2**, which indicates that the aromatic ligands may contribute to the related absorption bands in the excitation spectra of **1** and **2**, therefore ligand-to-metal charge transfer (LMCT) may occur between the 5d orbital of U^{6+} and the chromophoric pyridine-containing ligands,^[20] and the component of LMCT in the emission peak may contribute to the single peak nature of **2**,^[20] in which the pyridine nitrogen atom coordinates directly to the U^{6+} center. It is noteworthy that the excited-state lifetime (ca. 145 μs) of **1** is about six times that (ca. 24.4 μs) of **2** (see Figure S3; data were fitted with a single exponential decay function). This result is consistent with the long lifetime nature of the actinide ions.^[12] Several reasons may account for this difference. Firstly, the enhancement of the lifetime in **1** may be caused by the effect of infinite $\text{UO}(\text{OH})$ ribbons, which is consistent with our previous studies of 3d^{10} and 4d^{10} compounds^[11] as well as an aqueous fluorescence study of uranyl hydrolysis.^[21] Secondly, the chromophoric 2,4-pyda li-

Table 2. Selected bond lengths [Å] and angles [°] for **2**.^[a]

Compound 2			
U(1)–O(5)	1.766(8)	U(3)–O(1)	2.234(8)
U(1)–O(4)	1.779(7)	U(3)–O(3b)	2.390(7)
U(1)–O(1)	2.209(7)	U(3)–O(2)	2.403(7)
U(1)–O(1w)	2.355(8)	U(3)–O(12c)	2.440(9)
U(1)–O(2)	2.390(8)	U(3)–O(3)	2.510(7)
U(1)–O(10)	2.447(8)	U(1)···U(3)	3.7875(5)
U(1)–N(1)	2.617(9)	U(1)···U(2)	3.8865(6)
U(2)–O(6)	1.758(8)	U(2)···U(3)	3.8211(6)
U(2)–O(7)	1.795(7)	O(3)···O(3w)	2.68(1)
U(2)–O(1)	2.197(7)	O(3w)···O(7d)	3.05(1)
U(2)–O(13a)	2.357(7)	O(3w)···O(9a)	2.89(1)
U(2)–O(3)	2.406(7)	O(2)···O(5e)	3.36(1)
U(2)–O(2w)	2.422(9)	O(2w)···O(7f)	2.83(1)
U(2)–O(10)	2.612(7)	O(1w)···O(2g)	2.64(1)
U(3)–O(9)	1.772(7)	O(1w)···O(8e)	2.74(1)
U(3)–O(8)	1.778(7)		
O(5)–U(1)–O(4)	176.2(4)	O(7)–U(2)–O(10)	89.5(3)
O(5)–U(1)–O(1)	91.9(4)	O(1)–U(2)–O(10)	66.4(3)
O(4)–U(1)–O(1)	91.9(4)	O(13a)–U(2)–O(10)	147.5(3)
O(5)–U(1)–O(1w)	84.1(3)	O(3)–U(2)–O(10)	136.9(2)
O(4)–U(1)–O(1w)	92.7(3)	O(2w)–U(2)–O(10)	72.5(3)
O(1)–U(1)–O(1w)	149.5(3)	O(9)–U(3)–O(8)	178.1(4)
O(5)–U(1)–O(2)	90.8(3)	O(9)–U(3)–O(1)	90.2(4)
O(4)–U(1)–O(2)	90.7(3)	O(8)–U(3)–O(1)	91.6(3)
O(1)–U(1)–O(2)	69.5(3)	O(9)–U(3)–O(3b)	89.5(3)
O(1w)–U(1)–O(2)	80.3(3)	O(8)–U(3)–O(3b)	88.7(3)
O(5)–U(1)–O(10)	89.3(3)	O(1)–U(3)–O(3b)	134.9(2)
O(4)–U(1)–O(10)	91.8(3)	O(9)–U(3)–O(2)	86.1(3)
O(1)–U(1)–O(10)	69.4(3)	O(8)–U(3)–O(2)	95.2(3)
O(1w)–U(1)–O(10)	140.4(3)	O(1)–U(3)–O(2)	68.9(3)
O(2)–U(1)–O(10)	138.9(2)	O(3b)–U(3)–O(2)	155.9(2)
O(5)–U(1)–N(1)	90.5(3)	O(9)–U(3)–O(12c)	89.8(3)
O(4)–U(1)–N(1)	86.7(3)	O(8)–U(3)–O(12c)	89.1(3)
O(1)–U(1)–N(1)	133.8(3)	O(1)–U(3)–O(12c)	144.3(3)
O(1w)–U(1)–N(1)	76.6(3)	O(3b)–U(3)–O(12c)	80.8(3)
O(2)–U(1)–N(1)	156.6(3)	O(2)–U(3)–O(12c)	75.4(3)
O(10)–U(1)–N(1)	64.5(3)	O(9)–U(3)–O(3)	93.0(3)
O(6)–U(2)–O(7)	176.7(4)	O(8)–U(3)–O(3)	87.2(3)
O(6)–U(2)–O(1)	92.1(4)	O(1)–U(3)–O(3)	68.1(2)
O(7)–U(2)–O(1)	90.5(4)	O(3b)–U(3)–O(3)	66.9(3)
O(6)–U(2)–O(13a)	89.2(4)	O(2)–U(3)–O(3)	137.0(3)
O(7)–U(2)–O(13a)	87.5(4)	O(12c)–U(3)–O(3)	147.6(3)
O(1)–U(2)–O(13a)	145.9(3)	U(3)···U(1)···U(2)	59.71(1)
O(6)–U(2)–O(3)	84.3(3)	U(3)···U(2)···U(1)	58.86(1)
O(7)–U(2)–O(3)	94.7(3)	U(1)···U(3)···U(2)	61.43(1)
O(1)–U(2)–O(3)	70.6(3)	O(3)–H(3a)···O(3w)	164.6
O(13a)–U(2)–O(3)	75.6(3)	O(3w)–H(3wa)···O(7d)	145(13)
O(6)–U(2)–O(2w)	89.0(4)	O(3w)–H(3wb)···O(9a)	174(16)
O(7)–U(2)–O(2w)	90.3(3)	O(2)–H(2a)···O(5e)	148.6
O(1)–U(2)–O(2w)	138.9(3)	O(2w)–H(2wa)···O(7f)	163(11)
O(13a)–U(2)–O(2w)	75.2(3)	O(1w)–H(1wa)···O(2g)	152(10)
O(3)–U(2)–O(2w)	150.1(3)	O(1w)–H(1wb)···O(8e)	163(10)
O(6)–U(2)–O(10)	93.4(4)		

[a] Symmetry codes: a) $-x + 3/2, -y + 3/2, z + 1/2$; b) $-x + 1, y, -z + 1/2$; c) $x - 1/2, -y + 3/2, -z$; d) $x, 1 + y, z$; e) $-x, 1 + y, -z + 0.5$; f) $-x + 1.5, y + 0.5, z$; g) $-x, y + 2, -z + 0.5$.

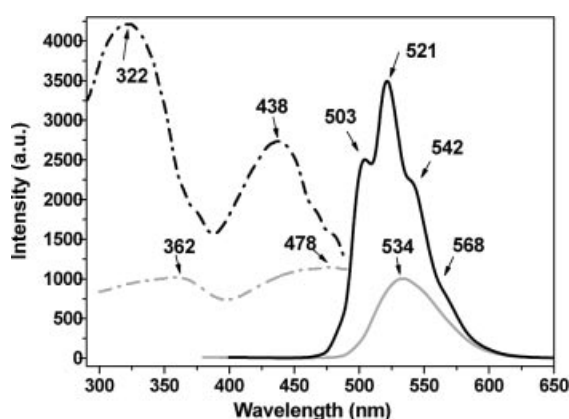
gand, which is a strong π -donor ligand that coordinates directly to the uranyl in the equatorial plane, would correlate well with the low luminescence quantum yield.^[12,20] Thirdly, the presence of the protonated pyridyl ring could enhance energy transfer from pyridinium to uranyl moieties in **1**.^[12] Finally, the existence of the lattice water molecules could partially quench the excited state in **2**.^[12,20]

Conclusions

Two new layered uranium–organic photoluminescent coordination polymers of 3,4- and 2,4-pyridinedicarboxylates, which contain infinite and finite UO(OH) polyhedra, respectively, have been hydrothermally synthesized and crystallographically characterized. This work reveals that

Table 3. A comparison of the densities and dimensions of representative UIFs and UOFs.

	Compounds	Dimensions	D_c [g cm ⁻³]	Ref.
UOFs	(C ₇ H ₁₆ N) ₆ [(UO ₂)(C ₈ H ₄ O ₉)] ₃ ·9H ₂ O	0D	1.346	[15d]
	(C ₆ H ₁₆ N) ₈ [(UO ₂)(C ₈ H ₄ O ₉)] ₄ ·2(CH ₃ OH)·2H ₂ O	0D	1.633	[15d]
	[UO ₂ F(C ₅ H ₆ O ₄)]·2H ₂ O	1D	2.324	[15a]
	[(UO ₂) _{1.5} (C ₈ H ₄ O ₄) ₂] ₂ [CH ₃ NCOH ₂]·H ₂ O	1D	2.400	[15a]
	[UO ₂ (C ₄ H ₄ O ₄)]·H ₂ O	3D	3.442	[15a]
	UO ₂ (C ₆ H ₄ NO ₃) ₂	2D	2.551	[12c]
	UO ₂ (C ₃ H ₅ O ₃) ₂	2D	2.898	[12c]
	UO ₂ (C ₆ H ₈ O ₄)(H ₂ O) ₂	1D	2.729	[15b]
	UO ₂ (C ₆ H ₈ O ₄)	3D	3.106	[15b]
	(ZnO ₂) ₂ (UO ₂) ₃ (C ₆ H ₄ NO ₂) ₄ (CH ₃ CO ₂) ₂	3D	2.918	[15c]
	UO ₂ Cu(C ₅ H ₂ N ₂ O ₄) ₂ (H ₂ O) ₂	2D	2.954	[12d]
	UO ₂ (C ₅ H ₂ N ₂ O ₄) ₂ (H ₂ O)	2D	3.548	[12d]
	[Ni ₂ (H ₂ O) ₂ (C ₇ H ₃ NO ₄) ₂ (C ₁₀ H ₈ N ₂)U ₅ O ₁₄ (H ₂ O) ₂ (C ₂ H ₃ O ₂) ₂]·2H ₂ O	3D	2.723	[15e]
	[(UO ₂) ₃ (O)(OH) ₂ (C ₇ H ₄ NO ₄)(C ₇ H ₃ NO ₄) _{0.5}]	2D	3.968	this work
	[(UO ₂) ₃ (O)(OH) ₂ (C ₇ H ₃ NO ₄)(H ₂ O) ₂]·H ₂ O	2D	4.071	this work
UIFs	(C ₄ H ₁₂ N ₂)UO ₂ F ₄ ·3H ₂ O ^[a]	0D	2.622	[14j]
	(C ₄ H ₁₂ N ₂)UO ₂ F ₄ ·3H ₂ O ^[b]	0D	2.643	[14j]
	(C ₄ H ₁₂ N ₂) ₂ U ₂ F ₁₂ ·H ₂ O	1D	2.922	[14j]
	(C ₄ H ₁₂ N ₂) ₂ (U ₂ O ₄ F ₅) ₄ ·11H ₂ O	2D	3.792	[14j]
	(C ₄ H ₁₂ N ₂) ₂ U ₂ O ₄ F ₆	3D	3.977	[14j]
	[(CH ₃) ₄ N][(C ₅ H ₅ NH) _{0.8} [(CH ₃) ₃ NH] _{0.2}]U ₂ Si ₉ O ₂₃ F ₄	3D	2.759	[14a]
	(C ₆ H ₁₄ N ₂)[UO ₂ (H ₂ O)(SO ₄)]	2D	2.78	[14d]
	(C ₅ H ₁₄ N ₂)[UO ₂ (H ₂ O)(SO ₄)]	1D	2.80	[14d]
	(C ₄ H ₁₂ N ₂)[UO ₂ (H ₂ O)(SO ₄)]	1D	2.95	[14d]
	(C ₅ H ₆ N)UO ₂ F ₃	1D	3.220	[12a]
	(C ₃ H ₅ N ₂)UO ₂ F ₃	1D	3.481	[12a]
	(C ₅ H ₁₄ N ₂)U ₂ O ₄ F ₆	1D	3.624	[12a]
	(C ₃ H ₅ N ₂)U ₂ O ₄ F ₅ ·1.75H ₂ O	1D	3.834	[14k]
	(C ₅ H ₆ N)U ₂ O ₄ F ₅	2D	4.020	[14k]
	(C ₆ H ₁₄ N ₂) ₂ [(UO ₂) ₆ (H ₂ O) ₂ F ₂ (PO ₄) ₂ (HPO ₄) ₄]·4H ₂ O	3D	3.557	[14h]
	[(UO ₂) ₃ (PO ₄)O(OH)(H ₂ O) ₂]·H ₂ O	3D	5.092	[14b]
	UO ₂ (IO ₃) ₂ (H ₂ O)	2D	5.300	[12b]
	UO ₂ (IO ₃) ₂	1D	5.786	[12b]
	Cs ₃ [(UO ₂) ₃ O ₂ (OH) ₃]Cl(H ₂ O) ₃	3D	5.590	[14c]
	(NH ₄) ₃ (H ₂ O) ₂ [(UO ₂) ₁₀ O ₁₀ (OH)][(UO ₄)(H ₂ O) ₂]	3D	6.252	[14c]
	Cs[(UO ₂) ₃ (HIO ₆)(OH)(O)(H ₂ O)]·1.5H ₂ O	3D	5.711	[14g]

Figure 3. The emission spectra (solid line) and excitation spectra (dash-dot line) of **1** (black) and **2** (gray).

the multitopic ligand has an important effect on the structures of uranium–organic coordination polymers and the lifetimes evidently increase with the polymerization of the UO(OH) polyhedra.

Experimental Section

General Remarks: The reagents and solvents employed were commercially available and used as received without further purification. The C, H, and N microanalyses were carried out with an Elementar Vario-EL CHNS elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm⁻¹ on a Bio-Rad FTS-7 spectrometer. X-ray powder diffraction (XRD) intensities for **1** and **2** were measured at 293 K on a Rigaku D/max-III A diffractometer (Cu-K α , λ = 1.54056 Å). The crushed, single-crystalline powder samples were prepared by crushing the crystals and scanned from 4–65° with a step of 0.1° s⁻¹. Calculated patterns for **1** and **2** were generated with PowderCell 2.3. The emission/excitation spectra were recorded on an F-4500 fluorescence spectrophotometer and the lifetimes were measured on an Edinburgh FLS-920 spectrophotometer equipped with a continuous Xe-900 Xenon lamp or a μ F900 microsecond flash lamp. Crushed single-crystalline powder samples of **1** and **2** and powder samples of the free ligands 2,4-pydaH₂ and 3,4-pydaH₂ were used for the photoluminescence measurements.

Synthesis: Complexes **1** and **2** were synthesized by heating a mixture of (UO₂)(CH₃COO)₂·2H₂O (0.203 g, 0.5 mmol), 3,4-pydaH₂ [or 2,4-pydaH₂ (0.083 g, 0.5 mmol)], and deionized water (9 mmol) in a molar ratio of 1:1:1000 in a 23-mL, Teflon-lined autoclave at

Table 4. Crystal and structure refinement data for compounds **1** and **2**.

Compound	1	2
Empirical formula	C _{10.5} H ₈ N _{1.5} O ₁₅ U ₃	C ₇ H ₁₁ NO ₁₆ U ₃
Formula mass	1109.26	1079.26
Temperature [K]	293(2)	293(2)
Wavelength [Å]	0.71073	0.71073
Crystal system	orthorhombic	orthorhombic
Space group	<i>Pccn</i> (no. 56)	<i>Pbcn</i> (no. 60)
<i>a</i> [Å]	18.168(2)	22.788(2)
<i>b</i> [Å]	12.635(1)	7.1468(5)
<i>c</i> [Å]	16.149(1)	21.627(1)
<i>V</i> [Å ³]	3707.0(5)	3522.1(4)
<i>Z</i>	8	8
<i>D</i> _{calcd.} [mg m ⁻³]	3.968	4.071
Absorption coefficient [mm ⁻¹]	22.229	27.603
<i>F</i> (000)	3804	3712
Crystal size [mm]	0.10 × 0.08 × 0.02	0.08 × 0.08 × 0.02
θ range for data collection [°]	1.96 to 27.50	1.79 to 27.50
Limiting indices	$-21 \leq h \leq 23$, $-16 \leq k \leq 15$, $-17 \leq l \leq 20$	$-29 \leq h \leq 17$, $-9 \leq k \leq 9$, $-27 \leq l \leq 28$
Reflections collected/unique	20920/4238 [<i>R</i> _{int} = 0.0850]	19029/4002 [<i>R</i> _{int} = 0.0513]
Completeness	99.2% (θ_{\max} = 27.50°)	98.9% (θ_{\max} = 27.50°)
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2002)	Multi-scan (<i>SADABS</i> ; Bruker, 2002)
Max. and min. transmission	0.6220 and 0.1790	0.6082 and 0.2162
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	4238/342/271	4002/9/262
Goodness-of-fit on <i>F</i> ²	1.048	1.070
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0618, <i>wR</i> ₂ = 0.1331 ^[a]	<i>R</i> ₁ = 0.0411, <i>wR</i> ₂ = 0.1002 ^[a]
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0833, <i>wR</i> ₂ = 0.1436 ^[a]	<i>R</i> ₁ = 0.0507, <i>wR</i> ₂ = 0.1050 ^[a]
Extinction coefficient	none	none
Largest diff. peak and hole [e Å ⁻³]	2.756 and -2.523	4.887 and -1.495

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

180 °C for 3 d. After slowly cooling down to room temperature within 12 h, yellow needle-like crystals of **1** (yield: 0.166 g, ca. 90% based on U) or yellow plate-like crystals of **2** (yield: 0.160 g, ca. 87% based on U) were filtered, washed with deionized water, and dried in the air.

1: C_{10.5}H₈N_{1.5}O₁₅U₃; calcd. C 11.37, H 0.73, N 1.89; found C 11.41, H 0.71, N 1.90. IR: $\tilde{\nu}$ = 911 cm⁻¹ U=O; 1374, 1427, 1551, 1582 C=C_(py) or C=N_(py); 1643, 1680 C=O; 2881, 3000, 3058, 3077 C–H or N–H; 3438, 3547 cm⁻¹ O–H.

2: C₇H₁₁NO₁₆U₃; calcd. C 7.79, H 1.03, N 1.30; found C 7.81, H 1.01, N 1.29. IR: $\tilde{\nu}$ = 930 cm⁻¹ U=O; 1322, 1384, 1479, 1542 C=C_(py) or C=N_(py); 1596, 1635 C=O; 2850, 2916, 3067 C–H; 3424, 3535, 3623 cm⁻¹ O–H_(H₂O) (for details, see Figure S4 in the Supporting Information).

X-ray Crystallographic Study: Diffraction intensities of **1** and **2** were collected on a Bruker Apex CCD area-detector diffractometer (Mo-*K*_α, λ = 0.71073 Å). Absorption corrections were applied by using the multiscan program *SADABS*.^[22] The structures were solved by direct methods and refined with a full-matrix least-squares technique with the *SHELXTL* program package.^[23] Anisotropic thermal parameters were applied to all non-hydrogen atoms. The organic hydrogen atoms were generated geometrically (C–H = 0.96 Å), as were the hydroxy oxygen atoms (O–H = 0.85 Å); the aqua hydrogen atoms were located from difference maps. For **1**, the proton on the pyridyl nitrogen of (3,4-pydaH)[–] was added in a geometrically idealized position. The disordered atoms of N2 and C11 were treated as each having an occupation of 50%. The crystallographic data for **1** and **2** are listed in Table 4.

CCDC270938 (for **1**) and -270939 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information Available: IR spectra, powder X-ray diffraction patterns, fluorescence spectra and lifetime spectra (with fitting results).

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