Syntheses, structures, and fluorescent properties of two uranium coordination polymers with carboxylic acids

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Syntheses, structures, and fluorescent properties of two uranium coordination polymers with carboxylic acids

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Two U(VI)-containing coordination polymers, $(UO_2)_2O_2(Suc)(2,2'-bipy)_2$ (**1**) and $UO_2(BC)_2(DMF)$ (**2**) (2,2'-bipy = 2,2'-bipyridine, H_2Suc = succinic acid, HBC = benzoic acid, DMF = *N,N*-dimethylformamide), have been synthesized and characterized *via* elemental analysis, infrared spectroscopy, UV-Vis spectroscopy, and single-crystal X-ray diffraction. Structural analyses show that **1** is a 1-D chain coordination polymer in which U(VI) ions are connected by succinic acid ligand and the 1-D chain is connected into a 3-D supramolecular network by CH···O hydrogen bonds between carbon of 2,2'-bipyridine and uranyl oxygen. For **2**, monomeric entities are further assembled into a 1-D supramolecular network by C–H···O hydrogen bonds between carbon of DMF molecule and coordinated carboxylate oxygen. Thermogravimetric analyses and photoluminescent properties of **1** and **2** are discussed.

Keywords: Uranium coordination polymers; Crystal structure; Photoluminescent properties; Hydrogen-bonding; Supramolecular assembly

1. Introduction

Interest in uranium coordination chemistry has increased, with the discovery of novel reagents, reactivity, and structural features [1–6]. Uranium exists in aqueous solution as the linear uranyl ion UO_2^{2+}, which has quite stable and unreactive uranium-oxygen double bonds [7, 8]. Uranium(VI) coordination polymers are dominated by the uranyl ion UO_2^{2+} [9, 10]. The coordination geometry of UO_2^{2+} is constrained by a linear shape, with four to six donors accommodated in the equatorial plane, thus giving classical polygons (tetragonal, pentagonal, or hexagonal). These geometries typically promote 1-D or 2-D structures [11–15]. Multidentate N- or O-donors not only have the capacity to bridge metal centers to form polymeric structures, but are also utilized as versatile linkers in constructing interesting coordination polymers with abundant hydrogen bonds [16–18]. Carboxylate-containing ligands have drawn much attention because of the diversity of bonding geometries, such as monodentate, chelating, bidentate bridging,

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monodentate bridging, and chelating bridging [19–23]. Consequently, in order to further study structural and spectral characterization of uranium(VI) coordination polymers, in this article, two uranium(VI) coordination polymers, $(UO_2)_2O_2(Suc)(2,2'\text{-bipy})_2$ (**1**) and $UO_2(BC)_2(DMF)$ (**2**), where $2,2'\text{-bipy} = 2,2'$-bipyridine, $H_2Suc =$ succinic acid, $HBC =$ benzoic acid, and $DMF = N,N$-dimethylformamide, were synthesized. Additionally, the photoluminescent properties and thermal stability of the complexes are investigated.

2. Experimental

2.1. *Materials and methods*

All chemicals purchased were of reagent grade or better and used without purification. C, H, and N analyses were made on a Perkin-Elmer 240 C automatic analyzer at the analysis center of Liaoning Normal University. Infrared (IR) spectra were recorded on a JASCO FT/IR-480 PLUS Fourier transform spectrophotometer with pressed KBr pellets from 200 to 4000 cm^{-1}. UV-Vis diffuse reflectance spectra were recorded with a JASCO V-570 UV-Vis/NIR spectrophotometer from 200 to 2500 nm. Luminescence spectra were reported on a JASCO FP-6500 spectrofluorimeter (solid). Thermogravimetric analysis (TGA) was performed under N_2 with a heating rate of $10°C\,min^{-1}$ on a Perkin Elmer Diamond TG/DTA. X-ray powder diffraction (XRPD) data were collected on a Bruker Advance-D8 with Cu-Kα radiation in the range $5° < 2\theta < 60°$, with a step size of $0.02°$ (2θ) and an acquisition time of 2 s per step.

2.2. *Synthesis*

2.2.1. Synthesis of $(UO_2)_2O_2(Suc)(2,2'\text{-bipy})_2$ (1). A mixture of a solution of $UO_2(CH_3COO)_2 \cdot 2H_2O$ (0.0848 g, 0.2 mmol), $2,2'$-bipyridine (0.0624 g, 0.4 mmol), and succinic acid (0.0472 g, 0.4 mmol) in deionized water (8 mL) and DMF (2 mL) was stirred for about 30 min at room temperature. The resultant solution was filtered and left to stand at room temperature. Yellow block crystals suitable for analysis were produced by slow evaporation of the solvent for 7 days in 45% yield (based on U). Elemental analysis for $C_{24}H_{20}N_4O_{10}U_2$ ($M_r = 1000.50$), Calcd (%): C, 28.81; H, 2.01; N, 5.60. Found (%): C, 28.43; H: 2.07; N, 5.58. IR data (KBr pellet, $\nu[cm^{-1}]$): 3434, 3120, 2923, 1598, 1575, 1529, 1496, 1476, 1449, 1437, 1401, 1319, 1298, 1157, 1014, 921, 859, 770, 736, 677, 426.

2.2.2. Synthesis of $UO_2(BC)_2(DMF)$ (2). A mixture of a solution of $UO_2(CH_3COO)_2 \cdot 2H_2O$ (0.0848 g, 0.2 mmol), benzoic acid (0.488 g, 0.4 mmol) in deionized water (8 mL), and DMF (2 mL) was stirred for 30 min at room temperature. It was filtered and then the filtrate was left undisturbed. Yellow block crystals suitable for analysis were produced by slow evaporation of the solvent for 7 days in 55% yield (based on U). Elemental analysis for $C_{17}H_{17}NO_7U$ ($M_r = 585.35$), Calcd (%): C, 34.88; H, 2.93; N, 2.39. Found (%): C, 34.82; H, 2.91; N, 2.41. IR data (KBr pellet, $\nu[cm^{-1}]$): 3435,

Table 1. Crystallographic data for **1** and **2**.

Complexes	**1**	**2**
Empirical formula	$C_{24}H_{20}N_4O_{10}U_2$	$C_{17}H_{17}NO_7U$
Formula weight $(g\,mol^{-1})$	1000.50	585.35
Crystal system	Monoclinic	Monoclinic
Space group	$P2/c$	$P2_1/c$
Unit cell dimensions $(\mathring{A}, °)$		
a	17.416(2)	9.3798(17)
b	10.8685(13)	9.5125(18)
c	14.9765(18)	21.297(4)
α	90	90
β	110.532(2)	92.625(2)
γ	90	90
Volume $(\mathring{A}^3)$, Z	2654.7(6), 4	1898.3(6), 4
Calculated density $(g\,cm^{-3})$	2.503	2.048
Absorption coefficient (Mo-Kα) (mm^{-1})	12.249	8.588
$F(000)$	1824	1096
Crystal size (mm^3)	$0.10 \times 0.06 \times 0.06$	$0.11 \times 0.07 \times 0.06$
θ range for data collection $(°)$	1.87–25.00	2.17–25.00
Reflection collected	13,005	9161
Independent reflection	4660	3328
Parameters	361	237
Goodness of fit on F^2	1.028	0.977
R_1[a]	0.0549 (0.0860)[c]	0.0290 (0.0464)[c]
wR_2[b]	0.1055 (0.1199)[c]	0.0530 (0.0562)[c]
$\Delta(\rho)$ $(e\,\mathring{A}^{-3})$	4.067 and −2.768	0.718 and −0.493

[a]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b]$wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{1/2}; [F_o > 4\sigma(F_o)]$.
[c]Based on all data.

1655, 1599, 1556, 1509, 1496, 1432, 1401, 1378, 1312, 1176, 1118, 920, 859, 720, 686, 572, 448, 408.

2.3. *X-ray crystallographic determination*

A single-crystal with dimensions $0.10 \times 0.06 \times 0.06\,mm^3$ for **1** was selected for structure determination. Reflection data were collected at room temperature on a Bruker AXS SMART APEX II CCD diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073\,\mathring{A}$) from $1.87 < \theta < 25.00°$. A total of 13,005 (4660 unique, $R_{int} = 0.0549$) reflections were measured. A yellow single crystal of **2** with dimensions $0.11 \times 0.07 \times 0.06\,mm^3$ was mounted on a glass fiber. Reflection data were collected at room temperature on a Bruker AXS SMART APEX II CCD diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073\,\mathring{A}$) from $2.17 < \theta < 25.00°$. A total of 9161 (3328 unique, $R_{int} = 0.0290$) reflections were measured. Empirical absorption corrections were applied using a multi-scan technique. All absorption corrections were performed using SADABS [24]. Crystal structures were solved by direct methods. All non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares calculations on F^2 using SHELXL-97. All hydrogen atoms were fixed at calculated positions with isotropic thermal parameters. All calculations were performed using the SHELX-97 program [25]. Crystal data and details of the data collection and the structural refinement are given in table 1.

Table 2. Selected bond distances (Å) and angles (°) of **1**.

U1–O8	1.634(14)	U1–O1	2.467(9)	U2–O6	2.362(13)
U1–O7	1.776(12)	U1–N2	2.614(12)	U2–O5	2.377(13)
U1–O5	2.297(12)	U1–N1	2.665(11)	U2–O4	2.445(9)
U1–O6	2.335(13)	U2–O10	1.651(14)	U2–O3	2.471(10)
U1–O2	2.466(10)	U2–O9	1.797(11)	U2–N3	2.595(11)
U2–N4	2.676(11)				
O8–U1–O7	175.6(6)	O6–U1–N2	68.2(4)	O6–U2–O4	121.4(4)
O8–U1–O5	94.1(6)	O2–U1–N2	172.3(4)	O5–U2–O4	156.9(4)
O7–U1–O5	90.1(5)	O1–U1–N2	134.1(4)	O10–U2–O3	87.4(5)
O8–U1–O6	94.7(6)	O8–U1–N1	85.6(5)	O9–U2–O3	93.3(5)
O7–U1–O6	87.9(5)	O7–U1–N1	90.1(5)	O6–U2–O3	70.4(4)
O5–U1–O6	37.2(4)	O5–U1–N1	166.2(4)	O5–U2–O3	106.7(4)
O8–U1–O2	93.0(5)	O6–U1–N1	129.0(4)	O4–U2–O3	52.2(3)
O7–U1–O2	89.6(5)	O2–U1–N1	125.2(3)	O10–U2–N3	82.7(5)
O5–U1–O2	68.6(4)	O1–U1–N1	73.6(3)	O9–U2–N3	96.8(4)
O6–U1–O2	105.7(4)	N2–U1–N1	60.8(4)	O6–U2–N3	107.1(4)
O8–U1–O1	89.1(5)	O10–U2–O9	178.2(6)	O5–U2–N3	71.1(4)
O7–U1–O1	89.7(5)	O10–U2–O6	99.2(7)	O4–U2–N3	131.4(3)
O5–U1–O1	120.3(4)	O9–U2–O6	82.7(5)	O3–U2–N3	169.3(4)
O6–U1–O1	157.3(4)	O10–U2–O5	99.0(6)	O10–U2–N4	101.2(6)
O2–U1–O1	51.7(3)	O9–U2–O5	82.4(5)	O9–U2–N4	77.0(4)
O8–U1–N2	92.2(4)	O6–U2–O5	36.3(4)	O6–U2–N4	154.4(4)
O7–U1–N2	85.5(5)	O10–U2–O4	90.1(5)	O5–U2–N4	124.2(4)
O5–U1–N2	105.4(4)	O9–U2–O4	88.9(5)	O4–U2–N4	73.9(3)
O3–U2–N4	125.6(3)	N3–U2–N4	60.9(4)		

Table 3. Selected bond distances (Å) and angles (°) of **2**.

U–O6	1.751(4)	U–O5	2.304(4)	U–O1	2.421(4)
U–O7	1.763(4)	U–O4	2.401(4)	U–O2	2.470(3)
U–O3	2.298(4)				
O6–U–O7	178.97(19)	O7–U–O4	89.39(18)	O4–U–O1	123.80(12)
O6–U–O3	88.71(18)	O3–U–O4	78.44(13)	O6–U–O2	90.69(15)
O7–U–O3	91.32(18)	O5–U–O4	160.09(13)	O7–U–O2	88.76(16)
O6–U–O5	91.26(16)	O6–U–O1	88.02(16)	O3–U–O2	149.34(13)
O7–U–O5	89.76(18)	O7–U–O1	92.34(16)	O5–U–O2	128.97(13)
O3–U–O5	81.69(14)	O3–U–O1	157.48(13)	O4–U–O2	70.90(13)
O6–U–O4	89.61(17)	O5–U–O1	76.12(12)	O1–U–O2	53.00(12)

Selected bond lengths and angles of **1** and **2** are listed in tables 2 and 3. The drawings were made with Diamond 3.2.

3. Results and discussion

3.1. *Crystal structure analysis*

Single-crystal X-ray diffraction analysis indicates that **1** possesses a 1-D framework, crystallizing in the monoclinic space group *P*2/*c*. It is a dinuclear complex, and the
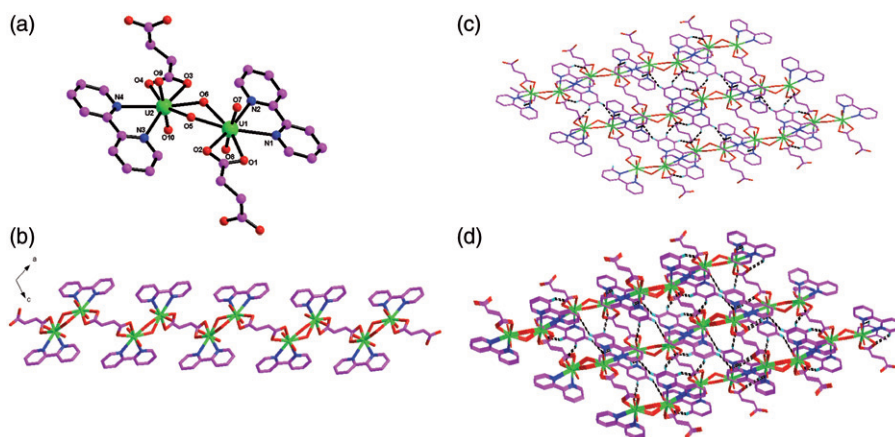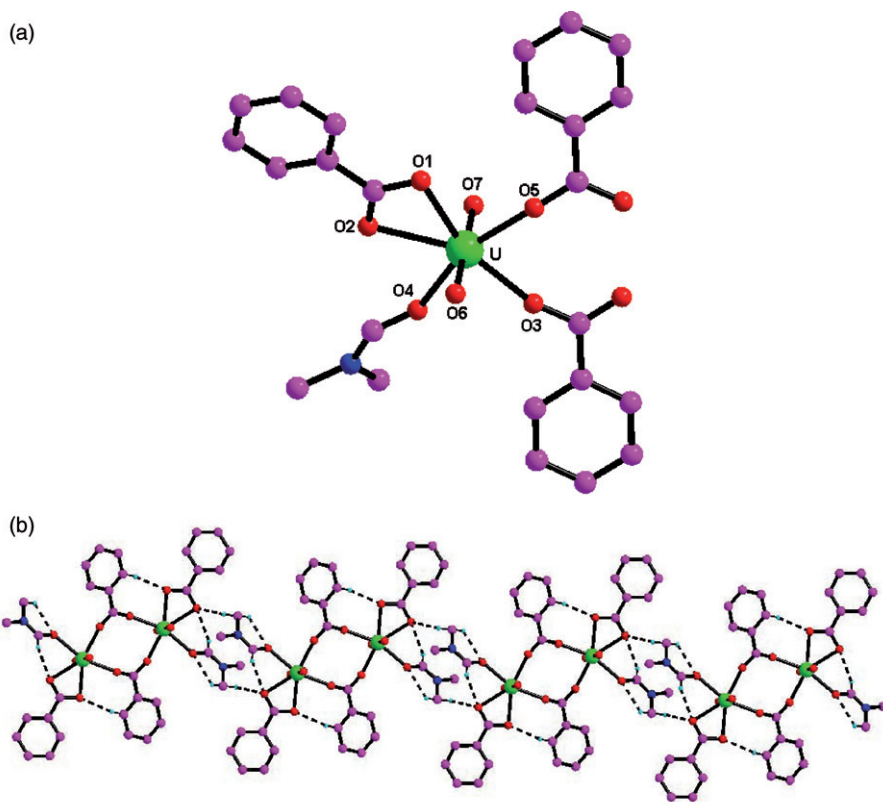
Figure 1. (a) Coordination environment of U in **1** (hydrogen atoms omitted for clarity), (b) 1-D infinite polymeric chain of **1** along the *b*-axis, (c) 2-D layer of **1** viewed along the *b*-axis formed by hydrogen-bonding, and (d) 3-D supramolecular structure of **1** viewed along the *b*-axis.

asymmetric unit of **1** contains two eight-coordinated uranium ions (U1 and U2), one succinic acid ligand, 2,2′-bipyridine, and two bridging oxygen atoms. U1 and U2 have similar coordination spheres as shown in figure 1(a). The coordination sphere of U1 consists of the uranyl oxygen atoms (O7 and O8), two oxygen atoms (O1 and O2) from one succinate, two nitrogen atoms (N1 and N2) from a 2,2′-bipyridine, and bridging O5 and O6. The U–O_{Suc} (from succinic acid) and U–N bond lengths are in the ranges 2.445(9)–2.471(10) Å and 2.595(11)–2.676(11) Å, respectively. Uranyl oxygen atoms (O7, O8, O9, and O10) are at an average distance of 1.745 Å from U. The O=U=O bond angles are 75.6(6)° and 178.2(6)°, respectively. The corresponding bond lengths and angles are close to those reported for uranium-containing complexes with succinate or other carboxylates [26–28]. Each succinate is coordinated bidentate to the UO_2^{2+} center. The bridging O5 and O6 (average distance 2.312 Å) link the UO_2^{2+} centers into pseudodimers. The pseudodimers are connected by succinate to form a 1-D chain running in the [010] direction, as shown in figure 1(b). The chain is further connected by extensive intermolecular hydrogen bonds (C–H···O) between carbons of 2,2′-bipyridine and the uranyl oxygen atoms to form a complicated 2-D layer as viewed along the *b*-axis (figure 1c). The layer is eventually linked by H-bonding interactions between carbons of 2,2′-bipyridine and uranyl oxygen atoms to yield a stable 3-D supramolecular network (figure 1d). In addition, the intramolecular H-bonding interactions further increase the connectivity of the structure. The detailed hydrogen bonds are listed in table 4.

The crystal structure of **2** reveals a discrete mononuclear complex, crystallizing in monoclinic system space group $P2_1/c$. An asymmetric unit $UO_2(BC)_2(DMF)$ (**2**) contains one seven-coordinate uranium, two benzoates, and one DMF. The coordination environment of U is shown in figure 2(a). The uranyl unit is coordinated by two oxygen atoms (O1, O2) of chelating bidentate carboxylates from one benzoate, two oxygen atoms (O3, O5) of monodentate carboxylates from two benzoates, and one oxygen atom (O4) of monodentate DMF. The coordination environment of uranium is pentagonal bipyramidal. The U–O_{BC} (from benzoic acid) and U–O_{DMF}

Table 4. Hydrogen-bonding distance (Å) and angle (°) data for **1** and **2**.

D–H⋯A	D–H	H⋯A	D⋯A	∠DHA	Symmetry codes
Complex 1					
C1–H1⋯O1	0.9300	2.2200	2.9171	131.00	
C1–H⋯O7	0.9300	2.4700	3.1157	126.00	$-x, 1-y, -z$
C8–H8⋯O8	0.9300	2.4400	3.2696	148.00	$x, -y, 1/2+z$
C9–H9⋯O10	0.9300	2.5000	3.3235	147.00	$x, -y, 1/2+z$
C10–H10⋯O3	0.9300	2.5600	3.1277	120.00	
C10–H10⋯O6	0.9300	2.0000	2.6258	123.00	
C11–H11⋯O2	0.9300	2.5900	3.1167	116.00	
C11–H11⋯O5	0.9300	2.4900	2.8866	106.00	
C12–H12⋯O7	0.9300	2.3900	3.2500	153.00	$x, 1-y, -1/2+z$
C13–H13⋯O9	0.9300	2.5300	3.3247	144.00	$x, 1-y, -1/2+z$
C14–H14⋯O9	0.9300	2.5300	3.3336	145.00	$1-x, 1-y, -z$
C20–H20⋯O4	0.9300	2.2800	2.9533	129.00	
Complex 2					
C12–H12⋯O1	0.9300	2.4100	3.3318	170.00	$-x, 1-y, -z$
C15–H15⋯O2	0.9300	2.4900	2.9238	109.00	
C17–H17A⋯O2	0.9600	2.4900	3.4118	161.00	$1-x, 2-y, -z$
C17–H17C⋯O4	0.9600	2.3400	2.7535	105.00	

Figure 2. (a) Coordination environment of U(VI) in **2** (hydrogen atoms omitted for clarity), and (b) 1-D hydrogen-bonded chain in **2** along the *b*-axis.

(from *N,N*-dimethylformamide) bond lengths are 2.298(4)–2.470(3) Å and 2.401(4) Å, respectively. The average bond length (U–O) of equatorial plane is 2.378 Å. Uranyl oxygen atoms (O6 and O7) are at an average distance of 1.757 Å from U. The $O=U=O$ bond angle is 178.97(19)°. These values are similar to reported uranium-benzoate complexes [29–32]. In **2**, benzoate as terminal ligand adopts two coordination modes, bridging bidentate (μ_1-η^1 : η^1) and bidentate (μ_2-η^1 : η^1). The benzoate bridges two U(VI) ions into a dinuclear unit, and then the units are linked by hydrogen bonds (C17–H17A···O2) between carbon of DMF and coordinated carboxylate into a 1-D hydrogen-bonded chain along the *b*-axis (figure 2b). Intramolecular H-bonding interactions are observed, further increasing the connectivity of the structure. The detailed hydrogen bonds are listed in table 4.

3.2. *XRPD study*

The XRPD data of **1** and **2** were measured (figures S1 and S2). The results show that **1** and **2** are in agreement with that calculated on the basis of their structural data, indicating that metal complexes have been obtained as pure crystalline phases.

3.3. *Thermal properties*

Thermogravimetric experiments were conducted to explore the stability of **1** and **2**, as an important parameter for metal-organic framework materials (figures S3 and S4). The TGA curve of **1** indicates that only one weight loss stage exists from 256°C to 684°C of 42.74%, corresponding to decomposition of 2,2′-bipyridine and succinate (Calcd 42.82%). The remaining UO_2^{2+} fragment is stable upon further heating until 800°C. The thermal decomposition process of **2** can be divided into two stages. The first weight loss of 13.55% between 149°C and 227°C corresponds to the release of one DMF (12.49%, theoretical weight loss). The second weight loss of 40.84% from 247°C to 763°C is attributed to release of two deprotonated benzoic acids (41.38%, theoretical weight loss).

3.4. *Photoluminescent properties*

To examine the luminescence of the uranyl-containing complexes, the solid-state fluorescence spectra of **1** and **2** at room temperature are depicted in figure 3. Under excitation at 326 nm, the luminescence spectrum of **2** shows a typical molecular structure characteristic of UO_2^{2+} with six visible broad emission peaks located at 493 (w), 515 (s), 538 (s), 563 (s), 590 (m) and 621 (w) nm. The successive bands correspond to electronic transitions $S_{11} \rightarrow S_{00}$ and $S_{10} \rightarrow S_{0v}$ ($v = 0$–4), respectively [33, 34]. The emission spectrum of **1** gives a strong emission peak at 546 nm upon excitation of 480 nm. It is remarkable that the emission spectrum of **1** is obviously different from that of **2**, attributed to the different coordination environment of UO_2^{2+}.
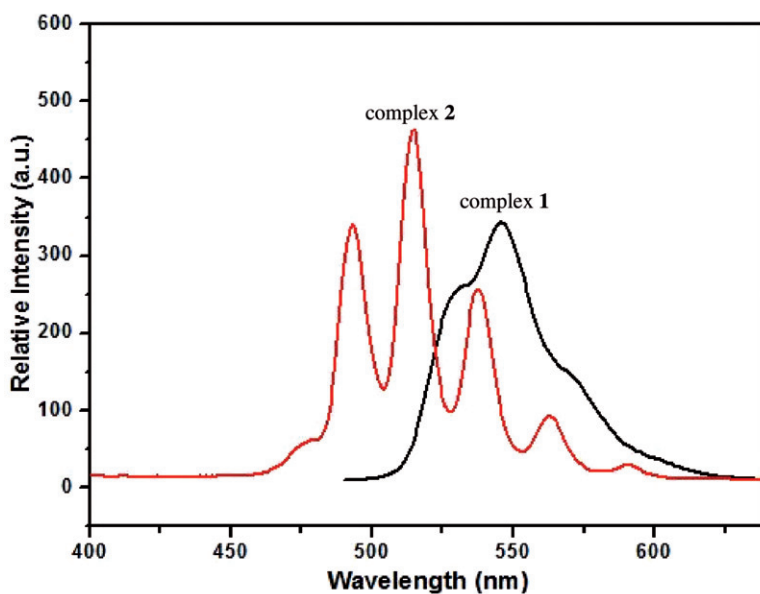
Figure 3. Fluorescence spectra of **1** and **2** (the spectra of **1** was excited at 480 nm and of **2** was excited at 326 nm).

3.5. *UV-Vis absorption spectra*

UV-Vis absorption spectra of **1** and **2** are recorded as solid samples. For **1**, bands at 208 and 294 nm are attributed to π–π* transition of 2,2′-bipyridine and n–π* transition of succinate, respectively. The band at 422 nm is assigned to ligand-to-metal charge transfer (LMCT) transitions. For **2**, bands at 210 nm and 294 nm are attributed to π–π* and n–π* transitions of benzoate, and the band at 420 nm is assigned to LMCT transitions.

3.6. *IR spectra*

Complexes **1** and **2** were characterized by IR spectroscopy. For **1**, the broad band at 3434 cm^{-1} is typical of hydroxyl. The bands at 2923 and 2854 cm^{-1} are absorptions of the ν_{C-H} vibration modes of –CH$_2$– groups within the carbon chain of succinate. The characteristic bands of carboxyl are shown at 1529 cm^{-1} for asymmetric stretching and 1437 cm^{-1} for symmetric stretching. The sharp and intense band at 921 cm^{-1} is due to asymmetric stretch of UO$_2^{2+}$. A medium band at 859 cm^{-1} can be ascribed to symmetric UO$_2^{2+}$ stretch because the uranyl units are not strictly linear. For **2**, the band with the maximum at 3435 cm^{-1} is typical of hydroxyl. Bands at 1556, 1509 cm^{-1} and 1432, 1401 cm^{-1} are attributed to asymmetric and symmetric stretching vibrations of carboxylates in benzoic acid ligand. The strong band at 920 cm^{-1} is assigned to asymmetric stretch of UO$_2^{2+}$ and medium band at 859 cm^{-1} can be ascribed to symmetric UO$_2^{2+}$ stretch.

4. Conclusion

We have demonstrated the syntheses and properties of two new uranium(VI) coordination polymers. The results indicate that they exhibit not only a high thermal stability but also interesting photoluminescent properties. Research is in progress with the aim of further exploring uranium coordination chemistry with different ligands.

Supplementary material

Tables of atomic coordinates, isotropic thermal parameters, and complete bond distances and angles have been deposited with the Cambridge Crystallographic Data Canter. Copies of this information may be obtained free of charge by quoting the publication citation and deposition numbers CCDC 851603 (**1**) and 851604 (**2**) from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

Acknowledgments

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