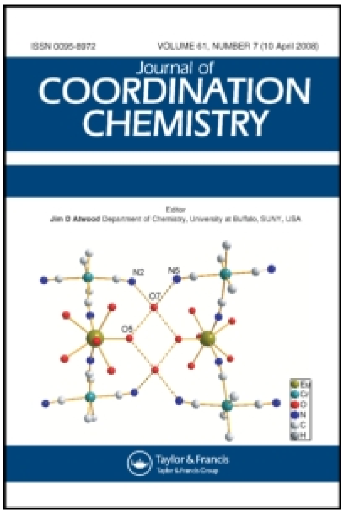

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U(VI) and Zn(II) coordination complexes with 5-[N-acetato(4-pyridyl)]tetrazolate anions

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U(VI) and Zn(II) coordination complexes with 5-[N-acetato(4-pyridyl)]tetrazolate anions

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A U(VI) mononuclear coordination complex $[UO_2(a4\text{-}ptz)_2 \cdot (H_2O)_3]$ (**1**) and a Zn(II) 1-D coordination polymer $[Zn(a4\text{-}ptz)_2 \cdot (H_2O)_2] \cdot 2H_2O$ (**2**) have been synthesized with 5-[N-acetato(4-pyridyl)]tetrazolate (a4-ptz) as ligand. Complex **1** has a slightly distorted pentagonal bipyramid around each U center. Complex **2** is octahedral with four a4-ptz and two water ligands. Each Zn center is linked by carboxylate-O(1) and tetrazolate-N(2) of a4-ptz forming a 1-D polymeric chain. Complexes **1** and **2** are self-assembled to form 3-D supramolecular structures through hydrogen bonds. The luminescence properties of **1** and **2** were investigated at room temperature in the solid state. The results suggest that **1** and **2** may be useful as photoactive materials.

Keywords: Uranium; Zincum; a4-ptz; Coordination complex; Fluorescence

1. Introduction

Tetrazole plays an increasingly important role in coordination chemistry as a ligand [1–9], in medicinal chemistry as a metabolically stable surrogate for a carboxylic acid group and in material science to make various products, including special explosives [10–13]. Transformations make tetrazoles versatile intermediates for substituted tetrazoles, in particular of other five-ring heterocycles via the Huisgen rearrangement [14]. Of interest to supramolecular chemists is the coordination ability of the tetrazolyl through four, electron-donating, nitrogens that allows it to serve as either a multidentate or a bridging building block in supramolecular assemblies. Metal complexes containing 5-(4-pyridyl)tetrazolate(4-ptz) such as $[Zn_2(OH)(4\text{-}ptz)_3]$ and $[Cu(4\text{-}ptz) \cdot 0.5(py)]$ [2], $[Cd(4\text{-}ptz)_2 \cdot (H_2O)_2]$ and $[Cd_3(OH)_2Cl_2(4\text{-}ptz)_2]$ [4b], $[Mn(4\text{-}ptz)_2(H_2O)_4](H_2O)_2$ and $[Cd(4\text{-}ptz)_2(H_2O)_4](H_2O)_2$ [9] have been reported. Following Sharpless's pioneering work [11], we have recently studied [2 + 3] cycloaddition reactions of 4-cyanopyridine to NaN_3 in the presence of $ZnCl_2$ as Lewis acid in aqueous solution. 5-[N-acetato(4-pyridyl)]tetrazolate anion (designated as a4-ptz anion) was obtained in the reaction of 4-ptz with chloroacetic acid in

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methanolic potassium hydroxide solution and reported the synthesis and structures of a series of copper(II), cadmium(II), and lead(II) complexes based on a4-ptz [15]. In this manuscript, we describe the syntheses, crystal structures, and luminescent properties of $[UO_2(a4\text{-}ptz)_2 \cdot (H_2O)_3]$ (**1**) and $[Zn(a4\text{-}ptz)_2 \cdot (H_2O)_2] \cdot 2H_2O$ (**2**).

2. Experimental

2.1. *Materials and general methods*

All materials and reagents were obtained commercially and used without purification. Infrared spectra were recorded as KBr discs using a Nicolet MagNa–IR 550 spectrometer. Thermogravimetric analyses (TGA) were performed with a SDT 2960 thermoanalyzer under N_2 (25–1100°C range) at a heating rate of 10°C/min. CHN microanalyses were performed on a Carlo-Erba EA1110 CHNO-S microanalyzer. The photoluminescence spectra were performed on a Perkin–Elmer LS55 spectrofluorometer.

2.2. *Synthesis*

2.2.1. Synthesis of ligands. 5-[N-acetato(4-pyridyl)]tetrazole potassium salt [K(a4-ptz)] was prepared from chloroacetic acid and 5-(4-pyridyl)tetrazole [16] in methanolic potassium hydroxide according to the literature method [2, 17].

2.2.2. Synthesis of $[UO_2(a4\text{-}ptz)_2 \cdot (H_2O)_3]$ (1). A mixture of a4-ptz potassium salt (0.0486 g, 0.2 mmol) and $UO_2(NO_3)_2 \cdot 6H_2O$ (0.0502 g, 0.1 mmol) was dissolved in distilled water (5 mL), heated at 100°C for 5 h with stirring, then cooled to room temperature and filtered. Slow evaporation of the filtrate in air gave light-yellow block crystals of **1**. The yield of **1** was 58% (0.043 g) based on the amount of $(UO_2)^{2+}$ consumed. Anal. Calcd for $C_{16}H_{22}N_{10}\ O_9U$: C, 26.09; H, 3.01; N, 19.02. Found (%): C, 26.18; H, 3.11; N, 18.89. IR (KBr, cm^{-1}): 3419 (s), 1638 (s), 1620 (s), 1473 (s), 1338 (m), 1315 (m), 1290 (m), 1193 (m), 1128 (m), 1024 (m), 943 (s), 735 (m).

2.2.3. Synthesis of $[Zn(a4\text{-}ptz)_2 \cdot (H_2O)_2] \cdot 2H_2O$ (2). The similar reaction of a4-ptz potassium salt (0.0486 g, 0.2 mmol) with $Zn(ClO_4)_2 \cdot 6H_2O$ (0.0437 g, 0.1 mmol) in H_2O (5 mL) was carried out as for preparation of **1**. Colorless crystals of **2** were obtained in 52% yield (0.028 g) based on Zn^{2+}. Anal. Calcd for $C_{16}H_{20}N_{10}O_8Zn$: C, 35.21; H, 3.69; N, 25.66. Found (%): C, 35.39; H, 3.77; N, 25.81. IR (KBr, cm^{-1}): 3419 (s), 1638 (s), 1620 (s), 1543 (m), 1479 (s) 1383 (s), 1317 (m), 1224 (m), 1090 (m), 1020 (m), 978 (m), 847 (s), 731 (m).

2.3. *X-ray crystallography*

Single crystal X-ray diffraction data were collected for **1** and **2** on a Rigaku Mercury CCD diffractometer operating at 50 kV and 30 mA using Mo-Kα radiation

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

Compound	**1**	**2**
Empirical formula	$C_{16}H_{22}N_{10}O_9U$	$C_{16}H_{22}N_{10}O_8Zn$
Formula weight	736.47	547.81
Crystal system	Monoclinic	Triclinic
Space group	$C2$	$P\bar{1}$
Unit cell dimensions (Å, °)		
a	13.571(3)	7.5076(3)
b	8.5729(16)	8.9556(2)
c	10.051(2)	8.9945(3)
α		71.582(13)
β	111.342(3)	66.754(14)
γ		69.359(13)
V (Å^3)	1089.2(4)	508.87(7)
Z	2	1
T (K)	193(2)	291(2)
D_{Calcd} (g cm^{-3})	2.246	1.788
μ (cm^{-1})	7.526	1.280
F (000)	704	282
Unique reflections (R_{int})	1928 (0.0311)	1995 (0.0403)
No. observations ($I > 2.00\sigma(I)$)	1928	1737
No. variables	171	175
R^a, Rw^b	0.0194, 0.0400	0.0421, 0.0909
GOF^c	0.950	1.046
Flack	0.000(9)	
$\Delta/\rho_{\max}$ (e Å^{-3})	0.609	0.517
$\Delta/\rho_{\min}$ (e Å^{-3})	−1.180	−0.375

Note: $^{a}R=\Sigma||F_o|-|F_c|/\Sigma|F_o||$; $^{b}Rw=\{\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$; $^{c}\text{GOF}=\{\Sigma w((F_o^2-F_c^2)^2)/(n-p)\}^{1/2}$, where n = number of reflections and p = total number of parameters refined.

($\lambda = 0.71070 \sim 0.71073$ Å) at 193 K (**1**) and 291 K (**2**), respectively. Data collection and reduction used SMART and SAINT software [18]. A multi-scan absorption correction was applied using SADABS [19]. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL program package [20]. Hydrogens were located from difference Fourier maps and a riding mode. Crystal parameters and details of the data collection and refinement are given in table 1.

3. Results and discussion

3.1. *Synthesis and structure descriptions*

Carboxylate and tetrazolate are multifunctional ligands [4h, 21]. Treatment of a solution of a4-ptz with 1/2 equivalent of metal salt in water by refluxing 5 h afforded a homogeneous solution; after filtration, evaporation of solvent from the filtrate afforded **1** and **2**, which are stable toward oxygen, and not soluble in common organic solvents and water. Elemental analyses of **1** and **2** are consistent with their chemical formulas. In the IR spectra of **1** and **2** a peak at 3419 cm^{-1} suggests lattice water or coordinated water is present. Formation of the tetrazole group is supported by a peak at 1620 and 1473 (1479) cm^{-1} in **1** and **2** [2, 4c, 9]. Strong peaks at 1638 cm^{-1} in **1** and **2** are consistent with the presence of carboxylate [4d].

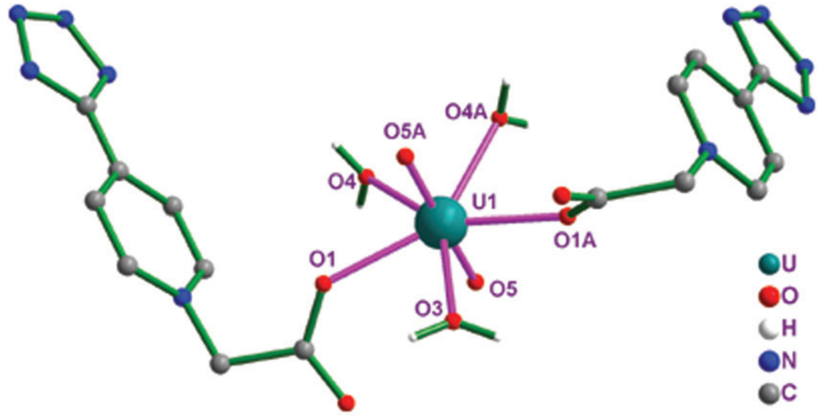

Figure 1. The structure of **1** showing the coordination environment of U(VI) and the coordination mode of a4-ptz$^-$.

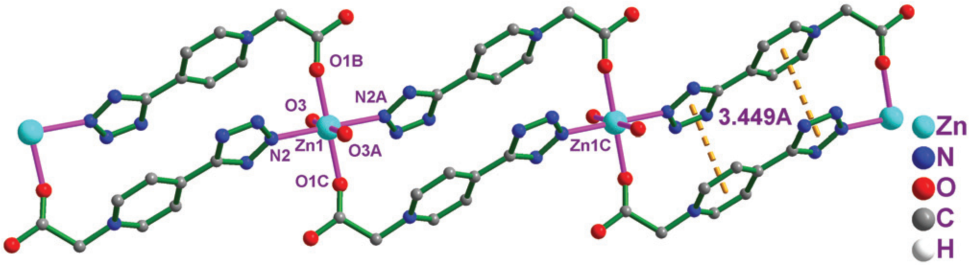

Figure 2. 1-D polymeric chain of **2** (hydrogen atoms omitted for clarity; π–π interactions indicated by dashed lines) showing the coordination environment of Zn(II) and the coordination mode of atza$^-$.

Complex **1** crystallizes in the monoclinic space group $C2$ and the asymmetric unit contains one-half of the [UO$_2$(a4-ptz)$_2\cdot$(H$_2$O)$_3$] formula unit, while **2** crystallizes in the triclinic space group $P\bar{1}$ and the asymmetric unit consists of a [Zn$_{0.5}$(a4-ptz)$\cdot$(H$_2$O)]$\cdot$H$_2$O molecule. X-ray crystallography shows that **1** is mononuclear (figure 1) and **2** is a 1-D polymeric chain structure (figure 2). Selected bond lengths and angles for **1** and **2** are given in table 2.

The solid-state structure of **1** has a slightly distorted pentagonal bipyramid coordination geometry around each U center, defined by seven oxygens from two carboxylate groups of a4-ptz, three H$_2$O and two oxo groups (axial). The uranyl bond distance of 1.770(3) Å and angle of 176.3(7)° are characteristic for a UO$_2^{2+}$ (1.750 ~ 1.794 Å) [4j, 22–25]. The U–O(H$_2$O) bond distances [U(1)–O(3) 2.418(5); U(1)–O(4) 2.395(4) Å] are longer than that of U–O(carboxylate-O) bond distance [U(1)–O(1) 2.381(3) Å]. These U–O bond distances are in the normal range and comparable to those found (2.332 – 2.544 Å) in (UO$_2$)(C$_7$H$_3$NO$_4$), (UO$_2$)$_2$(C$_7$H$_3$NO$_4$)(O)(H$_2$O), and (UO$_2$)(C$_7$H$_3$NO$_4$)$_2$(Cu(H$_2$O)$_4\cdot$4H$_2$O [24]. The four N-donors of the tetrazolate group are not coordinated to uranium, but act as acceptors of O–H$\cdots$N and C–H$\cdots$N hydrogen bonds. Each mononuclear unit [UO$_2$(a4-ptz)$_2\cdot$(H$_2$O)$_3$] is bridged through hydrogen bonds [O(4)$\cdots$N(4) 2.700(9) Å; O(4)$\cdots$O(2) 2.636(6) Å] to form a 2-D network extended along the ac plane with

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

Complex 1			
U(1)–O(1)	2.381(3)	U(1)–O(3)	2.418(5)
U(1)–O(4)	2.395(4)	U(1)–O(5)	1.770(3)
O(5)–U(1)–O(5A)	176.3(7)	O(5)–U(1)–O(1)	94.21(15)
O(1)–U(1)–O(4)	71.79(12)	O(4)–U(1)–O(4A)	71.00(19)
O(5A)–U(1)–O(1)	86.86(15)	O(5)–U(1)–O(3)	91.9(3)
O(1)–U(1)–O(1A)	146.64(16)	O(1)–U(1)–O(3)	73.32(8)
O(5)–U(1)–O(4 A)	92.6(3)	O(4)–U(1)–O(3)	144.50(9)
O(5)–U(1)–O(4)	84.4(3)	O(4A)–U(1)–O(3)	144.50(10)
O(1)–U(1)–O(4A)	141.25(12)		
Complex 2			
Zn(1)–O(3)	2.124(2)	Zn(1)–O(1B)	2.132(2)
Zn(1)–N(2)	2.157(2)		
O(3)–Zn(1)–O(3A)	180.0	O(3)–Zn(1)–O(1B)	90.60(10)
O(3)–Zn(1)–O(1C)	89.40(10)	O(3A)–Zn(1)–O(1C)	90.60(10)
O(1B)–Zn(1)–O(1C)	180.00(8)	O(3A)–Zn(1)–N(2)	86.93(10)
O(3A)–Zn(1)–N(2A)	93.07(10)	O(1B)–Zn(1)–N(2A)	93.39(9)
O(1C)–Zn(1)–N(2A)	86.61(9)	O(3)–Zn(1)–N(2)	93.07(10)
O(1C)–Zn(1)–N(2)	93.39(9)		

Note: Symmetry codes: **1**: A: $1-x$, y, $2-z$; **2**: A: $-x$, $-y$, $2-z$; B: $-x$, $1-y$, $1-z$; C: x, $-1+y$, $1+z$.

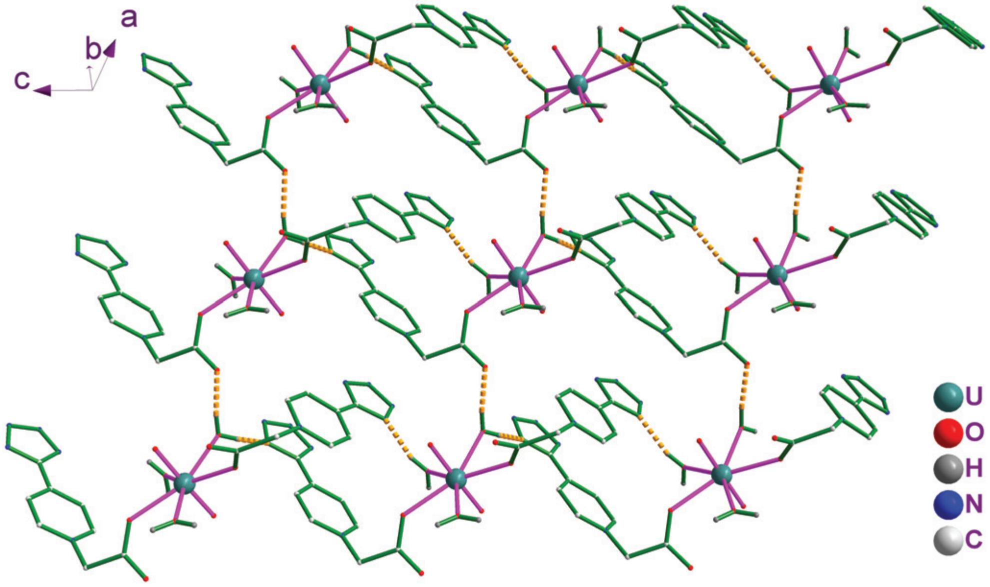

Figure 3. 2-D network structure of **1** extended along the *ac* plane by hydrogen-bonding interactions.

U ··· U dimensions of 8.026 × 10.051 Å (figure 3). In addition, other hydrogen bonding interactions (table 3) among H_2O, carboxylate, tetrazole, and oxo groups led to formation of a 3-D hydrogen bond network (figure S1).

As shown in figure 2, Zn resides on the center of symmetry of the octahedron with six positions occupied by [O(1C), O(1B), N(2), and N(2A)] from four equivalent ligands and [O(3), O(3A)] from two equivalent waters. These Zn–O [Zn(1)–O(1)

Table 3. Hydrogen bond lengths (Å) and angles (°) of **1** and **2**.

D–H···A	D–H	H···A	D···A	D–H···A
Complex 1				
O(3)–H(3A)···N(3)[a]	0.83(6)	1.99(5)	2.788(8)	162(8)
O(4)–H(4A)···N(4)[b]	0.82(4)	1.91(5)	2.700(9)	161(6)
O(4)–H(4B)···O(2)[c]	0.82(4)	1.82(4)	2.636(6)	173(6)
Complex 2				
O(3)–H(3A)···N(3)[d]	0.85(5)	2.55(4)	3.099(4)	123(4)
O(4)–H(4A)···O(2)[e]	0.85(5)	2.08(5)	2.768(3)	137(5)
O(3)–H(3C)···O(2)[f]	0.85(5)	2.21(5)	2.782(4)	125(4)
N(1)–H(1A)···O(4)[g]	0.87(4)	2.13(4)	2.812(4)	135(4)

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

2.131(2) Å; Zn(1)–O(3) 2.124(2) Å] and Zn–N 2.157(2) Å] distances for **2** are in agreement with literature values for Zn-tetrazole complexes [4d, 4e, 4h], whereas the C–C and C–N distances are unexceptional. Each Zn(II) is connected by two μ-a4-ptz ligands acting in end-to-end bridging mode via their carboxylate-O and tetrazolate-N atoms forming a 1-D Z-type polymeric chain with Zn···Zn distance of 10.498 Å. The 1-D structure of **2** is remarkably different from Zn(4-PTZ) (OH)(H_2O), where Zn is coordinated by one pyridyl-N, one tetrazolate-N, and two O atoms in a 2-D structure [4c]. $\pi\cdots\pi$ interactions (3.449 Å) between the pyridyl and tetrazolate from neighboring a4-ptz ligands can be regarded as a stabilizing factor for the 1-D structure.

These 1-D chains are connected by coordinated water (O3w) and crystallization water (O4w) via hydrogen-bonding interactions [O(3)···O(2) 2.782(4) Å; O(3)···N(3) 3.099(4) Å; O(4)···N(1) 2.812(4) Å; O(4)]···O(2) 2.768(3) Å] (table 3) into a 3-D supramolecular network structure with large cavities (3.45 × 10.54 Å) in the *ab* plane (figure 4).

3.2. *Fluorescence emission spectra (1) and (2)*

Pyridinecarboxylates are attractive ligands for studies of energy transfer because conjugation within the pyridine ring causes an 'antenna effect', a specific type of energy transfer which occurs through interaction between a donor and an acceptor whereby the emission spectrum of the donor (a4-ptz) overlaps the absorption spectrum of the acceptor (uranium) [24, 25]. The luminescence properties of **1**, **2**, and a4-ptz potassium salt were investigated at room temperature in the solid state. Upon excitation at 345 nm, Ka4-ptz shows a strong emission peak at 376 nm [15]; six characteristic emission peaks at 475–580 nm are observed for **1** (figure 5), which means the emission peaks of **1** are not from ligand donation, but typical for the uranyl fluorescence spectrum [4j, 22–27]. Furthermore, **1** is thermally stable up to 160°C (TGA measurement) (figure S2) and insoluble in common solvents such as ethanol, chloroform, ethyl acetate, acetone, acetonitrile, benzene, and water. The photoluminescence spectrum of powdered **2** (figure 6) shows a strong emission at 363 nm that can be assigned to an intraligand fluorescence emission. A relatively weak peak at 460 nm is also observed for **2**. This peak may be tentatively assigned to phosphorescence [4b]. The results suggest that these complexes may be useful as photoactive materials.

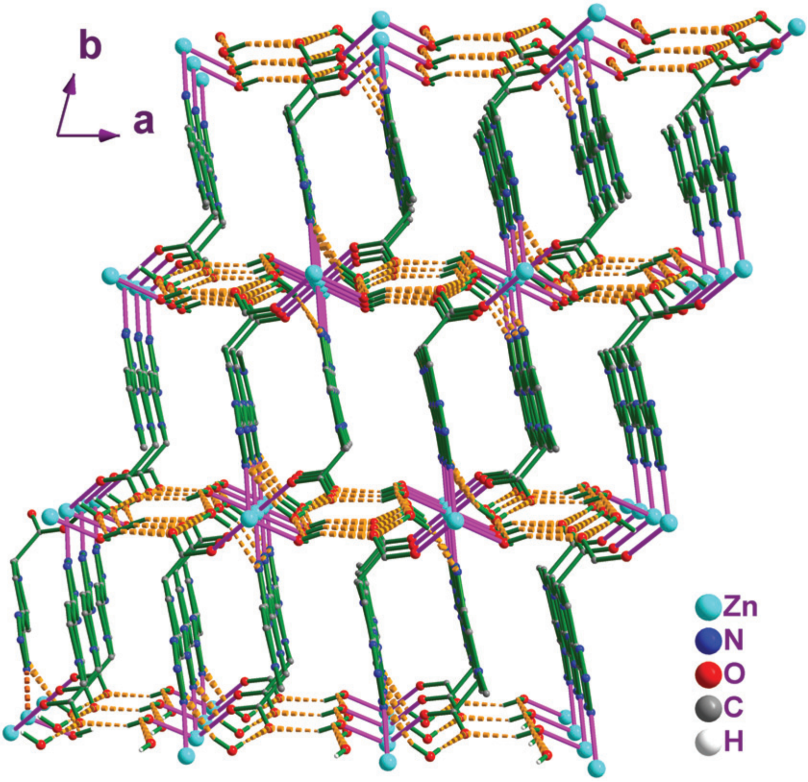

Figure 4. Hydrogen bond 3-D network structure of **2** looking down the *c* axis.

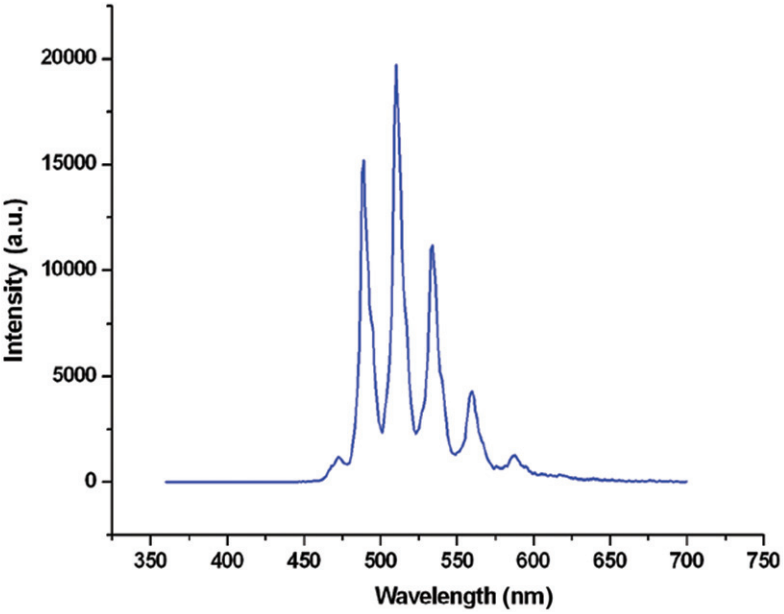

Figure 5. Solid state fluorescence emission spectra of **1** at room temperature ($\lambda_{ex} = 345\,nm$).

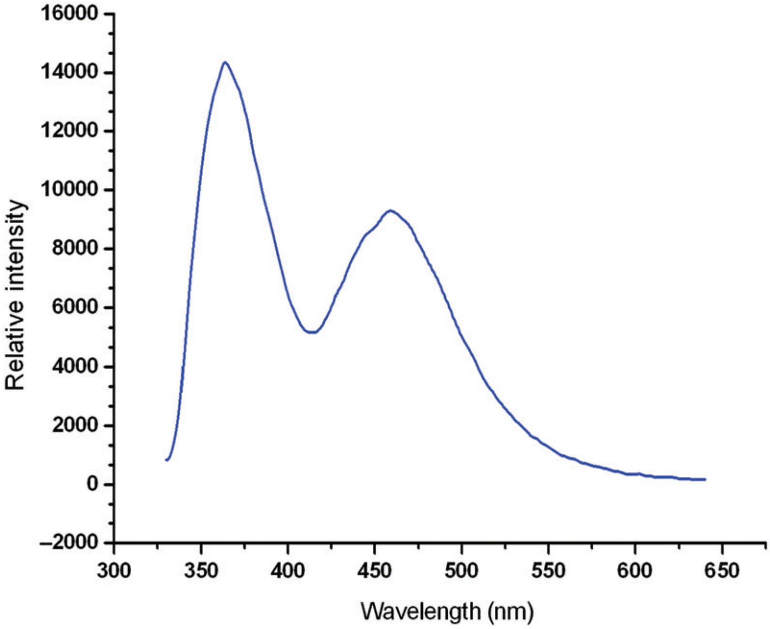

Figure 6. Solid state fluorescence spectrum of **2** at room temperature ($\lambda_{ex} = 345$ nm) in which an emission at 363 nm is fluorescent while the emission at 460 nm may be tentatively assigned to phosphorescence.

4. Summary

Two hydrogen-bonded supramolecular networks, $[UO_2(a4\text{-}ptz)_2 \cdot (H_2O)_3]$ (**1**) and $[Zn(a4\text{-}ptz)_2 \cdot (H_2O)_2] \cdot 2H_2O$ (**2**), have been synthesized and structurally characterized. Syntheses of **1** and **2** demonstrate that carboxylate-tetrazolate ligands provide multiple binding forces such as coordinate covalent, hydrogen bonding interactions and π–π stacking interactions with potential for assembling multi-dimensional supramolecular architectures. The luminescence properties at room temperature in the solid state show that **1** and **2** may be useful photoactive materials.

Supplementary material

CCDC 682414 and 686966 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223–336–033; or E-mail: deposit@ccdc.cam.ac.uk.

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