Syntheses, Structures and Photoluminescent Properties of the Two Novel Coordination Polymers $[Cd(pydc)_2(tu)]_n$ and $[Cd_2(SO_4)(nic)_2(tu)_{1.5}(H_2O)_2]_n$ (pydc = Pyridine-2,3-dicarboxylate, nic = Nicotinate, tu = Thiourea)

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Two novel cadmium coordination polymers, $[Cd(pydc)_2(tu)]_n$ (**1**) and $[Cd_2(SO_4)(nic)_2(tu)_{1.5}(H_2O)_2]_n$ (**2**) (pydc = pyridine-2,3-dicarboxylate, nic = nicotinate, tu = thiourea), have been synthesized under hydrothermal conditions and structurally characterized by X-ray diffraction analysis. **1** is a one-dimensional ladder coordination polymer in a two-dimensional network formed by hydrogen bonds. **2** consists of two kinds of Cd(II) centers in different coordination environments connected *via* nicotinate and sulfate to form a two-dimensional grid network integrated in a three-dimensional framework generated by hydrogen bonds. **2** shows intense fluorescent emission in the solid state at room temperature.

Key words: Cadmium, Pyridine-dicarboxylate, Synthesis, Crystal Structure, Coordination Polymer

Introduction

Coordination polymers (CPs) with transition metal ions have received much attention due to their intriguing architectures and various potential applications in separations, catalysis, gas adsorption, and magnetic materials [1 – 7]. The selection of organic building blocks plays a key role for designing different architectures. Pyridine-carboxylate ligands bearing both anionic and neutral donor atoms have been widely employed for the self-assembly of functional CPs [8 – 13]. In contrast to pyridine-2,4-, -3,4-, -2,5-, -2,6-, and -3,5-dicarboxylates [14 – 20], pyridine-2,3-dicarboxylate has been frequently used in CPs mainly because of its special coordination modes [21, 22]. In order to obtain poly-dimensional networks, typically inorganic bridging ligands such as CN^-, SCN^-, N_3^- and ClO_4^- are often used in the metal-pyridine carboxylate system [9, 23 – 27]. However, most of the common inorganic ligands are mono-anions, while the use of di- or tri-anionic ligands has been rather rare [28 – 31]. Besides metal-ligand combinations, hydrogen bonding, π-π stacking and metal-metal interactions also greatly influence the framework and dimensionality in CPs [32, 33]. To extend our former work, we employed thiourea molecules bearing as a bridging function the sulfur atom and offering the amine groups as hydrogen bonding donors. Furthermore, the $SO_4{}^{2-}$ dianion was used as a multi-bridging ligand for building CPs. In this paper we report the syntheses, structures and photoluminescent properties of two novel cadmium coordination polymers, $[Cd(pydc)_2(tu)]_n$ (**1**) and $[Cd_2(SO_4)(nic)_2(tu)_{1.5}(H_2O)_2]_n$ (**2**) (pydc = pyridine-2,3- dicarboxylate, nic = nicotinate, tu = thiourea).

Experimental Section

General

All chemicals were purchased from Alfa Aesar and used without further purification. All elemental analyses were carried out using a Perkin-Elmer 2400 CHN analyzer. Infrared spectra were recorded on a Digilab FTS-40 spectrophotometer with use of pressed KBr pellets. Fluorescence data were collected on an Edinburgh FLS-920 system.

*Preparation of $[Cd(pydc)_2(tu)]_n$ (**1**)*

A mixture of pyridine-2,3-dicarboxylic acid (H_2pydc) (1.0 mmol, 167 mg), $Cd(NO_3)_2{\cdot}4H_2O$ (0.4 mmol, 123 mg),

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Table 1. Crystallographic and structure refinement data for complexes $[\mathrm{Cd(pydc)_2(tu)}]_n$ (**1**) and $[\mathrm{Cd_2(SO_4)(nic)_2(tu)_{1.5}(H_2O)_2}]_n$ (**2**).

	1	**2**
Formula	$C_8H_7O_4N_3SCd$	$C_{13.5}H_{18}O_{10}N_5S_{2.5}Cd_2$
Mw	353.63	715.28
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$C2/c$
a, Å	8.2315(1)	23.999(3)
b, Å	17.1464(2)	7.9719(8)
c, Å	7.7013(1)	23.070(3)
β, deg	96.905(1)	100.338(5)
V, Å^3	1079.08(2)	4342.0(8)
Z	4	8
ρ_{calc}, g cm^{-3}	2.18	2.19
T, K	296(2)	296(2)
$\mu(\mathrm{Mo}K_\alpha)$, mm^{-1}	2.2	2.3
$F(000)$, e	688	2800
Refl. total / unique	10384 / 2474	20899 / 5033
R_{int}	0.0217	0.0219
Ref. parameters	154	325
$R1^{\mathrm{a}}$ / $wR2^{\mathrm{b}}$ $[I \geq 2\sigma(I)]$	0.0193 / 0.0451	0.0276 / 0.0624
$R1$ / $wR2$ (all data)	0.0235 / 0.0466	0.0315 / 0.0645
Goodness of fit (GoF)$^{\mathrm{c}}$	1.051	1.047
$\Delta\rho_{\mathrm{fin}}$ (max / min), e Å^{-3}	+0.44 / −0.27	+0.47 / −0.33

[a] $R1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$; [b] $wR2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (\mathrm{A}P)^2 + \mathrm{B}P]^{-1}$, where $P = (\mathrm{Max}(F_o{}^2,0) + 2F_c{}^2)/3$ and A and B are constants adjusted by the program; [c] $\mathrm{GoF} = S = [\Sigma w(F_o{}^2 - F_c{}^2)^2/(n_{\mathrm{obs}} - n_{\mathrm{param}})]^{1/2}$.

thiourea (0.5 mmol, 38 mg) and H_2O (5 mL) was stirred for *ca.* 15 min and then sealed in a 23-mL Teflon-lined stainless-steel autoclave. The vessel was heated at 110 °C for 3 d and then cooled to r. t. at a rate of 5 °C h^{-1}. Colorless flake-like crystals were obtained and air dried. Yield: 72 % based on cadmium. – Elemental analysis for $C_8H_7O_4N_3SCd$: calcd. C 27.2, H 1.9, O 18.1; found C 26.9, H 1.8, O 17.8.

Preparation of $[\mathrm{Cd_2(SO_4)(nic)_2(tu)_{1.5}(H_2O)_2}]_n$ *(**2**)*

A mixture of nicotinic acid (Hnic) (0.5 mmol, 62 mg), $CdSO_4$ (0.5 mmol, 104 mg) and thiourea (0.5 mmol, 38 mg) in H_2O (5 mL) was heated at 110 °C for 3 d in a 23 mL Teflon-lined stainless-steel autoclave and then cooled to r. t. at a rate of 5 °C h^{-1}. Colorless flake-like crystals were obtained and air dried. Yield: 65 % based on cadmium. – Elemental analysis for $C_{13.5}H_{18}O_{10}N_5S_{2.5}Cd_2$: calcd. C 23.7, H 2.6, O 23.4; found C 23.5, H 2.5, O 23.2.

X-Ray crystallography

The structures of **1** and **2** were determined by single-crystal X-ray diffraction. Diffraction data were collected on a Bruker SMART Apex CCD diffractometer with MoK_α radiation (λ = 0.71073 Å) at 296 K using the ω scan mode. The collected frames were processed with the software SAINT [34]. The data set was corrected for absorption using the program SADABS [35]. Structures were solved by Direct Methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package [36]. All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were generated geometrically (C_{sp^3}–H = 0.96, C_{sp^2}–H = 0.93 Å) and included in the structure factor calculations with assigned isotropic displacement parameters, but were not refined. Further details of the data collection, crystal data and structure refinement parameters are summarized in Table 1, selected bond lengths and angles for **1** and **2** in Tables 2 and 3, respectively.

Table 2. Selected bond lengths (Å) and bond angles (deg) for **1**$^{\mathrm{a}}$.

Cd(1)–S(1)	2.5092(5)	Cd(1)$^{\#4}$–O(3)	2.2381(15)
Cd(1)–O(1)	2.4621(15)	Cd(1)–O(2)$^{\#1}$	2.2174(15)
Cd(1)–N(1)	2.3027(17)	Cd(1)$^{\#3}$–O(2)	2.2174(15)
Cd(1)–O(3)$^{\#2}$	2.2381(15)		
O(2)$^{\#1}$–Cd(1)–O(3)$^{\#2}$	103.13(6)	N(1)–Cd(1)–O(1)	70.34(5)
O(2)$^{\#1}$–Cd(1)–N(1)	99.87(6)	O(2)$^{\#1}$–Cd(1)–S(1)	128.39(4)
O(3)$^{\#2}$–Cd(1)–N(1)	97.11(6)	O(3)$^{\#2}$–Cd(1)–S(1)	97.18(4)
O(2)$^{\#1}$–Cd(1)–O(1)	75.63(6)	N(1)–Cd(1)–S(1)	124.14(5)
O(3)$^{\#2}$–Cd(1)–O(1)	166.70(5)	O(1)–Cd(1)–S(1)	93.71(4)

[a] Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $x, -y+3/2, z-1/2$; $^{\#2}$ $x, y, z-1$; $^{\#3}$ $x, -y+3/2, z+1/2$; $^{\#4}$ $x, y, z+1$.

Table 3. Selected bond lengths (Å) and bond angles (deg) for **2**$^{\mathrm{a}}$.

Cd(2)–S(3)	2.6274(9)	Cd(2)–N(2)	2.325(3)
S(3)–Cd(2)$^{\#6}$	2.6274(9)	Cd(1)–N(1)	2.293(2)
Cd(2)–S(2)	2.5881(9)	Cd(1)–O(3)	2.291(2)
Cd(1)–O(8)$^{\#1}$	2.571(2)	Cd(2)–O(4)$^{\#2}$	2.262(2)
Cd(1)$^{\#5}$–O(8)	2.571(2)	Cd(2)$^{\#2}$–O(4)	2.262(2)
Cd(1)–O(10)	2.487(2)	Cd(1)–O(9)	2.372(3)
Cd(2)–O(2)	2.429(3)	Cd(1)–O(1)	2.360(2)
Cd(2)–O(5)$^{\#3}$	2.396(2)	Cd(1)–O(7)$^{\#1}$	2.346(2)
Cd(2)$^{\#4}$–O(5)	2.396(2)	Cd(1)$^{\#5}$–O(7)	2.346(2)
O(3)–Cd(1)–N(1)	96.97(9)	O(1)–Cd(1)–O(8)$^{\#1}$	82.95(9)
O(3)–Cd(1)–O(7)$^{\#1}$	83.73(9)	O(9)–Cd(1)–O(8)$^{\#1}$	162.84(9)
N(1)–Cd(1)–O(7)$^{\#1}$	138.73(8)	O(10)–Cd(1)–O(8)$^{\#1}$	132.81(7)
O(3)–Cd(1)–O(1)	173.70(9)	O(4)$^{\#2}$–Cd(2)–N(2)	91.84(10)
N(1)–Cd(1)–O(1)	88.35(9)	O(4)$^{\#2}$–Cd(2)–O(5)$^{\#3}$	86.25(10)
O(7)$^{\#1}$–Cd(1)–O(1)	90.04(9)	N(2)–Cd(2)–O(5)$^{\#3}$	82.90(9)
O(3)–Cd(1)–O(9)	102.17(9)	O(4)$^{\#2}$–Cd(2)–O(2)	166.11(11)
N(1)–Cd(1)–O(9)	86.37(9)	N(2)–Cd(2)–O(2)	87.59(10)
O(7)$^{\#1}$–Cd(1)–O(9)	134.05(8)	O(5)$^{\#3}$–Cd(2)–O(2)	79.90(9)
O(1)–Cd(1)–O(9)	81.47(10)	O(4)$^{\#2}$–Cd(2)–S(2)	96.28(8)
O(3)–Cd(1)–O(10)	90.70(8)	N(2)–Cd(2)–S(2)	86.85(7)
N(1)–Cd(1)–O(10)	139.87(8)	O(5)$^{\#3}$–Cd(2)–S(2)	169.52(6)
O(7)$^{\#1}$–Cd(1)–O(10)	81.17(8)	O(2)–Cd(2)–S(2)	97.54(8)
O(1)–Cd(1)–O(10)	87.37(8)	O(4)$^{\#2}$–Cd(2)–S(3)	92.95(7)
O(9)–Cd(1)–O(10)	53.53(8)	N(2)–Cd(2)–S(3)	168.02(7)
O(3)–Cd(1)–O(8)$^{\#1}$	94.01(8)	O(5)$^{\#3}$–Cd(2)–S(3)	86.46(6)
N(1)–Cd(1)–O(8)$^{\#1}$	86.02(8)	O(2)–Cd(2)–S(3)	85.13(7)
O(7)$^{\#1}$–Cd(1)–O(8)$^{\#1}$	52.90(7)	S(2)–Cd(2)–S(3)	103.52(3)

[a] Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $x, y-1, z$; $^{\#2}$ $-x+1, -y+2, -z+1$; $^{\#3}$ $x, -y+2, z+1/2$; $^{\#4}$ $-x+1, y, -z+3/2$; $^{\#5}$ $x, -y+2, z-1/2$; $^{\#6}$ $x, y+1, z$.

CCDC 806125 and 806126 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.

Results and Discussion

Single-crystal X-ray diffraction analysis has revealed that complex **1** crystallizes in the monoclinic space group $P2_1/c$. The central cadmium atom (Cd1) is coordinated by three oxygen atoms (O1, O2A, O3B) of carboxyl groups, one nitrogen atom (N1) of a pyridine moiety, and a sulfur atom from a thiourea molecule, forming a distorted trigonal bipyramid as shown in Fig. 1. The chelating Cd(1)–O(1) bond length of 2.4621(15) Å is obviously longer than the terminal Cd(1)–O(2A) and Cd(1)–O(3B) bond lengths of 2.2174(15) and 2.2381(15) Å, respectively. The Cd–N and Cd–S bond lengths in **1** are 2.3027(17) and 2.5092(5) Å, respectively. Although the pydc ligand has a total of 18 coordination modes which are summarized on the Cambridge Structural Database [22], a new coordination mode of the pydc ligand was found in **1**, as shown in Scheme 1. An oxygen atom of the carboxylate group in 2-position and the nitrogen atom of a pyridyl moiety chelate one cadmium atom while the second oxygen atom and an oxygen atom from the carboxylate in the 3-position bind two different cadmium atoms. The pydc ligand thus adopts both chelating and μ_3-bridging coordination modes to connect three individual cadmium atoms. A similar coordination mode of the pydc ligand was also found in the complex $[Cu(2,3\text{-pydc})_2][Na_2(H_2O)_6(\mu\text{-}H_2O)_2]$ [37]. The organization of the bridging pydc ligands at the cadmium atoms leads to the formation of a ladder-like chain, as shown in Fig. 2. Furthermore, these chains are joined by intermolecular hydrogen bonds N–H···O between terminal thiourea molecules and carboxylate oxygen atoms, forming an extended two-dimensional network, as shown in Fig. 3.

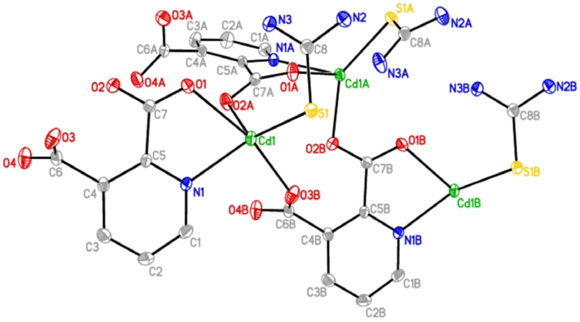
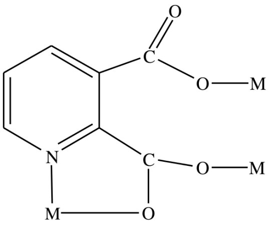


Fig. 1 (color online). Perspective view of the asymmetric unit of complex **1**.



Scheme 1. The coordination mode of the pydc ligand in **1**.

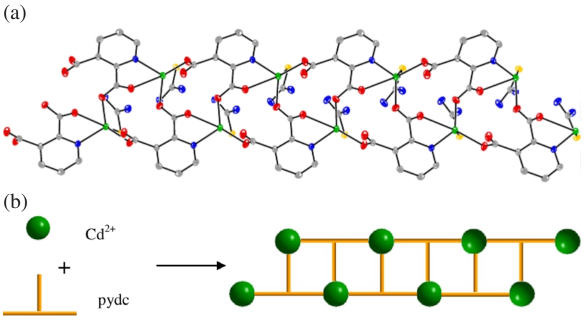


Fig. 2 (color online). (a) Perspective view of a chain in complex **1**; (b) organization of the building blocks to a ladder-like chain in complex **1**.

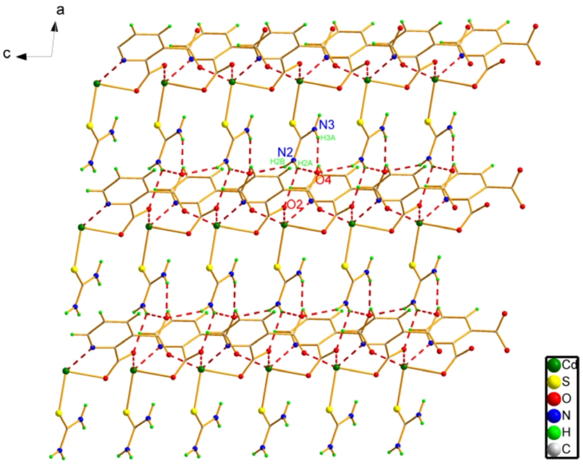


Fig. 3 (color online). The 2D network of complex **2** as viewed onto the *ac* plane.

Single-crystal X-ray diffraction has also revealed that there are two kinds of cadmium centers in the asymmetric unit of **2**, as shown in Fig. 4. The Cd(2) atom is in distorted octahedral geometry, coordinated by one nitrogen atom of a nic ligand, three oxygen atoms of two sulfate groups and one water molecule, and two sulfur atoms of thiourea ligands. Two adjacent

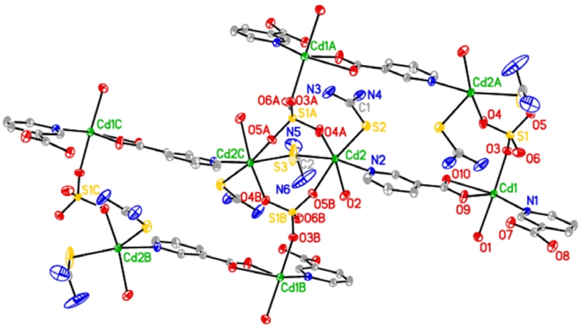
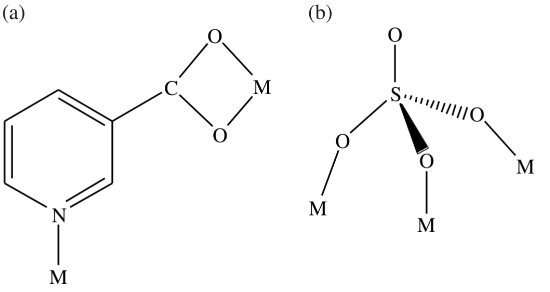


Fig. 4 (color online). ORTEP drawing of the coordination environment of the Cd(II) centers in complex **2**.

cadmium atoms are bridged by one μ-*S*,-$SC(NH_2)_2$ and two $\mu_3 - O,O,O\text{-}SO_4{}^{2-}$ groups. The Cd(1) atom is in a highly distorted pentagonal bipyramidal environment and thus seven-coordinated by six oxygen atoms and one nitrogen atom. Four oxygen atoms and one nitrogen atom from three different nic ligands are almost co-planar; two oxygen atoms from one sulfate group and one from a water molecule occupy axial positions. The average Cd–O_{water}, Cd–$O_{sulfate}$ and Cd–$O_{carboxyl}$ bond lengths are 2.395(2), 2.293(2) and 2.444(2) Å, respectively. The Cd–N bond lengths range from 2.293(2) to 2.325(3) Å, and the Cd–S bond lengths are in the range of 2.5881(9) – 2.6274(9) Å. Scheme 2 shows the bridging coordination modes of the nic ligand and the sulfate group in **2**. Obviously, two oxygen atoms of a carboxyl moiety chelate the Cd(2) atom, while the nitrogen atom of the pyridine group coordinates the Cd(1) atom. The sulfate group bridges three cadmium atoms. Both nic ligands and the sulfate group connect the cadmium atoms giving a typical two-dimensional framework, as shown in Fig. 5. Hydrogen bonds formed between water molecules and carboxyl groups yield a three-dimensional network structure, as shown in Fig. 6.



Scheme 2. (a) The coordination mode of the pdc ligand in **2**; (b) the coordination mode of the sulfate ligand in **2**.

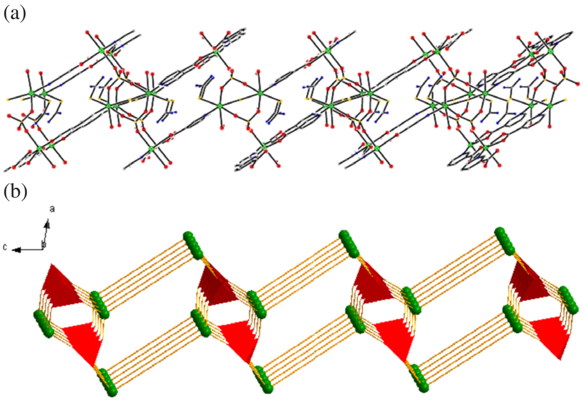


Fig. 5 (color online). (a) Side view of a sheet in complex **2** along the *ac* plane, all hydrogen and disordered carbon and nitrogen atoms of the thiourea molecules have been omitted for clarity; (b) schematic view of the sheets in **2**. All connections by nic ligands are replaced by connections between the Cd atoms, red polyhedra represent sulfate ligands.

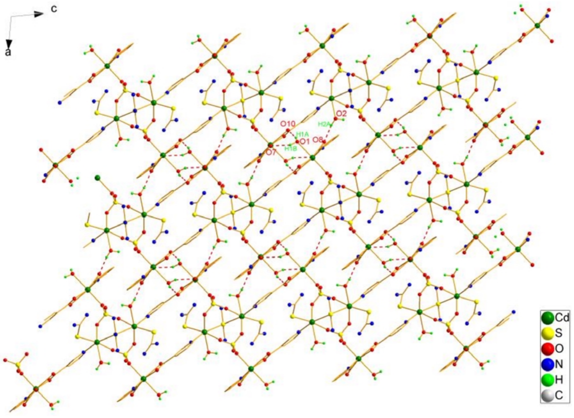


Fig. 6 (color online). The 3D network of complex **2**, interconnected by hydrogen bonds between the sheets. Hydrogen atoms of nic and tu ligands have been omitted for clarity.

In the IR spectra of the two complexes, the very strong peaks at 1615 and 1371 cm^{-1} for **1** and at 1630 and 1397 cm^{-1} for **2** correspond to the asymmetrical and symmetrical stretching vibrations of coordinated carboxyl groups, respectively, which are shifted to lower wavenumbers compared with the free carboxylate ligand [38]. The asymmetric and symmetric NH_2 stretching vibrations appear at 3291 and 3049 cm^{-1} for **1** and at 3294 and 3051 cm^{-1} for **2**. The bands observed in the range of 1410 – 1501 cm^{-1} are assigned to the asymmetric stretching vibrations of C=S and C–N units of the thiourea ligands. The ν_3 and ν_4 absorption bands associated with the sulfate group appear at 1113 and 615 cm^{-1} in the IR spectrum of **2**.

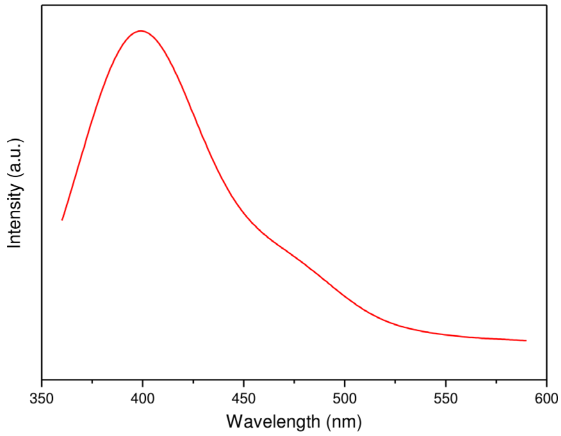


Fig. 7 (color online). The photoluminescence spectrum of **2** in the solid state at room temperature.

It is well known that coordination polymers based on d^{10} metals often exhibit intense photoluminescence and have great potential for applications as light-emitting materials [39, 40]. Many studies have revealed that the photoluminescence behavior is closely associated with the metal centers and the ligands coordinated to them [41]. In order to investigate the photoluminescence properties of the title complexes, their emission spectra have been measured in the solid state at r. t. Whereas complex **1** exhibits very weak emission, complex **2** exhibits intense luminescence with an emission maximum at 401 nm (λ = 350 nm) as illustrated in Fig. 7. The free nicotinic acid ligand shows a luminescence emission at 379 nm (λ = 330 nm) [42], indicating that the free ligand has no emission in the visible region. So the emission found in **2** can be related to a ligand-to-metal charge transfer absorption (LMCT).

In conclusion, we have synthesized under hydrothermal conditions and structurally characterized two novel coordination polymers, $[Cd(pydc)_2(tu)]_n$ (**1**) and $[Cd_2(SO_4)(nic)_2(tu)_{1.5}(H_2O)_2]_n$ (**2**). In **1**, thiourea and pydc ligands coordinate to the cadmium atoms to form a one-dimensional polymer. Pydc acts as a bridging ligand while thiourea functions as a hydrogen bond donor for construction of a two-dimensional network. In **2**, the sulfate and nic ligands coordinate to the cadmium atoms, both acting as bridging ligands and forming an interesting two-dimensional layered framework. Complex **2** displays intense luminescence with an emission maximum at 401 nm upon excitation at 350 nm. It reveals that complex **2** may be a good candidate for hybrid inorganic–organic photoactive materials.

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