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Design of metal-organic NLO materials: complexes derived from pyridine-3,4-dicarboxylate†

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Two new polymeric complexes, $[Zn(pydc)]_n$ (**1**) and $[Co(pydc)(H_2O)_2]_n \cdot nH_2O$ (**2**) (pydc = pyridine-3,4-dicarboxylate), have been synthesized and characterized. Complex **1** crystallizes in an acentric space group $Pna2_1$ and consists of a 3D network with unsymmetrical pydc linkers arranged in a parallel mode. Complex **2** crystallizes in the centric space group $P-1$, in which pydc ligands link Co(II) metal ions to generate a 2D layer structure with (4,4) topology nets. The Kurtz powder measurement shows that **1** exhibits a powder SHG efficiency about 5 times higher than that of potassium dihydrogen phosphate (KDP) and represents the first NLO-active 3D coordination network with parallel arrangement of dipolar ligands.

Introduction

Recently, there has been considerable interest in the design and elaboration of noncentrosymmetric solids, which are a stringent requirement for second-order nonlinear optical (NLO) bulk materials due to their potential applications in fields such as opto-electronics and other photonics-based technologies.[1–3] There is still a great challenge in constructing acentric solids. To date, crystal engineering has proved to be a powerful tool in designing and building networks with special topologies, and it has been related to the rational design of noncentrosymmetric solids for applications in NLO materials.[4–10] Among them, metal-organic coordination networks combine useful attributes of organic and inorganic components and have attracted much attention from chemists.

Metal ions are powerful 3D templates, with the ability to gather ligands in a variety of predetermined arrangements.[11] The arrangement of ligands is also important to maintain the acentricity of the network. Lin's group has synthesized 3D diamondoid, 2D grid and 1D chain helix acentric networks by combining unsymmetrical bridging ligands and metal ions with well-defined coordination spheres.[4] Nicoud and coworkers also have made a significant contribution to this field.[5]

Pyridine-3,4-dicarboxylate (pydc) ligands can act as multi-connectors to link metal ions to form extended high-dimensional networks, susceptible to exhibit higher thermal stability, resulting in readily practical applications. In addition, the pydc ligand, with its two carboxylate groups in the 3 and 4 positions, is structurally unsymmetrical and possesses a higher dipole moment than that of *m*-pyridinecarboxylate and *p*-pyridinecarboxylate.[5] Furthermore, NLO networks built with only pydc ligands can be considered as optimal, as pydc is an NLO-active ligand and the presence of NLO-inactive co-ligands would decrease the second harmonic generation (SHG) efficiency of the bulk material.[12] However, as far as we know, there has been only three reported centric coordination networks built exclusively with pydc ligands.[13] We report here the synthesis and characterization of two complexes, $[Zn(pydc)]_n$ (**1**) and $[Co(pydc)(H_2O)_2]_n \cdot nH_2O$ (**2**), along with the NLO property of **1**.

Experimental

General

All reagents were analytical grade and used as received. The hydrothermal reactions were performed in a 20 ml Teflon-lined stainless steel autoclave under autogenous pressure. The IR spectra were recorded using KBr pellets on a Magna 750 FT-IR spectrometer. C, H and N microanalyses were performed on a Vario EL III elemental analyzer. Thermogravimetric analyses were performed on a Perkin Elmer TGA/SDTA851 instrument. Fluorescent analyses were performed on an Edinburgh Instruments analyzer model FL920. The NLO property was measured by the Kurtz powder SHG method. A Q-switched mode-locked Nd-YAG laser (λ = 1064 nm) was used as the illuminating source and potassium dihydrogen phosphate (KDP) was used as the reference material.

Synthesis

$[Zn(pydc)]_n$ (1). A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.071 g, 0.24 mmol), pyridine-3,4-dicarboxylic acid (H_2pydc; 0.040 g, 0.24 mmol) and 1,2-bis(4-pyridyl)ethane (bpe, 0.022 g, 0.12 mmol.) in 10 ml H_2O at pH 3.0 (adjusted with HCl) was heated at 160 °C for 4 days. After cooling to room temperature at 5 °C h^{-1}, colourless crystals of **1** were filtered off the solution (yield 47.1% based on Zn). Anal. calcd for $C_7H_3NO_4Zn$: C, 36.48; H, 1.31; N, 6.08; found: C, 36.21; H, 1.04; N, 6.01%. IR (KBr, cm^{-1}): $\nu_s(COO^-)$ 1624 (vs.), $\nu_s(COO^-)$ 1597 (s), $\nu_{as}(COO^-)$ 1396 (vs.), γ(C–H) 856 (m), δ(py) 735 (m), γ(py) 611 (m).

$[Co(pydc)(H_2O)_2]_n \cdot nH_2O$ (2). A mixture of $Co(NO_3)_2 \cdot 6H_2O$ (0.070 g, 0.24 mmol) and H_2pydc (0.040 g, 0.24 mmol) in 10 ml H_2O and 1 ml pyridine was heated at 160 °C for 4 days. After cooling to room temperature at 5 °C h^{-1}, red crystals of **2** were filtered off the solution (yield 36.5%, based on Co). Anal. calcd for $C_7H_9NO_7Co$: C, 30.23; H, 3.26; N, 5.04; found: C, 30.11; H, 3.02; N, 5.00%. IR (KBr, cm^{-1}): ν(OH) 3288 (m, br), ν_s(COO–) 1622 (vs.), $\nu_s(COO^-)$ 1566 (s),

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† Electronic supplementary information (ESI) available: TGA/DSC of complexes **1** and **2**. See http://www.rsc.org/suppdata/nj/b4/b401802h/

Table 1 Crystal data and refinement parameters of **1** and **2**

	1	**2**
Formula	$C_7H_3NO_4Zn$	$C_7H_9NO_7Co$
FW	230.47	278.08
Crystal system	Tetragonal	Monoclinic
Space group	$Pna2_1$	$P-1$
T/K	293(2)	293(2)
a/Å	8.421(2)	7.111(1)
b/Å	6.575(1)	7.856(1)
c/Å	12.913(3)	9.031(2)
α/°	90.00	75.614(3)
β/°	90.00	68.570(4)
γ/°	90.00	76.107(4)
U/Å^3	715.0(3)	448.6(1)
Z	4	2
μ/mm^{-1}	2.141	2.059
Reflections collected	1586	2316
Unique reflections	1083	1565
Obs. reflections [$I > 2\sigma(I)$]	1038	1040
R_{int}	0.0191	0.0756
R_1[a] [$I > 2\sigma(I)$]	0.0258	0.0998
wR_2[a] [$I > 2\sigma(I)$]	0.0613	0.1782
Flack parameter	0.02(3)	

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 \Sigma w(F_o^4)]^{1/2}$.

$\nu_{as}(COO^-)$ 1408 (s), γ(C–H) 866 (m), δ(py) 737 (m), γ(py) 606 (m).

X-Ray crystallography‡

Single crystals of complexes **1** and **2** with approximate dimensions 0.40 × 0.34 × 0.32 and 0.10 × 0.06 × 0.05 mm^3, respectively, were used for X-ray diffraction analysis. Data were collected on a Siemens Smart CCD diffractometer with MoKα radiation (λ = 0.71073 Å) at 293(2) K. Empirical absorption corrections were applied by using the SADABS program for the Siemens area detector. The structures were solved with direct methods and all calculations were performed using the SHELXTL package.[14] The structures were refined by full-matrix least squares with anisotropic thermal parameters for non-hydrogen atoms. For **1**, all hydrogen atoms were generated geometrically and treated as riding. For **2**, no attempt was made to locate the hydrogen atoms of lattice water and coordinated water. Other hydrogen atoms were generated geometrically and treated as riding. The crystallographic data for **1** and **2** are summarized in Table 1, and selected bond distances and angles are listed in Table 2.

Results and discussion

Synthesis

In order to obtain NLO metal-pydc networks, we carried out the hydrothermal reaction of two different transition metal salts with pydc ligands. It was observed that the direct reaction of the Zn(II) salt and H_2pydc gave a white precipitate without any SHG effect. When the pyridyl-like ligand bpe was added to the reaction system, complex **1** in its crystalline form was successfully isolated in good yield. For the synthesis of the Co(II) analogue, a parallel reaction using the Co(II) salt gave rise to a pink precipitate. By replacing bpe by pyridine, crystals of **2** were isolated in satisfactory yield. Although detailed studies are still required to better understand this phenomenon, we propose that the rate of polymerization of transition metal ions with pydc is too fast to obtain crystalline products. According to this, different pyridyl-like ligands were introduced into the reaction system to coordinate with the transition metal ion first and then be replaced by pydc ligands, thus decreasing the rate of polymerization and leading to the formation of crystalline polymers **1** and **2**.

Table 2 Selected bond lengths (Å) and angles (°) for **1** and **2**[a]

1		**2**	
Zn–O3	1.989(3)	Co–O5	2.089(9)
Zn–N1A	2.037(4)	Co–O6	2.117(8)
Zn–O1C	1.971(3)	Co–O2B	2.209(8)
Zn–O2	2.207(3)	Co–N1	2.12(1)
Zn–O4B	2.059(3)	Co–O1A	2.149(9)
O3–Zn–N1A	105.4(2)	Co–O4C	2.022(9)
O3–Zn–O4B	84.0(1)	O4C–Co–O5	95.7(4)
N1A–Zn–O2	87.5(2)	N1–Co–O2B	91.5(3)
O1C–Zn–O4	99.9(2)	O6–Co–O1A	87.0(3)
O3–Zn–O2	84.2(1)	O4C–Co–N1	98.0(4)
O1C–Zn–O3	134.9(2)	O6–Co–O2B	83.2(3)
O1–Zn–O2	89.2(2)	O5–Co–O1A	85.9(4)
O1C–Zn–N1A	118.8(2)		
N1A–Zn–O4B	94.7(2)		
O4B–Zn–O2	168.2(1)		

[a] Symmetry codes for **1**: A = $-x + 1, -y + 2, z + 1/2$; B = $x - 1/2, -y + 5/2, z$; C = $x - 1/2, -y + 3/2, z$; for **2**: A = $x + 1, y - 1, z$; B = $-x + 1, -y + 1, -z + 1$; C = $x + 1, y, z$.

Crystal structures

In the crystal structure of **1**, there is one zinc metal ion and one pydc ligand in the asymmetric unit. The Zn(II) ion is five-coordinated by one nitrogen atom from one pydc ligand and four oxygen atoms from three distinct pydc ligands [Zn–O: 1.971(3)–2.207(3) Å] in a distorted trigonal bipyramidal geometry (Fig. 1), in which two oxygen atoms from two different pydc ligands occupy the axial positions [O2–Zn–O4B angle: 168.2(1)°]. Two carboxylate groups of the pydc ligand link three Zn(II) in syn-anti and anti-anti modes when the pyridyl nitrogen atom coordinates to Zn(II) as an N-donor, as illustrated in Fig. 2(a). Thus, the pydc ligand, by acting as a tetraconnector, links zinc ions to form a 3D network, as shown in Fig. 3. In a side view of the network, it is interesting to see that Zn ions are coplanar (parallel to the *ab* plane) and linked by carboxylate groups from pydc ligands, resulting in infinite 2D layers. The layers are extended to a 3D channel-like network through the Zn–N bonds, which are nearly plumb

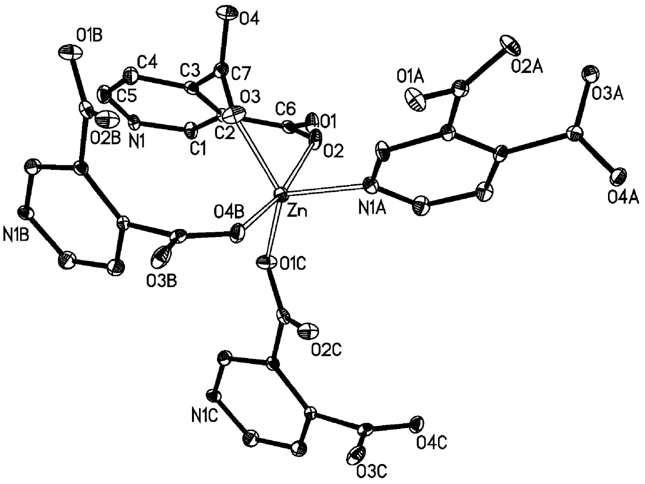

Fig. 1 Coordination environment of Zn(II) metal ion in **1**, symmetry codes: A = $-x + 1, -y + 2, z + 1/2$; B = $x - 1/2, -y + 5/2, z$; C = $x - 1/2, -y + 3/2, z$.

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‡ CCDC reference numbers are 230122 for **1** and 230123 for **2** . See http://www.rsc.org/suppdata/nj/b4/b401802h/ for crystallographic data in .cif or other electronic format.

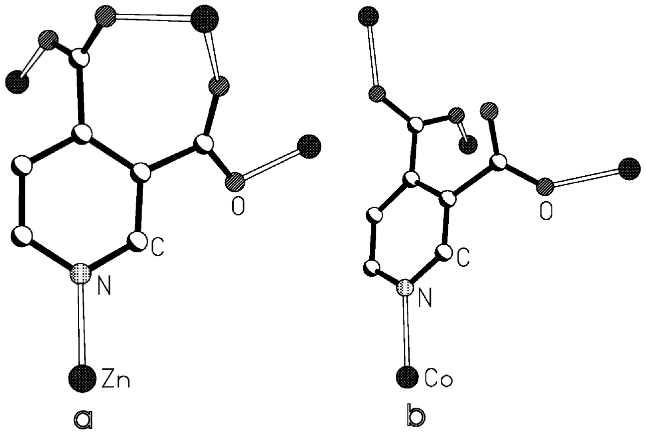

Fig. 2 Coordination modes of pydc ligand in (a) **1** and (b) **2**.

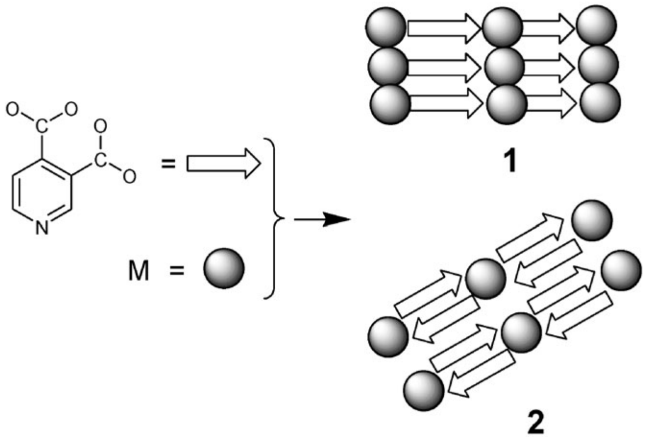

Fig. 5 Schematic representation of push-pull effects in **1** and **2**.

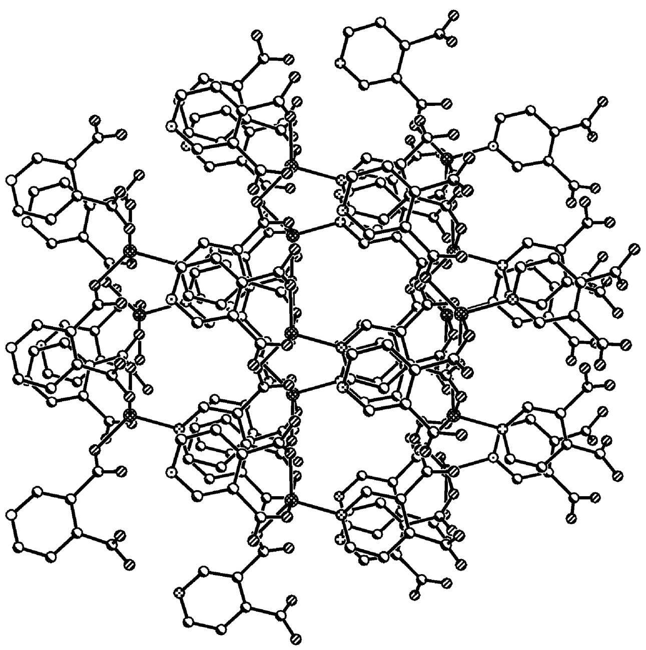

Fig. 3 View of the packing structure down the *a* axis in **1**.

to the local layer with the dihedral angle being 96.3°, as illustrated in Fig. 4. It is noteworthy that pydc ligands are arranged almost along the same direction. Such a parallel arrangement means that the dipole moment of **1** is stronger than that of the dipole-dipole repulsion. Furthermore, the parallel arrangement of unsymmetrical pydc ligands results in acentric networks, as illustrated in Fig. 5.

Complex **2** possesses 2D doubled-up layers with a Co(II) core as the building unit. In contrast with **1**, **2** crystallizes in centric space group $P-1$. There is one Co(II) metal ion, one pydc ligand, two coordinated water molecules and one lattice water molecule in the asymmetric unit. The Co(II) ion is six-coordinated by a nitrogen atom from one pydc ligand [Co–N1: 2.12(1) Å], three oxygen atoms from two bridging and one monodentate carboxylate groups from three distinct pydc ligands [Co–O: 2.022(9)–2.209(8) Å] and two cis terminal water molecules [Co–O: 2.089(9)–2.117(8) Å] to produce a distorted octahedral geometry (Fig. 6). The pydc ligand in **2** adopts different coordination modes from what was observed in **1**. The two carboxylate groups are in syn-anti and monodentate modes, as illustrated in Fig. 2(b). Two Co(II) ions are bridged by two μ-carboxylates from two distinct pydc ligands in an antiparallel mode to form a Co_2 unit with the Co···Co distance being 4.716(9) Å. The antiparallel arrangement leads to unfavorable inversion centers, which cancel the SHG activity of the pydc ligand (Fig. 5). The Co_2 units are interlinked *via* tetradentate pydc ligands to form 2D doubled-up layers parallel to the *ab* plane and containing tetragonal cavities (9.24 × 7.86 Å^2), as shown in Fig. 7. The topology of **2** can be simplified as (4,4) nets with Co_2 units as nodes. The coordinated water molecules form bifurcated hydrogen bonds with the lattice water molecule and the pydc carboxylate oxygen atom [O5–H···O3^{i} 2.75(1) Å and O5–H···O7^{ii} 2.77(1) Å; symmetry codes: i = $-x + 1, -y + 1, -z$; ii = $2 - x, -y, -z$]. The 2D layers are stacked into a 3D supramolecular architecture *via* interlayer hydrogen bonding (Fig. 8).

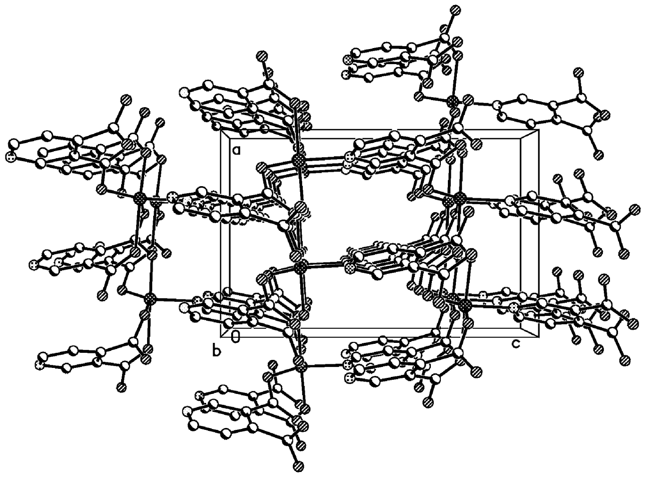

Fig. 4 View of the packing structure down the *b* axis in **1**.

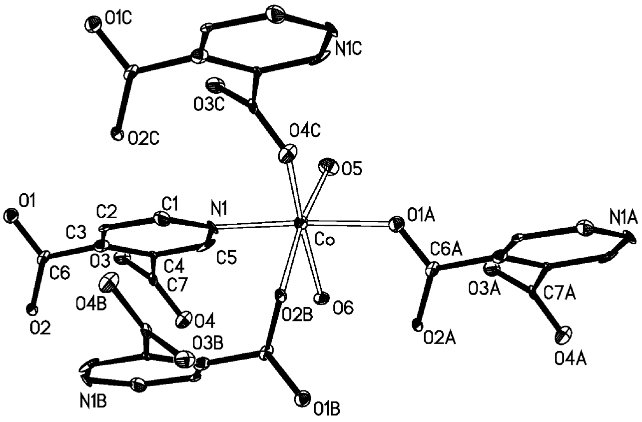

Fig. 6 Coordination environment of Co(II) metal ion in **2**, symmetry codes: A = $x + 1, y - 1, z$; B = $-x + 1, -y + 1, -z + 1$; C = $x + 1, y, z$.

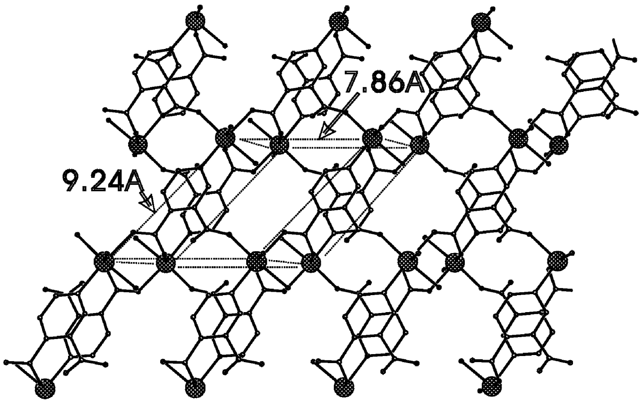

Fig. 7 View of the packing structure down the *c* axis in **2**.

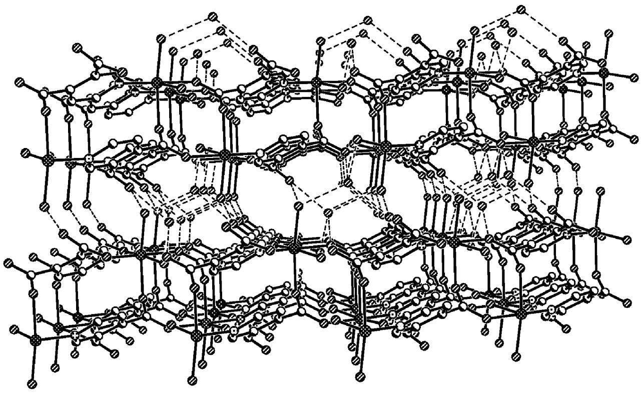

Fig. 8 View of the packing structure down the *a* axis in **2**.

Thermal properties

Thermogravimetric analysis (TGA)† shows that **1** has an onset decomposition temperature of 475 °C, indicating a remarkable thermal stability of the complex. The TGA of **2** shows a weight loss of *ca.* 19.1% in the range 100–220 °C, corresponding to the loss of two coordinated water molecules and one lattice water molecule per formula unit (calcd 19.4%). Subsequent to this, no obvious weight loss occurs up to 320 °C. Complete decomposition is observed at *ca.* 600 °C.

Optical properties

We studied the optical properties of **1** to evaluate its potential as an NLO material because it is colorless and is an acentric coordination network. The solid-state photoluminescent spectrum of **1** at room temperature is depicted in Fig. 9. The complex exhibits an intense luminescence with an emission maximum at *ca.* 431 nm upon excitation at 350 nm. This emission at *ca.* 431 nm can be attributed to the intraligand emission from the pydc ligand.[15] Free H_2pydc exhibits a weak luminescence at *ca.* 490 nm in the solid state at room temperature. The enhancement and blue-shift (from *ca.* 490 nm to 431 nm) of the emission of the pydc ligand in **1** compared to that of free H_2pydc may be attributed to the coordination bond between the pydc ligand and Zn(II), which increases the rigidity of the ligand and reduces the loss of energy by radiationless decay of the intraligand emission excited state.[16]

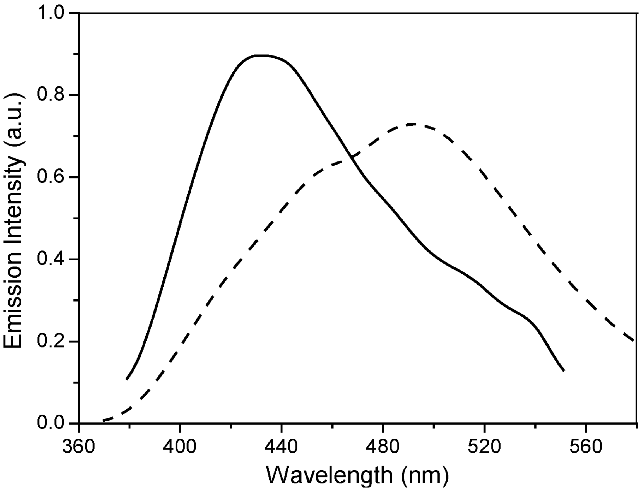

Fig. 9 The emission spectra (λ_{ex} = 330 nm) of **1** (—) and H_2pydc (- -) in the solid state at room temperature.

A Kurtz powder SHG measurement was performed on **1**.[17] The complex exhibits a powder SHG efficiency about 5 times higher than that of KDP, which confirms its structural noncentrosymmetry. In addition, **1** represents the first NLO-active 3D coordination network with parallel arrangement of dipolar ligands, resulting in a larger powder SHG efficiency than those of bis(isonicotinato)zinc and bis(nicotinato)zinc, which are 3 and 2 times that of KDP, respectively.[5] Complex **1** may be an attractive candidate as a potential NLO material, since it is highly stable thermally and insoluble in common solvents, with these properties originating from the polymeric structure.

Conclusion

In summary, a 3D acentric coordination network **1** was built by self-assembly of five-coordinate Zn(II) metal ions and unsymmetrical pydc ligands. Dipole moments of pydc ligands are enhanced thanks to a parallel arrangement mode. The Kurtz powder SHG measurement shows that **1** exhibits a moderate powder SHG efficiency about five times higher than that of KDP. Complex **2** consists of a 2D layers structure, in which pydc ligands are arranged in an antiparallel mode, resulting in a noncentrosymmetric network without any NLO activity.

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