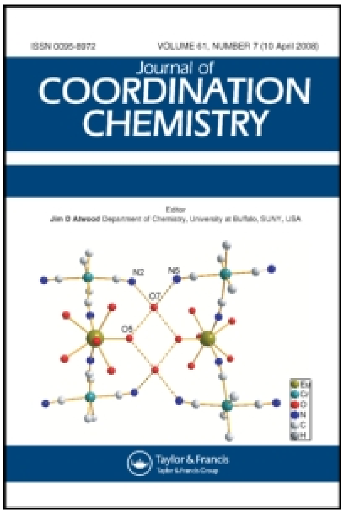

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Hydrothermal synthesis, crystal structure and third-order nonlinear optical properties of a 3D coordination polymer containing 3,3′,4,4′-benzophenone-tetracarboxylate (BPTC) and pyrazine ligands

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A mixed-ligand compound, $[Ni_2(BPTC)(pyz) \cdot 2H_2O]_n(0.5H_2O)_n$ (BPTC = 3,3′,4,4′-benzophenone-tetracarboxylate, pyz = pyrazine), has been prepared hydrothermally by assembly of BPTC, $NiCl_2{\cdot}6H_2O$ and pyz. X-ray diffraction analysis of a single crystal reveals the three-dimensional framework assembled from pyz-pillared two-dimensional sheets. Three types of channels in one direction are established inside the structure. The third-order nonlinear optical (NLO) properties in DMF have been studied by Z-scan technique using an 8 ns laser at 532 nm. The results reveal that the new compound exhibits strong NLO absorption and self-focusing refractive performance ($n_2 = 2.7 \times 10^{-17}\,m^2\,W^{-1}$).

Keywords: Nickel compound; Crystal structure; Hydrothermal synthesis; Mixed ligands; Optical property

1. Introduction

Interest has focused on design and synthesis of supramolecular complexes for their novel structural motifs and properties, such as ion exchange, adsorption, non-linear optics and magnetism [1–5]. Among these, three-dimensional (3D) metal-containing coordination polymers with well-defined pores are particularly attractive [6–8]. In construction of new supramolecular frameworks, polycarboxylate coordination solids are of special interest [9]. Aromatic or closed-ring aliphatic polycarboxylates have been widely investigated for design and synthesis of open framework complexes [10, 11]. The 3,3′,4,4′-benzophenonetetracarboxylate (BPTC) ligand, which has nine potential

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donor oxygen atoms, has not been previously investigated in detail. BPTC is a versatile ligand for construction of metal-organic hybrid compounds owing to its four carboxylate arms. Controlling the assembly of the bilayer motif and then utilizing linear bidentate ligands, such as pyrazine, as connectors to assemble the sheets into a 3D network is still a challenge [12, 13].

Herein, we report a new type of mixed-ligand 3D framework, $[Ni_2(BPTC)(pyz) \cdot 2H_2O]_n(0.5H_2O)_n$ (**1**) (pyz = pyrazine), with a 3D architecture generated by unusual pillared 2D bilayer motifs. Three types of channels in one direction are established inside the framework. The third-order nonlinear optical properties have been determined by *Z*-scan technique using an 8 ns laser at 532 nm.

2. Experimental

2.1. *General information and materials*

Commercially available chemicals and solvents were analytical reagents and used without further purification. Elemental analyses (C, H, N) were carried out on a Perkin-Elmer model 240 C analytical instrument. Infrared spectrum was recorded on a Bruker VECTOR22 FT-IR spectrophotometer using a KBr pellet ($400 \sim 4000\,\mathrm{cm^{-1}}$). TGA analysis was performed on a Perkin-Elmer thermal analysis instrument at a heating rate of $20^\circ\mathrm{C\,min^{-1}}$.

2.2. *Synthesis*

A mixture of 3,3′,4,4′-benzophenone-tetracarboxylate (0.2 mmol, 0.032 g), $NiCl_2 \cdot 6H_2O$ (0.2 mmol, 0.047 g), K_2CO_3 (0.2 mmol, 0.028 g), and pyrazine (0.2 mmol, 0.016 g) in water (10 ml) were sealed in a 25 ml stainless-steel reactor with a Teflon-lined autoclave. The reaction system was heated at 438 K under autogenous pressure for three days. Slowly cooling of the system to room temperature yielded green, rod-like crystals of the complex, which were collected by filtration. Yield: 88% (based on Ni). Elemental analysis (%) Calcd for $C_{42}H_{30}N_4Ni_4O_{23}$: C, 42.27; H, 2.53; N, 4.69. Found: C, 42.36; H, 2.43; N, 4.54. IR (KBr pellets, $\mathrm{cm^{-1}}$): 3291(vs), 1612(vs), 1552(s), 1535(s), 1490(m), 1429(m), 1405(vs), 1366(m), 1303(m), 1241(w), 1172(w), 1071(m), 827(w), 799(w).

2.3. *X-ray crystallography*

A crystal suitable for X-ray determination was mounted on the tip of a glass fiber. All data collection was performed on a Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 261(2) K. The structure was solved by direct methods and expanded with Fourier techniques using SHELXTL-97 [14]. The non-hydrogen atoms were derived from successive difference Fourier syntheses and refined with anisotropic thermal parameters. Hydrogen atoms were located at geometrically calculated positions and refined isotropically. The final cycle of full-matrix least-squares refinement on F^2 was based on 3282 observed reflections ($I > 2\sigma(I)$) and 340 variable parameters. $w = 1/[\sigma^2(F_o^{\,2}) + (0.04P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$. All calculations were performed with the SHELXTL-97 crystallographic software package [15]. Crystal data collection and structure determination summary for the complex are summarized in table 1. Selected bond lengths and angles for the complex are listed in table 2.

2.4. *Optical measurement*

A $3.6 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}$ DMF solution of ground sample was placed in a 2 mm quartz cuvette for NLO measurements. Their NLO properties were measured with

Table 1. Crystal data and structure refinement for **1**.

Compound	**1**
Empirical formula	$C_{42}H_{30}N_4Ni_4O_{23}$
M_r	1193.54
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	7.3096(17)
b (Å)	12.267(3)
c (Å)	13.891(3)
α (°)	82.960(4)
β (°)	80.951(4)
γ (°)	72.897(4)
V (Å^3)	1171.8(5)
Z	1
D_{Calcd} (g cm^{-3})	1.691
μ (mm^{-1})	1.673
F(000)	606
Crystal size (mm^3)	$0.32 \times 0.28 \times 0.26$
Method of collecting reflections	$\varphi - \omega$
θ Range for data collection	$2.2 \sim 26°$
Reflns. collected/unique	6286/4466 ($R_{\mathrm{int}} = 0.038$)
Observed reflns ($I > 2\sigma(I)$)	3282
Parameters refined	340
Goodness-of-fit on F^2	1.03
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0647$ $wR_2 = 0.1433$
Maximum peak (e Å^3)	0.62
Minimum peak (e Å^3)	−0.93

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

Ni1–O1	2.027(4)	Ni1–O4^b	2.060(4)	Ni2–O3	2.009(5)
Ni1–O10	2.091(4)	Ni2–O2	2.012(4)	Ni2–N2	2.053(6)
Ni1–O11	2.079(4)	Ni1–O9^a	2.044(4)	Ni2–O7^g	2.011(4)
Ni1–N1	2.082(4)				
O1–Ni1–O10	92.85(15)	O10–Ni1–N1	88.44(17)	O9^a–Ni1–N1	91.05(17)
O1–Ni1–O11	93.85(16)	O9^a–Ni1–O10	97.24(15)	O4^b–Ni1–N1	86.17(15)
O1–Ni1–N1	86.12(17)	O4^b–Ni1–O10	173.33(15)	O4^b–Ni1–O9^a	86.79(15)
O1–Ni1–O9^a	169.45(16)	O11–Ni1–N1	174.15(17)	O2–Ni2–O3	91.54(19)
O1–Ni1–O4^b	82.88(15)	O9^a–Ni1–O11	89.99(16)	O2–Ni2–N2	91.4(2)
O10–Ni1–O11	85.71(15)	O4^b–Ni1–O11	99.64(13)	O2–Ni2–O7^g	170.81(19)
O3–Ni2–N2	90.4(2)	O3–Ni2–O7^g	96.59(19)	O7^g–Ni2–N2	92.8(2)

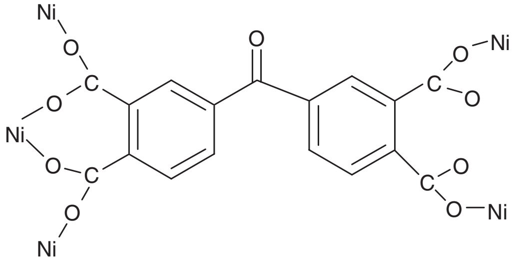
Symmetry transformation used to generate equivalent atoms: ^{a} $-2+x, 1+y, z$; ^{b} $-1+x, y, z$; ^{g} $1-x, -y, 2-z$.

an 8 ns pulse at 532 nm generated from a Q-switched frequency-doubled Nd-YAG laser. The spatial profiles of the optical pulses were nearly Gaussian after passing through a filter. The pulsed laser was focused on the sample cell with a 30 cm focal length mirror. Incident and transmitted pulsed energies were measured simultaneously by two energy detectors (RJP-735 energy probes, laser precision). The NLO properties of the sample were determined by performing *Z*-scan measurements. The sample was mounted on a translation stage that was controlled by the computer to move along the *Z*-axis with respect to the focal point. An aperture of 0.5 mm radius was placed in front of the transmission detector and the transmittance recorded as a function of the sample position on the *Z*-axis (closed aperture *Z*-scan). For measuring the NLO absorption, the *Z*-dependent sample transmittance was taken without the aperture (open aperture *Z*-scan) [16, 17].

3. Results and discussion

3.1. *Structure description*

Single-crystal X-ray analysis reveals that **1** is an interesting three-dimensional network containing three types of channels and a bilayer architecture, crystallizing in the $P\bar{1}$ space group. The coordination of BPTC in **1** is given in scheme 1. As shown in figure 1,



Scheme 1. The coordination mode of BPTC in **1**.

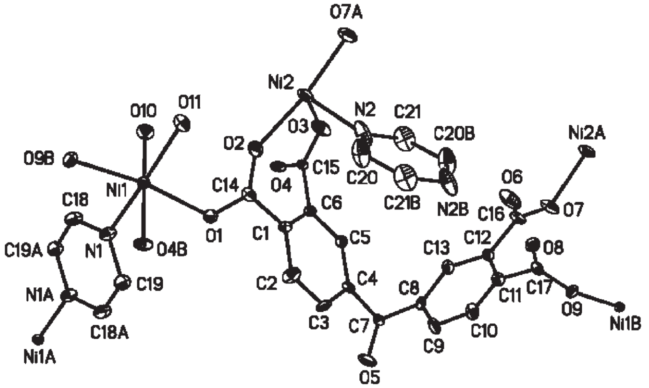


Figure 1. Crystal structure of **1** showing the atom labeling scheme with 30% probability ellipsoids. Hydrogen atoms and water were omitted for clarity.

each BPTC ligand binds to five Ni(II) centers through the O donors from carboxylate groups. The two phenyl rings in the same BPTC unit are twisted from each other by 59.89°. There are two crystallographically different Ni(II) centers in the structure. The Ni(1) center is coordinated by three BPTC ligands, two water molecules and one nitrogen atom of a μ_2–pyz ligand, displaying a slightly distorted [$NiNO_5$] octahedron. The equatorial positions are occupied by nitrogen, two oxygen atoms from two BPTC ligands, and one H_2O. Ni(1)–O bond lengths fall in the range 2.027(4)–2.091(4) Å; Ni(1)–N bond length is 2.082(4) Å. The Ni(2) center is attached to three carboxylate oxygen atoms of two different BPTC ligands, one nitrogen atom of one pyz. Ni(2)–O bond lengths fall in the range 2.009(5)–2.012(4) Å; Ni(2)–N bond length is 2.053(6) Å; O(7)–Ni(2)–O(2) bond angle is 170.83(17)°. The Ni(2) center can be viewed as an octahedron with two vacant *cis* sites. Ni(1) atoms are interconnected *via* T-shaped BPTC ligands, forming a 2D sheet (figure 2); Ni(1) atoms in the 2D sheet are coplanar. Three carboxylate groups from one BPTC ligand are coordinated to three Ni(1) atoms, the fourth being almost perpendicular to the 2D sheet, leads to a distinct 2D T-shaped layer. Two T-shaped layers are further linked through the O donors of the remaining carboxylate groups and other carboxylate groups on the other side coordinated to

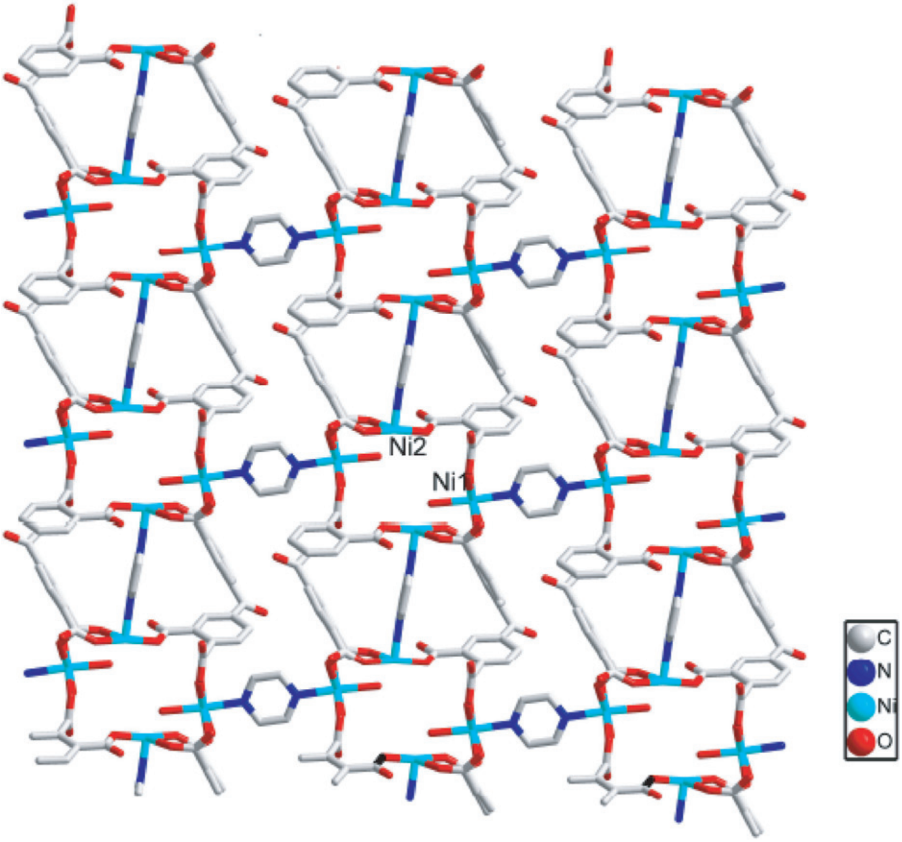


Figure 2. View of the 2-D T-shaped layer in **1**. Two crystallographically independent Ni(II) centers exhibit different patterns.

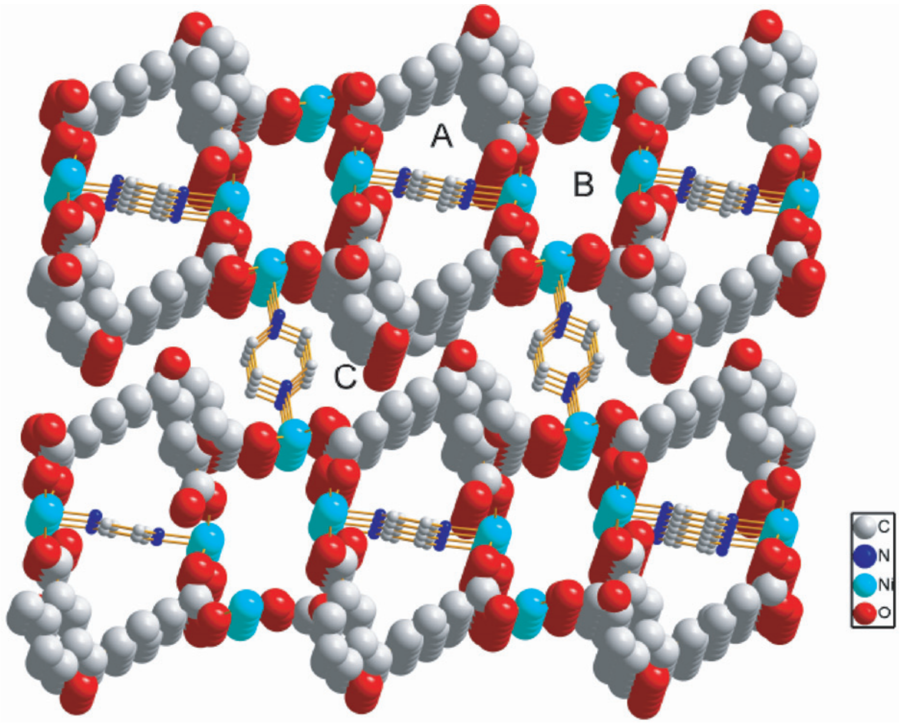


Figure 3. Space-filling diagram of the 3D framework of **1**. Water molecules in the channels and coordinated are omitted for clarity.

Ni(2) atoms in a face-to-face manner. This resulted in bilayer galleries, in which planar sheets separately define two types of 1D channels (A and B in figure 3). Interestingly, Ni(2) atoms integrated into two adjacent layers are not coplanar. In the parallelogram channel A with dimensions 5.39–9.36 Å, the pyz ligands connect symmetrically-opposed Ni(2) atoms so that they act not only as μ_2 bridges to support the framework, but also as guest molecules to fill the channel. Carboxylate groups link Ni(1) and Ni(2) atoms to form rectangular channel B with dimensions 7.77–10.36 Å, which is filled by free water molecules. The pyz ligands link bilayers together, thus completing the final 3D architecture (figure 3). Due to the participation of the pyz ligands, another irregular channel C emerges between the double layers. So, three types of channels are included in this compound. Taking into account the van der Waals radii of the atoms in the channel wall, the channel C is small. In this 3D structure there exist many C–H $\cdots$ O hydrogen bonds between H_2O and O atoms from carboxylate groups (table 3).

3.2. *Thermal and IR analysis*

To study the stability of **1**, thermogravimetric analysis (TGA) was performed on polycrystalline sample. The TGA curve exhibits three weight loss stages (figure 4). The first weight loss of 7.6% occurred over the temperature range 70–130°C, corresponding to removal of four bonded water molecules and one guest water in the channel (Calcd 7.5%). The second weight loss of 7.3% between 130 and 250°C is

Table 3. Hydrogen bonding for $[Ni_2(BPTC)(pyz) \cdot 2H_2O]_n(0.5H_2O)_n$ (Å, °).

Donor–H···Acceptor	D–H	H···A	D···A	D–H···A
O10–H10B···O8[a]	0.96(7)	1.97(8)	2.795(6)	143(6)
O10–H10C···O12[b]	0.96(8)	2.02(8)	2.949(14)	165(6)
O11–H11A···O3[c]	0.9600	1.9500	2.719(6)	135.00
O11–H11A···O6[d]	0.9600	2.5600	3.050(6)	112.00
O11–H11C···O2	0.9600	2.1000	2.869(6)	135.00
O12–H12A···O4[b]	0.8500	2.2100	3.006(13)	156.00

Symmetry transformation used to generate equivalent atoms: [a] $-2+x, 1+y, z$; [b] $-x, 1-y, 1-z$; [c] $-1+x, y, z$; [d] $-x, -y, 2-z$.

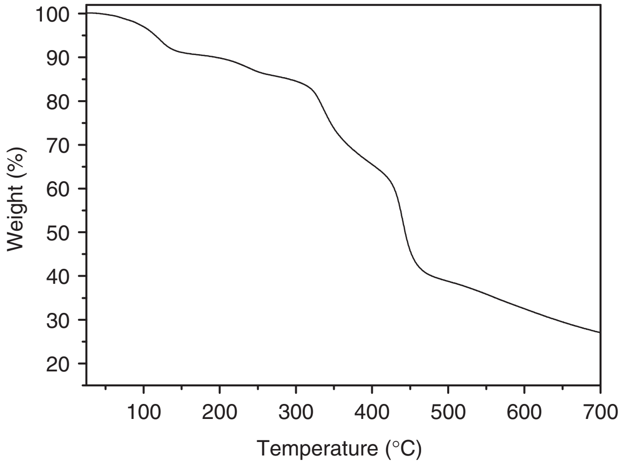


Figure 4. TGA diagram for **1**.

consistent with removal of one coordinated pyz linking bilayers together (Calcd 7.1%). The third weight loss of 38.2% occurred over the temperature range 250–450°C, corresponding to the removal of one pyz molecule linking two Ni(2) atoms, and one BPTC molecule (Calcd 38.1%). One BPTC molecule was lost between 450 and 700°C. The remaining weight of 26.1% corresponds to the percentage (26.2%) of the Ni and O components, indicating the final product is NiO. Infrared spectroscopy of **1** is determined within the frequency range 4000–400 cm^{-1}. Owing to the symmetric and asymmetric stretching-vibration of carboxyl groups, the infrared spectra show the expected strong characteristic absorption peaks at about 1612 and 1552 cm^{-1}. Some features at about 1535 and 1490 cm^{-1} are assigned to benzene ring or pyrazine vibrations. The absorption peaks at about 3291 are assigned to ν_{O-H} of coordinated water. Compared to the ligand, symmetric and asymmetric stretching-vibration of carboxyl groups in **1** have a blue shift (1787 and 1857 cm^{-1} for carboxyl groups in BPTC ligand).

3.3. *Nonlinear optical properties*

The UV-Vis spectrum of **1** in DMF solution shows a very strong absorption at about 290 nm and a relatively weak linear absorption from 300 to 800 nm. So **1** is transparent

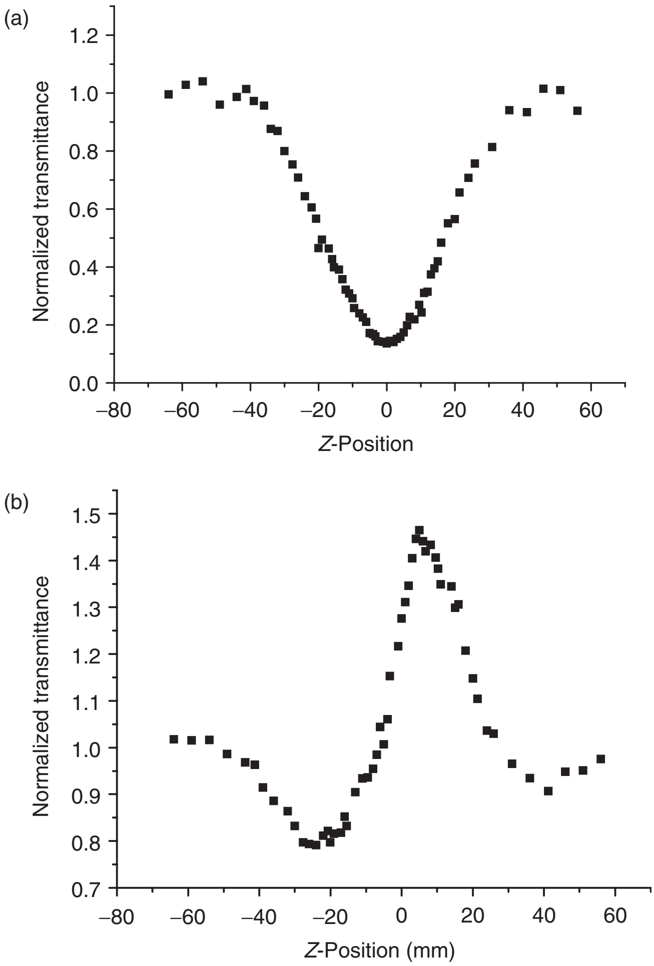


Figure 5. The normalized *Z*-scan data of **1** in DMF solution with 532 nm, 8 ns laser pulses. (a) The experimental data were measured with an open aperture. (b) The experimental data were measured with a closed aperture.

in a very large visible region, a great advantage for optical applications. The NLO properties of **1** are investigated with a 532 nm laser pulse in DMF solution of $3.60 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}$. Figure 5 shows the NLO optical behavior of **1**, which has a deep valley at open-aperture condition and exhibits strong nonlinear absorption (figure 5(a)). The NLO refractive property was assessed by dividing the normalized *Z*-scan data obtained under the closed aperture configuration by the normalized *Z*-scan data obtained under the open aperture configuration. The effective third-order non-linear refractive index n_2 values can be calculated according to equation (1):

$$n_2 = \frac{\lambda\alpha_0}{0.812\pi I_0(1 - e^{-\alpha_0 L})}\Delta T_{v-p} \tag{1}$$

where ΔT_{v-p} represents the difference between normalized transmittance values at valley and peak portions, L is the thickness of the sample, and α_0 is the linear absorption index. It can be seen from figure 5(b) that the difference of valley-peak positions, ΔZ_{v-p}, is 30 mm and ΔT_{v-p} is 0.65. Compound **1** has a positive sign for refractive non-linearity, which gives rise to self-focusing behavior. The third-order NLO refractive index is $2.7 \times 10^{-17}\,\mathrm{m}^2\,\mathrm{W}^{-1}$. Compound **1** has very strong third-order optical nonlinearity in DMF solution, comparable to those of reported NLO materials [18, 19].

4. Conclusions

In conclusion, a new three-dimensional compound containing three kinds of channels has been synthesized with two different ligands, the rigid pyz and the T-shaped flexible multi-carboxylate ligand H_4BPTC. Synthesis of the new compound demonstrates the potential of using mixed rigid and flexible ligands to assemble framework structures and provides an efficient route for preparing functional coordination polymers. We have also explored the NLO properties of **1** and believe that it could be used as a non-linear optical material.

Supplementary data

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 618064 for **1**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; Email: deposit@ccdc.cam.ac.uk or www: web: http://www.ccdc.cam.ac.uk).

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