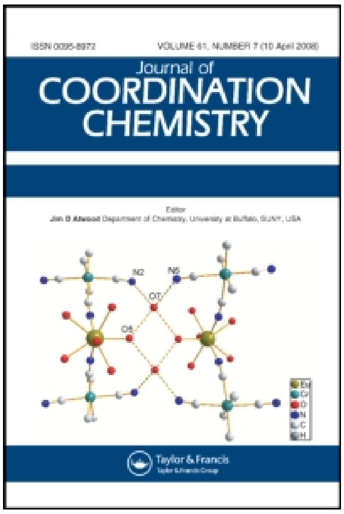

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Synthesis of novel copper compounds containing isonicotinic acid and/or 2,6-pyridinedicarboxylic acid: third-order nonlinear optical properties

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SYNTHESIS OF NOVEL COPPER COMPOUNDS CONTAINING ISONICOTINIC ACID AND/OR 2,6-PYRIDINEDICARBOXYLIC ACID: THIRD-ORDER NONLINEAR OPTICAL PROPERTIES

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Two novel compounds, $[Cu_2(pydc)_2(inta)_2(H_2O)_2]\cdot 3H_2O$ **1** (pydc = 2,6-pyridinedicarboxylic acid, inta = isonicotinic acid) and $[Cu(pydc)_2][Cu(H_2O)_5]\cdot 2H_2O$ **2**, have been synthesized in aqueous solution and characterized by single-crystal X-ray diffraction, elemental analyses and IR spectra. Compound **1** exhibits reverse saturable absorption and self-defocusing. X-ray structural analysis reveals that Compounds **1** and **2** both possess π–π stacking and hydrogen-bonding interactions forming three-dimensional (3D) networks. Crystal data for **1**: $a = 7.2345(14)$, $b = 12.219(2)$, $c = 17.069(3)$ Å, $\alpha = 90.44(3)$, $\beta = 91.82(3)$, $\gamma = 93.56(3)^\circ$, $Z = 1$, $R1 = 0.0435$, $wR2 = 0.1216$. Crystal data for **2**: $a = 8.3708(17)$, $b = 27.386(6)$, $c = 9.6170(19)$ Å, $\alpha = 90.00$, $\beta = 98.14(3)$, $\gamma = 90.00^\circ$, $Z = 3$, $R1 = 0.0742$, $wR2 = 0.2160$.

Keywords: π–π Stacking; Hydrogen-bonding interactions; Three-dimensional (3D) networks; 2,6-Pyridinedicarboxylic acid; Isonicotinic acid

INTRODUCTION

In recent years, crystal engineering of supramolecular architectures based on metal and organic building blocks has emerged rapidly as an exciting area of supramolecular chemistry because of the novel and diverse topologies and potential applications in host–guest chemistry, catalysis, electrical conductivity and magnetism [1,2]. Connections of metal–organic coordination networks based on complexes of transition metals and multidentate bridging ligands have proven to be a fertile field due to the intriguing network topologies and potential of new classes of materials. These metal-containing supramolecular frameworks can be constructed through two different interactions: (i) coordinate covalent bonds linking metal centers and organic ligands [3] and (ii) noncovalent intermolecular forces such as hydrogen bonding, π–π stacking

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and Coulombic interactions. These weaker noncovalent interactions, especially hydrogen bonds, play a crucial role in fundamental biological processes, such as expression and transfer of genetic information, and are essential for molecular recognition between receptors and substrates as well as construction of complicated supramolecular arrays through self-organization of molecules in supramolecular chemistry [4]. Rational design and synthesis of new extended supramolecular networks by means of both coordinative covalent and hydrogen-bonding interactions are of great interest and have brought forth a variety of such frameworks with fascinating structural motifs [5]. In general, extended networks possessing higher dimensionalities can be obtained by assembly of coordination polymers (or complexes) with lower dimensionalities via hydrogen-bonding interactions and π–π stacking [6]. However, it is still a challenge to control the final products. Studies on this aspect are limited because the assembly of molecules through weak interactions requires incorporation of many factors that cannot be completely controlled. Proper selection of metal ions and ligands are key issues in designing a system for self-assembly [7].

Both 2,6-pyridinedicarboxylic acid and isonicotinic acid are good hydrogen-bonding molecules and could form hydrogen-bonded networks with H-donors. However, reports on metal-based 2,6-pyridinedicarboxylic acid and isonicotinic acid in supramolecular compounds remain few; metal-based supramolecular frameworks constructed by both 2,6-pyridinedicarboxylic acid and isonicotinic acid ligands have not been reported. In view of the known coordination chemistry of 2,6-pyridinedicarboxylic acid and isonicotinic acid, we have used 2,6-pyridinedicarboxylic acid and isonicotinic acid as mixed organic building blocks to construct multidimensional supramolecular networks in the expectation that these two groups could generate covalent, hydrogen-bonding and/or) π–π stacking interactions with transition metal ions in the assembly process [8–13]. Herein, we report the syntheses and structures of two novel compounds, $[Cu_2(pydc)_2(inta)_2(H_2O)_2]\cdot 3H_2O$ **1** (pydc = 2,6-pyridinedicarboxylic acid, inta = isonicotinic acid) and $[Cu(pydc)_2][Cu(H_2O)_5]\cdot 2H_2O$ **2**. In the solid state, Compounds **1** and **2** show three-dimensional (3D) networks with unusual hydrogen bonding and π–π stacking. To our knowledge, Compound **1** represents the first metal-based supramolecular compound constructed from 2,6-pyridinedicarboxylic acid and isonicotinic acid ligands.

EXPERIMENTAL

General Procedures

All reagents were commercially available and used as received. C, H and N elemental analyses were performed on a Perkin-Elmer 2400 instrument. Copper was determined by a Leaman inductively coupled plasma (ICP) spectrometer. The FT-IR spectra were recorded as KBr pellets in the range 4000–400 cm^{-1} on an Alpha Centauri FT/IR spectrometer.

Synthesis of 1 and 2

$[Cu_2(pydc)_2(inta)_2(H_2O)_2]\cdot 3H_2O$, 1. Isonicotinic acid (0.094 g) was added to an aqueous solution of $CuCl_2\cdot 6H_2O$ (0.086 g) with stirring, and the resulting solution was then adjusted to pH $\approx$ 5.0 by addition of dilute HCl. 2,6-Pyridinedicarboxylic

TABLE I Crystal data and refinement summary for Compounds **1** and **2**

	Compound 1	*Compound 2*
Empirical formula	$C_{26}H_{26}Cu_2N_4O_{17}$	$C_{14}H_{20}Cu_2N_2O_{15}$
FW	793.57	583.39
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2(1)/c$
a (Å)	7.2345(14)	8.3708(17)
b (Å)	12.219(2)	27.386(6)
c (Å)	17.069(3)	9.6170(19)
α (°)	90.44(3)	90.00
β (°)	91.82(3)	98.14(3)
Γ (°)	93.56(3)	90.00
V (Å^3)	1505.1(5)	2182.4(8)
Z	1	1
T (K)	293(2)	293(2)
$R1$	0.0435	0.0742
$wR2$	0.1216	0.2160

acid (0.096 g) was added slowly to this reaction mixture and the mixture stirred for 30 min at room temperature. After filtration, a clear solution was obtained and allowed to stand at room temperature. On evaporation, blue, block-shaped single crystals were obtained after 2 weeks. Yield: 55% based on Cu. Anal. Calcd. for $[Cu_2(pydc)_2(inta)_2(H_2O)_2]\cdot 3H_2O$(%) **1**: C, 39.29; H, 3.27; Cu, 16.12; N, 7.05; O, 34.26. Found: C, 39.41; H, 3.01; Cu, 16.04; N, 7.08; O, 34.18.

*$[Cu(pydc)_2][Cu(H_2O)_5]\cdot 2H_2O$, **2**.* 2,6-Pyridinedicarboxylic acid (0.085 g) was added to an aqueous solution of $CuCl_2 \cdot 6H_2O$ (0.068 g) with stirring, and the resulting solution was then adjusted to pH ≈ 4.5 by addition of a dilute HCl solution, followed by further stirring for 30 min at room temperature. On evaporation, blue, block-shaped single crystals were obtained after 5 days. Yield: 58% based on Cu. Anal. Calcd. for $[Cu(pydc)_2][Cu(H_2O)_5]\cdot 2H_2O$(%) **2**: C, 28.77; H, 3.42; Cu, 21.88; N, 4.79; O, 41.09. Found: C, 28.78; H, 3.40; Cu, 21.89; N, 4.68; O, 41.02.

X-ray Crystallography

Crystals with dimensions $0.432 \times 0.356 \times 0.272\,mm^3$ for Compound **1** and $0.456 \times 0.378 \times 0.305\,mm^3$ for compound **2** were selected for intensity data collection at 293(2) K on a Rigaku R-AXIS RAPID IP diffractometer with Mo Kα radiation. Empirical absorption corrections were applied. The structures were solved by direct methods and refined by a full-matrix least-squares technique based on F^2 using the *SHELXL 97* program [16]. All nonhydrogen atoms were refined anisotropically. The positions of the hydrogen atoms attached to carbon atoms were fixed in the calculated positions in Compound **1** and found in a Fourier map in compound **2**. Detailed data collection and refinement of the compounds are summarized in Table I. Selected bond distances and angles are given in Table II.

RESULTS AND DISCUSSION

$[Cu_2(pydc)_2(inta)_2(H_2O)_2]\cdot 3H_2O$, 1. The basic structure unit of Compound **1** possesses two crystallographically independent Cu atoms (as shown in Fig. 1). The Cu_1 site

TABLE II Selected bond distances (Å) and angles (°) for **1** and **2**

Compound 1				*Compound 2*			
Cu1–N2	1.889(3)	N1–Cu1–O6	97.85(12)	Cu1–N1	2.014(4)	Cu(2)–O(12)	2.093(4)
Cu1–N1	1.951(3)	N2–Cu1–O3	81.02(11)	Cu1–N2	2.021(4)	Cu(2)–O(10)	2.096(4)
Cu1–O6	2.006(3)	N1–Cu1–O3	99.97(11)	Cu1–O4	2.118(4)	Cu(2)–O(13)	2.167(4)
Cu1–O3	2.016(3)	O6–Cu1–O3	161.88(10)	Cu1–O2	2.175(4)	N2–Cu1–O2	103.96(15)
Cu2–N3	1.904(3)	N3–Cu2–N4	168.15(14)	Cu1–O8	2.179(4)	O4–Cu1–O2	150.27(15)
Cu2–N4	1.969(3)	N3–Cu2–O10	81.23(12)	Cu1–O6	2.217(4)	N1–Cu1–O8	111.97(16)
Cu2–O10	2.003(3)	N4–Cu2–O10	97.69(12)	Cu2–O11	2.062(4)	N2–Cu1–O8	75.80(15)
Cu2–O7	2.069(3)	N3–Cu2–O7	79.46(11)	Cu2–O9	2.068(4)	O4–Cu1–O8	85.63(17)
Cu2–OW3	2.236(3)	Cu2–OW3	100.53(12)	Cu2–O5	2.088(4)	O2–Cu1–O8	94.69(16)

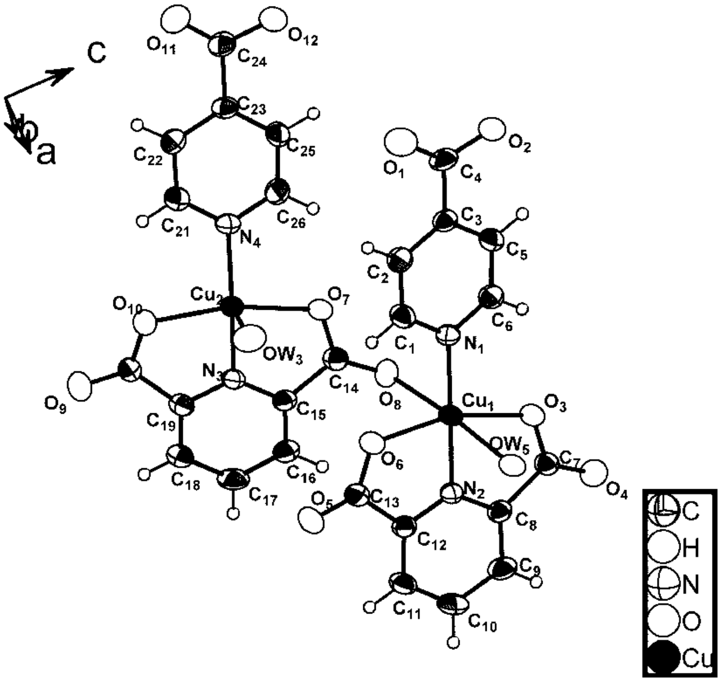
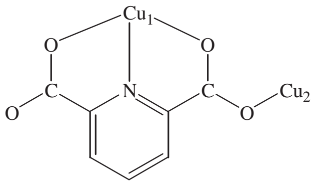
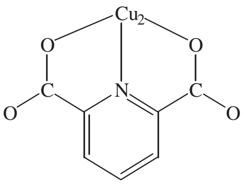


FIGURE 1 ORTEP drawing of Compound **1** with thermal ellipsoids at 50%.

is pentacoordinate with one nitrogen donor and two oxygen atoms of a pydc ligand, one oxygen atom of another pydc ligand, one nitrogen donor of isonicotinic acid and a terminal water. The second copper center Cu_2 is six-coordinate with one nitrogen donor and two oxygen atoms of a pydc ligand, one nitrogen donor of isonicotinic acid ligand, a terminal water and a bridging O_8. Each unit cell contains two units bridged through O_8.





The structure of **1** is composed of a unit cell bridged through hydrogen bonds. OW1–OW3 = 2.818 Å, OW1–OW4 = 2.994 Å, OW3–OW4 = 2.783 Å, OW5–O2 = 2.613 Å. The discrete molecules of **1** are bridged through hydrogen bonds and formed two-dimensional (2D) networks (Fig. 2). The extended 2D networks of Compound **1** are connected through not only hydrogen-bonding interactions but also π–π stacking; the distance between the benzene rings is 3.67 Å.

*$[Cu(pydc)_2][Cu(H_2O)_5]\cdot 2H_2O$, **2**.* The asymmetric unit of **2** (Fig. 3) exhibits two crystallographically independent Cu centers. The Cu_1 atom possesses distorted octahedral geometry and is coordinated to two nitrogen donor and four oxygen atoms of two pydc ligands. The Cu_2 site shows distorted octahedral coordination geometry with five terminal waters and one carboxyl oxygen atom.

The pydc ligands lie approximately on *ab* planes and are partially superimposed, displaying π–π interactions. A view of the unit cell along the *c* axis is shown in Fig. 4. The complex is stacked approximately parallel to the *ab* plane, indicating π–π interactions between pydc rings forming 3D networks. Both hydrogen-bonding and π–π interactions stabilize the lattice. The distance between the benzene rings is 3.75 Å.

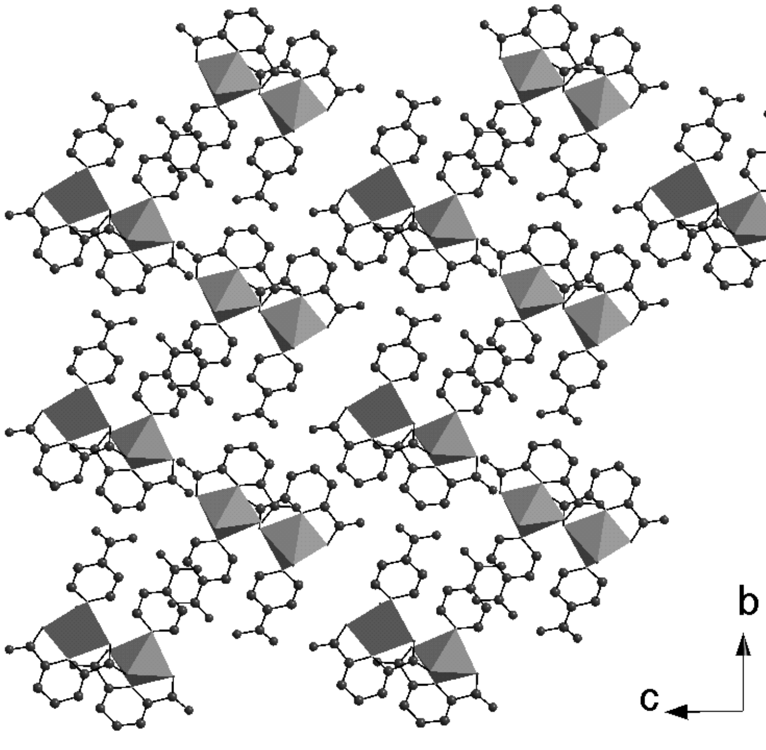


FIGURE 2 2D layered network in Compound **1** in the *ac* plane.

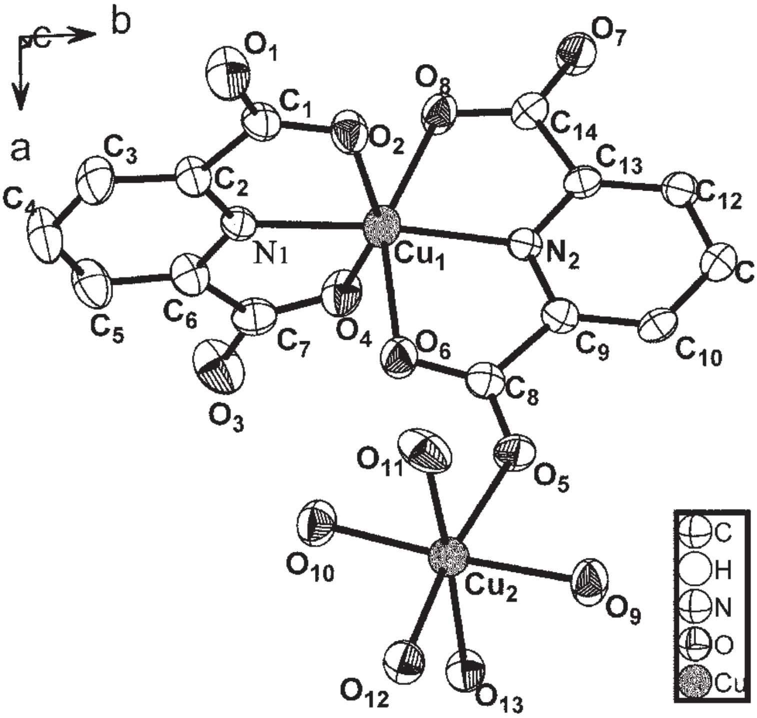


FIGURE 3 ORTEP drawing of Compound **2** with thermal ellipsoids at 50%.

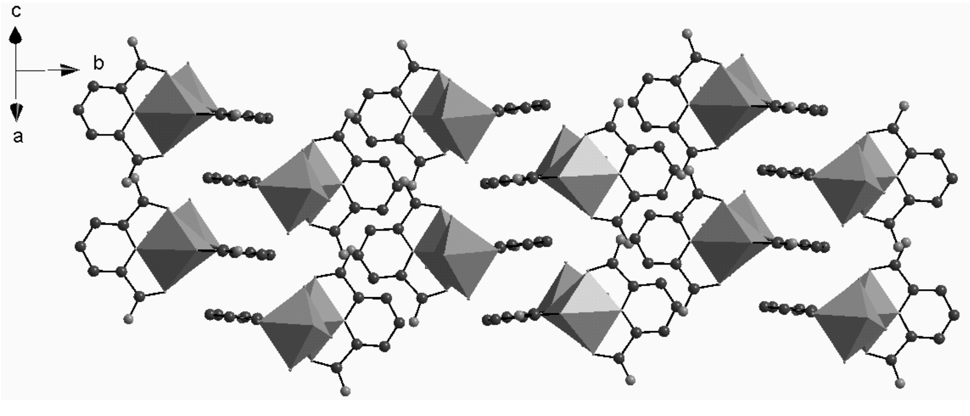


FIGURE 4 Views of packing in crystals of Compound **2** with Cu.

TABLE III Infrared spectroscopy (cm^{-1}) for Compounds **1** and **2**

	$\upsilon_{O\text{–}H}$			$\upsilon_{C\text{–}H}$	$\upsilon_{C\text{–}O}$	$\upsilon_{O\text{–}C\text{–}O}$	υ_{PR}		δ_{OH}	$\delta_{C\text{–}H}$		$\delta_{O\text{–}C\text{–}O}$	$\upsilon_{C\text{–}H}$
1	3354	3099		2487	1731	1678	1632	1598	916	1368	826	740	826
2	3395	3063	3039		1688	1664	1621	1596	917	1377	821	736	

IR Spectroscopy

IR data for Compounds **1** and **2** are listed in Table III. The characteristic carboxyl vibrations in the free pydc ligand are found at $1702\,cm^{-1}$ as a strong and broad vibration assigned to $\upsilon_{(C=O)}$ stretching vibrations [14,15].

The IR spectrum of **1** presents three distinguishable regions. In the high-energy bands, ranging from 3500 to $2700\,cm^{-1}$, there are three absorption peaks at 3354–$3099\,cm^{-1}$, due to $\upsilon_{O–H}$ of coordination water molecules and free water molecules. In the mid-energy range, $2487\,cm^{-1}$, absorption peaks originate from $\upsilon_{C–H}$. At lower energy, a series of absorption peaks is observed, including $\upsilon_{C–O}$ at $1731\,cm^{-1}$, $\upsilon_{O–C–O}$ at $1678\,cm^{-1}$, υ_{PR} at 1632 and $1598\,cm^{-1}$ (PR = pyridine ring), δ_{OH} at $917\,cm^{-1}$, and $\delta_{C–H}$ at 1368 and $826\,cm^{-1}$. The $\delta_{O–C–O}$ in-plane deformation vibration, which occurs as a strong sharp band at $701\,cm^{-1}$ in free H_2pdc, shifts to $740\,cm^{-1}$, which is also found in the literature [15].

The IR spectrum of Complex **2** presents two distinguishable regions. In the high-energy bands, ranging from 3500 to $2700\,cm^{-1}$, there are three absorption peaks at 3395, 3063 and $3039\,cm^{-1}$, due to $\upsilon_{O–H}$ of coordination water molecules and free water molecules. At low energy, a series of absorption peaks are observed, including $\upsilon_{C–O}$ at $1688\,cm^{-1}$, $\upsilon_{O–C–O}$ at $1664\,cm^{-1}$, υ_{PR} at 1621 and $1596\,cm^{-1}$, δ_{OH} at $916\,cm^{-1}$, and $\delta_{C–H}$ at 1377 and $821\,cm^{-1}$. The $\delta_{O–C–O}$ in-plane deformation vibration, which occurs as a strong sharp band at $701\,cm^{-1}$ in the free H_2pdc ligand, shifts to $736\,cm^{-1}$, as is found in the literature [15].

Third-order Nonlinear Optical Properties

Third-order nonlinear optical properties of Compound **1** were investigated (see Fig. 5) and we found α_2 $(m\,W^{-1}) = 0.15 \times 10^{-11}$, n_2 $(m^2 W^{-1}) = -2.50 \times 10^{-19}$, $\chi^3\,(esu) = 2.00 \times 10^{-13}$, $\chi^3\,(esu\,mol^{-1}\,dm^3) = 1.52 \times 10^{-10}$, and $\gamma\,(esu) = 8.35 \times 10^{-32}$. Compound **1** exhibits reverse saturable absorption and self-defocusing.

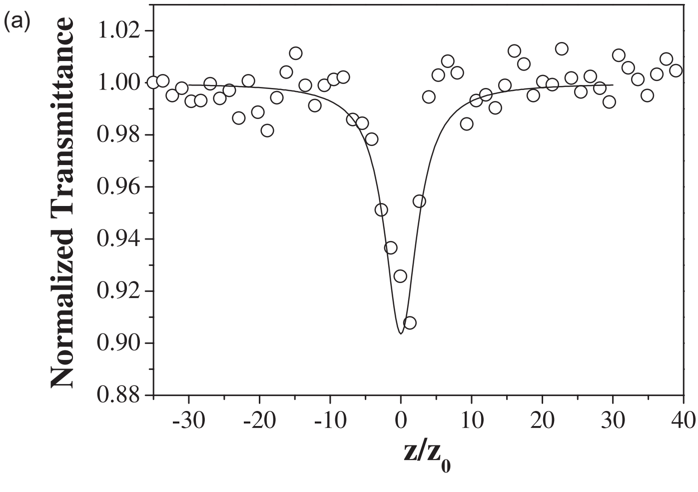


FIGURE 5 The third-order nonlinear optical property Z-scan data of $1.31 \times 10^{-3}\,mol\,dm^{-3}$ of Compound **1**: (a) collected under the open aperture configuration showing nonlinear optical absorption (the solid curve is a theoretical fit); (b) obtained by dividing the normalized Z-scan data obtained under the closed aperture configuration by the normalized Z-scan data in (a).

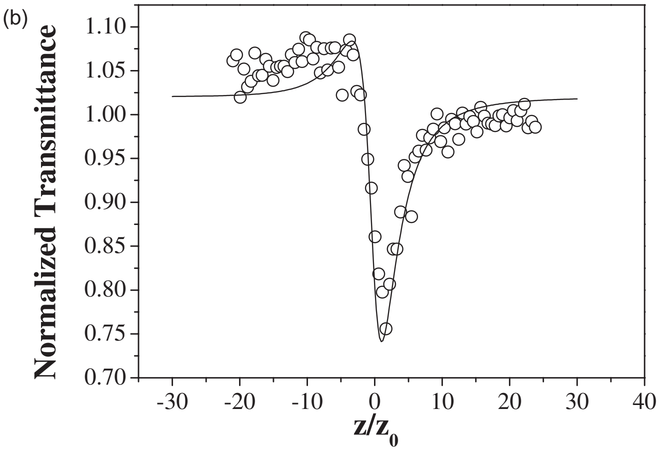


FIGURE 5 Continued.

CONCLUSIONS

In the present work, two novel hydrogen-bonded and π–π stacked 3-D supramolecular networks, Compounds **1** and **2**, have been synthesized and structurally characterized. Compound **1** exhibits reverse saturable absorption and self-defocusing. These syntheses demonstrate that the introduction of mixed ligands may provide multiple binding forces such as coordinate covalent, hydrogen-bonding interactions and π–π stacking, which has enormous potential for assembling multidimensional architectures. Furthermore, the use of pyridinedicarboxylic acid and isonicotinic acid groups contributes new features to the rapidly expanding area of supramolecular chemistry. In summary, we provide here a new strategy for the construction of coordination polymers. We are actively moving this synthetic strategy towards other related supramolecular coordination polymers.

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Supplementary Data

A figure and full lists of atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and observed and calculated factors are available from the authors on request. Deposition numbers CCDC 207520 and 207523.

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