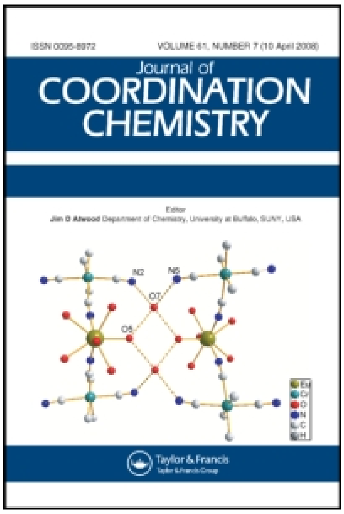

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A 3-D metal-organic framework constructed with cobalt(II), 1,3-di(4-pyridyl)propane (bpp) and 3,5-dinitrobenzoate (DNBA) with methyl-3,5-dinitrobenzoate (MDNBA) by <i>in-situ</i> synthesis as a guest

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A 3-D metal-organic framework constructed with cobalt(II), 1,3-di(4-pyridyl)propane (bpp) and 3,5-dinitrobenzoate (DNBA) with methyl-3,5-dinitrobenzoate (MDNBA) by *in-situ* synthesis as a guest

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A new 3-D cobalt(II) mixed ligand, metal-organic framework $\{[Co_2(bpp)_2(DNBA)_4H_2O] \cdot MDNBA\}$ (**1**), (bpp = 1,3-di(4-pyridyl)propane, DNBA = 3,5-dinitrobenzoate and MDNBA = methyl-3,5-dinitrobenzoate) was synthesized in aqueous-methanol medium. X-ray structural analysis of **1** revealed that the dinuclear cobalt clusters interlinked by two μ-carboxylates and a μ_2 water molecule, acting as a node, are connected to four other clusters through bridging bpp to generate an extended neutral 3-D network. MDNBA was *in-situ* synthesized and encapsulated in the framework as a guest molecule. Moreover, the fluorescence spectrum shows **1** exhibits blue fluorescent emission in the solid state at room temperature.

Keywords: *In-situ*; Hydrothermal synthesis; Metal-organic framework; Crystal structure

1. Introduction

The fabrication of multi-dimensional networks comprising metal ions as nodes and bridged ligands as spacers through self-assembly has made progress by detailed studies of their structural characteristics, such as diverse coordination modes and conformations, and their potential applications as catalysts, luminescent, sorption and magnetic materials [1–12]. Chemists are attracted by the particular beauty and intriguing topological structures which can be obtained by assembling metal ions and flexible bridging dipyridine ligands [13]. 1,3-Di(4-pyridyl)propane (bpp) is a good spacer for the formation of 0-D, 1-D, 2-D or 3-D [14–38] metal-organic frameworks and inorganic–organic hybrid materials [39, 40], owing to its conformational flexibility (see chart 1 a); 3,5-dinitrobenzoic acid (HDNBA) is also an excellent ligand to construct metal-organic frameworks, because it has one carboxylic group to bridge and two nitro-groups as H-bonding acceptors to diversify the metal complex architectures (see chart 1 b).

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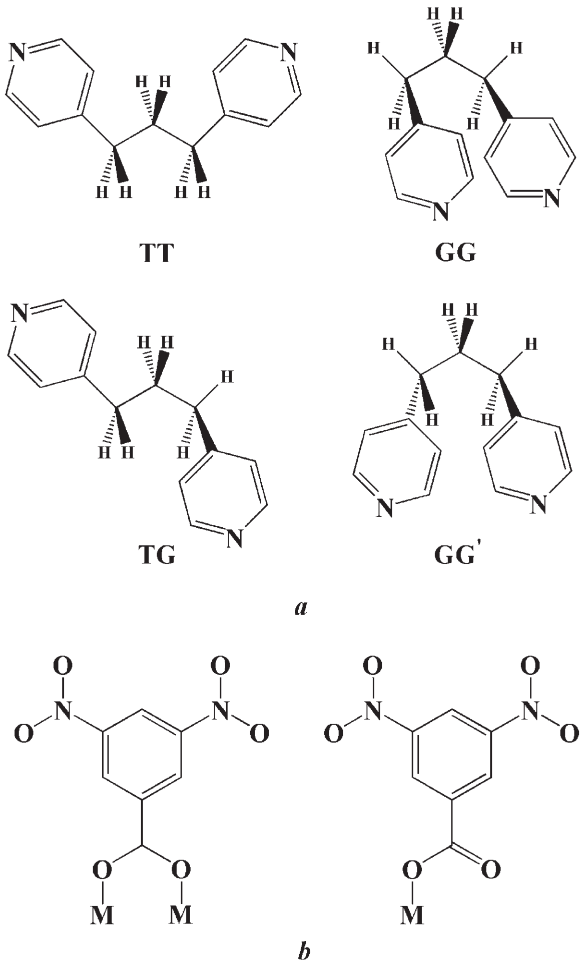

Chart 1. Different conformations of bpp, where T = *trans* and G = gauche (a) and coordination modes of 3,5-DNBA ligand in **1** (b).

Coordination polymers based on bpp or DNBA are well-known in the literature [41–58], but there is no report on Co^{II} coordination polymers using DNBA as building nodes and bpp as bridging spacers. In this context, we present the synthesis, crystal structure and properties of a new 3-D metal-organic framework $\{[Co_2(bpp)_2(DNBA)_4H_2O] \cdot MDNBA\}$ (**1**) with bpp and DNBA as ligands.

2. Experimental

2.1. *General procedures*

All solvents and reagents for synthesis were commercially available and used as received. The IR spectra were recorded in the range 400–4000 cm^{-1} on an FTIR-8400

(SHIMADZU) spectrometer with pressed KBr pellets; elemental analyses (C, H and N) were performed on a Perkin-Elmer 240 C analyzer. Thermogravimetric data were collected on a PYRIS DIAMOND thermal analyzer. Excitation and emission spectra were obtained on a HITACHI F-4500 spectrofluorometer equipped with a 150 W xenon lamp as the excitation source.

2.2. *Preparation of (1)*

A mixture of $CoCl_2 \cdot 6H_2O$ (0.1 mmol), bpp (0.1 mmol), HDNBA (0.2 mmol), H_2O (2.5 mL) and CH_3OH (2.5 mL) was stirred for 20 min, sealed in a Teflon-lined stainless steel autoclave (25 mL) and kept at 140°C for four days. After the mixture was slowly cooled to room temperature, red block crystals of **1** suitable for X-ray diffraction were obtained in 35% yield (based on Co^{II} salt). Anal. Calcd for $Co_2C_{62}H_{48}N_{14}O_{31}$: C, 46.41; H, 2.99; N, 12.23%. Found: C, 46.22; H, 2.78; N, 12.41%. IR (KBr, cm^{-1}): 3092m, 2951w, 2363w, 1643s, 1616s, 1547s, 1460m, 1427m, 1397s, 1348s, 1225w, 1074m, 1020w, 976w, 918w, 860w, 829w, 793w, 760w, 725s.

2.3. *X-ray crystallography*

The structure of **1** was determined by single crystal X-ray diffraction. Data were collected on a BRUKER SMART 1000 CCD detector with Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293 K in the range $1.70 < \theta < 25.00°$. A total of 33,475 (12,013 unique) reflections were measured ($-25 \leq h \leq 22$, $-14 \leq k \leq 16$, $-28 \leq l \leq 28$) for **1**. The structure was solved by direct methods and refined by full-matrix least squares on F^2 using SHELXL-97 [59, 60]. All non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were generated geometrically. A summary of the crystallographic data and structural determination for the title compound is provided in table 1. Selected bond lengths and angles are given in table 2. CCDC no. is 635735.

3. Results and discussion

3.1. *Preparation of (1)*

The self-assembly of $CoCl_2 \cdot 6H_2O$ with HDNBA and bpp in H_2O–CH_3OH mixed solution was performed under mild conditions with methanol as solvent and reactant in the *in situ* guest molecule reaction. If methanol was not added into the reaction system, only unknown ropy precipitate was obtained. If methanol was replaced by ethanol at the same conditions, we could not obtain single crystals.

3.2. *Structure description*

Single-crystal X-ray analysis reveals that **1** contains two crystallographically unique Co1 and Co2 atoms. Each cobalt in the dinuclear motif is coordinated by two oxygen atoms from two μ-carboxylate ends of different DNBA, one oxygen atom from

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

Compound	**1**
Empirical formula	$C_{31}H_{24}CoN_7O_{155}$
Formula weight	801.50
Temperature (K)	273(2)
Crystal system	Orthorhombic
Space group	*Pna*21
a (Å)	21.1573(8)
b (Å)	13.5422(6)
c (Å)	24.0112(10)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å^3)	6879.6(5)
Z	4
D_{Calcd} (g cm^{-3})	1.548
$F(000)$	3279
θ range (°)	1.70 to 25.00
Reflections collected/unique	33,475/12,013 ($R_{int} = 0.0619$)
Data/restraints/parameters	12,013/1/977
Goodness-of-fit on F^2	0.990
Final R indices [$I > 2\sigma(I)$]	$R^a = 0.0531$, $wR^b = 0.1067$
R indices (all data)	$R^a = 0.0973$, $wR^b = 0.1302$
Largest diff. peak and hole (e Å^{-3})	0.737 and −0.309

$^aR_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$; $^bwR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

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

Co(1)–O(2)	2.068(4)	Co(1)–O(8)	2.074(4)
Co(1)–O(14)	2.133(4)	Co(1)–O(1)	2.140(4)
Co(1)–N(10)	2.145(5)	Co(1)–N(9)	2.154(5)
Co(2)–O(3)	2.066(4)	Co(2)–O(9)	2.107(4)
Co(2)–O(1)	2.108(4)	Co(2)–N(12)#1	2.120(4)
Co(2)–O(20)	2.126(4)	Co(2)–N(11)#2	2.173(5)
O(2)–Co(1)–O(8)	88.60(16)	O(2)–Co(1)–O(14)	86.08(16)
O(8)–Co(1)–O(14)	174.62(16)	O(2)–Co(1)–O(1)	94.67(15)
O(8)–Co(1)–O(1)	89.68(15)	O(14)–Co(1)–O(1)	90.04(16)
O(2)–Co(1)–N(10)	176.48(18)	O(8)–Co(1)–N(10)	90.68(17)
O(14)–Co(1)–N(10)	94.68(17)	O(1)–Co(1)–N(10)	88.77(17)
O(2)–Co(1)–N(9)	93.42(16)	O(8)–Co(1)–N(9)	89.98(17)
O(14)–Co(1)–N(9)	91.04(17)	O(1)–Co(1)–N(9)	171.89(17)
N(10)–Co(1)–N(9)	83.13(18)	O(3)–Co(2)–O(9)	89.15(16)
O(3)–Co(2)–O(1)	91.05(15)	O(9)–Co(2)–O(1)	93.12(15)
O(3)–Co(2)–N(12)#1	90.89(18)	O(9)–Co(2)–N(12)#1	91.24(16)
O(1)–Co(2)–N(12)#1	175.25(17)	O(3)–Co(2)–O(20)	175.87(17)
O(9)–Co(2)–O(20)	86.76(16)	O(1)–Co(2)–O(20)	89.73(16)
N(12)#1–Co(2)–O(20)	88.64(17)	O(3)–Co(2)–N(11)#2	90.09(17)
O(9)–Co(2)–N(11)#2	176.82(18)	O(1)–Co(2)–N(11)#2	89.98(17)
N(12)#1–Co(2)–N(11)#2	85.68(18)	O(20)–Co(2)–N(11)#2	93.96(17)
Co(2)–O(1)–Co(1)	117.10(15)		

Symmetry code: #1: $-x - 3/2$, $y - 1/2$, $z + 1/2$; #2: $-x - 1$, $-y$, $z + 1/2$.

carboxylate (in a monodentate fashion) of DNBA, one oxygen atom from bridging water molecule (Co–O 2.066(4)–2.140(4) Å), and two nitrogen atoms from different bpp ligands (Co–N 2.120–2.173 Å), in a distorted octahedron geometry, as shown in figure 1. The dinuclear cobalt unit bridged by two μ-carboxylic groups and a μ_2 water molecule, constitute a bimetallic second building unit (SBU) $[Co_2(CO_2)_2(\mu_2\text{-}OH_2)N_4O_2]$

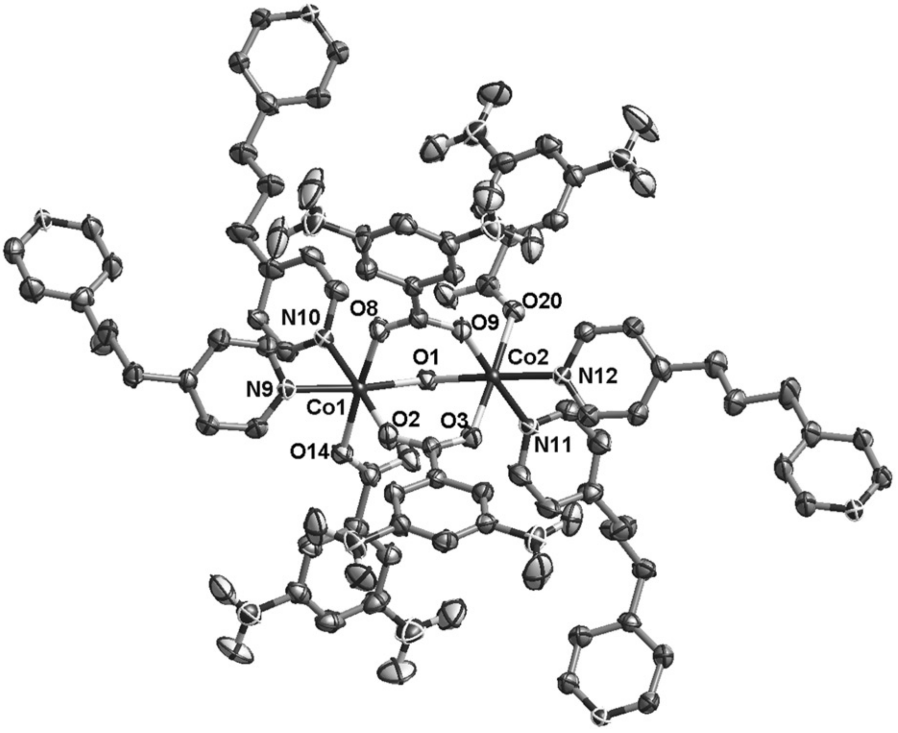

Figure 1. The coordination environment of **1**. Thermal ellipsoids are shown at 30% probability.

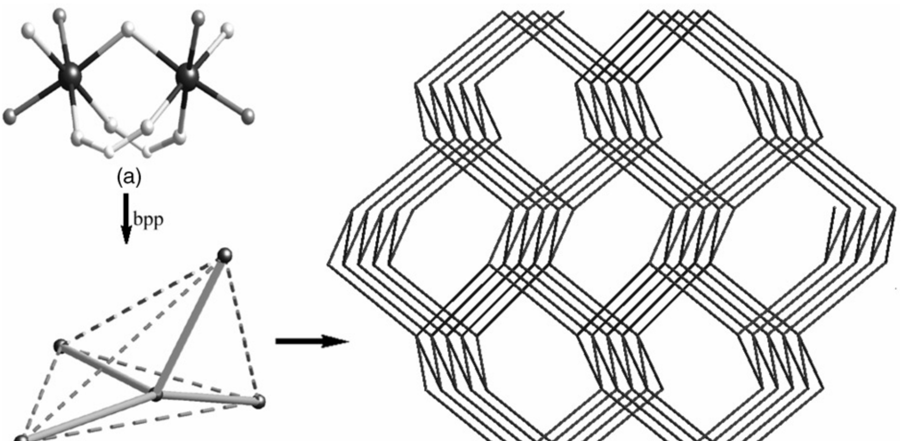

Figure 2. A schematic view of the 3-D framework.

figure 2(a), with Co1 ··· O1 ··· Co2 angle of 117° and non-bonding Co ··· Co distance of 3.624 Å. Moreover, bpp ligands are in TT and TG conformations owing to the free twist of propyl (–CH_2–CH_2–CH_2–) with N ··· N distances of 9.880 and 8.662 Å, respectively. The binuclear SBU, as a 4-connected node figure 2(b), is linked through bridging bpp to

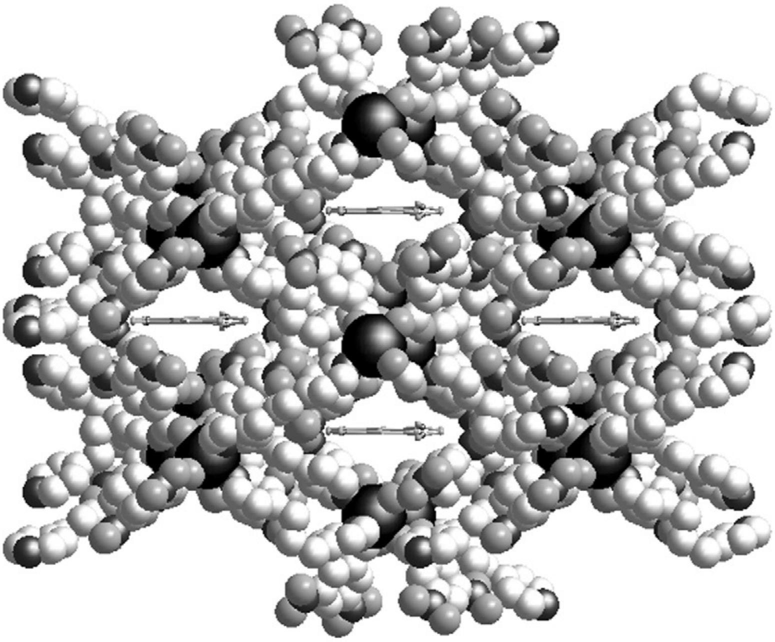

Figure 3. Space-filling view of the 3-D network along the [100] direction (H atoms were omitted for clarity), MDNBA were capsulated in the void of the 3-D framework as a guest molecule.

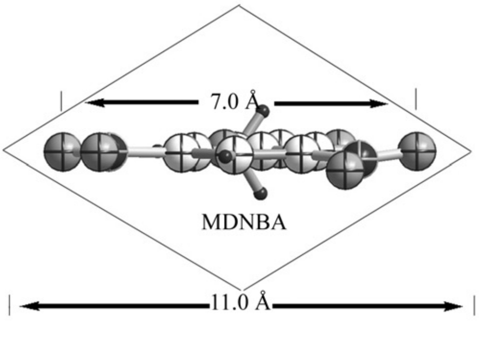

Figure 4. View of the pore size of 3-D network in the [100] direction, the rhombus rim represents the distorted rhombus cavities and the pore size is dependent on the distance (11.0 Å) between N8 derived from DNBA and C47 of bpp.

generate an extended neutral 3-D metal-organic framework figure 2(c), and the distances between two cores of SBU are 13.328 and 15.074 Å, respectively.

MDNBA was *in-situ* synthesized and inserted into the void of the 3-D framework as a guest molecule with distorted rhombus cavities approximately $8.0 \times 8.0\,\text{Å}^2$, as shown in figures 3 and 4. Calculations from X-ray structural parameters show that the solvent accessible void space in the 3-D framework is approximately 2.0% of the total crystal volume (18.6% for the MDNBA omitted). Long ligands usually lead to large voids and may further result in interpenetration and entangle structures [37]. In this report,

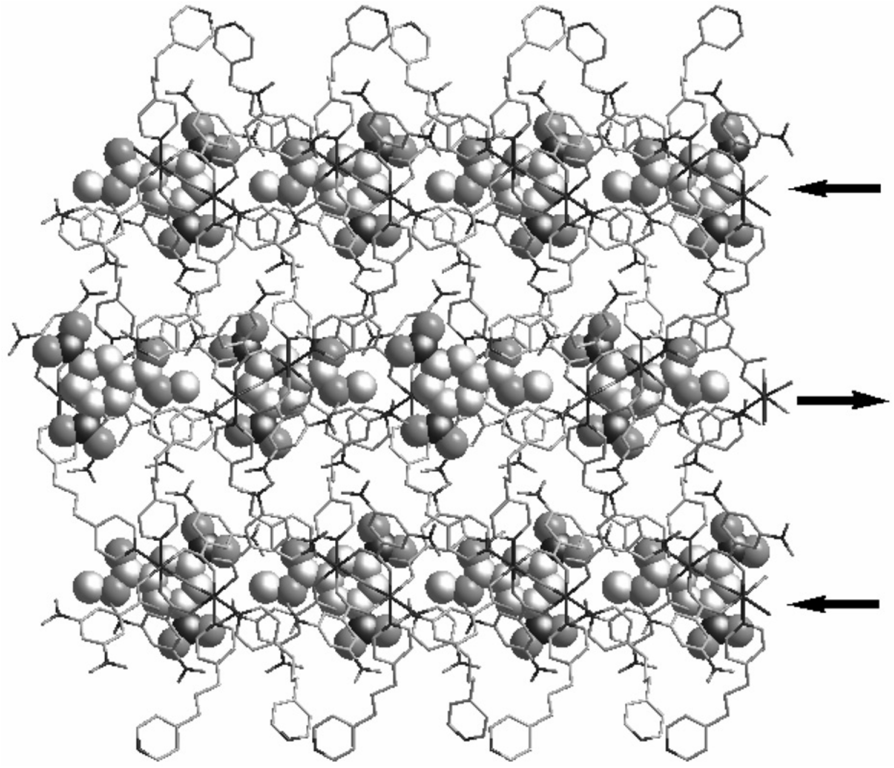

Figure 5. Two orientations of MDNBA in the network along the [010] direction (H atoms were omitted for clarity).

MDNBA *in-situ* synthesized may prohibit the interpenetration of 3-D framework by steric hindrance. Moreover, antiparallel MDNBA guest molecules have been found, probably from the asymmetry of the unit (figure 5). Reports on guest molecules *in-situ* synthesized and encapsulated in the framework are rare [61].

3.3. *The properties of (1)*

Compound **1** exhibits blue fluorescence emission around 452 nm upon excitation at 372 nm in the solid state at room temperature, similar to that of bpp ($\lambda_{em} = 455$ nm) [62], as shown in figure 6. Lin and co-workers have obtained similar results (emission around 426 upon excitation at 388 nm) with a minor shift of the emission compared to the title compound [62]. The different emission of **1** and the complex obtained by Lin may be due to the difference of their typological structures because the fluorescence behavior is closely associated with the metal ions and the ligands coordinated around them [63].

Thermogravimetric analysis (TGA) was performed at 40–600°C with a heating rate of 10°C min^{-1} to study the thermal stability of **1** (shown in figure 7). The TGA curve shows the weight of **1** is almost unchanged from 40 to 148°C. The stage that occurs

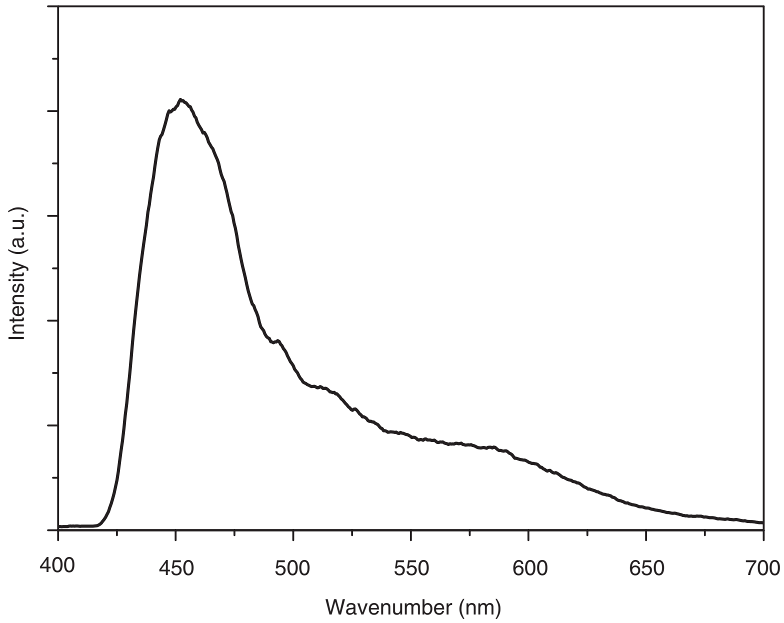

Figure 6. The photo-induced emission spectrum of **1** ($\lambda_{ex} = 372$, $\lambda_{em} = 452$).

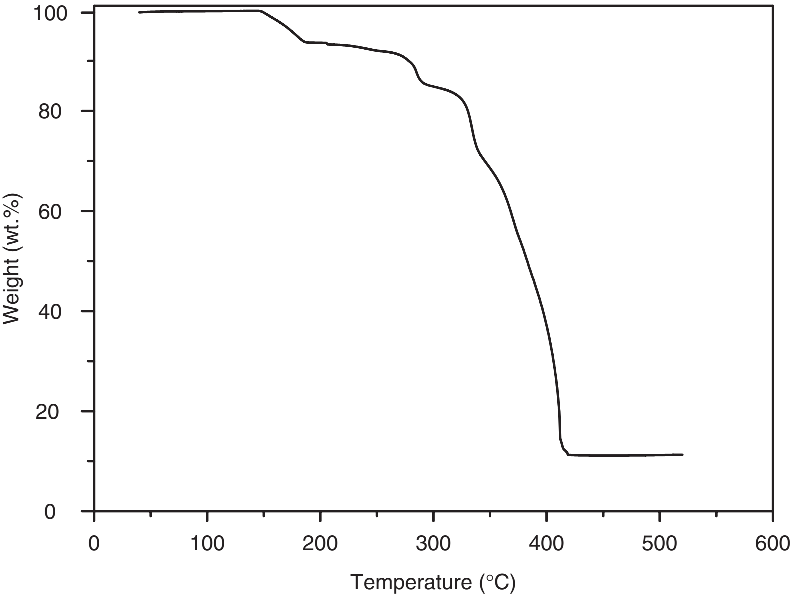

Figure 7. Thermogravimetric analysis of **1**.

between 148 and 297°C is attributed to the loss of a coordinated water molecule and a MDNBA guest molecule per formula. The overall observed value (15%) is in agreement with the calculated value (15.2%). The latter step, which occurs in the range 280–415°C, corresponds to the loss of DNBA and bpp ligands.

The IR spectrum shows characteristic bands of carboxylate at 1643 and 1472 cm^{-1} for asymmetric stretching and 1397 cm^{-1} for symmetric stretching. No strong absorptions around 1700 cm^{-1} for –COOH are observed, indicating that all carboxylates of DNBA are deprotonated. The broad bond at 3429 cm^{-1} is assigned to hydrogen bonds and coordinating water molecules in the compound. The absorption peaks at 1074 and 1224 cm^{-1} are assigned to symmetric and asymmetric stretching of C–O–C of MDNBA.

In summary, we isolated a new 3-D metal-organic framework in aqueous-methanol by hydrothermal synthesis; methyl-3,5-dinitrobenzoate spanning two different directions was *in-situ* synthesized and inserted into the void of the 3-D network as a guest molecule. Compound **1** exhibits blue fluorescence in the solid state at room temperature.

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