CrystEngComm

Cite this: *CrystEngComm*, 2012, **14**, 4719–4727

www.rsc.org/crystengcomm

PAPER

# A series of coordination polymers constructed from *in situ* amidation ligands: syntheses, structures and luminescent properties†

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***Received 24th December 2011, Accepted 17th April 2012***
**DOI: 10.1039/c2ce06730g**

From the hydrothermal *in situ* amidation reactions of aromatic polycarboxylates and hydrazine hydrate ($N_2H_4{\cdot}H_2O$), four complexes, dinuclear $[Cu(\mu_2\text{-}H_3bbch)(H_2O)]_2{\cdot}2H_2O$ (**1**), 3-D grid-like $[Fe_3(\mu_5\text{-}Hbbch)_2(\mu_2\text{-}H_2O)_2(H_2O)_2]{\cdot}2H_2O$ (**2**), 2-D layer $[Zn(\mu_2\text{-}H_2bbh)(\mu_2\text{-}N_2H_4)_{1/2}(H_2O)]{\cdot}2H_2O$ (**3**) and 3-D supramolecular structure $[Cd(H_2bch)_2(2,2'\text{-bpy})(H_2O)_2][Cd(\mu_2\text{-}H_2bch)(2,2'\text{-bpy})(H_2O)_2](H_2bch)$ (**4**) have been prepared. The two different *in situ* amidated ligands in **1**, **2** and **3**, benzene-4,5-bicarboxylate-1,2-hydrazide ($H_4bbch$) and benzene-1,2,4,5-bihydrazide ($H_4bbh$), were formed through adjusting the ratios of pyromellitic acid (PMA) and $N_2H_4{\cdot}H_2O$, of which $H_4bbch$ was generated through hydrothermal *in situ* amidation reactions for the first time. Benzene-4-carboxylate-1,2-hydrazide ($H_3bch$), displaying three new coordination modes in **4**, was also an *in situ* amidation product of benzene-1,2,4-tricarboxylic acid ($H_3btca$) and $N_2H_4{\cdot}H_2O$. **1–4** were characterized by elemental analysis, infrared spectroscopy, and thermogravimetric analysis. Their structures were determined by single-crystal X-ray diffraction. The fluorescence properties of compounds **1**, **3** and **4** were also investigated.

## Introduction

The rational design and synthesis of metal–organic frameworks (MOFs) is a current hot topic owing to their fascinating architectures and potential applications.[1] Recently, *in situ* synthesis of ligands under hydro- or solvo-thermal conditions is of great interest for the discovery of new organic reactions and for the preparation of unusual coordination complexes as such transformations are generally achieved in the presence of certain metal ions.[2–7] To date, an increasing number of *in situ* ligand reactions have occurred under hydrothermal conditions including hydroxylation,[3] hydrolysis,[4] formation of triazoles and tetrazoles,[5] formation of carbon–carbon bonds,[6] and so on. Using the ligands *in situ* in reactions between organic carboxylates and organic amines, several novel compounds have been generated.[7] However, to the best of our knowledge, only two kinds of *in situ* amidation cyclization reactions have been found and a series of coordination compounds were obtained under hydrothermal conditions. One type is where benzene-1,2,4-tricarboxylic acid ($H_3btca$) *in situ* reacts with *p*-phenylenediamine to give 2-(4-amino-phenyl)-1,3-dioxo-2,3-dihydro-1*H*-isoindole-5-carboxylic acid with one five-membered ring formed.[7h] Another type is that between hydrazine hydrate ($N_2H_4{\cdot}H_2O$) and polycarboxylic acids containing two adjacent carboxylic groups to form six-membered amide rings.[7a–7g] Several coordination complexes with amidated ligands generated from the *in situ* reactions of $N_2H_4{\cdot}H_2O$ and different polycarboxylic acids, including pyromellitic acid (PMA), $H_3btca$, phthalic acid, pyridine-2,3-dicarboxylic acid, pyridine-3,4-dicarboxylic acid, 4,5-dichlorophthalate, 5-ethylpyridine-2,3-dicarboxylic acid, 6-methylpyridine-2,3-dicarboxylic acid and 4,4′-oxydiphthalic anhydrous, were obtained. Interesting coordination modes of the amidated ligands and intriguing architectures of the corresponding metal complexes offer impetus for further research of similar reactions.[7]

Among these polycarboxylic acids, PMA has been widely used for the hydrothermal synthesis of coordination polymers of transition metals because of its multiform coordination modes.[8] It has two pairs of adjacent carboxylic groups which indicates that if we adjust the ratio of PMA and $N_2H_4{\cdot}H_2O$, different amidated ligands may be formed. Although several coordination polymers have been generated *via in situ* amidation cyclization between PMA and $N_2H_4{\cdot}H_2O$, only benzene-1,2,4,5-bihydrazide ($H_4bbh$) was obtained with one PMA and two $N_2H_4{\cdot}H_2O$.[7a–7d] On the other hand, another useful polycarboxylic acid, $H_3btca$ has three carboxylic groups containing one pair of neighbouring carboxylic groups. One $H_3btca$ can react with one $N_2H_4{\cdot}H_2O$ to

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† Electronic supplementary information (ESI) available. CCDC reference numbers 742273, 742939, 802479 and 802480. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ce06730g

give the *in situ* amidation cyclization ligand benzene-4-carboxylate-1,2-hydrazide ($H_3bch$), which has been proved to be a good candidate ligand.[7a,7e] Recently, we have been focusing on the investigation on the reaction systems containing multidentate aromatic polycarboxylates (PMA and $H_3btca$) and $N_2H_4 \cdot H_2O$, expecting to obtain new compounds with *in situ* amidation cyclization ligands. Finally, we successfully obtained four coordination compounds, $[Cu(\mu_2\text{-}H_3bbch)(H_2O)]_2 \cdot 2H_2O$ (**1**), $[Fe_3(\mu_5\text{-}Hbbch)_2(\mu_2\text{-}H_2O)_2(H_2O)_2] \cdot 2H_2O$ (**2**), $[Zn(\mu_2\text{-}H_2bbh)(\mu_2\text{-}N_2H_4)_{1/2}(H_2O)] \cdot 2H_2O$ (**3**) and $[Cd(H_2bch)_2(2,2'\text{-}bpy)(H_2O)_2][Cd(\mu_2\text{-}H_2bch)(2,2'\text{-}bpy)(H_2O)_2](H_2bch)$ (**4**), containing three *in situ* amidation cyclization ligands, $H_4bbch$, $H_4bbh$ and $H_3bch$, respectively. Notably, $H_4bbch$ and $H_4bbh$ were formed *via* two different *in situ* amidation cyclization reactions of PMA and $N_2H_4 \cdot H_2O$ through adjusting the ratio of the two reagents, of which $H_4bbch$ was generated through hydrothermal *in situ* amidation cyclization reaction to construct coordination polymers for the first time.[9] In this paper, we report the syntheses, crystal structures and thermogravimetric analyses of the four compounds, as well as the fluorescence properties of compounds **1**, **3** and **4**.

## Experimental section

### Material and physical measurements

All chemicals were obtained from commercial sources and used without further purification. IR (KBr pellets) spectra were recorded in the 4000–400 cm$^{-1}$ range using a Perkin-Elmer Spectrum One FT-IR spectrometer. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 elemental analyzer. Thermogravimetric (TG) behaviours were investigated on a Perkin-Elmer TGA-7 instrument with a heating rate of 10 °C min$^{-1}$ in air. Fluorescent data were obtained using a Cary Eclipse fluorometer at room temperature.

### Syntheses

**$[Cu(\mu_2\text{-}H_3bbch)(H_2O)]_2 \cdot 2H_2O$ (1).** A mixture of $CuSO_4 \cdot 5H_2O$ (0.25 g, 1.0 mmol), PMA (0.25 g, 1.0 mmol) and $H_2O$ (20 mL) was stirred for 2 h at room temperature. Its pH was then adjusted to 4 with an aqueous solution of $N_2H_4 \cdot H_2O$ (10%, 0.6 mL). The resulting mixture was sealed in a 25-mL Teflon-lined stainless steel autoclave and heated at 170 °C for 4 days, after which it was cooled over 12 h to room temperature. The product was obtained as orange block-shaped crystals in 40% yield (based on Cu). Anal. Calc. for $Cu_2C_{20}N_4O_{16}H_{18}$ (697.48): C, 34.44; H, 2.60; N, 8.03%; Found: C, 34.59; H, 2.71; N, 7.91%. IR (KBr, cm$^{-1}$): 3415 m, 1704 m, 1649 s, 1562 m, 1511 m, 1389 m, 1321 w, 1281 m, 1223 m, 1133 w, 1090 w, 929 w, 847 w, 773 w, 729 m, 684 w, 581 w.

**$[Fe_3(\mu_5\text{-}Hbbch)_2(\mu_2\text{-}H_2O)_2(H_2O)_2] \cdot 2H_2O$ (2).** Compound **2** was obtained in 58% yield (based on Fe) as brown block-shaped crystals by a similar procedure with $FeSO_4 \cdot 7H_2O$ (0.28 g, 1.0 mmol) in place of $CuSO_4 \cdot 5H_2O$. Anal. Calc. for $Fe_3C_{20}N_4O_{18}H_{18}$ (769.93): C, 31.25; H, 2.32; N, 7.25%; Found: C, 31.32; H, 2.28; N, 7.14%. IR (KBr, cm$^{-1}$): 3738 s, 1692 m, 1546 s, 1508 m, 1463 w, 1377 m, 1141 w, 9415 m, 838 m, 753 w, 696 m.

**$[Zn(\mu_2\text{-}H_2bbh)(\mu_2\text{-}N_2H_4)_{1/2}(H_2O)] \cdot 2H_2O$ (3).** Compound **3** was prepared analogously using a mixture of $ZnCl_2$ (0.14 g, 1.0 mmol), PMA (0.25 g, 1.0 mmol), $H_2C_2O_4$ (0.13 g, 1.0 mmol) and $H_2O$ (20 mL) (pH = 6, adjusted by using a 1.5 mL 10% aqueous solution of $N_2H_4 \cdot H_2O$). The product was obtained as yellow block-shaped crystals in 44% yield (based on Zn). Anal. Calc. for $ZnC_{10}N_5O_7H_{12}$ (379.62): C, 31.64; H, 3.18; N, 18.45%; Found: C, 31.71; H, 3.22; N, 18.34%. IR (KBr, cm$^{-1}$): 3638 s, 1622 s, 1559 s, 1491 s, 1379 m, 1376 m, 1300 m, 1173 m, 974 s, 887 m, 849 m, 721 m, 672 m, 585 m.

**$[Cd(H_2bch)_2(2,2'\text{-}bpy)(H_2O)_2][Cd(\mu_2\text{-}H_2bch)(2,2'\text{-}bpy)(H_2O)_2](H_2bch)$ (4).** Compound **4** was prepared analogously using a mixture of $CdCl_2 \cdot 2.5H_2O$ (0.23 g, 1.0 mmol), $H_3btca$ (0.21g, 1.0 mmol), 2,2′-bpy (0.16 g, 1.0 mmol) and $H_2O$ (20 mL) (pH = 7, adjusted by using a 0.5 mL 10% aqueous solution of $N_2H_4 \cdot H_2O$). The product was obtained as yellow block-shaped crystals in 53% yield (based on Cd). Anal. Calc. for $Cd_2C_{56}N_{12}O_{20}H_{44}$ (1429.83): C, 47.04; H, 3.15; N, 11.78%; Found: C, 47.15; H, 3.21; N, 11.87%. IR (KBr, cm$^{-1}$): 2991 m, 1657 s, 1610 m, 1582w, 1551 m, 1349 m, 1388 s, 1308 m, 1218 s, 1060 w, 816 m, 769 s, 650 m.

### X-Ray crystallography

Diffraction data for compounds **1** and **2** were collected at 293 K on a Rigaku R-AXIS RAPID IP diffractometer with Mo Ka radiation ($\lambda$ = 0.71073 Å). The data for **3** and **4** were collected at 293 K on a Bruker-AXS Smart CCD diffractometer (Mo-Ka, $\lambda$ = 0.71073 Å). Anisotropic thermal parameters were applied to all non-hydrogen atoms. In compounds **2–4**, all hydrogen atoms attached to C, N and O atoms were placed geometrically. In compound **1**, the hydrogen atoms attached to O2W and N1 were located from difference Fourier maps and refined isotropically, while those attached to other O and C atoms were placed geometrically. The structures were then refined on $F^2$ using SHELXL-97. CCDC numbers of compounds **1–4** are 742939, 742273, 802480 and 802479, respectively.† Details of the final refinement are given in Table 1. Selected bond lengths and angles are listed in Table S1.† Hydrogen-bonded parameters are listed in Table S2.†

## Results and discussion

### Synthesis

Aromatic polycarboxylic acids containing two neighbouring carboxylic groups can react *via in situ* amidation cyclization with $N_2H_4 \cdot H_2O$ to form amidated ligands.[7] PMA has two pairs of adjacent carboxylic groups which indicates that the two pairs of carboxylic groups or only one pair can react with $N_2H_4 \cdot H_2O$. $H_4bbh$, characterized with two newly-formed six-membered acylhydrazidate rings, has been reported before,[7a–7d] and was generated by one PMA and two $N_2H_4 \cdot H_2O$ through *in situ* amidation cyclization reaction in a nearly neutral environment. When we used one PMA and one $N_2H_4 \cdot H_2O$ at pH about 4, only one pair of adjacent carboxylic groups were *in situ* amidated and $H_4bbch$ with one newly-formed six-membered acylhydrazidate ring was hydrothermally generated for the first time by our group. The pH value is influential, in that $H_4bbch$ can be obtained at a pH value of about 4 and $H_4bbh$ at neutral pH. In

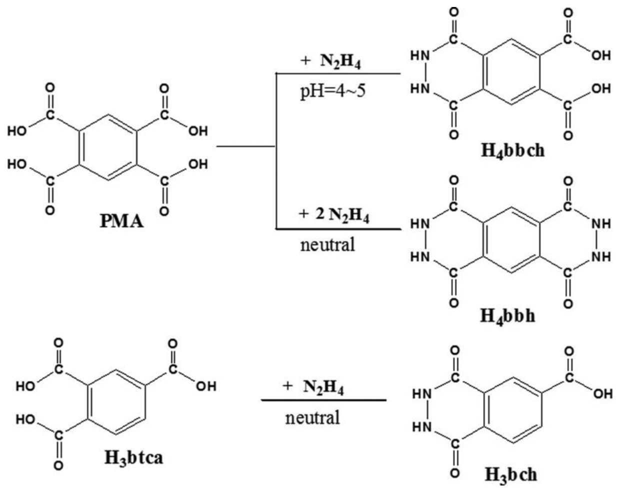
**Table 1** Crystal data collections and structure refinements for **1–4**

| | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Formula | $Cu_2C_{20}H_{18}N_4O_{16}$ | $Fe_3C_{20}H_{18}N_4O_{18}$ | $ZnC_{10}H_{12}N_5O_7$ | $Cd_2C_{56}H_{44}N_{12}O_{20}$ |
| $M$ | 697.48 | 769.93 | 379.62 | 1429.83 |
| $T/K$ | 293(2) | 293(2) | 296(2) | 293(2) |
| Crystal system | Triclinic | Triclinic | Monoclinic | Orthorhombic |
| Space group | $P\bar{1}$ | $P\bar{1}$ | $P2_1/c$ | $Pca2_1$ |
| $a$/Å | 6.6226(13) | 6.4427(13) | 9.4252(16) | 18.683(11) |
| $b$/Å | 9.6570(19) | 9.5515(19) | 20.219(3) | 7.826(5) |
| $c$/Å | 9.752(2) | 10.224(2) | 7.0187(12) | 37.85(2) |
| $\alpha$ (°) | 95.92(3) | 107.45(3) | 90 | 90 |
| $\beta$ (°) | 108.90(3) | 91.15(3) | 108.742(2) | 90 |
| $\gamma$ (°) | 94.26(3) | 101.70(3) | 90 | 90 |
| $V$/Å$^3$ | 583.1(2) | 585.5(2) | 1266.6(4) | 5534(5) |
| $Z$ | 1 | 1 | 4 | 4 |
| Dc/Mg m$^{-3}$ | 1.986 | 2.183 | 1.991 | 1.716 |
| $\mu$/mm$^{-1}$ | 1.921 | 1.943 | 1.992 | 0.861 |
| $F$(000) | 352 | 388 | 772 | 2880 |
| $\theta$ Range/° | 3.27–27.48 | 3.24–25.00 | 2.01–26.92 | 2.15–27.48 |
| Reflections collected | 5796 | 4630 | 7233 | 33 927 |
| Independent reflections ($R_{int}$) | 2658 (0.0459) | 2047 (0.0527) | 2739 (0.0515) | 12 231 (0.1062) |
| GOF | 1.005 | 1.033 | 0.963 | 1.048 |
| Final $R^{a,b}$ indices [$I > 2\sigma(I)$] | $R_1 = 0.0456$, w$R_2 = 0.1121$ | $R_1 = 0.0792$, w$R_2 = 0.2211$ | $R_1 = 0.0422$, w$R_2 = 0.0889$ | $R_1 = 0.0779$, w$R_2 = 0.1874$ |
| $R$ indices (all data) | $R_1 = 0.0689$, w$R_2 = 0.1242$ | $R_1 = 0.1030$, w$R_2 = 0.2358$ | $R_1 = 0.0715$, w$R_2 = 0.1016$ | $R_1 = 0.1097$, w$R_2 = 0.2439$ |

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F|$. [b] $wR_2 = |\sum w(|F_o|^2 - |F_c|^2)^2/\sum|w(F)^2|^{1/2}$.

the process of preparing compound **3**, we tried to only add one PMA and three $N_2H_4{\cdot}H_2O$ with the pH being 9 to react with $ZnCl_2$, but we obtained powders. Only when oxalic acid was added to adjust the pH to about neutral, was compound **3**, constructed with $H_4$bbh and $N_2H_4$, produced. $H_3$bch, with only one six-membered acylhydrazidate ring, can be produced from the reaction starting with one $H_3$btca and one $N_2H_4{\cdot}H_2O$ in a neutral environment according to this paper and references.[7a,7e] The reactions between PMA and $H_3$btca with $N_2H_4{\cdot}H_2O$ are shown in Scheme 1. We attempted to obtain the corresponding crystals of $H_4$bbch and $H_3$bch ligands with PMA, $H_3$btca and $N_2H_4{\cdot}H_2O$, but failed.

It should be noted that in addition to the ratio of the reagents, the nature of the metal ions and auxiliary ligands have also been shown to have significant influences on the reaction outcome. For example, we have used other metal salts such as $MnCl_2$ or $NiSO_4$ to react with PMA and $N_2H_4{\cdot}H_2O$, but no suitable crystals constructed with $H_4$bbch or $H_4$bbh were obtained. As another example, the *in situ* amidation cyclization reaction occurred hydrothermally using a mixture of $CdCl_2$, $H_3$btca, $N_2H_4{\cdot}H_2O$ and 2,2′-bpy at pH = 7, affording compound **4**. In the absence of 2,2′-bpy, however, we only got white powders.



**Scheme 1** The reactions between PMA ($H_3$btca) and $N_2H_4{\cdot}H_2O$.

## Structural description

**[Cu(μ$_2$-H$_3$bbch)(H$_2$O)]$_2$·2H$_2$O (1).** As shown in Fig. 1a, **1** possesses a dinuclear structure constructed by two Cu(I) ions coordinated with two $H_3bbch^-$ ligands generated *via in situ* amidation cyclization reaction. The identity of Cu(I) is verified by the sum of bond-valence calculation of 0.813 for Cu1.[10] Cu1 adopts a distorted trigonal planar geometry, being coordinated by one nitrogen atom (N2) from one $H_3bbch^-$ ligand, one oxygen atom (O2A) from the other $H_3bbch^-$ ligand, and one water molecule (O1W). The distance of Cu1–N2 (1.889(3) Å) is comparable to that of Cu1–O2A (1.862(3) Å). The Cu1–O1W distance (2.516(3) Å) is consistent with a weak bonding interaction between Cu1 and O1W.[11,12] In compound **1**, the coordination of Cu1 shows a T-shaped coordination geometry with the angles of N2–Cu1–O1W, O2A–Cu1–O1W, and N2–Cu1–O2A being 87.94(12), 103.15(12), and 168.75(12)°, respectively. This may not only be attributed to the rigid structure of $H_3bbch^-$ ligand, but also to the bidentate coordination mode of neighbouring N2 and O2 atoms in the $H_3bbch^-$ ligand. The $H_3bbch^-$ ligand adopts a μ$_2$-bidentate mode in which one amide group coordinates two Cu atoms using its monodentate O and N atoms. Two $H_3bbch^-$ ligands coordinate simultaneously to two Cu atoms, forming an octagon core of $Cu_2C_2N_2O_2$. The Cu···Cu distance of 2.6291(13) Å is shorter than the sum of the van der Waals radius of Cu(I) (2.8 Å), but slightly longer than the Cu–Cu separation of 2.56 Å in metallic copper, indicating weak Cu(I)···Cu(I) interactions.[13] The hydrogen bonding and π···π interactions play important roles in stabilizing **1**. The uncoordinated

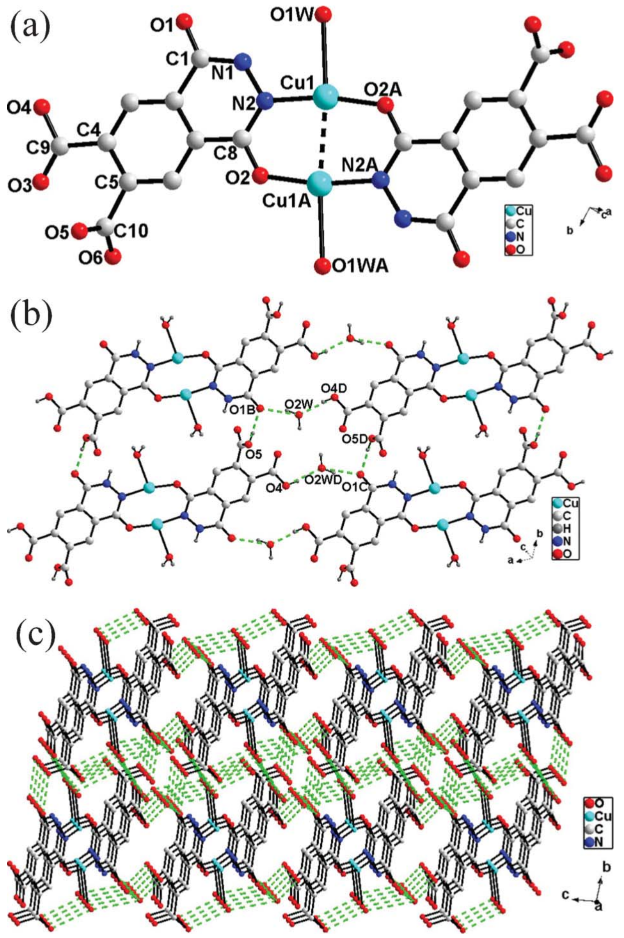


**Fig. 1** (a) The dinuclear structure of **1** (symmetry code: A, $3-x$, $-y$, $1-z$); (b) the 2-D supramolecular layer structure formed *via* intermolecular hydrogen bonds for **1** (symmetry codes: B, $x$, $1+y$, $z$; C, $-x$, $-y$, $-z$; D, $-x$, $1-y$, $-z$); (c) the 3-D supramolecular structure of **1** constructed through hydrogen bonds and the $\pi\cdots\pi$ interactions.

carboxylic O5 atom, acting as a hydrogen-bond donor, links the oxygen atom O1B of the uncoordinated amide group of a neighbouring molecule, forming a 1-D chain along the *b* axis (O5···O1B = 2.604(4) Å, O5–H5···O1B = 173.6°; symmetry code: B, $x$, $1+y$, $z$). Lattice water O2W, acting as both a hydrogen-bond donor and an accepter, simultaneously links O1B and O4D from neighbouring chains, leading to the observed 2-D supramolecular layers (O2W···O1B = 2.764(5) Å, O2W–H2WB···O1B = 162(8)°; O4D···O2W = 2.651(5) Å, O4D–H4D···O2W = 172.2°; symmetry codes: B, $x$, $1+y$, $z$; D, $-x$, $1-y$, $-z$) (Fig. 1b). Coordinated water O1W, acting as a hydrogen-bond donor, is bonded to O3E, O2WE, and O6F of neighbouring layers (O1W···O3E = 3.094(5) Å, O1W–H1WA···O3E = 127.6°; O1W···O2WE = 3.190(5) Å, O1W–H1WA···O2WE = 143.3°; O1W···O6F = 2.820(4) Å, O1W–H1WB···O6F = 142.1°; symmetry codes: E, $1+x$, $-1+y$, $z$; F, $2-x$, $-y$, $1-z$) (Table S2†). The 2-D supramolecular layers are self-assembled into a 3-D supramolecular network (Fig. 1c) *via* interlayer hydrogen bonds and, simultaneously, the offset face-to-face $\pi\cdots\pi$ stacking interactions, characterized by separation of 3.35 Å (Table S3†), between the aromatic rings of the two $H_3bbch^-$ ligands.

**$[Fe_3(\mu_5\text{-}Hbbch)_2(\mu_2\text{-}H_2O)_2(H_2O)_2]\cdot 2H_2O$ (2).** Compound **2** displays a 3-D structure. Fe1 displays a distorted octahedral coordination geometry; its two axial sites are occupied by two carboxylic oxygen atoms from two $Hbbch^{3-}$ ligands (Fe1–O6C = 2.125(6) Å; Fe1–O5E = 2.150(6) Å, symmetry codes: C, $-x$, $-y$, $2-z$; E, $1-x$, $-y$, $2-z$), while its equatorial sites are bonded to O1 and N1 from the third $Hbbch^{3-}$ ligand (Fe1–O1 = 2.120(6) Å; Fe1–N1 = 2.277(7) Å), O4D from the fourth $Hbbch^{3-}$ ligand (Fe1–O4D = 2.017(6) Å, symmetry code: D, $x$, $y$, $-1+z$), and one water molecule O3W (Fe1–O3W = 2.221(6) Å). Fe2 has a slightly distorted octahedral geometry with the coordination of four water molecules at equatorial sites and two carboxylic oxygen atoms from two $Hbbch^{3-}$ ligands at the axial sites. The Fe–O distances range from 2.017(6) to 2.289(6) Å. O3W and the carboxylic group (–C9O3O4) bridge three neighbouring Fe cations into a trinuclear cluster with a double six-member rings structure. The distance of Fe1···Fe2 is 3.79 Å. The $Hbbch^{3-}$ ligand adopts a special $\mu_5$-hexadentate bridging mode in which one amide group chelates one Fe atom while each of four the carboxylic oxygen atoms (O3, O4, O5 and O6) is monodentate. Fe1 atoms are linked by $Hbbch^{3-}$ ligands through one amide group (O1 and N1) and three carboxylic oxygen atoms (O4, O5 and O6), producing a grid-like 2-D double-metal layer structure (Fig. 2b). The neighbouring $Hbbch^{3-}$ ligands are stacked in opposite directions to realize strong face-to-face $\pi\cdots\pi$ interactions with distances of 3.21 and 3.22 Å (Table S3†). Through the bridging water (O3W and its symmetric partners) and the fourth carboxylic oxygen atom (O3 and its symmetric partners), the 2-D double layers are linked by Fe2 cations into a 3-D framework (Fig. 2b). If the $Hbbch^{3-}$ ligands can be considered as four-connected nodes and the trinuclear Fe clusters viewed as eight-connected nodes, the overall structure of **2** can be reduced to a (4, 8)-connected *flu* ($CaF_2$) network and a schematic diagram (OLEX) shows that the Schläfli symbol[14a] is $(4^6)_2(4^{12}, 6^{12}, 8^4)$ (Fig. 2c). As one of the most important structure types in minerals, the fluorite topology has met limited success in reported metal–organic frameworks, owing to its 8-connected node.[14c] To date, compounds with such connectivity are rare reported.[14b,14c]

**$[Zn(\mu_2\text{-}H_2bbh)(\mu_2\text{-}N_2H_4)_{1/2}(H_2O)]\cdot 2H_2O$ (3).** Compound **3** displays a 2-D layer structure. As shown in Fig. 3a, Zn1 exhibits a distorted tetrahedral geometry, surrounded by two acyl oxygen atoms (Zn1–O1 = 1.980(2) Å, Zn1–O3B = 1.948(2) Å, symmetry code: B, $2-x$, $1/2+y$, $3/2-z$) from two $H_2bbh^{2-}$ ligands, one nitrogen atom (N5) from one $N_2H_4$ ligand (Zn1–N5 = 2.042(3) Å), and one aqua ligand (Zn1–O1W = 2.103(3) Å). The $H_2bbh^{2-}$ ligand adopts a $\mu_2$-bidentate mode with its two *para* acyl oxygen atoms coordinated to two Zn atoms, each in a monodentate fashion; the Zn atoms are linked into a 1-D zigzag chain by $H_2bbh^{2-}$ ligands along the *b* axis. Complexes featuring $N_2H_4$ are relatively rare.[15] In **3**, $N_2H_4$ molecules not only take part in the *in situ* amidation reaction with PMA, but also act as $\mu_2$-bidentate bridging ligands for the coordination of Zn atoms of neighbouring chains and linking the zigzag chains into 2-D layers with $(4^4\cdot 6^2)$ topology in the *ab* plane as shown in Fig. 3b. Water molecules (O1W and its symmetric partners) coordinate Zn atoms from both sides of the layer planes. Two $N_2H_4$ and four $H_2bbh^{2-}$ ligands link six Zn atoms into a ring structure with

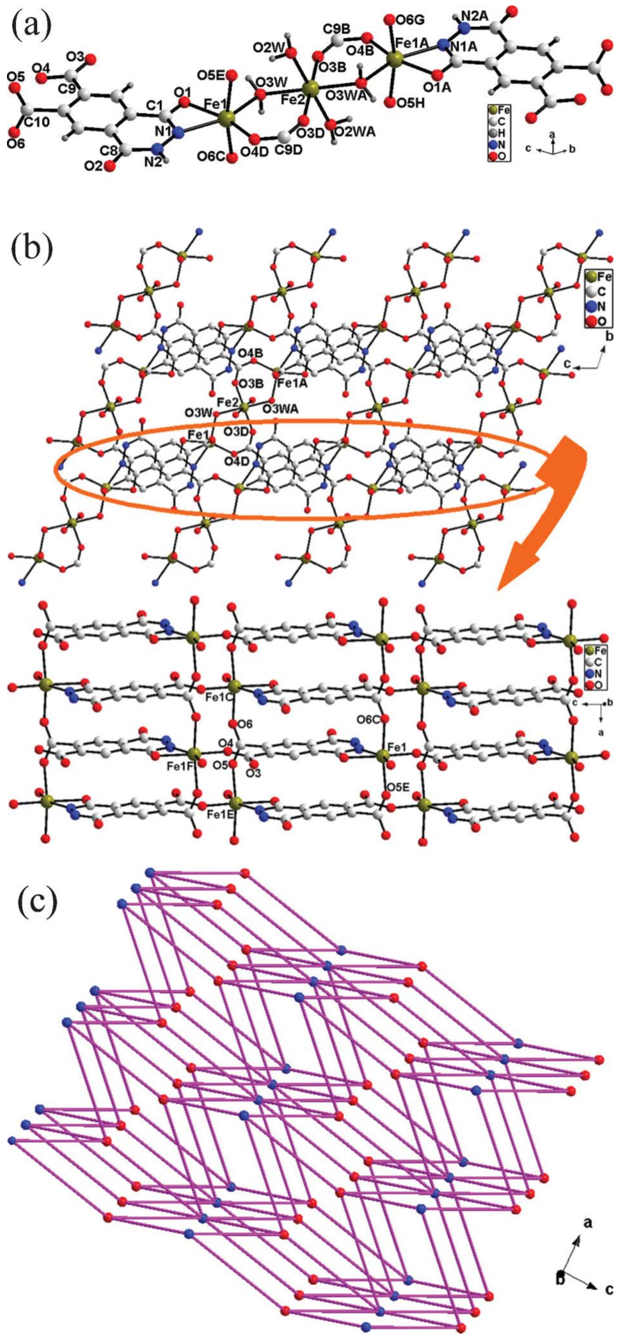


**Fig. 2** (a) The coordination environment of the Fe atoms in compound **2** (symmetry codes: A, 1 − *x*, 1 − *y*, 1 − *z*; B, 1 − *x*, 1 − *y*, 2 − *z*; C, −*x*, −*y*, 2 − *z*; D, *x*, *y*, −1 + *z*; E, 1−*x*, −*y*, 2 − *z*; G, 1 + *x*, 1 + *y*, −1 + *z*; H, *x*, 1 + *y*, −1 + *z*); (b) Fe2 cations link the 2-D grids-structure layers into a 3-D framework through the bridging water O3W and the carboxylic oxygen atom O3 (symmetry codes: C, −*x*, −*y*, 2 − *z*; E, 1 − *x*, −*y*, 2 − *z*; F, *x*, *y*, 1 + *z*); (c) a schematic view of the $(4^6)_2(4^{12}, 6^{12}, 8^4)$ topology of compound **2** (blue points represent the trinuclear Fe clusters and red points represent the $Hbbch^{3-}$ ligands).

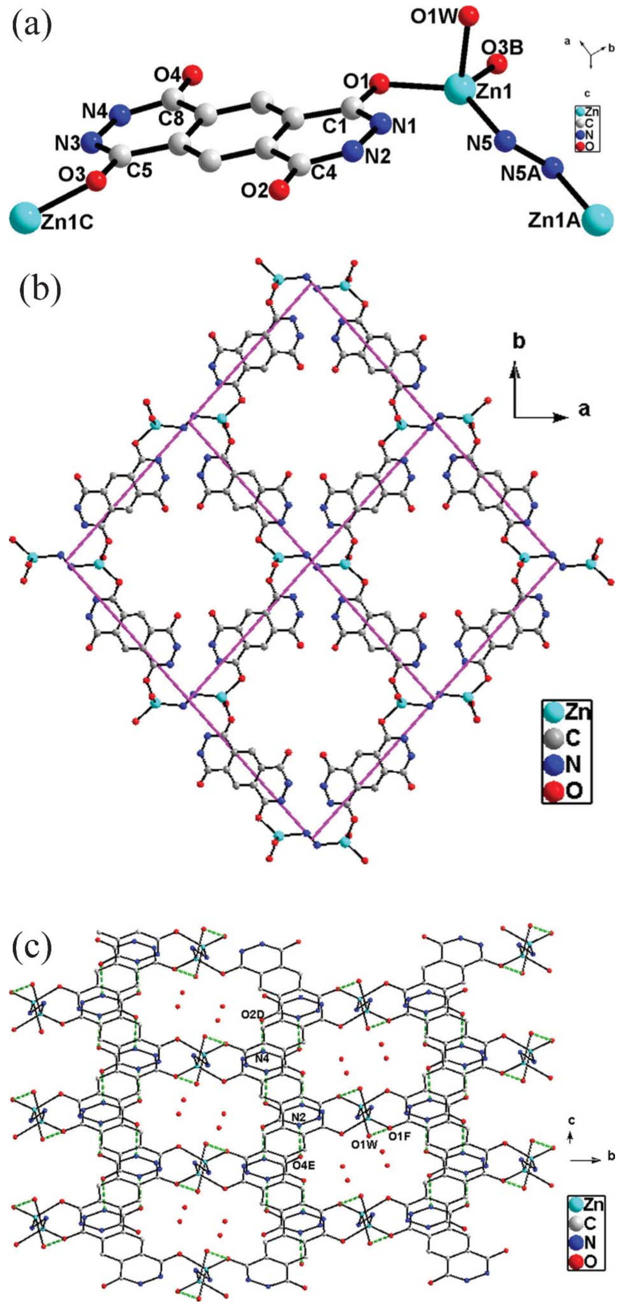


**Fig. 3** (a) The coordination environment of the Zn atoms in compound **3** (symmetry codes: A, 1 − *x*, 2 − *y*, 1 − *z*; B, 2 − *x*, 1/2 + *y*, 3/2 − *z*; C, 2 − *x*, −1/2 + *y*, 3/2 − *z*); (b) $N_2H_4$ acting as $\mu_2$-bidentate bridging ligands coordinate to Zn atoms of neighbouring zigzag chains into a 2-D layer; (c) the lattice waters fill in the tunnels of the supermolecule linked *via* hydrogen bonded interactions (symmetry codes: D, 1 + *x*, *y*, 1 + *z*; E, −1 + *x*, *y*, −1 + *z*; F, 2 − *x*, 2 − *y*, 1 − *z*).

opposite Zn···Zn distances at 13.16, 20.36 and 21.24 Å, respectively. The layers are staggered and all neighbouring aromatic rings of the $H_2bbh^{2-}$ ligands between layers are stacked with respect to each other. Strong π···π interactions are present with the face-to-face separation of 3.20 and 3.24 Å and the dihedral angle between $H_2bbh^{2-}$ ligands at 1.00° (Table S3†). N2, N4, and O1W acting as hydrogen-bond donors, respectively, are bonded to O4D, O2E and O3F of neighbouring layers (N2···O4E = 2.804(4) Å, N2–H2···O4E = 175.5°; N4···O2D = 2.838(4) Å, N4–H4···O2D = 176.3°; O1W···O1F = 2.718(3) Å, O1W–H1WB···O1F = 154.1°; symmetry codes: D, 1 + *x*, *y*, 1 + *z*; E, −1 + *x*, *y*, −1 + *z*; F, 2 − *x*, 2 − *y*, 1 − *z*), leading to an open structure with continuous tunnels along the *a* axis where the lattice waters are located (Fig. 3c). There are hydrogen bonding interactions between the lattice waters and the framework (Table S2†). The layers are self-assembled into a 3-D supramolecular network *via* the interlayer face-to-face π···π stacking interactions and hydrogen-bond interactions.

**$[Cd(H_2bch)_2(2,2'\text{-bpy})(H_2O)_2][Cd(\mu_2\text{-}H_2bch)(2,2'\text{-bpy})(H_2O)_2]$ $(H_2bch)$ (4).** The asymmetric unit of **4** contains one unit of $[Cd(H_2bch)_2(2,2'\text{-bpy})(H_2O)_2]$ (A), one unit of $H_2bch^-$ (B), and one cation $[Cd(\mu_2\text{-}H_2bch)(2,2'\text{-bpy})(H_2O)_2]^+$ (C), as shown in Fig. 4a. In part A, Cd1 is coordinated by two nitrogen atoms (N9 and N10) from a 2,2′-bpy ligand, two carboxylic oxygen atoms (O7 and O8) from one $H_2bch^-$ ligand, one acyl oxygen atom (O1) from another $H_2bch^-$ ligand, and two aqua ligands (O17 and O18), showing a distorted pentagonal bipyramidal coordination geometry. The distances of Cd–N [2.378(8)–2.418(8) Å] and Cd–O [2.292(7)–2.534(8) Å] in part A are in the normal range of those observed in reported Cd(II) compounds.[16b] It is very interesting that $H_2bch^-$ ligands display a bidentate-chelating coordination mode and a monodentate mode, respectively, avoiding linking Cd1 cations into a 1-D chain. There exit weak π···π interactions (Table S3†) with a distance of 3.57 Å between the two kinds of $H_2bch^-$ ligands of neighbouring molecules that link the discrete molecules into a 1-D supermolecule structure along the *a* axis (Fig. 4b). In part C, Cd2 is also coordinated by two nitrogen atoms (N11 and N12) from a 2,2′-bpy ligand, two carboxylic oxygen atoms (O11 and O12) from one $H_2bch^-$ ligand, one acyl oxygen atom (O10A) from another $H_2bch^-$ ligand, and two aqua ligands (O19 and O20), showing a distorted pentagonal bipyramidal coordination geometry. The distances of Cd–N [2.391(9)–2.418(8) Å] and Cd–O [2.354(8)–2.514(9) Å] are in the normal range of those observed in reported Cd(II) compounds. $H_2bch^-$ adopts a $\mu_2$-tridentate bridging mode in which the two carboxylic oxygen atoms coordinate Cd2 with a bidentate-chelating mode, and the oxygen atom of the amide group at the same site coordinates Cd2 in a monodentate fashion. The bridging $\mu_2$-$H_2bch^-$ ligands link Cd2 cations into a 1-D chain along the *b* axis, while 2,2′-bpy acting as auxiliary ligands chelate Cd2 on the opposite site of the chain (Fig. 4b). The dihedral angles between neighbouring 2,2′-bpy ligands and between neighbouring $H_2bch^-$ ligands in part C are 40.9 and 50.1°, respectively. There exist bpy–bpy π···π interactions between part A and part C with a distance of 3.59 Å. Part A and part C are linked into 2-D double metal supramolecular layers along the *b* axis through the π···π interactions. The $H_2bch^-$ anions, part B, acting as counter ions to part A, fill in the double metal supramolecular layers. It is very interesting that all $H_2bch^-$ anions of part B are almost parallel to the $H_2bch^-$ ligands of part C, arranged in the same direction with the dihedral angle being only 0.24°; π···π interactions with distances of 3.89 and 3.96 Å can be realized between them. The hydrogen bonds are also important for the supramolecular structure of **4**, and pertinent parameters are listed in Table S2.† In summary, the π···π interactions and hydrogen bonds both link the three parts of **4** into a stable 3-D supramolecular architecture.

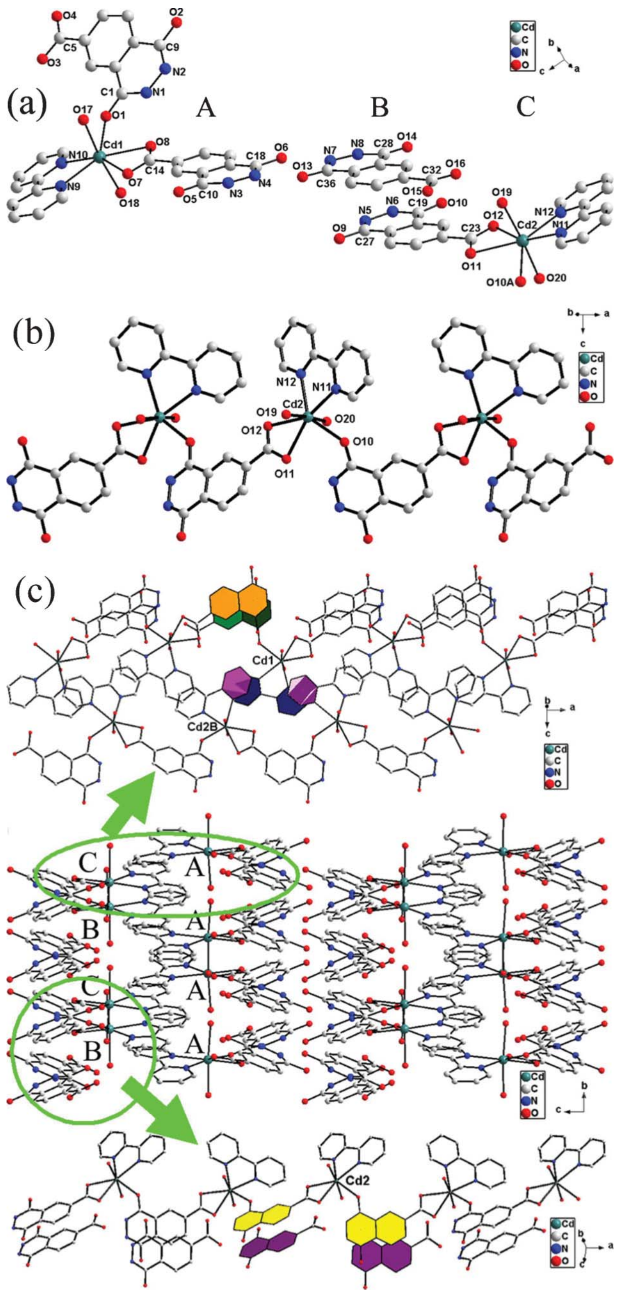
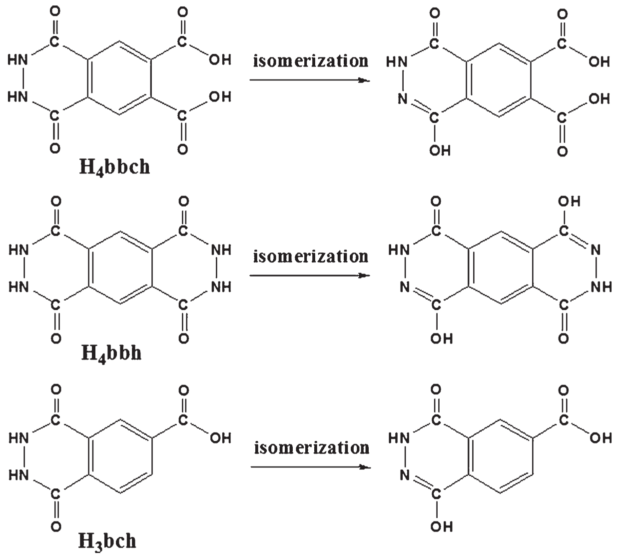


**Fig. 4** (a) The asymmetric unit of **4** (symmetric code: A, 1/2 + *x*, −*y*, *z*); (b) the 1-D chain structure of part C; (c) there exit π···π interactions in part A, between part A and C and between part B and C (symmetric code: B, 1 − *x*, 1 − *y*, 1/2 + *z*).

## Character of the acylhydrazidate ligands

Three different kinds of acylhydrazidate ligands ($H_4bbch$, $H_4bbh$ and $H_3bch$) were generated from *in situ* amidation cyclization reactions in the present study, as shown in Scheme 1. To the best of our knowledge, $H_4bbch$ was obtained for the first time by our group through the reaction of one PMA and one $N_2H_4$ under hydrothermal conditions. According to the reaction mechanism, the three *in situ* amidation cyclization ligands should exhibit a di-keto form (Scheme 2). But the X-ray analysis revealed that the two C–O bond lengths and the two C–N bond lengths of each acylhydrazidate group are not consistent with each other (Table

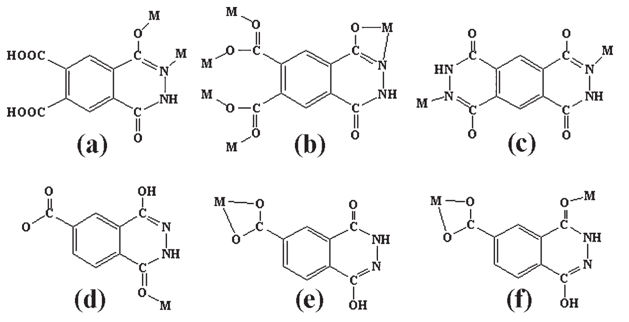


**Scheme 2** The isomerization equations of $H_4$bbch, $H_4$bbh and $H_3$bch.

S4†), all of which indicate that one acylamino group of the acylhydrazidate group isomerizes into a hydroxylimino group.

In compounds **1** and **2**, $H_4$bbch ligands adopt a $\mu_2$-bidentate mode and a $\mu_5$-hexadentate mode, respectively (Scheme 3 (a) and (b)). It appears that $H_4$bbch may be a good candidate for the construction of MOFs with diverse coordination modes. In compound **3**, $H_4$bbh ligands display a $\mu_2$-bidentate bridging mode (Scheme 3 (c)) which has been reported before.[7d] Five kinds of coordination modes of $H_3$bch have been found by Xu (Scheme S1†).[7a,7e] In compound **4**, three new coordination modes are observed, namely, bidentate-chelating, monodentate, and $\mu_2$-tridentate bridging modes (Scheme 3 (d)–(f)). $H_3$bch, exhibiting fascinating coordination modes, can coordinate one, two, three, four or five metal ions.

These acylhydrazidate ligands ($H_4$bbch, $H_4$bbh and $H_3$bch) all display fascinating coordination abilities. Firstly, they all present multiple coordinating points to construct novel metal–organic frameworks with various bridging modes. Secondly, the two or three rigid rings of the ligands are coplanar, so the $\pi\cdots\pi$ interaction in the compounds containing these ligands can be an important noncovalent one. In addition, the amido groups or carboxylic groups can easily form hydrogen bonding interactions compounds. The results described above show that $H_4$bbch, $H_4$bbh and $H_3$bch are good ligands for designing and constructing new MOF materials.



**Scheme 3** The coordination modes of the three acylhydrazidate ligands.

## Fluorescence properties

The luminescent properties of compounds with $d^{10}$ metal centers have been attracting great interest owing to their potential applications in chemical sensors, photochemistry, and electroluminescent displays. The solid luminescence at room temperature of compounds **1**, **3**, **4** and free $H_4$bbh has been investigated (Fig. 5 and Fig. S1†). Compound **3** exhibits blue light with one fluorescent emission band at $\lambda_{max}$ = 481 nm upon photoexcitation at 400 nm, and the emission band of **4** shows at $\lambda_{max}$ = 490 nm ($\lambda_{ex}$ = 403 nm). The emissions of **3** and **4** are neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal transfer (LMCT) in nature since the $Zn^{2+}$ or $Cd^{2+}$ ions with $d^{10}$ configuration are difficult to oxidize or reduce, but rather are assigned to intraligand emission.[16] Comparing with the maximum emission peak at 558 nm of free $H_4$bbh ligand (Fig. S1†) and the emission with $\lambda_{max}$ = 531 nm ($\lambda_{ex}$ = 394 nm) of 2-D layer compound $[Zn(\mu_4\text{-}H_2bbh)_{1/2}(\mu_2\text{-}H_2bbh)_{1/2}(H_2O)]_n$,[7d] the emission band of **3** is blue-shifted. This may be rationalized in terms of the charge transfer between $N_2H_4$ and $H_2bbh^{2-}$ ligands.

Different from compounds **3** and **4**, compound **1** exhibits a purple emission at 413 nm when excited at 300 nm. In order to understand clearly the emission mechanism, time-dependent density functional theory (TDDFT)[17] calculations were carried out in both the ground and the excited states of compound **1**. The calculation details are stated as below: in the calculations, the calculated complexes display $C_i$ symmetry, the ground and the excited states structures of **1** were optimized by the Becke's three parameter functional and the Lee–Yang–Parr functional (B3LYP)[18] and single-excitation configuration interaction (CIS) methods.[19] On the basis of the optimized excited-state structures, the spectroscopic properties related to the emission were carried out by using TDDFT method. The STO-3G basis sets were employed for C, H, O and N, and the LANL2DZ basis sets associated with the pseudopotential were employed for Cu. All calculations were performed with the Gaussian 03 (Revision C.02) software package.[20] The dimensional plots of molecular configurations and orbitals were generated with the GaussView program.[21] The TDDFT calculation results indicate that there is a strong emission at 405 nm ($f$ = 0.0425), corresponding to the

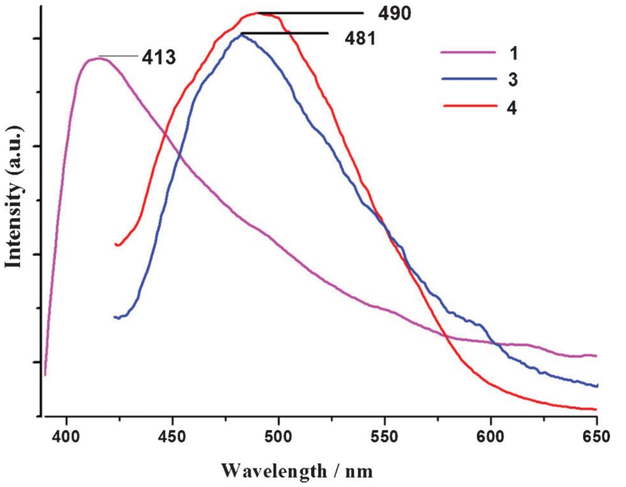


**Fig. 5** The fluorescent emissions of compound **1** ($\lambda_{ex}$ = 300 nm), **3** ($\lambda_{ex}$ = 400 nm) and **4** ($\lambda_{ex}$ = 403 nm) in the solid state at room temperature.

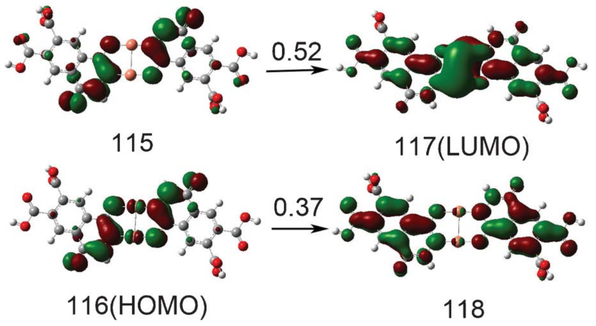


**Fig. 6** Single-electron transitions with |CI coefficient| > 0.2 in the TDDFT calculations for the 405 nm emission of **1**.

electronic transition from orbital 115 to orbital 117 and orbital 116 to orbital 118. Obviously, the emission peak is similar to the observed result (413 nm). Fig. 6 illustrates the characteristics of these orbitals for compound **1**. The electron densities of the occupied MO (115 and 116) are located at the $H_4$bbch ligand, while those of the unoccupied MO are distributed mainly on metal Cu for MO 117 and $H_4$bbch for MO 118. Therefore, the fluorescence emission at 405 nm of the compound **1** can be predominantly described as originating from ligand-to-metal and intraligand charge transfer (LMCT/ILCT) transition.

## TG analysis

Thermogravimetric analyses were performed to verify the thermal stability of the compounds. As shown in Fig. 7, **1** is thermally stable up to 220 °C, and **2** to 170 °C. Weight loss is *ca.* 9.08% (calc. 10.33%) for **1** between 220–305 °C and 12.06% (calc. 14.04%) for **2** between 170–220 °C, corresponding to the loss of the lattice water and coordinated water. The weight loss of 69.38% (calc. 71.45%) for **1** from 375–445 °C and 62.41% (calc. 64.20%) for **2** from 350–645 °C can be attributed to the decomposition of the organic ligand. We speculate that the final products of the thermal decomposition be metal oxide with the weight loss of 21.54% (calc. 22.81%) for **1** and 25.53% (calc. 27.99%) for **2**. For **3**, a weight loss of 13.08% (calc. 14.23%) was observed in the temperature range of 205–235 °C, corresponding to the release of both the lattice and coordinated water, and then the compound loss of 66.00% (calc. 68.54%) from 505–610 °C is attributed to the decomposition of $H_2bbh^-$ and $N_2H_4$ ligands; the final decomposition product (20.92%) might be ZnO (calc. 21.44%). Compound **4** was stable up to 218 °C, and then a weight loss of 5.50% (calc. 5.04%) was found between 218–282 °C, in agreement with the loss of the coordinated water molecules. The weight loss of 77.91% (calc. 79.23%) from 315–530 °C corresponds to the decomposition of $H_2bch^-$ and 2,2′-bpy ligands, producing CdO as the final decomposition product at the remaining weight of 16.59% (calc. 17.96%).

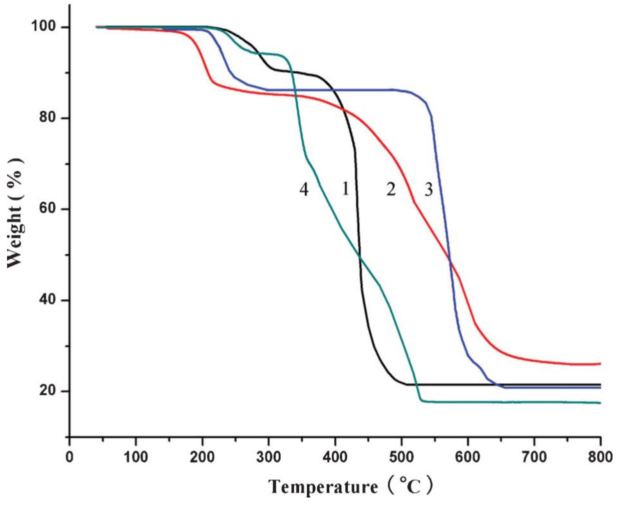


**Fig. 7** The TG analyses curves of compounds **1–4**.

## Conclusions

Presented here are the results from our continuous efforts in the study of *in situ* amidation reaction between polycarboxylic acids and $N_2H_4 \cdot H_2O$. It has been found that the ratio of polycarboxylic acids and $N_2H_4 \cdot H_2O$ has a significant influence on the reaction outcome in terms of the identity of the ligands produced *in situ* under hydrothermal conditions, and therefore, on the structure of the resulting complexes featuring these ligands. In this work, we report for the first time the synthesis of $H_4$bbch with one PMA and one $N_2H_4 \cdot H_2O$. On the other hand, $N_2H_4$ molecules can not only take part in the *in situ* amidation cyclization reaction with PMA to form $H_4$bbh, but also act as $\mu_2$-bidentate bridging ligands to coordinate metal ions. Three new kinds of coordination modes of $H_3$bch were observed. With the diverse coordination modes of these ligands, it is possible to construct MOFs with fascinating structures and interesting properties.

## Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (No. 21003056, 20771023 and 21071027), 863 program (2007AA03z218), 12th Five-Year Science and Technology Research Program for Department of Education of Jilin Province (No. 2012291 and No. 2012289) and analysis and testing foundation of Northeast Normal University.

## References

1 (*a*) For example: J. Kim, B. Chen, T. M. Reineke, H. Li, M. Eddaoudi, D. B. Moler, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2001, **123**, 8239–8247; (*b*) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319–330; (*c*) R. Kitaura, G. Onoyama, H. Sakamoto, R. Matsuda, S.-I. Noro and S. Kitagawa, *Angew. Chem., Int. Ed.*, 2004, **43**, 2684–2687; (*d*) S. Kitagawa, R. Kitaura and S.-I. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334–2375; (*e*) G.-H. Wang, Z.-G. Li, H.-Q. Jia, N.-H. Hu and J.-W. Xu, *Cryst. Growth Des.*, 2008, **8**, 1932–1939; (*f*) G.-X. Liu, H. Xu, H. Zhou, S. Nishihara and X.-M. Ren, *CrystEngComm*, 2012, **14**, 1856–1864.

2 (*a*) For exampleJ. Y. Lu, B. R. Cabrera, R.-J. Wang and J. Li, *Inorg. Chem.*, 1998, **37**, 4480–4481; (*b*) X.-M. Zhang, *Coord. Chem. Rev.*, 2005, **249**, 1201–1219; (*c*) X.-M. Chen and M.-L. Tong, *Acc. Chem. Res.*, 2007, **40**, 162–170; (*d*) Q.-F. Yang, X.-B. Cui, J.-H. Yu, J. Lu, X.-Y. Yu, X. Zhang, J.-Q. Xu, Q. Hou and T.-G. Wang, *CrystEngComm*, 2008, **10**, 1531–1538; (*e*) L.-F. Ma, L.-Y. Wang and M. Du, *CrystEngComm*, 2009, **11**, 2593–2596; (*f*) W.-T. Liu, Y.-C. Ou, Y.-L. Xie, Z. Lin and M.-L. Tong, *Eur. J. Inorg. Chem.*, 2009, 4213–4218; (*g*) X.-M. Liu, L.-H. Xie, J.-B. Lin, R.-B. Lin, J.-P. Zhang and X.-M. Chen, *Dalton Trans.*, 2011, **40**, 8549–8554; (*h*) Q.

Zhu, T. Sheng, C. Tan, S. Hu, R. Fu and X. Wu, *Inorg. Chem.*, 2011, **50**, 7618–7624; (*i*) D. Dang, P. Wu, C. He, Z. Xie and C. Duan, *J. Am. Chem. Soc.*, 2010, **132**, 14321–14323.

3 (*a*) X.-M. Zhang, M.-L. Tong and X.-M. Chen, *Angew. Chem., Int. Ed.*, 2002, **41**, 1029–1031; (*b*) J. Tao, Y. Zhang, M.-L. Tong, X.-M. Chen, T. Yuen, C. L. Lin, X. Huang and J. Li, *Chem. Commun.*, 2002, 1342–1343.

4 (*a*) W. Lin, Z. Wang and L. Ma, *J. Am. Chem. Soc.*, 1999, **121**, 11249–11250; (*b*) O. R. Evans, Z. Wang and W. Lin, *Chem. Commun.*, 1999, 1903–1904; (*c*) O. R. Evans and W. Lin, *J. Chem. Soc., Dalton Trans.*, 2000, 3949–3954; (*d*) M.-L. Tong, L.-J. Li, K. Mochizuki, H.-C. Chang, X.-M. Chen, Y. Li and S. Kitagawa, *Chem. Commun.*, 2003, 428–429; (*e*) D. Sun, R. Cao, Y. Liang, Q. Shi, W. Su and M. Hong, *J. Chem. Soc., Dalton Trans.*, 2001, 2335–2340.

5 (*a*) L. Cheng, W.-X. Zhang, B.-H. Ye, J.-B. Lin and X.-M. Chen, *Inorg. Chem.*, 2007, **46**, 1135–1143; (*b*) J.-P. Zhang, Y.-Y. Lin, X.-C. Huang and X.-M. Chen, *J. Am. Chem. Soc.*, 2005, **127**, 5495–5506; (*c*) J.-P. Zhang, S.-L. Zheng, X.-C. Huang and X.-M. Chen, *Angew. Chem., Int. Ed.*, 2004, **43**, 206–209; (*d*) L.-Z. Wang, Z.-R. Qu, H. Zhao, X.-S. Wang, R.-G. Xiong and Z.-L. Xue, *Inorg. Chem.*, 2003, **42**, 3969–3971; (*e*) H. Zhao, Z.-R. Qu, H.-Y. Ye and R.-G. Xiong, *Chem. Soc. Rev.*, 2008, **37**, 84–100.

6 (*a*) C.-M. Liu, S. Gao and H.-Z. Kou, *Chem. Commun.*, 2001, 1670–1671; (*b*) N. Zheng, X. Bu and P. Feng, *J. Am. Chem. Soc.*, 2002, **124**, 9688–9689; (*c*) O. R. Evans and W. Lin, *Cryst. Growth Des.*, 2001, **1**, 9–11.

7 (*a*) X.-X. Hu, J.-Q. Xu, P. Cheng, X.-Y. Chen, X.-B. Cui, J.-F. Song, G.-D. Yang and T.-G. Wang, *Inorg. Chem.*, 2004, **43**, 2261–2266; (*b*) X.-X. Hu, C.-L. Pan, J.-Q. Xu, X.-B. Cui, G.-D. Yang and T.-G. Wang, *Eur. J. Inorg. Chem.*, 2004, 1566–1569; (*c*) J.-H. Yu, Y.-C. Zhu, D. Wu, Y. Yu, Q. Hou and J.-Q. Xu, *Dalton Trans.*, 2009, 8248–8256; (*d*) X.-Y. Yu, L. Ye, X. Zhang, X.-B. Cui, J.-P. Zhang, J.-Q. Xu, Q. Hou and T.-G. Wang, *Dalton Trans.*, 2010, **39**, 10617–10625; (*e*) J. Jin, M.-J. Jia, Y. Peng, Q. Hou, J.-H. Yu and J.-Q. Xu, *CrystEngComm*, 2010, **12**, 1850–1855; (*f*) J. Jin, D. Wu, M.-J. Jia, Y. Peng, J.-H. Yu, Y.-C. Wang and J.-Q. Xu, *J. Solid State Chem.*, 2011, **184**, 667–674; (*g*) J. Jin, F.-Q. Bai, M.-J. Jia, Y. Peng, J.-H. Yu and J.-Q. Xu, *Dalton Trans.*, 2012, **41**, 2382–2392; (*h*) F. Liu, L. Duan, Y. Li, E. Wang, X. Wang, C. Hu and L. Xu, *Inorg. Chim. Acta*, 2004, **357**, 1355–1359.

8 (*a*) For example: R. Cao, D. Sun, Y. Liang, M. Hong, K. Tatsumi and Q. Shi, *Inorg. Chem.*, 2002, **41**, 2087–2094; (*b*) S. O. H. Gutschke, D. J. Price, A. K. Powell and P. T. Wood, *Eur. J. Inorg. Chem.*, 2001, 2739–2741; (*c*) D.-Q. Chu, J.-Q. Xu, L.-M. Duan, T.-G. Wang, A.-Q. Tang and L. Ye, *Eur. J. Inorg. Chem.*, 2001, 1135–1137; (*d*) X.-Y. Yu, J. Lu, J.-H. Yu, X. Zhang, J.-Q. Xu and T.-G. Wang, *Z. Anorg. Allg. Chem.*, 2007, **633**, 490–494; (*e*) L.-P. Zhang, J.-F. Ma, J. Yang, Y.-Y. Pang and J.-C. Ma, *Inorg. Chem.*, 2010, **49**, 1535–1550; (*f*) Q. Hua, Y. Zhao, G.-C. Xu, M.-S. Chen, Z. Su, K. Cai and W.-Y. Sun, *Cryst. Growth Des.*, 2010, **10**, 2553–2562; (*g*) X.-Y. Yu, X.-B. Cui, X. Zhang, L. Jin, Y.-N. Luo, J.-J. Yang, H. Zhang and X. Zhao, *Inorg. Chem. Commun.*, 2011, **14**, 848–851; (*h*) H.-B. Zhang, C.-B. Tian, S.-T. Wu, J.-D. Lin, Z.-H. Li and S.-W. Du, *J. Mol. Struct.*, 2011, **985**, 355–360.

9 A. C. Benniston, D. S. Yufit and J. A. K. Howard, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1999, **C55**, 1535–1536.

10 G. P. Shields, P. R. Raithby, F. H. Allen and W. D. S. Motherwell, *Acta Crystallogr., Sect. B: Struct. Sci.*, 2000, **B56**, 455–465.

11 (*a*) H.-Y. Liu, H. Wu, J.-F. Ma, Y.-Y. Liu, J. Yang and J.-C. Ma, *Dalton Trans.*, 2011, **40**, 602–613; (*b*) S.-L. Li, Y.-Q. Lan, J.-F. Ma, J. Yang, J. Liu, Y.-M. Fu and Z.-M. Su, *Dalton Trans.*, 2008, 2015–2025.

12 P. Jensen, S. R. Batten, B. Moubaraki and K. S. Murray, *J. Chem. Soc., Dalton Trans.*, 2002, 3712–3722.

13 (*a*) P. L. Jones, J. C. Jeffery, J. P. Maher, J. A. McCleverty, P. H. Rieger and M. D. Ward, *Inorg. Chem.*, 1997, **36**, 3088–3095; (*b*) X.-M. Zhang, M.-L. Tong, M.-L. Gong, H.-K. Lee, L. Luo, K.-F. Li, Y.-X. Tong and X.-M. Chen, *Chem.–Eur. J.*, 2002, **8**, 3187–3194.

14 (*a*) J. V. Smith, *Am. Mineral.*, 1978, **63**, 960–969; (*b*) C.-H. Zhan, M.-X. Jiang, Y.-L. Feng and J.-W. Cheng, *CrystEngComm*, 2010, **12**, 420–424; (*c*) L.-L. Liang, S.-B. Ren, J. Wang, J. Zhang, Y.-Z. Li, H.-B. Du and X.-Z. You, *CrystEngComm*, 2010, **12**, 2669–2671.

15 (*a*) F. Paulat, N. Lehnert, Y. Ishikawa, K.-I. Okamoto and K. Fujisawa, *Inorg. Chim. Acta*, 2008, **361**, 901–915; (*b*) B. T. Heaton, C. Jacob and P. Page, *Coord. Chem. Rev.*, 1996, **154**, 193–229.

16 (*a*) X. Shi, G. Zhu, Q. Fang, G. Wu, G. Tian, R. Wang, D. Zhang, M. Xue and S. Qiu, *Eur. J. Inorg. Chem.*, 2004, 185–191; (*b*) S. Su, W. Chen, X. Song, M. Zhu, C. Qin, S. Song, Z. Guo, S. Wang, Z. Hao, G. Li and H. Zhang, *CrystEngComm*, 2012, **14**, 1681–1686.

17 (*a*) M. E. Casida, C. Jamorski, K. C. Casida and D. R. Salahub, *J. Chem. Phys.*, 1998, **108**, 4439–449; (*b*) R. E. Stratmann, G. E. Scuseria and M. J. Frisch, *J. Chem. Phys.*, 1998, **109**, 8218–8224.

18 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652.

19 (*a*) J. F. Stanton, J. Gauss, N. Ishikawa and M. Head-Gordon, *J. Chem. Phys.*, 1995, **103**, 4160–4174; (*b*) J. B. Foresman, M. Head-Gordon, J. A. Pople and M. J. Frisch, *J. Phys. Chem.*, 1992, **96**, 135–149; (*c*) V. A. Walters, C. M. Hadad, Y. Thiel, S. D. Colson, K. B. Wiberg, P. M. Johnson and J. B. Foresman, *J. Am. Chem. Soc.*, 1991, **113**, 4782–4791.

20 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. Ochterski, P.Y. Ayala, K. MorokumaG. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *GAUSSIAN 03 (Revision C.02)*, Gaussian, Inc., Wallingford, CT, 2004.

21 R. Dennington, K. Todd, J. Millam, K. Eppinnett, W. L. Hovell, R. Gilliland, *GaussView, version 3.09*, Semichem, Inc., Shawnee Mission, KS, 2003.