Assembly of 1,2,3,4-Benzenetetracarboxylic Acid and Zinc(II) Metal Centers to a Chiral 3D Metal-organic Framework: Syntheses, Structure and Properties

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A new three-dimensional metal-organic framework $\{[Zn(mpda)_{0.5}(bix)]\cdot(H_2O)_{1.5}\}_n$ (**1**) (H_4mpda = 1,2,3,4-benzenetetracarboxylic acid, *m*-bix = 1,3-bis(imidazol-1-ylmethyl)-benzene) has been synthesized and characterized by single-crystal X-ray diffraction and IR spectra. In **1**, homochiral helical chains are formed in the Zn-mpda layer through spontaneous resolution by $mpda^{4-}$. Such layers are further connected through the second *m*-bix ligand to form a 3D chiral metal-organic framework. The individual (4,4)-connected net in **1** can be specified by the Schläfli symbol $(6^6)_2(6^4.8^2)$. Bulk material of **1** has good second-harmonic generation (SHG) activity, approximately 0.4 times that of urea. In addition, a thermogravimetric analysis was carried out, and the photoluminescent behavior of the complex was also investigated.

Key words: Homochiral, Helical, Metal-organic Framework, Topology, SHG, Photoluminescence

Introduction

The rational design and synthesis of metal-organic frameworks through self-assembly are currently attracting considerable attention [1 – 3]. Over the past decades, different complexes with fascinating structural topologies have been prepared. Some of them can find potential applications in nonlinear optics, catalysis, separation, magnetism, molecular recognition, ion exchange, sorption, and electrical engineering [4 – 8]. In recent years, in order to obtain metal-organic frameworks with interesting topologies and special physical properties, a variety of synthetic methods and strategies have been developed [9 – 13]. Many factors have been found to influence the structure of coordination polymers, such as the coordination number and geometries of the metal ions and the shape, functionality, and flexibility of the organic ligands [14]. Aromatic multicarboxylate ligands have often been selected as multifunctional organic linkers for metal ions. In comparison to 1,3-benzenedicarboxylic acid, 1,3,5-benzenetricarboxylic acid and other reported benzenemulticarboxylate ligands [15], 1,2,3,4-benzenetetracarboxylic acid (H_4mpda) has rarely been explored up to now [16, 17]. With the aim of further understanding the coordination chemistry of this new ligand and preparing new materials with interesting structural topologies and physical properties, we have recently become engaged in the research of coordination polymers based on it. In this paper, we describe the preparation and crystal structure of $\{[Zn(mpda)_{0.5}(bix)]\cdot(H_2O)_{1.5}\}_n$ (**1**). A thermogravimetric analysis was also carried out, and the photoluminescent behavior of the complex has also been investigated.

Experimental Section

All reagents used in the syntheses were of analytical grade. Elemental analyses for carbon, hydrogen and nitrogen atoms were performed on a Vario EL III elemental analyzer. The infrared spectra (4000∼500 cm^{-1}) were recorded by using KBr pellets on a Bruker model Vector22 FT-IR spectrophotometer. Thermal analysis was performed on a SDT 2960 thermal analyzer from r. t. to 800 °C with a heating rate of 20 °C min^{-1} under a nitrogen flow. Luminescence spectra of the solid samples were recorded on a Hitachi 850 fluorescence spectrophotometer. The circular dichroism (CD) spectrum of **1** was recorded at r. t. with a Jasco J-810(S) spectropolarimeter (KBr pellets).

Synthesis of $\{[Zn(mpda)_{0.5}(bix)]\cdot(H_2O)_{1.5}\}_n$ *(**1**)*

A mixture of H_4mpda (0.1 mmol, 33.0 mg), bix (0.2 mmol, 47.6 mg), $Zn(OAc)_2\cdot 2H_2O$ (0.2 mmol, 44.0 mg), and NaOH (0.4 mmol, 16.0 mg) in distilled water (8 mL) was placed in a Teflon-lined stainless-steel vessel, heated

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Table 1. Crystallographic data for complex **1**.

Empirical formula	$C_{38}H_{36}N_8O_{11}Zn_2$
Formula weight	911.49
Color, habit	colorless, block
Crystal size, mm^3	0.21 × 0.20 × 0.18
Crystal system	monoclinic
Space group	$C2$
a, Å	16.814(4)
b, Å	10.603(3)
c, Å	11.327(3)
β, deg	91.067(4)
V (Å^3)	2019.1(9)
Z	2
D_{calc} (g cm^{-3})	1.49
Absorption coeff., mm^{-1}	1.3
T (K)	293(2)
F(000)	936
Reflections collected	4967
Independent refl. / R_{int}	3228 / 0.0351
R_1 / wR_2 [$I \geq 2\,\sigma\,(I)$]	0.0434 / 0.1238
R_1 / wR$_2$ (all refl.)	0.0436 / 0.1244
Goodness-of-fit (GOF)	1.097
Flack parameter x	0.00(4)
Largest difference peak / hole, e Å^{-3}	+1.24 / −0.48

Table 2. Selected bond lengths (Å), bond angles (deg) and hydrogen bonding parameters for **1**[a].

Distances and angles:

Zn(1)–O(2)	2.332(4)	Zn(1)–N(1)	2.232(5)
Zn(1)–O(4)$^{\#2}$	2.255(5)	Zn(1)–N(4)$^{\#1}$	2.221(5)
Zn(1)–O(1)	2.438(4)		
O(4)$^{\#2}$-Zn(1)-O(2)	93.99(15)	N(1)–Zn(1)–O(4)	83.16(18)
N(4)$^{\#1}$-Zn(1)-O(1)	118.79(19)	O(4)$^{\#2}$-Zn(1)-O(1)	114.47(17)
N(1)–Zn(1)–O(4)$^{\#2}$	92.59(19)	O(2)–Zn(1)–O(1)	54.15(14)
N(4)$^{\#1}$–Zn(1)–N(1)	115.1(2)	N(1)–Zn(1)–O(2)	136.09(18)
N(4)$^{\#1}$-Zn(1)-O(4)$^{\#2}$	124.3(2)	N(4)$^{\#1}$-Zn(1)-O(2)	96.36(18)

Hydrogen bonds:

D–H···A	D–H	H···A	D···A	D–H···A
O2W-H2WA···O1W	0.86	1.97	2.83(2)	177.3
O2W-H2WB···O1W$^{\#3}$	0.85	2.44	3.12(3)	137.9
O1W-H1WB···O1$^{\#3}$	0.85	2.13	2.805(7)	135.7
O1W-H1WA···O2$^{\#4}$	0.85	2.20	2.859(8)	134.5

[a] Symmetry codes: $^{\#1}$ $x, y, z+1$; $^{\#2}$ $-x+1/2, y+1/2, -z+2$; $^{\#3}$ $-x, y, -z+1$; $^{\#4}$ $x, y, z-1$.

to 150 °C for 3 d, and then cooled to r. t. Colorless crystals of complex **1** were obtained. Yield: 47 %. – Anal. for $C_{38}H_{36}N_8O_{11}Zn_2$ (911.49): calcd. C 51.0, H 3.9, N 12.3; found C 51.1, H 3.9, N 12.5 %. – IR (KBr pellet): ν = 3432w, 2469w, 1659w, 1625w, 1589w, 1255w, 1120w, 675w, 512s cm^{-1}.

X-Ray crystallography

Single-crystal data of complex **1** was collected on a Bruker SMART APEX CCD diffractometer with Mo$K\alpha$ radiation using the ω scan mode in the range of $1.80° \leq \theta \leq 24.99°$. The structure was solved by Direct Methods, completed by difference Fourier maps and refined by ful1-matrix least-squares techniques using SHELXS-97 and SHELXL-97, respectively [18, 19]. Anisotropic displacement parameters were assigned to all non-hydrogen atoms. Analytical expressions of neutral atom scattering factors were employed, and anomalous dispersion corrections were incorporated. Crystal data and further information on the structure determination are summarized in Table 1. Selected bond lengths and bond angles are given in Table 2.

CCDC 752404 contains the supplementary crystallographic data for complex **1**. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

Structural description of {[Zn(mpda)$_{0.5}$(bix)] · (H$_2$O)$_{1.5}$}$_n$ (1)

Complex **1** shows a three-dimensional chiral framework based on 2D sheets and bix pillars. The asymmetric unit of **1** contains one Zn atom, half a mpda^{4-} ligand, one bix ligand, and one and a half solvate water molecules (Fig. 1a). The Zn1 atom adopts a distorted square-pyramidal coordination environment with the Zn–O bond lengths in the range of 2.255(5) – 2.438(4) Å and Zn–N bond lengths of 2.221(5) and 2.232(5) Å. As to the mpda^{4-} ligand, the four carboxylate groups have dihedral angles of 14.6, 76.3, 14.2, and 76.3° towards the plane of the corresponding phenyl ring. A dramatic twisting is observed between the O1–C1–O2 and O3–C2–O4 carboxylate groups with a dihedral angle of 70.9°. This twisting usually leads to helical chains in the assembly of metal-organic networks [20]. Complex **1** has a chiral sheet structure parallel to the *ab* plane (Fig. 1b), in which the Zn(II) ions are linked by adjacent carboxylate groups with *syn-anti* conformation of adjacent symmetry-related mpda^{4-} ligands to give infinite helical chains with a pitch of 10.603 Å along a 2_1 screw axis in the *b* direction. Within each layer, all Zn-mpda helical chains display the same chirality. Such layers are further connected through the bix ligands to give a chiral 3D metal-organic framework (Fig. 1c). A better insight into the nature of this framework can be achieved by the application of a topological approach reducing the multidimensional structures to simple node-and-connector nets. Taking the Zn atoms and the mpda^{4-} ligands as nodes, and the connector between metal centers as rods, the single framework topology representation for **1** is illustrated in Fig. 1d. From the above anal-

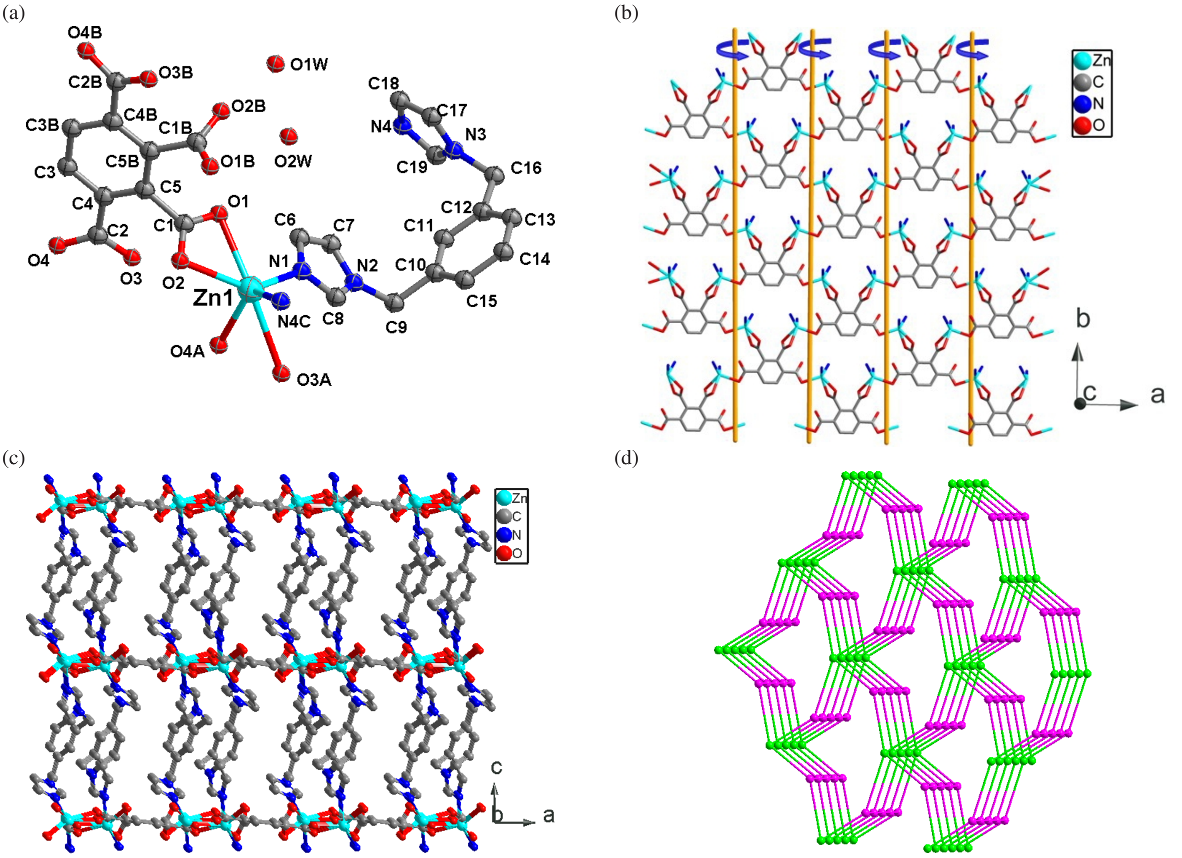

Fig. 1. (a) The molecular and crystal structure of **1**. Symmetry codes: A $0.5-x$, $0.5+y$, $2+z$; B $-x$, y, $2-z$; C x, y, $1+z$; (b) layer formation through right-handed helical chains parallel to the *ab* plane (all hydrogen atoms of oxygen atoms from water molecules are omitted for clarity); (c) view of the chiral 3D metal-organic framework; (d) topological analysis for **1**.

ysis, both the Zn(II) cation and the mpda^{4-} ligand can be defined as 4-connected tetrahedral nodes. Complex **1** therefore possesses a (4,4)-connected topology. The individual (4,4)-connected net in **1** can be specified by the Schläfli symbol $(6^6)_2(6^4.8^2)$ (Fig. 1d).

Thermogravimetric analysis

A thermogravimetric (TG) analysis of complex **1** was conducted under an N_2 atmosphere between 30 and 800 ℃. The weight loss corresponding to the release of water molecules occurred from 30 to 160 ℃ (observed, 3.8 %; calculated, 4.0 %), and the host framework started to decompose above 160 ℃.

Photoluminescent and SHG properties

Luminescent compounds composed of d^{10} metal centers and organic ligands are of great interest because of their potential applications in the areas of chemical sensors and photochemistry. Therefore, in the

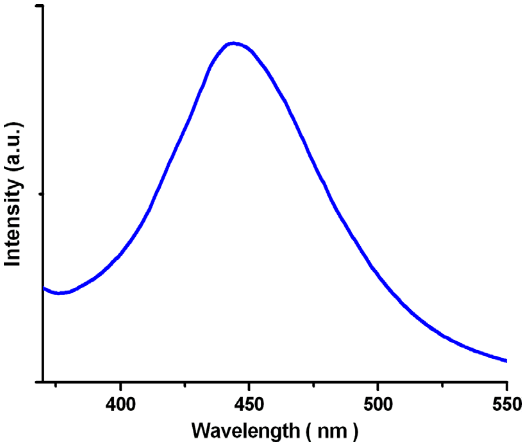

Fig. 2. Solid-state emission spectrum of complex **1** at r. t.

present work, the luminescent properties of complex **1** were investigated in the solid state at r. t. The emission and excitation peaks of H_4mpda have their maxima at 370 and 280 nm, respectively [17]. The emission maximum for compound **1** is located at 444 nm (λ_{ex} = 338 nm) and is red-shifted by 74 nm with respect to the band shown by the free ligand. This emission at 444 nm for **1** may be assigned to MLCT, and **1** therefore may be a candidate for fluorescent materials. Crystals derived by spontaneous resolution from achiral components may give a pronounced Cotton effect in their CD spectrum. Bulk material of **1** shows no visible Cotton effect in the CD spectrum. It is acentric and may have potential application as a NLO-active material. We have performed quasi-Kurtz SHG measurements on powdered samples to confirm its acentricity as well as to evaluate the potential application as a second-order NLO material [21]. Preliminary experimental results show that the bulk material of **1** displays weak powder SHG efficiencies of approximately 0.4 times that of urea.

Conclusions

In this paper, we have presented a new chiral three-dimensional Zn^{2+} coordination polymer constructed from H_4mpda and bix ligands. Results indicate that the mpda^{4-} ligand has the potential to form chiral metal-organic frameworks when it reacts with metal ions. The structure of compound **1** shows that the aromatic tetracarboxylic acid anion mpda^{4-} has the ability to freely adjust its coordination made and that the secondary ligand may also play an important role in determining the structural diversity of MOFs. The steric hindrance of the bix molecule may be responsible for the simple bridging fashion of the mpda^{4-} ligand. In conclusion, H_4mpda could be used as a versatile ligand to construct novel MOFs by an appropriate choice of metal centers and secondary ligands. Subsequent studies will be focused on the construction of new interesting coordination polymers by reacting H_4mpda and other auxiliary N-donor ligands with selected metal ions.

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[1] P. J. Hagrman, D. Hagrman, J. Zubieta, *Angew. Chem.* **1999**, *111*, 2798 – 2848; *Angew. Chem. Int. Ed.* **1999**, *38*, 2638 – 2684.

[2] O. M. Yaghi, G. Li, H. Li, *Nature* **1995**, *378*, 703 – 706.

[3] a) R. A. Heintz, H. Zhao, X. Ouyang, G. Grandinetti, J. Cowen, K. R. Dumbar, *Inorg. Chem.* **1999**, *38*, 144 – 156; b) L. F. Ma, L. Y. Wang, X. K. Huo, Y. Y. Wang, Y. T. Fan, J. G. Wang, S. H. Chen, *Cryst. Growth Des.* **2008**, *8*, 620 – 628.

[4] a) M. Du, X. H. Bu, Y. M. Guo, J. Ribas, *Chem. Eur. J.* **2004**, *10*, 1345 – 1354; b) T. K. Karmakar, B. K. Ghosh, A. Usman, H. K. Fun, E. Rivière, T. Mallah, G. Aromi, S. K. Chandra, *Inorg. Chem.* **2005**, *44*, 2391 – 2399.

[5] M. Kondo, T. Okubo, A. Asami, S. Noro, T. Yoshitomi, S. Kitagawa, T. Ishii, H. Matsuzaka, K. Seki, *Angew. Chem.* **1999**, *111*, 190 – 193; *Angew. Chem. Int. Ed.* **1999**, *38*, 140 – 143.

[6] a) N. L. Rosi, J. Eckert, M. Eddaoudi, D. J. Vodak, J. Kim, M. O'Keeffe, O. M. Yaghi, *Science* **2003**, *300*, 1127 – 1129; b) J. L. C. Rowsell, O. M. Yaghi, *Angew. Chem.* **2005**, *117*, 4748 – 4758; *Angew. Chem. Int. Ed.* **2005**, *44*, 4670 – 4679; c) A. C. Sudik, A. R. Millward, N. W. Ockwig, A. P. Cote, J. Kim, O. M. Yaghi, *J. Am. Chem. Soc.* **2005**, *127*, 7110 – 7118.

[7] a) G. Férey, M. Latroche, C. Serre, F. Millange, T. Loiseau, A. Percheron-Guégan, *Chem. Commun.* **2003**, 2976 – 2977; b) X. Zhao, B. Xiao, A. J. Fletcher, K. M. Thomas, D. Bradshaw, M. J. Rosseinsky, *Science* **2004**, *306*, 1012 – 1015; c) M. Dinca, A. F. Yu, J. R. Long, *J. Am. Chem. Soc.* **2006**, *128*, 8904 – 8913.

[8] L. Carlucci, G. Ciani, P. Macchi, D. M. Proserpio, *Chem. Commun.* **1998**, 1837 – 1843.

[9] A. Y. Robin, K. M. Fromm, *Coord. Chem. Rev.* **2006**, *250*, 2127 – 2157.

[10] P. J. Steel, *Acc. Chem. Res.* **2005**, *38*, 243 – 250.

[11] D. N. Dybtsev, H. Chun, K. Kim, *Chem. Commun.* **2004**, 1594 – 1595.

[12] Z. Lin, D. S. Wragg, R. E. Morris, *Chem. Commun.* **2006**, 2021 – 2023.

[13] J. Y. Lu, *Coord. Chem. Rev.* **2003**, *246*, 327 – 347.

[14] E. Psillakis, J. C. Jeffery, J. A. McCleverty, M. D. Ward, *Chem. Commun.* **1997**, 479 – 480.

[15] a) H. F. Zhu, J. Fan, T. A. Okamura, Z. H. Zhang, G. X. Liu, K. B. Yu, W. Y. Sun, N. Ueyama, *Inorg. Chem.* **2006**, *45*, 3941 – 3948; b) E. C. Yang, Y. N. Chan, H. Liu, Z. C. Wang, X. J. Zhao, *Cryst. Growth Des.* **2009**, *9*, 4933 – 4942.

[16] Y. Su, S. Q. Zang, C. Y. Duan, H. Z. Zhu, Q. J. Meng, *Inorg. Chem. Commun.* **2007**, *10*, 339 – 342.

[17] L. P. Zhang, J. F. Ma, J. Yang, Y. Y. Liu, G. H. Wei, *Cryst. Growth Des.* **2009**, *9*, 4660 – 4673.

[18] G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**. See also: G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467 – 473.

[19] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**. See also: G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112 – 122.

[20] S. Q. Zang, Y. Su, Y. Z. Li, H. Z. Zhu, Q. J. Meng, *Inorg. Chem.* **2006**, *45*, 2972 – 2978.

[21] S. K. Kurtz, T. T. Perry, *J. Appl. Phys.* **1968**, *39*, 3798 – 3813.