

Two New Solvent-modulated Zinc(II) Metal-Organic Hybrid Materials based on Rigid Tripodal Carboxylate Ligand and 2,2'-Bipy Co-ligand: Crystal Structures and Luminescent Properties

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Abstract. The zinc(II) coordination polymers [Zn(Htatb)(2,2'-bipy)·(NMP)·H₂O] (**1**) and [Zn₃(tatb)₂(2,2'-bipy)₃·H₂O] (**2**) (H₃tatb = 4,4',4''-s-triazine-2,4,6-triyl-tribenzoic acid; 2,2'-bipy = 2,2'-bipyridyl, NMP = N-methyl-2-pyrrolidon), were synthesized hydrothermally, and characterized by infrared spectroscopy (IR), powder X-ray

diffraction (PXRD), and single-crystal X-ray diffraction. Both compounds **1** and **2** possess expectant low dimensional coordination structures, which further connected into interesting 3D networks by hydrogen bond and strong π - π interactions. Moreover, the thermal stabilities and fluorescent properties of **1** and **2** were investigated.

1 Introduction

Coordination polymers (CPs) as one kind of solid state materials have developed exponentially over the past few decades in terms of both crystal engineering and supramolecular chemistry.^[1-7] In the design and synthesis of such solid state materials with new structures and varying functionalities, organic multi-carboxylate linkers are widely used as bridging ligands due to the high thermal and chemical stabilities of the carboxylate-metal fragment.^[8-11] Among the family of organic carboxylate, tri-angular carboxylate, especially H₃tatb (4,4',4''-s-triazine-2,4,6-triyl-tribenzoic acid), will remarkable improve the thermal stability and enhance the hydrogen uptake property, which has been proved by our group.^[12] In tatb³⁻, the three nitrogen atoms in the central triazine ring allow a nearly complete delocalization of π electrons and draw the positively charged carbon atoms, which obviously strong inter-ligand interaction and lead to those superiorities character.^[13-14] For this point, research and exploration of π - π interaction motif is necessary between tatb ligand to guide the synthesis of subsequent tatb-based CPs. However, the reported tatb-based CPs are all three-dimension framework by searching for CCDC database, which means that tatb molecular were not freedom on the process of self-assembling.^[15] Therefore, co-ligand, such as 2,2'-bipy ligands was employed by us as blocking agent to synthesis tatb-based low dimensional CPs.

Herein, the syntheses and structures of the low dimensional CPs [Zn(Htatb)(2,2'-bipy)·(NMP)·H₂O] (**1**) and [Zn₃(tatb)₂(2,2'-

bipy)₃·H₂O] (**2**) are reported. The thermal behaviors, luminescent properties and inter-ligand π - π interaction motif were studied.

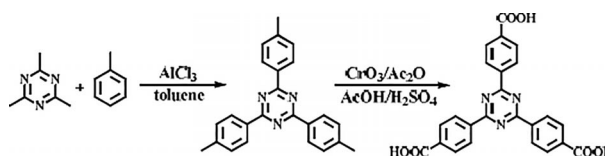
2 Experimental Section

2.1 Materials and Measurements

All the reagents and solvents employed were commercially available and used as received without further purification except H₃tatb. Infrared spectra were recorded with a Bruker VERTEX-70 spectrometer as KBr pellets in the frequency range 4000–400 cm⁻¹. Elemental analyses (C, H, and N) were determined with a CE instruments EA 1110 analyzer. Photoluminescence measurements were performed with a Hitachi F-7000 fluorescence spectrophotometer with solid powder on a 1 cm quartz round plate. TG curves were measured from 40 to 900 °C with a Mettler Toledo TGA instrument at a heating rate 10 K·min⁻¹ in a nitrogen atmosphere (100 mL·min⁻¹).

2.2 Synthesis of H₃tatb Ligand (4,4',4''-s-Triazine-2,4,6-triyl-tribenzoic Acid) (H₃tatb)

A 500 mL three-necked flask was charged with acetic acid (72.64 g), H₂SO₄ (4.4 mL), and 4,4',4''-s-triazine-2,4,6-tri-p-tolyl (2.783 g). Chromium oxide (7.2 g) and acetic anhydride (4.8 mL) were added with stirring, carefully keeping the temperature below 50 °C (Scheme 1). The resulting black-brown slurry was stirred overnight, poured into cold water (300 mL), well mixed, and filtered. The solid was washed with water and dissolved in 2 M NaOH solution (200 mL).



Scheme 1. Synthesis of H₃tatb.

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After the unreacted starting material was removed by filtration, the solution was acidified with HCl to give crude product. Recrystallization from DMF gave pure product as white solid (yield: 95%). **IR** (KBr): $\tilde{\nu}$ = 2858 (w), 2546 (w), 1684 (s), 1583 (m), 1507 (vs), 1407 (m), 1360 (s), 1282 (vs), 1016 (m), 790 (s), 762 (vs) cm^{-1} . **¹H NMR** (300 MHz, [D₆]DMSO): δ = 7.5 (d, 6 H), 8.7 (d, 6 H), 12.9 (br., 3 H).^[16]

2.3 Synthesis of Complexes 1 and 2

[Zn(Htatb)(2,2'-bipy)·(NMP)·H₂O] (1)

A mixture of Zn(NO₃)₂·6H₂O (23.5 mg, 0.079 mmol), 2,2'-bipy (33.2 mg, 0.21 mmol), and H₃tatb (11.7 mg, 0.027 mmol) was dissolved in NMP/H₂O mixed solvent (7 mL, v/v = 1/1). All reagents were sealed in a pressure-resistant glass tube and slowly heated to 120 °C from room temperature in 500 min. After keeping at 120 °C for 3000 min, the mixture was slowly cooled to 30 °C at a rate of 7 K·h⁻¹. Afterwards, the yellowish block crystals were collected after washed with acetone, and dried in air. (yield: 71%, based on zinc). C₃₉H₃₂N₆O₈Zn: calcd. C 61.22 (found 60.15); H 4.08 (4.11); N 10.99 (10.80)%. **IR** (KBr): $\tilde{\nu}$ = 3422 (s), 2032 (w), 1632 (m), 1560 (m), 1514 (m) cm^{-1} .

[Zn₃(tatb)₂(2,2'-bipy)₃·H₂O] (2)

A mixture of Zn(NO₃)₂·6H₂O (112.9 mg, 0.38 mmol), 2,2'-bipy (67.8 mg, 0.43 mmol), and H₃tatb (13.2 mg, 0.03 mmol) was dissolved in DMF/EtOH/H₂O mixed solvent (7 mL, v/v/v = 5/2/1). All reagents were sealed in a pressure-resistant glass tube and slowly heated to 120 °C from room temperature in 500 min. After keeping at 120 °C for 3000 min, the mixture was slowly cooled to 30 °C at a rate of 7 K·h⁻¹. Afterwards, the colorless transparent crystals were collected after washed with acetone, and dried in air (yield: 67%, based on zinc). C₇₈H₅₃N₁₂O₁₃Zn₃: calcd. C 60.21 (found 59.92); H 3.52 (3.39); N 10.88 (10.76)%. **IR** (KBr): $\tilde{\nu}$ = 3422 (s), 2330 (w), 2016 (w), 1624 (m), 1407 (w), 1342 (w), 1124 (w), 1086 (w), 766 (w), 599 (w) cm^{-1} .

2.4 X-ray Single-crystal Structure Determination

Single crystals of the complexes **1** and **2** with appropriate dimensions were chosen under an optical microscope and quickly coated with high vacuum grease (Dow Corning Corporation) before being mounted on a glass fiber for data collection. Data for **1** and **2** were collected with a SuperNova diffractometer equipped with a Molybdenum micro-focus X-ray sources (λ = 0.71073 Å) and an Eos CCD detector under 293 K. The data were collected with a ω -scan technique and an arbitrary ϕ -angle. Data reduction was performed with the CrysAlisPro package, and an analytical absorption correction was performed. The structures were treated anisotropically, whereas the aromatic and hydroxyl hydrogen atoms were placed in calculated, ideal positions and refined as riding on their respective carbon or oxygen atoms. Structure was examined using the Addsym subroutine of PLATON^[17] to assure that no additional symmetry could be applied to the models. Crystal data and collection and parameters are summarized in Table 1, and selected bond lengths and angles are given in Table S1 and Table S2 (Supporting Information).

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1054255 and CCDC-1054256 for complexes **1**

Table 1. Crystallographic data for **1** and **2**.

	1	2
Formula	C ₃₉ H ₃₂ N ₆ O ₈ Zn	C ₇₈ H ₅₃ N ₁₂ O ₁₃ Zn ₃
M	778.08	1562.43
Crystal system	triclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> / Å	8.6456(5)	25.7542(9)
<i>b</i> / Å	12.5274(6)	8.8192(2)
<i>c</i> / Å	17.6100(10)	38.2868(14)
α / °	110.576(5)	90.00
β / °	90.640(5)	121.123(2)
γ / °	93.301(5)	90.00
<i>V</i> / Å ³	1781.63(17)	7444.4(4)
<i>Z</i>	2	4
<i>D</i> / g·cm ⁻³	1.450	1.394
μ / mm ⁻¹	1.492	1.030
<i>R</i> _{int}	0.0366	0.0741
GOF	1.047	1.023
<i>R</i> ₁ ^a / <i>wR</i> ₂ ^b [<i>I</i> > 2 σ (<i>I</i>)]	0.0514, 0.1354	0.0875, 0.2514
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0774, 0.1531	0.1555, 0.3120

a) *R*₁ = $\sum ||F_o| - |F_c|| / \sum |F_o|$. b) *wR*₂ = $[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{0.5}$.

and **2** (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

Supporting Information (see footnote on the first page of this article): PXRD patterns and selected bond lengths and angles of complexes **1** and **2**.

3 Results and Discussion

3.1 Crystal Structure Descriptions

[Zn(Htatb)(2,2'-bipy)·(NMP)·H₂O] (1)

Single-crystal X-ray diffraction analysis reveals that complex **1** has a 1D chain structure, crystallizing in the triclinic *P* $\bar{1}$ space group. The asymmetric unit in complex **1** contains one crystallographic independent Zn^{II} ion, one Htatb²⁻ anion, one 2,2'-bipy ligand, one coordinated water molecule, and one uncoordinated NMP unit. As shown in Figure 1a, the Zn^{II} ion in **1** adopts a distorted trigonal bipyramidal arrangement. Each Zn^{II} ion is five-coordinated by two carboxylate oxygen atoms from two different Htatb²⁻ molecules, one oxygen atom from coordinated water molecule, and two nitrogen atoms from one chelating 2,2'-bipy ligand. The Zn–O and Zn–N distances range from 1.999(1) to 2.197(2) Å, in the order Zn–N > Zn–O_w > Zn–O_{Htatb}, with the O(or N)–Zn–O(or N) bond angles varying from 75.522(5)° to 168.787(6)°, which are comparable to those of reported Zn^{II} coordination polymers.^[18,19] The carboxylate ligands in complex **1** are partly deprotonated, adopting a monodentate mode to link two different central Zn^{II} atoms, coordinated water molecules and 2,2'-bipy occupy the left coordinated sites of the central metal ions, which interrupts to construct high-dimensional architecture. At last, the 1D infinite chains are further stacked into a three-dimensional supramolecular framework through π – π stacking and weak interactions.

[Zn₃(tatb)₂(2,2'-bipy)₃·H₂O] (2)

X-ray single-crystal diffraction reveals that complex **2** has a 2D wavy framework. Complex **2** crystallizes in the monoclinic

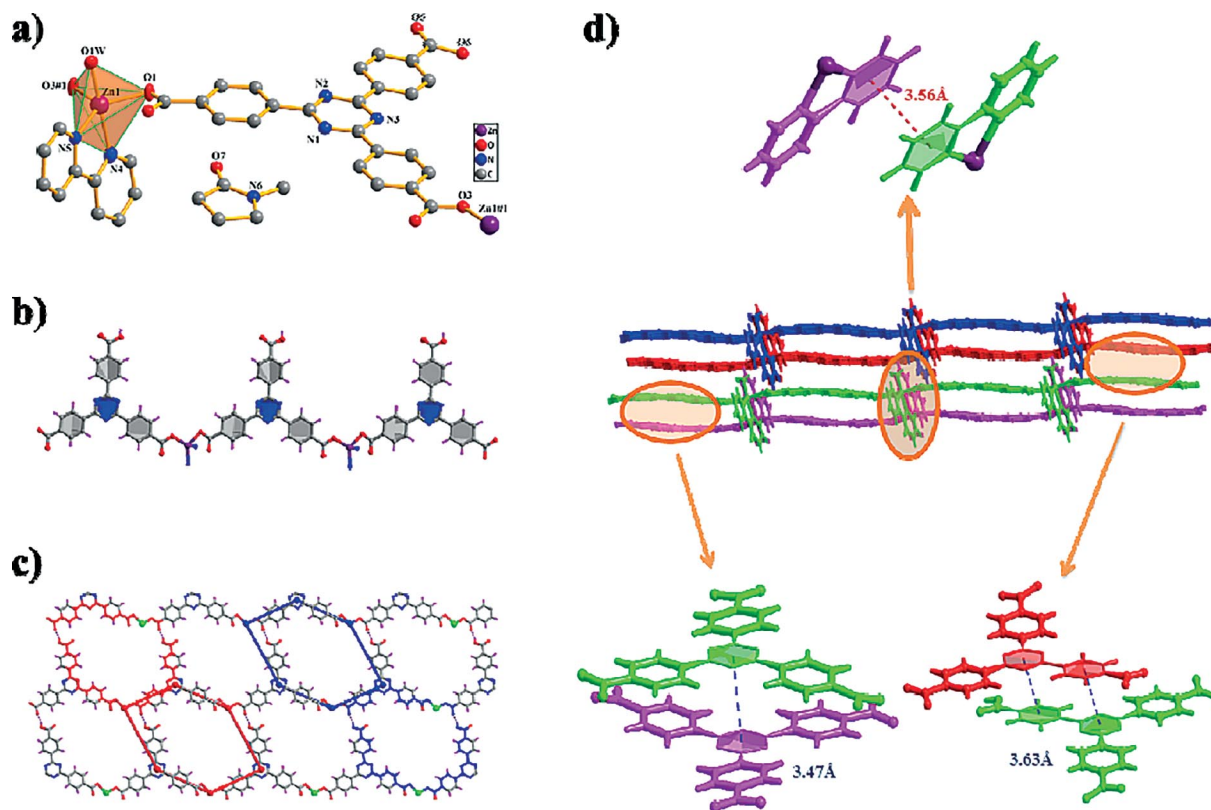


Figure 1. (a) Partial view of **1** with atom labeling of the asymmetric unit and metal coordination. (b) Perspective view of the Zn-tatb chain. (c) Perspective view of the 2D layered framework extended through O–H...O hydrogen bonds. (d) The 3D supramolecular architecture by π – π stacking interactions and different motif of π – π stacking.

$P2/c$ space group. The asymmetrical unit of **2** contains three dependent Zn^{II} atoms, two tatb^{3-} anion, three 2,2'-bipy ligands, and one lattice water molecule. The Zn2 atom is five-coordinated by three carboxylate oxygen atoms from three different tatb^{3-} molecules and two nitrogen atoms from one chelating 2,2'-bipy ligand, whereas Zn3 is six-coordinated by four carboxylate oxygen atoms from two different tatb^{3-} molecules and two nitrogen atoms from one chelating 2,2'-bipy ligand. Zn1 is four-coordinated by three carboxylate oxygen atoms from two different tatb^{3-} molecules and two nitrogen atoms from one chelating 2,2'-bipy ligand (Figure 2). The Zn–O and Zn–N distances range from 1.929(2) to 1.948(2) Å and 2.022(3) to 2.027(3) Å, respectively. The carboxylate group in compound **2** adopts μ_1 - η^1 - η^0 and μ_1 - η^1 - η^1 bridging modes to link different Zn_2O_4 , ZnO_4N_2 , and ZnO_3N_2 resulting in a wavy-like layer structure.

3.2 X-ray Power Diffraction Analyses and Thermogravimetric Analyses

The X-ray powder diffraction patterns of samples were recorded for checking the phase purities of **1** and **2** at room temperature. As shown in Figure S1 and Figure S2 (Supporting Information), the experimental patterns are in good agreement with simulated patterns generated from the results of single-crystal diffraction data, demonstrating the phase purity of the product nicely. The preferred orientation of the crystalline

powder samples perhaps caused the dissimilarities in intensity.^[10]

The thermal behavior of compounds **1** and **2** were studied by TGA in a nitrogen atmosphere with a heating rate of $10 \text{ K}\cdot\text{min}^{-1}$ (Figure 3). Complex **1** experienced a weight loss of 3.69% below 150°C corresponding to the release of the coordinated water molecules (calcd. 2.32%). Finally, the removal of uncoordinated NMP molecules and the pyrolysis of organic ligands occur in the range of 150 to 900°C . For complex **2**, there are only one obvious weight loss step with the 16.17% mass remnant corresponding to a deposition of ZnO (15.39%).

3.3 Photoluminescence Properties

It is reported that the luminescent properties of d^{10} transition metal have attractive fluorescence properties and potential applications in multiple fields, such as photochemistry and chemical sensors.^[20,21] The luminescent properties emission spectra of complexes **1** and **2** were examined in the solid state at room temperature, which is shown in Figure 4. The main emission peak of free rigid tatb is at 407 nm ($\lambda_{\text{exc}} = 247 \text{ nm}$), which can be assigned to the intra-ligand π – π^* transitions. Excitation of compound **1** and **2** at 247 nm produces two similar emission peak at 407 nm for **1** and 410 nm for **2**, probably attributed to intra-ligand charge transfer of the tatb , because the Zn^{II} is difficult to oxidize or to reduce due to its d^{10} configuration.^[22]

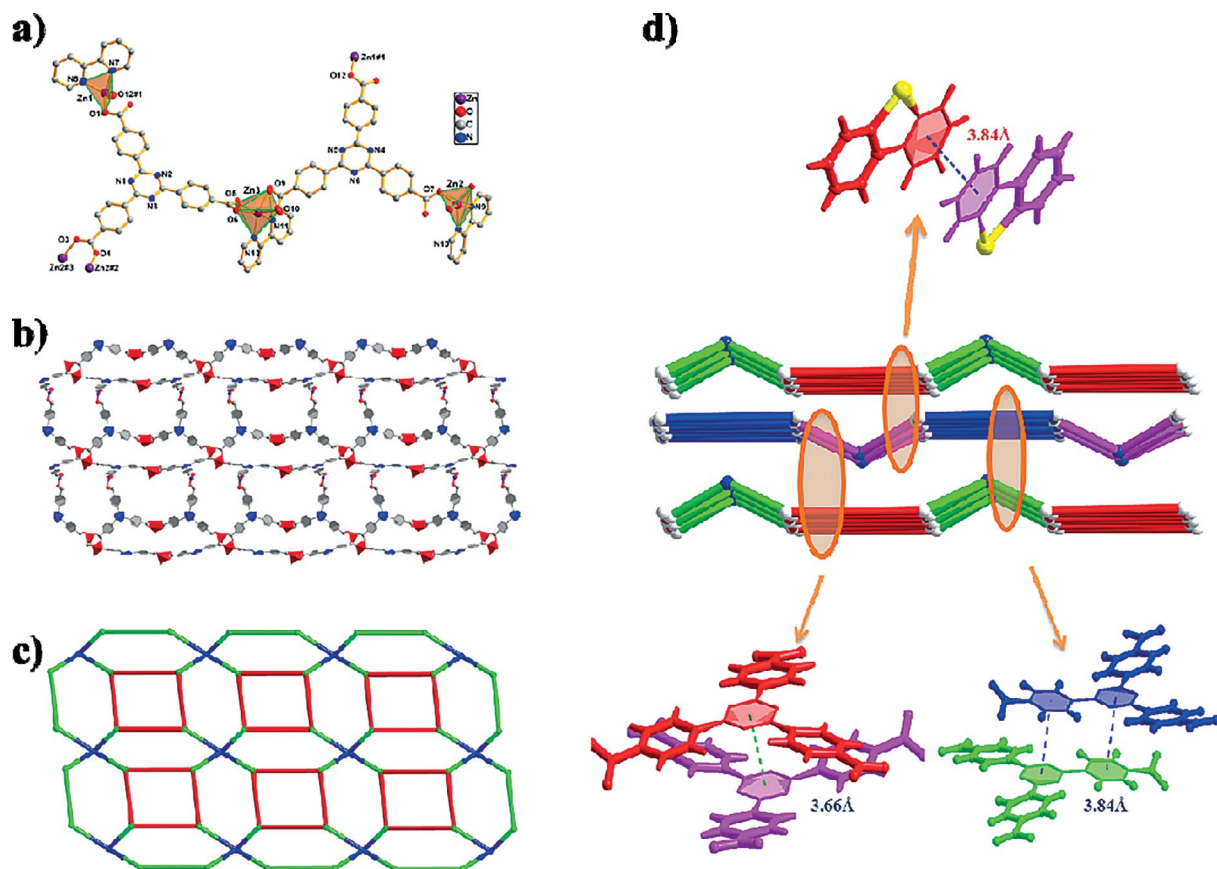


Figure 2. (a) Molecular structure of **2** with atom labeling of the asymmetric unit. (b) View of the 2D layer completed by the Zn^{II} ions and the tatb anions. (c) View of the 2D Zn-tatb layer simplified through topology. (d) View of the 3D supramolecular structure and $\pi\cdots\pi$ stacking motifs exist in the framework.

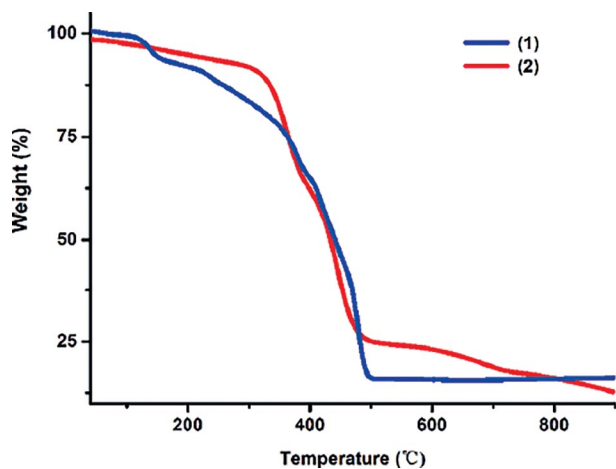


Figure 3. TGA curves for complexes **1** and **2**.

4 Conclusions

Two Zn^{II} coordination polymers based on 4,4',4''-s-triazine-2,4,6-triyl-tribenzoic acid (tatb) and N-donor co-ligand (2,2'-bipy) were obtained. Complex **1** has a 1D zigzag-like chain and **2** exhibits a 2D wave-like layer. To the best of our knowledge, complexes **1** and **2** are the first two low-dimensional coordination polymers composed by tatb ligands. Two kinds

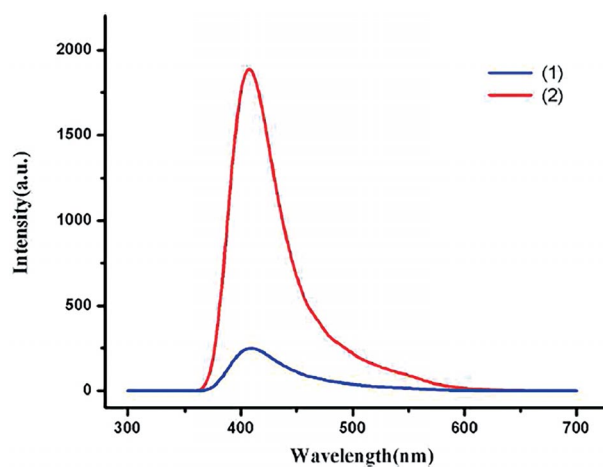


Figure 4. Solid-state fluorescence emissions recorded at room temperature for complexes **1** and **2**.

of $\pi\cdots\pi$ interaction motifs were observed in the crystal structures of **1** and **2**: the “Piedfort unit” and the “X-shape unit”. In the case of more freedom, the intensity of $\pi\cdots\pi$ interaction of the “Piedfort unit” (3.47–3.50 Å) is not stronger than that in reported 3D frameworks, and the “X-shape staking” motif was discovered, which did not exist in reported tatb-based structures.

Acknowledgements

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