Research paper

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Four congenetic zinc(II) MOFs from delicate solvent-regulated strategy: structural diversities and fluorescent properties

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ABSTRACT: Four new congenetic zinc(II) MOFs, namely $[Zn_5(bdcpp)_3(DMF)(H_2O)_4]_n \cdot x(solvent)$ (1), $[Zn_2(bdcpp)(Hbdcpp)]_n \cdot y(solvent)$ (2), $[Zn_2(bdcpp)(DMF)(H_2O)_2]_n$ (3),and $[Zn_2(bdcpp)(NMP)(H_2O)_2]_n$ (4) $(H_4bdcpp = 2,6-bis(2',4'-dicarboxylphenyl)pyridine, DMF =$ N,N'-dimethyl formamide, NMP = N-methyl-2-pyrrolidone), have been synthesized solvothermally with different solvent systems. Stabilized by Zn₂(COO)₄ paddle-wheel building blocks, the resulting MOFs 1–4 represent diverse structural features. Structurally, 1 is a rarely 3,4-c binodal 2D bilayered framework, 2 possesses a 4-c 2D (4,4) sql planar network accommodating two kinds of hetero chiral helix chains, 3 and 4 are iso-structural 1D loop ladder chains except different solvent molecules occupying the axial terminals of $Zn_2(COO)_4$ paddle-wheels. This approach based on solvent-regulated strategy aiming to allow the structural fine-tuning provides a good role model in reticular chemistry. Complexes 1–3 display excellent solid-state photoluminescence stemming from the metal-to-ligand charge transfer or intraligand charge transmission.

Keywords: Solvent-regulated strategy, Zn(II)-MOFs, Congenetic synthesis, Structural diversities, Fluorescent properties

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1. Introduction

Over the past two decades, metal-organic frameworks (MOFs) assembled by metal / metal clusters and organic ligands have attracted tremendous attention in the field of chemistry and materials science [1]. The regular highly-ordered structures of MOFs endow these crystalline functional materials potential applications in gas storage, separation, sensing, catalysis, photoelectric materials and so on [2]. The rapid development of MOFs benefits basically from the diversity and designability of metal nodes and linking blocks, which provides more options for the construction of MOFs owning fascinating frameworks and attractive functions [3]. It is apparently that some external factors may also have a positive impact on the synthesis trend and process, such as solvent (volume ratio, polarity, aprotic / protic), pH value, template, crystal seeds and cooling rate [4]. The ultimate aim of reticular chemistry is to achieve controllable molecular self-assembly of the solid materials [5]. What inspiring us is that some examples of the rational design of MOFs have already been achieved based on the design of metal containing SBUs and organic linkers in the unremitting efforts. Nevertheless, that is far from achieving the final expected results [4,5].

Solvent system has the characteristics of the widespread source, low cost and highly maneuverable. It means that the precise selection of the solvent is essential to the synthesis of final product [6]. Solvent system could perform different roles in the reaction process except for dissolving the raw materials to get crystalline MOFs: (i) participating in the reaction as ligands; (ii) filling the pores as guest molecules; (iii) dual roles with host bonding and guest adsorption; (iv) structure-director as a template [7]. In other words, the solvent does not only act as a carrier for chemical reaction, but also enhances the stability of the whole framework and even expands the variety of crystalline substances. According to the literatures, some researches on solvent effects for syntheses of MOFs are reported. However, the number of the MOF structures obtained from a solvent-based synthesis system are only in small numbers and even rarely more than three cases [7c,8]. Therefore, it is still desirable to explore new systems systematically to construct the MOFs in greater numbers and make clear the synthetic mechanisms.

It has been reported that the designing or modification of the ligands to obtain new MOFs in solvent-regulated strategies was feasible. Especially, owing to holding both hydrophobic molecular skeleton and two or more hydrophilic carboxylic groups, the aromatic polycarboxylates were given

innately the ability of the subtle control of solvent action, which was logically excellent research objectives to investigate the syntheses of solvent-regulated MOFs [8,9]. Aromatic polycarboxylates show comparable stability, diverse coordination ability, and adjustable deprotonation degree of carboxylic groups, which affords a stage for the solvent system to determine the structure type of **MOFs** like marionette [9c,10]. Accordingly, target V-shaped а we 2,6-bis(2',4'-dicarboxylphenyl)pyridine (H₄bdcpp), possessing embedded pyridyl acting as Lewis basic sites and two neighboring 2-carboxyls being favorable for the forming of M₂(COO)₄ paddle-wheels SBUs, which is very efficient for MOFs construction as functional building blocks. To date, just one case tethering the H_4 bdcpp ligand has been documented with a surfactant-introduction strategy for separating two pure MOFs [11]. In this context, four congenetic zinc(II)-based MOFs of $[Zn_5(bdcpp)_3(DMF)(H_2O)_4]_n \cdot x(solvent)$ (1), $[Zn_2(bdcpp)(DMF)(H_2O)_2]_n$ (3) $[Zn_2(bdcpp)(Hbdcpp)]_n \cdot y(solvent)$ (2)and $[Zn_2(bdcpp)(NMP)(H_2O)_2]_n$ (4) were successfully synthesized through the solvent-regulated strategy. The assembly of the precursors was deeply influenced by the solvent types and ingredients, and the products of MOFs 1-4 exhibit multifarious structural features. In addition, the physio-chemical properties were evaluated using FT-IR, TGA, PXRD and fluorescence spectrophotometer.

2. Experimental

2.1. Chemicals and physical measurements

All reagents and solvents were purchased commercially and used as received. **FT-IR** spectra (KBr pellets) were recorded in the 400-4000 cm⁻¹ region with a Nicolet Avatar360 **FT-IR** spectrometer. Thermogravimetric analyses (TGA) were performed on a METTLER-TOLEDO TGA/STDA 851^e Thermal Analysis at a heating rate of 10 °C/min under the protection of N₂ stream. Powder X-ray diffraction (PXRD) patterns were carried out in a Bruker D8 ADVANCE X-ray powder diffractometer (Cu-K α , 1.5418 Å). Photoluminescent spectra were investigated with a Hitachi F-7000 Fluorescence Spectrophotometer.

2.2. Synthesis of 2,6-bis(2',4'-dicarboxylphenyl)pyridine

The synthesis technique of H_4 bdcpp is similar to 3,5-di(2',4'-dicarboxylphenyl)benozoic acid [12]. The synthesis procedure of H_4 bdcpp is shown stepwise in Scheme 1.



Scheme 1. The scheme for the synthesis of 2,6-bis(2',4'-dicarboxylphenyl)pyridine (H₄bdcpp). Reaction conditions: (i) 4-bromoisophthalic acid (0.05 mol, 12.3 g), ethanol (250 mL), concentrated H₂SO₄ (5 mL), refluxing for 10 h; (ii) diethyl 4-bromoisophthalate (0.05 mol, 15.0 g), bis(pinacolato)diborane (0.025 mol, 6.4 g), CH₃COOK (0.15 mol, 14.7 g), dried 1,4-dioxane (250 mL), Pd(dppf)₂Cl₂ (7.0 mmol, 5.1 g), refluxing overnight, extracting thrice with ethyl acetate (150 mL) after pouring into H₂O (2000 mL), recrystallizing; (iii) (1) 4,4,5,5-tetramethyl-2-(diethyl-2,4-dicarboxylatephenyl)-1,3-dioxolane (0.05 mol, 17.40 g), 2,6-dibromopyridine (0.025 mol, 5.9 g), K₃PO₄ (0.1 mol, 21.2 g), 1,4-dioxane (250 mL), deaerating with N₂ for 20 min; (2) Pd(PPh₃)₄ (0.5 mmol, 0.6 g), refluxing for 6 d, recrystallizing; (iv) (1) tetraethyl 2,6-bis(2,4-dicarboxylphenyl)pyridine (0.05 mol, 26.0 g), NaOH (8 g), H₂O (500 mL), refluxing for 2 h; (2) neutralizing with concentrated HCl.

2.3. Synthesis of $[Zn_5(bdcpp)_3(DMF)(H_2O)_4]_n$: x(solvent) (1)

A mixture of H₄bdcpp (0.1 mmol, 0.0410 g), ZnSO₄·7H₂O (0.2 mmol, 0.0575g), and 0.05 mL HNO₃ (63%, aq.) in the solvent system of DMF (3.5 mL) / distilled water (1.5 mL) was introduced into a 25 mL Teflon-lined autoclaved stainless steel vessel, heated at 105 °C for 48 h, and then cooled naturally to room temperature. Colorless block crystals of **1** were obtained in 59% yield based on H₄bdcpp ligand. IR spectrum (cm⁻¹, KBr pellet):3778w, 3408s, 2796m,2487m,1656s, 1625s, 1438m, 1373s, 1254m, 1172w, 1102w, 1023w, 818w, 784m, 734w, 697m, 567w, 481w.

2.4. Synthesis of $[Zn_2(bdcpp)(Hbdcpp)]_n$ y(solvent) (2)

The same procedure as that of 1 was used except that solvent system was replaced by 5 mL DMF and 0.2 mL H_2O for 2. Colorless block crystals of 2 were obtained in 49% yield based on

H₄bdcpp ligand. IR spectrum (cm⁻¹, KBr pellet): 3404s, 3068m, 2790m, 2486w, 2359s, 1654s, 14387m, 1369s, 1253m, 1174w, 1102w, 1023w, 923w, 818m, 781m, 731w, 697m, 569w, 483m. *2.5. Synthesis of [Zn₂(bdcpp)(DMF)(H₂O)₂]_n (3)*

H₄bdcpp (0.1 mmol, 0.041 g), ZnSO₄·7H₂O (0.2 mmol, 0.0575 g), DMF (5 mL) and 0.05 mL HNO₃ (63%, aq.) were mixed uniformly and then sealed in a 25 mL Teflon-lined autoclaved stainless steel vessel. After being heated at 105 °C for 48 h, the mixture was cooled naturally to room temperature. Colorless block crystals of **3** were collected with 55% yield based on H₄bdcpp ligand. IR spectrum (cm⁻¹, KBr pellet): 3430s, 2934m, 2358w, 1666s, 1497m, 1437s, 1379s, 1253m, 1171w, 1103s, 1062w, 819m, 788s, 734m, 667m, 568w, 485m.

2.6. Synthesis of $[Zn_2(bdcpp)(NMP)(H_2O)_2]_n$ (4)

The synthetic procedure was similar to that of **3** except that 5 mL DMF was changed into the mixed DMF/NMP system (2.5 mL/2.5 mL). Very little colorless block crystals of **4** were obtained. *2.7. X-ray crystallographic Studies*

The crystal data for complexes **1–4** were collected at room temperature with a Bruker APEX IISMART CCD area detector diffractometer with graphite-monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073$ Å). The structures were solved by direct method using SHELXS-97, and then refined with full matrix least-square methods based on F² with SHELXL-97 [13]. The SQUEEZE program was applied to remove the scattering from the highly disordered guest solvent molecules and anion ions in the frameworks of complexes **1** and **2**. All hydrogen atoms except the coordinated water molecules were fixed theoretically, and the aqua hydrogen atoms were located from differential Fourier maps. Metal atoms Zn2, Zn3 and Zn4 of complex **1** situate special coordinate positions. The disordered methyl groups of DMF and coordinate water O1W and O2W in **1** are dealt with equal site occupancies into two positions. CCDC 1535086–1535089 for **1–4** contain the supplementary crystallographic data for this paper. The crystal data and refinement details for **1–4** are listed in **Table 1**. Selected bond lengths and bond angles of **1–4** are summarized in **Table S1**.

Complex	1	2	3	4
Empirical formula	$C_{66}H_{42}N_4O_{29}Zn_5$	$C_{42}H_{19}N_2O_{16}Zn_2$	$C_{24}H_{20}N_2O_{11}Zn_2$	$C_{26}H_{22}N_2O_{11}Zn_2\\$
М	1681.89	938.33	643.16	669.20
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	<i>C2/m</i>	Pī	<i>C2/c</i>	C2/c
<i>a</i> [Å]	22.888(4)	13.707(6)	28.917(14)	29.593(9)
<i>b</i> [Å]	25.631(4)	14.229(6)	16.436(8)	16.576(5)
<i>c</i> [Å]	16.944(3)	15.229(7)	19.031(9)	18.963(6)
α [°]	90	95.789(7)	90	90
β[°]	102.728(3)	106.877(7)	118.713(6)	120.983(5)
γ [°]	90	90.060(7)	90	90
$V \left[\text{\AA}^3 \right] / Z$	9696(3) / 4	2826(2) / 2	7933(7) / 8	7975(4) / 8
$d_{calcd}[g.cm^{-3}]$	1.152	1.103	1.077	1.115
$\mu [\mathrm{mm}^{-1}]$	1.283	0.904	1.251	1.247
<i>F</i> (000)	3392	946	2608	2720
θ Range [°]	1.21–28.47	1.41-26.02	1.48–25.68	1.47–25.38
Reflections collected	34739	16879	19187	19366
R _(int)	0.0874	0.0542	0.0797	0.1029
Goodness-of-fit on F ²	1.031	1.158	1.190	1.025
$R_1^{[a]}, w R_2^{[b]} [I > 2\sigma(I)]$	0.0762, 0.1865	0.0915,0.2143	0.0938, 0.2466	0.0839, 0.2139
$R_1^{[a]}, w R_2^{[b]}$ [all data]	0.1300, 0.2072	0.1093,0.2216	0.1561, 0.2649	0.1437, 0.2335

Table 1. Crystallographic data and structure refinement details for 1-4

^[a] $R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|;$ ^[b] $wR_2 = [\Sigma w (F_0^2 - F_c^2)^2 / \Sigma w (F_0^2)^2]^{1/2}$

3. Results and discussions

3.1. Syntheses

The aromatic polycarboxylate 2,6-bis(2',4'-dicarboxylphenyl)pyridine and $ZnSO_4 \cdot 7H_2O$ were used as precursor reagents in the synthetic process, and a lot of exploratory experiments have been made carefully to obtain the desired MOFs crystals (see Fig. 1). Direct mixing treatment of the organic materials and zinc salts in aqueous solution generates plenty of fine precipitates immediately, so the hydro(solvo)thermal techniques were applied to produce suitable crystals for X-ray analysis. Complexes 1–4 have been synthesized successfully under the same reaction conditions except for

different solvent systems. Using DMF / $H_2O(7:3, v/v)$ as solvent led to the regular block crystals of 1, while reducing water amount to several drops made for the block crystals of 2. For 3 and 4, DMF and DMF / NMP (1:1, v/v) served as the solvent systems, respectively. But unfortunately, the yield of 4 is too low despite various attempts. Although the experiments with the other solvent systems have also been carried out, only unknown deposits were obtained. Little additional concentrated acids in solvothermal system should contribute to the deprotonation decelerating of the carboxylic acids, which facilitates the formation of MOFs materials with high quality.



Fig. 1. Synthetic procedures of complexes 1–4.

3.2. Description of crystal structures

3.2.1. Crystal structure of complex 1

Single-crystal X-ray diffraction measurements show that complex 1 crystallizes in the monoclinic C2/m space group. The 2D zinc-based anionic MOF accommodates two kinds of dinuclear $Zn_2(COO)_4$ paddle-wheel units and one metal center, in which unknown cations might be inclosed presumably into the interlayers to balance the global charge of anionic framework. As revealed in Fig. 2a, there are two and half Zn^{2+} ions, one and half deprotonized bdcpp⁴⁻ ligands, half

DMF molecule, two coordinated water in the asymmetric unit. Zn1 ion is four-coordinated by three carboxylic O atoms from three bdcpp⁴⁻ ligands and one O atom from a water molecule. The coordination geometry of Zn1 can be described as a tetrahedral mode without regard to the elongated Zn1–O10 bond of 2.614(4) Å. The Zn2, Zn3 and Zn4 ions are coordinated with tetragonal pyramidal geometry affording different $Zn_2(COO)_4$ paddle-wheels, which two DMF molecule located at the axial sites in one paddle-wheel from two Zn2 ions and two different H₂O molecules coordinated axially to Zn3 and Zn4 ions in the other paddle-wheel (Zn3–O2W 2.022(8) Å and Zn4–O1W 1.957(6) Å).

Carboxylic groups of H₄bdcpp ligand adopt μ_1 - η^0 : η^1 , μ_2 - η^1 : η^1 , μ_1 - η^1 :(η^1)_(elongated Zn-O) coordinating modes (Scheme S1a and S1b) to bridge four Zn1 atoms and four paddle-wheels to give star-shaped SBUs being similar to macrocyclic porphyrin molecule (Fig. 2b). The diagonal dimensions of star-shaped SBUs are in mesoscale of 25.834 Å. The SBUs interlinking through 1D Zn1/bdcpp single strand lean against to form 1D ribbon-like chain along the crystallographic *c* axis (Fig. 2c and 2d). Further, these ribbons are extended into 2D bilayered structure by Zn2–Zn2 paddle-wheels (Fig. 2e). Topologically, the Zn1 centers and Zn₂(COO)₄ paddle-wheels serve as 3-connected and 4-connected nodes, respectively. Therefore, MOF **1** is an unusual binodal 3,4-*c* 2D bilayered network, which is not reported in RCSR database [14].





(b)



(c)



(d)



Fig. 2. (a) Coordination modes of Zn(II) ions in complex 1, symmetry codes: A x, y, z+1; B x, -y+1, z; C -x, -y+1, -z+2; D x, -y, z; (b) star-shaped stuctural unit similar to macrocyclic porphyrin molecule; (c) 1D polymeric ribbon by the cross-linking of star-shaped units; (d) 1D Zn-ligand straight chain; (e) 2D bilayer coordination network.

3.2.2. Crystal structure of complex 2

Single-crystal analysis revealed that complex 2 crystallizes in the triclinic PI space group, that the 2D anionic layer consists of typical $Zn_2(COO)_4$ paddle-wheel units. Similar to 1, the unknown cationic guest molecules fill into the micropores of the framework 2 to fit the global charge balance. The asymmetric unit of complex 2 contains two Zn^{2+} ions, one deprotonized bdcpp⁴⁻ ligand and one deprotonized-partially Hbdcpp³⁻ ligand (see Fig. 2a). The Zn1 and Zn2 adopt a distorted tetragonal pyramidal geometry with {ZnO₅} coordination mode. Two adjacent Zn1 centers are linked together by four carboxylic groups of two deprotonized bdcpp⁴⁻ to afford the Zn₂(COO)₄ paddle-wheel building units, and the carboxylic oxygen atoms of two Hbdcpp³⁻ ligands locate at the axial sites. But, the paddle-wheels from Zn2 centers are composed of the Hbdcpp³⁻ paddles and the bdcpp⁴⁻ fixed axes.

Carboxylic groups of bdcpp⁴⁻ and Hbdcpp³⁻ display μ_1 - η^0 : η^1 and μ_2 - η^1 : η^1 coordinating modes (Scheme S1c and S1d) to link paddle-wheel units to produce irregular square grids with the dimensions of 9.873(3) × 9.884(3) Å² (Fig. 2b). These fundamental square grids orient an ordered arrangement into 2D monolayers (Fig. 2c). The framework topology of **2** could be viewed as a 4-connected uninodal *sql* (4,4) net with Point Symbol of {4⁴.6²} by considering the Zn₂(COO)₄ unit

as a 4-*c* node. Interestingly, heterochiral helical chains appearing in couples through paddle-wheel units and ligand molecules coexist in the framework to produce mesomeric networks (Fig. 2d). The helices are made up of the repeated moieties " $-Zn_2(COO)_4$ —ligand— $Zn_2(COO)_4$ —ligand—" with the screw pitch of 13.7 Å.



(b)



(c)



Fig. 3. (a) Coordination environment of Zn(II) ions in complex **2**, symmetry codes: A -x+1, -y+1, -z+2; B -x, -y, -z+2; (b) quadrilateral unit from Zn₂(COO)₄ paddle-wheels and organic ligands; (c) 2D grid squares; (d) heterochiral helical chains appearing in couples through paddle-wheel units and ligand molecules.

3.2.3. Crystal structures of complexes 3 and 4

Utilization of pure organic solvents in synthetic systems yields isostructural MOFs **3** and **4**. Seeing Fig. 4 and 5, organic ligands bridge $Zn_2(COO)_4$ paddle-wheels and Zn ions to form identical 1D loop ladder chains except the axial DMF and NMP of paddle-wheels in **3** and **4** separately. Because the MOFs have the similar frameworks, only the structure of **3** is described here. The X-ray studies show that complex **3** belongs to the monoclinic *C2/c* space group and consists of two crystallographically independent Zn(II) ions, one deprotonized bdcpp⁴⁻ ligand, one coordinate DMF molecule and two coordinate water in the asymmetric unit. As shown in Fig. 4a, Zn1 shows a pyramidal geometry of $\{ZnO_5\}$, and two Zn1 ions linking four carboxylic groups of two bdcpp⁴⁻ ligands afford the $Zn_2(COO)_4$ paddle-wheel cluster. In view of the non-negligible Zn2–O6B (2.635 Å) , Zn2 bonds with two carboxylic groups of two bdcpp⁴⁻ ligands and two water molecules to produce the 5+1 {ZnO_6} modes with distorted octahedral environment.

Four carboxylic groups of deprotonized $bdcpp^{4-}$ link paddle-wheel clusters and Zn ions in $\mu_2-\eta^1:\eta^1$ and $\mu_1-\eta^1:(\eta^1)_{(elongated Zn-O)}$ coordinating modes to form 1D chains running along the *b* crystallographic axis (Scheme S1e). As Fig. 4b shows, the binuclear Zn(II) cluster connects to two

ligands in four directions as a 4-connected node, and Zn2 does in two directions as a linear linker. The framework of **3** could be viewed as a 1D loop ladder structures with the size of 9.38×16.44 Å² (defined by the diagonal distance of the rhombus grids).



Fig. 4. (a) Coordination environment of Zn(II) ions in complex 3, symmetry codes: A -x+1, y, -z+1/2; B x, y-1, z;
(b) 1D loop ladder chain from Zn₂(COO)₄ paddle-wheels and organic linkages.





Fig. 5. (a) Crystallographic environment around Zn(II) ions in complex **4**, symmetry codes: A -x, y, -z+1/2; B x, y-1, z; (b) view of 1D chain.

3.3. Effect of different solvent systems on the MOFs structures

According to the structural analyses of MOFs 1-4 above, different crystal structures were induced from the same precursors by the solvent interference. The solvent types and constitutes (v/v) in 1-4 are DMF / H₂O of 7:3, DMF with little water, DMF and DMF / NMP of 1:1, respectively. Complex 1 is an unusual 3,4-*c* binodal 2D bilayering framework, complex 2 represents a 4-*c* uninodal 2D (4,4) *sql* planar network possessing two kinds of chiral helix chains, however, complexes 3 and 4 are 1D loop ladder chains except different axial coordinate solvent molecules. In all MOFs, $Zn_2(COO)_4$ paddle-wheels acting as SBUs participate in the construction and structural reinforcement of crystal materials. The formation of paddle-wheel units should be ascribed to two neighboring 2-carboxylic groups of H₄bdcpp ligand, which exemplifies the component selection in the designed synthesis of MOFs.

Obviously, four congenetic zinc(II) MOFs are generated through delicate solvent-regulated strategy. Because of the insolubility of large-sized molecules, polar aprotic DMF was used as excellent mother solvent to promote the solubility and crystallization of the products. The appropriate amount of water adding into DMF solvent facilitates the ionization of polycarboxylic acids, thus the coordination ability and bonding degree of organic ligands were improved to form more complicated crystal structures [15]. This solvent-regulated strategy proposes a proper approach to the structural fine-tuning of MOFs with a given raw reactant in reticular chemistry.

3.4. Phase analyses and thermal stabilities

PXRD technique has been used to detect the phase purity of the bulk samples of MOFs **1-3** in the solid state (Fig. S1). The PXRD patterns of as-synthesized powders of **1-3** match well with those of the single-crystal simulated, which confirms the crystalline phase purities.

Thermogravimetric analyses (TGA) were carried out to testify the thermal stability of complexes 1-3 (Fig. 6). 1 and 2 keep stable below ca. 60 °C and with the temperature increasing, the sustained mass loss of MOFs materials began soon. The solvent escaping and framework collapse last until 530 °C and 550 °C with the final remnant 22.0 % and 17.2 %, respectively. The TG curve of **3** presents a platform in the range of ambient temperature to 120 °C and the framework starts to decompose until 530 °C. A final weight residual of 25.8 % corresponds rightfully to the ZnO solid.



Fig. 6. TG curves of MOFs 1-3.

3.5. Photoluminescent properties

The solid-state emission spectra of free ligands and complexes 1-3 were examined at room temperature (Fig. 7). The free H₄bdcpp powders display an emission maximum at 390 nm upon excitation at 340 nm, which is assigned to ligand-centered π - π * electronic transitions. Under the irradiation of 290 nm ultraviolet light, bulk samples of complexes 1-3 exhibit a sharp emission at 357 nm, 363 nm and 353nm, respectively. The blue shift of 33 nm, 27 nm, and 37 nm of complexes 1-3, compared with the emission spectra of free ligand, should be attributed to metal-to-ligand charge transfer (MLCT) or intraligand (π - π *) charge emission (ILCT) [16]. The enhanced luminescent emission of the MOFs, far stronger than free H₄bdcpp, may be originated from Zn/bdcpp coordination, strong interaction of Zn₂(COO)₄ paddle-wheels and compact crystal packing. These results indicate that such MOF materials could be good candidates for potential photoactive

fluorescent probes [17].



Fig. 7. Fluorescent emission spectra of MOFs 1–3 and free H₄bdcpp in the solid state.

4. Conclusions

In conclusion, an intriguing MOF system was constructed from $Zn_2(COO)_4$ paddle-wheels SBUs and V-shaped tetracarboxylate linker. The judiciously solvent-regulated strategy induced four congenetic zinc(II)-based MOFs with various frameworks including 1D loop ladder chains, 2D *sql* plane and 2D bilayered structure. The results exemplified the solvent types and constitutes in synthetic system play an important role in the microstructural fine-tuning of MOFs. Compared with free ligand, bulks of synthesized MOFs present excellent luminescent emission with the higher intensity. A deeper exploration of solvent effect in the syntheses of MOFs crystalline materials with aromatic polycarboxylates will lead to the discovery of more controllable framework architectures.

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Appendix A. Supplementary material

Supplementary pictures and tables for 1-4. See http://dx.doi.org/???. The crystal and refining data of complexes 1-4 can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc. cam.ac.uk/data_request/cif.

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Highlights:

• Four new solvent-regulated congenetic zinc(II)-based MOFs were synthesized solvothermally.

- MOFs materials were characterized by single-crystal XRD, elemental analysis, FT-IR, PXRD, TGA and photoluminescent techniques.
- Various frameworks including 1D loop chains, 2D *sql* plane and 2D bilayered structure were created.
- This approach for solvent-regulated strategy to allow the structural fine-tuning provides a good role model in reticular chemistry.

Graphical Abstract - synopsis

Four congenetic zinc(II) MOFs from delicate solvent-regulated strategy: structural diversities and fluorescent properties

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Yao-Yu Wang

A judiciously solvent-regulated strategy induced four congenetic zinc(II)-based fluorescent MOFs including 1D loop chains, 2D *sql* plane and 2D bilayer.

Graphical Abstract - pictogram

