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# Structural Diversity in Six Mixed Ligand Zn(II) Metal-Organic Frameworks Constructed by Rigid and Flexible Dicarboxylates and Different N, N' Donor Ligands

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## ABSTRACT

Three different N.N'-donor ligands with Zn(NO<sub>3</sub>)<sub>2</sub> 6H<sub>2</sub>O and two different dicarboxylates, flexible succinate (suc) and rigid fumarate (fum) afforded six different metal-organic frameworks (MOFs). Among the N,N'-donor ligands, one is bent 1,4-bis(3-pyridyl)-2,3diaza-1,3-butadiene (3-bpdb), gives two isostructural 2D MOFs,  $\{[Zn(3-bpdb)]$  $(suc)].(H_2O)_2_n$  (1) and  $\{[Zn(3-bpdb) (fum) (H_2O)_2]\}_n$  (2). The use of straight N,N'-donor ligand, *ie* 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene (4-bpdb) results two 3D MOFs, {[Zn<sub>4</sub>(4 $bpdb_{2}(suc)_{3}(OH)_{2}].5(H_{2}O)_{n}$  (3) and  $\{[Zn(4-bpdb)(fum)].(H_{2}O)_{2}\}_{n}$  (4). Here, 3 is a pillared layer structure whereas 4 has fivefold interpenetrated dimondoid network. For both the bent and straight N,N'-donor ligands there are imine alike motif is embedded in the structure. When this motif is replaced by C-C double bond by using the ligand, the ligand 1,2-bis(4pyridyl)ethylene (bpee), it produces two MOFs,  $\{[Zn(bpee)(suc)]_2, (H_2O)_3\}_n$  (5) and  $\{[Zn_2(bpee)_2(fum)_2], (H_2O)\}_n$  (6), having similar structural relation like 3 and 4 respectively, 5 with pillared layer structure and 6 with five-fold interpenetrated dimondoid network. All the compounds have been thoroughly characterized by powder X-ray diffraction (PXRD), elemental analysis, infrared (IR) spectroscopy, UV-vis spectroscopy, thermogravimetric (TG) analyses. The gas/solvent vapor sorption studies have been carried out for compounds 3-6 those having 3D structures. In case of  $\mathbf{3}$  an interesting reversible crystalline to crystalline transformation was observed which has been thoroughly studied by PXRD analysis, IR and UV-vis spectroscopy. Solid state emission spectral analysis for all the complexes has been performed at room temperature.

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#### INTRODUCTION

From the past decade, metal-organic frameworks (MOFs) have remained in the effective domain of interest for the chemists, due to their fascinating property<sup>1-8</sup> as well as their applications in several areas of modern importance.<sup>9-20</sup> The structure-property relationship<sup>21-</sup> <sup>23</sup> of these MOFs are one of the major criteria for the investigation of such system for their possible real world applications. In connection to that it has been found that although, some of the physical properties of MOFs have been well interpreted on the basis of their structures,<sup>21-23</sup> but many of those are yet to know. It has been also observed that the careful design with the use of suitable linkers/co-linkers along with appropriate metal ions may originate materials with desired structural arrangement which will endorse specific application of interest as well<sup>21-22</sup>. In a MOF, structural arrangement of the building unit and the resultant overall framework topology is generally the key factor for the bulk-property of that particular system<sup>24</sup> and that is why it is always important to analyze the topology of the system. Therefore, logical design of MOFs with the use of well established strategies of reticular chemistry,<sup>25-29</sup> i.e. through judicious metal-ligand combination; produces recurrent structural diversity with captivating topologies<sup>25-29</sup> and tunable properties<sup>30-31</sup> for the achievement of next generation materials.9, 32

It is worth to mention that the MOFs with various functional pores, always remained in the limelight for their various applications<sup>2,4,9</sup> and in the synthesis of such MOFs, the use of multi- carboxylic acid donors and pyridyl-containing co-ligands have been proven to be an efficient strategy.<sup>33-35</sup> Successful synthesis of the materials incorporating the aforesaid verity of ligands will serve the purpose of design and also important to classify the core architecture or the topologies.<sup>33-35</sup> The ligands with acyclic multi-carboxylate donors provide topologically appealing structures,<sup>26,36</sup> and the employment of pyridyl co-linkers can enhance this diversity in a multiplicative manner.<sup>37</sup> In addition to that, on changing the position of donor atom<sup>38</sup> and/or introduction of double bond,<sup>39</sup> and/or atom replacement<sup>40</sup> in a ligand motif may enhance functionality as this effectively changes the coordination pattern and hence the nature of bulk or surface property of the system.<sup>38-40</sup> On the other hand, type of metal ion is also an active factor to create the overall structure, affecting functionality as well.<sup>24,35</sup> It has been observed that the Zn(II) containing MOFs are found with enormous possibility of various application like host–guest chemistry,<sup>9,41</sup> luminescent materials,<sup>9,42</sup> OLED or NLO materials,<sup>39,43</sup> heterogeneous catalysis<sup>15,44</sup> so on and so forth.



Scheme 1. Synthetic outline of complexes 1-6



Scheme 2. Ligand used for the synthesis of complexes 1-6

With an attempt for a detailed investigation of the above mentioned understanding, Zn(II) has been chosen as the metal centre in this present work and we have synthesized six MOFs (Scheme 1) with three different N, N' donor ligands and a flexible and rigid dicarboxylate namely succinate and fumarate respectively (Scheme 2). The use of a bent coordinating 1,4-bis(3-pyridyl)-2,3-diaza-1,3-butadiene (3-bpdb) along with succinate (suc) and fumarate

(fum) results the formation of two isostructural two dimensional MOFs, {[Zn(3-bpdb)]  $(suc)].(H_2O)_2_n$  (1) and  $\{[Zn(3-bpdb)(fum)(H_2O)_2]\}_n$  (2). The use of straight chain 1,4-bis(4pyridyl)-2,3-diaza-1,3-butadiene (4-bpdb), along with the same dicarboxylates used in previous case results the formation of three dimensional MOFs  ${[Zn_4(4$  $bpdb_4(suc)_3(OH)_2[.5(H_2O)]_n$  (3) and  $\{[Zn(4-bpdb)(fum)], (H_2O)_2\}_n$  (4). Here 3 shows a pillared layer structure and 4 is a fivefold interpenetrated dimondoid network. Now moving to the use of a shorter length ligand straight linker; 1,2-bis(4-pyridyl)ethylene (bpee), along with suc and fum produced two MOFs,  $\{[Zn(bpee)(suc)]_2, (H_2O)_3\}_n$  (5) and  $\{[Zn_2(bpee)_2(fum)_2], (H_2O)\}_n$  (6), where similar structural difference like 3 and 4 has been found. The 5 shows a pillar-layer structure and fum containing 6 produced five fold interpenetrated dimondoid network. All these observations are based upon the characterization of the above compounds single crystal X-ray diffraction, powder X-ray diffraction (PXRD), elemental analysis, infrared (IR) spectroscopy, UV-vis spectroscopy, thermogravimetric (TG) analyses. The gas/solvent vapor sorption study has been performed for all four 3D compounds (3-6). In case of 3 an interesting reversible crystalline to crystalline transformation was observed which has been thoroughly investigated by PXRD analysis, IR spectroscopy and UV-vis spectroscopy. Photoluminescence of all the compounds along with their constituent ligands has also been studied.

#### **EXPERIMENTAL SECTION**

**Materials** Highly pure  $Zn(NO_3)_2 \cdot 6H_2O$ , 1,2-bis(4-pyridyl)ethylene (bpee), pyridene-4aldehyde and pyridene-3-aldehyde were purchased from the Sigma-Aldrich Chemical Co. All other reagents and solvents were purchased from commercial sources and were used without further purification. 1,4-bis(3-pyridyl)-2,3-diaza-1,3-butadiene (3-bpdb) and 1,4-bis(4pyridyl)-2,3-diaza-1,3-butadiene (4-bpdb) were synthesized by typical condensation reaction between pyridene-4-aldehyde or pyridene-3-aldehyde and hydrazine hydrate following the reported procedure.<sup>45,36</sup> Na<sub>2</sub>-suc or Na<sub>2</sub>-fum was synthesized by the slow addition of solid NaHCO<sub>3</sub> to the corresponding acid (H<sub>2</sub>-suc and H<sub>2</sub>-fum respectively) in water in a 2:1 ratio and was allowed to evaporate until dryness.

**Physical Measurements** Elemental analyses (carbon, hydrogen, and nitrogen) were performed using a Heraeus CHNS elemental analyzer. Infrared spectra (4000–400 cm<sup>-1</sup>) were taken on KBr pellet, using Perkin–Elmer Spectrum BX-II IR spectrometer. Thermal analysis (TGA) was carried out on a METTLER TOLEDO TGA 850 thermal analyzer under nitrogen atmosphere (flow rate: 30 cm<sup>3</sup> min<sup>-1</sup>) at the temperature range 30-600° C with a heating rate

of 2° C/min. X-ray powder diffraction (PXRD) patterns in different states of the samples were recorded on a Bruker D8 Discover instrument using Cu-K $\alpha$  radiation ( $\lambda = 1.5406$  Å), operating at 40 kV and 40 mA. Absorption spectra of the solid samples were collected in Perkin–Elmer Lamda-35 instrument with integrating sphere arrangement. Fluorescence measurements were done using Horiba FluoroMax 4.

# Synthesis of $\{[Zn(suc)(3-bpdb)], (H_2O)_2\}_n$ (1).

An aqueous solution (4 ml) of disodium salt of succinic acid (Na<sub>2</sub>-suc) (0.25 mmol, 41 mg) was mixed slowly with a methanolic solution (4 ml) of 3-bpdb (0.25 mmol, 53 mg) and stirred for 30 min to prepare the mix-ligand solution.  $Zn(NO_3)_2 \cdot 6H_2O$  (0.25 mmol, 75 mg) was dissolved in 4 mL water and then in a long crystal tube 4 ml of Zn(II) solution was slowly and cautiously layered with the 8 ml of aforesaid mixed-ligand solution, separated by 2 mL of a 1:1 water-methanol buffer. Yellow-colored needle-shaped single crystals suitable for X-ray diffraction analysis were obtained from the junction of the layer after one week. The crystals were separated and washed with copious amounts of cold 1:1 (v/v) water and methanol, and dried under air (yield = 71% based on Zn). Anal. Cal. for C<sub>16</sub>H<sub>18</sub>N<sub>4</sub>O<sub>6</sub>Zn (427.73), **1** : C, 44.93; H, 4.24; N, 13.10. Found: C, 44.81; H, 4.42; N, 13.29. IR spectra (KBr pellet, 4000–400 cm<sup>-1</sup>): 3138 (m), 1632 (s), 1599 (s), 1551 (m), 1468 (s), 1430 (s), 1397 (m), 1313 (s), 1238 (s), 1190 (s), 1162 (m), 1126 (s), 1051 (s), 1027 (m), 974 (m), 946 (m), 874 (m), 812 (m), 701 (m), 661 (m), 641 (m), 407 (s).

# Synthesis of $\{[Zn(fum)(3-bpdb)(H_2O)_2]\}_n$ (2).

Compound **2** has been synthesized using the same procedure as that of **1**, using disodium salt of fumaric acid (Na<sub>2</sub>-fum) (1 mmol, 160 mg) instead of disodium salt of succinic acid (Na<sub>2</sub>-suc). After 14 days, needle shaped yellow crystals were obtained from the middle of the tube and were separated and washed with methanol (yield = 67% based on Zn). Anal. Cal. for  $C_{16}H_{16}N_4O_6Zn$  (625.71), **2** : C, 45.14; H, 3.79; N, 13.16. Found: C, 45.02; H, 3.88; N, 13.37. IR spectra (KBr pellet, 4000–400 cm<sup>-1</sup>): 3180 (b), 1632 (s), 1599 (s), 1580 (m), 1555 (s), 1467 (s), 1431 (s), 1385 (s), 1313 (s), 1206 (m), 1189 (m),1126 (m), 1052 (s), 1028 (s), 970 (s), 944 (s), 875 (s), 803 (s), 699 (s), 680 (s), 642(s), 592 (s), 405 (s).

#### Synthesis of $\{[Zn_4(4-bpdb)_2(suc)_3(OH)_2] \cdot 5H_2O\}_n$ (3).

Compound **3** has been synthesized by the same procedure as that of **1** using 4-bpdb (1 mmol, 210 mg) instead of 3-bpdb. Unlike the compounds, here the yellow colored block crystals were obtained after a longer time. After seven weeks the crystals were obtained from the middle of the tube and were separated and washed with methanol (yield = 69% based on Zn). Anal. Cal. for  $C_{36}H_{44}N_8O_{19}Zn_4$  (1154.33), **3** : C, 37.46; H, 3.84; N, 9.71. Found: C, 36.99; H,

4.11; N, 9.33. IR spectra (KBr pellet, 4000–400 cm<sup>-1</sup>): 3377 (b), 3260 (b), 2985 (m), 1613 (m), 1570 (s), 1434 (s), 1416 (m), 1383 (s), 1308 (s), 1292 (s), 1226 (m), 1170 (m), 1068 (s), 1027 (m), 960 (m), 880 (s), 814 (m), 691 (s), 670 (m), 532 (m), 505 (m).

# Synthesis of $\{[Zn(fum)(4-bpdb)], (H_2O)_2\}_n$ (4).

Compound **4** has been synthesized adopting the same procedure as that of **1**, using disodium salt of fumaric acid (Na<sub>2</sub>-fum) (1 mmol, 160 mg) instead of disodium salt of succinic acid (Na<sub>2</sub>-suc) and 4-bpdb (1 mmol, 210 mg) instead of 3-bpdb . After 7 days, yellow needle alike crystals were obtained from the middle of the tube and were separated and washed with methanol (yield = 76% based on Zn). Anal. Cal. for  $C_{16}H_{16}N_4O_6Zn$  (625.72), **4** : C, 45.14; H, 3.79; N, 13.16. Found: C, 45.37; H, 3.63; N, 13.29. IR spectra (KBr pellet, 4000–400 cm<sup>-1</sup>): 3435 (b), 1616 (s), 1596 (s), 1428 (s), 1366 (s), 1335 (m), 1228 (m), 1192 (m), 1063 (s), 1029 (s), 957 (m), 823 (s), 799 (s), 693 (s), 517 (s), 427 (s).

# Synthesis of $\{[Zn(suc)(bpe)]_2, (H_2O)_3\}_n$ (5).

Compound **5** has been synthesized using the same procedure as that of **1**, using 1,2-bis(4pyridyl)ethylene (bpee) (1 mmol, 182 mg) instead of 3-bpdb. After 14 days, white block crystals were obtained from the middle of the tube and were separated and washed with 1:1 methanol/water (yield = 76% based on Zn). Elemental analysis calculated for  $C_{32}H_{34}N_4O_{11}Zn_2$  (781.36), **5**: C, 49.19; H, 4.39; N, 7.17. Found: C, 49.36%; H, 4.27%; N, 7.32%. IR spectra (KBr pellet, 4000–400 cm<sup>-1</sup>): 3391 (b), 1613 (s), 1506 (s), 1432 (s), 1402 (m), 1292 (s), 1253 (s), 1221 (s), 1206 (s), 1189 (s), 1153(m), 1070 (s), 1028 (s), 984 (m), 879 (m), 840 (s), 629 (m), 568 (m), 553 (m).

#### Synthesis of $\{[Zn_2(fum)_2(bpee)_2], (H_2O)\}_n$ (6).

Compound **6** has also been synthesized using the same procedure as that of **1**, using 1,2bis(4-pyridyl)ethene (bpee) (1 mmol, 182 mg) instead of 3-bpdb and disodium salt of fumaric acid (Na<sub>2</sub>-fum) (1 mmol, 160 mg) instead of disodium salt of succinic acid (Na<sub>2</sub>-suc). After 10 days, white block shaped crystals were obtained from the middle of the tube and were separated and washed with 1:1 methanol/ H<sub>2</sub>O (yield = 65% based on Zn). Anal. Cal. for  $C_{32}H_{26}N_4O_9Zn_2$  (741.35), **6** : C, 51.84; H, 3.53; N, 7.56. Found: C, 51.63; H, 3.68; N, 7.37. IR spectra (KBr pellet, 4000–400 cm<sup>-1</sup>): 3550 (b), 3055 (m), 1614 (m), 1593 (m), 1432 (m), 13798 (m), 1254 (s), 1208 (s), 1187 (s), 1068 (s), 1026 (s), 981 (m), 841 (s), 798 (s), 695 (s), 552 (m).

The bulk compounds of **1-6** have been synthesized in powder form by the direct mixing of the corresponding solution of ligands and metal salt in water at their equal molar ratio. For all the compounds a precipitate appeared within 10 minutes of mixing and the

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solution is then stirred further for three hours; except the **3**. For compound **3** the stirring is continued for overnight. The compounds were separated by filtration and it is washed with small amount of 1:1 (v/v) methanol/water and dried in air. Compounds purity was verified by PXRD, which give good correspondence between simulated and bulk-phase PXRD. The purity of the bulk sample was further confirmed by the results of elemental analysis and IR spectra as well, which is also found in accordance with the data obtained for the single crystals.

Single-Crystal Structure Analysis The single crystals of compounds 1-6 were mounted on thin glass fibers with commercially available super glue. single crystal X-ray data collection of all of these six crystals were collected at room temperature using Bruker APEX II diffractometer, equipped with a normal focus, sealed tube X-ray source with graphite monochromated Mo-K $\alpha$  radiation ( $\lambda$ = 0.71073Å). The data were integrated using SAINT<sup>46</sup> program and the absorption corrections were made with SADABS.<sup>47</sup> All six structures were solved by SHELXS 2014<sup>48</sup> using Patterson method and followed by successive Fourier and difference Fourier synthesis. Full matrix least-squares refinements were performed on F<sup>2</sup> using SHELXL-2014<sup>48</sup> with anisotropic displacement parameters for all non-hydrogen atoms. Potential solvent accessible area or void space was calculated using PLATON<sup>48</sup> multipurpose crystallographic software. All the hydrogen atoms were fixed geometrically by HFIX command and placed in ideal positions in case of all structures. Calculations were carried out using SHELXL 2014,<sup>48</sup> SHELXS 2014,<sup>48</sup> PLATON v1.15,<sup>49</sup> ORTEP-3v2,<sup>50</sup> WinGX system Ver-1.80<sup>51</sup> and TOPOS.<sup>52,53</sup> Data collection and structure refinement parameters along with crystallographic data for **1-6** are given in Table 1.

#### **Sorption Measurements**

Ambient pressure volumetric N<sub>2</sub> gas adsorption study was carried out at 77 K with the desolvated samples of **3** (**3'**), **4**, **5** and **6**, maintained by a liquid-nitrogen bath, in the relative pressures ranging from 0 to 1 using a Quantachrome Autosorb-iQ adsorption instrument.  $CO_2$  sorption measurements were also performed at 195 K (dry ice-acetone cold bath) with same pressure range and on same instrument. High purity gases were used for the adsorption measurements (nitrogen, 99.999%; carbon dioxide, 99.95%). For water vapor sorption measurement, experiment was performed at 298 K in the pressure range 0 to 0.9 with the same instrument. Extent of adsorption was determined by monitoring the change in pressure at the equilibrium state of the sample tube containing adsorbates. All operations were computer-controlled and automatic.

Table 1. Crystallographic and Structural Refinement Parameters for 1-6								
	1	2	3	4	5	6		
formula	$C_{16}H_{18}N_4O_6Zn$	C <sub>16</sub> H <sub>16</sub> N <sub>4</sub> O <sub>6</sub> Zn	$C_{36}H_{44}N_8O_{19}Zn_4$	$C_{16}H_{16}N_4O_6Zn$	$C_{32}H_{34}N_4O_{11}Zn$	$C_{32}H_{26}N_4O_9Zn_2$		
formula weight	427.73	425.72	1154.33	425.71	781.413	741.35		
crystal system	monoclinic	monoclinic	mriclinic	monoclinic	orthorhombic	triclinic		
space group	$P2_{1}/n$	$P2_{1}/n$	Pī	C2/c	Fdd2	Pī		
<i>a</i> / Å	9.0977(2)	9.0519(7)	8.6199(9)	25.540(5)	37.910(3)	11.3553(2)		
a/Å	8.9913(2)	9.0401(7)	10.1025(10)	5.831(5)	8.2837(5)	11.4115(2)		
<i>c</i> / Å	11.2330(2)	11.1496(8)	14.4797(15)	15.508(5)	21.1744(15)	13.1231(2)		
α/°	90	90	81.768(7)	90	90	104.149(1)		
β/°	105.660(1)	105.451(5)	82.393(6)	118.202(5)	90	99.867(1)		
γ/°	90	90	87.194(7)	90	90	100.074(1)		
V/ Å3	884.75(3)	879.40(12)	1236.4(2)	2035.3(19)	6649.5(8)	1582.14(5)		
Ζ	2	2	1	2	8	2		
$D_{\rm c}$ / g cm <sup>-3</sup>	1.606	1.608	1.537	1.376	1.549	1.552		
$\mu$ /mm <sup>-1</sup>	1.431	1.439	1.994	1.243	1.509	1.577		
F(000)	440	436	578	856	3168	752		
$\theta$ range/°	2.6-27.5	2.6-27.6	1.4-27.8	1.8-27.5	2.1-27.8	1.6-27.5		
reflections collected	13680	14654	18786	15091	26012	26875		
unique reflections	2036	2022	5635	2345	3898	7232		
reflections $I > 2\sigma(I)$	1582	1336	3122	2122	3562	5704		
R <sub>int</sub>	0.043	0.088	0.070	0.022	0.055	0.033		
goodness- of-fit $(F^2)$	1.03	1.05	0.97	1.02	1.05	1.05		
$\frac{R1}{2\sigma(I)}^{a}$	0.0299	0.0495	0.0819	0.0548	0.0337	0.0341		
$wR2(I > 2\sigma(I))^a$	0.0690	0.1387	0.2602	0.1740	0.0890	0.0854		
$^{a}$ R	$\mathbf{L}_1 = \boldsymbol{\Sigma} \mid  F_0  -  F_0 $	$   /\Sigma  F_{o} , WR_{2}$	$_{2} = [\Sigma (w (F_{o}^{2} - F_{o}))]$	$(c^2)^2)/\Sigma w (F_0^2)^2$	<sup>2</sup> ] <sup><sup>1</sup>/<sub>2</sub></sup> .			

# TablesTable 1. Crystallographic and Structural Refinement Parameters for 1-6

#### **RESULTS AND DISCUSSION**

# Synthesis

At room temperature Zn(II) along with salt of two dicarboxylic acids and three different N,N'-donor linkers, 3-bpdb (1 and 2), 4-bpdb (3 and 4), and bpee (5 and 6) in methanol/water medium are used for synthesis of all the compounds 1-6 employing slow diffusion technique (Scheme 1).

Structural description of  $\{[Zn(3-bpdb)(suc)(H_2O)_2]\}_n$ (1) {[Zn(3and bpdb)(fum)(H<sub>2</sub>O)<sub>2</sub>]}<sub>n</sub> (2). Single-crystal X-ray structural analysis revealed that compounds 1 and 2 are isostructural having monoclinic  $P2_1/n$  space group with only difference in the nature of dicarboxylate linkers (succinate in 1 and fumarate in 2). Both the compounds show the formation of a two-dimensional (2D) structure of Zn (II) ions linked by 3-bpdb linker and bridging succinate in the case of 1 and fumarate in the case of 2. Here, in both cases Zn(II)center is located in a special position (1, 0, 1) and the asymmetric unit contains half of Zn(II) along with half 3-bpdb linker, half dicarboxylate ligand and one coordinated water molecule. Here, each hexa-coordinated Zn(II) centers with ZnN<sub>2</sub>O<sub>4</sub> binding set displays a distorted octahedral geometry created by two carboxylate O atoms (O1 and  $O1^{a}$ ) from two different dicarboxylate (suc in 1 and fum in 2), two symmetry generated coordinated water molecules (O1W and O1W<sup>a</sup>) and two 3-pyridyl nitrogen atoms (N1 and N1<sup>a</sup>) from two 3-bpdb linkers (Figure 1a for 1 and Figure 1b for 2).



**Figure 1.** View of the coordination environment around Zn(II): (a) for compound **1**, (b) for compound **2**; Zn (green), N (blue), O (red), C (gray). (Symmetry code a = 2-x, -y, 2-z.)

In **1** and **2**, Zn–O bond lengths vary from 2.0522(14)–2.0985(15) Å and 2.056(3)–2.095(3) Å, respectively, and the corresponding Zn–N bond lengths are 2.2093(18) (Table S1) and 2.200(4) (Table S2) for **1** and **2**, respectively. The selected bond lengths and bond angles are reported in Table S1 for **1** and Table S2 for **2**. Here, each dicarboxylate ligand binds in a bridging monodentate fashion in between two Zn(II) centers resulting the formation of a 1D metal carboxylate chain (Figure S2a for **1** and Figure S2b for **2**). The 1D metal-carboxylate

chains are joined by the 3-bpdb linkers to form a 2D arrangement in the crystallographic *ab* plane (Figure 2a for **1** and Figure 2b for **2**).



Figure 2. Two-dimensional sheet structure viewed along c axis: (a) for compound 1, (b) for compound 2. Schematic view of the 4-Connected 2D net: (c) for compound 1, (d) for compound 2.

The TOPOS<sup>52,53</sup> analysis reveals that both the structures can be represented as a 4-connected uninodal net (Figure 2c for 1 and Figure 2d for 2) with point symbol  $\{4^4.6^2\}$ . In the crystal packing, the coordinated water are attached with the free carboxylate oxygen atoms by means of H-bonding forming a supramolecular 3D structure in the crystallographic *ac* plane for both of them (Table S3 for 1 and Table S4 for 2; Figure 3 for 1 and Figure S3 for 2).



**Figure 3.** (a) 1D metal carboxylate chains stitched by lattice water molecules in **1**. (b) Supramolecular 3D arrangement in **1** (H bonding: cyan dotted lines).

It is worth to mention that although there is some rigidity in the fum relative to the suc, the positional effect and the bent nature of the 3-bpdb linker circumvent the effect of the double bond present in the fumarate, resulting similar bonding nature and net topology.

# Structural description of $\{[Zn_4(4-bpdb)_2(suc)_3(OH)_2] \cdot 5H_2O\}_n$ (3) and $\{[Zn(4-bpdb)(fum)], (H_2O)_2\}_n$ (4)

Taking a straight chain linker 4-bpdb instead of bent angular linker 3-bpdb, there is a change in binding mode as well as an enhancement of the flexibility of the N,N'-donor linker occurs which exerts a marked effect on the overall structure of the MOFs. This features, probably, acting for the rising of dimensionality for both the structures obtained with 4-bpdb. Single crystal X-ray structure determination of compound **3** reveals that it is a three-dimensional (3D) network made up of Zn(II), suc dianion and 4-bpdb spacer and the crystal belongs to the triclinic  $P_{\overline{1}}$  space group. In the asymmetric unit, there are two crystallographic independent Zn(II) ions (Zn1 and Zn2), one 4-bpdb linker, one and half of suc and a bridging OH group. Two Zn(II) centers are in two different geometrical arrangements. The hexacoordinated Zn1 centers are in a distorted octahedral geometry with ZnO<sub>5</sub>N<sub>1</sub> binding set and the coordination is provided by one 4-pyridyl nitrogen (N1) of 4-bpdb spacer, three carboxylate oxygen (O3, O4<sup>b</sup> and O6) atoms from three different suc ligands and two oxygen of bridging hydroxyl group (O1 and O1<sup>c</sup>) (Figure 4a). Every hydroxyl groups farther connect



**Figure 4.** (a) Coordination environment around Zn(II) ions in **3**; Zn (green), N (blue), O (red), C (gray). (b) 2D sheet constructed by the Zn(II) and succinate dianion. (c) Threedimensional (3D) structure in **3** with water filled 1D channels. (d) Schematic view of the 4connected 3D network of **3**. (Symmetry code: a = 1+x, 1+y, -1+z; b=1-x, 1-y, -z; c = 2-x, 1-y, -z.)

one more Zn1 and a tetrahedral Zn2 centre. The four-coordinated Zn2 is with a  $ZnO_3N_1$  binding set which is satisfied by the hydroxyl group, two carboxylate oxygen atoms (O2 and

O5<sup>b</sup>) from two bridging suc ligands and one 4-pyridyl nitrogen (N4<sup>a</sup>) atom of 4-bpdb (Figure 4a). The details of Zn–O and Zn–N bond lengths are depicted in Table S5. Among them, the Zn1–O bond length are in the range of 2.048(5) - 2.218(6)Å and Zn1–N bond lengths are 2.136(6) Å. However, the Zn2–O bond lengths lies in the range of 1.912(5) - 1.980(5) Å, and Zn2–N the bond lengths are 2.031(6) Å. Thus two set of  $Zn_2$  (Zn1 and Zn2), connected with the help of hydroxyl group, forms the secondary building unit (Figure S4) having the unit formula  $Zn_4N_4O_{12}$ . Two such units are connected by bridging suc and extend the structure along crystallographic a axis. A set of two connected suc farther, bonded to two Zn1 atoms of two different SBU and extend the structure to a Zn-suc sheet in *ab* direction (Figure 4b). Such sheets are farther linked up by 4-bpdb linkers along c axis to form the ultimate 3D structure (Figure 4c). Beyond that, the structure is further stabilized by the intermolecular  $\pi$ - $\pi$ interaction (Figure S5) and details about that is presented in the Table S6. From the topological analysis by TOPOS<sup>52,53</sup> it is revealed that this 3D structure can be represented as bi-nodal 5,7-c net (Figure 4d) with the Schläfli symbol  $\{3^4, 4^4, 5^2\}$   $\{3^5, 4^5, 5^5, 6^6\}$ . The distances of two Zn1 through the two-connected suc is 8.99Å and Zn1-Zn2 through 4-bpdb is 15.457Å. These large distances eventually create quadrilateral pores along a direction which are occupied by lattice water molecules (Figure 4c). On removal of the free water molecules, the solvent-accessible void space of **3** calculated by PLATON<sup>49</sup> is 286 Å<sup>3</sup> which is about 23.1% of the total unit cell volume.

Now, on introduction of double bond, in the dicarboxylate by use of more rigid fum instead flexible suc along with 4-bpdb and Zn(II) yielded yellow colored crystal of compound **4** having a fivefold interpenetrated diamond-type framework, which crystalises in monoclinic space group *C2/c*. Structural analysis illustrates that the asymmetric unit of **4** consists of one and half of Zn(II), fum, 4-bpdb ligands and two one-half of guest water molecules (Figure 5a). Here, each Zn(II) center exhibits a four coordinated distorted tetrahedral geometry with an N<sub>2</sub>O<sub>2</sub> donor set bonded to two oxygen atoms (O1, O1<sup>*a*</sup>) from two different fum ligands by monodentate bridging fashion and two nitrogen atoms (N1, N1<sup>*a*</sup>) from two different 4-bpdb linkers (Figure 5a). Here all the Zn-O and Zn-N bonds are 1.946(3)Å and 2.041(3) respectively. All the bond distances and bond angles around Zn(II) centers are presented in Table S7.



**Figure 5.** (a) The coordination environment around Zn1 and Zn2 atoms in 4; Zn (green), N (blue), O (red), C (gray). (b, c) Perspective view of a single diamondoid cage formed via coordination of fum and bpee to Zn(II) centres in 4. (d) A single 3D-diamondoid network showing large voids in 4. (e) Space-filling model of the five-fold interpenetrated 3D framework of 4. (f) Topological representation of the five-fold interpenetrating nets in 4 (five different 3D nets are shown in five different colours). (Symmetry code: a = 2-x, 1+y, 1/2-z)

Each fum and 4-bpdb bridges two Zn(II) centers and the arrangement finally leads to large adamantane-like cages (Figure 5b). In such an adamantane cage, Zn…Zn distances through 4-bpdb and fum are ~15.4 and ~8.8 Å, respectively. These adamantoid cages are interconnected and extended to form 3D diamondoid network with large hexagonal channels of dimension about  $18.9 \times 14.4$  Å<sup>2</sup> (Figure 5c). Topologically the framework can be presented as a 4-connected uninodal net with the Schläfli symbol {6<sup>6</sup>}(Figure 5f). Every diamondoid 3D networks are interpenetrated with another four equivalent diamondoid networks to form a Class Ia fivefold interpenetrated dimondoid network (Figure 5e-f). Notably, the channels dimension 9.6×7.3 Å<sup>2</sup> along *b* axis is outcome and guest water molecules are resides in these channels (Figure 5d). By PLATON<sup>49</sup> the solvent-accessible void space of **4** was calculated and found as 27.5% of the total crystal volume.

**Structural description of**{ $[Zn_2(bpee)_2(suc)_2]$ .(H<sub>2</sub>O)<sub>3</sub>}<sub>*n*</sub> (5) Compound 5 crystallizes in the orthorhombic *F*dd2 space group and the single-crystal X-ray structure analysis reveals the formation of a three dimensional (3D) network structure with Zn(II) metal ions connected by

suc dianion and bpee linkers. The asymmetric unit of **5** contains one Zn(II) atom, one bridging bpee ligand, one succinate and one and half latiice water molecules. As shown in Figure 6a, each Zn(II) center with  $O_2N_2$  binding set is coordinated with two 4-pyridyl



**Figure 6.** (a) Coordination environment around Zn(II) ions in **5**, where Zn (green), N (blue), O (red), C (gray); (b) View of  $[Zn(bpee)]_n$  two-dimensional (2D) grid in **5**; (c)Threedimensional (3D) structure in **5** with water filled 1D channels. (d) Schematic view of the 4connected 3D network of **5**. (Symmetry code: a = -1/4+x,5/4-y,-1/4+z; b = 3/4-x,1/4+y,-1/4+z).

nitrogen atoms (N1 and N2<sup>*b*</sup>) from two different linear bpee linkers and two carboxylate oxygen atoms (O1 and O3<sup>*a*</sup>) from two different bridging succinate displaying a distorted tetrahedral geometry. The Zn-O bond lengths lie in the range of 1.929(3) to 1.947(3) Å whereas Zn-N bond lengths are 2.029(3)-2.066(2) Å (Table S8). Other bond lengths and angles of Zn(II) coordination spheres are listed in Table S8. Here, each suc dianion binds two Zn(II) centers in a bridging monodentate fashion to yield a undulating  $[Zn(suc)]_n$  chain (Figure S7a), which is further cross linked by bpee co-ligands along two different directions (Figure 6b) to develop a 3D porous framework with the 1D channel along the crystallographic *b*-axis, which are occupied by lattice guest water molecules (Figure 6c). As calculated by PLATON<sup>49</sup>, without these lattice water molecules, the solvent-accessible void space of **5** is found as 7.8% of the total crystal volume. The structure is farther stabilized by the  $\pi$ - $\pi$  weak interaction (Figure S7b). Details are provided in the Table S9. The TOPOS<sup>52,53</sup>

analysis reveals that the structure can be represented as a 4-connected uninodal net (Figure 6d) with Schläfli symbol for net  $\{4^2, 8^4\}$ .

**Structural description of**  $\{[Zn_2(bpee)_2(fum)_2].(H_2O)\}_n$  (6) Compound 6 crystallizes in the triclinic *P*<sup>T</sup> space group and the single crystal X-ray structure determination reveals a three-dimensional (3D) fivefold interpenetrating diamondoid network made up of Zn(II), fum dianion and bpee spacer. The asymmetric unit contains two crystallographically independent Zn(II) ions (Zn1 and Zn2), one complete fum ligand, halves of two fum ligands with other environment, one complete bpee linker, halves of two other bpee linkers and one guest water molecule (Figure 7a). The penta-coordinated Zn1 center is in a distorted square pyramidal



**Figure 7.** (a) The coordination environment around Zn1 and Zn2 atoms in **6**; Zn (green), N (blue), O (red), C (gray). (b) Perspective view of a single diamondoid cage formed via coordination of fum and bpee to Zn(II) centres in **6**. (c) A single 3D-diamondoid network showing large voids in **6**. (d) Space-filling model of the five-fold interpenetrated 3D framework of **6**. (e) Topological representation of the five-fold interpenetrating nets in **6** (five different 3D nets are shown in five different colours). (Symmetry code: a = 1+x, 1+y, 1+z)

geometry with 0.32 Addison parameter (tau) value<sup>54</sup> and  $O_3N_2$  binding set satisfied by four carboxylate oxygen (O3, O7 and O8) atoms from two bridging fum ligands and two 4-pyridyl nitrogen (N2 and N3) atoms from two different bpee spacers (Figure 7a). The hexa-coordinated Zn2 shows a distorted octahedral geometry with a  $O_4N_2$  binding set and the coordination is provided by four carboxylate oxygen atoms (O1, O2, O5 and O6) from two

bridging fum ligands and two 4-pyridyl nitrogen (N1 and N4<sup>a</sup>) atoms from two different bpee spacers (Figure 7a). The Zn–O and Zn–N bond lengths and related angles for Zn1 and Zn2 centers are slightly different (Table S10). Among them, the Zn1–O and Zn1–N bond lengths are in the range of 1.9524(17)-2.6041(19) Å and 2.0466(18)-2.0609(18) Å, respectively. However, the Zn2–O bond lengths lies 2.116(2)–2.5352(19) Å, and Zn2–N the bond lengths are 2.0468(18) and 2.0886(19) Å. Other bond lengths and angles within the coordination spheres are listed in Table S10. Both the Zn(II) ions act as 4-connected nodes which are connected with each other by the fum and bpee linkers to generate a large adamantane-like cages (Figure 7b and S8a-b). Topological analysis by TOPOS<sup>52,53</sup> reveals that the structure can be represented as a 4-connected dia net topology (Figure 7c, 7e) with the Schläfli point symbol  $\{6^6\}$ . Due to the crystallographic difference between the fum dianion ligands, the Zn…Zn distances through fum are 8.747, 8.902 and 9.148 Å; whereas, Zn…Zn distances through the three crystallographically different bpee ligands are 13.377, 13.437 and 13.439 Å. These adamantoid cages are interlinked and extended to form 3D diamondoid network with large hexagonal channels of about  $16.7 \times 19.4$  Å<sup>2</sup> (Figure 7d-e), which facilitate further nucleation in the void spaces and allow the formation of equivalent diamondoid net in those regions to generate a Class Ia fivefold interpenetrated dimondoid network (Figure 7d-e). Calculation by PLATON<sup>49</sup> suggests that this system contain 5.5% solvent accessible void of total crystallographic volume without the lattice water molecules.

From the above discussion of all the structures it is evident that the ligands have marked influence on the overall structure of the compounds. In case of 1 & 2, the ultimate structure is influenced by the bent nature of the 3-bpdb ligand, resulting same structure thumping the effect rigid or flexible co-linkers. On moving to straight coordinating N, N' donor ligand, the enhancement in flexibility, may leads to the formation of the higher dimensional structures. Structural similarity in 3 & 5 and 4 & 6 pairs suggests here the overall structures is less directed by the N, N' donor ligand in comparison to that of 1 & 2. As described earlier in last two pairs both succinate containing 3 & 5 gives pillared layer 3D structures whereas fumarate containing 4 & 6 forms Class Ia fivefold interpenetrated structure. The rigidity of the fumarate is possibly responsible for the formation of rigid large hexagonal channels which finally turns into the interpenetrated structures.

## 

# Thermogravimetric Analysis (TG) and Powder X-ray Diffraction (PXRD) Study

To study the framework stability of the compounds **1-6**, thermo gravimetric analyses (TGA) and powder X-ray diffraction (PXRD) studies are carried out. For both the studies crystalline powder sample is used and TGA have been carried out in the range of 25–650 °C (Figure S9). Single crystal analysis has shown that iso-structural compound 1 and 2 have no solvent molecule and TGA is consistent with this and there is no significant weight-loss up to  $\sim 200$ °C for both of them and then a steady decrease of weight-loss have been observed in the TGA. Eventually, compound **3** shows a gradual weight-loss with a step of 7.66% (40–80 °C). which corresponds to the escape of guest water molecules and the weight lose is equivalent to  $\sim$ 5 (4.88) water molecules. The desolvated framework is stable up to 150 °C and after that it steadily disintegrates to unrecognized product. TGA curve (Figure S9) of the compound 4 shows there is no significant weight loss up to 90 °C and then it starts gradual weight-loss with a step of 8.12% up to 190 °C, corresponds to ~2 water molecules. This dehydrated framework is stable up to 270 °C. Afterwards it continuously dissociate to unidentified product. The TG analysis of 5 depict that guest water molecules are started to escape just after 40 °C and continuous up to 137 °C. A certain change in slope at ~137 °C temperature indicate that guest molecules are completely removed from the system with  $\sim$ 7 % weight loss which is equivalent to  $\sim 3$  water molecules. Afterwards with almost same rate (but not equal) it dissociates to unrecognized products. From TGA it has been revealed that compound 6shows a sharp weight-loss with a step of 2.48 % (60–90  $^{\circ}$ C), corresponds to the escape of one guest water molecules from the compound. This dehydrated framework is stable up to 370 °C with no significant weight lose. This is followed by a sharp weight loss, caused by unrecognized product probably due to the decomposition of the frameworks.

For all the compound bulk phase purity is confirmed by the PXRD pattern of the simulated and as-synthesized data and it is clearly observable the bulk phase is good accordance with the single crystal XRD data (Figure 8).



Figure 8. Powder X-ray diffraction patterns of all the compounds (a) 1, (b) 2, (c) 3, (d) 4, (e) 5 and (f) 6.

## Study of crystalline to crystalline transformation in 3

The PXRD pattern of desolvated phase of **3** (**3'**) displays shifting of a few peak positions along with the appearance of some new peaks in comparison to the as-synthesized pattern of **3** (Figure 9), signifying, rather than disintegration structural transformation after removal coordinated molecules has taken place. Indexing of the PXRD data of **3'** (Figure S10) using TREOR program<sup>52, 53</sup> implies a structural contraction along *c* axis by 23.48% (Table S11) associated with the reduction of 21.11% in volume after the removal of the solvent molecules.



Figure 9. Powder X-ray diffraction patterns of 3 in different state.

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On immersion of **3'** to water as well as water-methanol mixture, there is a formation of compound, **3''** which have PXRD pattern similar to that of the major peak found for the simulated pattern of **3** (Figure 9). That is on rehydration of **3'** it again restored to its original phase. There is an additional peak at  $2\theta = 7.2^{\circ}$  for both the water as well as water-methanol mixture immersed product, which is possibly due to unorganized crystal packing.

This transformation is also monitored using IR and UV-vis spectroscopy. In IR spectroscopy broadening of peak with shift in some peak is observed (Figure S11) which suggests there is a change in coordination environment around metal centre. In UV-vis spectroscopy, there is a  $\sim 20$  nm shift in the maxima has been observed for the **3'** respect to the **3** of the peak at  $\sim 370$  nm. The maximum at  $\sim 330$  nm is totally absent in **3'** (Figure S12). Again on rehydration the maxima position are restored as that of assynthesized (Figure S12). Thus the mentioned transformation is reversible in respect of treatment with water and water-methanol mixture.

Among the structures reported here, only **3** and **6** consists of two crystallographically independent metal  $(Zn^{II})$  centers whereas the others have only one independent metal centers in their unit cell. Upon dehydration of **3** there may be a possibility of reorganization in the structure through the flexible sucinate dianion linkage. This conversion may lead to form an uniform Zn(II) centre in the transformed phase (**3'**) which is somehow supported by the contraction of cell volume in the activated form of compound **3** (**3'**). But compound **6** being a dense interpenetrated structure consisting of rigid fumarate, is not prone to show such dynamicity; which has been observed in **3**.

## **Adsorption Properties**

As revealed from the single crystal-XRD structural analysis, **3**, **4**, **5** and **6** have water filled cavities and the pore dimensions are comparable to the kinetic diameter of the gases and solvent vapors of recent interest. Along with, except the **3**, all other's framework stability is supported by TGA and PXRD measurements. As stated earlier, **3** undergoes a structural transformation during the dehydration; although the transformed framework, **3'**, is quiet stable up to a certain high temperature. With all of the dehydrated frameworks sorption study has been performed using different gases (N<sub>2</sub> at 77K and CO<sub>2</sub> at 195 K) and vapors (H<sub>2</sub>O at 298 K). All of these samples shows negligible amount of N<sub>2</sub> uptake with a type-II surface adsorption (Figure 10a).





**Figure 10.** Sorption isotherms for (a)  $N_2$  at 77 K; (b)  $CO_2$  at 195 K and (c)  $H_2O$  at 298 K, for **3'** (red), **4** (violet), **5** (black) and **6** (blue).

Similar phenomenon is observed for the  $CO_2$  also; which also ends up with a very low uptake (Figure 10b). Despite of large pore, low N<sub>2</sub> uptake may be due to low thermal energy of N<sub>2</sub> at 77 K may not overcome the high diffusion barrier causing exclusion whereas for  $CO_2$  the blocking of the windows of unidirectional pore channels to the incoming larger sized  $CO_2$  gas molecules may be the reason for such low uptake. Besides, although **3** has a very large pore,

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due to change of structure during the dehydration process by the pore volume is mostly compromised resulting a low adsorption.

However, the water adsorption shows enhancement of amount of adsorption accompanied with some interesting phenomenon. The H<sub>2</sub>O adsorption profile for **3'**, exhibits a gate opening phenomenon; no uptake (~5 mL g<sup>-1</sup>) at low pressure and then at P/P<sub>0</sub> ~ 0.422, a sharp rise takes place upto P/P<sub>0</sub> ~ 0.599, associated with an uptake of amount of 207 mL g<sup>-1</sup> and the final uptake amount reaches to 235.6 mL g<sup>-1</sup> (Figure 10c). The final uptake amount is equivalent to a total no of 12 water molecules *i.e.* the converted structure can uptake more number of water molecules than the number present in its mother compound. For **4**, a type II adsorption is observed with a final uptake of ~69.3 mL g<sup>-1</sup>. There is a certain interesting scenario with **5**; it uptake water up to P/P<sub>0</sub> ~ 0.17 with a continuous rate of amount ~61 mL g<sup>-1</sup>, equivalent to 2.1 water molecule, then there is a change in rate of adsorption which ends at P/P<sub>0</sub> ~0.35 an amount of ~85 mL g<sup>-1</sup>, equivalent to a total of three water molecules (Figure 10c). Again a change of rate is observed and final amount reaches ~150.3 mL g<sup>-1</sup> at P/P<sub>0</sub> ~ 0.90 which is equivalent to ~5 (5.2) molecule of water. No significant adsorption is observed for **6**; final amount is ~38.6 (Figure 10c).

This is clearly visible that all these metal-organic frameworks with succinate linker have greater affinity towards water relative to the coordination polymer containing fumarate linker with identical co-ligand. Although, double bond containing fumarate should have greater tendency to adsorb polar water molecule but a lower adsorption is observed. This may be corroborated to the fact that all the fumarate containing systems are interpenetrated in nature which may block the pore window hence such lower adsorption is observed.

#### Luminescence Study

Optical properties of MOFs with d<sup>10</sup> metal centres and recent successful use of them in various applications,<sup>41,42</sup> have brought them one more time under the spotlight of interest of researchers. Solid state photoluminescence study of the d<sup>10</sup> complexes **1-6** and free respective ligands here been performed at room temperature (Figure 11). The ligand 3-bpdb and corresponding complexes **1** and **2** show emission maxima at 398 nm ( $\lambda_{ex} = 255$  nm), 405 nm ( $\lambda_{ex} = 265$  nm) and 408 nm ( $\lambda_{ex} = 265$  nm) respectively (Figure 11a). Similar emission spectra is found for the 4-bpdb and its complexes **3** and **4**. Complexes **3** and **4** exhibit the emission maxima at 396 nm ( $\lambda_{ex} = 255$  nm) and 407 nm ( $\lambda_{ex} = 265$  nm) respectively and the ligand 4-bpdb at 394 nm ( $\lambda_{ex} = 250$  nm) (Figure 11b). For the rest, ligand bpee shows

emission spectra at 396 nm ( $\lambda_{ex} = 260$  nm) where its complex **5** and **6** shows emission maxima at 401 nm ( $\lambda_{ex} = 260$  nm) and 396 nm ( $\lambda_{ex} = 250$  nm) respectively (Figure 11c).



Figure 11. Emission spectra for complex 1-6 with constituent free N,N'-donor linker.

It is cleared from the emission spectrum of the three ligand and their complexes 1-6, exhibit similar type of spectra with slightly red shifted compared to the ligand. The emission spectrum of free ligands with aromatic architecture may be originated from the  $\pi^*$ -n or  $\pi^*$ - $\pi$ 

transition. Since the d<sup>10</sup> metal ions are difficult to be reduced or oxidized there is less possibility to occur the metal-associated MLCT/LMCT charge transfer.<sup>55</sup> Thus, the emission property of these compounds may be allocated primarily to the intra ligand charge transition (ILCT) and ligand-to-ligand charge transfer (LLCT).

#### CONCLUSION

Here syntheses of six Zn(II) MOFs constructed by succinate and fumarate along with three different N,N' donor co-ligands, among them one is bent coordinating and other two are straight coordinating. The ligand differs by chain length and constituent atoms as well. The structural diversity was discussed and different physicochemical analysis has been performed on them for proper characterization. It is also found that, one of the compounds, shows reversible structural transformation on dehydration and rehydration which is also thoroughly investigated by different techniques. Besides, results from the gas and solvent vapor sorption experiments are found quiet interesting and consistent with the structural features. From the study it is interesting to note that, despite of use of the both flexible and rigid dicarboxylate linkers along with same bent coordinating ligand, 1 and 2 are found isostructural and rigidity or flexibility of a ligand seems to have no effect on the overall structure. Although, the compounds with straight coordinating linker have structural similarity as succinate containing pair 3 & 5, and fumarate containing pair 4 & 6. The flexible succinate containing compounds are portrayed pillared layer structure whereas fumarate containing compounds shows fivefold interpenetrated structure. It has been quite ubiquitous that the pillared layer structure is more likely to be formed by a rigid ligand and flexibility in ligand favors interpenetration, but here; exactly opposite trend is observed. Another interesting phenomenon is worth to note, **3** & **5** is made of succinate and linear flexible linker, but for **3** the flexibility is transferred to the constructed MOF but 5 does not have any structural flexibility as found in 3. Also, 4 with same N,N'-donor linker does not show any structural flexibility like 3. Therefore it is evident from the present study that a rigid linker can able to create a flexible structure in a favorable condition and vice versa.

## ASSOCIATED CONTENT

#### **Supporting Information**

The figures related to IR, UV-Vis spectral study; PXRD patterns, and TGA of compounds along with different structural figures and tables related to the crystal structures reported in

this paper are available as SI. CCDC 1572901-1572906 contains the supplementary crystallographic data for this paper in CIF format.

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# **Table of Contents**

# Structural Diversity in Six Mixed Ligand Zn(II) Metal-Organic Frameworks Constructed by Rigid and Flexible Dicarboxylates and Different N, N' Donor Ligands

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Study of the structure diversity for six functionalized metal-organic frameworks of Zn(II), synthesized using one rigid or flexible dicarboxylates along with three different N,N'-donor ligand. Various physicochemical analyses suggest their properties are consistent with the structural outcome.