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Construction of a 2D Interwoven and 3D Interpenetrated Metal-Organic Frameworks of Zn(II) by Varying N,N'-Donor Spacers

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Abstract

Four new metal-organic frameworks (MOFs) of Zn(II) ion, $[Zn_2(muco)_2(azopy)_2].3DMF.2H_2O$ (**1**), $[Zn(muco)(bpee)].4H_2O$ (**2**), [Zn(muco)(3bpdh)] (**3**), and $[Zn_4(muco)_4(4bpdh)_4].4bpdh.2H_2O$ (**4**) (where, muco = *trans, trans*-muconate dianion, azopy = 4,4'-bisazobipyridine, bpee = 1,2-bis(4-pyridyl)ethylene, 3bpdh = 2,5-bis(3-pyridyl)-3,4-diaza-2,4-hexadiene, and 4bpdh = 2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadiene) have been synthesized using mixed ligand systems and characterized structurally by single-crystal X-ray diffraction. Compound **1** has a 2D network with 2-fold interwoven, (4,4)-connected, $\{4^4.6^2\}$-**sql** net topology. Compounds **2** and **3** have a 3D diamondoid (**dia**) structure with interesting 5-fold and 3-fold interpenetrated net, respectively. Whereas, compound **4** has a 3D cubic (**pcu**, α-Po) structure with 2-fold interpenetrating, 6-connected, $\{4^{12}.6^3\}$ net topology. Topological analyses of **2** and **3** reveal a 4-connected net with 6^6 topology. In spite of interweaving/interpenetration, compounds **1** and **2** possess rectangular channels with dimension 3.9 × 4.5 $Å^2$ and 4.3 × 7.0 $Å^2$ respectively. Photoluminescence study showed the emissions of **1-4** and the thermal stabilities of the compounds were also examined.

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Introduction

The design and synthesis of porous coordination polymers (PCPs) or metal-organic frameworks (MOFs) by connecting the metal ions as nodes or clusters (SBU) with variety of organic ligands as linkers has attracted a great deal of interest in the past two decades due to their intriguing network topology and novel functionality.[1] The network topology and the functionality can be tuned by the judicious choice of bridging organic linkers and metal containing secondary building units.[2] Having the merits of both organic and inorganic building units combined with high surface area, tailored pore volume makes MOFs useful materials for hydrogen storage,[3] selective adsorption of carbon dioxide,[4] separation,[5] heterogeneous catalysis,[6] sensing[7] as well as drug delivery[8] applications. Recently, considerable efforts have also been made to construct MOFs with structural diversity/flexibility by employing mixed ligand systems that have carboxylate ligand combined with various bipyridyl N,N'–donor spacer ligands.[9] Furthermore, it has been observed that the use of long organic linkers has often resulted in the formation of interpenetrated/entangled networks.[10] In this context, rigid spacer ligands, such as, trans, trans-muconic acid (mucoH_2) has been found to be quite useful in construction of MOFs with interpenetration, `due to its moderately longer spacer length and diverse binding modes.[11] The origin of interpenetration in a framework has been attributed to the presence of large voids in it and oftentimes the interpenetration does not prevent the possibility of obtaining porous frameworks.[12] However, the factors that influence the resulting degree of interpenetration remain unknown. Literature survey reveals that about more than 60% of interpenetrated frameworks bear a diamondoid topology.[13] MOFs with diamondoid motif have gained a special interest not only from the topological point of view but also due to their robust structural motifs and the possible applications in nonlinear optical (NLO) properties.[14] Diamondoid frameworks with various degrees of interpenetration such as, 2-5-fold, 7-9-fold, 11-fold as well as 12-fold degeneracy have been reported.[15]

Herein, we report design and syntheses of four new MOFs based on Zn(II) ion, $[Zn_2(muco)_2(azopy)_2].3DMF.2H_2O$ (**1**), $[Zn(muco)(bpee)].4H_2O$ (**2**), [Zn(muco)(3bpdh)] (**3**), and $[Zn_4(muco)_4(4bpdh)_4].4bpdh.2H_2O$ (**4**) (muco = *trans, trans*-muconate dianion, azopy = 4,4'-bisazobipyridine, bpee = 1,2-bis(4-pyridyl)ethylene, 3bpdh = 2,5-bis(3-pyridyl)-3,4-diaza-2,4-hexadiene, and 4bpdh = 2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadiene) by changing the bipyridine spacers (Scheme 1). Compounds **1**, **3** and **4** were synthesized under solvothermal conditions. Whereas, compound **2** was constructed by self-assembly of Zn(II) ion with muconate dianion and bpee spacer (Scheme 2). Compound **1** has a 2-fold interwoven 2D network with $\{4^4.6^2\}$ topology. Compounds **2** and **3** possess a 3D diamondoid net with 5-fold and 3-fold interpenetrating nets, respectively. Whereas, compound **4** has a 2-fold interpenetrated 3D pillar-layered framework with $\{4^{12}.6^3\}$ topology. Interestingly, inspite of interweaving/interpenetration, compounds **1** and **2** possess a rectangular 1D channels of dimension 3.9 × 4.5 $Å^2$ and 4.3 × 7.0 $Å^2$, respectively occupied by guest solvent molecules. Solid state photoluminescence study shows the emissions by **1**- **4**.

Experimental

Materials

All the reagents employed were commercially available and used as provided without further purification. The Zn(II) salts, *trans, trans*-muconic acid, 1,2-bis(4-pyridyl)ethylene (bpee) were obtained from Sigma Aldrich chemical Co. 4,4'-bisazobipyridine (azpy), 2,5-bis(3-pyridyl)-3,4-diaza-2,4-hexadiene (3bpdh) and 2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadiene) (4bpdh) have been synthesized following previously reported procedure.[16]

Physical Measurements

Elemental analysis was carried out using a Thermo Fischer Flash 2000 Elemental Analyzer. IR spectra were recorded on a Thermo Scientific Nicolet iS10 *FT-IR* Spectrometer in the region 4000-400 cm^{-1}. Thermogravimetric analysis (TGA) was carried out using Metler Toledo thermogravimetric analyzer in nitrogen atmosphere (flow rate = 50 mL min^{-1}) in the temperature range 30 – 500 °C (heating rate = 3°C min^{-1}). Powder XRD pattern of the compounds were recorded by using Cu Kα radiation (k = 1.542 Å; 40 kV, 20 Ma) using PANalytical's X'PERT PRO diffractometer. The patterns were agreed with those calculated from single crystal structure determination (See supporting information).Solid state photoluminescence (PL) spectra of the samples were recorded on a Perkin-Elmer LS 55 spectrofluorometer.

Synthesis of [Zn_2(muco)$_2$(azopy)$_2$].3DMF.2H_2O (1)

Compound **1** was synthesized under solvothermal conditions at 125°C. $Zn(NO_3)_2.6H_2O$ (0.074 g, 0.25 mmol) was dissolved in 4 ml of deionized water to which a DMF solution (2ml) of H_2muco (0.036g, 0.25mmol) was added with constant stirring. To this solution an ethanolic solution (2 ml) of azopy (0.046g, 0.25 mmol) was added and the contents were stirred for 30min and then taken in a 30 mL glass vial sealed with parafilm and heated at 125^{o}C for 2 days. After being cooled to room temperature, orange block crystals of **1** were isolated. Anal. Calcd. for $C_{41}H_{49}N_{11}O_{13}Zn_2$: C, 47.59; H, 4.77; N, 14.89 Found: C, 46.91; H, 4.23; N,14.32. Yield (74%) IR (cm^{-1}): ν(H_2O), 3219(b); ν(CH-Ar), 3002 (w); ν(C=N), 1611(s), ν(N=N), 1570(s); ν(C=C), 1516-1387(s); ν(C-O), 1342-1214(s).

Synthesis of [Zn(muco)(bpee)].4H_2O (2)

Compound **2** was prepared at room temperature using layering method. Stock solutions of $Zn(OAc)_2{\cdot}2H_2O$ (0.055 g, 0.25 mmol) in 25ml H_2O, H_2muco (0.036 g, 0.25 mmol) neutralized with NaOH (0.020 g, 0.5 mmol) in 12.5 ml of H_2O and bpee (0.045 g, 0.25 mmol,) in 12.5ml of ethanol were prepared. The bpe and the H_2muco solutions were mixed together and stirred for 30 min. Then 2ml of this solution was slowly and carefully layered over 2 ml of metal solution using 1 ml of 2:1 (v/v) buffer solution of H_2O and ethanol. The colorless block crystals of **2** were obtained after four weeks. Yield (70%). Anal. Calcd. for $C_{18}H_{30}N_2O_8Zn$: C, 46.21; H, 6.46; N, 5.98 Found: C, 47.01; H, 6.03; N, 6.72. IR (cm^{-1}): ν(H_2O), 3394(b); ν(CH-Ar), 3050 (w) ; ν(C=N), 1614(s), ν(C=C), 1560-1433(s); ν(C-O), 1365-1255(s).

Synthesis of [Zn(muco)(3bpdh)] (3)

Compound **3** was synthesized under solvothermal condition**s** at 110°C. $Zn(OAc)_2.2H_2O$ (0.055g, 0.25 mmol) was dissolved in 4 ml of deionized water to which a DMF solution (2ml) of H_2muco (0.036g, 0.25mmol) was added with constant stirring. To this solution, an ethanolic solution (2 ml) of 3bpdh (0.060g, 0.25 mmol) was added and the contents were stirred for 30min and then taken in a 30 mL glass vial sealed with parafilm and heated at 110 ^{o}C for 2 days. After being cooled to room temperature, light yellow block crystals of **3** were isolated. Yield(60%). Anal. Calcd. for $C_{20}H_{18}N_4O_4Zn$: C, 54.13; H, 4.08; N, 12.62 Found: C, 53.6; H, 4.64; N, 13.02. IR (cm^{-1}): ν(CH-Ar), 3100-3031(bw); ν(C=N), 1613 (s), ν(C=C), 1575-1435(s); ν(C-O), 1335-1282(s).

Synthesis of $[Zn_4(muco)_4(4bpdh)_4].4bpdh.2H_2O$ (4)

Compound **4** was synthesized under solvothermal conditions at 100°C. $Zn(NO_3)_2.6H_2O$ (0.074 g, 0.25 mmol) was dissolved in 4 ml of deionized water to which an aqueous solution (2ml) of H_2muco (0.036g, 0.25mmol) neutralised with NaOH (0.020 g, 0.5 mmol), was added with constant stirring. To this solution an ethanolic solution (2 ml) of 4bpdh (0.060g, 0.25 mmol) was added and the contents were stirred for 30min and then taken in a 30 mL glass vial sealed with parafilm and heated at 100°C for 3 days. After being cooled to room temperature, yellow block crystals of **4** were isolated. Yield (70%). Anal. Calcd. for $C_{94}H_{86}N_{20}O_{18}Zn_4$: C, 55.20; H, 4.23; N, 13.69 Found: C, 55.80; H, 3.93; N, 14.23. IR (cm^{-1}): ν(H_2O), 3400-3200 (bw) ; ν(CH-Ar), 3022(w) ; ν(C=N), 1612(s) ; ν(C=C), 1565-1421(s) ; ν(C-O), 1339-1220(s).

X-ray Crystallography

X-ray single crystal structural data of all the compounds **1-4** were collected on a CMOS based Bruker D8 Venture PHOTON 100 CMOS diffractometer equipped with a INCOATEC micro-focus source 1μs with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) operating at 50 kV and 30 mA. The program SAINT[17] was used for integration of diffraction profiles and absorption correction was made with SADABS[18] program. All the structures were solved by SIR 92[19] and refined by full matrix least square method using SHELXL-97[20] and WinGX system, Ver 1.70.01.[21] All the non hydrogen atoms were located from the difference Fourier map and refined anisotropically. All the hydrogen atoms were fixed by HFIX and placed in ideal positions and included in the refinement process using riding model with isotropic thermal parameters. Potential solvent accessible area or void space was calculated using the PLATON multipurpose crystallographic software.[22] All the crystallographic and structure refinement data of compounds **1-4** are summarized in Table 1. Selected bond lengths and angles are given in Table S1-S4, respectively. The crystallographic information files are deposited with the CCDC 973248-973251.

Results and discussion

Synthesis and crystal structure

Compounds **1**, **3** and **4** were synthesized by solvothermal reaction of Zn(II) with deprotonated H_2muco ligand and N,N'-donors (azpy, 3bpdh and 4bpdh, respectively) at temperatures of 100-125°C (Scheme 2). It is worth mentioning that solvothermal preparation of **1** and **3** in

H_2O/Ethanol did not yield the desired products and use of DMF in combination with H_2O/Ethanol gave the products indicating the role of DMF in their formation. This is also supported by the presence of three DMF molecules of crystallization in compound **1**. Similarly, solvothermal reaction of Zn(II) with H_2muco and bpee in H_2O/DMF/Ethanol at 110°C yielded the reported 3D framework, [Zn(muco)(bpe)].DMF.H_2O which host DMF molecules in the open channels.[11c] On the contrary, room temperature reaction in the absence of DMF yielded the structurally different compound, [Zn(muco)(bpee)].4H_2O, **2** which hosts only H_2O molecules. Therefore, the solvent molecules play an important role in the formation of compounds **1-4**.

Crystal structure of [Zn_2(muco)$_2$(azopy)$_2$].3DMF.2H_2O (1)

Compound **1** crystallizes in the Orthorhombic crystal system with the non-centrosymmetric, Pca21 space group. X-ray structure determination reveals a two-dimensional (2D) network constituted by a muconate (muco) dianion and an azopy spacer. The asymmetric unit consists of two Zn(II) ions, two muconate dianions and two azopy spacers along with three guest DMF and two water molecules of crystallization. Both Zn1 and Zn2 center are in a distorted tetrahedral geometry with ZnO_2N_2 chromophore satisfied by two carboxylate oxygen atoms O1 and O2 for Zn1 (O3 and O4a, where a = x,-1+y,z, at Zn2) from two bridging muconate dianions and two nitrogen atoms N1 and N2 for Zn1 (N3 and N4 at Zn2) from the azopy spacer (Fig. 1a). The Zn1-O and Zn1-N bond lengths are in the range 1.952(5)-1.969(4) Å and 2.016(6)-2.021(6) Å, respectively. The Zn2-O/N and Zn2-N bond distances are in the range 1.958(5)-1.976(4) Å and 2.011(6)-2.017(6) Å, respectively. The degree of distortion from an ideal tetrahedral geometry can be seen from the tetrahedral angles which varies from 100.39(19) to 115.7(2)º and from 97.66(19) to 114.2(2)º for Zn1 and Zn2, respectively. The muconate dianion acts as a monodentate ligand which bridges Zn1 and Zn2 centers through μ_1-O fashion forming a 1D [Zn(muco)]$_n$ zig-zag chains that are connected by azopy spacers to form a 2D [Zn(muco)(azopy)]$_n$ network (Fig. 1b). That houses large rectangular 1D channels of dimension ~ 8.0 × 10.7 $Å^2$ along the crystallographic *b*-axis (Fig. 1b). The presence of large rectangular channels along with bent shape of azopy spacer facilitate interweaving of one 2D net over another to generate a 2-fold interwoven 2D network (Fig. 1c and 1d). As a result of 2-fold interweaving the size of the 1D channels has been reduced to ~ 3.9 × 4.5 $Å^2$ as shown in Fig.2a. Topological analysis by TOPOS[23] suggests that each Zn(II) center acts as a 4-connecting node and the overall structure has a (4,4)-connected 2D interwoven network with Schläfli point symbol {$4^4.6^2$} (Fig. 2b). Interestingly, in spite of 2-fold interweaving, the structure exhibit effective solvent accessible void volume of ~ 38.9 % (4802.1 $Å^3$) per unit cell volume calculated using PLATON[22] after removal of guest DMF and water molecules. The distance between two adjacent Zn….Zn centers along Zn…muco…Zn and along Zn…azopy…Zn are 11.770 Å and 11.070 Å, respectively. The structure shows C-H…O hydrogen bonding interactions involving the aromatic C-H bonds with the carboxylate oxygens of muco ligand, and the guest water (O2w) molecule (Table S5).

Crystal structure of [Zn(muco)(bpee)].4H_2O (2)

Compound **2** crystallizes in the monoclinic crystal system with the C2/c space group. X-ray structure determination reveals a 3D framework constituted by a bridging muconate dianion and a bpee spacer. The asymmetric unit consists of a Zn(II) ion, a muconate dianion and a bpee spacer and two guest water molecules which are residing in special positions. The geometry around the Zn(II) center is a distorted tetrahedron with ZnO_2N_2 chromophore satisfied by two oxygen (O1 and O1a, where a = 1-x,y,1/2-z) atoms from a bridging muconate and two nitrogen (N1 and N1a, where a = 1-x,y,1/2-z) atoms of a bpee linker (Fig. 3a). The Zn-O/N bond lengths are 1.933(2)/1.969 (9) Å, respectively. The extend of distortion from a regular tetrahedral geometry can be seen in the tetrahedral angles at the Zn(II) center which vary from 98.93(4) to 124.48(4)°. Similar to **1**, the muconate dianion coordinates to two Zn(II) centers through monodentate μ_1-O fashion. Thus the Zn(II) centers acts as a 4-connected node which are connected with each other in 3D by muconate and bpee linkers to generate a 3D diamondoid framework (Fig. 3b and c). Topological analysis by TOPOS[23] suggests that each Zn(II) center acts as a 4-connecting node and the overall structure has the diamondoid **(dia)** net topology with Schläfli point symbol {6^6} (Fig. 3b and c). As it can be seen from the Fig. 3, the 3D **dia** framework possesses a large cavity inside which assist further nucleation in the vacant spaces and allow the formation of new 3D nets in those regions. The void space is large enough to generate a complex 5-fold interpenetrated, 3D framework (Fig. 4a). Interpenetration analysis with TOPOS suggests the presence of a 5-fold interpenetration with Schläfli extended point symbol [6(2).6(2).6(2).6(2).6(2).6(2)] (Fig. 4b). Interestingly, in spite of 5-fold interpenetration, the framework possesses rectangular channels with dimension ~ 4.3 × 7.0 $Å^2$ occupied by guest water molecules along the crystallographic *b*-axis (Fig. 5a). The guest water molecules (O1w and O2w) are located in the special positions and actively engaged in hydrogen bonding between each other and with the non-coordinating carboxylate oxygen (O2) atom of the muconate ligand forming a 1D zig-zag chain of water molecules in the open channels of the framework (Fig. 5b, Table S6). The distance between two adjacent Zn….Zn centers along Zn…muco…Zn and along Zn…bpee…Zn are 10.976 and 13.453 Å, respectively. The effective solvent accessible void volume calculated using PLATON[22] is ~ 27.9 % (2038.5 $Å^3$) per unit cell volume after removal of guest water molecules.

Crystal structure of [Zn(muco)(3bpdh)] (3)

Compound **3** crystallizes in the monoclinic crystal system with the C2/c space group. X-ray structure determination reveals a 3D framework constituted by a muconate dianion and a 3bpdh spacer. The asymmetric unit consists of a Zn(II) ion, a muconate dianion and a 3bpdh spacer. Similar to **1** and **2**, the Zn(II) center is in a distorted tetrahedral geometry with ZnO_2N_2 chromophore completed by two oxygen (O1 and O1a, where a = 1-x,y,3/2-z) atoms of a muconate and two nitrogen atoms (N1 an N1a, where a = 1-x,y,3/2-z) from the 3bpdh spacer (Fig. 6a). The Zn-O and Zn-N bond distances are 1.933(2) Å and 2.052(2) Å, respectively. The extent of distortion from the regular tetrahedral geometry can be seen from the tetrahedral angles at the Zn center which vary from 99.95(4) to 123.95(4)º. Similar to **2**, the Zn(II) nodes are connected each other in 3D by muconate and 3bpdh to form a 3D **dia** framework (Fig. 6). Topological analysis by TOPOS[23] suggests that each Zn(II) atom acts as a 4-connected node and the overall structure has **dia** net with Schläfli point symbol for the net is $\{6^6\}$ (Fig. 6b). Interestingly, due to the angular nature of 3bpdh linker compared to that of a linear linker, bpee, the void space in the **dia** net of **3** is relatively smaller than that of **2** and it is sufficient enough to allow penetration of two other independent nets to generate a 3-fold interpenetrated 3D framework (Fig. 7a). Interpenetration analysis with TOPOS[23] suggests the presence of a 3-fold interpenetration with Schläfli extended point symbol [6(2).6(2).6(2).6(2).6(2).6(2)] (Fig. 7b). The distance between two adjacent Zn….Zn centers along Zn…muco…Zn and along Zn…3bpdh…Zn are 11.882Å and 12.063 Å, respectively. Calculation using PLATON[22] reveal that the framework does not possess any void space (See Fig. S1).

Crystal structure of $[Zn_4(muco)_4(4bpdh)_4].4bpdh.2H_2O$ (4)

Compound **4** crystallizes in the Triclinic crystal system with the P1̄ space group. X-ray structure determination reveals a 3D framework constituted by the muconate dianion and the 4bpdh spacer. The asymmetric unit consists of four Zn(II) ions, four muconate dianions and four

4bpdh spacers along with a guest molecule of 4bpdh and two water molecules. The geometry around all the four Zn(II) centers can be best described as a distorted octahedron with ZnO_4N_2 chromophore satisfied by four carboxylate oxygen atoms, O1,O2,O3 & O4 (at Zn1), O5, O6, O7 & O8 (at Zn2), O9, O10, O11 & O12 (at Zn3) and O13, O14, O15 & O16 (Zn4) in the equatorial positions from four different bridging muconates and two nitrogen atoms, N1, N2 (Zn1), N3, N4 (Zn2), N5, N6 (Zn3) and N7, N8 (Zn4) in the axial positions from four different 4bpdh spacers (Fig. 8a). The extent of distortion from the regular octahedral geometry at the Zn centers can be seen from the *cisoid* and *transoid* angles which are in the range 58.34(8)- 121.97(9)º, and 145.78(9)-175.58(9)º (for Zn1); 55.89(8)-123.17(9)º and 138.03(9) -176.32(10)º (for Zn2); 58.35(8) - 114.16(9)º and 149.89(9)- 175.88(9)º (for Zn3); 58.11(8) - 94.09(8)º and 150.30(8)–171.74(9)º for Zn4, respectively. Zn1 and Zn2 are connected by two muconate dianions, one of which coordinates through chelating bidented, μ_2-O fashion and the other one through monodentate μ_1-O bridging mode forming a 2D $[Zn1Zn2(muco)_2]_n$ sheet (Fig. 9a). Similarly, Zn3 and Zn4 are connected by two other muconate dianions resulting an another 2D $[Zn3Zn4(muco)_2]_n$ sheet. These two 2D sheets are pillared by 4bpdh linkers to form a 3D pillar-layered framework which houses almost rectangular 1D channels of dimension ~ 3.4 × 11.0 $Å^2$ along the crystallographic *b*-axis (Fig. 9b). The void space is sufficient enough to allow penetration of another 3D framework to generate a 2-fold interpenetrated 3D pillar-layered framework as shown in Fig. 9c. Topological analysis by TOPOS suggests the presence of two types of Zn(II) ions which acts as 6-connecting nodes and the overall structure has cubic (**pcu** α-Po) net topology with Schläfli point symbol for the net {4^12.6^3} (Fig. 9c). Interpenetration analysis with TOPOS suggests the presence of 2-fold interpenetration with Schläfli extended symbol [4.4.4.4.4.4.4.4.4.4.4.4.6(4).6(4).6(4)] (Fig. 9d). Interestingly, a guest molecule of 4bpdh has been located in the open channels of the framework and it is involved in C-H**…**O and C-H**…**N hydrogen bonding interactions with the guest water molecule (O2W) and the nitrogen atom of (-N=N-) group of the 4bpdh spacer in the framework, respectively (Fig. S3, Table S7). The distance between two adjacent Zn….Zn centers along the Zn…muco…Zn due to bridging and chelating muconates are 4.056 and 11.300 Å, respectively and along the Zn…4bpdh…Zn are 15.503 Å and 15.516 Å. The effective solvent accessible void volume calculated using PLATON[22] is ~ 27.9 % (2038.5 $Å^3$) per unit cell volume after removal of guest 4bpdh and two water molecules.

Effects of N, N'-donor spacers on the structures of MOFs 1-4

It is interesting to note that the N,N'-donor spacers play important role in directing the final structures of compounds **1**-**4**. Here, four kinds of N,N'-donor (azopy, bpee, 3bpdh and 4bpdh) spacers were selected to investigate their effects on the structure and topology of the resulting frameworks **1-4** (Scheme **1**). The composition of all the four MOFs can be generalized as [Zn(muco)(N,N'-donor)] (leaving the guest molecules). In compounds **1**-**3** the Zn(II) center acts as a 4-connected node, whereas in **4** the Zn(II) centers are 6-connected by the muconate dianion and 4bpdh spacer. The bent shape of azopy spacer resulted the 2D network of **1**, which houses 1D channels which are large enough to allow interweaving of another 2D net to generate a 2-fold interwoven 2D network with $\{4^4.6^2\}$-**sql** net topology. On the other hand, both **2** and **3** have 3D **dia** structure with 6^6 topology but differ in the degree of interpenetration. This difference can be attributed due to the angular coordination of 3bpdh spacer compared to that of linear spacer bpee. As a result, the void space in the **dia** net (Fig. 3b) of **2** is relatively large to facilitate interpenetration four other 3D nets to generate a 5-fold interpenetrating net. Whereas the smaller void space in **3** (Fig. 6b) can facilitate interpenetration of only two other 3D nets to result 3-fold interpenetrating net. In **4** though the 4bpdh spacer is linear like bpee, the presence of the extra -CH_3 group reduces the void space of the rectangular pores (Fig.9b) and they can allow interpenetration of only one 3D net to form a 2-fold interpenetrating net with $\mathbf{\{4^{12}.6^3\}}$ net topology.

Photoluminescence properties of MOFs

Recently, luminescent compounds, particularly, those containing d^{10} metals are gaining much interest due to their potential applications, including chemical sensors, electroluminescence displays and so on.[24] Therefore, the luminescence properties of compounds **1**-**4** along with their corresponding ligands were measured in the solid state at room temperature (Fig. 10). As shown in the Fig.10 fluorescent emissions at 438-467 nm, 350-475 nm, 450-490 nm and 445-490 nm were observed from **1**-**4**, respectively. According to literature muconic acid shows a broad emission at 447—463 nm.[25] Therefore, the emissions from compounds **1**- **4** might be arising due to mixture characteristics of intraligand and ligand-to-ligand charge transitions (LLCT), as has been observed in literature.[25] As the Zn(II) ion is in d^{10} configuration it is less prone to undergo oxidization or reduction. Hence, the emissions of **1**-**4** are neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT) in nature.

Framework stability and Power X-ray diffraction (PXRD) analysis

TGA of compound **1** shows a weight loss of ~ 4.0 % around 80ºC which corresponds to the loss of two guest water molecules (calc. wt% 3.48) (Fig. S3, ESI). The second weight loss of ~ 21 % was observed in the temperature regime 80-300 ºC corresponding to the loss of 3DMF molecules (calc. wt% 21.16). Compound **2** shows a weight loss of ~ 8.0 % around 80-180 ºC which corresponds to the loss of two guest water molecules (calc. wt% 8.4) (Fig. S3, ESI) and the dehydrated framework, $[Zn(muco)(bpee)]_n$ is stable upto 240 °C. The second weight loss of ~ 30.5 % in the temperature regime 240-350 ºC corresponds to the loss of muconate ligand (calc. wt% 30.9). Sample **3** does not show any weight loss upto temperature of 300 ºC supporting the absence of guest solvent molecules and relatively high framework stability. In the temperature range of 300-350 °C a weight loss of ~ 53.2 % was observed which corresponds to the loss of 3bpdh linker (calc. wt% 53.69) (Fig. S3). Compound **4** shows a weight loss of ~ 2.0 % around 80-170 ºC which corresponds to the loss of two guest water molecules (calc. wt% 1.7) (Fig. S3, ESI). The second weight loss of ~ 12.0 % in the temperature regime 180-240 ºC corresponds to the loss of 4bpdh ligand (calc. wt% 11.6). The PXRD patterns of the compounds **1**-**4** match with the one simulated from single-crystal diffraction data (Fig.S4-S7, ESI).

Conclusions

We have constructed four new MOFs of Zn(II) ion using mixed ligand systems and structurally characterized. Structural analyses revealed that compound **1** has a 2-fold interwoven 2D network with **sql-**net topology. Compounds **2** and **3** have a 3D **dia** framework with interesting 5-fold and 3-fold interpenetrating net, respectively. Whereas, compound **4** has a 3D cubic (**pcu**, α-Po) structure with 2-fold interpenetrating net. In spite of interweaving/interpenetration, compounds **1** and **2** possess rectangular channels with dimension 3.9 × 4.5 $Å^2$ and 4.3 × 7.0 $Å^2$, respectively. Solid state photoluminescence study carried out at room temperature showed the emissions from **1**-**4**. The present study demonstrates that by a suitable choice of different building units (metal ion) and organic linkers, it has been possible to tune the network topology, dimensionality and the degree of interpenetration of the resulting MOFs.

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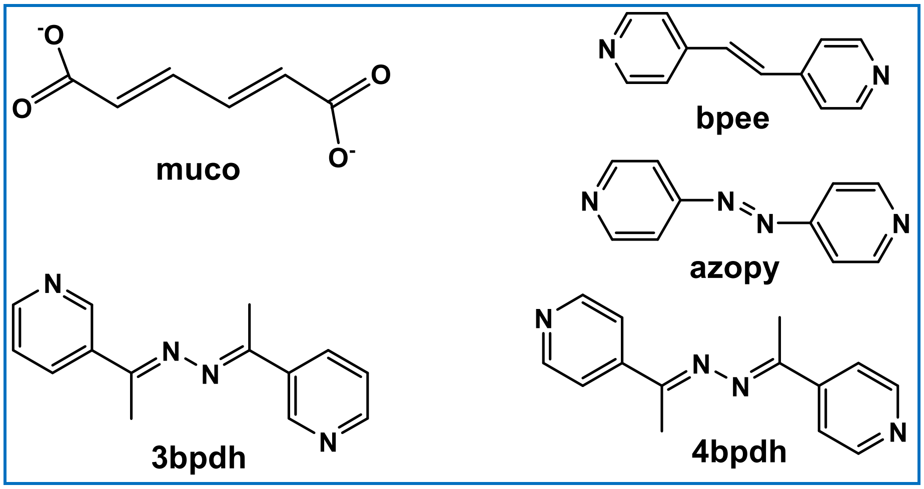
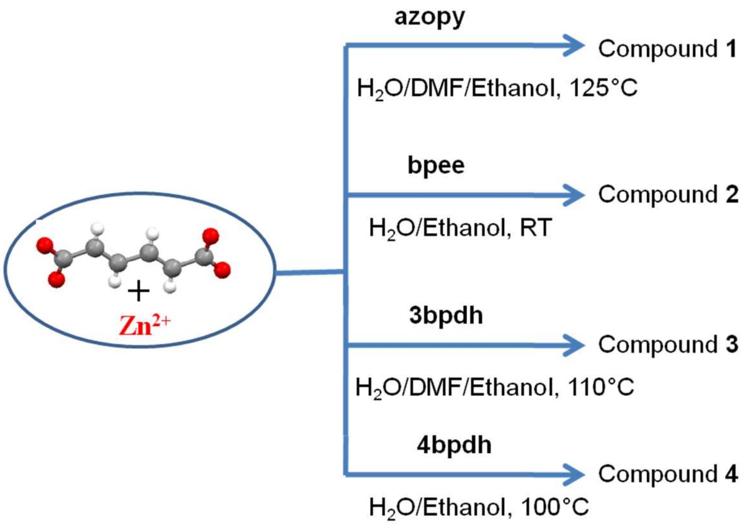
Table 1: Crystal data and structure refinement parameters of compounds **1**- **4**.

Parameters	**1**	**2**	**3**	**4**
Chemical formula	$C_{41}H_{49}N_{11}O_{13}Zn_2$	$C_{18}H_{22}N_2O_8Zn$	$C_{20}H_{18}N_4O_4Zn$	$C_{94}H_{86}N_{20}O_{18}Zn_4$
Formula mass	1034.65	459.75	443.75	2045.31
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclinic
Space group	Pca21(No.29)	C2/c(No.15)	C2/c (No.15)	P-1(No.2)
a /Å	11.0697(6)	22.2190(13)	16.000(5)	10.7575(4)
b /Å	22.2083(11)	5.5243(3)	5.452(5)	15.3180(6)
c /Å	19.5333(11)	18.471(10)	22.025(5)	29.3906(13)
α (°)	90	90	90	81.112(1)
β (°)	90	115.962(2)	107.74(5)	87.711(1)
γ(°)	90	90	90	84.536(1)
V(Å^3)	4802.1(4)	2038.5(2)	1830.3(18)	4761.6(3)
Z	4	4	4	2
D_c (g cm^{-3})	1.426	1.498	1.610	1.427
μ(mm^{-1})	1.071	1.252	1.379	1.073
F(000)	2128	952	912	2108
T(K)	293	293	293	293
λ(Mo K_α)(Å)	0.71073	0.71073	0.71073	0.71073
Θ_{min} (°)	2.3	2.4	2.7	2.2
Θ_{max}(°)	28.4	28.3	28.4	28.4
Total data	128645	17871	15873	135441
Unique data	11361	2548	2292	23865
R_{int}	0.053	0.026	0.022	0.079
Data[I>2σ(I)]	8870	2489	2248	15835
$^aR_1$	0.0661	0.0225	0.0227	0.0525
$^bwR_2$	0.1906	0.0581	0.0602	0.1337
S	1.06	1.07	1.09	1.06

$^aR_1 = \sum \lVert F_o| - |F_c\rVert / \sum |F_o|$, $^bwR_2 = [\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$



Scheme1. Chemical structures of muconate dianion and other N,N'-donor spacers



Scheme2. Synthetic conditions for the compounds **1**-**4**.

Figures with caption

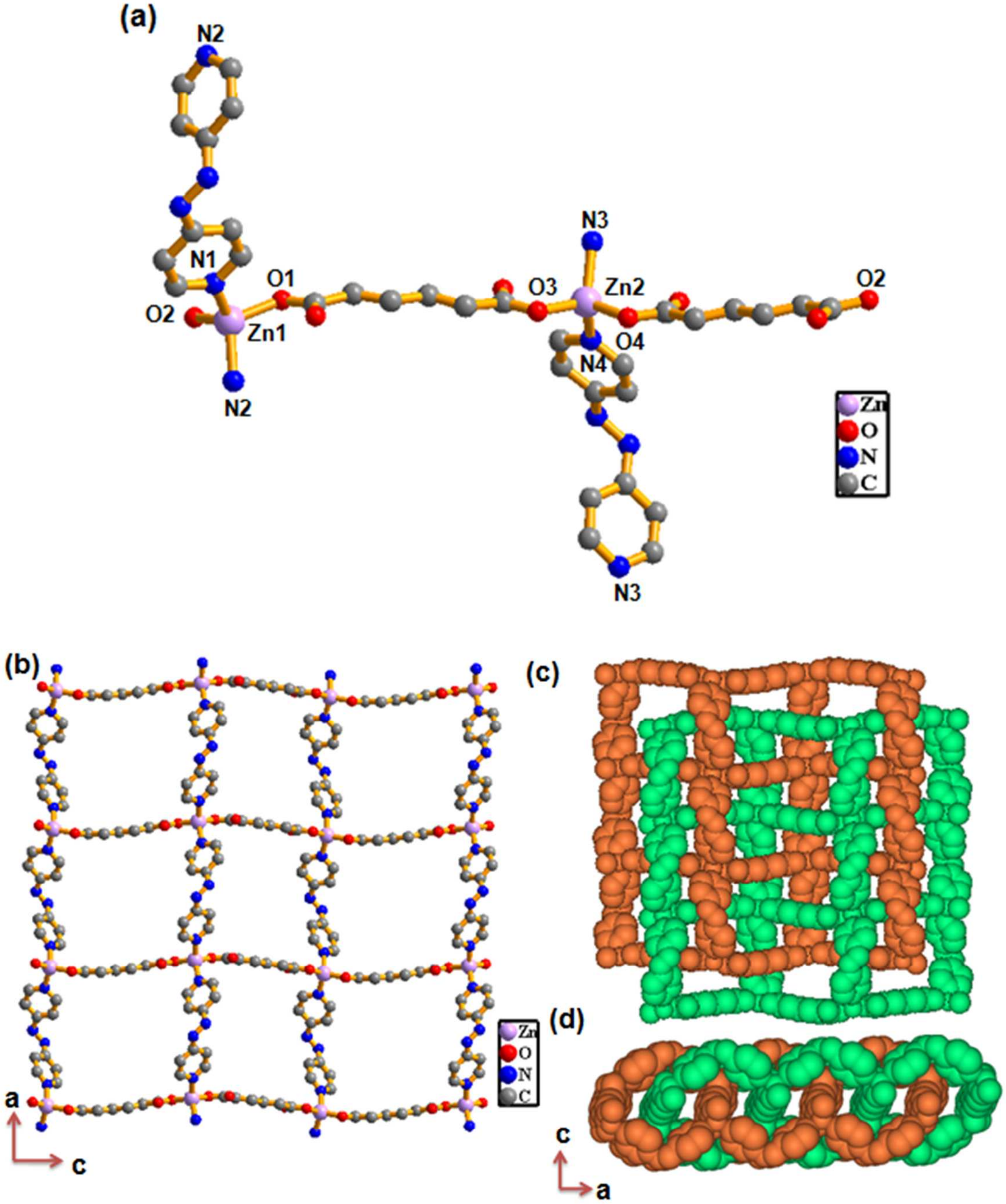


Fig. 1 (a) The coordination environment around Zn1 and Zn2 atoms in **1**: the hydrogen (H) atoms and solvent molecules are omitted for clarity. (b) View of a single 2D network constructed by Zn(II), muco, and azopy linkers (H atoms and solvent molecules are omitted for clarity. (c) and (d) show CPK view of the 2-fold interwoven 2D networks (two different 2D nets are shown in two different colors).

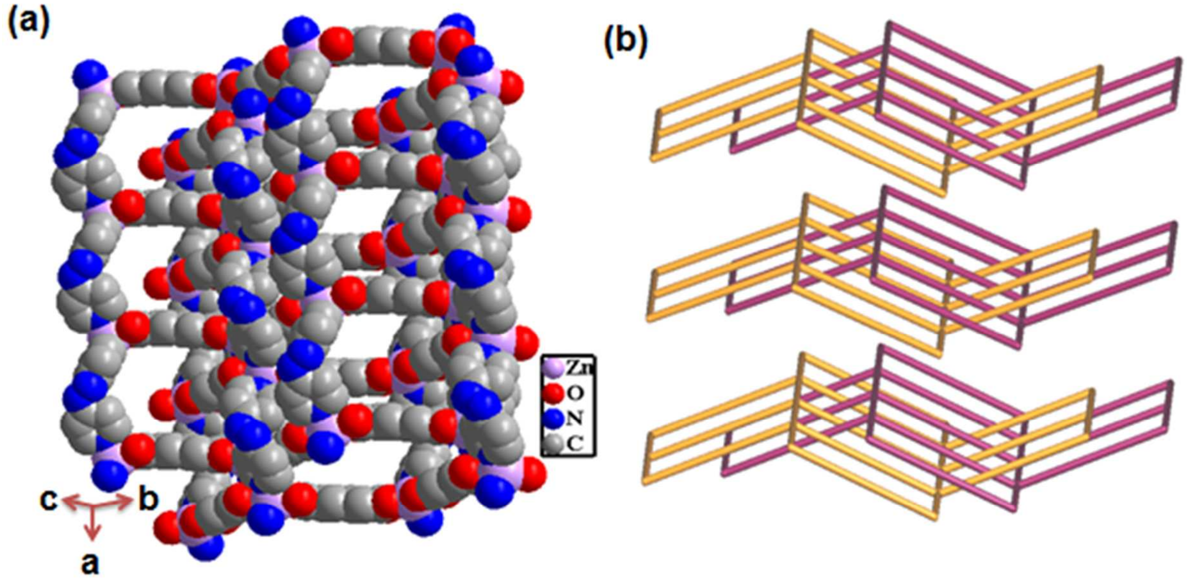
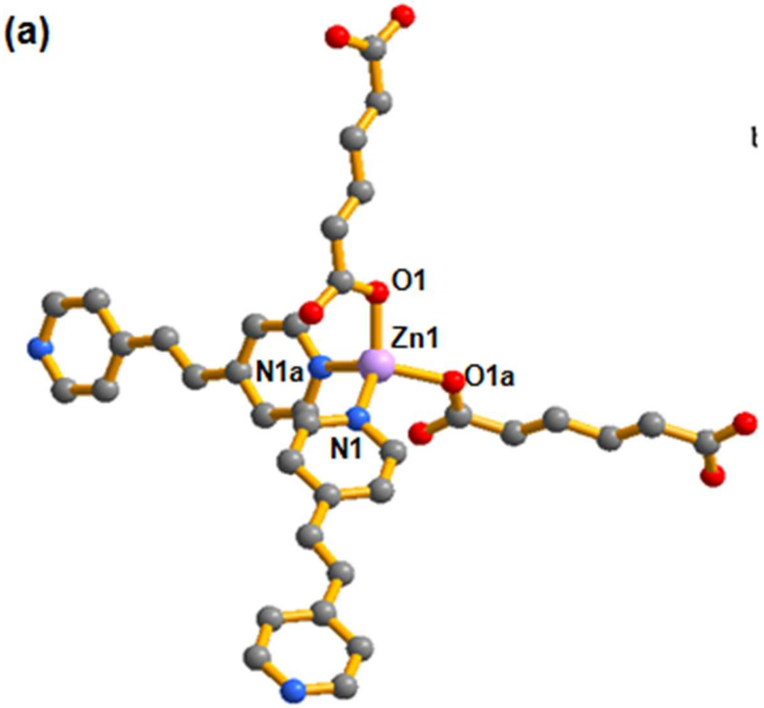


Fig. 2 (a) Space-fill model of the 2-fold interwoven 2D network showing the void space in **1**. (b) Topological representation of the 2-fold interwoven nets in **1** (two different 2D nets are shown in different colors.



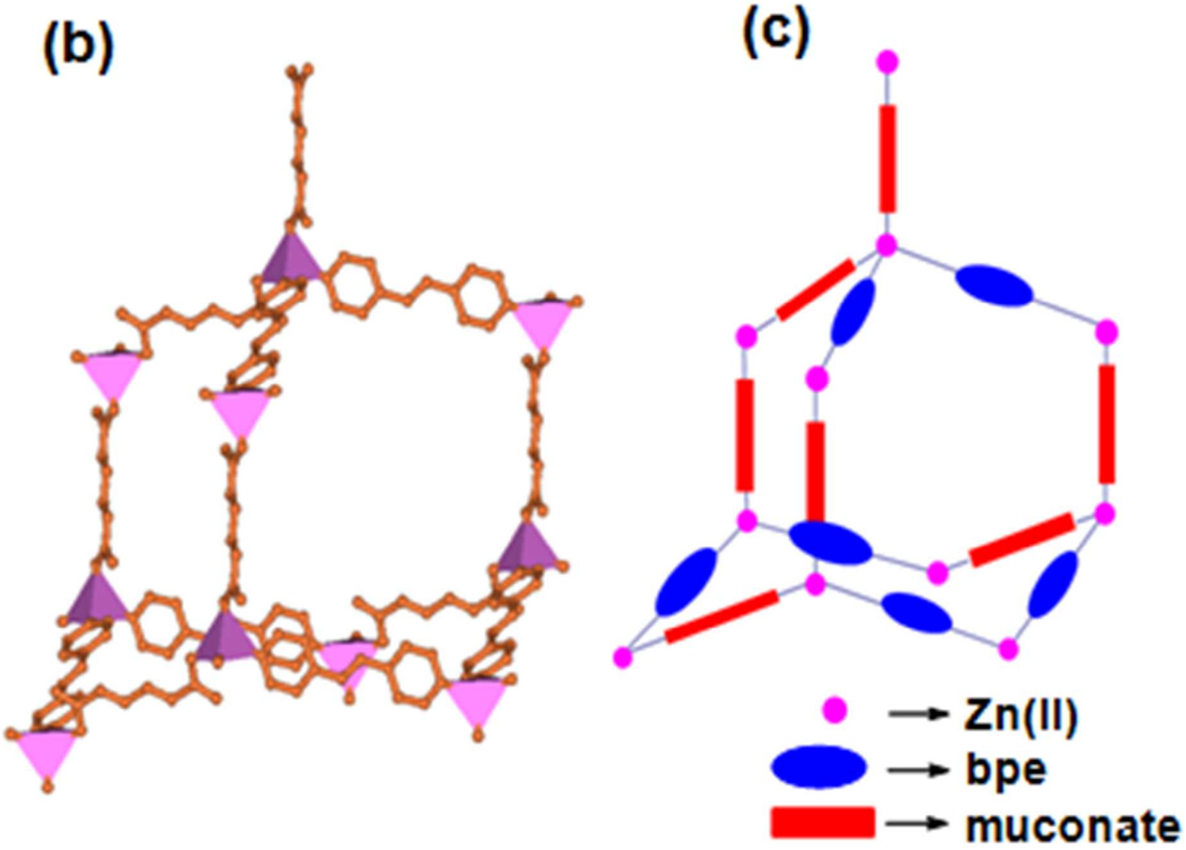


Fig. 3 (a) View of the coordination environment around the Zn(II) atom of **2**; the H atoms and the solvent molecules are omitted for clarity: (b) Perspective view of a single **dia** cage constructed by Zn (II), muco and bpee linkers: (c) Simplified view of the 4-connected single **dia** net.

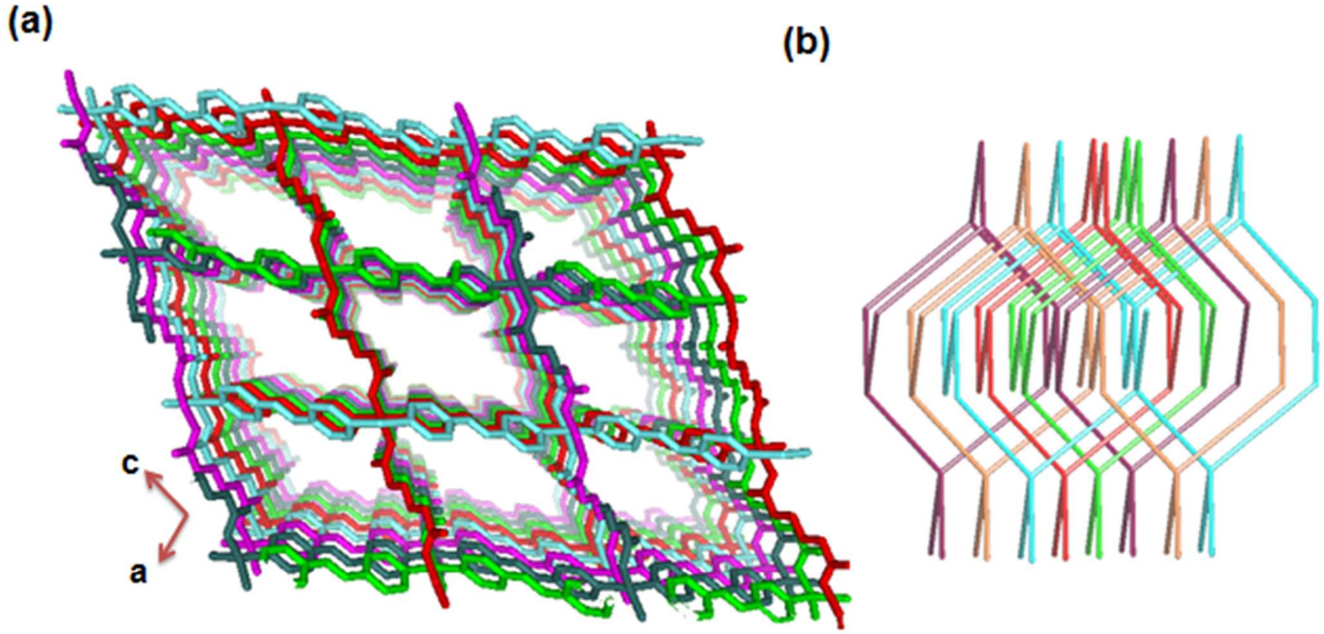


Fig. 4 (a) View of the 5-fold interpenetrated 3D framework of **2** showing the rectangular channels along *b*-axis. (b) Topological representation of the 5-fold interpenetrating nets in **2** (five different 3D nets are shown in five different colors).

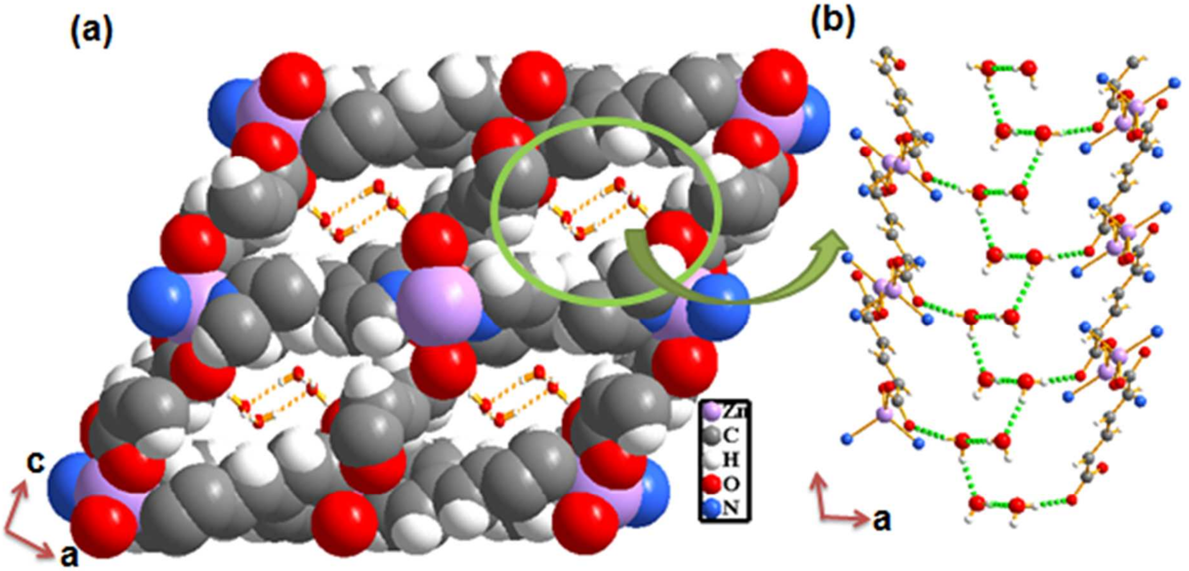


Fig. 5 (a) Space-fill model showing rectangular 1D channels occupied by guest water molecules in **2** (b) View of the 1D chain of guest water molecules via hydrogen bonding between them and with the carboxylate oxygen atom of muconate ligand.

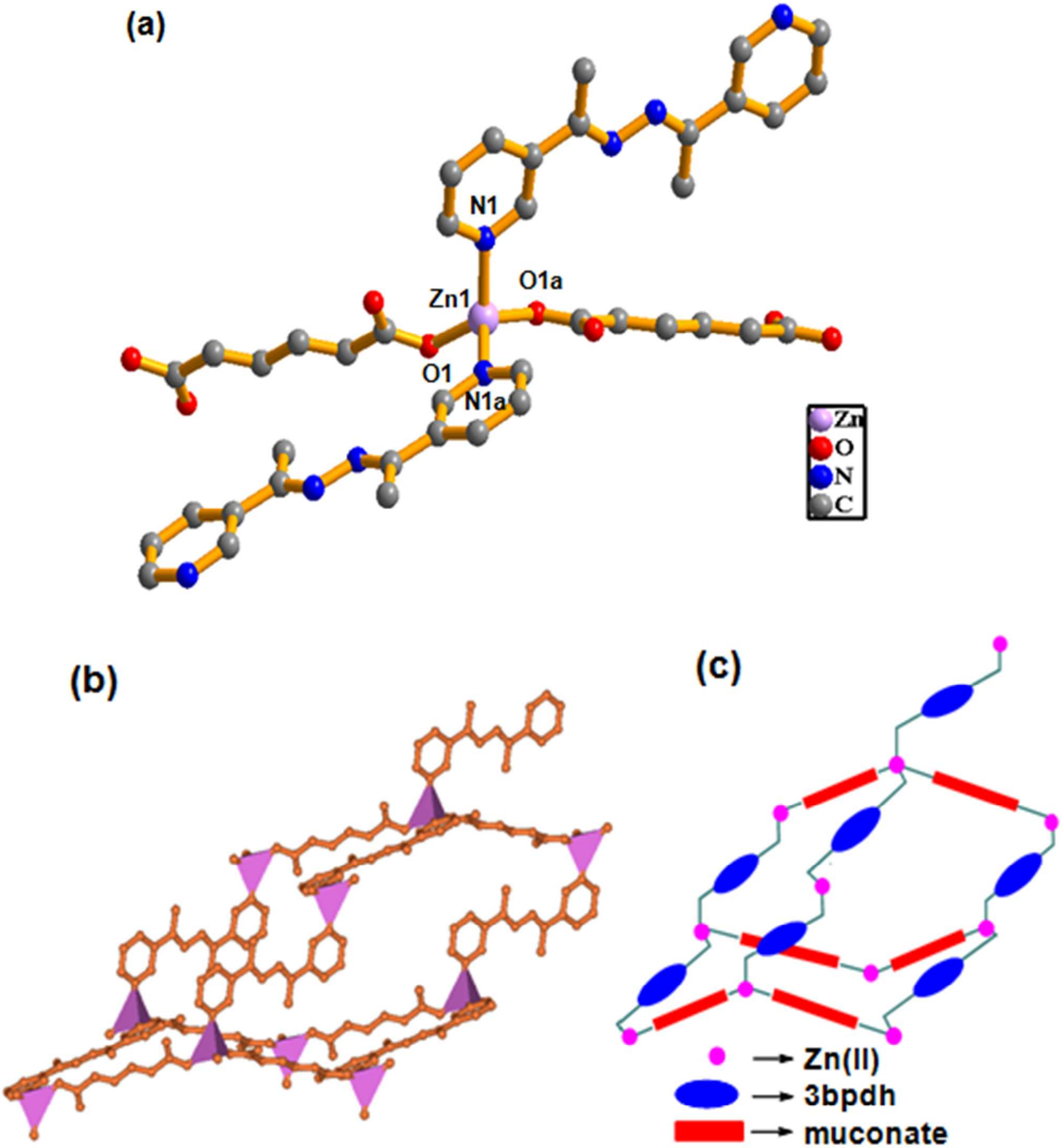


Fig. 6 (a) Coordination environment around the Zn(II) atom in **3**; the H atoms are omitted for clarity. (b) Perspective view of the single **dia** cage. (c) Simplified view of the 4-connected single **dia** net.

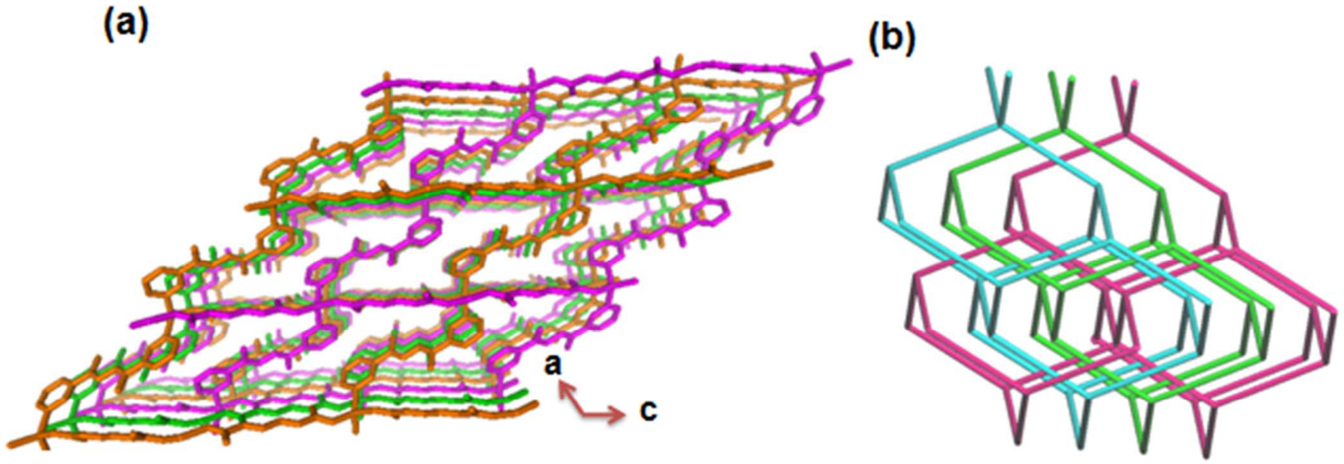


Fig. 7 (a) View of the 3-fold interpenetrated 3D framework of **3** showing the open channels along *b*-axis. (b) Topological representation of the 3-fold interpenetrating net in **3** (three different 3D nets are shown in three different colors.

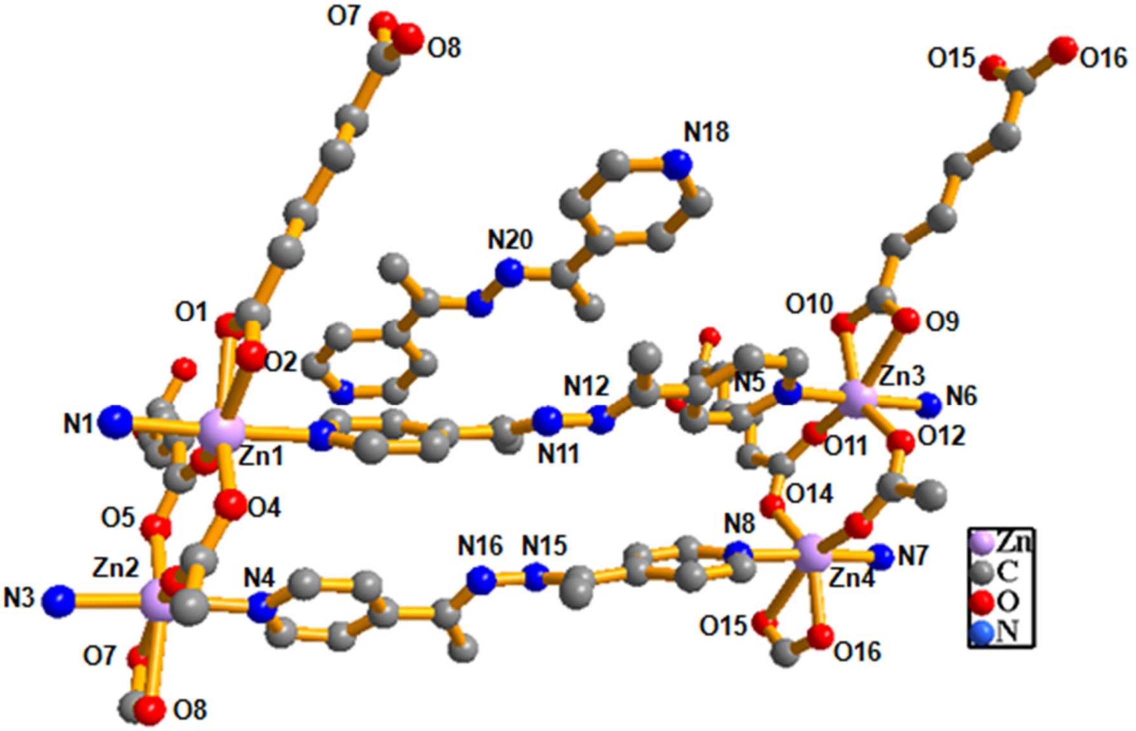


Fig. 8 (a) The coordination environment around Zn1, Zn2, Zn3 and Zn4 atoms of **4**: only the nitrogen atoms of two more bridging 4bpdh spacers are shown for clarity. The H atoms and the guest water molecules are omitted for clarity.

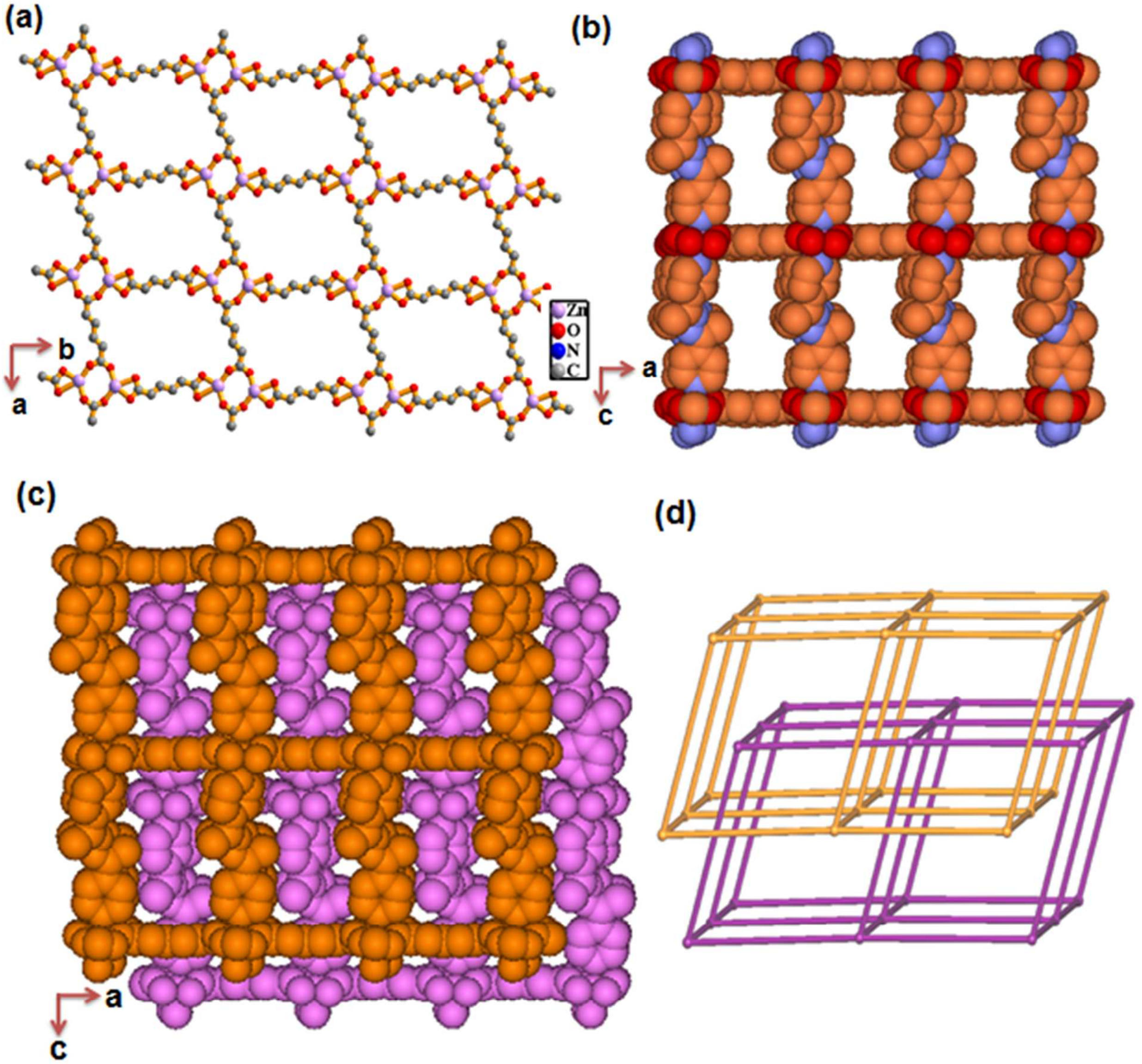


Fig. 9 (a) View of the single $[Zn_2(muco)_2]_n$ 2D sheet in the *ab*-plane, the 4bpdh pillar, solvent molecules and the H atoms are omitted for clarity. (b) CPK view of a single 3D pillar-layered framework in **4**. (c) CPK view showing the 2-fold interpenetrating 3D frameworks and (d) shows the topological representation of the 2-fold interpenetrating nets (two different colors are used to show 2 different 3D nets).

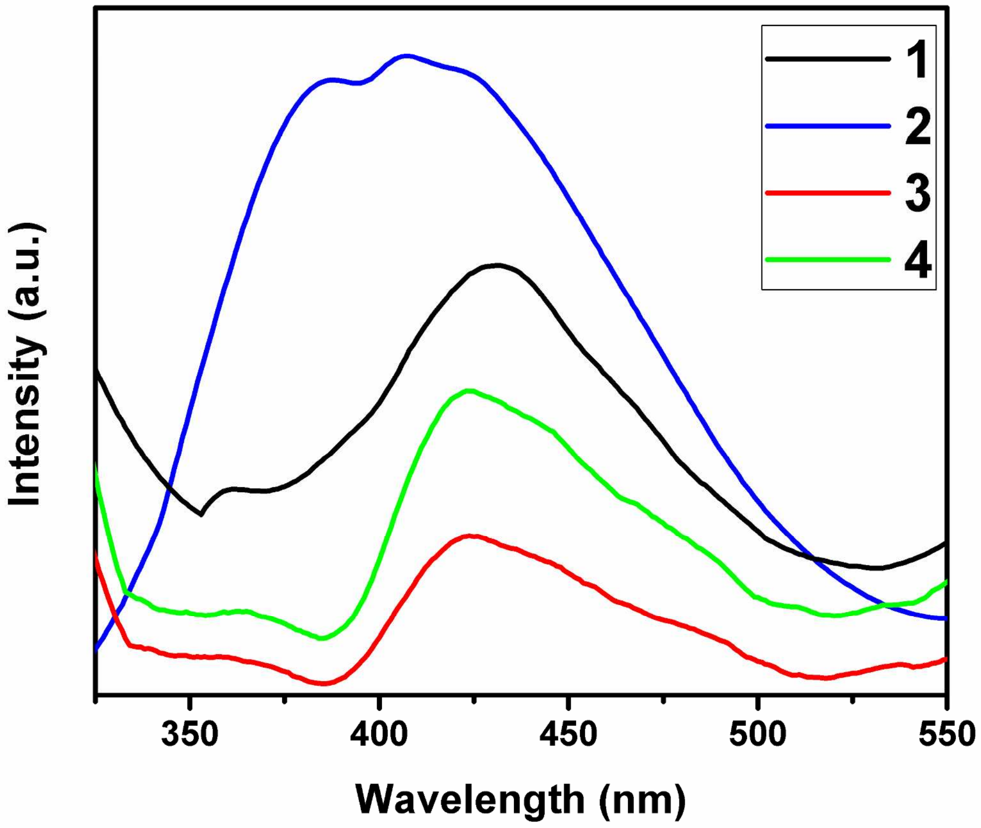


Fig.10 Room temperature solid-state photoluminescence spectra of compounds **1-4.**

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For graphical abstract

Four new MOFs of Zn(II) with different degrees of interpenetration have been synthesized using *trans, trans*-muconic acid and different N,N'-donors.