Exploring conformationally flexible hydrogen-bond-functionalized ligand and counter anions in metal–organic frameworks of Cu(II)†

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Single crystal structures of six metal–organic frameworks (MOFs) derived from *N*,*N*′-bis(3-pyridyl)urea **L1** and Cu(II) salts having different counter ions have been investigated to study the plausible role of conformationally flexible hydrogen-bond-functionalized ligand **L1** and counter ions on the resultant topologies of the MOFs. The ligand adopts the energetically least stable *syn–syn* conformation in most of the MOFs. The 1 : 2 metal–ligand coordination polymers display looped chain topologies with square-pyramidal metal center whereas 1 : 1 metal–ligand coordination polymers show 1D zigzag infinite chain. Although the urea functionality of the ligand does recognize the anions *via* various N–H···O/F interactions, the counter anions do not influence the primary framework structures.

Introduction

Metal–organic frameworks (MOFs) are important to study in the context of designing and synthesizing new materials with desired structures and properties. Syntheses of MOFs with intriguing supramolecular topologies are the results of spontaneous self-assembly processes of metal centers and ligands *via* metal–ligand coordination bond formation and other nonbonded interactions such as hydrogen bonding, π–π interactions *etc*. Research in deliberate synthesis of desired supramolecular architectures and properties of MOFs are intensified in recent times due to their various potential applications.[1] Concepts of supramolecular chemistry[2] and crystal engineering[3] are exploited to generate such useful MOFs.[4] Because of the dynamic nature of the metal–ligand bonds, various coordination geometries of the metal centers, nature and ligating topologies of the ligands used, metal–ligand ratio, nature of the counter ions and various experimental conditions such as the solvents, temperature and crystallization methods influence the final supramolecular assemblies, it is often difficult to predict the final outcome.

When linkers are neutral, the resultant MOFs are cationic. To balance the charge, the counter anions either coordinate to the metal center or remain in the frameworks *via* electrostatic interactions and hydrogen bonding (in suitable cases) thereby greatly influencing the resultant supramolecular architectures. Thus it is important to study the influence of anions on the final supramolecular architectures of the resultant MOFs.

Recently Chen and Mak showed the importance of counter anions in tuning the helical pitches of single-strand helical complexes.[5] Schröder's group studied the influence of anions on long-range chain orientation in 1D coordination polymers,[6] on coordination polymers of Ag(I) with 1,4-dithiacyclohexane,[7] on interpenetration and framework topology of scandium derived coordination frameworks.[8] Hannon and coworkers demonstrated that anions could help form spiral arrays in Ag(I) complexes of simple terpyridine.[9] Vilar's group demonstrated anions as template in synthesizing Ni/Pd containing metalloamacrocycles[10] and also discussed the influence of anions on the resultant structures of Cu(II) MOFs.[11] A switch from discrete complex to a directional 1D network as a function of anions was demonstrated by Josseini *et al.*[12] Recent interests in the study of anion binding modes in the coordination frameworks[13] demonstrated by Steed *et al.*,[13b,c] Gale *et al.*,[13f] Beer and Hayes,[13e] and others are fueled by the possible application of MOFs as anion exchanger.[14]

As a part of our ongoing program on synthesizing new MOFs,[15] we have recently shown[16] supramolecular structural diversity in some Zn(II) MOFs derived from two topologically variant urea functionalized bipyridyl ligands. In this study, the ligating topologies of the ligands were dependent on the relative positions of the pyridyl N atoms. One such ligand namely *N*,*N*′-bis(3-pyridyl)urea **L1** is capable of having different ligating topologies depending on its conformation. Thus, to study the plausible supramolecular structural diversity in MOFs influenced by conformationally flexible ligating topology, flexible coordination geometry of the metal center, counter anions with various shapes and sizes, anion binding modes with the hydrogen bonding functionality of the ligand used, we have reacted a conformationally flexible ligand namely *N*,*N*′-bis(3-pyridyl)urea **L1** with various Cu(II) salts having different counter ions such as perchlorate, triflate, hexafluorosilicate, sulfate and nitrate in 1 : 2 metal–ligand molar ratio. Single crystal structures of six MOFs synthesized in this context are discussed in this paper.

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Results and discussion

Structural characterization of the coordination polymers using single crystal X-ray diffraction techniques

Single crystals suitable for X-ray diffraction studies were grown by slow evaporation of the solution of the reactants at room temperature (see experimental).

Crystal structure of $\{[Cu(\mu L1)_2(H_2O)]\cdot(ClO_4)_2\cdot H_2O\}_n$ 1

Crystals of **1** belong to centrosymmetric monoclinic space group $P2_1/c$. The metal center Cu(II) displays a slightly distorted square pyramidal geometry [∠N–Cu–N = 88.1(1)–90.7(1)°; ∠O–Cu–N = 91.8(1)–95.6(1)°]; the equatorial positions are occupied by **L1** and the axial position is coordinated by a water molecule. The Cu–N distances vary from 2.023(2)–2.032(2) Å whereas the Cu–O distance is 2.352(2) Å. Both the crystallographically independent ligands display *syn–syn* conformation. While one of these two ligands shows reasonably planar molecular geometry with pyridine–urea dihedral angles of 5.9° and 7.0°, the other one adopts a significantly nonplanar geometry with the corresponding dihedral angles of 15.2° and 23.8°. Both the crystallographically independent ligands **L1** connect adjacent metal centers so that a zigzag 1D MOF having metal–organic macrocyclic backbone is formed. In the groove of the 1D looped chain framework are located one water molecule coordinated to the metal center, one solvate water molecule and two perchlorate ions. While the solvate water molecule is held in the groove by hydrogen bonding interactions with the oxygen atoms of the urea moiety of **L1** and one of the perchlorate ions [O···O = 2.898(3)–2.930(3) Å; ∠O–H···O = 153(4)–165(4)°], the perchlorate ions form hydrogen bond with the coordinated water molecule [O···O = 2.805(3)–2.821(3) Å; ∠O–H···O = 143.8–167(3)°]. Such 1D tapes are packed in parallel fashion along the *b*-axis and stabilized further by N–H···O hydrogen bond involving perchlorate ion of one tape and urea moiety of the neighbouring tape [N···O = 2.922(3)–2.941(3) Å; ∠N–H···O = 147.9–158.7°] resulting in a formation of 2D layer structures. Such layers when packed along the *a*-axis are held strongly with hydrogen bond interactions of the type N–H···O involving perchlorate ion of one layer and urea functionality of the top layer [N···O = 2.884(3)–3.028(3) Å; ∠N–H···O = 155.1–163.8°] (Fig. 1). Thermal analysis of **1** indicate the loss of both metal-bound and solvate water molecules at the peak temperature of 111.2° C with experimental weight loss of 4.7% which agrees well with that obtained from X-ray structure (calc. 4.9%).

Crystal structure of $\{[Cu(\mu L1)_2(H_2O)]\cdot(CF_3SO_3)_2\cdot H_2O\}_n$ 2[17]

Single crystal data of **2** reveals that the crystals belong to a centrosymmetric monoclinic space group $P2_1/c$. The metal center Cu(II) displays a slightly distorted square pyramidal geometry with ∠N–Cu–N = 88.7(1)–91.0(1)°; ∠O–Cu–N = 90.4(1)–94.1(1)°; the equatorial positions are occupied by **L1** and the axial position is coordinated by a water molecule. The Cu–N distances are within the range of 2.025(2)–2.040(2) Å whereas the Cu–O distance is 2.452(2) Å. Two crystallographically independent ligands **L1** display *syn–syn* conformation. Both the ligands show nonplanar molecular geometry (pyridine–urea dihedral angle of 8.7°, 19.9° and 7.4°, 17.2°). A 1D zigzag looped chain framework having two Cu(II) metal nodes connected by the bidentate ligands **L1** is formed. In the groove of the framework are located two water molecules—one coordinated to the metal center and the other hydrogen bonded to oxygen atoms of urea functionalities and triflate anion [O···O = 2.987(3)–2.980(3) Å; ∠O–H···O = 144(4)–165(4)°], and two triflate anions hydrogen bonded to coordinated water molecule [O···O = 2.809(3)–2.884(3) Å; ∠O–H···O = 166(3)–168(3)°]. The 1D infinite tapes of the MOFs are further packed in parallel fashion along the *b*-axis and stabilized further by N–H···O hydrogen bonding involving the triflate oxygen atoms of one tape and urea functionality of the neighbouring tape [N···O = 2.876(3)–2.934(3) Å; ∠N–H···O = 154.1–155.3°]; as a result, a 2D hydrogen bonded network of the 1D zigzag ribbon is formed. The 2D layers are further packed on top of each other down the *b*-axis further supported by N–H···O hydrogen bonding involving triflate oxygen atoms of one layer with the urea functionality of the next layer [N···O = 2.907(3)–2.939(3) Å; ∠N–H···O = 161.3–170.6°] (Fig. 2). Thermal analysis of **2** indicates the loss of both metal-bound and solvate water molecules at the peak temperature of 148.3 °C with experimental weight loss of 4.2% which agrees well with that obtained from X-ray structure (calc. 4.4%).

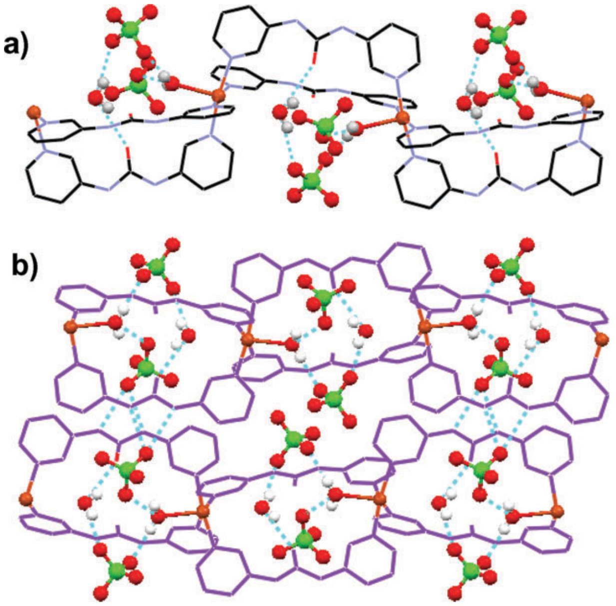


Fig. 1 Crystal structure illustration of **1**; (a) looped chain topology of the framework; (b) self-assembly of the 1D chain *via* various hydrogen bonding involving counter ions and urea functionality.

Crystal structure of $\{[Cu(\mu L1)_2(H_2O)]\cdot(SiF_6)\cdot H_2O\cdot 2EG\}_n$ 3

Reaction of $CuSiF_6$ and ligand **L1** in 1 : 2 molar ratio in EG–H_2O–EtOH mixture (EG = ethylene glycol) afforded single crystals of **3** which belonged to centrosymmetric monoclinic space group $C2/c$. The Cu(II) metal center shows a characteristic of slightly distorted square pyramidal geo-

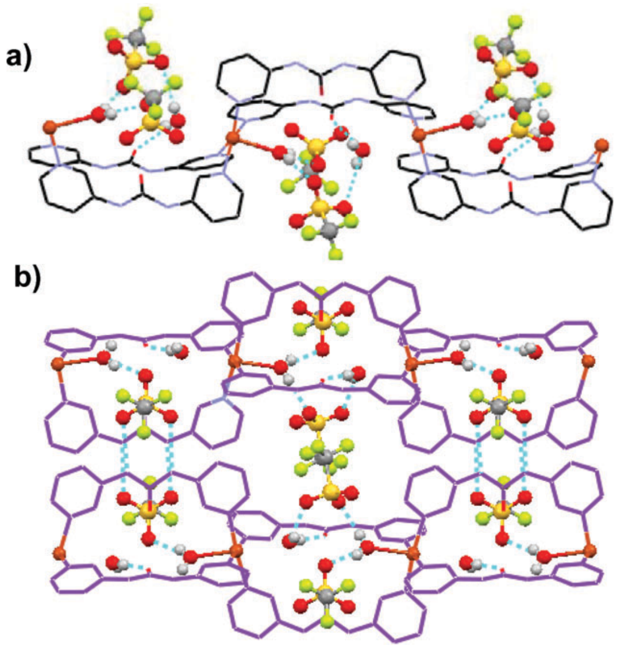


Fig. 2 Crystal structure of **2**; (a) 1D zigzag polymeric chain having looped chain topology; (b) packing of the 1D chain *via* various hydrogen bonding involving counter ions and urea functionality.

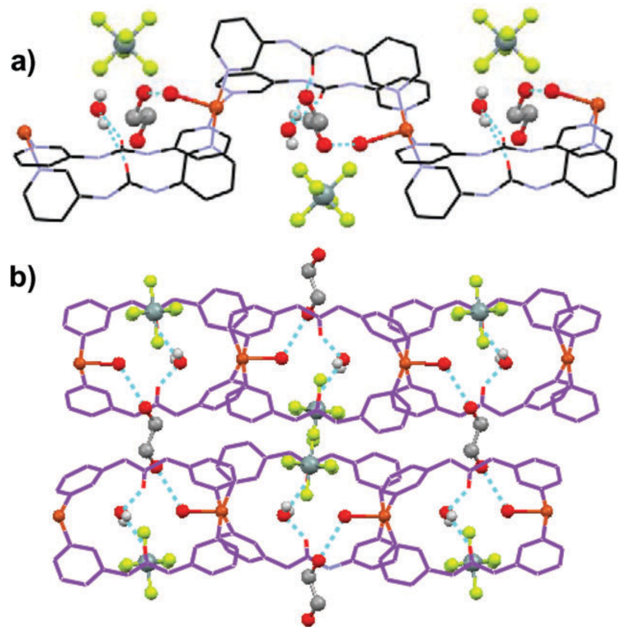


Fig. 3 Crystal structure of **3**; (a) 1D zigzag polymeric chain having looped chain topology; (b) parallel packing of the 1D chain bridged by solvate EG molecule *via* hydrogen bonding and also by various hydrogen bonding involving counter ions and urea functionality.

metry with ∠N–Cu–N = 87.3(2)–93.6(2)°; ∠O–Cu–N = 94.7(2)–97.9(2)°; N-donor bidentate ligands **L1** occupy the equatorial coordination sites whereas one water molecule coordinates to the axial site of the metal center. The corresponding Cu–N distances are within the range of 2.000(4)–2.029(4) Å whereas the Cu–O distance is 2.249(4) Å. The molecular geometries of the ligands are found to be quite nonplanar with pyridine–urea dihedral angles of 3.1°, 11.3° and 21.2°, 30.5° and display *syn–syn* conformation. Each ligand **L1** connects adjacent metal centers in such a way that a 1D zigzag polymeric framework having metal–organic macrocycle is formed. In the groove of the frameworks are located one solvate water molecule hydrogen bonded with the oxygen atoms of the urea functionalities of the crystallographically independent ligands **L1** [O···O = 2.924(6)–2.969(6) Å; ∠O–H···O = 126.2–147.0°], one EG molecule (with high thermal parameters; refined isotropically) hydrogen bonded to metal bound water molecule [O···O = 2.919(9) Å; ∠O–H···O = 143(4)°] and one SiF_6^{2-} ion which appears to be hydrogen bonded with the urea functionality, solvate and metal bound water molecules *via* N–H···F and O–H···F interactions, respectively [N···F = 2.908(6)–3.108(6) Å; ∠N–H···F = 121.2–175.4°; O–H···F = 2.827(5)–3.163(5) Å; ∠O–H···F = 126.0(5)–164.0(6)°].

At the final stage of the refinement, significant electron densities were left in the Fourier map and they could not be assigned to any reasonable model of included solvent molecules. Therefore, SQUEEZE[18] was performed to refine rest of the structure. It indicates the presence of 290 e/unit cell which amounts to 36 e/repeat unit of the coordination polymer. These electron densities may be assigned to one EG molecule (calc. 34 e). The 1D zigzag ribbon frameworks are further packed in a parallel fashion along the *b*-axis sustained by hydrogen bonding involving solvate EG molecules and metal-coordinated water molecules of the neighbouring ribbons [O···O = 2.919(9) Å; ∠O–H···O = 143(4)°]; as a result, 2D hydrogen bonded layers of 1D zigzag ribbons are formed which are further packed on top of each other down the *a*-axis (Fig. 3). Thermal analysis of **3** was not possible due to fast desolvation of the crystals.

Crystal structure of $\{[Cu(\mu L1)_2(H_2O)]\cdot(SiF_6)\cdot 5H_2O\}_n$ 4

When the reaction of $CuSiF_6$ and **L1** (1 : 2 molar ratio) was performed in EtOH–water mixture, crystals of **4** were formed. Crystallographic parameters of **4** indicate that it is iso-structural with **3**, displaying similar cell dimensions and identical space group (monoclinic *C*2/*c*). The metal center displays a slightly distorted square pyramidal geometry with ∠N–Cu–N = 87.2(1)–94.0(1)°; ∠O–Cu–N = 93.8(1)–98.6(1)°; the equatorial positions are occupied by **L1** and the axial site is coordinated by a water molecule. The Cu–N and C–O distances are 2.014(3)–2.039(3) Å and 2.232(2) Å, respectively. The pyridine–urea dihedral angles of 1.3°, 13.9° and 12.9°, 24.6° for the ligands which display *syn–syn* conformation, indicate their significant nonplanarity. The spontaneous self-assembly of metal salt and ligand resulted in a 1D zigzag ribbon architecture having metal–organic macrocyclic backbone. Two solvate water molecules, one counter ion SiF_6^{2-} and one metal-coordinated water molecule occupy the groove of the network.

One of the solvate water molecules is found to be hydrogen bonded with the urea oxygen atom of **L1** [O···O = 2.894(3)–2.974(3) Å; ∠O–H···O = 133.0–135.1°] and F atom

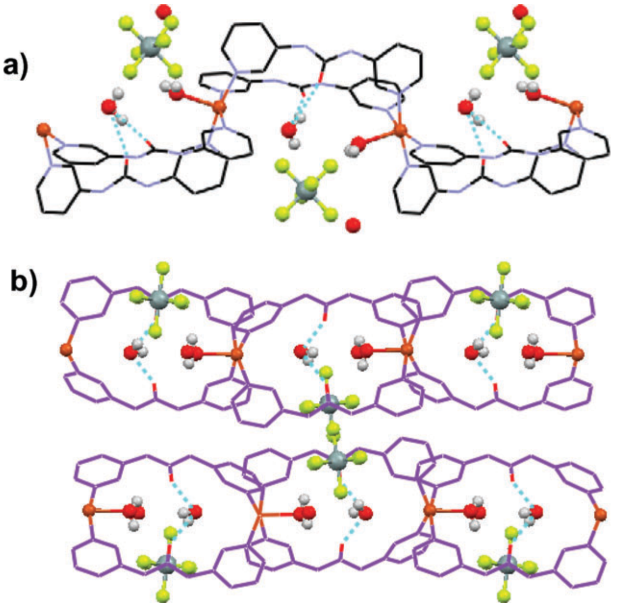


Fig. 4 Crystal structure of **4**; (a) 1D zigzag polymeric chain having looped chain topology; (b) parallel packing of the 1D chain by various hydrogen bonding involving counter ions and urea functionality.

of the counter ion [O···F = 2.978(3) Å; ∠O–H···F = 164.5°]. The second one forms hydrogen bond with the counter ions *via* O–H···F interactions [O···.F = 2.895 Å]. The metal-bound water shows O–H···F interactions with the counter ion [O···F = 2.823(3) Å; ∠O–H···F = 178.7°]. The unaccounted electron densities at the final stage of refinement were subjected to SQUEEZE calculations which indicated the presence of 240 e/unit cell which amounts to 30 e/repeat unit of the coordination polymer. These unaccounted electrons may be assigned as three water molecules (calc. 30 e). Thermal analysis indicates the loss of all water molecules (coordinated, uncoordinated and disordered) with a weight of 14.5% as multistep process with peak temperatures of 78.7 °C and 177.7° C. This value agrees well with the calculated value of 14.9%. The 1D ribbons are further packed in parallel fashion along the *c*-axis sustained by various inter-ribbon N–H···F interactions involving the counter ions and urea functionality of the neighbouring ribbons [N···F = 2.855(3)–3.082(4) Å; ∠N–H···F = 122.3–169.8°](Fig. 4).

Crystal structure of $\{[Cu(\mu L1)\cdot(SO_4)]\cdot MeOH\}_n$ 5

Crystals of **5** were afforded when $CuSO_4$ and **L1** were reacted in 1 : 2 molar ratio in water–MeOH. Crystallographic analysis revealed that **5** belonged to a centrosymmetric monoclinic space group $P2_1/c$ and the ligand and metal salt reacted in 1 : 1 instead of 1 : 2 molar ratio. The metal center Cu(II) displays a slightly distorted square pyramidal geometry with ∠N–Cu–O = 88.0(1)–91.4(1)° (involving Cu and equatorial atoms) and 87.8(1)–99.2(2)° (involving Cu, axial and equatorial atoms); the *trans* equatorial positions are coordinated by the pyridyl N atoms and O atoms of water and sulfate respectively. The axial position is occupied by one water molecule. While equatorial Cu–N/O distances are within the range of 1.995(3)–2.019(3) Å, the axial Cu–O distance is 2.184(3) Å. The ligand **L1** displays a *syn–anti* conformation with slightly nonplanar molecular geometry with pyridine–urea dihedral angles of 7.3°, 15.6°. The MOF can be best described as 1D zigzag chain coordination polymer which are further packed along the *b*-axis sustained by hydrogen bonding involving sulfate ions and urea functionality of the neighbouring chains *via* N–H···O interactions [N···O = 2.836(4)–3.012(5) Å; ∠N–H···O = 146.2–178.7°]. One MeOH molecule is found to be present in the crystal lattice stabilized *via* various O–H···O hydrogen bonding involving metal coordinated water molecules and sulfate ion [O···O = 2.787(5)–2.871(5) Å; ∠O–H···O = 171.0(6)–176.8°] (Fig. 5). Thermal analysis for the crystals of **5** could not be performed due to fast desolvation of the crystals.

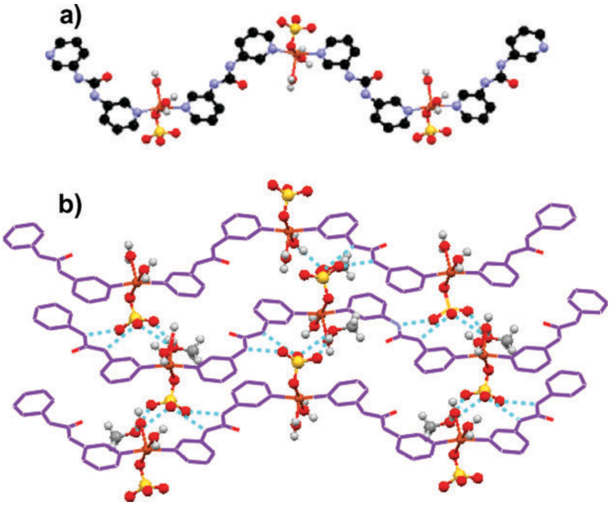


Fig. 5 Crystal structure of **5**; (a) 1D zigzag polymeric chain; (b) parallel packing of the 1D chain by various hydrogen bonding involving counter ions and urea functionality.

Crystal structure of $\{[Cu(\mu L1)(H_2O)_4Cu(\mu L1)(H_2O)_2(NO_3)_2]\cdot(NO_3)_2\cdot MeOH\cdot H_2O\}_n$ 6

$Cu(NO_3)_2$ also reacted with **L1** in 1 : 1 molar ratio when the components were mixed in 1 : 2 (metal–ligand) molar ratio in MeOH–nitrobenzene mixture and afforded crystals of **6**. X-Ray crystallographic studies revealed that **6** belonged to a centrosymmetric triclinic space group $P\bar{1}$. Crystallographically independent two metal centers, Cu(1) and Cu(2), are present in the crystal structure of **6**. Both the metal centers sit on a special position and display slightly distorted octahedral geometry. In Cu(1), the equatorial positions are occupied by water molecules and the axial positions are coordinated by the ligand **L1**. The equatorial angles ∠O–Cu–O range from 89.9(1)–90.1(1)° and the axial angles ∠N–Cu–N is 180.0°. While the equatorial sites of Cu(2) are occupied by two nitrate and two water molecules, the axial positions are coordinated by the pyridyl moiety of the ligand **L1**.

The equatorial angles ∠O–Cu–O range from 86.4(1)–93.6(1)° and the axial angles ∠N–Cu–N is 180.0°.

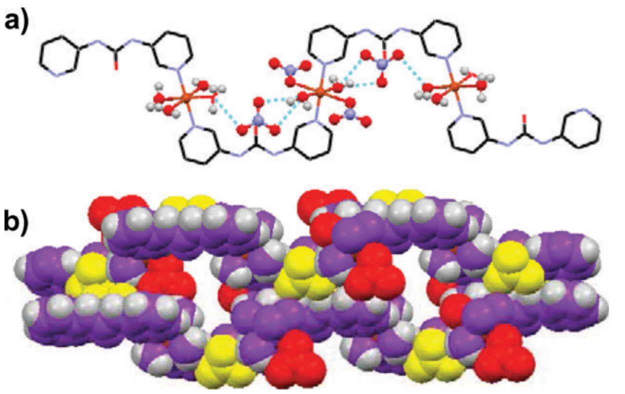
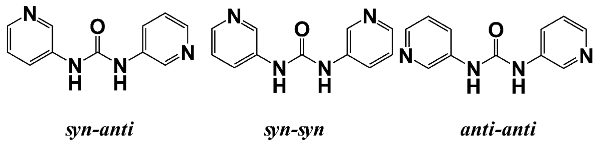


Fig. 6 Crystal structure of **6**; (a) 1D zigzag polymeric chain; (b) parallel packing of the 1D chain by various hydrogen bonding involving counter ions and urea functionality leading to the formation of channel type of microporous network; uncoordinated nitrate is shown in yellow.

The Cu–N and Cu–O distances in both the metal centers are in the ranges of 2.006(2)–2.024(2) and 1.999(2)–2.407(2) Å, respectively. The unaccounted electron densities in the Fourier map at the final stage of refinement were found to be 56 e/unit cell (SQUEEZE calculations) which amounts to 28 e/repeat unit of the coordination polymer. This could be attributed to one MeOH (calc. 18 e) and one water (10 e) molecule. Due to instability of the crystals, thermal analysis could not be performed. The ligand **L1** displays a *syn–syn* conformation with significantly nonplanar molecular geometry displaying pyridine–urea dihedral angles of 15.9°, 16.8°. The MOF can be best described as 1D zigzag framework which is packed further in parallel fashion along the diagonal of the unit cell. As a result, a channel type of microporous network down the *a*-axis is formed. The solvent molecules are presumably located in these channels. Uncoordinated nitrate ion is found to be interacting with the metal bound water and urea functionality *via* O–H···O and N–H···O hydrogen bond [O···O = 2.882(3)–3.016(3) Å; ∠O–H···O = 124.6–158.8(2)°; N···O = 2.845(3)–2.928(3) Å; ∠N–H···O = 166.4–170.2°]. The uncoordinated O atoms of coordinated nitrate form hydrogen bonding interactions with two metal bound water molecules of the neighbouring chain [O···O = 2.735(4)–2.943(3) Å; ∠O–H···O = 136.8–145.2°] (Fig. 6).

Conformation of *N*,*N*′-bis(3-pyridyl)urea L1 and its role on network formation

Considering the relative positions of N atoms of pyridine rings with respect to urea O atom, the hydrogen bond functionalized bidentate ligand **L1** can adopt three possible conformations namely *syn–syn*, *syn–anti* and *anti–anti* (Scheme 1). Computationally these conformations display perfectly flat molecular geometries and *anti–anti* conformer is found to be the most stable one whereas *syn–syn* is reported to be the least stable. However, energy differences among the conformers are not significantly high;[13d] *syn–anti* and *syn–syn* being 1.6 and 3.2 kcal mol^{-1} higher in energy compared to *anti–anti*, respectively. It can be easily envisaged that both *syn–syn* and *anti–anti* conformation can assume a 1D looped chain topology in the resultant MOFs when reacted in 1 : 2 (metal–ligand) molar ratio whereas *syn–anti* conformer might adopt a grid type 2D network. In all these cases, the metal center is assumed to be square-planar, square-pyramidal or octahedral. On the other hand, all the conformations are expected to form 1D framework when reacted in 1 : 1 (metal–ligand) molar ratio with different topologies such as linear or zigzag.



Scheme 1

It is interesting to note that the free ligand structure of **L1** reported for the first time by our group[19] displays the least stable *syn–syn* conformation with not-so-flat molecular geometry with pyridine–urea dihedral angle of 11.5°. In the present study, the ligand **L1** adopts mostly *syn–syn* conformation irrespective of their metal–ligand ratio in the MOFs **1–4** and **6**. In **5**, however, it assumes *syn–anti* conformation. In all the cases, the ligand geometries are not-so-flat displaying pyridine–urea dihedral angles ranging from as low as 1.3° to as high as 30.5°. As a result of such conformations and metal centers (either square-pyramidal in **1–5** and octahedral in **6**) frameworks of these structures adopt 1D ribbon topologies in **1–4** and zigzag 1D topology in **5** and **6**.

Role of counter anions

The counter anions such as perchlorate, triflate, hexafluorosilicate, sulfate and nitrate used in the present study are of various sizes and shapes. Except hexafluorosilicate, all of them are oxoanions and therefore, are expected to be recognized by the aryl substituted urea[20] functionality of the ligand **L1** *via* N–H···O hydrogen bonding. Due to enhanced electron withdrawing effect of the aryl groups, the urea functionality in **L1** is also expected to bind F atoms of hexafluorosilicate through N–H···F interactions. As a result, they are likely to greatly influence the resultant supramolecular structures of the MOFs. As can be seen from Fig. 7 urea functionalities in these MOFs do recognize the anions either *via* N–H···O or N–H···F interactions and display mostly chelate hydrogen bonding topologies. In addition to chelate hydrogen bonding motif, bifurcated hydrogen bonding topology is also observed in **1**. In **3** and **4**, the urea functionality interacts with three F

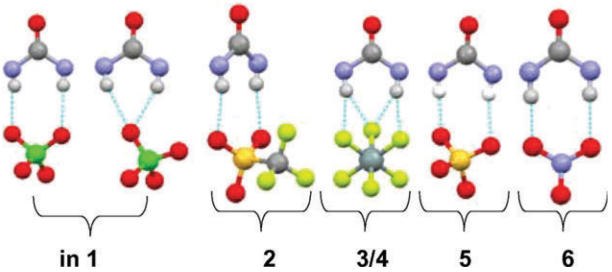


Fig. 7 Anion binding modes with urea functionalities in the MOFs.

atoms presumably due to the octahedral geometry of the anion hexafluorosilicate.

However, it is clear from the structures of MOFs **1–4** that counter anions do not have much influence on the primary framework structures. Thus, all these MOFs display 1D ribbon type of framework having metal–organic macrocyclic backbone. On the other hand, in 1 : 1 metal–ligand coordination polymers namely **5** and **6**, the sulfate and nitrate anions are coordinated to the metal centers and help in stabilizing the 1D zigzag polymeric chains *via* various hydrogen bonding interactions. It may be noted that considerably weak interactions such as C–H···O interactions further contribute to the overall stabilization of the crystal structures of all the MOFs studied herein.

Conclusions

The fact that all the MOFs **1–4** display looped chain framework topologies indicate that the counter anions, although differ from each other in size, shape and coordination ability, do not influence the primary framework structures. In all the MOFs **1–4**, the ligand adopts the least stable *syn–syn* conformation. In 1 : 1 metal–ligand MOFs **5–6** the ligand adopt *syn–anti* in **5** and *syn–syn* in **6**. Conformation of the ligands in these MOFs appears to be dictated by the geometry of the metal center (mostly square-pyramidal) as well as the metal–ligand ratio. Perchlorate, triflate and hexaflurosilicate[21] remain uncoordinated presumably because of their poor coordination ability and strong hydrogen bonding interactions with the urea backbone of the ligand **L1**. In all the cases, the counter anions whether coordinated or noncoordinated are recognized by the urea functionality of the ligand backbone.

Experimental

Materials and methods

Synthesis, characterization of the ligand **L1**, has been previously reported by our group.[19] All chemicals were commercially available (Aldrich) and used without further purification. Microanalyses were performed on a Perkin-Elmer elemental analyzer 2400 Series II. FT-IR spectra were recorded using Perkin-Elmer Spectrum GX and TGA analyses were performed on a Mettler Toledo TGA/SDTA851^e. Powder X-ray patterns were recorded on a XPERT Philips (CuKα radiation, λ = 1.5418 Å) diffractometer.

Syntheses of the coordination polymers‡

{[Cu(μL1)$_2$(H$_2$O)]·(ClO$_4$)$_2$·H$_2$O}$_n$ 1. Coordination polymer **1** was synthesised by layering an ethanolic solution (10 mL) of the ligand **L1** (42.8 mg, 0.2 mmol) over an aqueous solution of Cu(ClO$_4$)$_2$·6H$_2$O (37.0 mg, 0.1 mmol). After a period of one week X-ray quality single crystals were obtained (45.7 mg, yield: 63%) Anal. Calc. for $C_{22}H_{24}Cl_2CuN_8O_{12}$: C, 36.35; H, 3.33; N, 15.41. Found: C, 35.47; H, 3.27; N, 14.85. FT-IR (cm^{-1}): 3584w, 3519m, 3432b, 3365b, 3135w, 3099w, 2973w, 2925w, 2855w, 1722s, 1693m, 1615m, 1587vs, 1550vs, 1482vs, 1428vs, 1368m, 1335s, 1279vs, 1211vs, 1140w, 1109b, 1069w, 923m, 808s, 745s, 700vs, 671w, 652m, 624s, 540m, 511w, 468m, 426m.

{[Cu(μL1)$_2$(H$_2$O)]·(CF$_3$SO$_3$)$_2$·H$_2$O}$_n$ 2. Coordination polymer **2** was synthesised by layering an ethanolic solution (10 mL) of the ligand **L1** (42.8 mg, 0.2 mmol) over an aqueous solution of Cu(CF$_3$SO$_3$)$_2$ (36.1 mg, 0.1 mmol). After a period of one week X-ray quality single crystals were obtained (51 mg, yield: 61.7%) Anal. Calc. for $C_{24}H_{24}CuF_6N_8O_{10}S_2$: C, 34.89; H, 2.93; N, 13.56. Found: C, 35.06; H, 2.17; N, 13.17. FT-IR (cm^{-1}): 3573w, 3505b, 3349w, 3308vs, 3228m, 3119s, 3040m, 2977w, 1925b, 1855w, 1721vs, 1679w, 1648vs, 1619s, 1588vs, 1557vs, 1483vs, 1427vs, 1337vs, 1276m, 1250m, 1228b, 1185w, 1166s, 1069s, 1029vs, 917m, 810vs, 763m, 703vs, 636vs, 576s, 542w, 518s, 426m.

{[Cu(μL1)$_2$(H$_2$O)]·(SiF$_6$)·H$_2$O·2EG}$_n$ 3. Coordination polymer **3** was synthesised by layering an ethanolic solution (10 mL) of the ligand **L1** (42.8 mg, 0.2 mmol) over an aqueous ethylene glycol solution (20 mL) containing a mixture of Cu(BF$_4$)$_2$·6H$_2$O (34.5 mg, 0.1 mmol) and (NH$_4$)$_2$SiF$_6$ (17.8 mg, 0.1 mmol). After a period of one week X-ray quality single crystals were obtained (43.6 mg, yield: 54.9%). Anal. Calc. for $C_{26}H_{36}CuF_6N_8O_8Si$: C, 39.32; H, 4.57; N, 14.11. Found: C, 38.15; H, 4.149 N, 14.86. FT-IR (cm^{-1}): 3525b, 3352b, 3123m, 1720s, 1620s, 1589vs, 1561vs, 1484vs, 1430vs, 1338vs, 1279vs, 1219s, 1135b, 1072m, 1043m, 918b, 813s, 741s, 702m, 652s, 478s.

{[Cu(μL1)$_2$(H$_2$O)]·(SiF$_6$)·5H$_2$O}$_n$ 4. Coordination polymer **4** was synthesised by layering an ethanolic solution (10 mL) of the ligand **L1** (42.8 mg, 0.2 mmol) over an aqueous solution (20 mL) containing a mixture of Cu(BF$_4$)$_2$·6H$_2$O (34.5 mg, 0.1 mmol) and (NH$_4$)$_2$SiF$_6$ (17.8 mg, 0.1 mmol). After a period of one week X-ray quality single crystals were obtained (38 mg, yield: 50.1%).

Anal. Calc. for $C_{22}H_{32}CuF_6N_8O_8Si$: C, 35.60; H, 4.35; N, 15.10. Found: C, 34.95; H, 3.43; N, 14.37. FT-IR (cm^{-1}): 3525m, 3353b, 3120b, 2971m, 2363b, 1722s, 1621m, 1589vs, 1561vs, 1484vs, 1430vs, 1219vs, 1135b, 1072m, 919s, 814s, 741b, 701m, 651s, 544m, 476vs, 429w.

{[Cu(μL1)(SO$_4$)(H$_2$O)$_2$]·MeOH}$_n$ 5. Coordination polymer **5** was synthesised by layering a methanolic solution (10 mL) of the ligand **L1** (42.8 mg, 0.2 mmol) over an aqueous solution of Cu(SO$_4$)$_2$·5H$_2$O (49.8 mg, 0.2 mmol). After a period of two weeks X-ray quality single crystals were obtained (10.5 mg, yield: 10.7%) Anal. Calc. for $C_{11}H_{14}CuN_4O_7S\cdot0.5CH_3OH$: C, 32.43; H, 3.79; N, 13.16. Found: C, 31.76; H, 3.05; N, 12.13. FT-IR (cm^{-1}): 3353b, 3248b, 3132w, 3072m, 2979m, 2854w, 2362m, 1787b, 1675s, 1629vs, 1591vs, 1484vs, 1442vs, 1343vs, 1294s, 11232m, 1111b, 1034s, 970s, 919vs, 892m, 824m, 755s, 695s, 644s, 615m, 596m, 420s.

{[Cu(μL1)(H$_2$O)$_4$Cu(μL1)(H$_2$O)$_2$(NO$_3$$^-$)$_2$]·(NO$_3$)$_2$·MeOH·H$_2$O}$_n$ 6. Coordination polymer **6** was synthesised by layering of a methanolic solution (10 mL) of Cu(NO$_3$)$_2$·3H$_2$O (48.2 mg, 0.2 mmol) over a nitrobenzene–methanol (10 : 2, v/v) solution (10 mL) of the ligand **L1** (42.8 mg, 0.2 mmol). After a period of two weeks few X-ray quality single crystals were obtained along with precipitate (crystal yield: 5%). Although

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‡ Yield of the crystals is calculated based on Cu salt.

Table 1 Crystallographic parameters for **1–6**

Crystal data	**1**	**2**	**3**	**4**	**5**	**6**
Empirical formula	$C_{22}H_{24}Cl_2CuN_8O_{12}$	$C_{24}H_{24}CuF_6N_8O_{10}S_2$	$C_{23}H_{24}CuF_6N_8O_5Si$	$C_{22}H_{24}CuF_6N_8O_{4.50}Si$	$C_{12}H_{18}CuN_4O_8S$	$C_{11}H_{16}CuN_6O_{10}$
Formula weight	726.93	826.17	698.13	678.12	441.90	455.84
Crystal size/mm	0.44 × 0.33 × 0.21	0.42 × 0.30 × 0.19	0.24 × 0.18 × 0.09	0.32 × 0.18 × 0.08	0.25 × 0.18 × 0.06	0.36 × 0.21 × 0.06
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$C2/c$	$C2/c$	$P2_1/c$	$P\bar{1}$
a/Å	8.7969(6)	9.0522(6)	21.398(2)	21.2107(14)	7.704(4)	8.3292(7)
b/Å	17.9832(13)	18.0988(12)	17.9035(17)	17.9344(12)	21.708(11)	9.7989(8)
c/Å	17.5198(12)	19.5538(13)	17.4386(17)	17.5455(12)	12.165(5)	13.155(1)
α/°						80.124(1)
β/°	90.364(1)	95.286(1)	105.302(2)	104.877(1)	122.77(2)	74.892(1)
γ/°						88.202(1)
Volume/$Å^3$	2771.5(3)	3190.0(4)	6443.9(11)	6450.6(7)	1710.7(14)	1021.11(4)
Z	4	4	8	8	4	2
$D_{calc.}$/g cm^{-3}	1.742	1.720	1.439	1.397	1.716	1.483
$F(000)$	1484	1676	2840	2760	908	466
μ MoKα/mm^{-1}	1.061	0.919	0.794	0.790	1.450	1.128
Temperature/K	100(2)	100(2)	100(2)	100(2)	298(2)	100(2)
Range of h, k, l	−7/11, −20/22, −22/22	−11/11, −23/23, −23/25	−28/27, −14/22, −22/23	−22/22, −12/19, −16/18	−10/9, −27/26, −15/16	−10/10, −7/13, −14/16
θ min/max	1.62/28.31	2.09/28.31	1.51/28.36	1.99/22.50	1.88/28.11	1.63/28.20
Reflections collected/ unique/observed ($I > 2\sigma(I)$)	16591/6375/5033	19144/7415/5630	19036/7419/3660	12238/4136/3686	9427/3849/2175	6085/4444/3765
Data/restraints/ parameters	6375/0/419	7415/0/476	7419/0/395	4136/0/389	3849/0/247	4444/0/263
Goodness of fit on F^2	1.026	1.021	0.921	1.064	0.902	1.108
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0406$ $wR_2 = 0.0970$	$R_1 = 0.0427$ $wR_2 = 0.0970$	$R_1 = 0.0726$ $wR_2 = 0.1677$	$R_1 = 0.0403$ $wR_2 = 0.1124$	$R_1 = 0.0472$ $wR_2 = 0.1060$	$R_1 = 0.0428$ $wR_2 = 0.1307$
R indices (all data)	$R_1 = 0.0575$ $wR_2 = 0.1042$	$R_1 = 0.0632$ $wR_2 = 0.1053$	$R_1 = 0.1446$ $wR_2 = 0.1931$	$R_1 = 0.0442$ $wR_2 = 0.1162$	$R_1 = 0.0942$ $wR_2 = 0.1230$	$R_1 = 0.0495$ $wR_2 = 0.1394$

the X-ray quality crystal yield is poor in this case, a fast reaction resulted a crystalline precipitate; XRPD of which matches reasonably well with that of the simulated pattern obtained from single crystal structure of **6**. No satisfactory analytical data could be obtained presumably because of fast desolvation of the crystals. FT-IR (cm^{-1}): 3855w, 3749m, 3650w, 3284m, 3251m, 3090m, 2361m, 1715vs, 1619s, 1589vs, 1562vs, 1482s, 1430vs, 1362b, 1308m, 1279vs, 1216vs, 1137s, 1112w, 1070m, 1042m, 916m, 817s, 792m, 748w, 693vs, 654w, 544w, 507w, 421m.

Single crystal X-ray diffraction

X-Ray single crystal data were collected using MoKα (λ = 0.7107 Å) radiation on a SMART APEX diffractometer equipped with CCD area detector. Crystals were selected from the mother liquor and immediately immersed in Paratone oil. Data collection, data reduction, structure solution/refinement were carried out using the software package of SMART APEX.

All structures were solved by direct methods and refined. In most of the cases, nonhydrogen atoms were treated anisotropically. Whenever possible, the hydrogen atoms were located on a difference Fourier map and refined. In other cases, the hydrogen atoms were geometrically fixed. Crystallographic parameters are listed in Table 1.

CCDC reference numbers 612481–612486.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b606150h

In **3**, the solvent water molecule and the EG molecule were located on the Fourier map and refined. Due to the high thermal parameters, EG molecule was refined isotropically. At the final stage of the refinement, 11 extra electron density peaks amounting to 27.88 e $Å^{-3}$ (ranging from 4.05–1.39 e $Å^{-3}$) were left. However, attempts to assign these electron densities to any proper model were unsuccessful. PLATON/SQUEEZE was used to refine the coordination polymer framework along with the solvate EG and water molecules by excluding the disordered solvent electron densities. This calculations resulted 290 e/unit cell or 36 electron/monomer unit of the coordination polymers. This may be attributed to one EG molecule (34 electrons) per monomer unit.

In **4**, two solvate water molecules were refined anisotropically. At the final stage of the refinement, the excess electron densities amounting to 23.59 e $Å^{-3}$ (ranging from 3.99–1.64 e $Å^{-3}$) were left. Attempts to assign proper model for these peaks were unsuccessful. PLATON/SQUEEZE was performed to refine the coordination polymer framework along with the solvate water molecules by excluding the disordered solvent electron densities. These calculations indicate the presence of 240 e/unit cell or 30 electron/monomer unit of the coordination polymer. This may be attributed to three water molecules per monomer unit of the MOF.

In **6**, the solvate molecules were found to be disordered and attempts to assign proper model for these peaks were unsuccessful. At the final stage of the refinement, 11 excess electron density peaks amounting to 26.49 e Å^{-3}ranging from 6.05–1.12 e Å^{-3}were left. In order to refine the MOF, PLATON/SQUEEZE was performed excluding all the contribution of the disordered solvents which amounts to 56 e/unit cell or 28 e/monomer unit of the coordination polymer. This may be attributed to one methanol molecule (18 e) and one water molecule (10 e).

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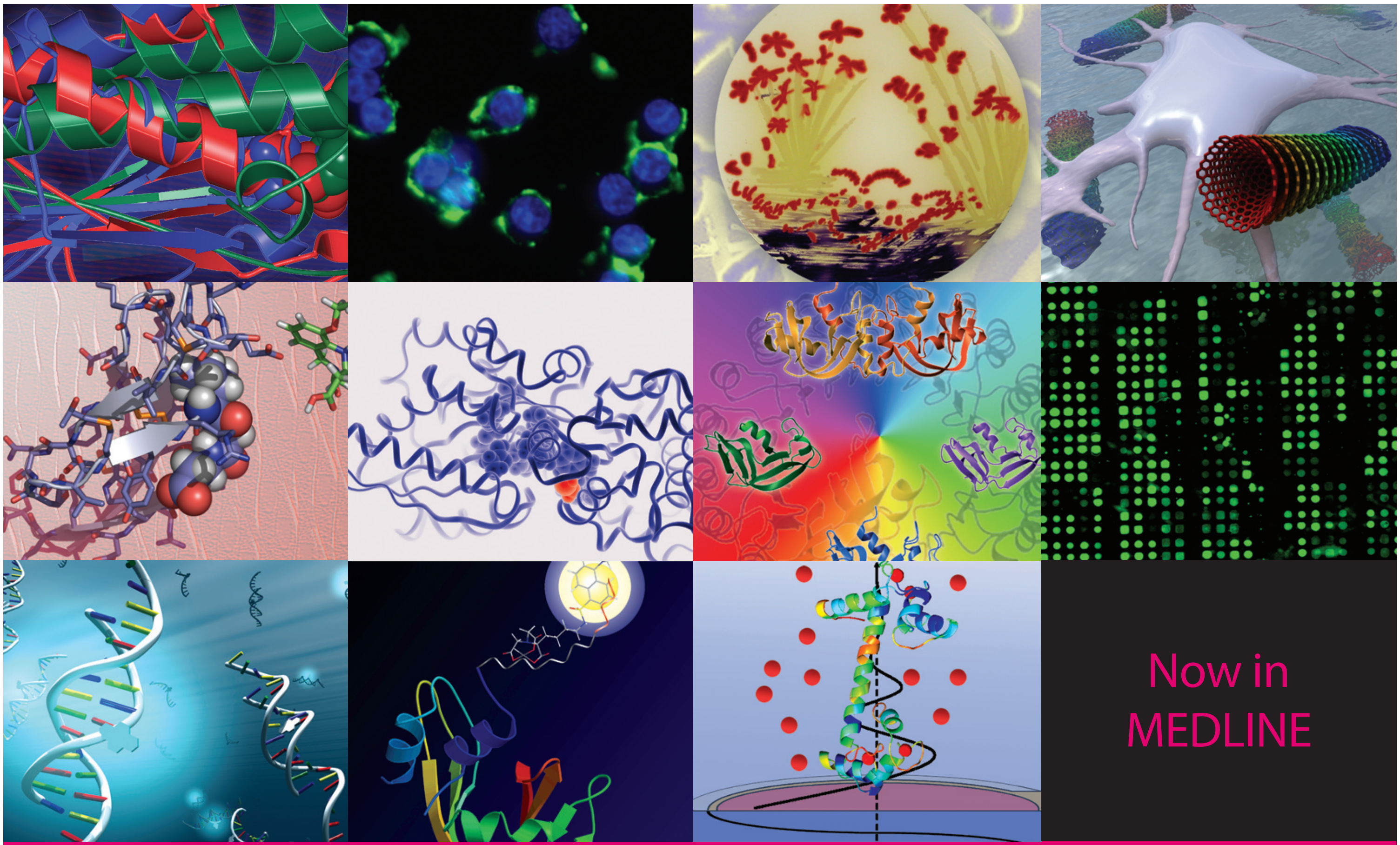
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