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Structural diversities in Cu(I) and Ag(I) sulfonate coordination polymers and anion exchange properties

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Two new Cu(I), [Cu₂(bds)(bpy)₂]-2H₂O (**1**), [Cu₄(bds)₂(azpy)₄]-6H₂O (**3**) (where bds = benzene-1,3-disulfonate, bpy = 4,4'-bipyridine and azpy = 4,4'-azopyridine) and four Ag(I), [Ag₂(bds)(bpy)₂]-2H₂O (**2**), [Ag₂(bds)(azpy)₂]-4H₂O (**4**), [Ag(bds)_{1/2}(bpe)]-3H₂O (**5**), [Ag₄(bds)₂(tmdp)₄]-9H₂O (**6**) (where bpe = 1,2-di(4-pyridyl)ethylene and tmdp = 4,4'-trimethylenedipyridine), compounds have been synthesized, structures determined and characterized by elemental analysis, IR, UV-vis and thermal studies. Structure of compounds change from 1D (**1** and **2**) to 2D (**3-5**) and interpenetrated 3D (**6**). In the case of **5**, solid-state [2+2] photochemical cycloaddition reaction has been performed. Compound **2** exhibits reversible anion exchange for perchlorate and permanganate whereas other compounds (**1**, **3-6**) exhibit irreversible anion exchange behaviour for perchlorate. Catalytic studies on **2** indicate Lewis acidity.

Introduction

The design, synthesis, and investigation of the properties of coordination polymers have gained a lot of attraction due to their new and novel network topologies and interesting properties in the areas of catalysis, luminescence, magnetic, gas sorption and separation, and molecular recognition.¹⁻⁶ The coordination polymers have structures built from ligands containing pyridyl and/or carboxylate units that allow scientists both structural as well as coordination flexibility. The coordination polymers formed employing sulfonate linkers are limited, possibly due to the weak coordination abilities of the sulfonates with transition metal ions.⁷ The sulfonate units, however, appear to coordinate better with alkali metal ions and Ag(I).^{1a,8}

The binding modes and the topological arrangement of the silver(I)-sulfonates, can be effectively tailored employing neutral N-containing secondary ligands.^{8d,8i,9} In many of the structures, the sulfonates behave either as a noncoordinating counter anion or exhibit simple coordination modes.^{1a,8,9} Though, there are reports of silver sulfonate compounds in the literature, the studies on Cu(I) coordination polymers with sulfonate ligands are limited.¹⁰ This promoted us to investigate compounds based on Cu(I) as well as Ag(I). As part of this study, different bipyridine ligands were employed which could offer flexibility as well as connectivity to alter the dimensionality of the structures. Our investigation have been successful and presently we have isolated six new compounds, [Cu₂(bds)(bpy)₂]-2H₂O (**1**), [Ag₂(bds)(bpy)₂]-2H₂O (**2**), [Cu₄(bds)₂(azpy)₄]-6H₂O (**3**), [Ag₂(bds)(azpy)₂]-4H₂O (**4**), [Ag(bds)_{1/2}(bpe)]-3H₂O (**5**) and [Ag₄(bds)₂(tmdp)₄]-9H₂O (**6**) exhibiting one (**1** and **2**), two (**3-5**) and three dimensional (**6**) extended structures. In this manuscript, we present the synthesis, structure and other related studies of the compounds.

Experimental

Synthesis and Characterization

All the reagents and solvents were procured from different sources and used as received. The compounds **1** and **3** were prepared employing the solvothermal method. In a typical synthesis for [Cu₂(bds)(bpy)₂(H₂O)]-H₂O (**1**), Cu(NO₃)₂·6H₂O (0.100 g, 0.41 mmol), sodium benzene-1,3-disulfonate (Na₂bds, 0.175 g, 0.62 mmol) and 4,4'-bipyridine (0.065 g, 0.41 mmol) were added to 7 mL of DMF and 3 mL distilled water. The solution was stirred for 30 minutes, transferred to a PTFE-lined stainless steel 23 mL autoclave, sealed and heated to 120°C for 3 days, followed by slow cooling to room temperature. The reaction yielded yellow rectangular crystals which were filtered, washed (water and methanol) and dried under vacuum. Similar synthesis procedure was employed for the preparation of the compounds **3** (Table 1).

The compounds **2** and **4-6** were prepared at room temperature with a similar procedure (Table 1). In a typical synthesis for [Ag₂(bds)(bpy)₂]-2H₂O (**2**), to a mixture of sodium benzene-1,3-disulfonate (0.141 g, 0.50 mmol) and AgNO₃ (0.170 g, 1.0 mmol) in 2 mL of water was added a solution of 4,4'-bipyridine (0.156 g, 1.00 mmol) in 5 mL of methanol with stirring which immediately led to the formation of a white precipitate. The precipitate was dissolved by the drop wise addition of an aqueous solution of NH₃ and the clear solution was kept for crystallization in dark. After a week, colorless, rectangular crystals were obtained. The crystals were filtered, washed (water and methanol) and dried under vacuum.

Initial characterizations were carried out by elemental analysis, powder X-ray diffraction (XRD), thermogravimetric analysis (TGA), IR and UV-Vis spectroscopic studies. Powder X-ray diffraction patterns were recorded in the 2θ range of 5-30° using Cu-Kα radiation (Philips X'pert Pro). Mercury software was used to generate the simulated powder X-ray diffraction patterns from the structures determined using the single crystal XRD studies. The experimental PXRD patterns and the simulated PXRD patterns matched well for all the compounds, suggesting phase purity (ESI, Figure S1).

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Electronic Supplementary Information (ESI) available: Tables for selected bond distances and bond angles, hydrogen bonds and UV-visible bands, PXRD patterns, additional figures for structural description, TGA, UV, ¹H NMR and PL plots of the compounds. See DOI: 10.1039/x0xx00000x

Table 1: Synthesis composition and conditions employed for the compounds 1-6

Compounds	Composition	Temp (°C)	Time	Yield (%) ^a
[Cu ₂ (bds)(bpy) ₂]-2H ₂ O, 1	Cu(NO ₃) ₂ ·6H ₂ O + 1.5bds + bpy + 221DMF + 407H ₂ O	120	72 hr	67
[Ag ₂ (bds)(bpy) ₂]-2H ₂ O, 2	2Ag(NO ₃) + bds + bpy + 222H ₂ O + 248MeOH	RT	7 days	83
[Cu ₄ (bds) ₂ (azpy) ₄]-6H ₂ O, 3	Cu(NO ₃) ₂ ·6H ₂ O + 1.5bds + Azbpy + 252DMF + 271H ₂ O	120	72 hr	64
[Ag ₂ (bds)(azpy) ₂]-4H ₂ O, 4	2Ag(NO ₃) + bds + Azbpy + 222H ₂ O + 248MeOH	RT	7 days	87
[Ag(bds) _{1/2} (bpe)]-3H ₂ O, 5	2Ag(NO ₃) + bds + bpe + 222H ₂ O + 248MeOH	RT	7 days	83
[Ag ₄ (bds) ₂ (tmdp) ₄]-9H ₂ O, 6	2Ag(NO ₃) + bds + tbp + 222H ₂ O + 248MeOH	RT	7 days	79

^aYields are calculated based on the respective metals. Compositions given are molar compositions. CHN analysis for **1**: Calc(%) C 43.88; H 3.40; N 7.87, Found: C 43.71; H 3.49; N 7.97. IR (cm⁻¹): 1603(s), 1527(w), 1482(w), 1409(m), 1246(m), 1220(s), 1199(s), 1165(m), 1037(s) 993(w); for **2**: Calc(%) C 39.02; H 3.02; N 7.00, Found: C 38.93; H 3.05; N 7.13. IR (cm⁻¹): 1603(m), 1534(w), 1487(w), 1414(m), 1247(m), 1223(s), 1200(s), 1171(m), 1035(s) 993(w); for **3**: Calc(%) C 39.74; H 3.34; N 14.26, Found: C 39.45; H 3.51; N 14.72. IR (cm⁻¹): 1603(s), 1521(m), 1479(m), 1424(s), 1215(s), 1183(m), 1027(s), 992(w); for **4**: Calc(%) C 34.99; H 3.16; N 12.56, Found: C 34.93; H 3.19; N 12.92. IR (cm⁻¹): 1595(s), 1566(m), 1487(m), 1414(m), 1244(m), 1220(s), 1202(s), 1168(m), 1037(s), 1005(m); for **5**: Calc(%) C 41.39; H 3.47; N 6.44, Found: C 41.34; H 3.49; N 6.57. IR (cm⁻¹): 1603(s), 1558(w), 1500(w), 1424(w), 1249(m), 1223(s), 1204(s), 1168(m), 1037(s), 1011(w), 849(s); for **6**: Calc(%) C 41.35; H 4.45; N 6.03, Found: C 41.38; H 4.47; N 6.12. IR (cm⁻¹): 1603(s), 1558(w), 1495(w), 1422(m), 1243(m), 1225(s), 1195(s), 1168(m), 1037(s), 1003(w).

The room temperature IR spectra (Perkin Elmer Spectrum 1000) exhibited sharp characteristic bands. The various observed bands can be identified with the functional groups. Thus, the broad bands at ~3386-3400 cm⁻¹ can be identified with the O-H stretching of water. In addition, The characteristic vibrations of ν₃(SO₃⁻) are observed at 1247-1215, 1225-1220 and 1183-1168 cm⁻¹; further ν_{as}(SO₃⁻) signals are also observed at 1037-1027 and 1011-992 cm⁻¹ in all compounds along with other characteristic bands.

Thermogravimetric analysis (TGA) (Mettler-Toledo) was carried out under oxygen atmosphere (flow rate = 50 mL/min) in the temperature range 30-850°C (heating rate = 10°C/min). In the case of compound **1**, we observed a three step weight loss. The first weight loss of 2.9% observed around 100°C corresponds to the loss of the lattice water molecule (calcd 2.5%). The second weight loss of 29.7% observed around 360°C could be due to the loss of one of the bipyridyl as well as one lattice water molecule (calcd 27%). The total observed weight loss of 72% around 420°C corresponds well with the

loss of all the organic species. Similar decomposition patterns were also found in other complexes (ESI, Figure S2) which are summarised in Table S1 (ESI).

The UV-Vis spectra were recorded in the solid state at room temperature (Perkin-Elmer model Lambda 35). Compound **1** exhibited absorption bands at 420, 327 (shoulder) and 248 nm. The other compounds have similar absorption (ESI, Fig S3) bands, which have been summarized in Table S2 (ESI). The higher energy absorption band (~250 and ~350 nm) may be assigned to the intra-ligand n → π* and π → π* transition whereas the lower energy band (~450 nm) could be due to the metal to ligand charge transfer transitions, involving the possible promotion of the lone pair of electrons of the metal to the π* orbital of the ligand.

The photoluminescence spectra for all the compounds were recorded on solid samples at room temperature (Perkin-Elmer, LS 55). The compound **1**, when excited at 250 nm, emitted an intense band at 394 nm along with a weak band centered at 488 nm (ESI, Figure S4). Similar emission bands were also observed in the other compounds when they were excited at 250 nm which are given in Table 2. While 4,4'-bipyridine shows an emission band at 390 nm when excited at 248 nm which is due to π* → π transition.¹¹ The strong emission peaks in between 390-398 nm are observed in all the compounds, similar to that of 4,4'-bipyridine, which indicates that the origin of these emissions involves emissive state derived from ligand-centered [π-π*] transition. The weak band at ~488 nm, are could be due to MLCT or LMCT transitions.

Table 2: Emission bands of compound 1-6

Compounds	Emission bands (nm)
1	394, 488(weak)
2	396, 488(weak)
3	393
4	398
5	398, 488(weak)
6	390, 421(shoulder), 486(weak)

Anion Exchange: In separate 10 mL solution of 0.1 M NaNO₃ or NaClO₄ or KMnO₄, 50 mg of compounds were soaked without stirring at room temperature for 7 days. The crystalline products were isolated by filtration and rinsed with water/methanol. The solid products after the exchange were placed in a 0.1 M solution of Na₂bds. The mixture was stirred for 3 days, followed by filtration to isolate the solid product.

Heterogeneous Catalysis: Compound, **2** was selected for the study of Lewis acid catalysis by carrying out the ketal formation reaction with various substrates. 50 mg (0.06 mmol) of the as-synthesized catalyst, 35 mmol of ketone (2-butanone, 2-pentanone or acetone), and 35 mmol of ethylene glycol were reacted in 40 mmol of toluene as a solvent. The reaction was refluxed at 110°C under Dean-Stark conditions for 12 h. All the products were analysed employing ¹H NMR spectroscopy (ESI, Figure S5-S7).^{9a,10}

Table 3: Crystal Data and Structure Refinement Parameters for 1-6

	1	2	3	4	5	6
Empirical formula	C ₂₆ H ₂₄ Cu ₂ N ₄ O ₈ S ₂	C ₂₆ H ₂₄ Ag ₂ N ₄ O ₈ S ₂	C ₅₂ H ₄₀ Cu ₄ N ₁₆ O ₁₈ S ₄	C ₂₆ H ₂₈ Ag ₂ N ₈ O ₁₀ S ₂	C ₁₅ H ₁₂ AgN ₂ O ₅ S	C ₆₄ H ₈₂ Ag ₄ N ₈ O ₂₁ S ₄
T/K	293	293	293	293	293	293
Crystal System	Triclinic	Triclinic	Triclinic	Triclinic	Monoclinic	Triclinic
Space Group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>P</i> 2 ₁ /m	<i>P</i> -1
a/Å	8.208(12)	8.250(8)	10.645(2)	7.022 (7)	7.399(3)	14.564(6)
b/Å	9.870(14)	10.248(11)	15.367(3)	13.245(14)	18.503(6)	14.723(6)
c/Å	17.377(19)	16.795(2)	19.590(4)	19.101(18)	12.632(5)	19.551(8)
α/°	83.411(10)	86.545(6)	80.844(10)	71.555(4)		72.143(2)
β/°	82.267(10)	86.590(6)	83.690(11)	79.412(2)	98.79(2)	70.919(2)
γ/°	73.463(13)	75.057(5)	85.182(10)	74.632(2)		77.780(2)
V/Å³	1333.0(3)	1368.2(3)	3137.5(10)	1615.3(3)	1709.1(11)	3742.1(3)
Z	2	2	2	2	4	2
μ(Mo-Kα)/mm⁻¹	1.812	1.643	1.553	1.409	1.328	1.218
Reflections						
Collected/unique	14250 / 7075	26353 / 6232	53662 / 14450	51866 / 7512	13793 / 4047	77533 / 17167
R (int)	0.0827	0.0630	0.0754	0.2107	0.1722	0.1687
Final R indices	R1 = 0.0939	R1 = 0.0327	R1 = 0.0588	R1 = 0.0585	R1 = 0.0931	R1 = 0.0589
[I > 2σ(I)]	wR2 = 0.1892	wR2 = 0.0708	wR2 = 0.1407	wR2 = 0.0638	wR2 = 0.2080	wR2 = 0.1131
R indices (all data)	R1 = 0.1579	R1 = 0.0448	R1 = 0.1190	R1 = 0.2282	R1 = 0.2800	R1 = 0.1918
	wR2 = 0.2334	wR2 = 0.0774	wR2 = 0.1691	wR2 = 0.0888	wR2 = 0.2860	wR2 = 0.1507
GOF on F2	1.033	0.999	1.021	0.973	0.918	0.952

Single-Crystal Structure Determination

A suitable single crystal of each compound was carefully selected under a polarizing microscope and glued to a glass fiber. The Single-crystal X-ray data of **1** was collected with Oxford Xcalibur (Mova) diffractometer equipped with an EOS CCD detector whereas those of **2-6** were collected on Bruker AXS smart Apex II CCD diffractometer using graphite monochromated MoK α radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods and refined using SHELXL2013 present in the WinGX suit of programs (version 2013.3).¹² All hydrogen positions were initially located in the difference Fourier maps, and for the final refinement, the hydrogen atoms were placed in geometrically ideal positions and refined in the riding mode. Final refinement included atomic positions for all the atoms, anisotropic thermal parameters for all the non-hydrogen atoms and isotropic thermal parameters for all the hydrogen atoms. Full-matrix least squares refinement against $|F^2|$ was carried out using the WinGx package of programs.¹³ Details of the structural parameters and final refinements for the compounds are presented in Table 3. Crystallographic data for the compounds **1-6** (CCDC Nos. 1401642-1401647) can be obtained free of charge from Cambridge Crystallographic Data Center (CCDC) via www.ccdc.cam.ac.uk.

Results and discussion

Structure of [Cu₂(bds)(bpy)₂]·2H₂O, **1**

The asymmetric unit of **1** has 42 non-hydrogen atoms, which includes two Cu⁺ ion, one benzene-1,3-disulfonate anion, two 4,4'-bipyridine and two water molecules (ESI, Figure S8). Selected bond lengths and bond angles are given in Table S3 (ESI). In **1**, Cu-O bond distances (Cu1-O1 = 2.561, Cu₁-O1 = 2.490, Cu₂-O2 = 2.771 and Cu₂-Ow1 = 2.563 Å) are longer

than the reported coordination bonds in Cu(I) sulfonates (2.03 - 2.22 Å)^{10,14} but still fall in the secondary bonding range (the sum of the van der Waals radii of Cu and O is 2.92 Å). Copper atoms have slightly distorted linear two coordination geometry.

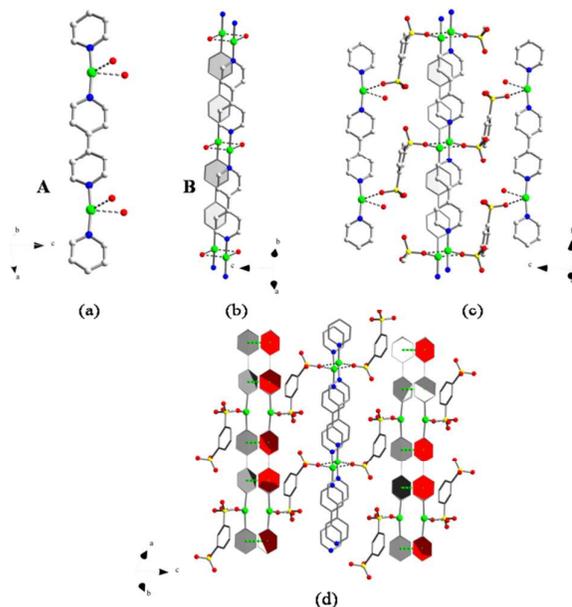


Figure 1: (a) 1D chain formed by [Cu(bpy)]_n, (b) Double layer 1D chain (c) Three chain 1D structure (d) 2D sheet due to π - π stacking

The connectivity between copper and bpy ligands gives rise to a one dimensional chain (A-chain, Figure 1a). A second one-dimensional double chain was formed by [Cu(bpy)]_n (B-chain), supported through weak interactions between oxygen from sulfonate and Cu(I) along with π - π interactions (phenyl centroid-centroid distance of 3.758 Å) (Figure 1b). The A-chains and B-chains are bridged by sulfonate ligands through

weak interaction alternatively (A \cdots B \cdots A) and form a triple chain one-dimensional structure (Figure 1c). Due to $\pi\cdots\pi$ (centroid-centroid distance = 3.863 Å) interactions between pyridine rings of terminal [Cu(bpy)]_n layers, it further extend to a supramolecular two-dimensional double layer structure (Figure 1d).

Structure of [Ag₂(bds)(bpy)]₂·2H₂O, **2**

The asymmetric unit of **2** has 42 non-hydrogen atoms, which includes two Ag⁺ ion, one benzene-1,3-disulfonate anion, two 4,4'-bipyridine and two water molecules (ESI, Figure S8). In **2**, Ag-O bond distances (Ag1-O1 = 2.671, Ag1-O₁ = 2.682, Ag2-O4 = 2.863, Ag2-Ow1 = 2.780 Å) are longer than the covalent radii of the two atoms (2.13 Å). In Comparison to the usual Ag-O coordination bond distances observed in silver sulfonates spanning the range 2.3-2.7 Å,¹⁵ the present Ag1-O1 and Ag1-O₁ bond distances are within the range whereas Ag2-O4 and Ag2-Ow1 distances are slight longer but still fall in the secondary bonding range (the sum of the van der Waals radii of Ag and O is 3.24 Å). Compound **2** is also a three chain one-dimensional coordination polymer similar to **1** in which two different coordination geometry around silver are present (Figure 2). One silver has distorted tetrahedral geometry whereas the other has linear coordination geometry. In comparison to a similar compound with benzene-1,4-disulfonate {[Ag₂(bpy)₂(H₂O)₂](1,4-bds)·(2H₂O)}, in which sulfonate ligands have only weak interactions with silver without Ag \cdots Ag interactions and silver has T-shaped coordination geometry.⁸¹ Here two middle [Ag(bpy)]_n layers are stacked by bridged oxygen from sulfonate ligands along with a weak interaction between two silver atoms (Ag-Ag distance is 3.356 Å, which is shorter than the sum of van der Waals radii (3.40 Å) of two atoms) and $\pi\cdots\pi$ interactions (centroid-centroid distance = 3.755 Å).

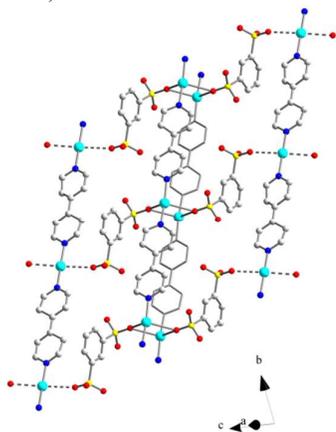


Figure 2: Three chain 1D structure of **2**

Structure of [Cu₄(bds)₂(azpy)]₄·6H₂O, **3**

The asymmetric unit of **3** has 94 non-hydrogen atoms, which includes four Cu⁺ ions, two benzene-1,3-disulfonate anion, four 4,4'-azobipyridines and six lattice water molecules (ESI, Figure S8). The Cu atoms exist in +1 oxidation state and has a 3-coordination (T-shaped geometry) through two nitrogen atoms from two different 4,4'-azobipyridyl ligand and an oxygen atom from the sulfonate ligand. A One-dimensional chain is formed by the connectivity between copper atoms and 4,4'-azobipyridine (Figure 3a). The chains, [Cu(azpy)]_n are further bridged by the sulfonate ligands giving rise to a two dimensional structure (Figure 3b and 3d). The two-dimensional structure resembles a stair-case wherein the copper azobipyridyl chains, [Cu(azpy)]_n form the steps of the stair (Figure 3c).

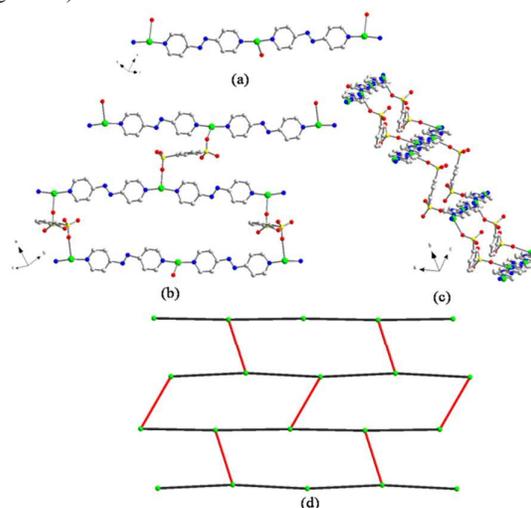


Figure 3: (a) 1D chain formed by Cu and azpy (b) 2D structure of **3** (c) Stair like structure of **3** (d) A schematic of the structure of **3** (The red sticks are represent bds and black sticks represent azpy)

Structure of [Ag₂(bds)(azpy)]₂·4H₂O, **4**

The asymmetric unit of **4** has 48 non-hydrogen atoms, which includes two Ag⁺ ion, one benzene-1,3-disulfonate anion, two 4,4'-azobipyridine and four lattice water molecules (ESI, Figure S8). Silver has a slightly distorted T-shaped geometry constituted by two nitrogens from 4,4'-azobipyridyl and an oxygen from a sulfonate ligand. The Ag-O bond distances (Ag-O: 2.794, 2.786 Å) are slightly longer than the reported values but it affects the geometry around Ag and the orientation of [Ag(azpy)]_n chains. Compounds **2** and **4** have the same bridging ligands but have different two-dimensional structures. Compound **2** has stair like 2D structure whereas, in case of **4**, one-dimensional chains formed by [Ag(azpy)]_n are arranged in two layers with an angle of 31.89° with respect to each other (Figure 4a). The double layer, crossed [Ag(azpy)]_n chains are connected by sulfonate ligands as a bent pillars and form the double layered two dimensional structure of **4** (Figure 4b and 4c).

In compound **4**, water channels are formed across the two dimensional sheet by hydrogen bonding between water molecules and sulfonate ligands. It is interesting to note that four water molecules and two sulfonate groups compose a five membered ring *via* hydrogen bonds, which is parallel to the *ab* plane (Figure 4d).

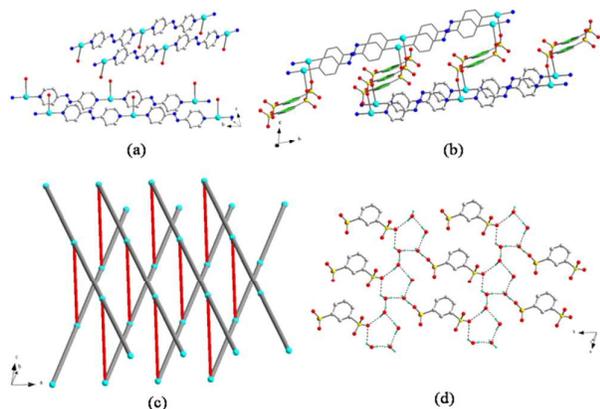


Figure 4: (a) Orientation of 1D $[\text{Ag}(\text{azpy})]_n$ chains (b) 2D criss-crossed structure of **4** (c) A schematic of the structure of **4** (The red sticks are represents bds and gray sticks represents azpy) (d) Water channels formed in between two SO_3 groups

Tetrameric $(\text{H}_2\text{O})_4$ water units exist in the structure of **4**. The geometrical parameters of the water tetramer and its association with sulfonate ligands are provided in the Table S4 (ESI). As shown in Figure 4d, four lattice water molecules assemble into a tetramer with an $\text{Ow}\cdots\text{Ow}$ distances of 2.699, 2.846 and 2.875 Å, whereas these distances in regular ice, liquid water, and water vapor are 2.74, 2.85 and 2.98 Å, respectively.¹⁶ It is well known that water molecules frequently show a three coordinated mode through hydrogen-bond interactions.¹⁷ Four oxygen atoms of the tetramer show four or two coordinated modes. Each tetramers are further hydrogen bonded to other tetramer with a $\text{Ow}\cdots\text{Ow}$ distance of 2.674 Å to form 1D water channels.

Structure of $[\text{Ag}(\text{bds})_{1/2}(\text{bpe})] \cdot 3\text{H}_2\text{O}$, **5**

The asymmetric unit of **5** has 24 non-hydrogen atoms, which includes one Ag^+ ion, half of a benzene-1,3-disulfonate anion, one 1,2-di(4-pyridyl)ethylene and three lattice water molecules (ESI, Figure S8). Silver is coordinated by two nitrogens from 1,2-di(4-pyridyl)ethylene ligands and exhibits linear geometry. Unexpectedly, the crystal structure indicates that the $\text{Ag}(\text{I})$ center is not coordinated by the SO_3 group and instead has a strong interaction with a water molecule (Ag1-Ow1 2.838 Å). Due to $\text{Ag}\cdots\text{O}(\text{sulfonate})$ weak interaction with a distance of 3.146 Å, a double chain one-dimensional coordination polymer formed (Figure 5a). In compound **5**, there are $\text{Ag}\cdots\text{Ag}$ interactions with a distance of 3.339 Å which is shorter than the van der Waals radii of two atoms (3.40 Å) and $\pi\cdots\pi$ interactions between two pyridine rings (centroid-centroid distance = 3.632 Å) along with two ethylene (3.609 Å) which are almost parallel. A $[\text{Ag}(\text{bpe})]_n$ double layer chain is formed through $\text{Ag}\cdots\text{Ag}$ and

$\pi\cdots\pi$ interactions which further extend to form the 2D structure through $\text{Ag}\cdots\text{O}(\text{sulfonate})$ interactions (Figure 5b).

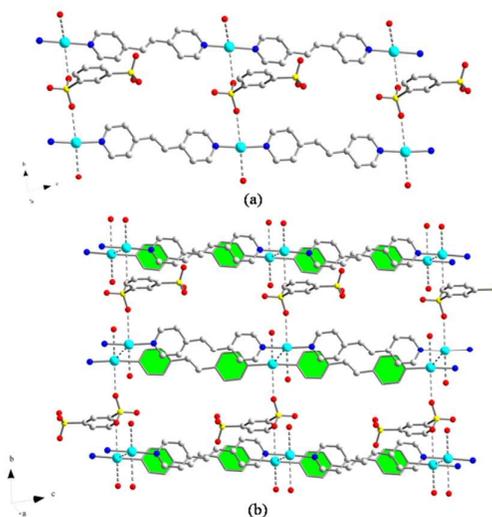


Figure 5: (a) 1D structure of **5** due to $\text{Ag}\cdots\text{O}(\text{sulfonate})$ interactions (b) Double layer 2D structure of **5** due to $\text{Ag}\cdots\text{Ag}$ and $\text{Ag}\cdots\text{O}(\text{sulfonate})$ interactions

Structure of $[\text{Ag}_4(\text{bds})_2(\text{tmdp})_4] \cdot 9\text{H}_2\text{O}$, **6**

The asymmetric unit of **6** has 101 non-hydrogen atoms, which includes four Ag^+ ion, two benzene-1,3-disulfonate anion, four 4,4'-trimethylenedipyridine and nine lattice water molecules (ESI, Figure S8). It is interesting to note that two structurally similar molecules are co-crystallized in **6**, both having similar structures but with different Ag-O bond lengths. In one of the molecule, Ag-O bond distances are 2.633 and 2.688 Å, which are within range as reported for silver sulfonate compounds¹⁵ whereas in the other one, Ag-O bond distances are 2.815 and 2.829 Å which are slightly longer, but still fall in the secondary bonding range. Each Ag atom has a T-shape geometry constituted by two nitrogens from *tbp* and one oxygen from a sulfonate ligand. At a glance, structure of **6** is similar to the reported structure with naphthalene-1,5-disulfonate ($[\text{Ag}(\text{tmdp})](\text{nds})_{1/2} \cdot 2\text{H}_2\text{O}$, **6a**)⁸ⁱ but a lot of difference are observed. In **6**, two types of molecules are co-crystallized; in one sulfonate ligands are directly bonded to silver whereas in the other one having weak interaction only and it is similar to **6a** ($\text{Ag-O} = 2.792$ Å). Each *tmdp* ligand adopts a TG (*T* = *trans* and *G* = *gauche*) conformation similar to **6a** with an $\text{N}\cdots\text{N}$ separation of 8.615-8.752 Å¹⁸ bridges two different silver atoms, yielding one-dimensional sinusoidal chains with $[\text{Ag}(\text{tmdp})]_n$ repeat units. These $[\text{Ag}(\text{tmdp})]_n$ one dimensional chain are bridged by sulfonate ligand and form two dimensional structure (Figure 6a). The $\text{Ag}\cdots\text{Ag}$ separation (3.165 and 3.236 Å) in **6** is notably shorter than the sum of the van der Waals radii of two Ag atoms (3.44 Å), indicating the presence of argentophilic interactions. Due to weak $\text{Ag}\cdots\text{Ag}$ interactions, adjacent one-dimensional chains generate a two-dimensional undulating brick-wall layer composed of $[\text{Ag}(\text{tmdp})]_n$ approximately in the *bc* plane (Figure 6b). Besides $\text{Ag}\cdots\text{Ag}$ interactions, aromatic $\pi\cdots\pi$ interactions with centroid-centroid

distances ranging from 3.595 to 3.851 Å between the pyridyl rings of neighbouring tmdp ligands, also exist between the chains in **6** and helping to strengthen the resulting 2D layer. Each pair of Ag atoms (connected by Ag \cdots Ag interactions) are connected through oxygen of sulfonate ligands (Figure 6c) either *via* direct bonding or through weak interaction between Ag and O(sulfonate), generated three dimensional interpenetrated structure (Figure 6c).

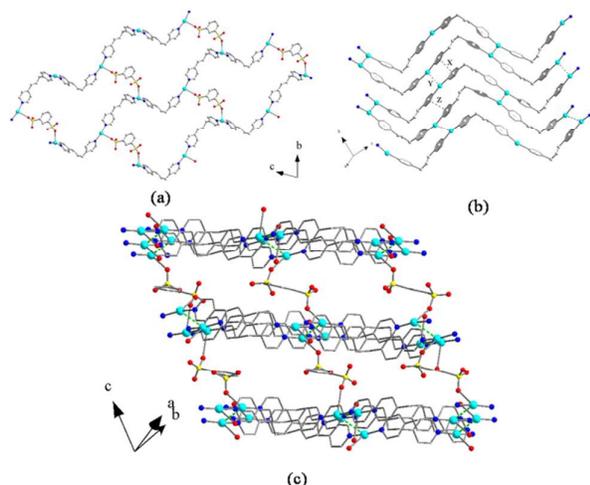


Figure 6: (a) 2D structure of **6** (b) A view of the 2D undulating [Ag(tmdp)]_n layer, with the interchain Ag \cdots Ag and π \cdots π interactions (c) 3D structure of **6**

Nine water molecules are present in the lattice of **6** which are connected by hydrogen bonding through each other and with sulfonate ligands (ESI, Table S4). All water molecules and oxygen of sulfonate ligands, assembled with an O \cdots O distance range of 2.718–2.969 Å. Between four sulfonate ligand one six member and two five member rings are formed due to hydrogen bonding (Figure 7).

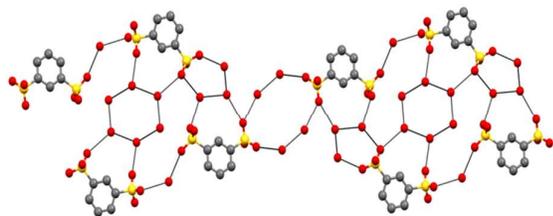


Figure 7: Water channels between SO₃ groups in **6**

Photochemical [2+2] cycloaddition in **5**

Solid-state photochemical [2+2] cycloaddition reaction is a unique solvent-less and a green way of synthesizing regio- and stereospecific cyclobutane derivatives.¹⁹ Structurally, the C=C bonds of 1,2-di(4-pyridyl)ethylene are separated by 3.609 Å. This distance satisfies the distance criterion for [2+2] cycloaddition reaction in a solid.²⁰ In addition, the Ag(I) appears to have Ag \cdots Ag interactions which guides the stacking of the C=C units in the structure. Our attempts to carry out the single-crystal-to-single-crystal [2+2] cycloaddition reaction were not successful due to the poor crystal quality of the product after irradiation by UV light. The complete solid-state

photochemical [2+2] cycloaddition was confirmed by ¹H NMR (In d⁶-DMSO) (Figure 8). The formation of the cyclobutane ring was confirmed by the disappearance of the olefinic protons (δ = 7.60 ppm) and the emergence of signals for the cyclobutane protons (δ = 4.64 ppm).

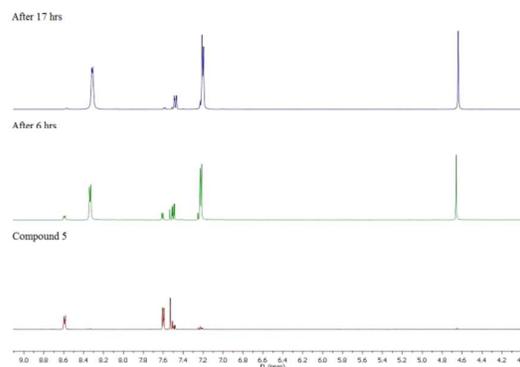


Figure 8: NMR spectra of solid state photochemical [2+2] cycloaddition

Anion Exchange

Anionic pollutants such as perchlorate (ClO₄⁻), arsenate (AsO₄³⁻) and chromate (CrO₄²⁻) are progressively more problematic and are included in EPA list (U.S. Environmental Protection Agency) as priority pollutants whereas pertechnetate (TcO₄⁻) is radioactive pollutant.^{10,21} It is interesting to design coordination polymers which can trap or exchange inorganic and organic anions because of only a few have been investigated for reversible/irreversible anion exchange.^{10,22} Here we investigated anion exchange for all compounds with NO₃⁻, ClO₄⁻ and MnO₄⁻ (analogous to pertechnetate) anions. In this study we find that there is no any exchange occurred for the nitrate anion. Only **2** is showing reversible anion exchange for perchlorate and permanganate whereas others show irreversible anion exchange for perchlorate. For the exchange of permanganate only compound **2** is showing reversible exchange while in the case of others after exchange of permanganate, compounds become amorphous.

FTIR and PXRD pattern of the solid products after exchange of the bds in **2** for perchlorate are shown in figure 10. The four singlet bands at 1603, 1534, 1487, and 1414 cm⁻¹ are aromatic C=C and C=N bending, confirming the presence of 4,4'-bipyridine during the exchange. The strong, broad band at ~1211 cm⁻¹ is characteristic of the SO₃⁻ group, confirming the presence of benzene-1,3-disulfonate anions in the initial framework (Figure 9a). Both FTIR and PXRD indicate that the bds anions in **2** were completely exchanged by ClO₄⁻ anions after keeping crystals of **2** in 0.1 M NaClO₄ solution at room temperature for 6-7 days (Figure 9b). The broad ~1209 cm⁻¹ band disappears and a new broad peak appeared at ~1115 cm⁻¹ which is characteristic for ClO₄⁻ (Cl-O stretch). PXRD further supports a complete and reversible exchange between bds and perchlorate anions. Due to low crystal quality of the exchanged product, structure could not be solved by X-ray crystallography. The resultant PXRD pattern of exchanged product (Figure 9b) exactly matches with the simulated PXRD pattern of the

previously reported $\{[Ag_3(bpy)_3](ClO_4)_3 \cdot 2H_2O\}_n$.²³ Just immersing the perchlorate exchanged product into a 0.1 M sodium benzene-1,3-disulfonate aqueous solution reforms the compound **2** which is confirmed by both FTIR and PXRD (Figure 9c) analysis.

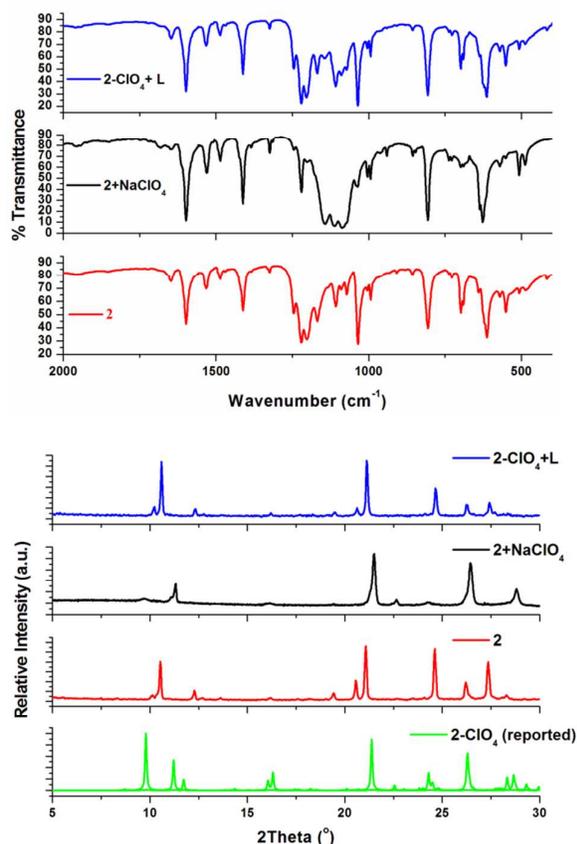


Figure 9: PXRD and FTIR of **2** for anion exchange with perchlorate. (a) Initial compound **2** (red) (b) exchange products $2-ClO_4$ (black) (c) the solid product after exchange reaction between $2-ClO_4$ and 0.1 M bds anion (blue) (d) Theoretical PXRD patterns of $2-ClO_4$ (green, from reported structure) in the bottom figure

Compound **2** also reforms when the perchlorate exchanged product is placed into a mixed aqueous solution of 0.1 M bds disodium salt and 0.1 M $NaClO_4$. Based on these observations, we can conclude that the exchange reaction with perchlorate depends on concentration rather than a stronger interaction between the cationic framework and anion. The other compounds (**1**, **3-6**) are showing irreversible anion exchange for the perchlorate anions which are confirmed by FTIR and PXRD analysis (ESI, Figure S9).

The compound **2** also shows reversible anion exchange for permanganate besides perchlorate. Color of crystalline products was changed from colorless to dark red after exchange of MnO_4^- anion (Figure S10, ESI). Here four singlet bands at 1604, 1534, 1486, and 1410 cm^{-1} are observed, which confirms the presence of 4,4'-bipyridine during the exchange (Figure 10). Disappearance of bands at $\sim 1221\text{ cm}^{-1}$ and appearance of intense bands at $\sim 900\text{ cm}^{-1}$ (Mn-O stretch) clearly indicate the

complete exchange of bds anion by MnO_4^- (Figure 10b).¹⁰ PXRD pattern of exchange product is exactly matching with previously reported.¹⁰

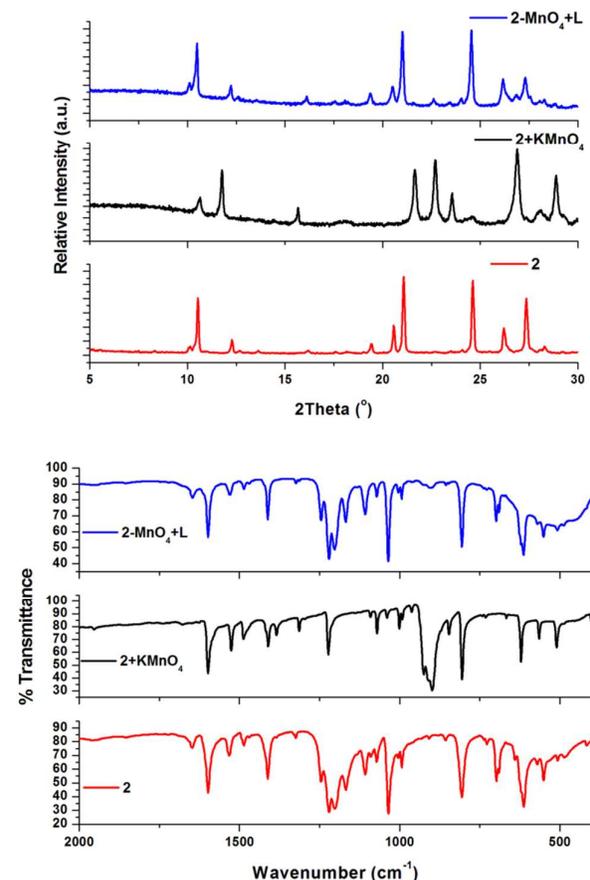
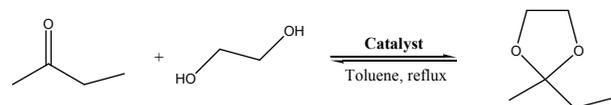


Figure 10: PXRD and FTIR of **2** for anion exchange with permanganate. (a) Initial compound **2** (red) (b) exchange products $2-MnO_4$ (black) (c) the solid product after exchange reaction between $2-MnO_4$ and 0.1 M bds anion (blue).

Heterogeneous Catalysis

Metal-organic frameworks are versatile supramolecular platforms for heterogeneous catalysis in a variety of organic reactions, especially for liquid-phase reactions. One of the most significant features of MOFs is their extremely high porosity.^{9a,10,24} Ketalization is a significant method to protect carbonyl groups in organic synthesis and drug design.²⁵ Here we have studied heterogeneous Lewis acid catalytic activity of **2** for activation of 2-butanone, 3-pentanone and acetone to form corresponding ketal products with ethylene glycol (Scheme 1, Table 4). All the ketal products form in good yield, which shows that compound **2** is an excellent Lewis acid catalyst. A blank experiment without catalyst under the same conditions and time yielded negligible amount of product.^{9a,10} Compound **2** is a heterogeneous catalyst and easily separated from the product. The catalyst can be reused without further treatment after catalytic runs as confirmed by PXRD.



Scheme 1: Lewis Acid Catalyzed Ketal Formation between 2-Butanone and Ethylene Glycol

Table 5: Conversion Yields for Catalytic Reactions

Compound	Ketones	Time (h)	Conversion yield (%)
No catalyst ^{9a,10}	2-butanone	12	1
	3-pentanone	12	0
	acetone	12	0
2	2-butanone	12	95
	3-pentanone	12	92
	acetone	12	89

Conclusions

Two new Cu(I), [Cu₂(bds)(bpy)₂·2H₂O (**1**), [Cu₄(bds)₂(azpy)₄·6H₂O (**2**) and four Ag(I), [Ag₂(bds)(bpy)₂·2H₂O (**3**), [Ag₂(bds)(azpy)₂·4H₂O (**4**), [Ag(bds)_{1/2}(bpe)]·3H₂O (**5**), [Ag₄(bds)₂(tmdp)₄·9H₂O (**6**), compounds have been synthesized and characterized by different techniques. From a single crystal X-ray diffraction study, we find that compounds **1** and **2** are triple chain one-dimensional coordination polymers where as **3** and **4** (having same ligands system) are two-dimensional coordination polymer with different arrangement: **2** has stair-case structure whereas, **4** is criss-crossed 2D structure. Compound **5** has similar ligand system as **4** but has a one-dimensional structure which extends to form a double layer two-dimensional sheet by weak interactions. An interpenetrated 3D structure is formed by employing flexible ligands in **6**. In case of **5**, [2+2] photodimerization in the solid state occurred because of argentophilic interactions, which guide stacking of olefins in the coordination polymer. Emission spectra of the compounds have been studied in solid states and show strong emission bands at ~394 nm which are ligand centered. Only compound **2** shows reversible anion exchange for perchlorate and permanganate (model compound for removal of pertechnetate) whereas others (**1**, **3-6**) show irreversible anion exchange for perchlorate. We have checked catalytic activity for **2** which has proved to be a good Lewis acid catalyst because of the presence of unsaturated coordination sites.

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The Cu(I)/Ag(I) sulfonate CP have been synthesized and characterized. One of the CP exhibits reversible anion exchange for perchlorate and permanganate

