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Tuned synthesis of two coordination polymers of Cd(II) using substituted bent 3-pyridyl linkers and succinate: structure and their applications in anion exchange and sorption properties

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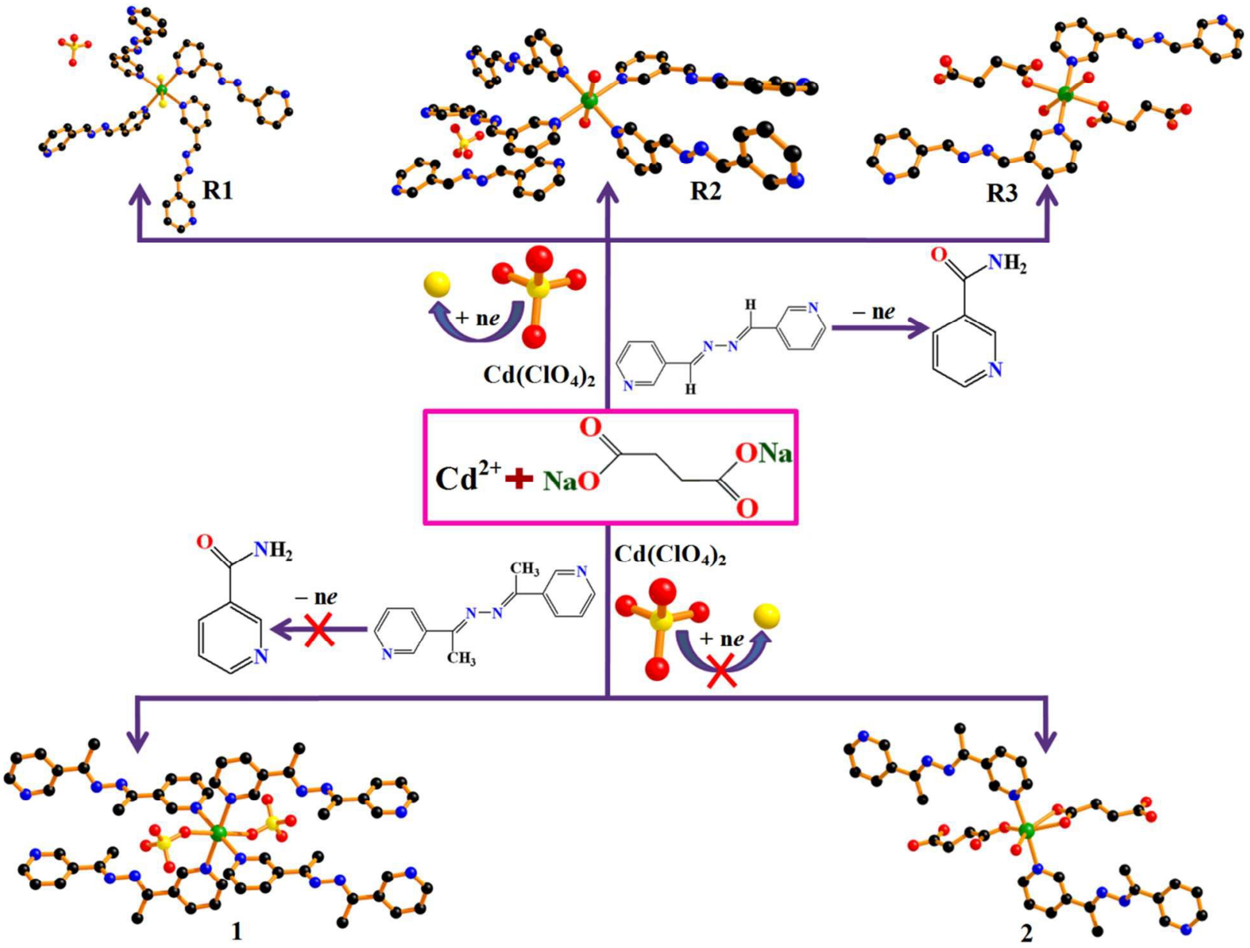
Two new Cd(II) coordination polymers namely $[Cd(3\text{-bpdh})_2(ClO_4)_2]_n$ **(1)** and $\{[Cd(3\text{-bpdh})(suc)(H_2O)]^{\cdot}3(H_2O)\}_n$ **(2)** have been synthesized using substituted bent N,N´-donor ligand 2,5-bis-(3-pyridyl)-3,4-diaza-2,4-hexadiene (3-bpdh) and aliphatic dicarboxylate disodium succinate (suc) with Cd(II) perchlorate salts at room temperature by a slow diffusion technique for the exploration of our previous reported work. Both the structures were determined by single-crystal X-ray diffraction analysis and also by other physicochemical methods. Structure analysis revealed that complex **1** is a 1D chain structure containing coordinated perchlorate with metal centre and complex **2** shows a porous 3D framework with encapsulation of lattice water molecules into the void along crystallographic *a*-axis. PXRD study shows the bulk purity of both the complexes and TGA analysis of **2** exhibits that the structure is thermally stable up to 250 °C. Complex **1** shows nice anion exchange property with replacement of weakly coordinated perchlorate with the inclusion of new anions; and the anion exchanged solids were characterised by FT-IR, PXRD and photoluminescence properties. The desolvated framework of **2** exhibits sorption of CO_2, water vapor and a surface adsorption of N_2 corroborating the nature of the pore environment present in **2**. The photoluminescence study has been also done for both the complexes in solid state which exhibits ligand based emissions at room temperature.

Introduction

Applications are one of the strongest driving forces of synthetic chemical research. This has been reflected in enormous thirst for the design of coordination polymers (CPs) in recent years, because of their multifunctional potential applications, in gas storage and separation,[1] ion exchange,[2] heterogeneous catalysis,[3] magnetism,[4] conducting materials,[5] optical materials[6] and sensors[7] etc. To achieve such functionalities, the control over the structure is highly necessary; and that ease of design in the synthesis of CPs, are made them extremely popular to the contemporary researchers. The design of the structure of CPs are mostly done by tuning the structure of the organic ligands,[8] but there are many other crucial factors such as the metal ions,[9] nature of organic ligands,[10] pH of the medium,[11] reaction temperatures,[12] solvents[13] and counter anions[14] may also contributes significantly to create structural diversities in CPs. Thus it is very crucial to understand the interplay of all possible factors which may sometime take significant role for the formation of the structures of CPs. To explore the nonconventional factors in the organization of the structure of CPs, a couple of years back we had reported[15] a reaction of Cd(II) with succinate (suc) and 1,4-bis-(3-pyridyl)-2,3-diaza-1,3-butadiene (3-bpdb) which gave three frameworks having 1D, 2D and 3D structure respectively. It is worth mentioning that in the said 3D structure, there was an interesting emergence of chloride integrated framework, which was originated by the reduction of ClO_4^- along with the oxidation of imine group of 3-bpdb. To explore the role of the electron supplier in the aforesaid process we have modified the linker and made the same reaction which does not facilitate the formation of Cl^- integrated product. Here, by the same reaction with methylated 3-bpdh we got only two products; one is 1D chain and the other is a 3D framework with water filled channels. In both the present and reported work the perchlorate salt of Cd(II) was used. It had also been observed in our other previous report[16] that the slight change in the counter anion (ClO_4^- to NO_3^-) with the same reaction as the present report, yielded a single product with completely different structure and functionality. Therefore, our present work is an attempt to address and correlate some crucial factors during the synthesis of CPs which has not been explored much.

Herein we have synthesized $[Cd(3\text{-bpdh})_2(ClO_4)_2]_n$ (**1**) and $\{[Cd(3\text{-bpdh})(suc)(H_2O)].3(H_2O)\}_n$ (**2**) by the reaction of Cd(II) perchlorate with succinate and a substituted N,N′-donor ligand 3-bpdh. It is interesting to note that here **1** shows excellent anion exchange property and **2** exhibits gas and water vapor sorption properties.

The anion exchange property has been significantly studied for CPs having coordinated anions with metal centres.[17] It has been revealed from such reports that the exchange of anions with the metal centre may depends on the size, shape, and coordinating abilities of the anions and here ClO_4^- being a comparatively weakly coordinated anion, can easily be exchanged with other anions. On the other hand gas sorption properties of mixed ligand CPs is one of the most important and widely explored functionality as this class of material shows their performance in executing selective gas adsorption properties.[18] Considering the burning issue of rise of CO_2 level in environment, the design of CPs which can uptake CO_2; has become very much contemporary in this particular field.[19]



Scheme 1. Synthetic scheme of complexes **1**-**2** with our previous reported work (**R1**[15], **R2**[15] and **R3**[15]: previous reported complexes)

Experimental section

Materials and methods

2,5-bis-(3-pyridyl)-3,4-diaza-2,4-hexadiene (3-bpdh) was synthesized by the procedure reported earlier.[20] High purity cadmium(II) perchchlorate hexahydrate; succinic acid; 3-acetylpyridine were purchased from Sigma-Aldrich Chemical Co. Inc. and used as received. Na_2suc was synthesized by the slow addition of solid Na_2CO_3 to aqueous solution of H_2suc in a 1:1 ratio and was allowed to evaporate until dryness. All other chemicals including solvents were of AR grade and used as received. Ultrapure water obtained from a Milliopore water purification system (≥18 MΩ, Milli-Q, millipore) was used in synthesis as well as in all experiment.

Physical measurements. Microanalyses (C, H, N) were performed on a Heraeus CHNS analyzer. Infrared spectra (4000–400 cm^{-1}) were taken on KBr pellet, using Perkin–Elmer Spectrum BX-II IR spectrometer. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 Discover instrument with Cu-Kα radiation. Thermogravimetric analysis (TGA) was carried out on a METTLER TOLEDO TGA 850 thermal analyzer in the temperature range of 30-600 °C under N_2 atmosphere at a heating rate of 10 °C min^{-1}. The solid state emission was recorded on HORIBA Jobin Yvon (Fluoromax-3) instrument. GC-MS analysis was performed using a Perkin Elmer CLARUS 680 instrument. ESI mass spectra were recorded with Waters QTOF Micro YA263 equipment.

Sorption measurements. The adsorption isotherms of N_2 (77 K), CO_2 (195 K) and water vapor (298 K) were measured using the dehydrated sample of **2** in Quantachrome Autosorb iQ instrument. In the sample tube ~40 mg sample of **2** were placed which had been prepared at 130°C under a 1×10^{-1} Pa vacuum for about 4 hours prior to measurement of the isotherms. Helium gas (99.999% purity) at a certain pressure was introduced in the gas chamber and allowed to diffuse into the sample chamber by opening the valve. The amount of gas/vapor adsorbed was calculated from the pressure difference ($P_{cal} - P_e$), where P_{cal} is the calculated pressure with no gas adsorption and P_e is the observed pressure at equilibrium. All operations were computer-controlled and automatic.

Synthesis

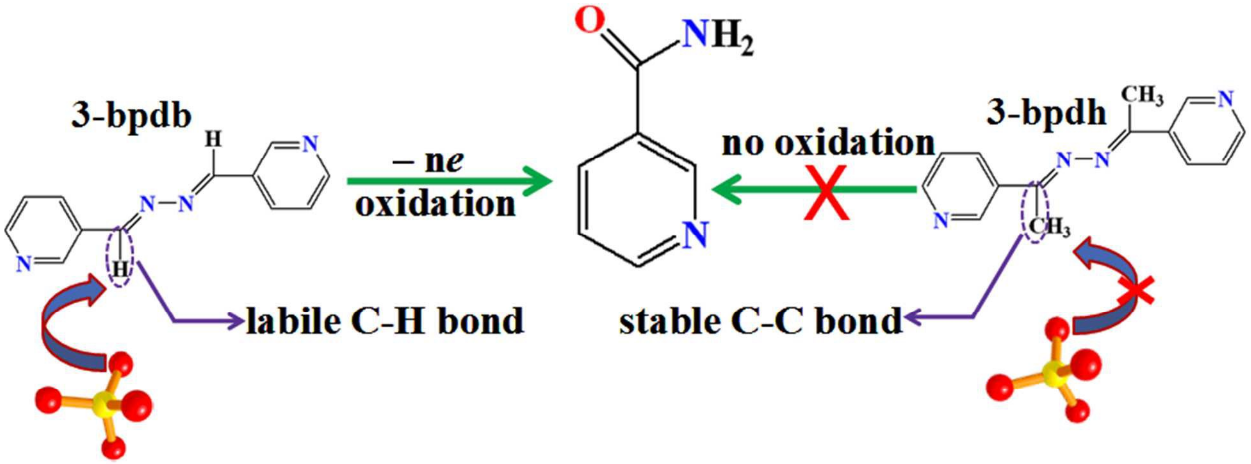
$[Cd(3\text{-}bpdh)_2(ClO_4)_2]_n$ (1) and $\{[Cd(3\text{-}bpdh)(suc)(H_2O)]^{\cdot}3(H_2O)\}_n$ (2). Compounds **1** and **2** were synthesized in a same reaction. A methanolic solution (20 mL) of 2,5-bis-(3-pyridyl)-3,4-diaza-2,4-hexadiene (3-bpdh) (1 mmol, 0.238 g) was mixed with an aqueous solution (20 mL) of disodiumsuccinate (Na_2suc) (1 mmol, 0.162 g) and the resulting solution was stirred for 1 hour to mix well. $Cd(ClO_4)_2 \cdot 6H_2O$ (1 mmol, 0.419 g) was dissolved in 20 mL water in a separate beaker. 6 mL of this mixed ligand solution was slowly and carefully layered above 3 ml of metal solution using 5 mL buffer (1:1 MeOH of and H_2O) in a glass tube. After three weeks, white colored block shaped single crystals of **1** (yield. 30%) and simultaneously yellowish block shaped single crystals of **2** (yield. 42%) were obtained at the wall of the tube; they were separated manually using microscope and washed with methanol–water (1:1) mixture and dried. Anal. calcd for $C_{28}H_{28}N_8O_8Cl_2Cd$ (**1**, %): C, 42.69; H, 3.58; N, 14.22. Found: C, 42.63; H, 3.62; N, 14.19. IR for **1** (KBr pellet, cm^{-1}): ν(CH-Ar), 3089; ν(C=N), 1609; ν(C=C), 1479-1420 and ν(ClO_4), 1121-1049. Anal. Calc. for $C_{18}H_{26}N_4O_8Cd$ (**2**, %): C, 40.12; H, 4.86; N, 10.4. Found: C, 40.17; H, 4.91; N, 10.36. IR for **2** (KBr pellet, cm^{-1}): ν(H_2O), 3422; ν(CH-Ar), 3063; ν(C=N), 1575; ν(C=C), 1575-1421 and ν(C-O), 1288-1045.

Crystallographic data collection and refinement. The single crystals of compounds **1** and **2** were mounted on the tips of glass fibers with commercially available glue. X-ray data collection of two single crystals were performed at room temperature using Bruker APEX II diffractometer, equipped with a normal focus, sealed tube X-ray source with graphite monochromated Mo-Kα radiation (λ= 0.71073Å). The data are integrated using SAINT[21] program and the absorption corrections are made with SADABS.[22] Both the structures are solved by SHELXS-97[23] using Patterson method and followed by successive Fourier and difference Fourier synthesis. Full matrix least-squares refinements were performed on F^2 using SHELXL-97[23] with anisotropic displacement parameters for all non-hydrogen atoms. All the hydrogen atoms are fixed geometrically by HFIX command and placed in ideal positions for both cases. Calculations are carried out using SHELXS 97,[23] SHELXL 97,[23] PLATON v1.15,[24] ORTEP-3v2,[25] and WinGX system Ver-1.80.[26] Data collection and structure refinement parameters along with crystallographic data for both the complexes are given in Table 1. The selected bond lengths and angles are given in Table 2-3.

Results and discussion

Discussion regarding synthesis of the compounds

As mentioned before, in our earlier work[15] we had reported an *in situ* perchlorate to chloride transformation supported by the metal organic framework, where a single reaction produced three different compounds (Scheme 1). The role of the N,N′-donor ligand has been discussed vividly in the previous case for the said reduction. There was a clear evidence of the oxidation of the 3-bpdb (Scheme 2), which may have facilitated the said framework assisted perchlorate to chloride reduction. With extension of our curiosity in this particular point here we have used a methyl substituted ligand 3-bpdh which is much more difficult to oxidize to form nicotinamide due to the presence of more stable C-C bond, rather than C-H bond in case of 3-bpdb.[15] Following our line of thinking that occurs when we made a reaction of $Cd(ClO_4)_2$ and succinate with 3-bpdh. We got only two products (Scheme 1) without any chloride containing product, which was found in case of 3-bpdb. Here complex **1** exhibits a 1D chain which contains bridging 3-bpdh ligand and coordinated perchlorate ions and complex **2** contains succinate and 3-bpdh to form a three dimensional structure. There is no existence of any structure with chlorides ions, rejecting the possibility for reduction of perchlorate to chloride and oxidation for imine group containing 3-bpdh ligand to amide. This has been convincingly proved by GC-MS study and ESI mass spectra (Fig. S2-S5) taking the residue of reaction mixture after drying. In all studies only the existence of 3-bpdh ligand has been established whereas in our previous work with 3-bpdb, imine group of this linker was oxidized to form amide which was confirmed by GC-MS experiment and ESI mass spectra. So, comparing our previous work it can be ascertained that the reduction of perchlorate must be inspired by the use of non methylated 3-bpdb linkers; which is not possible here with a methylated 3-bpdh linkers.



Scheme 2. Representing diagram to show the oxidation process favored by non methylated 3-bpdb[15] instead of methylated 3-bpdh

Crystal structure descriptions of [Cd(3-bpdh)$_2$(ClO$_4$)$_2$]$_n$ (1). Compound **1** crystallizes in monoclinic *P21/n* space group with Z value 2 and the structure analysis reveals that the compound **1** exhibits one dimensional (1D) structure of Cd(II) connected by doubly bridging 3-bpdh ligand. In asymmetric unit of **1** Cd(II) ions are in special position (1,0,1) with their half occupancy along with one 3-bpdh linker and one coordinated perchlorate ion. The hexa-coordinated Cd(II) with CdO$_2$N$_4$ coordination environments shows a distorted octahedral geometry (Fig. 1a) created by four nitrogen atoms (N1, N1^a, N4^b and N4^c where *a* = 2-x, -y, 2-z; *b* = -1+x, y, -1+z; *c* = 3-x, -y, 3-z) of four different 3-bpdh linker which creates the basal plane. The axial positions are occupied by two symmetry related oxygen atoms (O1, O1^a where *a* = 2-x, -y, 2-z) of two coordinated perchlorate ion. In **1**, the Cd-N bond length varies from 2.319(3) - 2.342(3) Å and the Cd-O bond length is 2.394(3) Å (Table 2). The other selected bond lengths and bond angles are reported in Table 2. Here two adjacent Cd(II) centers are connected by two 3-bpdh linkers and resulting the formation of 1D chain structure containing pendant perchlorate ion (Fig. 1b). Structural analysis with TOPOS[27] suggests that the overall framework exhibits a 2,4-c binodal net (Fig. 1c) with stoichiometry (2-c)2(4-c) and the corresponding Schläfli symbol for the net is $\{4^2\}\{4\}$.

Crystal structure descriptions of {[Cd(3-bpdh)(suc)(H$_2$O)]$^\cdot$3(H$_2$O)}$_n$ (2). Compound **2** crystallizes in the orthorhombic *Pna21* space group with Z value 4 and the structure analysis reveals that the compound **2** exhibits a porous three dimensional (3D) framework of Cd(II) connected by bridging succinate (suc) and bent bis-(3-pyridyl) N,N′-donor ligand (3-bpdh). The asymmetric unit of **2** contains one Cd(II) ion, one 3-bpdh linker, one succinate, one coordinated water molecule and three lattice water molecules. The hexa-coordinated Cd(II) with CdO$_4$N$_2$ coordination environments shows distorted octahedral geometry (Fig. 2a) created by four oxygen atoms (O1, O2, O4^a and O1W where *a* = -1-x, -y, -1/2+z) of two different succinate and one coordinated water molecule, which creates the basal plane. The axial positions are occupied by two nitrogen atoms (N1, N4^b where *b* = -1/2-x, 1/2+y, 1/2+z) of two different 3-bpdh ligands. In compound **2**, the Cd-O bond length varies from 2.224(3) - 2.507(3) Å and the Cd-N bond lengths are in the range from 2.332(3) - 2.358(3) Å (Table 3). The other selected bond lengths and bond angles are reported in Table 3. Here each succinate ligand bridges in between two Cd(II) centers where one end of carboxylate binds in a monodentate fashion and another end in a chelating fashion and resulting the formation of 1D chain along *c*-axis (Fig. 2b). The bent 3-bpdh ligands connects alternate Cd(II) centers in crisscross fashion to make a overall 3D framework (Fig. 2c). The resultant 3D framework contains water filled 1D channels oriented along *a* axis having a cannel dimension of around 4.8 × 3 Å^2 (Fig. S6a). Without the water molecules the total solvent accessible void value is estimated by PLATON is 458.2Å^3 which is 20.57% of the total crystal volume of 2228 Å^3. The 3D framework is also additionally stabilized through intramolecular π-π interactions in between two 3-pyridyl aromatic rings of two different 3-bpdh linkers (Fig. S6b and Table S1). Structural analysis with TOPOS[27] suggests that the overall framework exhibits a 4-c uninodal net (Fig. 2d) with Schläfli symbol for the net is $\{6^5.8\}$.

Powder X-ray diffraction (PXRD) analysis

Powder X-ray diffraction (PXRD) analysis was carried out to confirm the phase purity of the bulk materials both complexes at room temperature. The experimental PXRD patterns of complexes **1** and **2** are in good agreement with the simulated ones from their corresponding single crystal structures (Fig. S7), confirming the phase purity of the complexes. For **2** the PXRD pattern has also been collected after heating the sample at 130°C which is also in agreement with the as synthesized form of **2** (Fig. S7). This clearly indicates the thermal stability of the framework even after the removal of volatiles (water) at 130°C.

Thermogravimetric analysis

Caution! The TGA experiment was not carried out in case of **1** because there has no solvent molecule and it contains coordinated perchlorate ion which is explosive on heating; so for safety reasons we have ignored this measurement.

The TGA curve of complex **2** (Fig. S8) exhibits a weight loss of ~13.11% at ~104 °C, which reveals the presence of three lattice and one coordinated water molecules (calc. wt% 13.36) and the dehydrated framework is stable up to 250 °C without any weight loss suggesting the complete removal of all water molecules during activation process. After further heating the dehydrated framework collapses and decomposed into unidentified products.

Anion exchange and luminescence studies

As revealed from the single crystal structure analysis of **1**, the perchlorate anions are coordinated with Cd(II) centre. Since complex **1** is insoluble in water and common organic solvents so it is expected to exhibit anion exchange properties due to the presence of labile coordinated perchlorate ion.[28] The well-ground powder of complex **1** (~ 60 mg) was suspended in 5 ml

0.01M aqueous solution (taking ion free water) of Na-salt of different anions viz. NaN_3, NaNCO, NaSCN, $NaNO_3$ and Na_2CrO_4; separately and stirred gently for 24 hours at room temperature to permit the anion exchange. After that each mixture was filtered and washed with de-ionized water for three times. The completion of anion exchange with the parent complex **1** was monitored by FT-IR spectroscopy (Fig. 3) and PXRD measurement. In IR spectra of **1** intense band at ~1121 and ~1049 cm^{-1} is appeared which corroborates the presence of ClO_4^- anions. After the anion exchange, the IR spectra of the exchanged solids (Fig. 3) exhibit significant weakening of the ClO_4^- bands present in parent complex and emergence of new characteristic peak at ~2033 cm^{-1} for N_3^- (**1@N$_3$**), ~2187 cm^{-1} for NCO$^-$ (**1@NCO**), ~2043 cm^{-1} for SCN$^-$ (**1@SCN**), ~1429 to 1367 cm^{-1} for NO_3^- (**1@NO$_3$**) and at ~891 to 855 cm^{-1} for CrO_4^{2-} (**1@CrO$_4$**) respectively. The weakening of ClO_4^- bands and the generation of new characteristic bands of respective anions used for the exchange validated the progression of anion exchange process. Other peaks in the spectra remained virtually unchanged, which indicates that the framework structure of the MOF remained intact after the exchange process. After completion of anion exchange process with the corresponding foreign anions, the filtrates are collected in each case and dried to check the IR spectra. The presence of significant amount of perchlorate in all IR spectrums of the filtrates (Fig. S9); also support the exchange of perchlorate with the corresponding anions. From the PXRD pattern (Fig. S10) it is noticed that **1**@ NO_3 and parent **1** is closely isostructural which has been confirmed by indexing with the use of TREOR program.[29] The indexing shows same crystal system with very close cell parameters (Fig. S11, Table S2) between **1@NO$_3$** and **1**. The PXRD patterns (Fig. S10) of other anion exchanged products except **1@N$_3$** and **1@CrO$_4$** are quite similar with the PXRD pattern of **1** which also corroborates the retention of skeletal structures of the frameworks.

In case of N_3^-, the slight variation in PXRD pattern attributes probably due to the different size, shape and coordinating tendency of N_3^- compared to the other anions. The N_3^- being a strongly coordinating anions can easily remove the coordinated ClO_4^- from the respective parent frameworks and may facilitate a structural change in the framework, after the anion exchange process. In case of CrO_4^{2-} the variation is probably due to the different charge and large size compared to the other anions. The CrO_4^{2-} being a bulky binegative anion, must attached to the central metal atom with a different ratio than the others, resulting a structural change in the framework after the anion exchange process. However the anion exchange could not be monitored by single crystal structure due to the loss of single crystalinity of the compounds during anion exchange process.

The solid state fluorescence spectra of both complexes **1** and **2** as well as the 3-bpdh ligand has been measured at room temperature, which shown in Fig. S12. The free 3-bpdh ligand and complexes **1-2** were excited at 325 nm, 241 nm and 330 nm respectively. The fluorescent emissions were found with a maximum at 394 nm and 391 nm for free 3-bpdh ligand and both of the complexes respectively. The emission spectrum of 3-bpdh ligand with π-conjugated backbones is may be due to from the lowest singlet excited state to the singlet ground state i.e. intra ligand π*-π or π*-n transition and both the complexes **1** and **2** also show the ligand based emission may be due to the same π*-π or π*-n transition. The photoluminescence spectra of its anion exchanged products of complex **1** were also investigated in solid state at room temperature (Fig. 4). Like complex **1** all the anion exchanged products are excited at λ_{ex} = 241 nm. For **1@NO$_3$** and **1@CrO$_4$** the emission maxima were obtained at 391 nm and 390 nm respectively with a lesser emission intensity compared to **1** whereas in case of **1@NCO**, **1@SCN** and **1@N$_3$** the emission maxima were at 390 nm with an enhancement of emission intensity compared to **1**. The observed emission intensity order for the anion exchanged solids and parent complex with free 3-bpdh ligand was **1@NCO> 1@SCN> 1@N$_3$> 1> 1@CrO$_4$> 1@NO$_3$> 3-bpdh**. The probable rationale to the difference in luminescence intensities of parent **1** with its anion exchange solids can be ascribed to the various electronic interactions of the corresponding anions with the framework and metal node, as well as with their different characteristic coordinating modes, shapes, sizes, and geometries.[28]

Gas and water vapor sorption studies

The single crystal X-ray diffraction analysis reveals that the 3D framework of **2** have one-dimensional pores occupied by the guest water molecules. Prior to gas and vapor sorption experiments, guest water molecules of **2** was removed by solvent exchange using dry acetone and then thermal activation at 130 ^{o}C, under dynamic vacuum (1×10^{-1} Pa).

The desolvated framework of **2** was permitted to N_2 and CO_2 gas and water vapor adsorption experiments. It was found nonporous with respect to N_2 at 77 K probably due to its pore aperture (i.e. 4.8×3 Å^2) very close to the kinetic diameter of N_2 (kinetic diameter = 3.6 Å). Besides this the presence of unidirectional channel in the 3D structure make it unavailable for further inclusion of the N_2, after blocking the pore windows by incoming N_2 during adsorption.

As a result, the porosity was unavailable with respect to N_2 due to the absence of multi dimensional channel (Fig. S13). Thus in complex **2**, only surface adsorption for N_2 molecules has been observed (Fig. S14). The CO_2 adsorption isotherms has been measured for **2** at 195 K show reversible uptake of 4.7 (23.87cm^3 g^{-1}) wt % of CO_2, as the pressure approaches to 1 atm (Fig. **5**). The CO_2 molecules have comparatively smaller kinetic diameter (3.3 Å) than N_2 (3.6 Å) and it has a quadruple moment which may show a strong interaction with the N-based electron riched polar azine moiety [-(Me)C=N-N=C(Me)-] of 3-bpdh and uncoordinated oxygen atom of succinate in **2**. These two collective phenomena are probably responsible for the enhanced CO_2 adsorption of **2**. There was a hysteresis in CO_2 adsorption-desorption isotherm of **2** which can be corroborated to the strong interaction between quadrupolar CO_2 and the basic polar azine moiety present in the framework (Fig. 5).

The water vapor adsorption of **2** has also been studied at 298 K to understand the nature of interaction of water with the pore wall of the framework. It shows a steep rise in the uptake of water vapor of ~36 cm^{3}g^{-1} at very low pressure ($P/P_0 \approx 0.32$), which has been corroborated with the high water affinity of the desolvated framework. In the crystal structure, there is a coordinated water molecule which released in sample preparation temperature (130°C) and creates an open metal site in the framework. This open metal site is responsible for the said rise of water uptake in very low pressure. Thereafter, a sharp increase in the vapor adsorption profile was observed which reaches finally up to ~94 cm^{3}g^{-1} which corresponds to around two molecules of H_2O per formula unit of **2** (Fig. 6). This moderately high water uptake of **2** is accountable due to the presence of open metal site in the desolvated form, presence of polar azine moiety in the framework and also due to the presence of flexible succinate with uncoordinated oxygen atom. Similarly in water vapor sorption profile there occurs a large hysteresis which may be due to the flexible frameworks and the strong interaction between the framework and the guest or diffusion barrier.[30]

Conclusion

To explore the nonconventional factors in the organization of the structure of CPs, we have synthesized here two Cd(II) based CPs with different topology using a substituted bent 3-pyridyl linker (3-bpdh) instead of previously used non substituted 3-bpdb[15] and disodium succinate (suc). From aforesaid discussion it is revealed that in our previous work we had obtained three different CPs including 1D, 2D and 3D framework using same reaction as present except use of

3-bpdb ligand instead of 3-bpdh. It is note worthy that in our said previous work, there was an interesting appearance of Cl^{-} integrated 3D framework, which was generated by the reduction of ClO_4^{-} along with the oxidation of imine group of 3-bpdb to nicotinamide. To verify the formation of this Cl^{-} integrated 3D framework mentioned through electron taking reduction process, we have used the methylated linker (3-bpdh) instead nonmethylated linker (3-bpdb) and performed the same reaction as previous which does not lead to the formation of Cl^{-} integrated product. At present reaction with methylated 3-bpdh we have obtained only two products; one is 1D chain and the other is a 3D structure having water filled channels. Another interesting observation had been shown in our other previous work[16] that when we made same reaction except taking $Cd(NO_3)_2$ instead of $Cd(ClO_4)_2$ then a totally different single product with different functionality had been found. As a result our present work is an attempt to address and correlate some crucial factors during the synthesis of CPs which has not explored much. Two complexes **1**-**2** at present are not only interesting for their structure of formation and topology but also applicable for their excellent anion exchange property and gas sorption properties respectively. The one dimensional complex **1** contains coordinated perchlorate ions with Cd(II) centers and performs well anion exchange with the inclusion of foreign anions retaining the same skeleton structure. On the other hand, Complex **2** shows nice sorption of CO_2, water vapor and a surface adsorption of N_2 which is commensurate to its pore size and pore environment. In summary this work is a nice example of cogent design of functional CPs by controlling such factors which are not so conventional.

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Electronic supplementary information (ESI) available:

The IR, PXRD patterns, Photoluminescence spectra of complexes **1**-**2** and TGA of complex **2** along with different application based figures of both complexes and tables related to the crystal structure reported in this paper are available as ESI. The structure reported in this paper having the CCDC reference numbers 1426873 and 1426874. For ESI and crystallographic data in CIF or other electronic format see DOI:

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Figures and Tables:

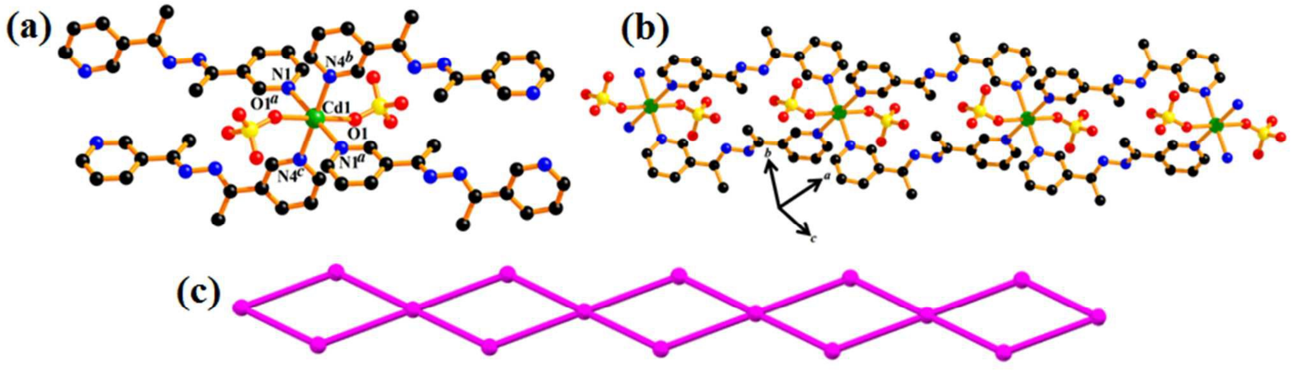

Fig. 1 (a) Coordination environment around the Cd(II) ions in **1**; Cd (green), N (blue), O (red), C (black), Cl (yellow); (b) 1D chain structure constructed through 3-bpdh ligand and coordinated perchlorate ions in **1**; (c) Simplified topological representation of 1D chain in **1**.

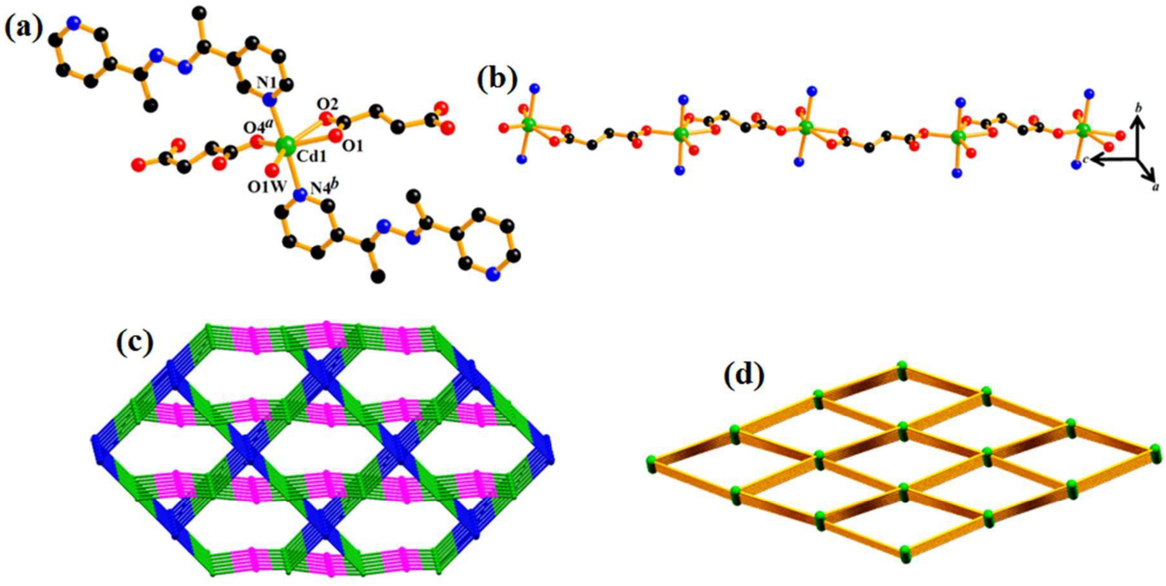

Fig. 2 (a) Coordination environment around the Cd(II) ions in **2**; Cd (green), N (blue), O (red), C (black); (b) 1D metal carboxylate chain along *c*-axis in **2** (3-bpdh ligands are omitted for clarity); (c) 3D framework of **2** constructed by both succinate and 3-bpdh ligand viewing by topos diagram (green: Cd(II) metal; pink: succinate and blue: 3-bpdh ligand); (d) Topological representation of 4-connected uninodal net in **2**.

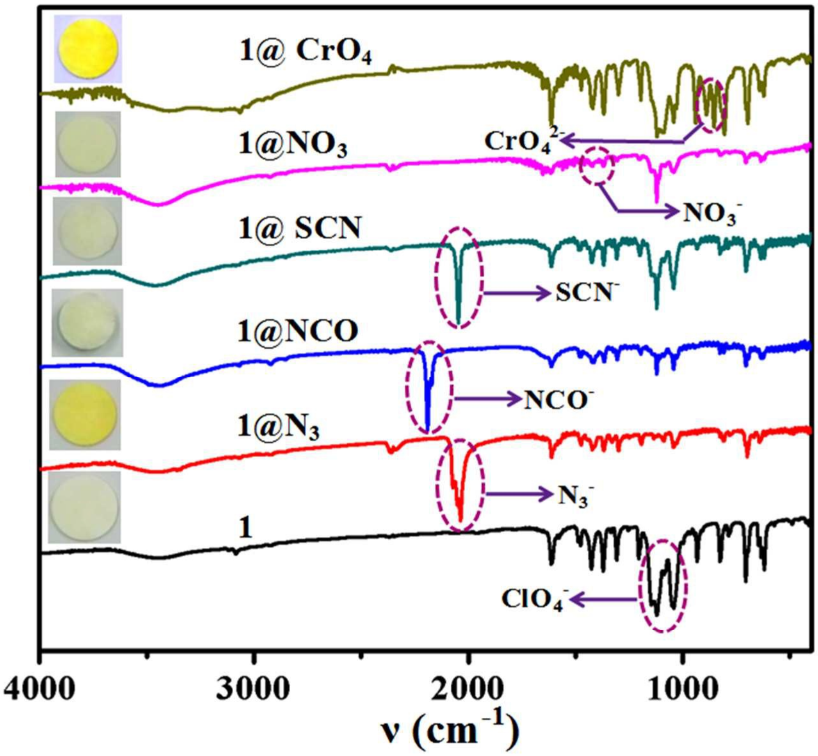

Fig. 3 Combined FT-IR spectra of parent complex **1** and its anion-exchanged solids with highlighted bands of the corresponding anions.

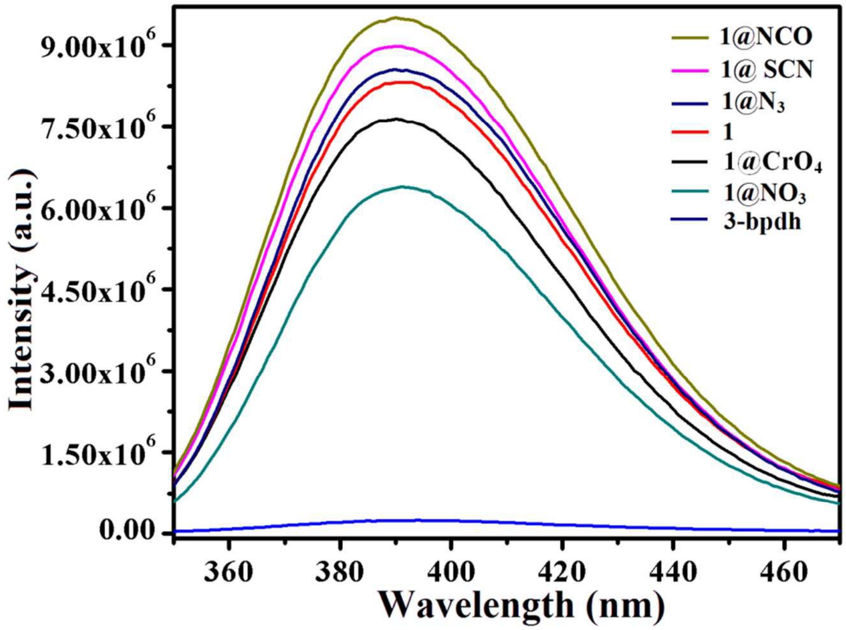

Fig. 4 Combined photoluminescence spectra of complex **1** and its anion exchanged solids with free 3-bpdh ligand.

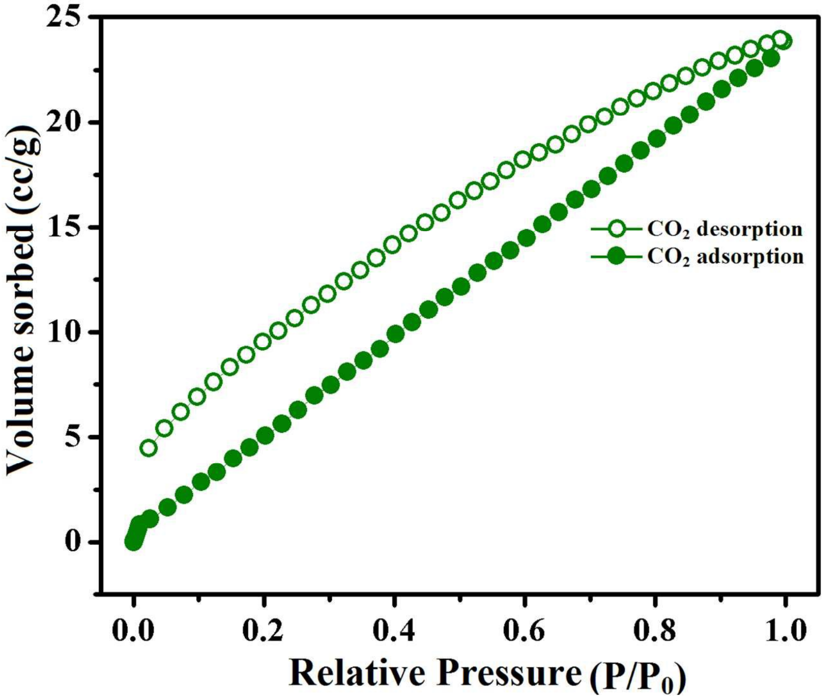

Fig. 5 CO_2 sorption isotherms of **2;** filled and open circles represent adsorption and desorption respectively.

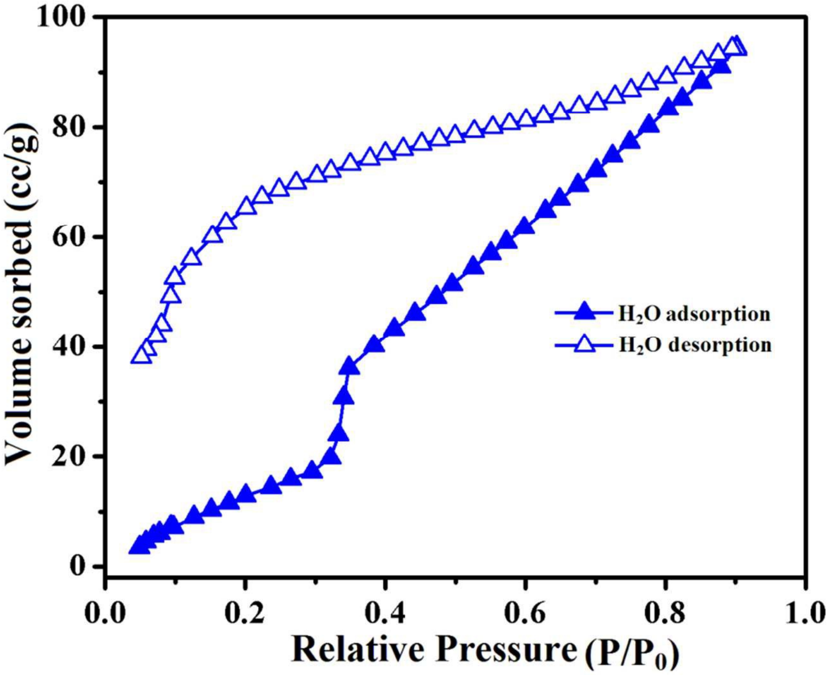

Fig. 6 Water sorption isotherms of **2;** filled and open triangles represent adsorption and desorption respectively.

Table 1 Crystallographic and structural refinement parameters of complexes **1-2**

	1	**2**
Formula	$C_{28}H_{28}N_8O_8Cl_2Cd$	$C_{18}H_{26}N_4O_8Cd$
Formula Weight	787.89	538.84
Crystal System	Monoclinic	Orthorhombic
Space group	*P21/n*	*Pna21*
a/ Å	8.840(5)	7.087(5)
b/Å	17.934(5)	17.669(5)
c/ Å	10.458(5)	17.793(5)
α/°	90	90
β/°	98.701(5)	90
γ/°	90	90
V/ Å^3	1638.9(13)	2228.0(18)
Z	2	4
D_c/ g cm^{-3}	1.597	1.600
μ /mm^{-1}	0.890	1.031
$F(000)$	796	1088
θ range/°	2.3-27.6	1.6-27.6
Reflections collected	28123	35046
Unique reflections	3780	5146
Reflections $I > 2\sigma(I)$	3131	4818
R_{int}	0.034	0.021
goodness-of-fit (F^2)	1.06	1.07
$R1$ ($I > 2\sigma$(I)) [a]	0.0387	0.0204
$wR2$($I > 2\sigma$(I)) [a]	0.1087	0.0578
$\Delta\rho$ min / max /e Å^3	-0.58, 0.89	-0.28, 0.35

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma(w(F_o^2-F_c^2)^2)/\Sigma w(F_o^2)^2]^{½}$

Table 2 Selected bond lengths (Å) and bond angles (°) for complex **1**

Cd1-O1	2.394(3)	Cd1-N1	2.342(3)
Cd1-N4^b	2.319(3)	Cd1-O1^a	2.394(3)
Cd1 -N1^a	2.342(3)	Cd1-N4^c	2.319(3)
O1-Cd1-N1	92.27(10)	O1-Cd1-N4^b	94.76(10)
O1-Cd1-O1^a	180.00	O1-Cd1-N1^a	87.73(10)
O1-Cd1-N4^c	85.24(10)	N1-Cd1-N4^b	87.35(8)
O1^a-Cd1 -N1	87.73(10)	N1-Cd1-N1^a	180.00
N1-Cd1-N4^c	92.65(8)	O1^a-Cd1-N4^b	85.24(10)
N1^a-Cd1-N4^b	92.65(8)	N4^b-Cd1 -N4^c	180.00
O1^a-Cd1-N1^a	92.27(10)	O1^a-Cd1-N4^c	94.76(10)
N1^a-Cd1-N4^c	87.35(8)		

Symmetry code: *a* = 2-x, -y, 2-z; *b* = -1+x, y, -1+z; *c* = 3-x, -y, 3-z.

Table 3 Selected bond lengths (Å) and bond angles (°) for complex **2**

Cd1-O1	2.338(3)	Cd1-O1W	2.302(3)
Cd1-O2	2.507(3)	Cd1-N1	2.332(3)
Cd1-O4^{a}	2.224(3)	Cd1-N4^{b}	2.358(3)
O1-Cd1-O1W	95.09(9)	O1-Cd1-O2	53.49(7)
O1-Cd1-N1	90.45(10)	O1-Cd1-O4^{a}	139.40(10)
O1-Cd1-N4^{b}	90.92(10)	O1W-Cd1-O2	148.57(8)
O1W-Cd1-N1	91.24(6)	O1W-Cd1-O4^{a}	125.19(11)
O1W-Cd1-N4^{b}	83.50(7)	O2-Cd1-N1	89.78(7)
O2-Cd1-O4^{a}	86.09(9)	O2-Cd1-N4^{b}	95.19(7)
O4^{a} -Cd1-N1	93.31(9)	N1-Cd1-N4^{b}	174.66(6)
O4^{a} -Cd1-N4^{b}	89.01(9)		

Symmetry code: *a* = -1-x, -y, -1/2+z; *b* = -1/2-x, 1/2+y, 1/2+z.

For Table of Content Use

Tuned synthesis of two coordination polymers of Cd(II) using substituted bent 3-pyridyl linkers and succinate: structure and their applications in anion exchange and sorption properties

Dilip Kumar Maity, Biswajit Bhattacharya, Arijit Halder and Debajyoti Ghoshal