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One-dimensional Water Cages with Repeat unit of $(H_2O)_{24}$ Resembling Pagodane in 3D Coordination Polymer: Proton Conducting and Tunable Luminescence Emission by Absorption of Anionic Dyes

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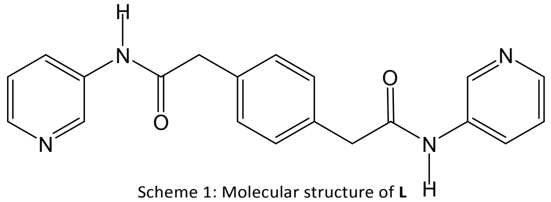
A 3D-coordination polymer was shown to trap one-dimensional polyhedral water cages consisting of a repeat unit of $(H_2O)_{24}$, the geometry of which resembles exotic organic molecule pagodane. Further, this material exhibitted proton conducting ability and tunable luminescence emission by absorption of anionic dyes such as fluorescein dianion.

In recent years special attention has been paid for the design and synthesis of microporous materials, in particular, metal-organic frameworks (MOFs) or covalent organic frameworks (COFs) for the gas storage and separation purposes.[1] These materials contain well-defined pores and possess the ability to incorporate several guest molecules and assemblies of guest molecules otherwise can't be realized.[2] For example, a variety of water clusters with different sizes and shapes have been reported in the past which affords some information related to the anomalous behaviour of bulk water, but still it is a meagrely understood liquid.[3] On the other hand, infinite chains of water molecules, hydrogen bonded water clusters and metal-coordinated water molecules were shown to have a potential to act as proton carriers in humid conditions as well as in anhydrous conditions.[4] Proton-conducting materials are of importance for developing electrochemical cells such as fuel cells, electrochemical sensors, electrochemical reactors, and electrochromic devices. Fuel cells are thought to be one of the alternative energy sources for the next generation.[5-6] Proton conductivity can mediate the process of conversion of energy from one form into another by involving the transfer of protons in proton exchange membrane fuel cells (PEMFCs) where the proton conducting materials are being used as the membrane electrolyte. The proton conduction within a hydrogen-bonded water cluster are anticipated with the formation of H_3O^+ within the network where transfer of the proton occurs with simultaneous rearrangement between nearby H_2O molecules following the Grotthuss or proton-hopping mechanism.[7-8]

In MOFs and COFs, the hydrophobic nature of the channels/cavities can be effectively tailored to hydrophilic nature by introducing the functional groups that are capable of forming hydrogen bonding on to the backbone of the linear exo-bidentate ligands. The organic back bone, in MOFs, serves as an anchor for the inclusion and self-organization of free water molecules into various ordered aggregates *via* hydrogen bonding.[9] To date, several variety of water clusters consisting of discrete assemblies such as tetramers, pentamers, hexamers, octamers, decamers and polyhedral cages, one-dimensional chains and helices and two-dimensional layers have been also identified in the crystal lattices of MOFs.[10] However, to the best of our knowledge no one-dimensional polyhedral cage structure of water molecules was reported to date. Herein we report one such example of 3D-coordination polymer containing one-dimensional water cage with a repeat unit of $(H_2O)_{24}$, the geometry of which resembles organic molecule pagodane. Further, this material was also shown to exhibit appreciable proton conductivity and anionic dye absorption from aqueous solution of dye which helps in fine tuning the emission properties.

In continuation of our efforts in synthesizing and exploring the properties of CPs containing amide and bis-pyridyl functional groups, the molecule **L** (scheme 1) has been synthesized in anticipation of 3D-networks, due to its inherent flexibility, with



Scheme 1: Molecular structure of **L**

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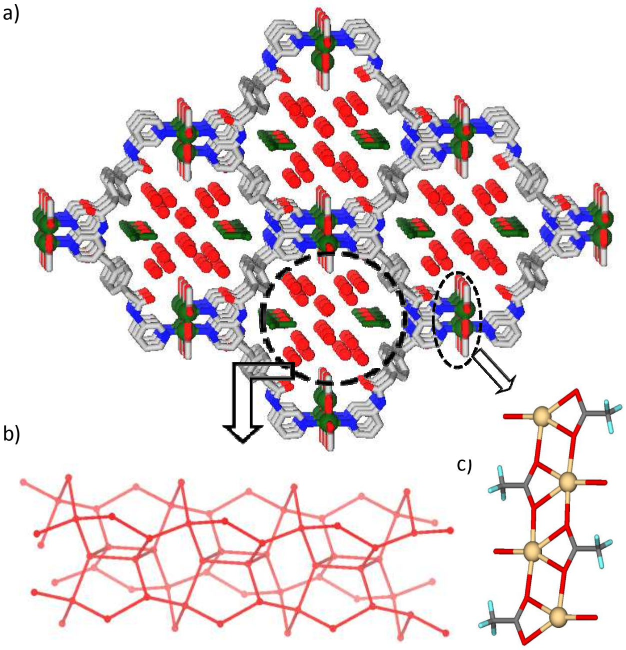

Fig. 1 Illustrations for the crystal structure of 1: (a) 3D-coordination polymer containing huge channels filled by water molecules (red spheres) and acetate ion (green, cylinder mode); (b) Hydrogen bonded (shown as bonds) one-dimensional polyhedral water cage with a repeat unit of $(H_2O)_{24}$; (c) one-dimensional planar chains of Cd(OAc) units via μ^2-oxo bridging.

hydrophilic channels given the presence of amide functionalities on the back bone. The reaction of **L** (17.32 mg, 0.05 mmol) with $Cd(OAc)_2$ (13.33 mg, 0.05 mmol) in MeOH (10 ml) resulted in the single crystals of a coordination polymer **1**, $\{[Cd(\mathbf{L})(OAc)(H_2O)]OAc\cdot 9H_2O\}_n$. Single-crystal X-ray diffraction analysis of **1** revealed that it crystallizes in the C2/m space group, and the asymmetric unit is composed of half unit each of **L** and Cd(II), two half units of acetate ions, and seven water molecules: three with full occupancy and four with half occupancy (six free and one coordinates to Cd(II)). Among the two acetate ions, one does not coordinate and the other coordinates to Cd(II) in chelating mode (Cd-O: 2.475 & 2.488 Å) which further bridges neighbouring Cd(II) ions via μ^2-oxo bridging (Cd-O: 2.366 & 2.405 Å) such that it results in the formation of one-dimensional chains of Cd(OAc) units. It is interesting to note here that the crystal structure of $Cd(OAc)_2.2H_2O$ exhibits such one-dimensional Cd(OAc) chains but the chains are spiral as only one O-atom of the acetate participates in the bridging. To date no double bridging Cd(OAc) planar chain similar to the one that is observed in **1** was reported. Further, the geometry of the chain observed here has a close resemblance with one that is observed in a CP of $LaNO_3$.[11]

As a consequence, each Cd(II) is connected to five O-atoms (four form acetate and one from water) which are in plane. The two apical positions of Cd(II) are connected to two pyridyl units (Cd-N: 2.288 Å) of **L** which links these one-dimensional chains into three-dimensional network containing channels of dimension 11X16.7 Å and overall the Cd(II) is seven coordinated with distorted pentagonal by-pyramidal geometry (Fig. 1).

The channels are exclusively occupied by six free water molecules (33% of crystal volume) and free acetate ion. The free acetate ion found to form hydrogen bonds with N-H group of **L** and remain in the channels. Interestingly, the water molecules in the channels exhibited cage like one-dimensional aggregates, which propagates along *c*-axis, via O_w-H…O_w hydrogen bonds (Table S2). The repeat unit $(H_2O)_{24}$ of these one-dimensional H_2O cages found to have geometry of exotic organic molecule called [2.2.2.2]pagodane $(C_{24}H_{28})$.[12] These one-dimensional chains were anchored by walls of the channels *via* O-H…O hydrogen bonds between free water molecules and coordinated water molecules, amide O-atoms or free acetate ion. Notably, with the exception of O5w all the other five free water molecules found to engage in four hydrogen bonds. The O5w forms only three hydrogen bonds: two with neighbouring water molecules and one with amide C=O moiety. Over all the supramolecular pagodane contains fused rings of six, five and four membered rings in 4:4:1 combination (Fig. 2). Unlike in covalent pagodane, in non-covalent pagodane the top positions involving O5w are not connected with each other and remain 7.3 Å apart. From TGA analysis it is evident that the crystals of **1** are stable up to 80 °*C* and loose the water molecules between 80 to 120 °*C*(Fig. S4).

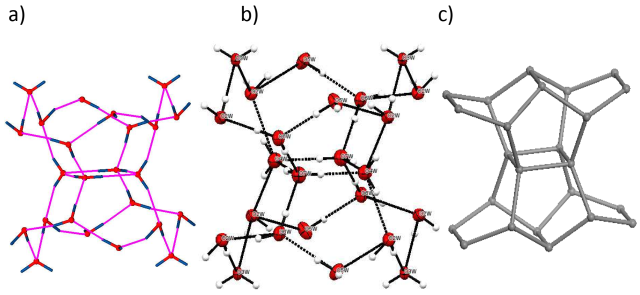

Fig. 2. Illustrations for the water cluster ($(H_2O)_{24,}$ pagodane like) observed in 1: (a) hydrogen bonding (pink lines) between the water molecules in the cluster (red= O and blue= H); (b) ORTEP view of water cluster $(H_2O)_{24}$; (c) structure of pagodane $C_{24}H_{28}$ as observed in it crystal structure.[12]

Further, single crystal data collection at room temperature also indicates that the water cluster was intact with albeit relatively somewhat higher thermal parameters. In order to verify the source of water molecules in the formation of crystals of **1**, the reaction of **L** with $Cd(OAc)_2$ was conducted in anhydrous MeOH. This reaction resulted in the coordination polymer **2**, $\{[Cd_2(L)_2(OAc)_4]\cdot 2MeOH\}_n$. As expected it does not contain water, and forms a 2D-square grid network in which the Cd(II) atoms act as a bi-metallic SBU. The SBUs are linked by **L** units to form square grids of dimension 19X20 Å and the layers pack on each other in off-set mode being interdigitated to each other (Fig. 3). The interdigitated layers interact with each other via amide-to-amide hydrogen bonds (Table S3).

The presence of highly ordered hydrogen bonded water molecules in the close proximity within the hydrophilic cavity of CP **1** prompted us to investigate the proton conductivity

(PC) on this material. Recently, it was shown that the CPs containing water chain or clusters have a potential to good PC materials.[4d,e]

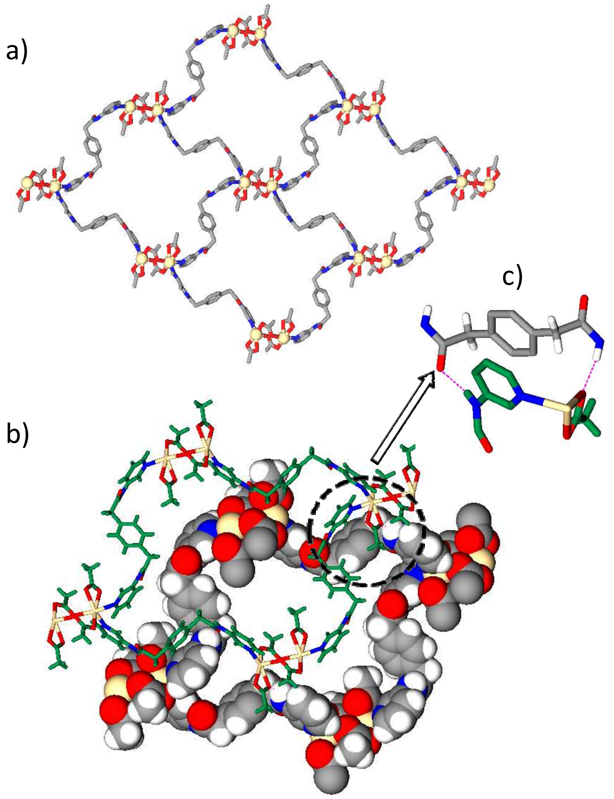

Fig. 3 Illustrations for crystal structure of **2**: (a) two dimensional network containing grids of dimension of 19X20 Å^2; b) interdigitation of 2D-layers via hydrogen bonding and other weak interactions; c) N-H-O hydrogen bonds between amide groups.

The PC of CP **1** was calculated by conducting AC impedance analysis on a pressed pellet of the powered sample using a frequency response analyzer via a quasi-four-probe method, at different relative humidity (RH) and temperatures. The conductivity value was evaluated from the Nyquist plots. The measured PC for this material is about 0.719 $\times 10^{-4}$ S cm^{-1} at 110 *°C* and RH of 98%. However, the conductivity value found to drop sharply with lowering of temperature as well as relative humidity. The dropping of the PC at lower temperatures and RH values indicate that these factors are important in stimulating the proton-conducting mechanism of the included water molecules in the CP (Fig. 4).

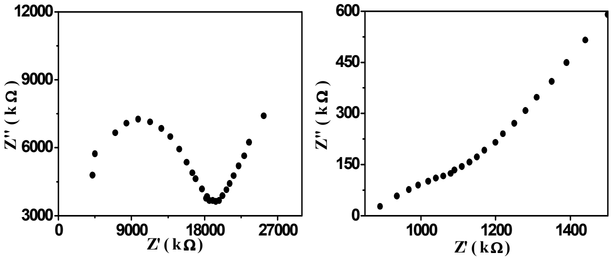

Fig. 4 Nyquist plots for **1** at (a) 25 *°C and 98% RH and* (b) 110 *°C* and 98% RH.

For example, the observed PC for CP **1** at ambient temperature and 60% of RH is 1.02x10^{-5} S cm^{-1}. The temperature dependence study for PC was performed over the temperature range of 25 to 110 *°C* (RH = 98%). These studies reveal that at 25 *°C*, it exhibits lowest PC value (1.52 $\times 10^{-5}$ S cm^{-1}) which increases to maximum (0.719 $\times 10^{-4}$ S cm^{-1}) as the temperature increases gradually to 110 *°C* and this is a very rare phenomenon and desired one. The PC value is comparable to that of reported Zn-MOFs and Cu-MOFs containing water chains.[4d,e]

The presence of one-dimensional channels that are occupied by hydrophilic water clusters prompted us to study the dye absorption ability of these materials from aqueous solutions. For this purpose the anionic dye such as fluorescein dianion (FSD) was considered as the network is cationic with one of the acetate ions remains in the channels.[13] Further, it was anticipated that the inclusion of the FSD into the CP-**1** enhances the luminescence of CP-**1** to result in functional materials with electro-optic properties. Therefore, the crystals of CP-**1** (15 mg) were immersed in the aqueous solution of FSD (10 ml, 10^{-3} M solution). It was observed that as the time progresses the colourless CP changed to orange coloured material (**3**) (Fig. S6). The single crystals found to be intact during the absorption process but not suitable for single crystal X-ray diffraction. The retaining of network structure in **3** was confirmed by comparing its XRPD with that of CP **1**.

The solid-state luminescence of **1** and **3** were investigated at room temperature with excitation wavelengths of 350 and 440 nm respectively. Both were found to display different emission profiles, **1** exhibited strongest emission peak at 415 nm whereas **3** shows an intense emission peak at 554 nm (λ_{ex} = 440 nm). For **3**, emission was observed with a red shift by 139 nm, with respect to **1**, due to the charge-transfer interactions between cationic framework and the anionic FSD. The emission profile of pure FSD was recorded by exciting it at 440 nm for the sake of comparison with that of **3**. Pure FSD was found to exhibit emission maximum at 586 nm which is in the yellow region (Fig. 5). Therefore, the complex **3** (green region) exhibits emission maximum which is in between that of **1** (violet region) and FSD (yellow region). Such type of intermediate emission was reported recently in case of cationic (DMASM) dye absorbed MOF.[13b] It is also interesting to note here that the intensity of emission can be also fine tuned by controlling the absorption quantities of dye. For example, the complex **1** exhibits 9 $\times 10^{6}$ a.u., while **3**, when prepared at 10^{-3} M conc. of FSD shows 6.5 $\times 10^{5}$ a.u.. The luminescence intensity of **3** is found to be much lower when the material of **3** was prepared by immersing **1** in highly conc. aqueous solution of FSD. We note here that the physical mixture of **1** and FSD does not exhibit either such shifting of emission wavelengths or change in intensities as the emission profile was similar to that of **1** and FSD at excitation wavelengths of 350 and 440 nm respectively.

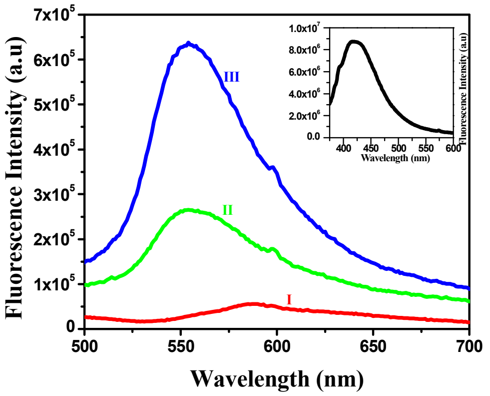

Fig. 5 Solid state emission profiles of I) pure FSD (red); II) of **3** at high conc. of FSD (green) and III) of **3** at 10^{-3} M conc. of FSD at 440 nm. The inset shows the emission profile of CP **1** at 350 nm.

In addition to FSD, **1** was also found to absorb another anionic dye methyl orange (MO) (Fig. S9, S10). The solid-state luminescence of MO absorbed materials of **1** were also found to exhibit similar emission profiles and trends as those of **3** (Fig. S12). As a matter of fact, the CP **1** did not absorb cationic dyes such as methylene blue or crystal violet which exemplifies the selectivity of **1** towards the nature of dye.

In conclusion, the CP **1** reported here had exhibited an unique feature of encapsulating a one-dimensional water cages in which the repeating unit contains the geometry of organic molecule pagodane. Further, the material **1** shows appreciable proton conductivity due to the presence of such water cages. It also exemplifies the role of one-dimensional planar chains of Cd(OAc) units in promoting the formation of three-dimensional porous structures. Furthermore, the cationic framework of CP has shown the capability of selectively absorbing anionic dyes, which helps in fine tuning the emission profiles of the materials. The exploration of gas sorption properties is underway in our laboratory.

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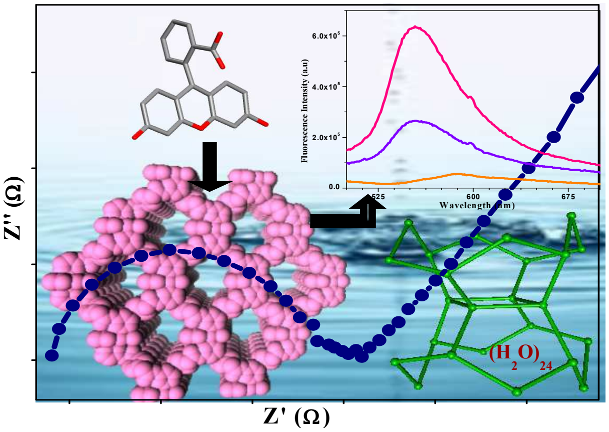
Z'' (Ω)
Z' (Ω)
Fluorescence Intensity (a.u)
6.0x10^5
4.0x10^5
2.0x10^5
0.0
525
600
675
Wavelength (nm)
(H2O)24