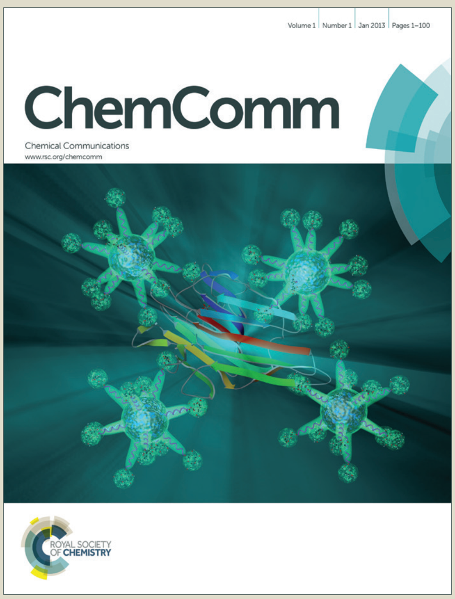
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ARTICLE TYPE

Novel Zeotype Frameworks with Soft Cyclodiphosphazane Linkers and Soft Cu_4X_4 Clusters as Nodes

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Two novel cyclodiphosphazane cluster frameworks with Cu_4X_4 clusters as tetrahedral nodes and ferrocenyl cyclodiphosphazane [Fe(η^5-C_5H_4)$_2$(PN^{t}Bu)$_2$] as ditopic linkers have been synthesized. These frameworks having sodalite topology displays a unique integration of porosity and redox activity and offer new opportunities for the synthesis of zeotype frameworks with soft phosphorus-based ligands.

Metal–organic frameworks (MOFs) have been the focus of intense interest because of their novel framework topologies and potential applications in gas storage, separation, CO_2 sequestration and catalysis.[1] These are generally synthesized by using bipyridine and carboxylate derived linkers with hard donor atoms like N or O,[2] but examples of MOFs with soft Lewis base linkers derived from P^{III} ligands are scarce.[3] The major constraints behind scarcity of phosphine-based MOFs is the lack of suitable linkers with rigid framework (such as 4,4'-bipyridine) as the pyramidal geometry at the phosphorus atom and free rotation about the P–C bonds allows a range of accessible orientations of lone pairs bringing a disambiguity in the coordination behavior.[3c] Cyclodiphosphazanes, which are rigid four membered rings having alternate phosphorus and nitrogen atoms (P_2N_2) in their cyclic skeleton can be utilized as bidentate linkers in the construction of phosphorus-based MOFs. These are capable of performing as neutral and anionic ligands towards both main group as well as transition metals[4] and have been used as building blocks in designing a variety of inorganic macrocycles, clusters and cages.[5]

The CuX complexes of phosphorus ligands display a wide range of structures depending on stoichiometry, reaction conditions and solvents employed. These generally form rhomboid dimeric or polymeric $[Cu_2X_2L_2]_n$ and tetrameric complexes $[Cu_4X_4L_4]_n$, displaying simple cubane or polymeric staircase structures.[6] As a result of these competing crystallization processes, it is highly challenging to construct MOFs by using metal halide clusters. Recently, Bu and coworkers have reported the synthesis of cluster organic framework (COZ-1) by using halide clusters as tetrahedral building blocks and DABCO as linkers.[7] Surprisingly, MOFs based on $[Cu_4X_4]$ clusters with bisphosphane as linkers are not known in the literature.

Herein, we demonstrate the use of ferrocenyl cyclodiphosphazane as ditopic linkers with Cu_4X_4 clusters as tetrahedral nodes for the synthesis of novel zeolitic cyclodiphosphazane cluster frameworks featuring sodalite (**sod**) topology. Ferrocenyl-cyclodiphosphazane [Fe(η^5-C_5H_4)$_2$(PN^{t}Bu)$_2$] was synthesized according to literature procedure.[8] Slow diffusion of acetonitrile solution of copper halide into a solution of [Fe(η^5-C_5H_4)$_2$(PN^{t}Bu)$_2$] in dichloromethane at room temperature afforded red crystals of [{Cu_4X_4}{Fe(η^5-C_5H_4)$_2$(PN^{t}Bu)$_2$}$_2$]$_n$, (**1**, X = Br and **2**, X = I).

Single crystal X-ray diffraction studies have shown that **1** and **2** crystallize in *I-43m* (Nr. 217) space group. The asymmetric unit consists of one crystallographically unique Cu atom, one iodine atom and half of the ligand. The overall three dimensional framework consists of Cu_4I_4 tetrahedral units linked in all four directions by ditopic P_2N_2 ligands to form a sodalite type network (Figure 1). Each tetrahedral Cu_4I_4 unit consists of four tetrahedrally coordinated Cu atoms, each bonded by three μ_3-I atoms and one P atom from the ditopic ligand. The Cu-P bond length in **1** and **2** are 2.182(4) Å and 2.214(4) Å, respectively. The average Cu···Cu distances in **1** and **2** are ~3.37 and ~3.43 Å, which are larger than the same in COZ-1 (2.6 Å).[7] The ^{31}P{^{1}H} NMR spectra of **1** and **2** showed broad single resonances at 137.1 and 143.3 ppm, with coordination shifts of 51 and 45 ppm (for [Fe(η^5-C_5H_4)$_2$(PN^{t}Bu)$_2$], δ_P = 188 ppm), respectively. ^{1}H NMR spectra displayed single resonances around 1.43 ppm for the ^{t}Bu groups and two singlets around 4.41 and 4.43 ppm for ferrocenyl protons.

The overall network of the framework consists of large supercages with eight distorted hexagonal faces and six square faces shared with neighbouring cages. A prominent structural feature of these frameworks is the presence of large cages made up of Cu_4X_4 clusters and cyclodiphosphazane ligands. Each cage contains 24 Cu_4X_4 clusters connected by 32 cyclodiphosphazane linkers forming an inner sphere of approximately 2.4 nm diameter (Figure 1c), making up a pore volume of ~7.2 nm^3. The presence of alternative ^{t}Bu and ferrocenyl groups in hexagonal faces decreases the aperture size to 5.7 Å, whereas the same is decreased to 3.9 Å in tetragonal faces due to the presence of bulky ^{t}Bu groups. The pore limiting diameter and maximum pore diameter according to the Poreblazer software are 18.2 Å and 2.89 Å, respectively. Size of these apertures in **1** and **2** are comparable with those of reported sodalite MOFs (3.4 and 6.4 Å

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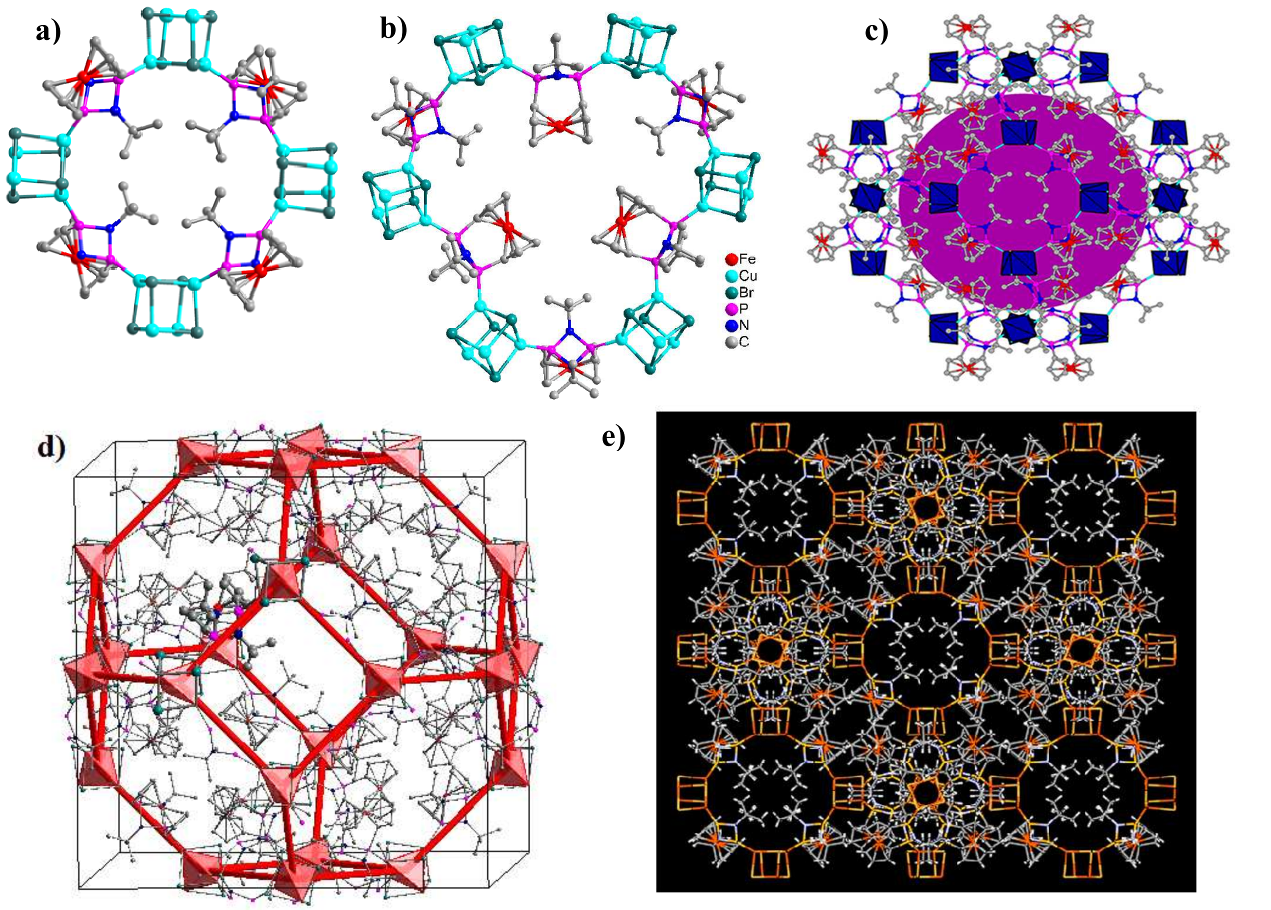

Fig. 1 a) Square window and (b) hexagonal window in **1**, some of the ^{t}Bu groups have been omitted for clarity (c) and (d) Sodalite cage (the violet ball represents large empty voids (2.4 nm), Cu_4X_4 and Cu_4 units are represented as polyhedra. (e) 3D framework of **1**.

for ZIF-8 and IFMC-1, respectively).[9] The solvent accessible volume of **2** was estimated by platon to be ~55 % of the total crystal volume.

The thermal gravimetric analysis of the frameworks shows loss of guest solvent molecules up to 200°C, the loss of ^{t}Bu groups is observed around 300 °C followed by the decomposition of the linker (Figure S1, S2 ESI). The phase purity of bulk material was confirmed by powder X-ray diffraction (Figure S3, S4 ESI). The UV-Visible spectrum of **1** and **2** in acetonitrile show adsorption bands in the region 220–260 nm due to ligand centered $\pi\rightarrow\pi^*$ transitions (Figure S5 ESI).

Prior to the adsorption measurements, the compounds were evacuated at 80 °C under vacuum to obtain fully desolvated frameworks. To ensure the integrity and the efficiency of solvent removal, **1** and **2** were also activated using supercritical CO_2. The nitrogen adsorption/desorption behavior of **1** and **2** at 77K can be classified as the type IV isotherm with type H2 hysteresis according to IUPAC classifications (Figure 2, 3). Obviously, the very narrow windows (ca. 3 Å) which connect the large pores (ca. 24 Å) in the structure are responsible for such hysteresis pointing to pore-blocking or cavitation effects.[10] Similar adsorption behavior was also observed for IFMC-1a MOF possessing sodalite topology as well.[9b] The differences in the maximum nitrogen uptake for the samples activated thermally and dried

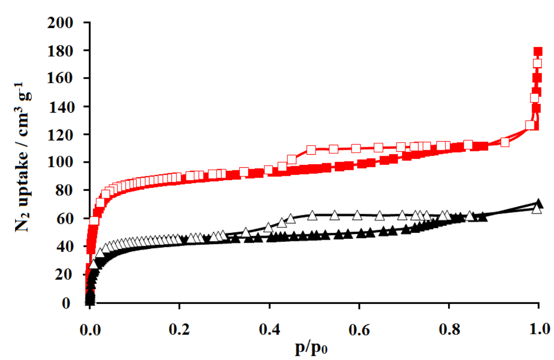

Fig. 2 a) The N_2 physiosorption isotherm of **1** activated at 80 °C (black circles) and supercritically dried (red diamonds) at 77 K.

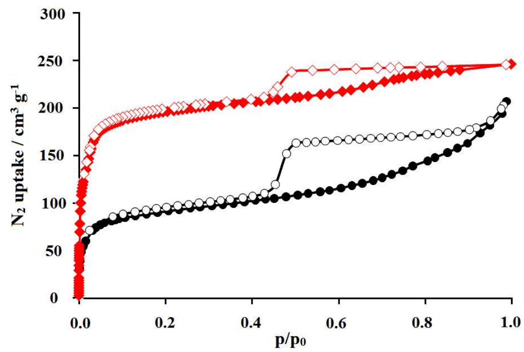

Fig. 3 a) The N_2 physiosorption isotherm of **2** activated at 80 °C (black triangles) and **2** supercritically dried (red squares) at 77 K.

supercritically can be explained by the insufficient solvent removal at 80 °C or by partial structure collapse during the evacuation at elevated temperature. The Brunauer-Emmett-Teller (BET) area of thermally activated samples was found to be 169 and 482 m^2g^{-1} for **1** and **2**, respectively. The supercritical dried samples show the BET surface area of 347 (**1**) and 759 m^2g^{-1} (**2**). The geometrical surface area calculated using Poreblazer V1.2 program[11] for **2** is 1221 m^2g^{-1}. The calculated pore volume for **2** is 0.53 cm^3g^{-1}. The pore volume for supercritically dried samples derived from nitrogen adsorption isotherms is 0.18 cm^3g^{-1} for **1** and 0.37 cm^3g^{-1} for **2**.

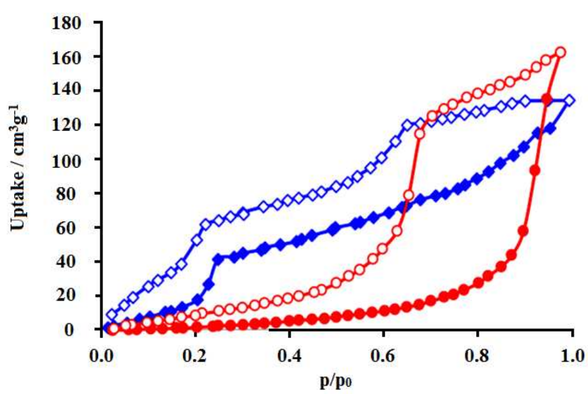

Fig. 4 The water vapor (red circles) and methanol vapor (blue squares) physisorption isotherms of **1** at 298 K. Solid and open symbols denote adsorption and desorption, respectively.

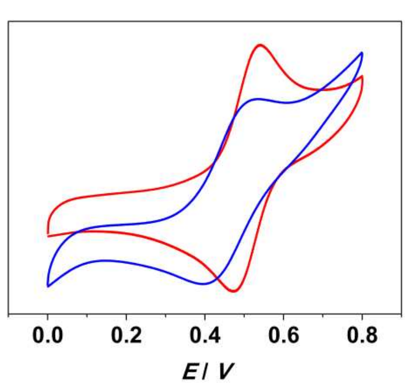

Fig. 5 Cyclic voltammetry curves of Ligand (red) and **1** (blue) in phosphate buffer solution (pH = 7.4)

The water and methanol vapor physisorption isotherms were measured at 298 K on thermally activated samples (Figure 4). The water adsorption starts at high relative pressure displaying the hydrophobicity of the framework. The methanol adsorption isotherm shows one distinct step at p/p_0 0.2, corresponding to the filling of two different sizes of pores.

MOFs based on ferrocenyl linkers are very scarce, post synthetic modifications have been made in few cases for the synthesis of ferrocenyl based MOFs and ferrocene has also been included as guest molecules in the pores.[12] The presence of redox ferrocenyl linkers makes these frameworks stable materials for electrochemical studies. The solid state electrochemical behavior was investigated by immobilizing these compounds on glassy carbon electrode. The reversible one electron redox ferrocene-ferrocenium(Fc/Fc^+) couple for the free ligand and **1** have been observed at 0.50 V and 0.46 V, respectively (Figure 5). The small shift of 45 mV towards negative potential may be due to immobilization of frameworks.

In summary, we have synthesized two new sodalite MOFs with soft donor phosphorus ligands as linkers. These zeolitic cyclodiphosphazane cluster frameworks (**1** and **2**) are constructed by using metal halide clusters (Cu_4X_4) as tetrahedral nodes and ferrocenyl cyclodiphosphazanes as ditopic linkers. These frameworks with large cages of diameter 2.4 nm represent a unique combination of redox activity and porous properties. These are ideally suited for electrocatalysis, electrochemical splitting of water and for fabricating energy storage devices.[13] These results have further demonstrated that MOFs can also be synthesized from soft phosphorus-based ligands which can open up new areas for designing attractive materials for heterogeneous catalysis as well.

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Notes and references

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† *Electronic Supplementary Information (ESI) available: Experimental procedures, NMR spectra, TGA plots, PXRD data. For ESI and Crystallographic data in CIF format see DOI: 10.1039/b000000x/*

‡ Crystal data for **1**: $C_{18}H_{26}Br_2Cu_2FeN_2P_2$, M = 675.1, Cubic, space group *I-43m*, a = b = c = 28.8993(5) Å, V = 24135.8(7) $Å^3$, Z = 24, Dc = 1.115 g cm^{-3}, μ(Mo Kα) = 3.474 mm^{-1} F(000) = 7968, T= 150 K, GoF = 1.113, final R_1 = 0.0414 and wR_2 = 0.0822 for $I > 2\sigma(I)$, R_1 = 0.0707, wR_2 = 0.0965 for all data. CCDC: 979416. Crystal data for **2**: M = 400.54, Cubic, space group *I-43m*, a = b = c = 29.2489(4) Å, V = 25022.4(10) $Å^3$, Z = 48, Dc = 1.276 g cm^{-3}, μ(Mo Kα) = 2.921 mm^{-1}, F(000) = 9216, T= 150 K, GoF = 1.119, final R_1 = 0.0680 and wR_2 = 0.1517 for $I > 2\sigma(I)$, R_1 = 0.0972, wR_2 = 0.1860 for all data. CCDC: 979417

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Two novel zeolitic phosphane cluster frameworks have been synthesized by using ferrocenyl cyclodiphosphazanes $[Fe(\eta^5\text{-}C_5H_4)_2\{P(\mu\text{-}N^tBu)\}_2]$ as ditopic linkers and $[Cu_4X_4]$ as tetrahedral nodes.