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ARTICLE

Copper based pillared-bilayer metal organic framework: synthesis, sorption property and catalytic performance

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A new 2D pillared-bilayer flexible open metal organic framework $\{[\text{Cu}(\text{tdc})(\text{bpe})]_n \cdot 2n(\text{H}_2\text{O}) \cdot n(\text{MeOH})\}$ (compound **1**) [H_2tdc = 2,5 thiophenedicarboxylic acid; bpe = 1,2-Bis(4-pyridyl)ethane] has been synthesized through solvent diffusion technique and structurally characterized. Structure analysis reveals that the tdc ligands formed bilayers with the $\text{Cu}(\text{II})$ ions along b -direction and the layers are further pillared by bpe linkers and resulted a 2D pillared-bilayer porous framework with four connected uninodal $\text{sq}1/\text{Shubnikov}$ tetragonal plane net with Schläfli symbol $\{4^4.6^2\}$. The framework is enclosed with large square shaped channels ($13.7 \times 8.35 \text{ \AA}^2$) along the bc -plane and the channels are occupied by guest solvent molecules. Adsorption studies reveal that compound **1** shows selective adsorption for CO_2 over CH_4 at room temperature and it also shows hysteretic sorption for few protic solvents (H_2O , EtOH) and Type-1 isotherm for an aprotic solvent (CH_3CN). Catalytic performance of compound **1** for Glaser type homo-coupling reactions have also reported.

Introduction

Recently, Porous Coordination Polymers (PCPs) or Metal Organic Frameworks (MOFs) have attracted much attention due to their potential applications in storage,¹ separation,² catalysis³ etc. In this regard, 2D MOFs have some additional advantages because of their flexibility⁴ resulted from promising movement of the 2D networks in addition to shifts in angles and local bond lengths or alteration during guest removal or accommodation.^{5a} MOFs are excellent candidates for heterogeneous catalysis in chemical reactions⁶ because of their poor solubility in common solvents and having tunable and uniform pore sizes. In spite of the great potential, a very few MOFs have been explored for catalytic applications as it remains a big challenge to incorporate catalytically active strong Lewis acid or Brønsted acid sites with in MOFs. One of the most common strategy is to utilize the metal connecting points with unsaturated coordination environments as catalytically active Lewis acid sites. This method implicates bigger synthetic challenges, but, once the product is obtained, handling and recycling of catalyst could be much easier.

The Glaser-type coupling is a classic reaction to prepare 1,3-diynes through homo-coupling reaction from terminal alkynes. These types of coupling reactions are being used in numerous reactions from total synthesis of polyene natural products to the straight forward amplification of highly conjugated new

materials.⁷ However, most of the reported Cu-catalysed systems are homogeneous⁸ and there are some difficulties in product separation, catalyst recycling as product contamination caused by the residual components of the catalysts.⁹ For this reason, heterogeneous catalysts have been increasingly used to promote this type of reactions, which mainly occur at the effective surface energy at preferential sites.¹⁰ Even though there are adequate number of Cu-MOFs described in the literature,¹¹ to the best of our knowledge, there is no report available on Glaser type homo-coupling reactions using Cu-MOFs as catalyst.

Herein, for the first time we are reporting synthesis and characterization, adsorption and catalytic property study of a new bi-layer open framework $[\text{Cu}(\text{tdc})(\text{bpe})]_n \cdot 2n(\text{H}_2\text{O}) \cdot n(\text{MeOH})$ (compound **1**) [H_2tdc =2,5 thiophenedicarboxylic acid; bpe = 1,2-Bis(4-pyridyl)ethane], for Glaser type coupling reactions.

Results and discussions

Synthetic aspects

Blue colored crystals of compound **1** was prepared by the reaction of Na_2tdc and bpe with $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ in 1:1:1 molar ratio through solvent diffusion technique using a methanol/water (1:1) mixture at room temperature. Following characteristic peaks were identified in FT-IR spectra 3441 cm^{-1} (free O-H), 1623 cm^{-1} (uncoordinate C=O (tdc)), 1566 cm^{-1}

(C=N of bpe) and 1393 cm^{-1} (chelated C-O groups) (Fig. S1). Powder X-ray diffraction (PXRD) experiments were carried out on compound **1**. All major peaks in experimental PXRD of compound **1** match well with simulated PXRD which indicates equitable crystalline phase purity (Fig. S2). TG analysis of compound **1** shows a gradual weight-loss of ~15% (calc. ~14%) at around 50-100 °C, which corresponds to the loss of two guest water molecules and one MeOH molecule (Fig. S3). The dehydrated framework was found to be stable up to 230 °C followed by a sharp weight loss which might be due to the decomposition of the framework. The desolvated phase of compound **1** was obtained by heating the samples for 24h at 110 °C under reduced pressure (Fig. S3). The PXRD data of desolvated compound matches well with the as-synthesized one (Fig. 7), and confirms of the stability desolvated framework. The compound **1** has also been characterized by SEM technique. SEM micrograph showed well block shaped crystals with crystal sizes ranging between approximately 70 and 80 μm (Fig. 1).

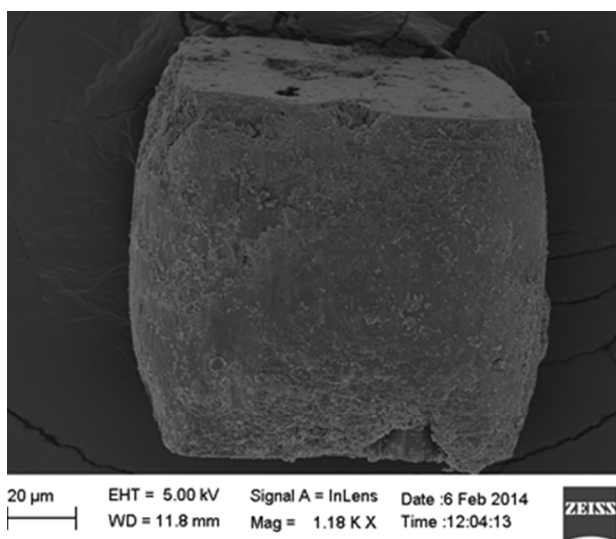


Fig. 1 SEM micrograph of compound **1**.

distance between two Cu(II) centres bridged by tdc ligands are $10.496(1)\text{ \AA}$.

Table 1 Crystallographic data for compound **1**:

CCDC	929621
Formula	$\text{C}_{19}\text{H}_{22}\text{CuN}_2\text{O}_7\text{S}$
weight (g/mol)	486.00
Crystal shape	Block
Color	Blue
Size	$0.42 \times 0.37 \times 0.24$
Crystal system	Triclinic
Space group	<i>P</i> -1
Cell length a (Å)	10.0921(3)
Cell length b (Å)	10.4958(3)
Cell length c (Å)	10.8431(3)
Cell angle alpha (°)	86.403(2)
Cell angle beta (°)	79.041(2)
Cell angle gamma (°)	81.993(2)
Cell volume V (Å ³)	1115.86(6)
Cell formula units Z	2
Temperature (K)	298(2)
λ (Mo K α) (Å)	0.71073
μ (mm ⁻¹)	1.496
Dc (g cm ⁻³)	1.339
crystal_F_000	458
Measured reflections	5772
Unique reflections	3450
R_1 [I > 2 σ (I)] ^a	0.0823
R_w [I > 2 σ (I)] ^b	0.2467

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad ^b R_w = \frac{[\sum \{w(F_o^2 - F_c^2)^2\} / \sum \{w(F_o^2)^2\}]^{1/2}}$$

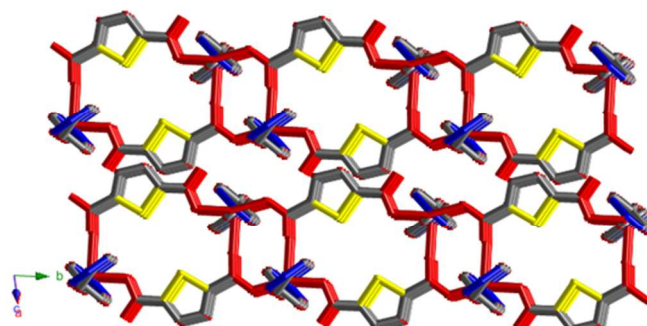


Fig. 2 View along the *b*-axis. Water molecules are omitted for clarity. Colour code: Cu-O (red), Cu-N (blue), C-S (yellow), C-O (red), C-C (gray) and C-N (blue).

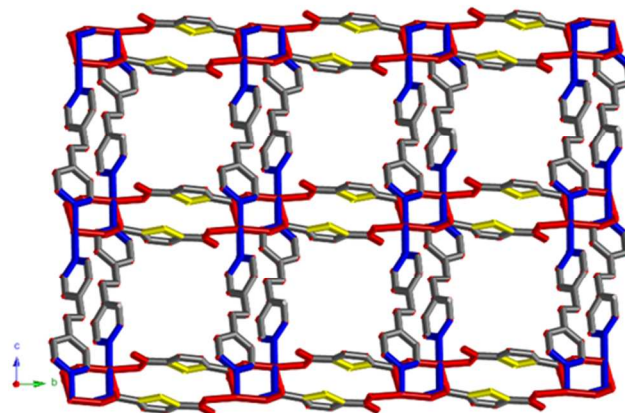


Fig. 3 View along the *bc*-plane. Colour code; same as in Fig.2

Structural description of compound **1**

Single crystal X-ray analysis reveals that the compound **1** crystallizes in triclinic system, with space group *P*-1. The asymmetric unit comprises of one Cu(II) ion, one tdc ligand, one bpe linker and two guest water molecules (Fig. S4). Each Cu(II) centre is penta coordinated by three monodentate carboxylate oxygen atoms from three different tdc ligands and two nitrogen atoms from two different bpe linkers. It was found that around each Cu(II) center the carboxylate oxygen atoms of tdc ligand are in the equatorial positions whereas the nitrogen atoms of the bpe linkers are in the axial positions and overall it results a distorted trigonal bipyramidal geometry [distortion (τ) = 0.266].¹² Each tdc ligands coordinates to three Cu(II) centers in both mono-dentate and bi-dentate fashion (Fig. S5a). The

Similarly each bpe ligand linked to two Cu(II) centres having a separation of 13.335(1) Å. It was also found that, two nearby Cu(II) centres are connected through two bi-dentate carboxylate groups of two different tdc ligands in $\{(\kappa^1)-(\kappa^1-\kappa^1)-\mu_3\text{-TDC}^{2-}\}$ coordination mode¹³ leading to a dinuclear unit (Fig. S5b). These di-nuclear units are connected to their subsequent neighbors through another tdc ligand and generate a 1D chain having small continuous channels (8.41 x 3.77 Å²; distance between Cu...Cu centres and cg...cg distance between tdc ligands respectively) along the *b*-direction (Fig. 2). These 1D chains are further connected by axial bpe linkers and results a 2D pillared-bilayer framework along the *bc*-plane (Fig. 3 and Fig. S6). These 2D pillared-bilayers encompass extended square shaped channels (13.7 x 8.35 Å²) along *bc*-plane, which are occupied by guest solvent molecules. The channel size has been calculated by taking the cg...cg distance between tdc ligands and CH₂...CH₂ separation between bpe ligands (Fig. S10). These water molecules are stabilized by hydrogen bonding interactions (O4...O5 = 2.70(2) Å; O5...O5A = 3.03(3) Å) with uncoordinated carboxylate oxygen atoms of tdc ligand (Fig. S7). Careful analysis reveals that the overall framework originates from a single motif [Cu₂(tdc)₄(bpe)₄]; and can be called as secondary building unit (SBU) (Fig. S8). Each SBU is connected to four neighboring SBUs by tdc, bpe ligands and that leads to formation of a four connected uninodal 2D coordination framework with point Schläfli symbol $\{4^4.6^2\}$ (Fig. S9a). This network is identified by topological type, sq1/Shubnikov tetragonal plane net in the Reticular Chemistry Structure Resource (RCSR) database¹⁴ (Fig. S9b). PLATON analysis revealed that compound **1** exhibits pore accessible void volume of 111.8 Å³ that represent 17.1% per unit cell volume.

Gas Adsorptions Studies

The adsorption experiment for N₂, CO₂ and CH₄ at low temperature were performed which reveals very less uptake for N₂ (kinetic diameter, 3.6 Å) at 77 K. Based on the structural feature of the framework (as calculated from pore size distribution as shown in Fig. S10), such type of behavior was unexpected but could be due to the fact that at low temperature (77 K) N₂ molecules might be strongly interacting with pore aperture and block other molecules to pass through, which results only surface adsorption.^{1h, 1i} However, 1.7 wt% uptake was obtained in case of CH₄ at 195 K and two step sorption isotherm observed in case of CO₂ at 195 K. In step-1 which ranges from 0 to 0.12 bar, compound **1** adsorbs 8.6 wt% of CO₂ whereas at the second step which ranges from 0.15 bar to 1 bar it adsorbs 13.1 wt% (Fig. 4). The adsorption selectivity of compound **1** towards CO₂ and CH₄ over N₂ can be justified by considering the large quadrupole moment (-1.4×10^{-35} C·m)¹⁵ of CO₂ and good polarizability value of CH₄ and both the gases are expected to interact strongly with hydrophilic/polar pores of the framework.¹⁶ The sorption experiments of CO₂ and CH₄ for compound **1** were also performed at 273 K and 298 K. The CO₂ sorption amount attained a value of ~5.6 wt% and ~4.2 wt% at 273 K and 298 K respectively. Interestingly, no uptake was observed for CH₄ at those temperatures (Fig. 5). For better

understanding, we calculated isosteric heat (Q_{st}) of adsorption for CO₂ and CH₄ at 273 K by using Clausius–Clapeyron method¹⁷ as shown in Fig. S11. The adsorption enthalpy for CO₂ at zero loading is approximately to -41.79 k J mol⁻¹ whereas -12.02 kJmol⁻¹ in case of CH₄. Based on this observation we concluded that CO₂ interacts more strongly than CH₄ with the framework due to the existence of a quadrupole moment for the former but not for CH₄. The adsorption selectivity of CO₂ over CH₄ was calculated by using the equation $S_{ij} = K_H(\text{CO}_2)/K_H(j)$ ¹⁸ (Table S1) based on Henry's law. The CO₂/CH₄ separation selectivity attained a value of 32 at 273 K and 28 at 298 K respectively. The selectivity values are closer to the highest values reported for Cu-based MOFs¹⁹ (Table S2) till date.

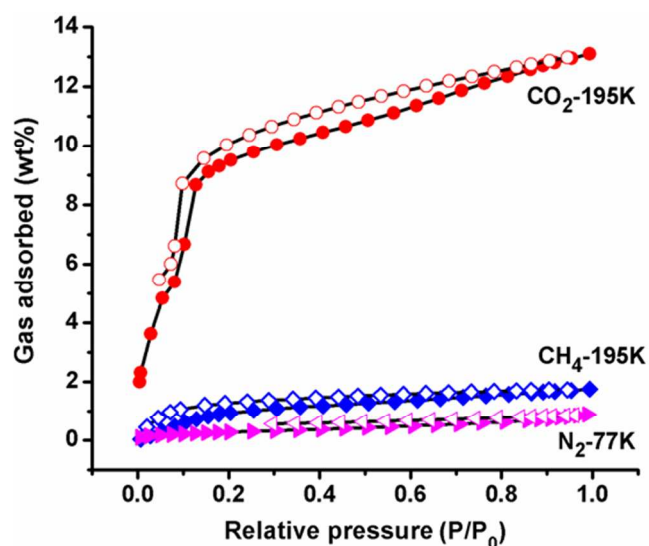


Fig. 4 Gas sorption isotherms at low temperature, N₂ at 77 K (magenta), CH₄ at 195 K (blue) and CO₂ at 195 K (red).

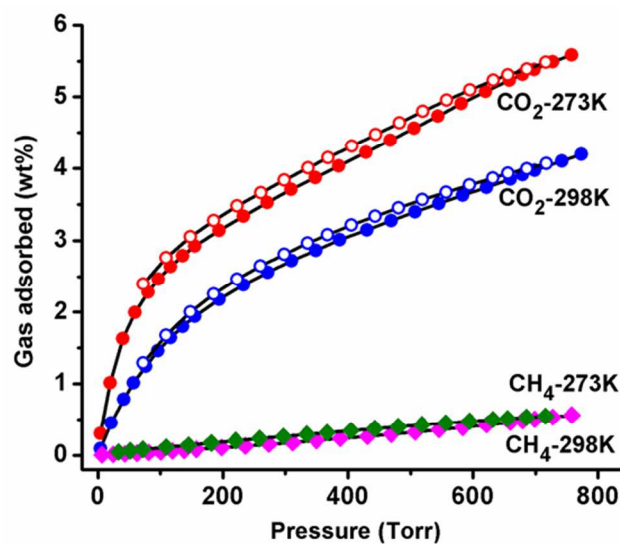


Fig. 5 Gas sorption isotherms at around room temperature, CO₂ at 273 K (red), 298 K (blue) and CH₄ at 273 K (green), 298 K (magenta).

To further investigate the polar nature of the pore surfaces, we carried out vapour sorption studies with protic (H_2O , EtOH) and aprotic solvents (CH_3CN) at 298 K (Fig. 6). The sorption profile of H_2O shows an abrupt jump at $P/P_0 = 0.15$ bar and reaches to a value of 150 mL g^{-1} at $P/P_0 \approx 1.0$ bar and desorption isotherm does not retrace the adsorption profile. This is predictable as the coordinated water molecules are not estimated to go away from the framework at 298 K.

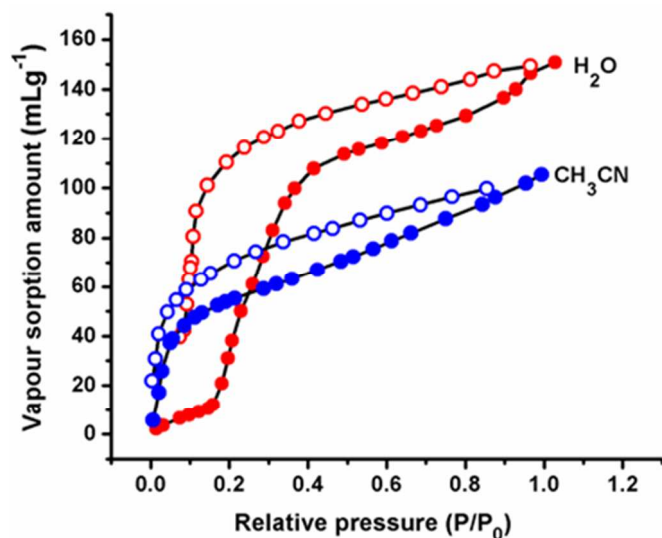


Fig. 6 Vapor sorption isotherms at 298 K, H_2O (red) and CH_3CN (blue)

To follow the detailed structural transformation upon adsorption of H_2O , we took powder XRD patterns by interrupting the measurement at step-1 (compound $\mathbf{1}'$) (Fig. 7 inset). Careful analysis of the resulting PXRD pattern reveals that, the peak at [001], which gives information about the Cu-O(tdc) (Fig. S12) bond lengths was shifted to lower 2θ values ($2\theta = 8.45$ to $2\theta = 7.48$) (Fig. 7). This indicates a severe expansion of the framework during the transformation of compound $\mathbf{1}$ to $\mathbf{1}'$ by gate opening phenomenon²⁰. The sorption

isotherm with EtOH shows a similar profile like CO_2 isotherm with small hysteresis whereas Type-I profile was obtained in case of CH_3CN . The isotherm with EtOH showed two noticeable steps at $P/P_0 = 0.0028$ bar and 0.1 bar with the sorption amount of 102 mL g^{-1} at 1 bar pressure (Fig. S13). The lower gate opening pressure in the case of H_2O in comparison with EtOH and CO_2 is mostly allied with the strong (O-H...O) hydrogen bonding interaction with the free carboxylate oxygen atoms of tdc ligands at the pore surface. The same gate opening pressure observed in case of CO_2 and EtOH because of their large size and weaker hydrogen bonding ability.^{20d} The observed Type-I profile in case of CH_3CN ($\sim 105 \text{ mL g}^{-1}$) could be due to the absence of hydrogen bonding interactions and the adsorption amount can be accounted for filling out the 1D channels by adsorbate molecules.⁵

To check the structural transformation after organic vapour adsorption, the dehydrated samples were exposed to different organic vapours for 4 days and are subjected to PXRD analysis. The PXRD patterns of all the vapour exposed samples of compound $\mathbf{1}$ is almost similar with the PXRD pattern of as synthesized compound which indicates that compound $\mathbf{1}$ restores the original structure after completion of adsorption steps (Fig. S14).

Catalytic property of compound $\mathbf{1}$

It has been reported that, coordinative unsaturated Cu-MOFs are excellent catalyst²¹ for organic reactions. This anticipation encouraged us to further evaluate the catalytic property of compound $\mathbf{1}$ for Glaser type of homocoupling reactions. When a mixture containing phenylacetylene (1 mmol) and K_2CO_3 (2 mmol) in toluene were allowed to stir at 110°C for 6 h under atmosphere in presence of activated compound $\mathbf{1}$ (5 mol%), 82% (based on NMR analysis) of the Glaser products were isolated. It was found that under same reaction conditions only 9% Glaser products were isolated in the absence of compound $\mathbf{1}$.

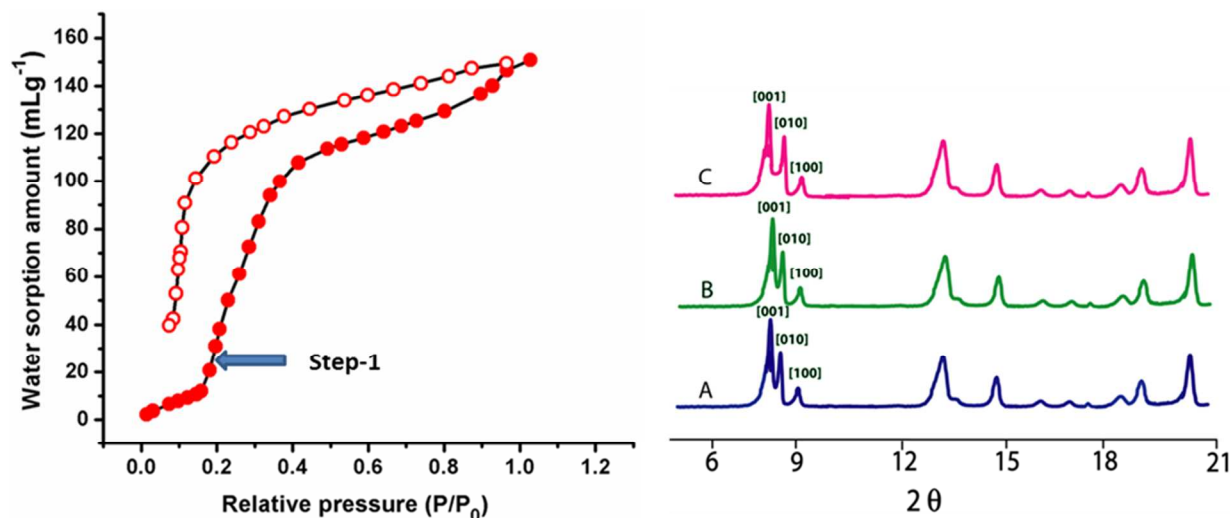
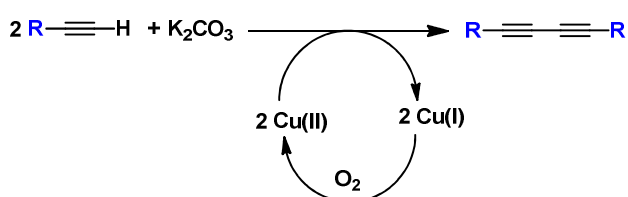


Fig. 7 Water sorption isotherm (left) and related PXRD Patterns (right). (A) As synthesized, (B) after pre-treatment at 110°C for 24h, (C) at step-1.

Recently, Corma et al.²² have used a lamellar MOF [Cu(BDC)] (BDC = benzene dicarboxylate) for same type of reaction and couldn't able to isolate any coupling product after several attempts even for longer reaction time similarly the reported Cu-BTC (HKUST-1)^{11a} MOF contains equal number of Cu(II) sites as compare to compound **1**, its catalytic properties for such Glaser type of coupling reactions were not explored. Hence, it can be concluded that, in both [Cu(BDC)] MOF and Cu-BTC (HKUST-1) MOF, copper centers are stable at +2 oxidation state which makes them inactive for Glaser type of coupling reaction. Although in the present case, compound **1**, contains copper centers in +2 oxidation state, it shows good catalytic activity for Glaser type of coupling reaction. To check whether the Cu(II) existing in the compound **1** played a key role in the catalysis, a few similar reactions were carried out in the presence of Cu(NO₃)₂·2.5H₂O (metal precursor). Surprisingly, we have not seen any substantial change in the yields associated to reactions without catalyst. This observation suggests that presence of electron rich ligands (tdc and bpe) might facilitates the in situ reduction of Cu(II) to Cu(I) state which is responsible for Glaser type coupling reactions. However, all our attempts to detect in situ generated Cu(I) ions during this heterogeneous reaction by EPR as well as UV-Vis spectroscopic analyses failed^{21j}.

Although we couldn't able to trace the in situ generated Cu(I) ions during the reaction, the formation of Glaser type products in presence of compound **1**, suggests that O₂/air probable play a vital role to re-oxidize the in situ formed Cu(I) ions to regenerate compound **1** (Scheme 1). In more precise, during the above Glaser type reaction, the electron rich ligands (tdc and bpe) possibly facilitated the in situ reduction of Cu(II) to Cu(I) ion and after the catalytic reaction the Cu(I) species might be immediately reoxidized in presence of O₂/air to Cu(II) ions²¹ to regenerate compound **1**.



Scheme 1. Possible mechanism for Glaser oxidative coupling reaction.

Even though the role of cuprous ions for this above Glaser type homo-coupling reaction is crucial, the effect of base should not be neglected. The role of base in Glaser type of homo-coupling reaction is here to deprotonate the terminal alkynes. Therefore, the influence of the bases on the terminal alkynes homo-coupling reaction was also investigated. Among the inorganic bases, it was found that K₂CO₃ shows excellent yield over other bases (Table S3).

For a more comprehensive study for the catalytic activity of compound **1** in the above reactions, recycling test with four consecutive runs was performed (Fig. 8). As mentioned before,

the yield of the Glaser product up to 82% is achieved after 6 h. In second runs, no substantial change in the yield was observed after the same reaction time. In third runs, a fall in the yields of the products has been detected (up to ~60%). However in fourth runs a marginal fall in the yields (~40%) was noticed. The decrease in yields of the reaction might be due to the loss in catalytic efficiency of compound **1** after three cycles of reaction.

To ascertain the heterogeneous mechanism of the compound **1**, the MOF was filtered off after the completion of reactions and the PXRD patterns (Fig. S15) and FT-IR bands (Fig. S16) of the recovered catalyst suggest that its structure is well maintained after several cycles of reactions. Leaching is a common problem in heterogeneous catalysis, especially for C-C coupling reactions. The simplest and most effective test for leaching is in situ catalyst filtration and re-addition. Since Cu(I) ions are known to catalyze Glaser type alkyne homo-coupling reaction, any leaching would be easily observed by monitoring the activity of the filtrate. To ensure it, after 1 h of the reaction, compound **1** was filtered while the reaction mixture is still hot and the reaction was allowed to further stir without compound **1** for 5 h at 110 °C. As illustrated in Fig. 9, stirring of the reaction was stopped after 5 h and there after no substantial increase in the yield was observed. Further, compound **1** was added to the reaction mixture after 3h of standing without it. It was found that after addition of compound **1** a sudden increase in the yield of products was noticed. Overall, the stepped reaction profile in Fig. 9C shows that removing the compound **1** from reaction mixture, stops the reaction and addition of filtered compound **1** back to the reaction mixture restarts it. This simple test shows that the copper catalyst under reaction is heterogeneous in nature.

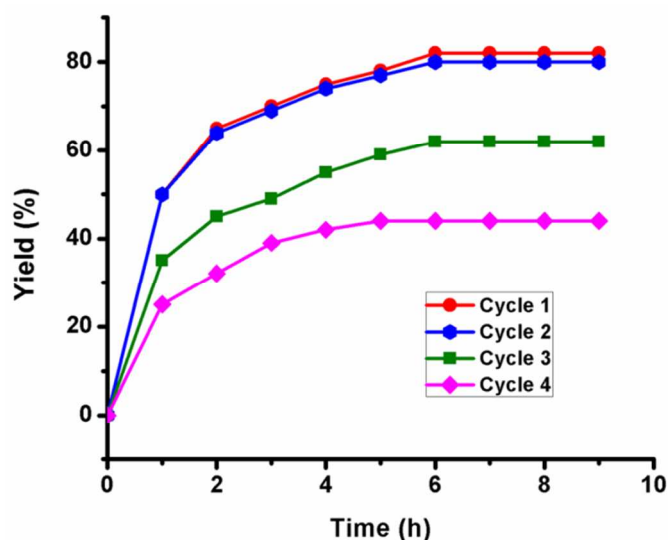
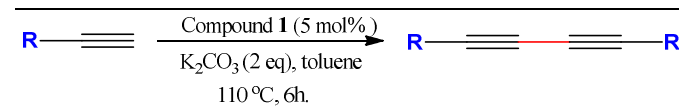


Fig. 8 Kinetic profiles in four consecutive reaction cycles employing compound **1** as catalyst.

Table 2 Glaser type coupling reactions with different alkynes.

S. No.	Substrate (R)	Without compound 1 (%) ^a	With compound 1 (%) ^a
1		9	82
2		8	78
3		10	72
4		7	65
5		8	25
6		6	6
7		6	6
8		9	9

^a Isolated yields from NMR analysis

To explore the catalytic activity of compound 1 to other alkynes, a variety of other aromatic alkynes derivatives are used as substrates. Good conversion and good selectivity to the homo-coupling product has been observed. The results are illustrated in Table 2. It has been found that, the reaction rate and yield depends on the nature of the substrate used. However, in case of 3,4-dimethoxyphenylacetylene (Table 2, entry 5), comparatively low yield was noticed, that might be due to the presence of two bulky methoxy group which restricts the π - π interaction²³ of the substrate with compound 1. Additionally, a few similar reactions were carried out with aliphatic alkynes.

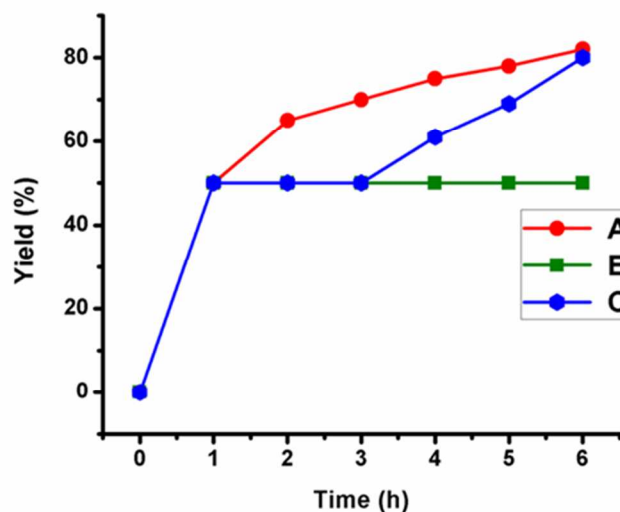


Fig. 9 Leaching test indicated no contribution from homogeneous catalysis of active species (A) in presence of compound 1. (B) catalyst filtration (after 1h) (C) re-addition of compound (after 3h).

Surprisingly; no substantial improvement in the yields was observed compared to reactions without compound 1. This might be due to the absence of extended π -cloud in case of aliphatic alkynes in comparison to aromatic one and in turn causes weak interaction with compound 1. Further, the above observation suggests the lack of catalytic activity of compound 1 in the coupling of aliphatic alkynes.

Conclusion

In conclusion, we have synthesized a new pillared-bilayer 2D Cu(II) MOF which exhibits gas uptake capacities for CO₂ and CH₄ at low temperature and selective adsorption of CO₂ over CH₄ around room temperature, revealing that the current material can be potentially useful in a CO₂ sequestration process. We also have highlighted the differences in adsorption behavior between protic and aprotic solvents. Catalytic property of compound 1 reveals that it is an efficient heterogeneous catalyst for Glaser type homocoupling reactions of aromatic alkynes. Further works upon the catalytic properties of a series of newly synthesized MOFs are under progress.

Experimental section

Materials

All the reagents and solvents for synthesis were purchased from commercial sources and used as supplied without further purification. Cu(NO₃)₂·2.5H₂O, 2,5-thiophenedicarboxylic acid (tdc), 1,2-Bis(4-pyridyl)ethane (bpe) and different alkynes were obtained from the Sigma-Aldrich Chemical Co. India. The elemental analysis was carried out on Elementar Micro vario cube elemental analyzer. FT-IR spectra (4000 - 400 cm⁻¹) was recorded on a KBr pellet with a Perkin Elmer Spectrum BX spectrometer. Powder X-ray diffraction (PXRD) data was collected on a PANalytical EMPYREAN instrument using Cu-K α radiation. For Scanning Electron Microscopy (SEM), The

crystals were dried inside vacuum desiccator for 24h and dried crystals were spread on carbon tape and gold coated for 120 s. The images were taken on Carl Zeiss (Ultraplus) FE-SEM used at 5 kV.

Synthesis of compound 1 $\{[\text{Cu}(\text{tdc})(\text{bpe})\cdot 2(\text{H}_2\text{O})\cdot (\text{MeOH})]_n\}$. An aqueous solution of (10 mL) Na_2tdc of (0.1 mmol, 21.6 mg) was mixed with methanol solution (10 mL) of bpe (0.1 mmol, 18.4 mg) and the resulting solution was stirred for 1h to mix well. $\text{Cu}(\text{NO}_3)_2\cdot 2.5\text{H}_2\text{O}$ (0.1 mmol, 24.1 mg) was dissolved in 10 mL of water in a separate beaker. 2 mL of the above mixed ligand solution was slowly and carefully layered above 2 mL of metal solution in a narrow glass tube using 2 mL of buffer (1:1 H_2O and MeOH) solution. Dark blue colored, block shaped single crystals (compound **1**) were obtained from the junction of the layer after 5 days. The crystals were separated and washed with MeOH and air-dried (Yield 70%). The bulk amount of the compound **1** was prepared by the direct mixing of the reagents in methanol/water mixed solution with stirring for 24h. **Elemental analysis:** Anal. Calcd.(%). C, 46.99; N, 5.76; S, 6.60; H, 4.56; Found (%): C, 46.15; N, 5.12; S, 6.5; H, 4.01; FT-IR(KBr pellet, cm^{-1}) 3441 (b), 1623 (s), 1566 (s), 1393 (s), 1221 (s), 1071 (b), 839 (w), 783 (w).

Activation of compound 1. As synthesized compound **1** (by using the above mentioned method) was washed several times with H_2O and the resulting powder were evacuated for 24h at 383 K under 10^{-2}KPa continuous vacuum using BelPrepvac II and purged with N_2 on cooling.

General procedure for Glaser type homo coupling reactions. Aromatic alkynes (1 mmol) and K_2CO_3 (2 mmol) were taken in 4 mL toluene. To that 20 mg (0.05 mmol) of activated compound **1** was added. The final mixture was stirred at 110 °C for 6h and the completion of the reaction was monitored by TLC (eluent = hexane). The reaction mixture was cooled to room temperature, filtered to remove compound **1**, concentrated under vacuum. Yields of catalysed and non-catalysed reactions were calculated based NMR analysis. Finally, the products were purified by preparative TLC using silica gel as stationary phase and hexane was used as eluent. The recovered catalyst was washed with diethyl ether, dried, and reused without further purification. Moreover, the recovered catalysts were characterized by the powder X-ray diffraction (PXRD) analysis, elementary analysis and FT-IR spectroscopic studies which show identical results to those of the fresh samples. **Elemental analysis:** Anal. Calcd.(%). C, 46.99; N, 5.76; S, 6.60; H, 4.56; Found (%): C, 46.15; N, 5.12; S, 6.5; H, 4.01; FT-IR (KBr pellet, cm^{-1}) 3441 (b), 1623 (s), 1566 (s), 1393 (s), 1221 (s), 1071 (b), 839 (w), 783 (w).

Single crystal X-ray diffraction

Single crystal data for compound **1** was collected on a Bruker APEX II diffractometer equipped with a graphite monochromator and Mo- $\text{K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$, 296 K) radiation. Data collection was performed using φ and ω scan. Non-hydrogen atoms are located from the difference Fourier maps

were refined anisotropically by full-matrix least-squares on F^2 , using SHELXS-97.²⁴ All hydrogen atoms were included in the calculated positions and refined isotropically using a riding model. Determinations of the crystal system, orientation matrix, and cell dimensions were performed according to the established procedures. Lorentz polarization and multi-scan absorption correction were applied. All calculations were carried out using SHELXL 97,²⁵ PLATON 99,²⁶ and WinGXsystemVer-1.64.²⁷ During the final stages of refinement, some Q peaks having high electron densities were found, which probably correspond to highly disordered solvent molecules and are removed by SQUEEZE²⁷ program. From the TG analysis we speculate that one non-coordinated methanol molecules is present as the reaction was performed in methanol medium and hence these are included in the molecular formula. Data collection and structure refinement parameters and crystallographic data in Table 1 and selected bond lengths and bond angles for compound **1** are given Table S4.

Sorption measurements.

Gas adsorption measurements were performed by using BelSorp-max (BEL Japan) automatic volumetric adsorption instrument. All the gases used were of ultra-pure research grade (99.999%). HPLC grade solvents were used for vapor adsorption studies. Before every measurement sample was pretreated for 24h at 383K under 10^{-2}KPa continuous vacuum using BelPrepvac II and purged with N_2 on cooling.

NMR measurements

^1H and ^{13}C NMR spectra were recorded on 400 and 500 MHz spectrometers with ^{13}C operating frequencies of 100 and 125 MHz, respectively. Chemical shifts (δ) are reported in ppm relative to the residual solvent (CDCl_3) signal ($\delta = 7.26$ for ^1H NMR and $\delta = 77.0$ for ^{13}C NMR). Data for ^1H NMR spectra are reported as follows: chemical shift (multiplicity, coupling constants, number of hydrogen). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). High Resolution Mass Spectrometry (HRMS) data were recorded on MicrOTOF-Q-II mass spectrometer using methanol as solvent.

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ARTICLE

Copper based metal organic framework with selective, hysteretic sorption and heterogeneous catalyst for Glaser type homo coupling reactions.

