Design and *In situ* Synthesis of Cu-Based Porous Double Chain Magnetic Framework

(Supporting Information: 45 pages including this page)

Chandan Dey, ^a Raja Das, ^a Binoy Krishna Saha, ^b Pankaj Poddar^{*}, ^a Rahul Banerjee^{*a} ^a Physical/Materials Chemistry Division, National Chemical Laboratory, Dr. Homi Bhabha Road, Pune-411008, India.

^b Department of Chemical, Pondicherry University, R. V. Nagar, Kalapet, Pondicherry-605014.
 E-mail: <u>p.poddar@ncl.res.in</u> Fax: + 91-20-25902636; Tel: + 91-20-25902580
 E-mail: <u>r.banerjee@ncl.res.in</u> Fax: + 91-20-25902636; Tel: + 91-20-25902535

Section S1.	Detail of Synthetic and Characterization Procedure of Cu	-DCM2-4
Section S2.	Design of Cu-DCM Synthesis	5-6
Section S3.	Single Crystal X-ray Diffraction Data Collection, Structure Solution and Refinement procedures	7-15
Section S4.	TGA Data and the Thermal Stability of Cu-DCM	16-17
Section S5.	Adsorption Study of Cu-DCM	18-21
Section S6.	Magnetic Property of As-synthesized, Evacuated and Re-solvated Cu-DCM	22-40
Section S7.	IR Spectroscopy	41
Section S8.	Investigation of Microstructure and Topography of As-synthesized, Evacuated Cu-DCM	42-45

Section S1. Detail of Synthetic and Characterization Procedure of Cu-DCM

Materials and general methods: All reagents were commercially available and used as received. Powder X-ray diffraction (PXRD) patterns were recorded on a Phillips PANlytical diffractometer for Cu K α radiation ($\lambda = 1.5406$ Å), with a scan speed of 2° min⁻¹ and a step size of 0.02° in 20. Thermogravimetric (TGA) experiments were carried out in the temperature range of 25–700 °C on a SDT Q600 TG-DTA analyzer under N₂ atmosphere at a heating rate of 10 °C min⁻¹. All low pressure gas adsorption experiments (up to 1 bar) were performed on a Quantachrome Quadrasorb automatic volumetric instrument. All the magnetic measurements were done using a Physical Property Measurement System (PPMS) from Quantum Design Inc. San Diego, USA equipped with a 7 Tesla superconducting magnet and a vibrating sample magnetometer. The magnetic signal from the sample holder was negligible to affect our data accuracy. These measurements were taken at 500 Oe field in field cooled (FC) and zero field cooled (ZFC) modes with heating/cooling rate of 2 K per minute. Magnetizations vs. field loops were taken in a field sweep from -50 kOe to +50 kOe at a rate of 75 Oe/sec.

In Situ Hydrothermal Synthesis: Current studies prove that hydrothermal synthesis under high pressure and moderate temperature (~150°C) is an effective method for *in situ* ligand generation.¹ *In situ* ligand preparation not only provides an easy route for synthesis of organic links which are not readily accessible but also represents a possible new crystal engineering ² approach for novel MOF synthesis. *In situ* ligand synthesis is advantageous since it minimizes the steps, time of the reaction and sometimes minimizes the difficulties of using hazardous chemicals, like azide, cyano etc.³ However the example of in *situ* ligand synthesis via oxidation and subsequent MOF formation is very rare.⁴

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Synthesis of $Cu_2(Phen-COOH)_2(BTC).3H_2O$: $Cu_2(Phen-COOH)_2(BTC).3H_2O$ was prepared using mixture of $Cu(NO_3)_2.xH_2O$ (1 mmol), neocuproine (0.4 mmol), Na₂MoO₄ (2 mmol) and 1,3,5-BTC (0.9 mmol) in 18ml deionised water in hydrothermal condition at 170°C for 4 days. We tried the reaction in the pH range of 1.45 to 3.25. However, we could able to isolate the product in 2.90-3.05 pH range. The quality of the crystal suitable for X-ray diffraction was obtained when pH was equal to 2.95. The possible reason for in situ oxidation could be the presence of MoO_4^{2-} ion which in presence of Cu^{2+} and HCl acts as catalyst for the oxidation of two methyl groups of neocuproine.

FT-IR: (KBr 4000-600 cm⁻¹): 3212 (m br), 1662 (s), 1564 (s), 1435 (s), 1363 (s), 1290 (s), 1103 (s), 908 (m), 848 (m), 753 (m), 721 (s), cm⁻¹.

Element Analysis: Found (%) C= 48.20, H= 2.81, N= 6.70; Calc. (%) C= 48.80, H= 2.67, N= 6.50.



Section S2. Design of Cu-DCM synthesis

Figure S1: a) Expected Product where neocuproine after *in situ* oxidation becomes 2,9-dicarboxy phenanthroline. This link acts as bulky terminal ligand to prevent the growth of the structure in two or three dimensions. Since all the coordinating functionalities of this link points inwards. BTC provides an opportunity to connect three units. b) But during the process one of the carboxylic acid of oxidized neocuproine got decarboxylated to 2-carboxy phenanthroline, BTC connects two units to make double chain structure. The third carboxylate of BTC remain free inside the structure



Figure S2. Comparison of the experimental PXRD pattern of as-synthesized Cu-DCM (top) with the one simulated from its single crystal structure (bottom). One extra pick in experimental PXRD data compare to simulated data (at $2\theta = 9^{\circ}$) could be attributed as some phase change in the bulk material during grinding.

Section S3. Single crystal X-ray diffraction data collection, structure solution and refinement procedures

General Data Collection and Refinement Procedures:

Single crystal data were collected on Bruker SMART APEX three circle diffractometer equipped with a CCD area detector and operated at 1500 W power (50 kV, 30 mA) to generate Mo K_{α} radiation (λ =0.71073 Å). The incident X-ray beam was focused and monochromated using Bruker Excalibur Gobel mirror optics. The Crystals of Cu-DCM reported in the paper was mounted on nylon CryoLoop (Hampton Research) with Paraton-N (Hampton Research).

Initial scans of each specimen were performed to obtain preliminary unit cell parameters and to assess the mosaicity (breadth of spots between frames) of the crystal to select the required frame width for data collection. In every case frame widths of 0.5° were judged to be appropriate and full hemispheres of data were collected using the *Bruker SMART*¹ software suite. Following data collection, reflections were sampled from all regions of the Ewald sphere to redetermine unit cell parameters for data integration and to check for rotational twinning using *CELL_NOW*². In no data collected frames the resolution of the dataset was judged. Data were integrated using Bruker *SAINT*³ software with a narrow frame algorithm and a 0.400 fractional lower limit of average intensity. Data were subsequently corrected for absorption by the program *SADABS*⁴. The space group determinations and tests for merohedral twinning were carried out using *XPREP*³. In these cases, the highest possible space group was chosen.

Structures were solved by direct methods and refined using the *SHELXTL* 97⁵ software suite. Atoms were located from iterative examination of difference F-maps following least squares refinements of the earlier models. Final model was refined anisotropically (if the number of data permitted) until full convergence was achieved. Hydrogen atoms were placed in calculated positions (C-H = 0.93 Å) and included as riding atoms with isotropic displacement parameters 1.2-1.5 times U_{eq} of the attached C

atoms. In some cases modeling of electron density within the voids of the frameworks did not lead to identification of recognizable solvent molecules in these structures, probably due to the highly disordered contents of the large pores in the frameworks. Highly porous crystals that contain solvent-filled pores often yield raw data where observed strong (high intensity) scattering becomes limited to ~1.0 Å at best, with higher resolution data present at low intensity. A common strategy for improving X-ray data, increasing the exposure time of the crystal to X-rays, did not improve the quality of the high angle data in these cases, as the intensity from low angle data saturated the detector and minimal improvement in the high angle data was achieved. Additionally, diffuse scattering from the highly disordered solvent within the void spaces of the framework and from the capillary to mount the crystal contributes to the background and the 'washing out' of the weaker data. The only optimal crystals suitable for analysis were generally small and weakly diffracting. Unfortunately, larger crystals, which would usually improve the quality of the data, presented a lowered degree of crystallinity and attempts to optimize the crystal growing conditions for large high-quality specimens have not yet been fruitful. Single Crystal X-ray Diffraction data for Cu-DCM was collected at 293(2) K. The foremost errors in all the models are thought to lie in the assignment of guest electron density. Structures were examined using the ADDSYM subroutine of PLATON⁷ to assure that no additional symmetry could be applied to the models. All ellipsoids in ORTEP diagrams are displayed at the 50% probability level unless noted otherwise. For these structures we noted that elevated R-values are commonly encountered in MOF crystallography for the reasons expressed above by us and by other research groups.⁸⁻¹⁷ Table S1 contains crystallographic data for Cu-DCM.

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Experimental and Refinement Details for Cu-DCM

A green needle-like crystal $(0.12 \times 0.07 \times 0.03 \text{ mm}^3)$ of Cu-DCM was placed in a 0.7 mm diameter nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). The loop was mounted on a SMART APEX three circle diffractometer equipped with a CCD area detector and operated at 1500 W power (50 kV, 30 mA) to generate Mo K α radiation ($\lambda = 0.71073$ Å). A total of 8914 reflections were collected of which 3947 were unique and 1815 of these were greater than $2\sigma(I)$. The range of θ was from 2.72 to 27.79. Analysis of the data showed negligible decay during collection. The structure was solved in the triclinic *Pnma* space group, with Z = 4, using direct methods. All non-hydrogen atoms were refined anisotropically with hydrogen atoms generated as spheres riding the coordinates of their parent atoms. An asymmetric unit of Cu-DCM contains one Cu(II) atom, one 2-carboxy phenanthroline, half BTC and three free water molecules. Due to the high data to noise ratio the attempts made to model the guests (solvent molecules) lead to identification of guest entities in this structure. Since the solvent is neither bonded to the framework nor tightly packed into the voids, solvent disorder can be expected for these structures. It should be noted that the precision of this model is low; however, the structure is reported to display the framework for Cu-DCM as isolated in the crystalline form. This challenge, which is typical of porous crystals, lies in the raw data where observed strong (high intensity) scattering becomes limited to ~ 1.0 Å at best (completeness 98.3%), with higher resolution data present but weak (low intensity). As is a common strategy for improving X-ray data, increasing the exposure time of the crystal to X-rays did not improve the quality of the high angle data in these cases, as the intensity from low angle data saturated the detector and minimal improvement in the high angle data was achieved. Additionally, diffuse scattering from the highly disordered solvent in the void spaces within the crystal and from the capillary used to mount the crystal contributes to the background noise and the 'washing out' of high angle data. The only optimal crystals suitable for analysis were generally small and weakly diffracting, and unfortunately, larger crystals, which would usually improve the quality of the data, presented a lowered degree of crystallinity and attempts to optimize

the crystal growing conditions for large high-quality specimens has not yet been fruitful. Other supporting characterization data (*vide infra* Materials and Methods) are consistent with the crystal structure. Final full matrix least-squares refinement on F^2 converged to $R_1 = 0.0413$ ($F > 2\sigma F$)) and $wR_2 = 0.1231$ (all data) with GOF = 1.069. Crystallographic data (excluding structure factors) for the structures are reported in this paper have been deposited with the CCDC as deposition No. CCDC 818302. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 IEZ, U.K. [fax: b 44 (1223) 336 033; e-mail: <u>deposit@ccdc.cam.ac.uk</u>].

Empirical formula	C35 H23 Cu2 N4O15			
Formula weight	866.67			
Temperature	293(2) K			
Wavelength	0.71073 Å			
Crystal system	Orthorhombic			
Space group	Pnma			
	$a = 7.1889(10) \text{ Å} \ \alpha = 90^{\circ}$			
Unit cell dimensions	$b = 24.444(3)$ Å $\beta = 90^{\circ}$			
	$c = 18.818(2)$ Å $\gamma = 90^{\circ}$			
Volume	3306.7(7)			
Z	4			
Density (calculated)	1.729			
Absorption coefficient	1.372			
F(000)	1732			
Crystal size	$0.12 \times 0.07 \times 0.03 \text{ mm}^3$			
Theta range for data collection	2.72 - 27.79			
Index ranges	$-9 <= h <= 8, \ -32 <= k <= 18, \ -25 <= l <= 13$			
Reflections collected	8914			
Independent reflections	3947			
Completeness to theta = 25.00°	98.3 %			
Absorption correction	Semi-empirical from equivalents			
Refinement method	Full-matrix least-squares on F ²			
Data / restraints / parameters	8914 / 0/ 259			
Goodness-of-fit on F ²	0.843			
Final R indices [I>2sigma(I)]	$R_1 = 0.0554, wR_2 = 0.1026$			
R indices (all data)	$R_1 = 0.1304, wR_2 = 0.1151$			
Largest diff. peak and hole	0.088 and -0.598 e.Å ⁻³			

Table S1. Crystal data and structure refinement for Cu-DCM



Figure S3. ORTEP drawing of the asymmetric unit of Cu-DCM.



Single crystal structures of Cu-DCM

Figure S4. Packing diagram of Cu-DCM showing the arrangement of 1-D ladders in bc-plane, Hydrogen atoms, solvent molecules are omitted for clarity. The distance between two closest pores through crystallographic *b-axis* is 18.82 Å and through the diagonal of the *bc-plane* is 15.56 Å. Color code: Cu (green), N (blue), O (red), C (black).



Figure S5. Orientation of four double chain ladders in Cu-DCM structure. The green balls are copper atoms. The *intra* and *inter* chain 'Cu-Cu' distances in one Cu-DCM unit are 3.99 Å and 8.39 Å respectively.



Figure S6. Space-Fill model of four interdigitated double chains in Cu-DCM. Four different Cu-DCM units are represented by four different colors. The 'cyan' color balls inside the Cu-DCM are copper atoms.

Section S4. Thermal gravimetric analysis (TGA) data and the thermal stability of Cu-DCM



Figure S7. Thermal stability and the thermal gravimetric analysis (TGA) data of Cu-DCM.



Figure S8. Comparison of the PXRD patterns of as-synthesized Cu-DCM (Cu-DCM-EXPT), evacuated Cu-DCM (Cu-DCM-Eva) and re-solvated Cu-DCM (Cu-DCM-RSol) with respected to simulated PXRD pattern (Cu-DCM-RSol) obtained from single crystal X-ray data. The evacuated sample is crystalline but the structure of different

Section S5. Adsorption Study of Cu-DCM

 N_2 , H_2 , and CO_2 Adsorption Measurements: Hydrogen adsorption-desorption experiments were conducted at 77K using Quantachrome Quadrasorb automatic volumetric instrument. Ultrapure H_2 (99.95%) was purified further by using calcium aluminosilicate adsorbents to remove trace amounts of water and other impurities before introduction into the system. For measurements at 77 K, a standard low-temperature liquid nitrogen Dewar vessel was used. CO_2 adsorption-desorption measurements were done at room temperature (298 K). To check the porosity of Cu-1D MOF, it was exchanged with anhydrous dichloromethane in 3 hours interval for 2 days. Before gas adsorption measurements, the sample was activated at 30 °C (for 12 h) under ultrahigh vacuum (10⁻⁸ mbar) overnight. About 75 mg of samples were loaded for gas adsorption, and the weight of each sample was recorded before and after out gassing to confirm complete removal of all guest molecules.



Figure S9. Hydrogen absorption isotherms of Cu-DCM at 77K. Absorption and desorption is completely reversible in nature. The filled and open shapes represent adsorption and desorption, respectively.



Figure S10. Nitrogen absorption isotherms (Type-I) of Cu-DCM at 77K. The filled and open shapes represent adsorption and desorption, respectively.



Figure S11. CO_2 absorption data of Cu-DCM at 298K, The filled and open shapes represent adsorption and desorption, respectively. P/P₀, relative pressure at the saturation vapour pressure of the adsorbate gas.

Section S6. Magnetic Property of As-synthesized, Evacuated and Re-solvated Cu-

DCM

We anticipated that in contrast to SCMs, the interplay of competing *intra* and *inter* chain magnetic interactions within a DCM framework might present more complex, interesting, tunable behavior at low temperature. Indeed, we observed a unique and interesting magnetic behavior where below the paramagnetic region Cu-DCM behaves quite similar to conventional SCMs down to certain temperature.

To investigate the nature of the 3D magnetic ordering in Cu-DCM and to probe the field dependence of the magnetic susceptibility, we measured ZFC and FC χ at different applied fields. It is observed that the peak position in ZFC does not change appreciably beyond an applied field of 1000 Oe but the peak shows significant broadening along with the strong bifurcation of ZFC-FC curves, showing irreversibility of ZFC and FC magnetization curves. The bifurcation temperature becomes weaker with increasing field strength. At 10 kOe field, the complete disappearance of bifurcation of ZFC-FC curves and disappearance of the onset of ferromagnetic transition around 14 K and inflection point around 8 K (which is seen for 500, 1000 Oe data) indicates that a sufficiently higher field (1T) can overcome both intra and inter chain magnetic interactions as at this field the Zeeman energy will be higher than uniaxial anisotropy energy therefore increasing number of spins will orient in the field direction with decreasing temperature. Below 15 K, the FC magnetization curve shows a gradual increase and changes its slope further at 8 K and shows no saturation effect till the lowest measured temperature. Similar to FC curve, the ZFC magnetization also shows upright behavior, till it reaches a maximum at 12 K, then decreases beyond 8 K which is followed by an increase till 3 K. The maxima at 12 K in the ZFC- χ is signature of long-range antiferromagnetic ordering induced by π - π interaction of two parallel '...- μ_2 -OCO-Cu(II)- μ_2 -OCO-...'chains within a double chain.¹ This type of ZFC-FC divergence has been observed in few cases and one such example being $[Ni(\mu-N_3)(bmdt)(N_3)]_n(DMF)_n$, where ZFC- χ reaches a peak at 14 K and diverges out from FC- χ at 16 K but the ZFC- χ does not show any upright behavior at low temperature.²

To further investigate the *intra-* and *inter*-chain magnetic interactions in various temperature regions, we performed isothermal magnetization experiment at different temperatures around which magnetic transition was observed in magnetic susceptibility study. At 12 K the magnetization starts showing non linear behavior due to the onset of ferromagnetic coupling. On the other hand at 15 K the magnetization shows complete linear behavior. At 3 K the magnetization shows strong non-linearity however the magnetization does not saturate up to 5 T for all the measured temperatures. The value of coercive field (H_C) at 12 K is 60 Oe which increases up to 422 Oe at 8 K, then again decreases to 296 Oe at 3 K which is consistent with the features shown by χ -T curves. The decrease in the coercivity below 8 K suggests the reduction in the uniaxial effective anisotropy. The higher value of H_C at 8 K shows the enhanced ferromagnetic ordering around the transition temperature which was also observed in temperature dependent magnetization as high μ_{eff} value. The remnant magnetization (H_r) decreases continuously from 105 emu mol⁻¹ at 3 K to 8 emu mol⁻¹ at 12 K.

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Figure S12: The temperature dependence of the χT for Cu-DCM at 500 Oe applied field. The χT value for two Cu (II) of Cu-DCM at 300 K is 1.08 emu K mol⁻¹ Oe⁻¹. Upon cooling, the χT (ZFC) value remains almost constant down to ~ 120 K, followed by a gradual decrease till ~ 40 K. Below 40 K, the χT (ZFC) value falls with an increased rate down to 15 K, again increases with a peak at 12 K in χ T (ZFC) value below which it falls rapidly till 8 K and then again rises till temperature of 3 K. The rapid increase of χT (ZFC) below 14 K shows the signature of the onset of ferromagnetic exchange interactions between the closest Cu (II) atoms within a chain, [Cu(II)-Cu(II) distance 3.99 Å].^[18] The peak at 12 K indicates occurrence of antiferromagnetic transition due to the *inter* chain magnetic interaction. The rise below 8 K indicates the second order phase transition to a totally magnetically ordered state. The reason for this ferromagnetic behavior is due to the parallel and stacked orientation of two ' $\dots -\mu_2$ -OCO-Cu(II)- μ_2 -OCO- \dots 'chains in Cu-DCM [with Cu-Cu distance of 8.39Å]. However, below 8 K, due to the increasing influence of *inter*-chain interactions within a DCM, magnetic behavior shows a modified-SCM behavior. However, upon cooling, the γT (FC) value remains almost constant down to ~ 120 K, followed by a gradual decrease till ~ 40 K. Below 40 K, the γ T value falls rapidly with a minima at 15 K, again increases with a peak at 8 K in χ T value below which it falls rapidly till a temperature of 3 Κ.

SL	Formula	Structure	Interaction	χT	Journal
NO				at 300 K	
1	$[Cu_{4}(OH)_{2}\{(py)C(CN)NO\}_{2}(O_{2}CPh)_{4}]_{2n}$ $\cdot n[Cu_{4}(OH)_{2}\{(py)C(CN)NO\}_{2}(O_{2}CPh)_{4}]$ $(U4)_{2}(OH)_{$	Chain	Anti- ferromagnetic	0.08 emu K mol ⁻¹	Inorg. Chem., 2011, 50 , 2468
2	$\{[Cu(4-imidazole-1-yl-benzoate)_2]\}_n$	2D- Structure	No interaction	0.39 emu K mol ⁻¹	New J. Chem., 2010, 34, 2502
3	Cu ₂ (PTMMC) ₂ (O ₂ CH ₃) ₂ (H ₂ O) ₂ PTMMC=Perchlorinated monocarboxylic triphenylmethyl radical	Complex	Anti- ferromagnetic	0.225 emu K mol ⁻¹	Chem.Comm 2002, 2958
4	Cu(L)(N ₃)(H ₂ O) _{0.5}] _n L=Isonicotinate N-oxide	Chain	ferromagnetic	0.64 emu K mol ⁻¹	Inorg. Chem., 2006, 45, 246694
5	Cu(L)(N ₃)(H ₂ O) _{0.5]n} L=Nicotinate N-oxide	Chain	ferromagnetic	0.57 emu K mol ⁻¹	Inorg. Chem., 2006, 45, 246694
6	Cu-DCM	Ladder	ferromagnetic	0.54 emu K mol ⁻¹	Current Paper

Table S2: Structural and magnetic aspects of Cu-carboxylate based MOFs



Figure S13: Temperature dependence of the effective magnetic moment μ_{eff} for Cu-DCM at 500 Oe. At 300 K, μ_{eff} values were calculated as 2.95 μ_B for Cu-DCM, which is appreciably lower than the theoretical value of 3.46 μ_B for two magnetically isolated Cu (II) atoms. On cooling the μ_{eff} (FC) values gradually decrease to a minimum of 2.84 μ_B at 14 K, then rise to maxima of 3.94 μ_B at 8 K and after that it decreases till a temperature of 2 K. However, the μ_{eff} (ZFC) value remains almost constant down to ~ 120 K, followed by a gradual decrease down to 14 K, then increases with a peak at 12 K in μ_{eff} (ZFC) value below which it falls rapidly till 8 K and then again rises till temperature of 3 K.



Figure S14: MH loops taken at temperatures 3, 8, 10, 12 and 15 K for Cu-DCM. Below 12 K the magnetization starts showing non linear behavior due to the onset of ferromagnetic coupling. At 3 K the magnetization shows strong non-linearity however the magnetization does not saturate up to 5 T for all the measured temperatures.



Figure S15: Initial magnetization of the MH curves at 3, 8, 10, 12 and 15 K. Below 12 K the magnetization starts showing non linear behavior. At 3 K the magnetization shows strong non-linearity.



Figure S16: Low field region isothermal magnetization plots taken at temperatures 3, 8, 10, 12 and 15 K for Cu-DCM. The value of coercive field (H_C) at 12 K is 60 Oe which increases up to 422 Oe at 8 K, then again decreases to 296 Oe at 3 K.



Figure S17: Inverse susceptibility $1/\chi$ with straight line behavior above 50 K. The $\chi^{-1}T$ plot above 50 K follows the Curie-Weiss law with C = 0.91 emu K mol⁻¹ Oe⁻¹, θ = 1.5 K. Small positive θ value suggests a weak ferromagnetic exchange among the two Cu(II) ions, which may be due to the short Cu(II)-Cu(II) distance in the chain.



Figure S18: The temperature dependence of the magnetic susceptibility χ (left axis), the χT (right axis) for Cu-DCM. ZFC-FC shows interesting bifurcation below 12 K, showing irreversibility of ZFC and FC magnetization. Below 15 K, the FC magnetization curve shows a gradual increase and changes its slope further at 8 K and shows no saturation effect till the lowest measured temperature. Like FC, ZFC magnetization also shows upright behavior, till it reaches a maximum at 12 K, then decreases beyond 8 K and then again increases till 3 K. The maxima at 12 K in the ZFC can be due to long-range magnetic ordering induced by π - π interaction of two parallel '...- μ_2 -OCO–Cu(II)– μ_2 -OCO–...'chains within a double chain.



Figure S19: The temperature dependence of the magnetic susceptibility χ for Cu-DCM at different applied fields. It is observed that the peak position in ZFC does not change appreciably up to an applied field of 1000 Oe but the peak shows significant broadening along-with the strong bifurcation of ZFC-FC curves, showing irreversibility of ZFC and FC magnetization curves. The bifurcation temperature becomes weaker with increasing field strength. At 10 kOe field, the complete disappearance of bifurcation of ZFC-FC curves and disappearance of the onset of ferromagnetic transition around 14 K and inflection point around 8 K (which is seen for 500, 1000 Oe data) indicates that a sufficiently higher field (1T) can overcome both *intra* and *inter* chain magnetic interactions as at this field the Zeeman energy will be higher than uniaxial anisotropy energy therefore increasing number of spins will orient in the field direction with decreasing temperature.



Figure S20: The temperature dependence of the magnetic susceptibility χ for Cu-DCM, Cu-DCM-Eva and Cu-DCM-RSol. However, the magnetic study of as-synthesized, evacuated and resolvated Cu-DCM shows that the magnetic behavior of these three phases remains largely unchanged with a little difference at low temperatures. This indicates that even the removal of guest molecule does not affect the *intra* and *inter chain* magnetic coupling. Moreover, these results also present indication of absence of any magnetic cross talking (dipolar or exchange) outside these isolated double chain magnets in 3D and the magnetic behavior seen by us in this study is purely from individual Cu-DCM chain.



Figure S21: Low field region isothermal magnetization plots of Cu-DCM, Cu-DCM-Eva and Cu-DCM-RSol at 3K. The behavior of the isothermal magnetization plots remains almost same. There is a small increase in the value of coercive field in evacuated and resolvated samples. This increase in coercivity value in evacuated and resolvated samples is due to the increase in defects sites in the samples.

Note: Zeng *et al* (*Inorg. Chem.* 2010, *49*, 6436) showed in Co (II) based compound $[Co_3(pybz)_2(pico)_2]_n$ the ferromagnetic interaction between Co (II) ions is transported by μ_2 -hydroxy and/ or μ_2 -carboxylate oxygen bridges. In this compound the Co (II) ions are not connected to each other by oxygen atom, whereas in our system the Cu (II) ions are not connected via same oxygen atom. So this type of interaction is not possible in our system. Liu *et al* (*Adv. Mater.* 2006, *18*, 2852) showed that *EE* azide bridges is responsible for antiferromagnetic interaction and the tilting of the coordination octahedral of Ni (II) resulting in a lack of an inversion center between the *EE* azide bridged Ni (II) ions giving rise to spin-canted weak ferromagnetism (this interaction was spin glassy in nature). In our system as there is particular stacking (intertwining) of Cu (II) ions in the double chains of DCM. So as pointed out by Drillon *et al* (*J. Appl. Phys.* 1988, *63*, 3551) this type ferromagnetic/ferromagnetic interaction can come in the system due to stacking of Cu (II) ions.

AC Magnetization for Cu-DCM and Cu-DCM-Eva

The ac magnetisation for Cu-DCM and Cu-DCM-Eva are measured at the ac amplitude of 10 Oe and in the frequencies range from 100 to 10,000 Hz. The in-phase component of the susceptibility (χ ') exhibits maxima at ~11 K and 7 K in case Cu-DCM where as in Cu-DCM-Eva showed one maxima ~ 11 K. The imaginary part of susceptibility (χ '') in both Cu-DCM and Cu-DCM-Eva exhibits one clear peak at ~11 K but the peak at 7 K is not visible due to relatively small signal to noise ratio. In both the cases, we did not observe any frequency dependence from 100 to 10000 was observed, confirming the absence of any spin glass behaviour.



Figure S22: Temperature dependence of real part of a.c. susceptibility for Cu-DCM.



Figure S23: Temperature dependence of imaginary part of a.c. susceptibility for Cu-DCM.



Figure S24: Temperature dependence of real part of a.c. susceptibility for Cu-DCM-Eva.



Figure S25: Temperature dependence of imaginary part of a.c. susceptibility for Cu-DCM.



Figure S26: Comparison of temperature dependence real part of a.c. susceptibility measured at 10 Oe and 101 Hz for Cu-DCM and Cu-DCM-Eva.



Figure S27: Comparison of temperature dependence imaginary part of a.c. susceptibility measured at 10 Oe and 101 Hz for Cu-DCM and Cu-DCM-Eva.

Section S7. IR Spectroscopy



Figure S28: Comparison of the IR Spectra of as-synthesized sample (Cu-DCM), evacuated sample (Cu-DCM-Eva) and re-solvated sample (Cu-DCM-RSol)

Section S8. Investigation of Microstructure and Topography of Cu-DCM and Cu-DCM-Evacuated

To further investigate microstructure and topography, we used the FEI (model Tecnai F30) high resolution transmission electron microscope (HRTEM) equipped with field emission source operating at 300 KV voltage to image the drop coated dilute solution of Cu-DCM and Cu-DCM evacuated in ethanol on carbon-coated copper TEM grid.

Selected Area Electron Diffraction (SAED) pattern of the Cu-DCM and Cu-DCM-Eva shows the crystallinity of the samples. These gives further proof that the Cu-DCM-Eva remains crystalline after evacuation even though there is change in crystalline structure. The TEM image has shown in figure S25c,d & S24, we observed the rod like structure for both Cu-DCM and Cu-DCM-Eva. In Cu-DCM each rod like structure is made up of several small diameter rods which bundles together to form the microcrystalline Cu-DCM rods. The Cu-DCM evacuated samples images show that after evacuation these bundles of rods are separated and forms individual rods nanocrystalline rods. The sizes of individual rods are from 30 to 40 nm in diameter and several hundred nanometer in length.



Figure S29: (a) & (b) SAED patterns of Cu-DCM and Cu-DCM-Eva respectively, shows the crystalline nature of the crystals, (c) & (d) bright field and dark field image of the Cu-DCM-eva taken at the same portion of sample shows the crystallinity of the crystals.



Figure S30: (a) & (b) TEM images of Cu-DCM shows that the crystals are made up of bundles of rods. (c) & (d) TEM images of Cu-DCM-Eva shows that after evacuation the bundles break apart and forms nanocrystalline rods which are of 30-40 nm in diameter and several hundred nanometer length.



Figure S31: a) TEM image of as-synthesized compound showing the crystalline form of Cu-DCM before evacuation b) TEM image of nanocrystalline phase of Cu-DCM after evacuation c) TEM image showing edges of nanocrystal of evacuated Cu-DCM d) Zoomed nanocrystal of evacuated Cu-DCM