# **Reversible Phase Transformation in Proton Conducting Strandberg-type POM Based Metal Organic Material**

(Supporting Information: 46 pages)

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# Section S1. Synthesis of Strandberg Polyoxometalate based MOF (Cu<sub>3</sub>Mo<sub>5</sub>P<sub>2</sub>)

All reagents and solvents for synthesis and analysis were commercially available and used as received. The Fourier transform (FT) IR spectra (KBr pellet) were taken on a *PERKIN ELMER FT-IR SPECTRUM* (Nicolet) spectrometer. Powder X-ray diffraction (PXRD) patterns were recorded on a Phillips PNAlytical diffractometer for Cu K $\alpha$  radiation ( $\lambda = 1.5406$  Å), with a scan speed of 2° min<sup>-1</sup> and a step size of 0.02° in 2 $\theta$ . Thermo-gravimetric experiments (TGA) were carried out in the temperature range of 25–700 °C on a SDT Q600 TG-DTA analyzer under N<sub>2</sub> atmosphere at a heating rate of 10 °C min<sup>-1</sup>. All low-pressure gas adsorption experiments (up to 1 bar) were performed on a *Quantachrome Quadrasorb* automatic volumetric instrument.

Synthesis of  $[Mo_5P_2O_{23}][Cu(phen)(H_2O)]_3 \cdot 5H2O$  (Cu<sub>3</sub>Mo<sub>5</sub>P<sub>2</sub>): A mixture phosphomolybdic acid hydrate (0.2 gm), CuCl<sub>2</sub>.2H<sub>2</sub>O (0.032gm), conc. H<sub>3</sub>PO<sub>4</sub> (0.5ml), 1, 10-Phenanthroline (0.023gm) and 18ml water was stirred for 30 minutes. The pH of the reaction medium was maintained to 2.83 by using 2M NaOH solution. Then the reaction mixture was put to 25ml hydrothermal bomb and kept at 160 °C for 120 hours. Blue tiny needle like crystals were obtained after cooling to room temperature for 24 hours. Few best crystals were washed with water for single crystal data collection. *FT-IR* : (KBr 4000-450cm<sup>-1</sup>): 3463(br), 3051(w), 1623(s), 1513(m), 1422(w), 1150(m), 1098(w), 1037(m), 910(s), 871(s), 845(m), 721(s), 664s), 563(w). **Elemental Analysis:** Found (%) C= 24.39, H= 1.59, N= 4.62; Calc. (%) C= 24.38, H= 1.52, N= 4.74.



Figure S1: Simulated (bottom) and experimental (top) PXRD pattern of Cu<sub>3</sub>Mo<sub>5</sub>P<sub>2</sub>

# Section S2. Single crystal X-ray diffraction data collection, structure solution and refinement procedures.

#### **General Data Collection and Refinement Procedures**:

Data was collected on a 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 $\alpha$  radiation ( $\lambda = 0.71073$  Å). The incident X-ray beam was focused and monochromated using graphite monochromator. The crystal reported in this paper was mounted on nylon CryoLoops (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. *Bruker SMART*<sup>1</sup> software was used suite to carry out overlapping  $\varphi$  and  $\omega$  scans at detector (2 $\theta$ ) settings (2 $\theta$  = 28). 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*<sup>2</sup>. In no data collection was evidence for crystal decay encountered. Following exhaustive review of collected frames the resolution of the dataset was judged. Data were integrated using Bruker SAINT<sup>3</sup> 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<sup>4</sup>. The space group determination and tests for merohedral twinning were carried out using *XPREP*<sup>3</sup>.

The structure was solved by direct methods and refined using the *SHELXTL* 97<sup>5</sup> software suite. Atoms were located from iterative examination of difference F-maps

following least squares refinements of the earlier models. Final models were refined anisotropically (if the number of data permitted) until full convergence was achieved. The structure was examined using the *Adsym* subroutine of PLATON<sup>6,7</sup> to assure that no additional symmetry could be applied to the models. All ellipsoids in ORTEP diagrams are displayed at the 30% probability level unless noted otherwise. Crystallographic data (excluding structure factors) for the structures are reported in this paper have been deposited with the CCDC as deposition No. CCDC 839380. 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: deposit@ccdc.cam.ac.uk].

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#### Cu<sub>3</sub>Mo<sub>5</sub>P<sub>2</sub> (MONOCLINIC)

#### Experimental and Refinement Details for Cu<sub>3</sub>Mo<sub>5</sub>P<sub>2</sub>

A yellow needle like crystal ( $0.20 \times 0.04 \times 0.05 \text{ mm}^3$ ) of **Cu<sub>3</sub>Mo<sub>5</sub>P<sub>2</sub>** was placed in 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 $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 273(2) K in a liquid N<sub>2</sub> cooled stream of nitrogen. A total of 48058 reflections were collected of which 8984 were unique and 8034 of these were greater than  $2\sigma(I)$ . The range of  $\theta$  was from 1.71 to 24.99. Analysis of the data showed negligible decay during collection. The structure was solved in the monoclinic P2(I)/c space group, with Z = 2, using direct methods. All non-hydrogen atoms were refined anisotropically with hydrogen atoms generated as spheres riding the coordinates of their parent atoms. Final full matrix least-squares refinement on  $F^2$  converged to  $R_1 = 0.0888$  ( $F > 2\sigma F$ ) and  $wR_2 = 0.1724$  (all data) with GOF = 1.256.

| Empirical formula                     | C72 H54 Cu6 Mo10 N12 O61 P4                            |
|---------------------------------------|--|
| Formula weight                        | 3527.86  |
| Temperature / K                       | 273.0  |
| Crystal system                        | Monoclinic   |
| Space group                           | <i>P2</i> <sub>1</sub> /c                              |
| a/Å, b/Å, c/Å                         | 8.501(7), 29.47(2), 20.745(16)                         |
| $\alpha$ /°, $\beta$ /°, $\gamma$ /°  | 90, 100.744(14), 90.00                                 |
| Volume / Å <sup>3</sup>               | 5106(7)  |
| Ζ                                     | 2  |
| $\rho calc / mg mm^{-3}$              | 2.295  |
| $\mu/mm^{-1}$                         | 2.579  |
| F(000)                                | 3480   |
| Crystal size / mm <sup>3</sup>        | $0.15\times0.05\times0.04$                             |
| $\Theta$ range for data collection    | 1.71 to 24.99 °  |
| Index ranges                          | $-10 \le h \le 10, -34 \le k \le 35, -24 \le l \le 23$ |
| Reflections collected                 | 48058  |
| Independent reflections               | 8984 [R(int) = 0.1001]                                 |
| Data/restraints/parameters            | 8984/0/ 721  |
| Goodness-of-fit on F <sup>2</sup>     | 1.253  |
| Final R indexes [I>2 $\sigma$ (I)]    | $R_1 = 0.0888, wR_1 = 0.1675$                          |
| Final R indexes [all data]            | $R_2 = 0.1001, wR_2 = 0.1724$                          |
| Largest diff. peak/hole / e Å $^{-3}$ | 0.243/ -1.137  |
|                                       |  |

#### Table S1. Crystal data and structure refinement for $Cu_3Mo_5P_2$



**Figure S2**: ORTEP drawing of the asymmetric unit of **Cu<sub>3</sub>Mo<sub>5</sub>P<sub>2</sub>**. [Color code: blue:C, Red:O, Black:Mo, Orange:P, Yellow:Cu, White:H]



Figure S3: Three different type of connectivity are reported in the literature with Strandberg type of Polyoxometalate a) two POM are connected via one metal centre b) two POM are connected via two metal centre but both of the metal are connected same oxygen of one POM c) two POM are connected via two metal centre and both of the metal are connected different oxygen of one POM, In Cu<sub>3</sub>Mo<sub>5</sub>P<sub>2</sub> connectivity is last type(c-type). The  $[CuP_{2}Mo_{5}O_{23}(H_{2}O)_{2}(H_{2}V)_{4}]_{n}$  structure consists of P<sub>2</sub>Mo<sub>5</sub>O<sub>23</sub> and [Cu(H<sub>2</sub>O)<sub>2</sub>(Cyt)<sub>2</sub>] subunits, the axial coordination of Cu(II) atoms are saturated by two oxygen atoms from P<sub>2</sub>Mo<sub>5</sub>O<sub>23</sub> to form 1D chain.<sup>1</sup> The crystal structures of  $[H_2en]_2[{Cu(en)(OH_2)}Mo_5P_2O_{23}]\cdot 4H_2O$  and  $[H_2en]-[{Cu(en)_2}Mo_5P_2O_{22}(OH_2)]\cdot 2H_2O$  are constructed from  $[Mo_5P_2O_{23}]^{6-}$  cluster,  $\{Cu(en)(OH_2)O_2\}^{2+}$  square pyramid and  $\{Cu(en)_2O_2\}^{2+}$  octahedra respectively. In  $[\{Cu(en)(Hen)\}_2-Mo_5P_2O_{23}]\cdot 3H_2O$  structure one  $[Mo_5P_2O_{23}]^{6-}$  cluster is connected to four {Cu(en)(Hen)}<sup>3+</sup> to form 2D layers.<sup>2</sup> In {Cu(DETA)}<sub>2</sub>[{Cu(DETA)(H<sub>2</sub>O)}-Mo<sub>5</sub>P<sub>2</sub>O<sub>23</sub>]·4.5H<sub>2</sub>O the POMs are connected by two Cu(DETA)<sup>2+</sup> complexes via Cu–O–P bonds to from 1D structure.<sup>3</sup> In the structure  $[H_2bpy]_2[{Cu(bpy)_2}Mo_5P_2O23] \cdot 4H_2O$  (bpy = 4,4bipyridine) Cu and bpy form 2D sheets, [Mo<sub>5</sub>P<sub>2</sub>O<sub>23</sub>]<sup>6-</sup> clusters act as pillar to connect 2D sheets in 3D network.<sup>4</sup> In  $Cu_3Mo_5P_2$  one POM is connected to next POM via one [Cu(Phen)(H<sub>2</sub>O)(O)<sub>2</sub>] square pyramid and one  $[Cu(Phen)(H_2O)(O)_3]$  octahedra. One  $[Cu(Phen)(H_2O)(O)_2]$  square pyramid, present in  $Cu_3Mo_5P_2$  is connected to a single POM, but does not contribute to network connectivity.

#### Refenences:

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**Figure S4**: a) Ball-stick model of one dimensional structure of Cu(II) connected POM in  $Cu_3Mo_5P_2$  b) Polyhedral model of one dimensional structure of Cu(II) connected POM in  $Cu_3Mo_5P_2$  c) Space fill model of one dimensional structure of Cu(II) connected POM in  $Cu_3Mo_5P_2$  [Color Code: Green:Mo, Yellow:P, Red:O, Blue:Cu, Deep blue:N, Black/Grey:C]



**Figure S5**: Arrangement of Cu<sub>3</sub>Mo<sub>5</sub>P<sub>2</sub> in *bc-plane*. [Color Code: Green:Mo, Yellow:P, Red:O, Blue:Cu, Deep blue:N, Black/Grey:C]



**Figure S6**: Space-fill model of Cu<sub>3</sub>Mo<sub>5</sub>P<sub>2</sub> in *bc-plane* showing the interdigitation of phenanthroline. [Color Code: Green:Mo, Yellow:P, Red:O, Blue:Cu, Deep blue:N, Black/Grey:C white:H]



**Figure S7**: Showing the position of water in the one dimensional channel surrounded by four interdigitated one dimensional chain. [Color Code: Green:Mo, Yellow:P, Red:O, Blue:Cu, Deep blue:N, Black/Grey:C Pink:H]



Figure S8: Interdigitation of four one dimensional channels via Cu(II) connected phenanthroline rings of  $Cu_3Mo_5P_2$ 



Figure S9: One dimensional channel of water in Cu<sub>3</sub>Mo<sub>5</sub>P<sub>2</sub> through crystallographic *a-axis*.



**Figure S10**: One 1D POM unit is surrounded via six parallel water channel. [POM units are removed for clarity]

| SL No | Donor | н     | Acceptor | D – H (Å) | HA (Å) | DA (Å)    |
|-------|-------|-------|----------|-----------|--------|-----------|
| 1     | O(2)  | H(2A) | O(32)    | 0.82      | 1.9    | 2.694(14) |
| 2     | O(6)  | H(6)  | O(12)    | 0.82      | 2.19   | 2.942(13) |
| 3     | O(6)  | H(6)  | O(21)    | 0.82      | 2.45   | 3.092(13) |
| 4     | O(24) | H(24) | O(19)    | 0.82      | 2.02   | 2.741(12) |
| 5     | O(30) |       | O(34)    |           |        | 3.43(5)   |
| 6     | O(30) |       | 0(11)    |           |        | 2.861(15) |
| 7     | O(30) |       | 0(11)    |           |        | 2.861(15) |
| 8     | O(30) |       | 0(31)    |           |        | 2.88(2)   |
| 9     | O(31) |       | O(10)    |           |        | 2.85(2)   |
| 10    | O(32) |       | O(4)     |           |        | 3.179(14) |
| 11    | O(32) |       | O(34)    |           |        | 3.18(4)   |
| 12    | O(32) |       | O(34)    |           |        | 3.18(4)   |
| 13    | O(34) |       | O(33)    |           |        | 3.41(5)   |

## Table S2. H-Bonding in Cu<sub>3</sub>Mo<sub>5</sub>P<sub>2</sub>

## Table S3: $\pi$ - $\pi$ stacking parameter

| Serial No | Centroid of aromatic ring           | Closest atom of<br>parallel ring | Distance |
|-----------|-------------------------------------|----------------------------------|----------|
| 1         | C22,C17,C16,C21,C35,C18<br>centroid | C16                              | 4.049 Å  |
| 2         | C32,C33,C34,C26,C27,C28<br>centroid | N4                               | 3.595 Å  |
| 3         | C9, C2,C1A, C12,N4,C8<br>centroid   | C33                              | 4.178 Å  |

# Section S3. Thermal stability of Cu<sub>3</sub>Mo<sub>5</sub>P<sub>2</sub> and the thermal gravimetric analysis (TGA) data



Figure S11. Thermal Gravimetric Analysis curve for Cu<sub>3</sub>Mo<sub>5</sub>P<sub>2</sub> (Scan Rate:10 °C/min).



**Figure S12.** Thermal Gravimetric Analysis curve for as-synthesized  $Cu_3Mo_5P_2$  shows ~8% weight lose (all the coordinated and non-coordinated water molecules) in 30-160 °C temperature range (Scan Rate: 5 °C/min).



**Figure S13.** Thermal Gravimetric Analysis curve for rehydrated  $Cu_3Mo_5P_2$  shows ~8% weight lose (all the coordinated and non-coordinated water molecules) in 30-160 °C temperature range (Scan Rate: 2 °C/min).



Section S4. Scanning Electron Microscopy (SEM) imaging of Cu<sub>3</sub>Mo<sub>5</sub>P<sub>2</sub>

**Figure S14 :** a) SEM image of as-synthesied  $Cu_3Mo_5P_2$  showing bulk morphology. b) SEM image of as-synthesied  $Cu_3Mo_5P_2$  showing crystalline edge. c) SEM image of evacuated  $Cu_3Mo_5P_2$ . d) SEM image of evacuated  $Cu_3Mo_5P_2$  where the crystalline edges are not prominent. e) SEM image of resolvated  $Cu_3Mo_5P_2$ . f) SEM image of  $Cu_3Mo_5P_2$  after methanol treatment



**Figure S15.** Microscopic images for as-synthesized  $Cu_3Mo_5P_2$  taken at different temperature shows noticeable color change beyond 130 °C.



Figure S16. Energy-Dispersive X-ray spectroscopy (EDAX) on the as-synthesized shows the presence of only Mo and Cu as metal in  $Cu_3Mo_5P_2$ .



Section S5. IR Spectroscopy of Cu<sub>3</sub>Mo<sub>5</sub>P<sub>2</sub>

**Figure S17:** IR Spectroscopy of as-synthesized  $Cu_3Mo_5P_2$ . Characteristic FTIR bands at 3463 (br), 1623(br), 1513, and 1422 cm<sup>-1</sup> confirmed the presence of 1, 10-phenanthroline and water, and bands at 947, 910, 871, 712, 664, and 563 cm<sup>-1</sup> are characteristic of phosphomolybdate anion.

#### Section S6. Adsorption studies on Cu<sub>3</sub>Mo<sub>5</sub>P<sub>2</sub>

 $H_2$  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  $Cu_3Mo_5P_2MOF$ , it was exchanged with anhydrous dichloromethane in 3 hours interval for 2 days. Before gas adsorption measurements, the sample was activated at 120 °C (for 12 h) under ultrahigh vacuum (10<sup>-8</sup> mbar) overnight.



**Figure S18:**  $H_2$  Adsorption isotherm for  $Cu_3Mo_5P_2$  at 77K. Filled dots are for absorption and blank dots are for desorption.



**Figure S19:**  $CO_2$  absorption data of  $Cu_3Mo_5P_2$  at 298K, The filled and open shapes represent adsorption and desorption, respectively. P/P<sub>0</sub>, relative pressure at the saturation vapor pressure of the adsorbate gas.



**Figure S20:** HO<sub>2</sub> vapor absorption data of  $Cu_3Mo_5P_2$  at 298K, The filled and open shapes represent adsorption and desorption, respectively. P/P<sub>0</sub>, relative pressure at the saturation vapor pressure of the adsorbate gas



Section S7. Solvent exchange experiment with Cu<sub>3</sub>Mo<sub>5</sub>P<sub>2</sub>

**Figure S21:** When the  $Cu_3Mo_5P_2$  was treated with different organic solvent like acetone, dimethyl formamide, chloroform, dichloromethane, acetonitrile, ethanol, methanol etc, it shows distinct color change with methanol.



Figure S22: Significant difference in color of  $Cu_3Mo_5P_2$  in methanol and  $D_2O$ 





**Figure S23:** Proton conductivity plot at 301 K (room temperature) [ $\sigma$ =2.2×10<sup>-5</sup> S cm<sup>-1</sup>]



**Figure S24:** Proton conductivity plot at 299K showing decrease in proton conductivity with respect to room temperature [ $\sigma$ =2.1×10<sup>-5</sup> S cm<sup>-1</sup>]



**Figure S25:** Proton conductivity plot at 297K showing decrease in proton conductivity with respect to room temperature [ $\sigma$ =2×10<sup>-5</sup> S cm<sup>-1</sup>]



**Figure S26:** Proton conductivity plot at 295K showing decrease in proton conductivity with respect to room temperature [ $\sigma$ =1.9×10<sup>-5</sup> S cm<sup>-1</sup>]



**Figure S27:** Proton conductivity plot at 297K showing decrease in proton conductivity with respect to room temperature [ $\sigma$ =1.8×10<sup>-5</sup> S cm<sup>-1</sup>]



**Figure S28:** Proton conductivity plot at 297K showing decrease in proton conductivity with respect to room temperature [ $\sigma$ =1.7×10<sup>-5</sup> S cm<sup>-1</sup>]



**Figure S29:** Proton conductivity plot at 297K showing decrease in proton conductivity with respect to room temperature [ $\sigma$ =1.6×10<sup>-5</sup> S cm<sup>-1</sup>]



**Figure S30:** Proton conductivity plot at 303K showing decrease in proton conductivity with respect to room temperature [ $\sigma$ =2.1×10<sup>-5</sup> S cm<sup>-1</sup>]



**Figure S31:** Proton conductivity plot at 305K showing decrease in proton conductivity with respect to room temperature [ $\sigma$ =1.9×10<sup>-5</sup> S cm<sup>-1</sup>]



**Figure S32:** Proton conductivity plot at 307K showing decrease in proton conductivity with respect to room temperature [ $\sigma$ =1.8×10<sup>-5</sup> S cm<sup>-1</sup>]



**Figure S33:** Proton conductivity plot at 309K showing decrease in proton conductivity with respect to room temperature [ $\sigma$ =1.7×10<sup>-5</sup> S cm<sup>-1</sup>]



**Figure S34:** Proton conductivity plot at 311K showing decrease in proton conductivity with respect to room temperature [ $\sigma$ =1.7×10<sup>-5</sup> S cm<sup>-1</sup>]



**Figure S35:** Proton conductivity plot at 315K showing decrease in proton conductivity with respect to room temperature [ $\sigma$ =1.4×10<sup>-5</sup> S cm<sup>-1</sup>].



**Figure S36:** Proton conductivity plot at lower temperature range showing decreasing trend in proton conductivity with respect to room temperature.



**Figure S37:** Proton conductivity plot at higher temperature range showing decreasing trend in proton conductivity with respect to room temperature.



**Figure S38:** Proton conductivity at different relative humidity showing decreasing trend of proton conductivity with decrease in humidification at room temperature (unit=  $S \text{ cm}^{-1}$ ).



**Figure S39:** Proton conductivity measurement of evacuated Cu<sub>3</sub>Mo<sub>5</sub>P<sub>2</sub> shows no semi-circle indicating no proton conduction in absence of one dimensional water channel(at 301K under 98% RH).



**Figure S40:** Proton conductivity measurement of rehydrated  $Cu_3Mo_5P_2$  shows same proton conductivity [ $\sigma$ =2.2×10<sup>-5</sup> S cm<sup>-1</sup>] as the as-synthesized  $Cu_3Mo_5P_2$  (at 301K under 98% RH).