Supporting Information (SI)

The Fate of Giant $\{Mo_{72}Fe_{30}\}$ Type Polyoxometalate Cluster in an Aqueous Solution at Higher Temperature: Understanding Related Keplerate Chemistry – from Molecule to Material

Raju Mekala, Sabbani Supriya* and Samar K. Das*

S1. Experimental Section

A. Materials and instrumental methods

The chemicals (ferric chloride hexa-hydrate, ammonium heptamolybdate, ammonium acetate, hydrazene sulfate, acetic acid, sodium acetate trihydrate) for syntheses were purchased from Sigma-Aldrich and were used as received. Millipore water was used throughout the experiments. All chemicals have been used as received without any further purification. Field emission scanning electron microscope (FESEM) imaging with energy dispersive X-ray spectroscopy (EDXS) or (EDS) was carried out on a Carl Zeiss model Ultra 55 microscope. The materials were prepared as KBr pellets and FT-IR spectra were collected in transmission mode using a JASCO FT-IR-5300 spectrometer; wavenumbers (ν) are given in cm^{-1}. Powder X-ray diffraction patterns were recorded on a Bruker D8-Advance diffractometer using graphite mono-chromated CuKα1 (1.5406 Å) and Kα2 (1.54439 Å) radiations.

B Synthesis of $[Fe_2(MoO_4)_3]$.

An aqueous solution of $\mathbf{[Mo_{72}Fe_{30}O_{252}(CH_3COO)_{12}\{Mo_2O_7(H_2O)\}_2\{H_2Mo_2O_8(H_2O)\}(H_2O)_{91}]\cdot 150\ H_2O}$ $\{Mo_{72}Fe_{30}\}$ is prepared by dissolving 2 g of rhombohedral-shaped $\{Mo_{72}Fe_{30}\}$ crystals in 50 mL of water. The pH of the clear yellow color $\{Mo_{72}Fe_{30}\}$ solution was recorded as 3.5. The $\{Mo_{72}Fe_{30}\}$ solution is then refluxed at 100 ^oC for 36 hours. Slowly pale yellow color $[Fe_2(MoO_4)_3]$

compound precipitates after 36 hours of reflux. The reaction mixture is cooled to room temperature. The precipitate was separated through filtration and quickly washed with ice cold water. The filtered compound was dried at room temperature. Yield is 0.55 gms (52% based on $\{\mathbf{Mo_{72}Fe_{30}}\} \rightarrow 15\ [Fe_2(MoO_4)_3]$) .

S2. Spectral observations

A. Infrared Spectroscopy:

In the IR spectra of ferric molbdate, the major peaks, which appear in the region of 900-800 cm^{-1}, are the characteristics peaks of Mo=O peaks as shown in Fig. S1.

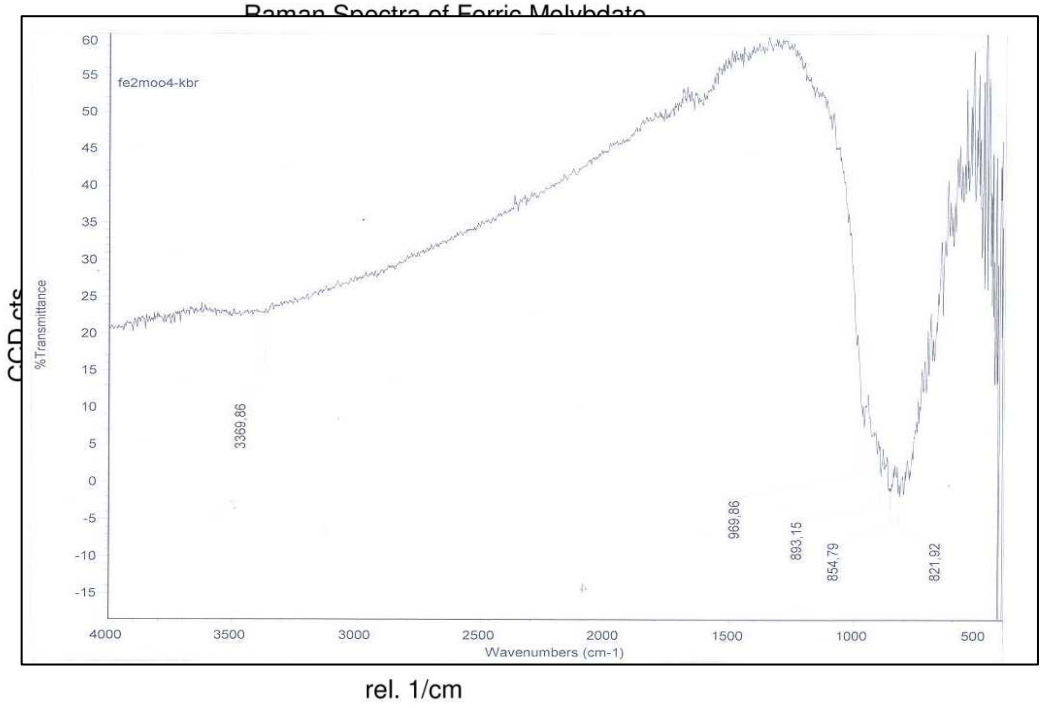


Figure S1. Infrared spectrum of ferric molybdate showing the characteristics Mo=O peaks in the range of 900-800 cm^{-1}.

B. Raman Speroscopy:

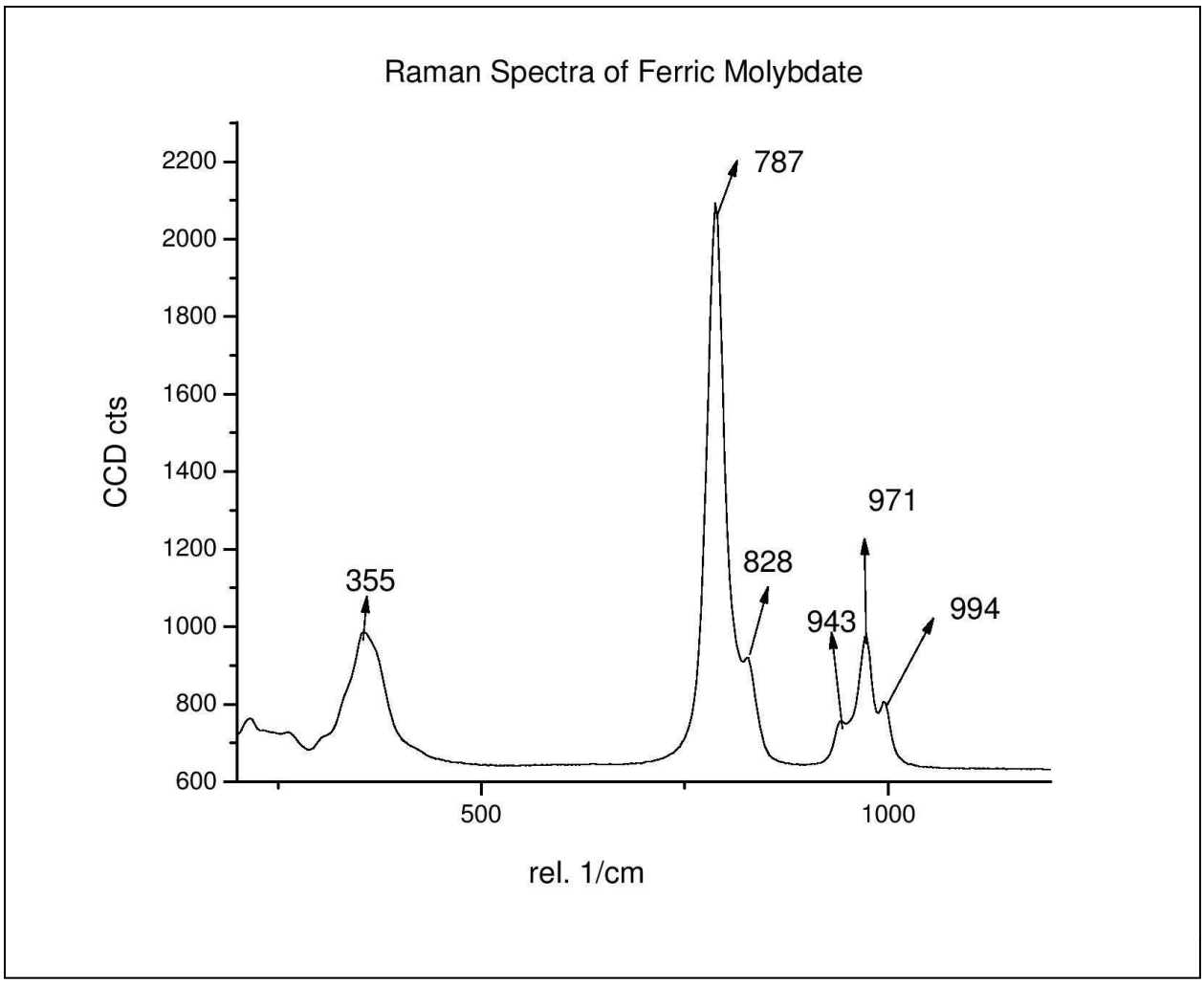


Figure S2. UV **(385 nm)** Raman spectrum of bulk ferric molybdate.

S3. Diffraction studies

Powder X-Ray Diffraction Studies:

The PXRD of the $Fe_2(MoO_4)_3$ synthesized from $\{Mo_{72}Fe_{30}\}$ cluster containing compound . All the peaks of the PXRD pattern are indexed to monoclinic ferric molybdate, which is in good agreement with relevant literature values (JCPDS file Card No. 35-0183) as shown in Fig. S4.

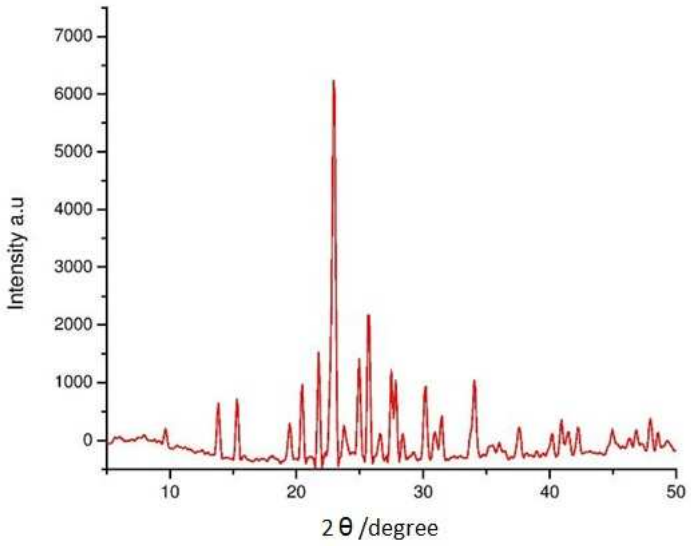


Figure S3. Powder X-Ray diffraction pattern of the ferric molybdate.

Table S1. X-ray powder diffraction data with d_{hkl} (CuKα1 (1.5406 Å)

d (Å)	I	h	k	l	Comments
6.40000	15	2	0	0	
5.79000	20	-2	1	2	
4.57000	10	-2	0	4	
4.35000	25	-3	1	3	
4.09000	30	-2	1	4	
3.92600	50	-2	2	2	
3.87200	100	-1	1	4	Strongest line.
3.71100	15	-4	0	4	
3.57300	20	-4	0	1	
3.46700	70	-3	2	2	
3.35300	12	2	2	1	
3.24700	50	-2	2	4	
3.20600	40	4	0	0	
3.14700	9	-4	1	5	
2.96700	20	-5	0	5	
2.89600	15	-1	3	2	
2.84700	18	1	3	1	
2.63400	20	-5	1	6	
2.39100	9	-5	2	1	
2.30900	10	-1	0	7	
2.24400	4	1	2	5	
2.20700	15	4	3	0	

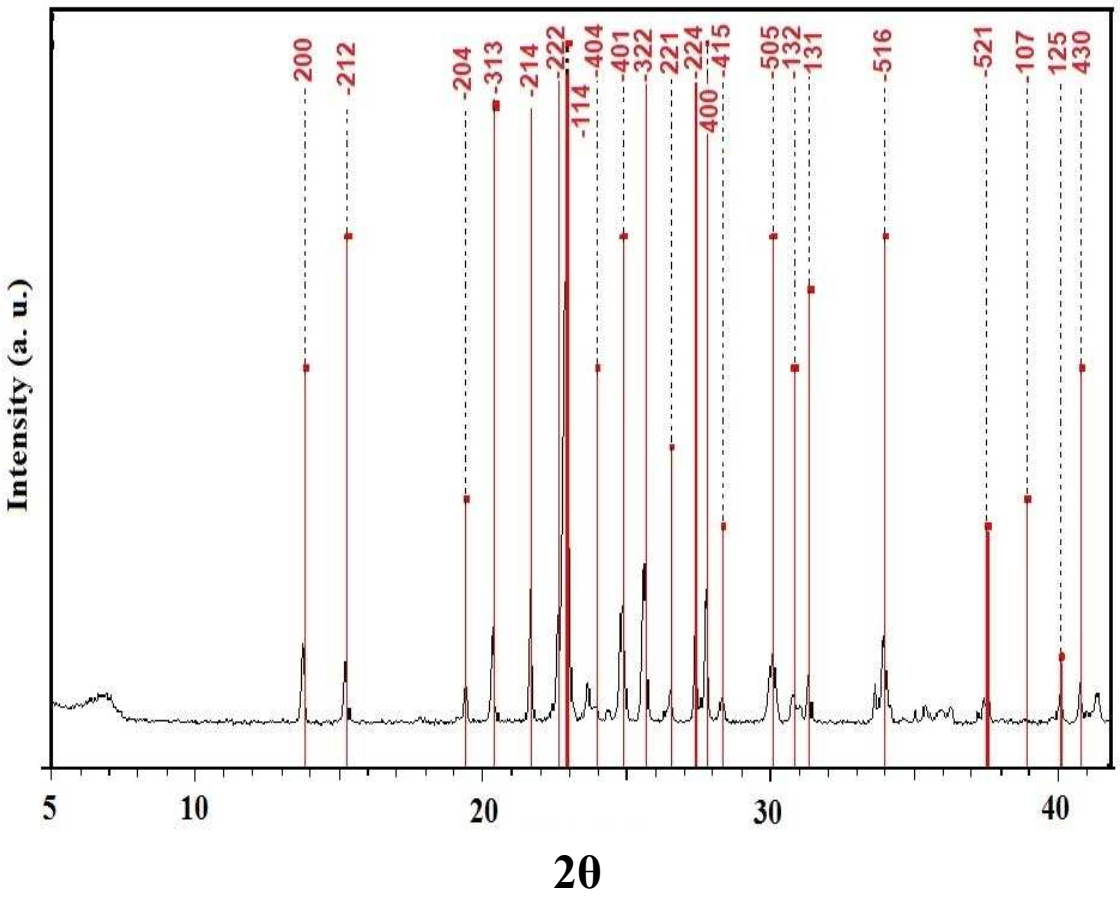
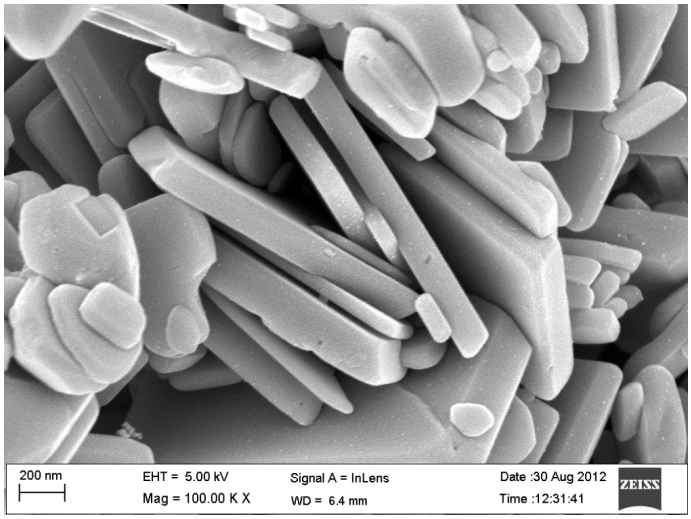


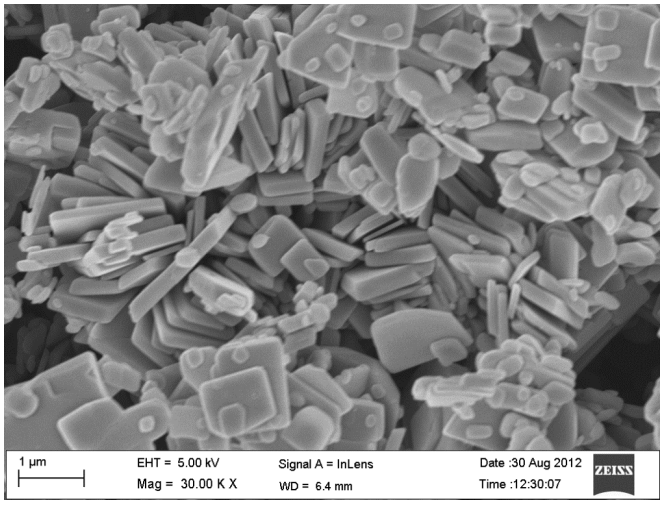
Figure S4. The powder X-ray diffraction patterns of ferric molybdate (red, simulated, JCPDS file Card No. 35-0183; black, observed, present study).

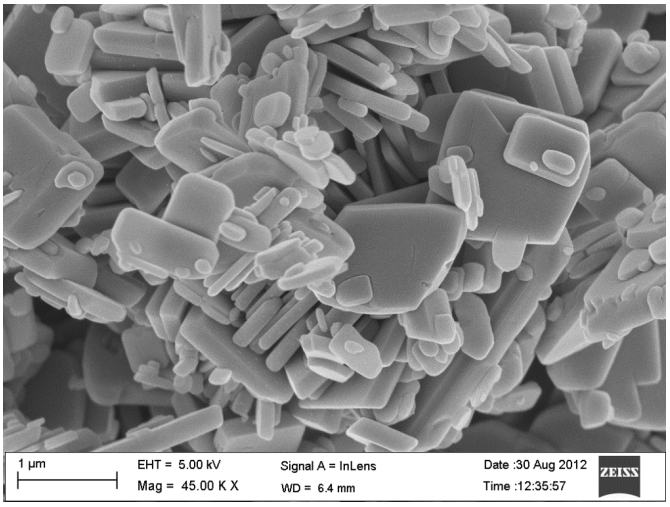
S4. Microscopic observations

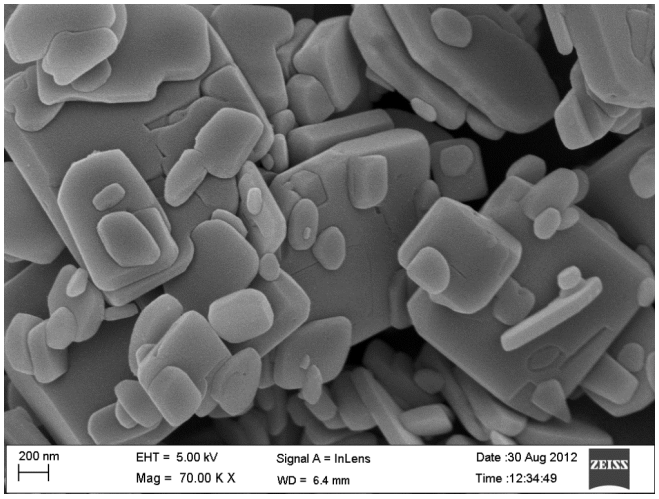
A. Field Emission Scanning Electron Microscopy (FESEM):

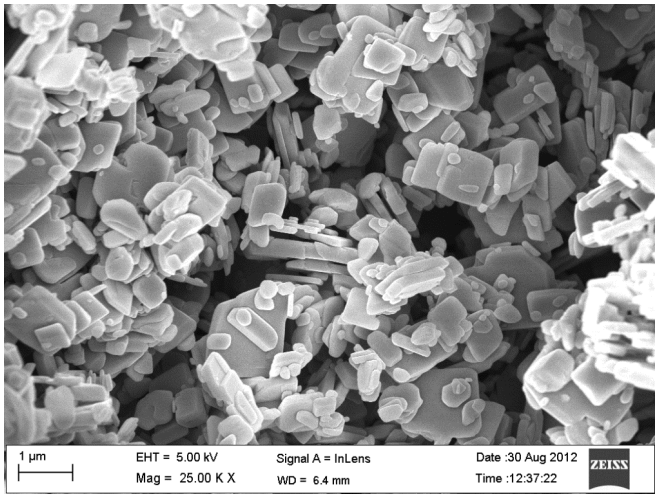
FESEM Images of ferric molybdate particles, synthesized from $\{Mo_{72}Fe_{30}\}$ compound exhibiting tablet morphology with varied size distribution. It is obvious from the images these are in the range of 100 to 200 nm in size.


200 nm
EHT = 5.00 kV
Mag = 100.00 K X
Signal A = InLens
WD = 6.4 mm
Date :30 Aug 2012
Time :12:31:41
ZEISS


1 µm
EHT = 5.00 kV
Mag = 30.00 K X
Signal A = InLens
WD = 6.4 mm
Date :30 Aug 2012
Time :12:30:07
ZEISS


1 µm
EHT = 5.00 kV
Mag = 45.00 K X
Signal A = InLens
WD = 6.4 mm
Date :30 Aug 2012
Time :12:35:57
ZEISS


200 nm
EHT = 5.00 kV
Mag = 70.00 K X
Signal A = InLens
WD = 6.4 mm
Date :30 Aug 2012
Time :12:34:49
ZEISS


1 µm
EHT = 5.00 kV
Mag = 25.00 K X
Signal A = InLens
WD = 6.4 mm
Date :30 Aug 2012
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ZEISS

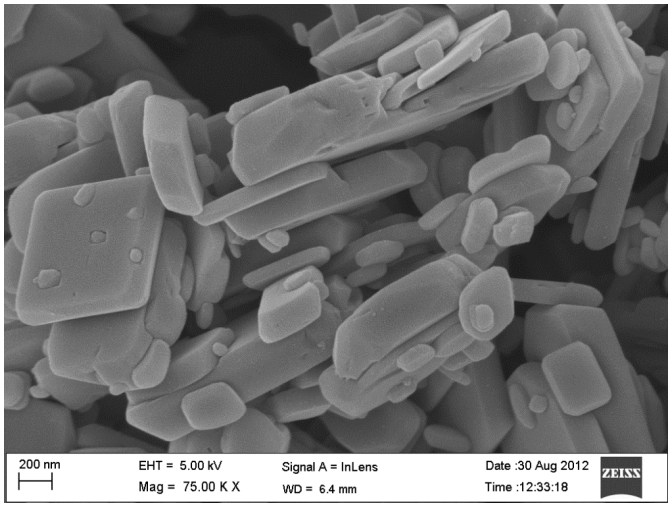
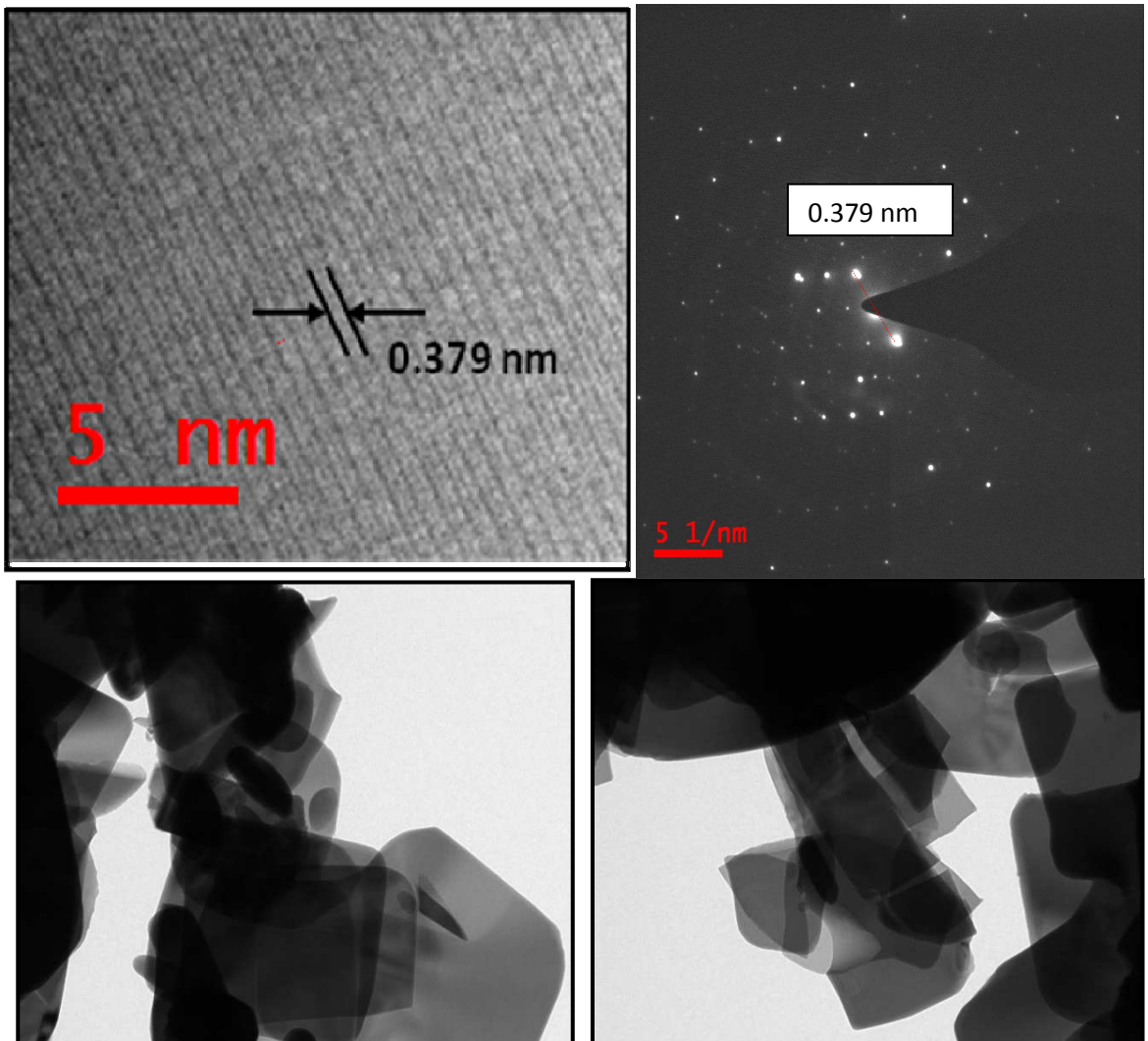
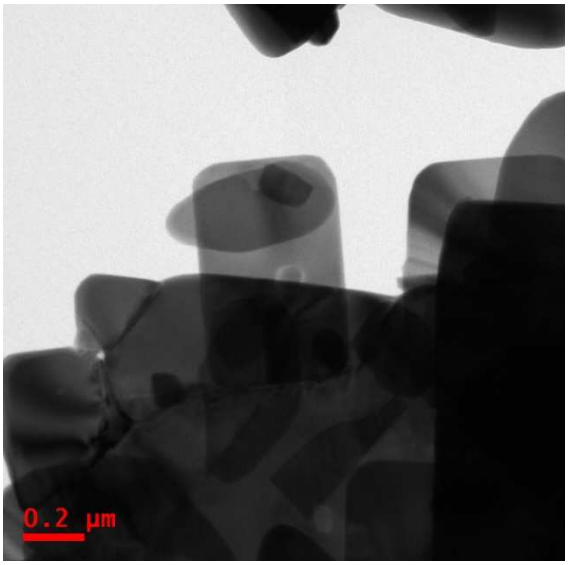

200 nm
EHT = 5.00 kV
Mag = 75.00 K X
Signal A = InLens
WD = 6.4 mm
Date :30 Aug 2012
Time :12:33:18
ZEISS

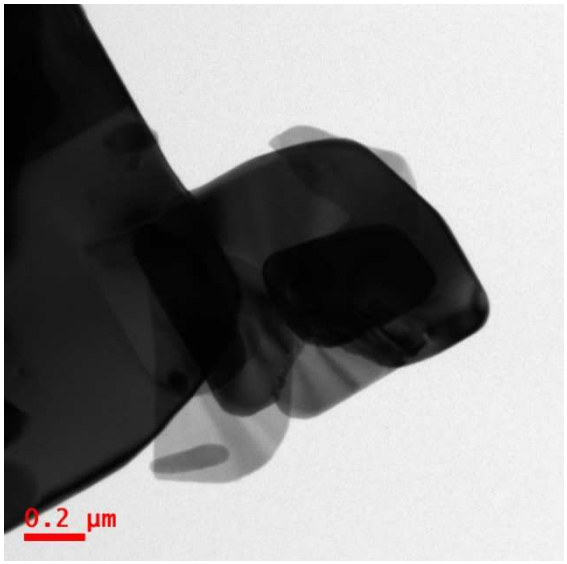
Figure S5. The images, shown above, are the FESEM images of ferric molybdate as synthesized powder taken on carbon tape; images are taken by coating with gold.

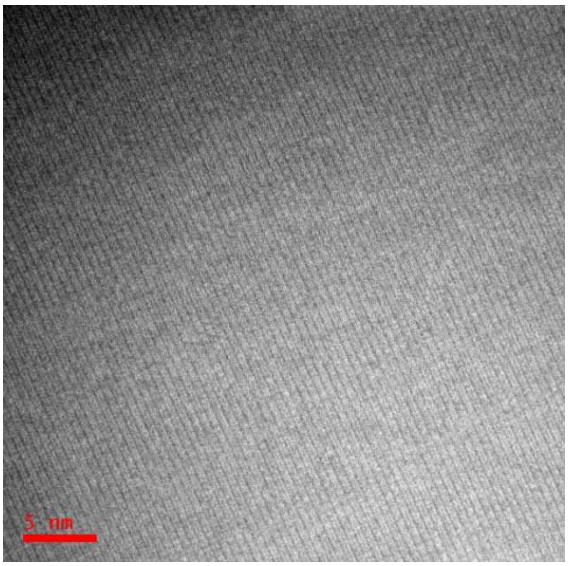
B. Transmission Electron Microscopy (TEM):

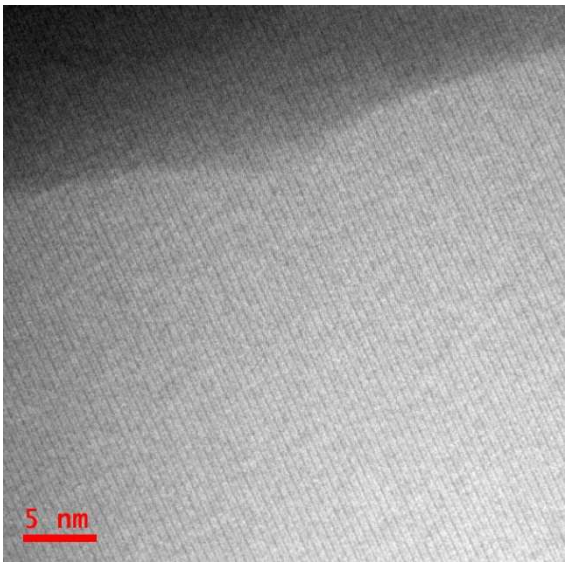
As shown from the TEM images of ferric molybdate , shown below, the shape of the particles are in well agreement with the morphology observed in FESEM images. The selective area electron diffractions (SAED) shows the crystalline nature of the particles and the d_{hkl} value obtained from the TEM are in agreement with the d_{hkl} values obtained from the experitmental PXRD indexed to the relevant literature values (JCPDS file Card No. 35-0183). The HRTEM (high resolution transmission electron microscope) of the particles shows the lattice fringes with d spacing of 0.379 nm corresponding to -114 plane of monoclinic ferric molybdate. The d_{hkl} value calculated with SAED is in accordance with the d_{hkl} value obtained from HRTEM establishing that the nano particles obtained are monoclinic form of ferric molybdate.




0.2 µm


0.2 µm


5 nm


5 nm

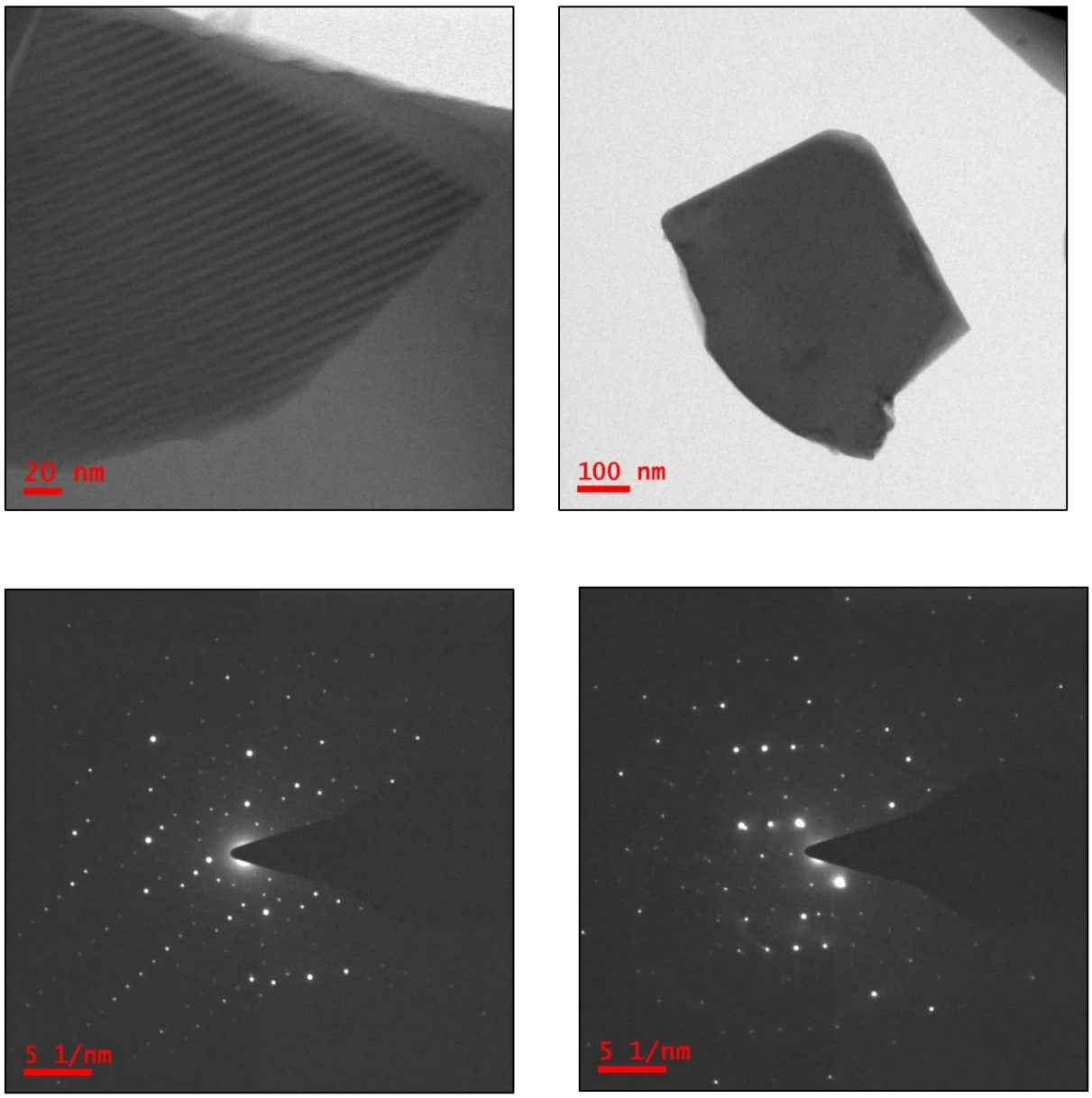


Figure S6. The images, shown above, are the TEM images of ferric molybdate as synthesized powder taken on copper grid.

C. Energy dispersive X-ray Spectroscopy (EDS) : Elemental composition of ferric molybdate particles imaged through FESEM and TEM studies.

Table S2. Elemental composition of ferric molybdate quantified after EDS taken from FESEM; some of the elements have been deleted from table, which are impurities that are there in preparation as well as in coating for microscopic studies.

Element	Weight %	Atomic %
Iron(Fe)	17.52	13.28
Molybdenum(Mo)	49.96	22.05
Oxygen (O)	23.49	62.17

(i) EDS of the selected area as shown in the FESEM image given below:

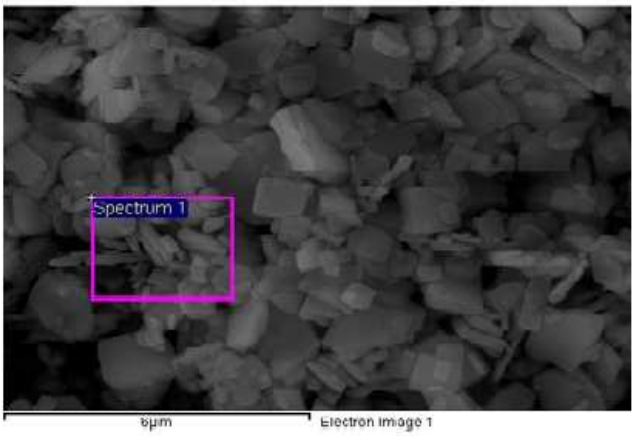


Figure S7. FESEM image for EDS analysis.

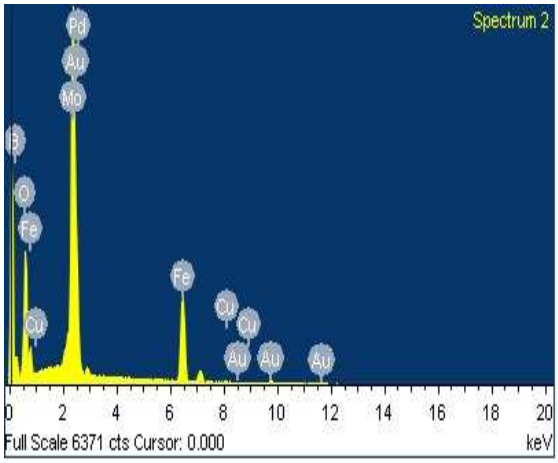
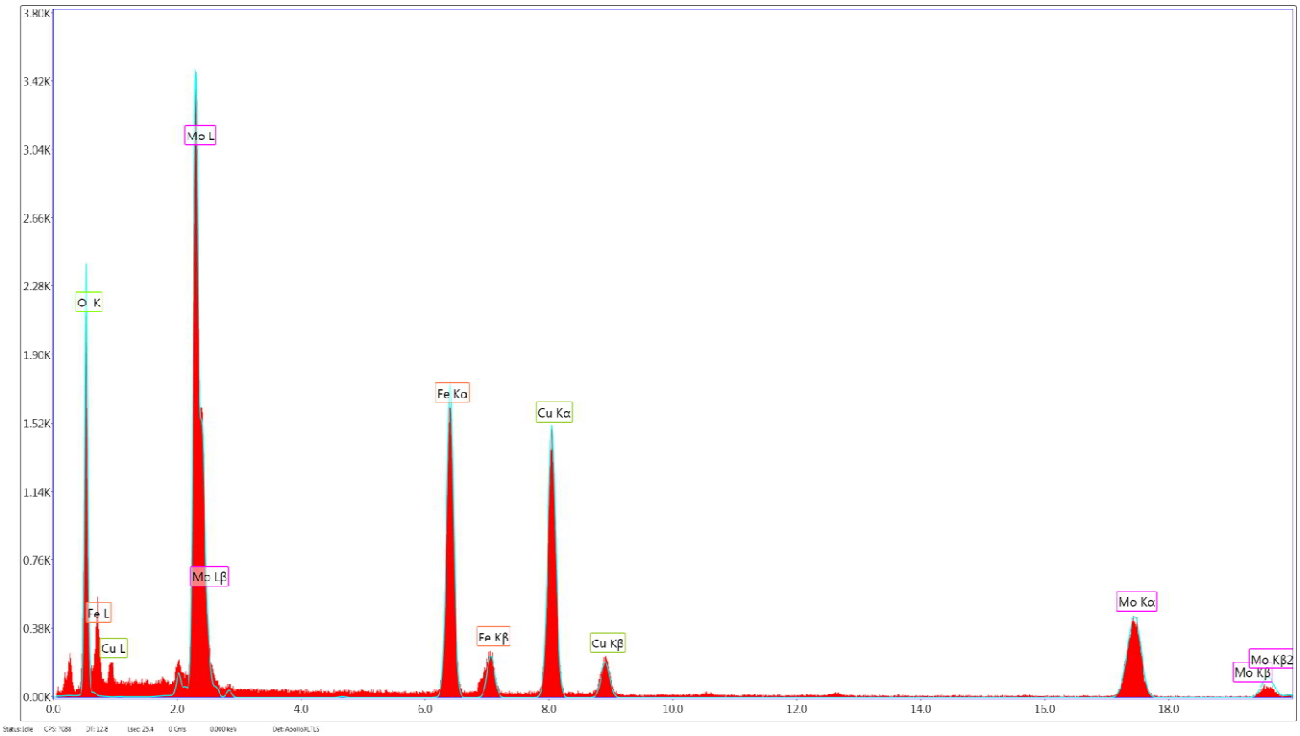
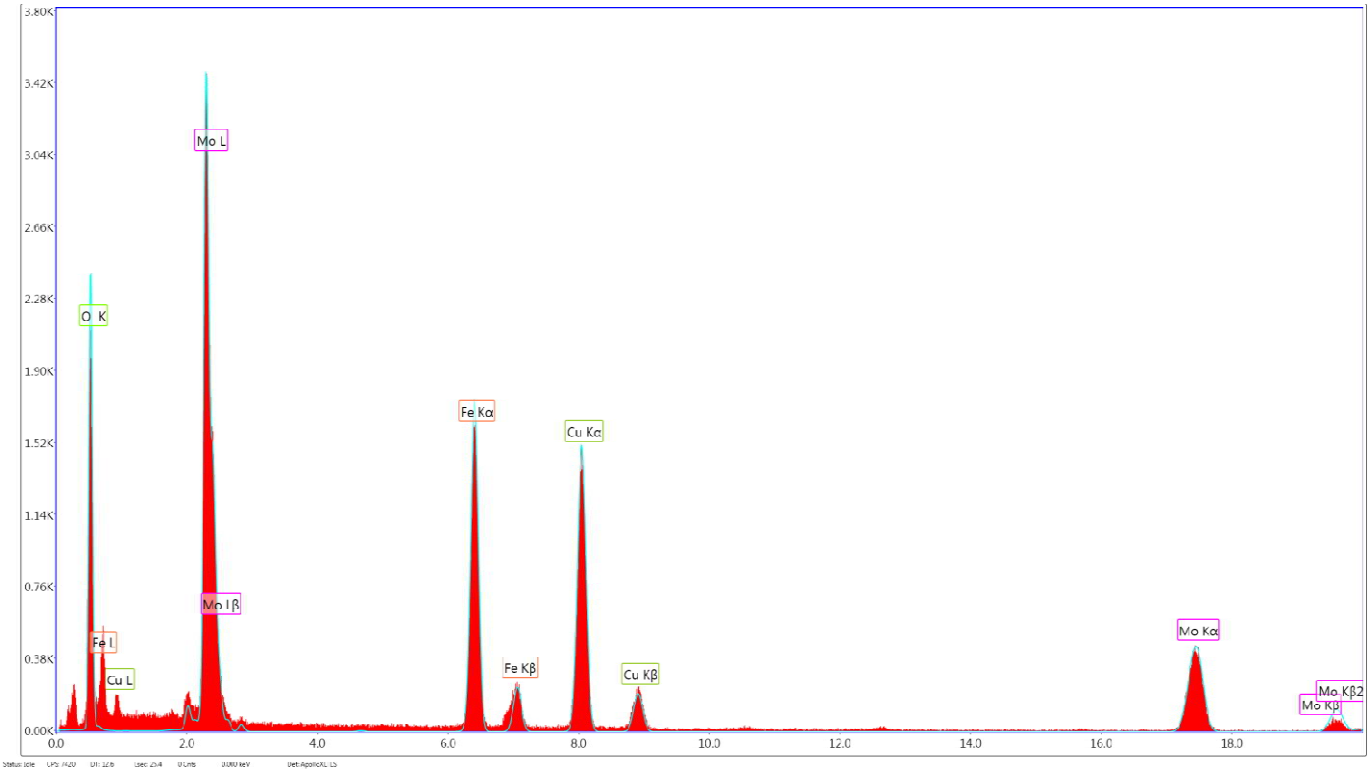


Figure S8. FESEM EDS Spectrum.

(ii) Given below are the EDAX obtained from TEM studies





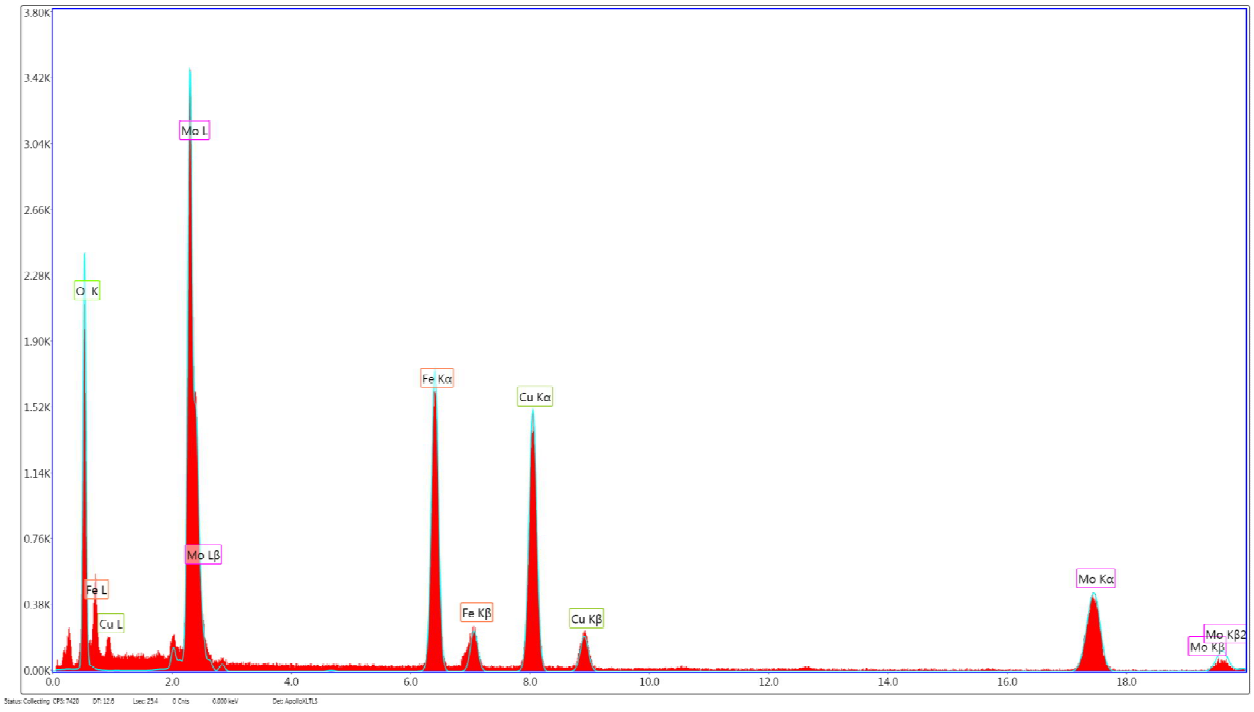


Figure S9. EDAX obtained from TEM studies.

D. Line Scanning of Transmission Electron Microscope (STEM)

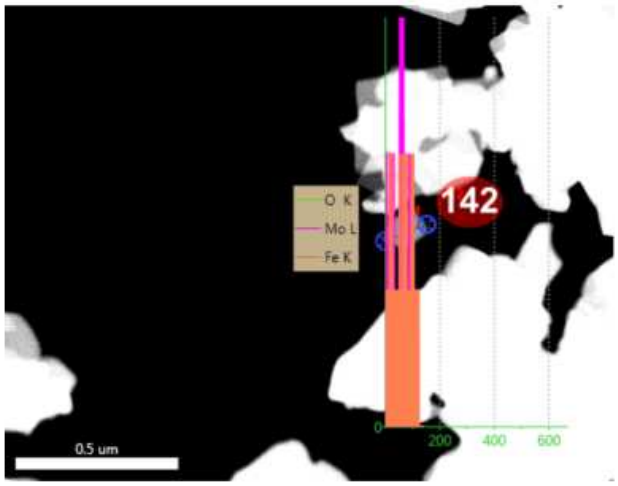
Line Scanning is a special tool in the Transimission Electron Microscopy (TEM) in which it shows the elemental distribution throughout the molecule image which gives the elemental profile plot as shown below.

FeMo

Author: CFNTEM
Creation: 11/30/2012

Sample Name: FeMo

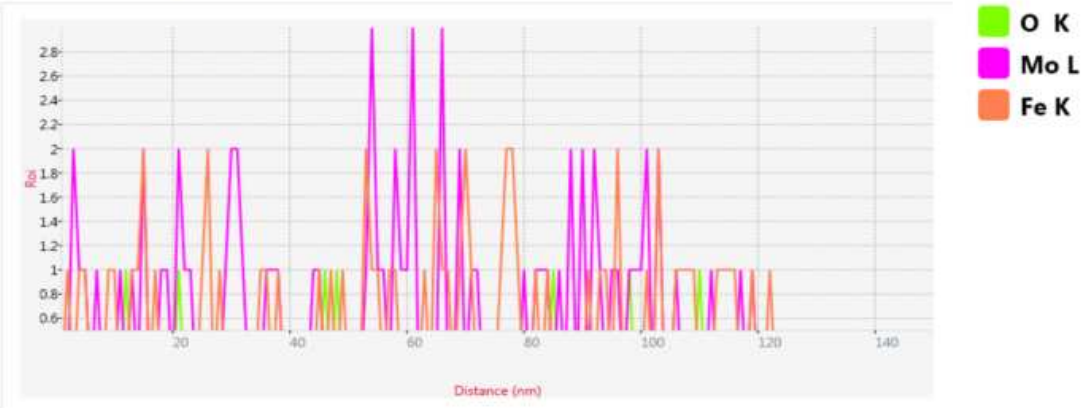
Area 1



Notes:

LineScan 1

Element profile plot

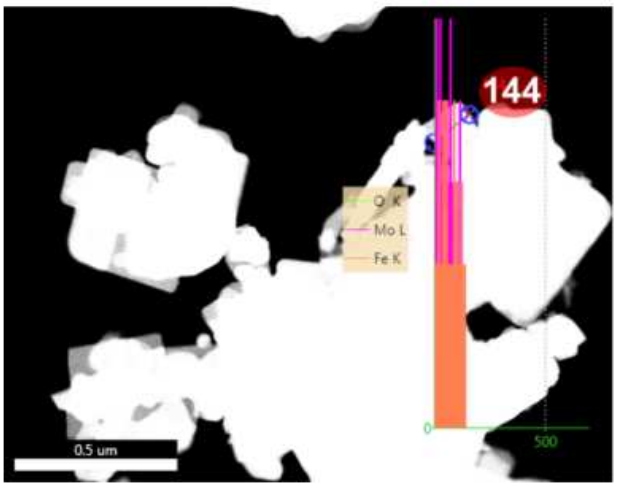


FeMo

Author: CFNTEM
Creation: 11/30/2012

Sample Name: FeMo

Area 2



Notes:

LineScan 1

Element profile plot

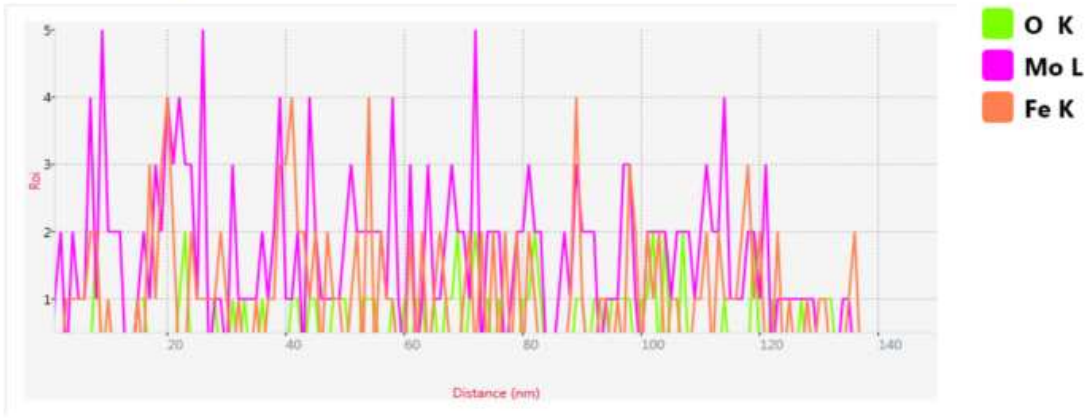
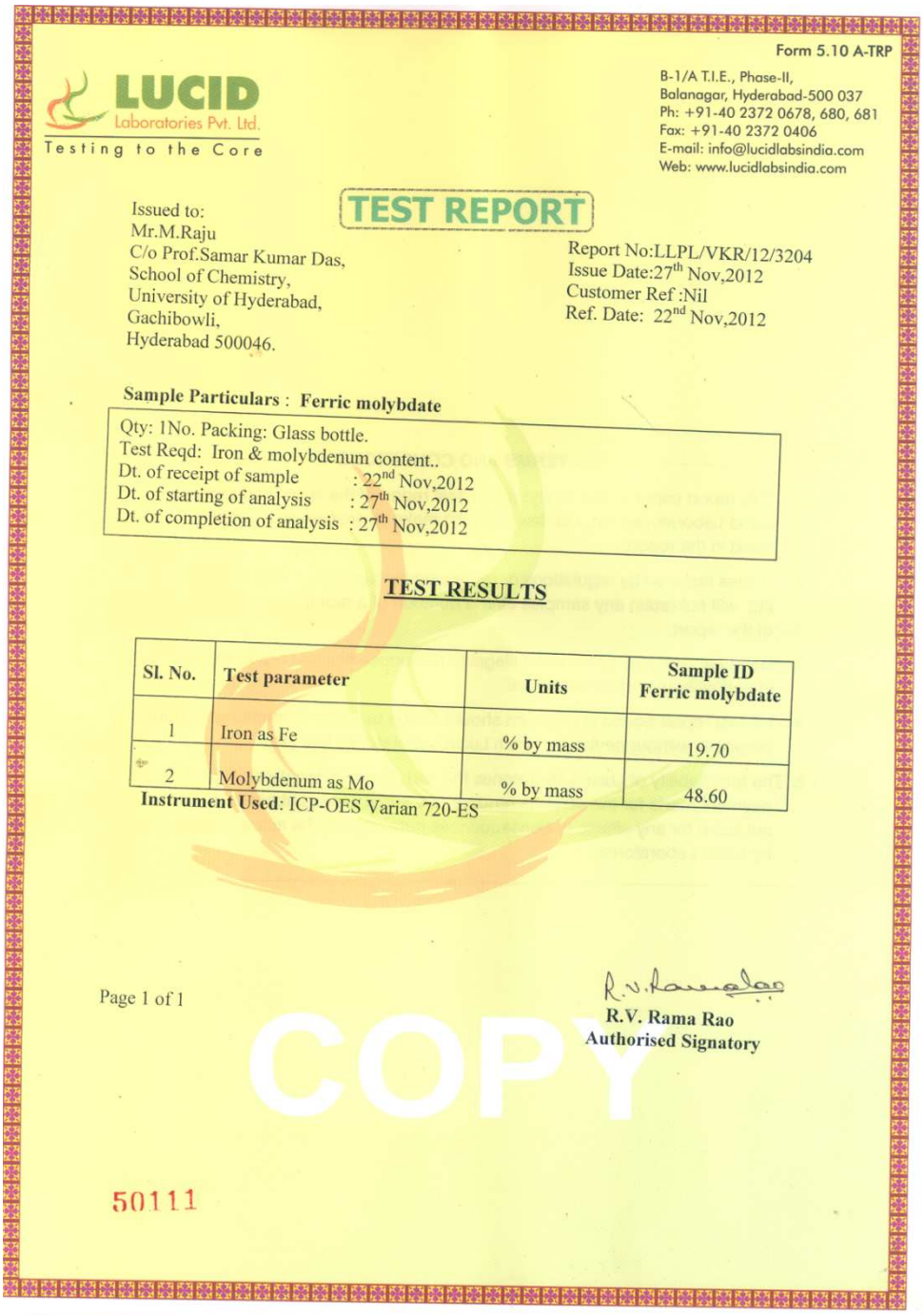


Figure S10. Elemental profile plot from line scanning of TEM.

S5. Inductively coupled plasma mass spectrometry (ICP-MS):



Form 5.10 A-TRP

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Testing to the Core

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E-mail: info@lucidlabsindia.com
Web: www.lucidlabsindia.com

TEST REPORT

Issued to:
Mr.M.Raju
C/o Prof.Samar Kumar Das,
School of Chemistry,
University of Hyderabad,
Gachibowli,
Hyderabad 500046.

Report No:LLPL/VKR/12/3204
Issue Date:27th Nov,2012
Customer Ref :Nil
Ref. Date: 22nd Nov,2012

Sample Particulars : Ferric molybdate

Qty: 1No. Packing: Glass bottle.
Test Reqd: Iron & molybdenum content..
Dt. of receipt of sample : 22nd Nov,2012
Dt. of starting of analysis : 27th Nov,2012
Dt. of completion of analysis : 27th Nov,2012

TEST RESULTS

Sl. No.	Test parameter	Units	Sample ID Ferric molybdate
1	Iron as Fe	% by mass	19.70
2	Molybdenum as Mo	% by mass	48.60

Instrument Used: ICP-OES Varian 720-ES

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R.V. Rama Rao
Authorised Signatory

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Figure S11. Results of ICP-MS that gives the metal proportion.

Table.S3. Process of estimation metals in ICP-MS

VARIAN 720-ES,Fe-27-11-12@720/725/730/735-ES@Quant@

Blank (Blk) **11/27/2012, 5:48:46 PM** **Tube 1**

Label	Sol'n Conc.	Units	SD(Int)	%RSD(Int)	Int. (c/s)
Fe 238.204	0.000000	mg/L	16.653	18.0	92.3108

Standard 1 (Std) **11/27/2012, 5:51:19 PM** **Tube 2**

Label	Sol'n Conc.	Units	SD(Int)	%RSD(Int)	Int. (c/s)
Fe 238.204	5.00000	mg/L	677.549	0.8	90033.7

Standard 2 (Std) **11/27/2012, 5:52:33 PM** **Tube 3**

Label	Sol'n Conc.	Units	SD(Int)	%RSD(Int)	Int. (c/s)
Fe 238.204	10.0000	mg/L	701.262	0.4	178466

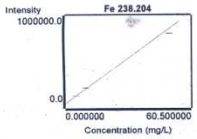
Standard 3 (Std) **11/27/2012, 5:53:59 PM** **Tube 4**

Label	Sol'n Conc.	Units	SD(Int)	%RSD(Int)	Int. (c/s)
Fe 238.204	50.0000	mg/L	3225.790	0.4	793768

Fe 238.204 Calibration (mg/L) **11/27/2012, 5:53:59 PM** **Correlation Coefficient: 0.999701**

Label	Flags	Int. (c/s)	Std Conc.	Calc Conc.	Error	%Error
Blank		92.3108	0.000000	0.000000	-	-
Standard 1		90033.7	5.00000	5.31992	0.319918	6.4
Standard 2		178466	10.0000	10.5506	0.550563	5.5
Standard 3		793768	50.0000	46.9449	-3.05512	-6.1

Curve Type: Linear Equation: y = 16906.5 x + 92.3



Blank (Samp) **11/27/2012, 6:00:38 PM** **Tube 7**
Weight: 1 **Volume: 1** **Dilution: 1**

Label	Sol'n Conc.	Units	SD	%RSD	Int. (c/s)
Fe 238.204	0.053302	mg/L	0.001134	2.1	993.468

Ferric molybdate/5di (Samp) **11/27/2012, 6:17:38 PM** **Tube 9**
Weight: 1 **Volume: 1** **Dilution: 1**

Label	Sol'n Conc.	Units	SD	%RSD	Int. (c/s)
Fe 238.204	18.1482	mg/L	0.142085	0.8	306916

P.V.V. Satya Kumari 27/11/2012

R.V. Rao 27/11/2012

S5. Thermo Gravimetric Analysis (TGA)

From the TGA plot, given below, we can say that the ferric molybdate particles (obtained in the present study) are stable up to 900^{o}C temperature, indicating that it is a stable material have extended linked structure.

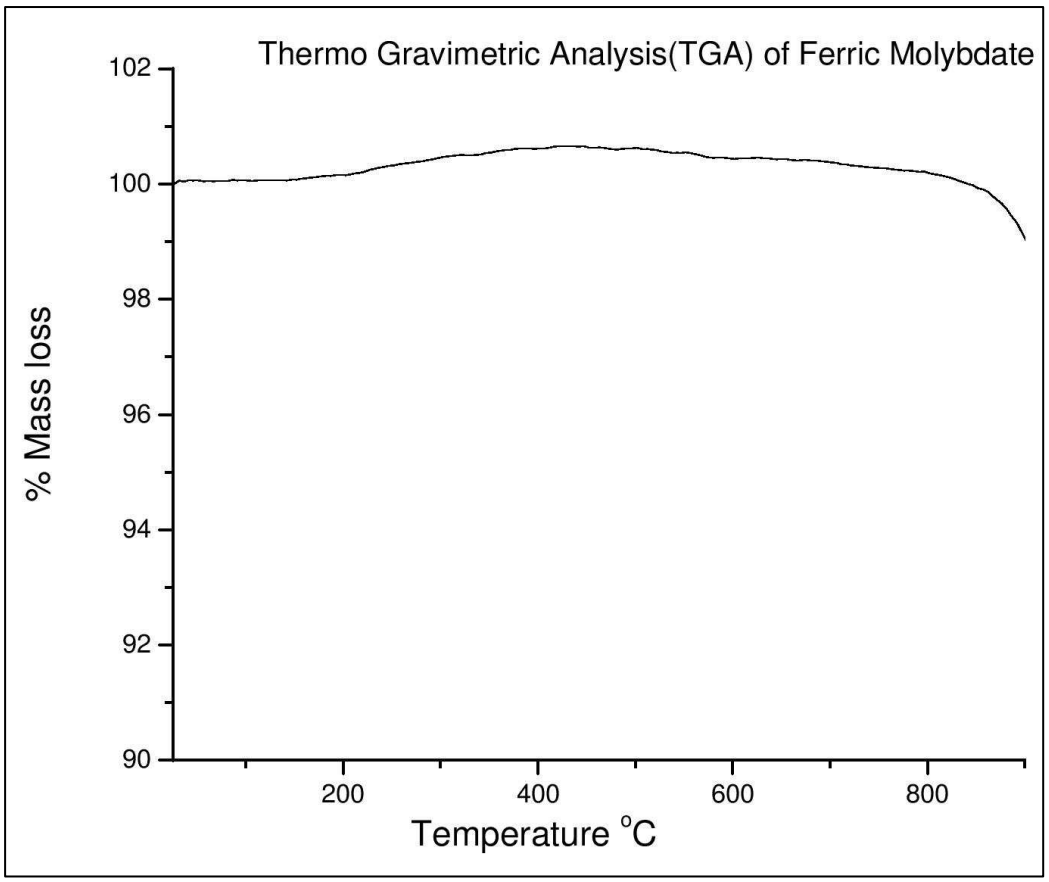
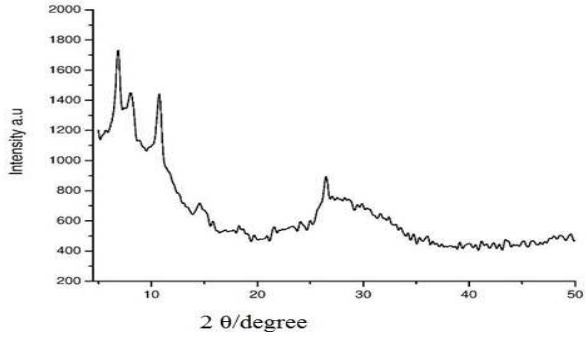


Figure S12. Thermo gravimetric (TG) plot of ferric molybdate.

S6. The PXRD and IR studies of the crude product, obtained from the solution / filtrate after separating / filtering the ferric molybdate of the refluxed solution.



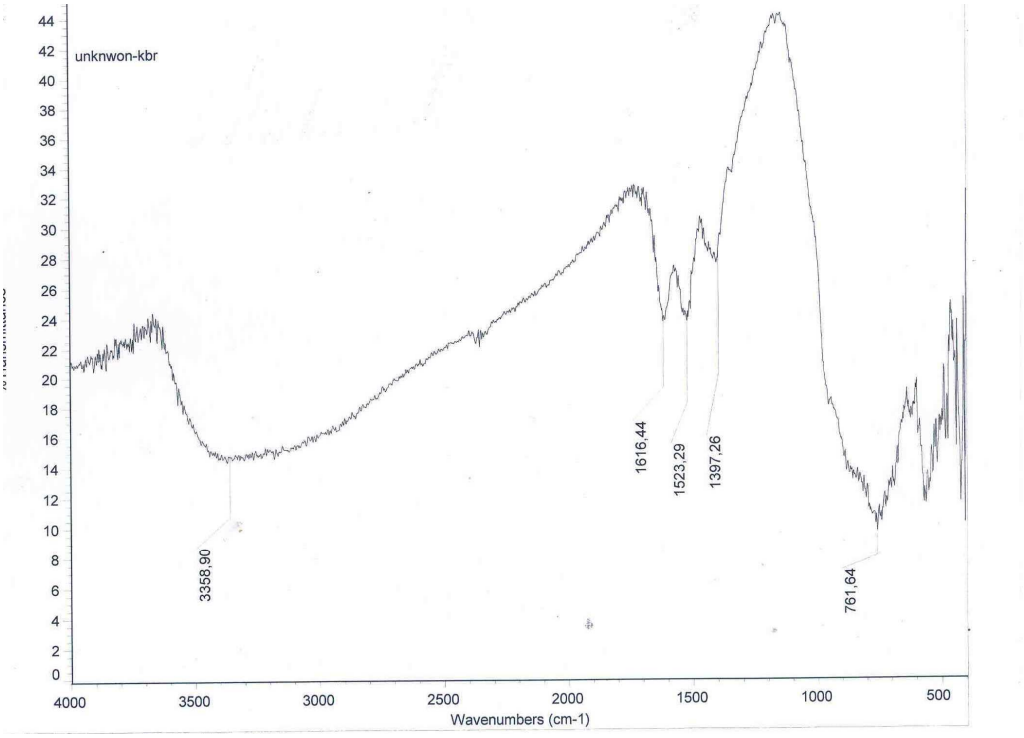


Figure S13. The PXRD pattern (top) and IR spectrum (bottom) of the crude product, obtained by evaporating the filtrate (after separating the nano-ferric molybdate) to dryness.

S7. An attempt to synthesize $[Fe_2(MoO_4)_3]$ in presence of added acetic acid in the reaction mixture

An aqueous solution of **$[Mo_{72}Fe_{30}O_{252}(CH_3COO)_{12}\{Mo_2O_7(H_2O)\}_2\{H_2Mo_2O_8(H_2O)\}(H_2O)_{91}] \cdot 150\ H_2O$** $\{Mo_{72}Fe_{30}\}$ was prepared by dissolving 2 g of rhombohedral-shaped $\{Mo_{72}Fe_{30}\}$ crystals in 50 mL of water; to that solution, 5 ml of 100% acetic acid was added. The solution was then refluxed at 100 ^oC for 36 hours. There is no change in the reaction mixture and no precipitation of ferric molybdate was observed.

IR spectrum and powder X-ray diffraction pattern of the solid, obtained by evaporation of above-described solution are shown below.

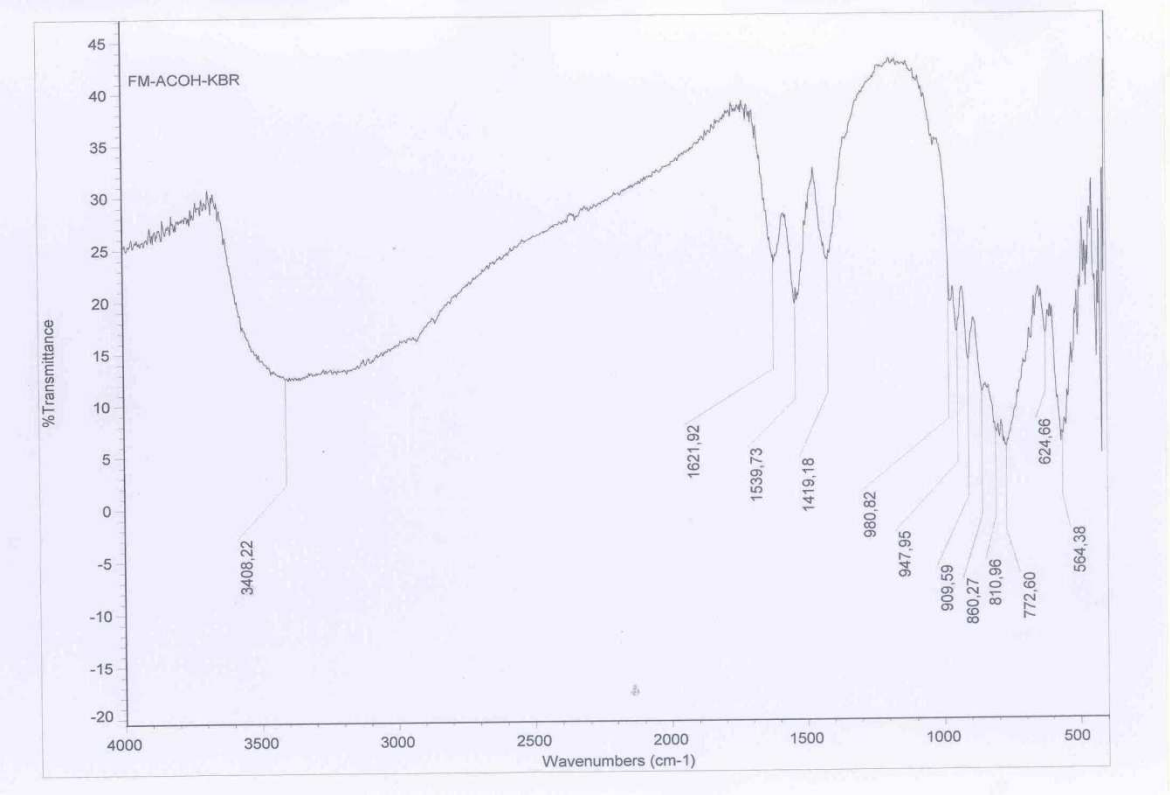


Figure S14. The IR spectrum of the solid, obtained by evaporating the solution to dryness, which was refluxed in the presence of acetic acid.

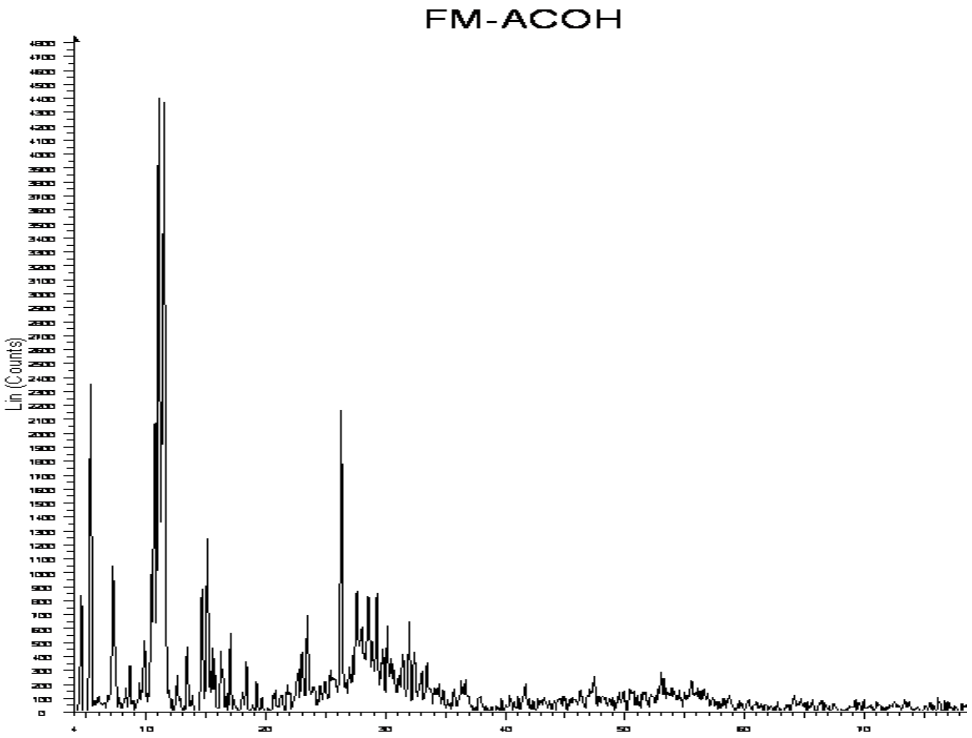


Figure S15. The powder X-ray diffraction pattern of the solid, obtained by evaporating the solution to dryness, which was refluxed in the presence of acetic acid.

S8. Synthesis of $[Fe_2(MoO_4)_3]$ in presence of added hydrochloric acid in the reaction mixture

An aqueous solution of **$[Mo_{72}Fe_{30}O_{252}(CH_3COO)_{12}\{Mo_2O_7(H_2O)\}_2\{H_2Mo_2O_8(H_2O)\}(H_2O)_{91}] \cdot 150\ H_2O$** $\{Mo_{72}Fe_{30}\}$ is prepared by dissolving 2 g of rhombohedral-shaped $\{Mo_{72}Fe_{30}\}$ crystals in 50 mL of water. To this solution, 1 ml of 1M of hydrochloric acid was added and the resulting reaction mixture was then refluxed at 100°C for 36 hours. Slowly pale-yellow colored $[Fe_2(MoO_4)_3]$ compound precipitates after 36 hours of reflux. The reaction mixture was cooled to room temperature. The precipitate was separated through filtration and quickly washed with ice cold water. The filtered compound was dried at room temperature. Yield 0.94 g (98% based iron). The IR spectrum of the solid, obtained by evaporation of above-described solution (after separation of ferric molybdate by filtration) is shown below.

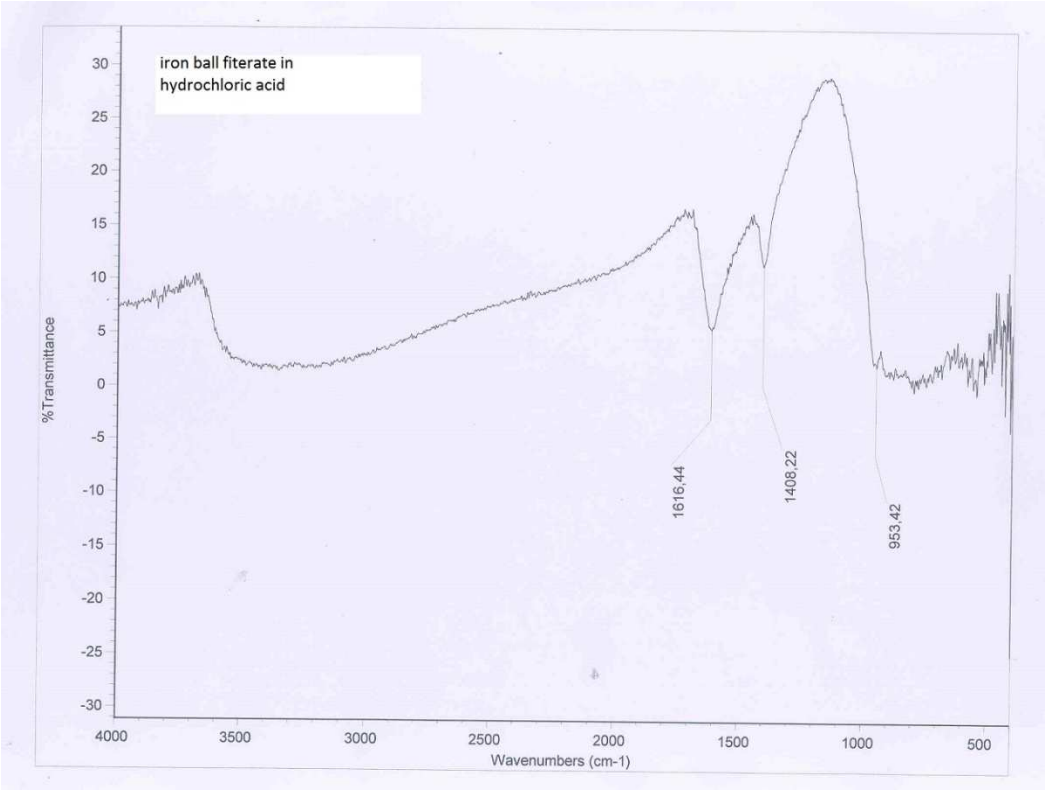


Figure S16. The IR spectrum of the solid, obtained by evaporating the solution (after separation of ferric molybdate) to dryness, which was refluxed in the presence of HCl acid.

**********End of SI**********