Supporting information

A nanoscopic icosahedral {$Mo_{72}Fe_{30}$} cluster catalyzes aerobic synthesis of benzimidazoles

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Experimental

1. General remarks. All chemicals were purchased from Merck and Across Chemical Companies. The FT-IR spectra were recorded on a Shimadzu 800 FT-IR system using a KBr pellet. Raman spectra were recorded on a Takram P50C0R10 spectrometer with laser wavelength of 532 nm. Powder X-ray diffraction (XRD) was performed on a Bruker D8-advance X-ray diffractometer with Cu Ka (λ= 1.5406 Å) radiation. The analysis of surface area was detected by the nitrogen adsorption-desorption measurements, which were measured at 77 K on a Belsorp-mini II (Bel Japan). Diffuse reflectance spectra (DRS) were obtained with an Avant's spectrophotometer (Avaspec-2048-TEC. The TGA measurements were obtained by a TGA-50 (Shimadzu) at the heating rate of 10 °C/min under 20 mL/min flowing air.TEM images were obtained by Department of Electron Microscopy Zeiss EM-10 West Germany. SEM and EDS performed by Scanning Electron Microscope TESCAN Vega Model. Magnetic susceptibility measurements were made by using a Lake Shore 7400 magnetometer at a field of 1 Tesla in 298 K.

2. Synthesis of amorphous {$Mo_{72}Fe_{30}$}.[1] 2.09 g $FeCl_3$-$6H_2O$ (7.7 mmol) was added under vigorous stirring to a solution of 3 g Na_2MoO_4-$2H_2O$ (12.3 mmol) in 25 mL water acidified with 15 mL of 100 % acetic acid (final pH ca. 2) which led to immediate precipitation of a yellow precipitate. It was filtered off after 30 min, thoroughly washed with distilled water and dried in air. The yellow solid characterized by FT-IR (Fig. S1),[1] Raman (Fig. S2),[2] UV-DRS (Fig. S3),[1,2], XRD (Fig. S4),[1] TGA (Fig. S5),[2] EDS (Fig. S6), VSM (Fig. S7), SEM (Fig. S8),[2] TEM (Fig. S9),[2] BET (Fig. S10).[2]

3. Synthesis of crystalline {$Mo_{72}Fe_{30}$}.[3] To a stirred orange-red solution of 1.1 g $FeCl_3.6H_2O$ (4.1 mmol) and 1.1 g $NaCH_3COO.3H_2O$ (8.1 mmol) in 75 mL H_2O, 1.4 g the ammonium salt of {Mo_{132}} (0.05 mmol) was added. The resulting mixture was vigorously stirred in an open 100-mL Erlenmeyer flask (wide-necked) for 24 h. After acidification with HCl (1M, 1 mL) and addition of NaCl (2.0 g), the stirred reaction mixture was heated to 90 ± 5 °C and then filtered whilst still hot. The golden yellow filtrate was cooled to 20 °C, and yellow crystals formed over a period of 2-3 days. The crystals were collected by filtration through a glass frit, washed twice with a little iced water (to remove the adhering NaCl), and dried in air. The yellow solid characterized by FT-IR (Fig. S11),[3] Raman (Fig. S12),[2] UV-DRS (Fig.13), XRD (Fig. S14),[1] TGA (Fig. S15), EDS (Fig. S16), FESEM (Fig. S17),[2] TEM (Fig. S18),[2] BET (Fig. S19).

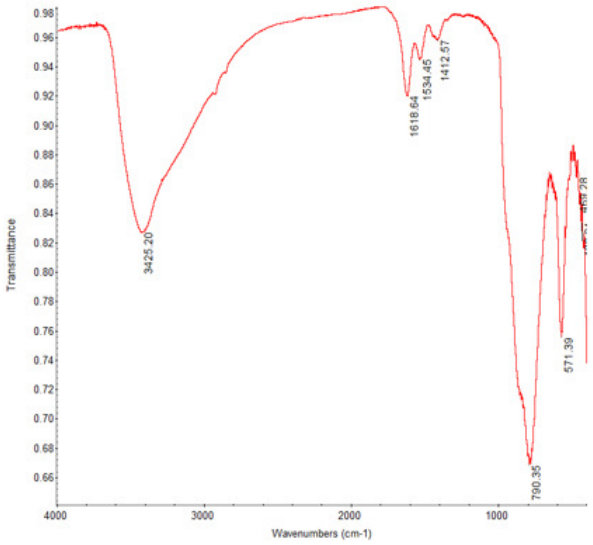


Fig. S1. FT-IR spectra of amorphous {$Mo_{72}Fe_{30}$}

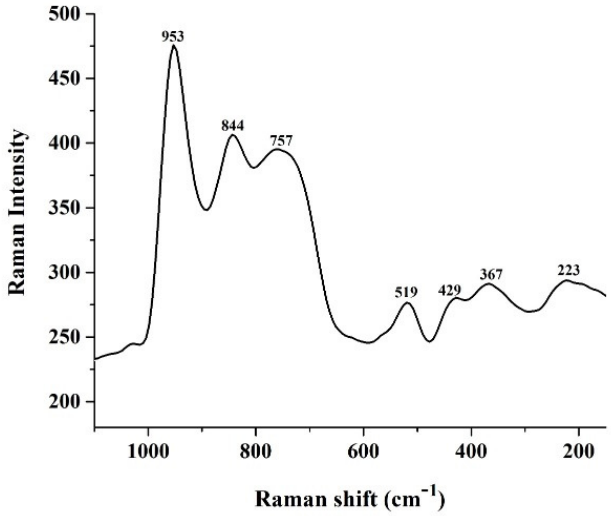


Fig. S2. The Raman spectrum of amorphous {$Mo_{72}Fe_{30}$}

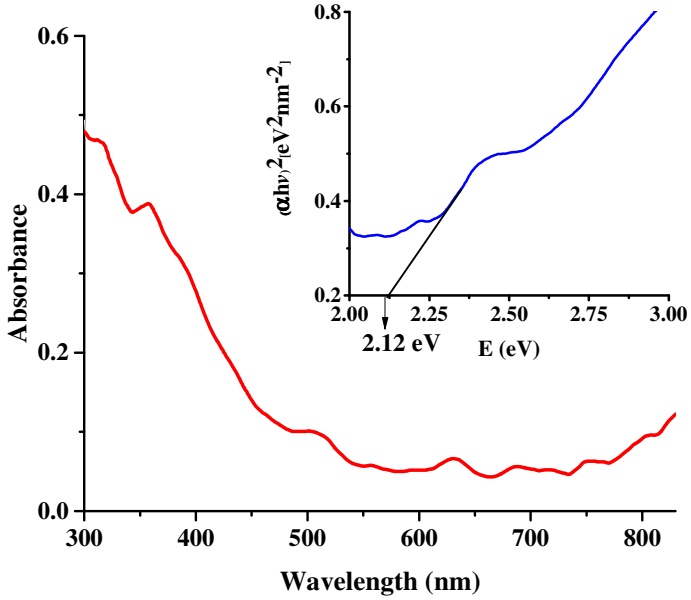


Fig. S3. Diffuse reflectance UV-vis spectra of amorphous {$Mo_{72}Fe_{30}$} (the inset is the Tauc's plots).

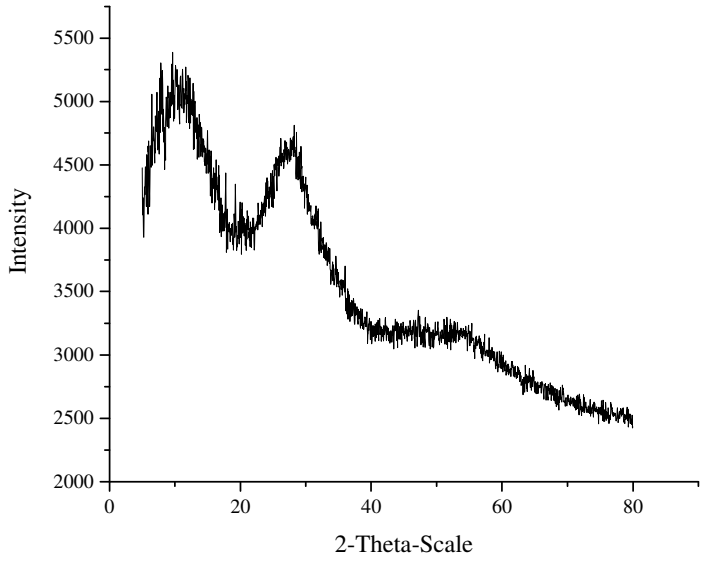


Fig. S4. X-ray diffraction pattern of amorphous {$Mo_{72}Fe_{30}$}

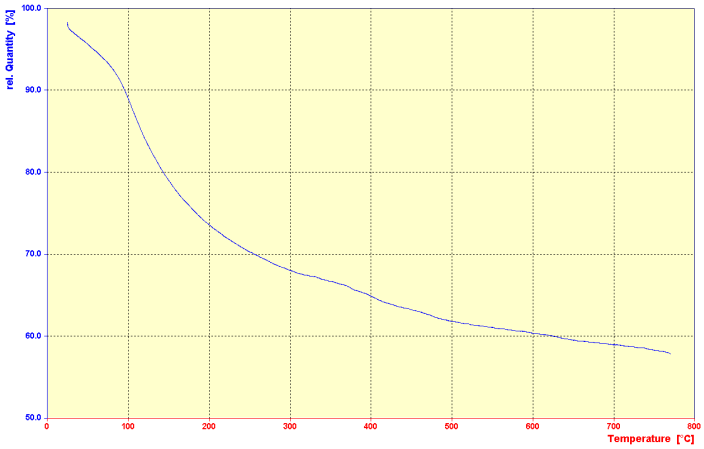
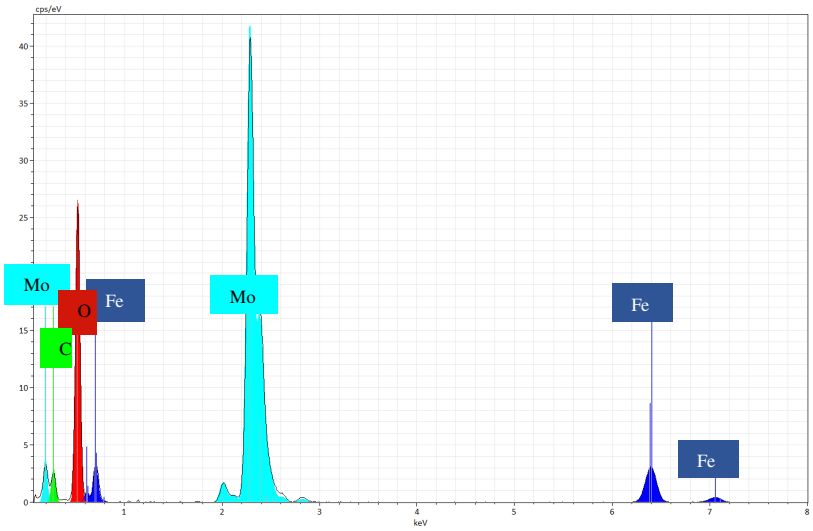


Fig. S5. The TGA of amorphous {$Mo_{72}Fe_{30}$} nanocluster; The first stage of water removal is observed up to ~100°C and results in a 7% weight loss. Then there is second stage of water and carbon dioxide (360°C) removal. The weight loss was 27%.



Element	W%	A%
C	5.15	11.72
O	41.45	70.85
Fe	10.72	5.25
Mo	42.68	12.18

Fig. S6. EDS elemental analysis of amorphous {$Mo_{72}Fe_{30}$}

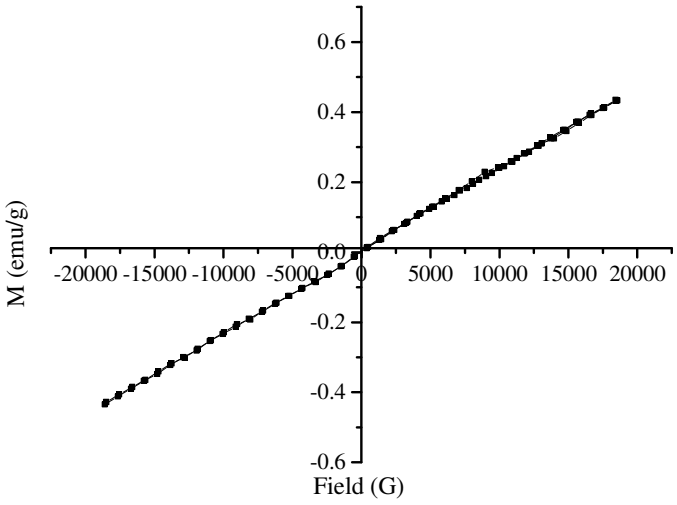


Fig. S7. Magnetization curve of amorphous {$Mo_{72}Fe_{30}$}

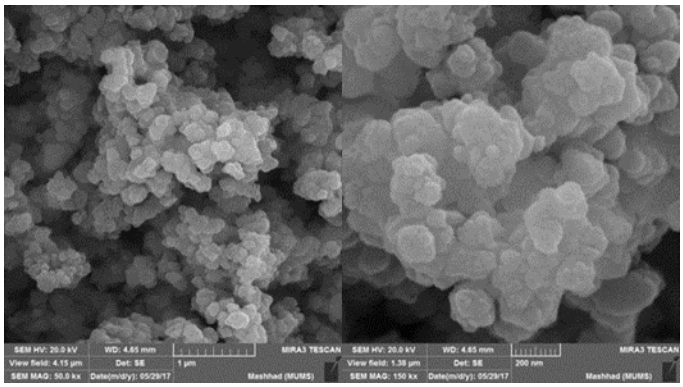


Fig. S8. HRSEM image of amorphous {$Mo_{72}Fe_{30}$}

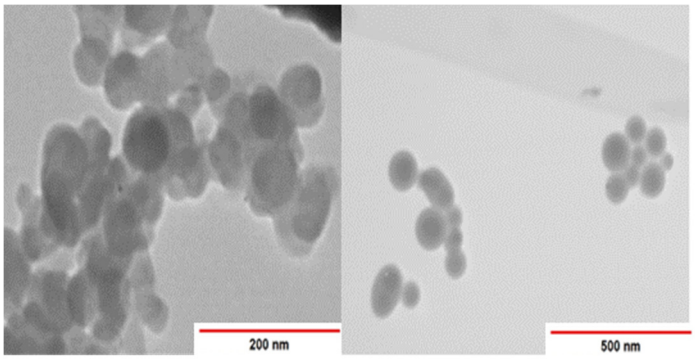


Fig. S9. TEM images of amorphous {$Mo_{72}Fe_{30}$}

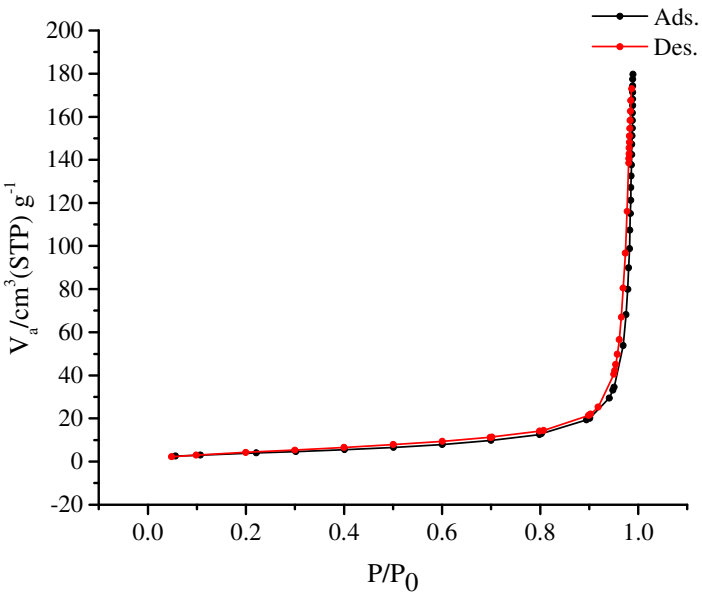


Fig. S10. N_2 adsorption–desorption isotherms of amorphous {$Mo_{72}Fe_{30}$}

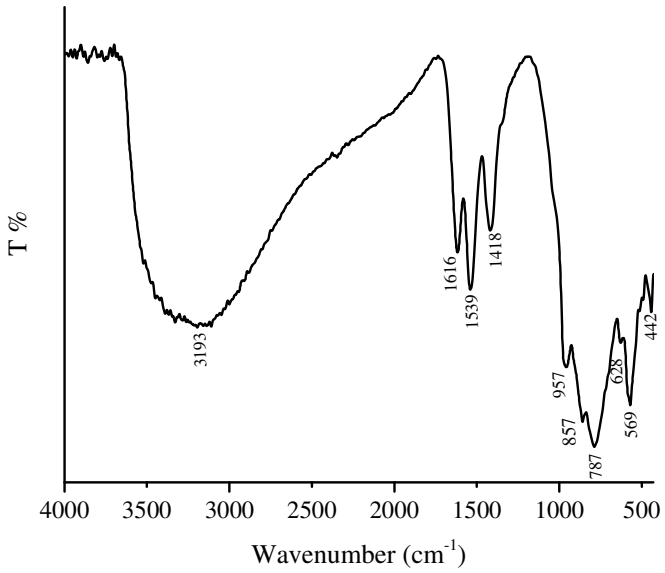


Fig. S11. FT-IR spectra of crystalline {$Mo_{72}Fe_{30}$}

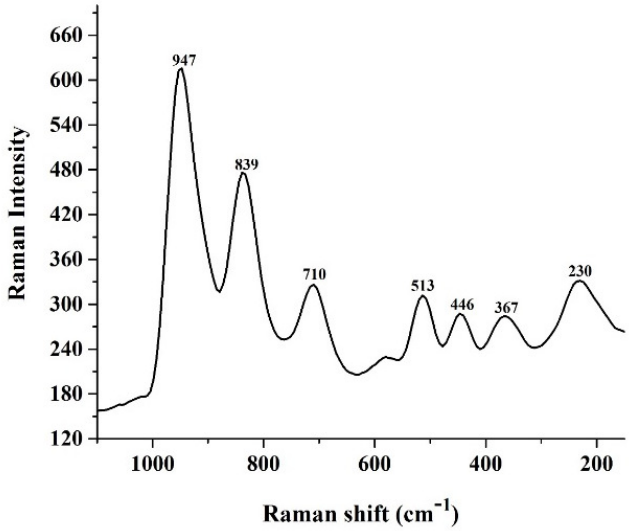


Fig. S12. Raman spectra of crystalline {$Mo_{72}Fe_{30}$}

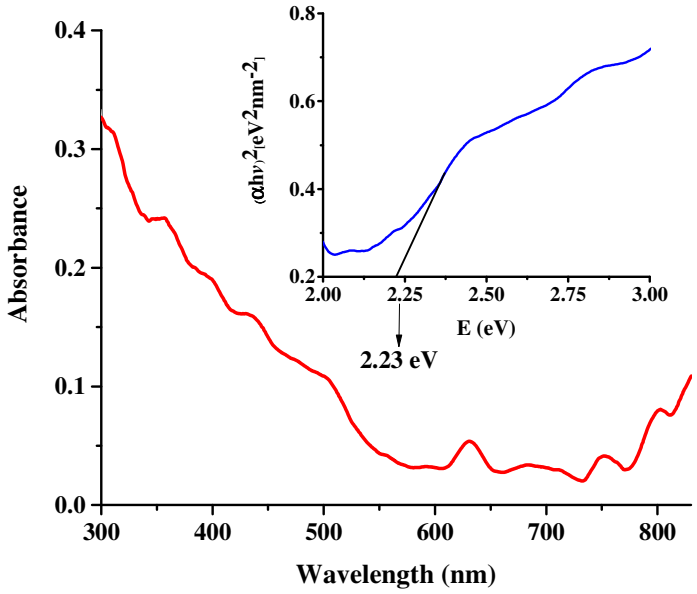


Fig. S13. Diffuse reflectance UV-vis spectra of crystalline {$Mo_{72}Fe_{30}$} (the inset is the Tauc's plots).

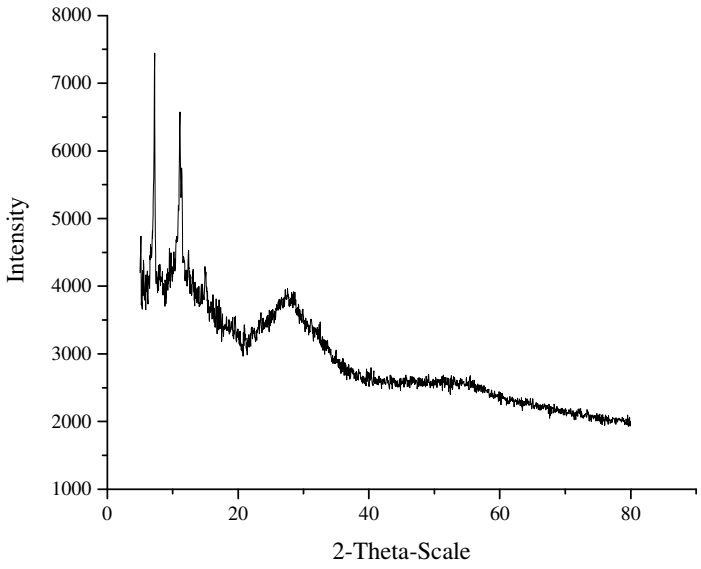


Fig. S14. X-ray diffraction pattern of crystalline {$Mo_{72}Fe_{30}$}.

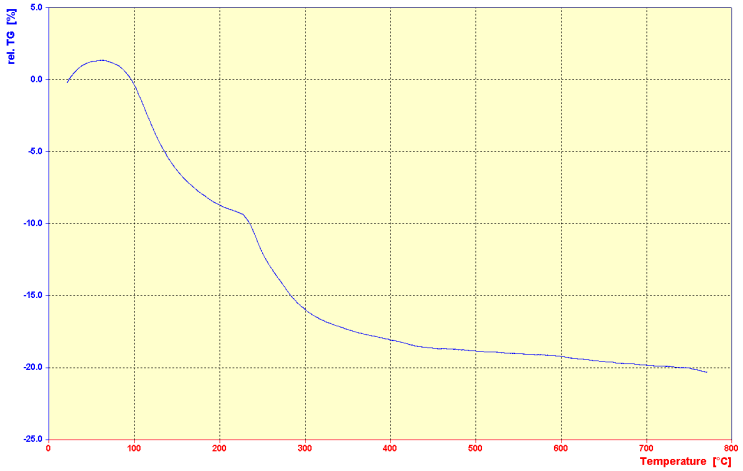
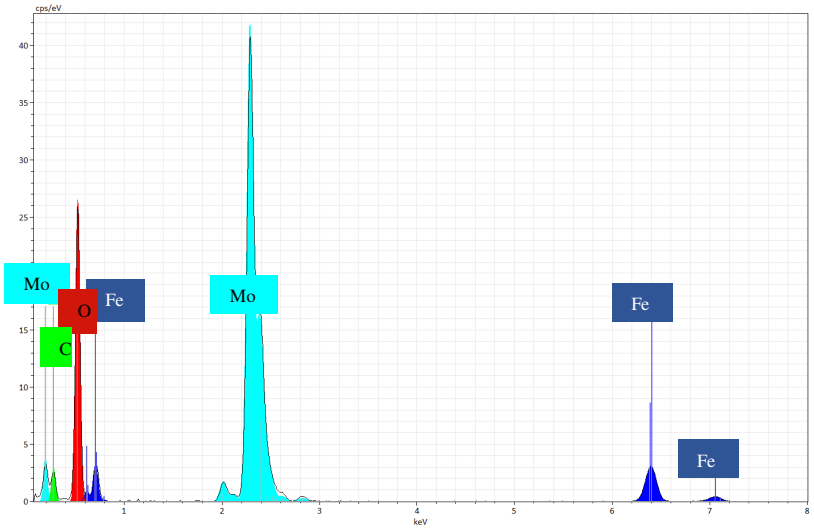


Fig. S15. The TGA of crystalline {$Mo_{72}Fe_{30}$}.



Element	W%	A%
C	5.72	12.86
O	41.65	70.32
Fe	9.91	4.80
Mo	42.72	12.02

Fig. S16. EDS analysis of crystalline {$Mo_{72}Fe_{30}$}

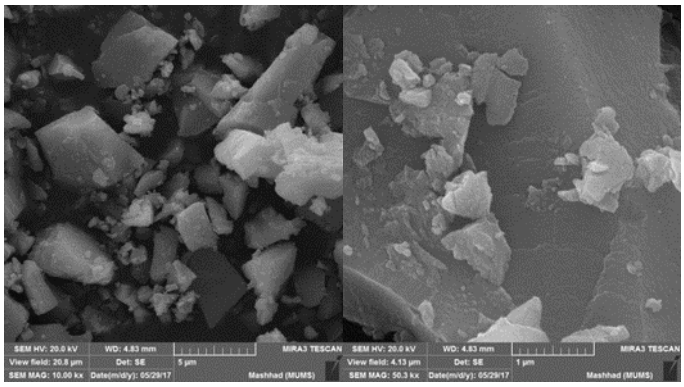


Fig. S17. HRSEM image of crystalline {$Mo_{72}Fe_{30}$}

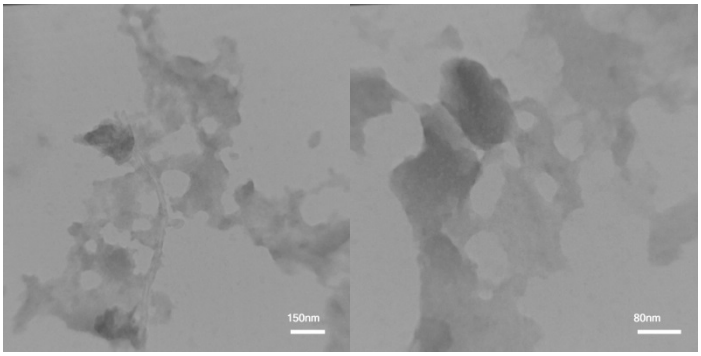


Fig. S18. TEM image of crystalline {$Mo_{72}Fe_{30}$}

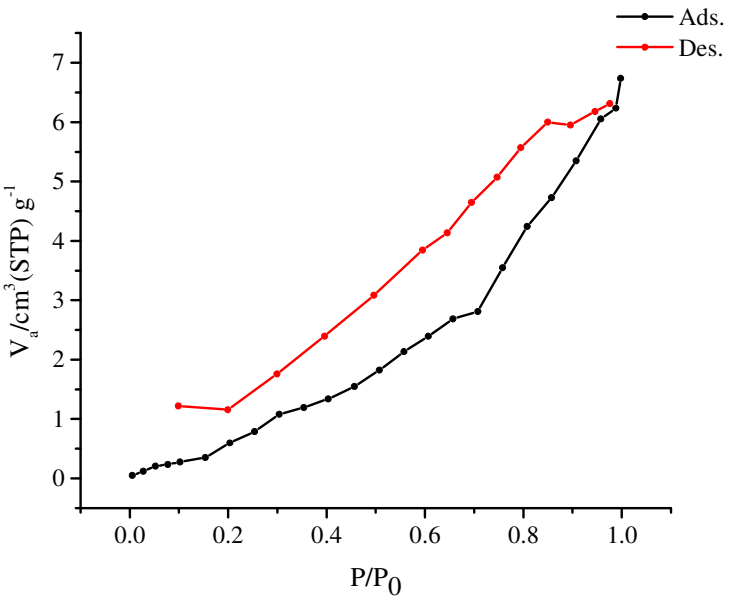


Fig. S19. N_2 adsorption–desorption isotherms of crystalline {$Mo_{72}Fe_{30}$}

References:

1 K. Kuepper, M. Neumann, A. J. M. Al-Karawi, A. Ghosh, S. Walleck, T. Glaser, P. Gouzerh and A. Müller, *J. Clust. Sci.*, 2014, **25**, 301–311.

2 R. Mekala, S. Supriya and S. K. Das, *Inorg. Chem.*, 2016, **55**, 12504–12507.

3 A. Müller, S. Sarkar, S. Q. N. Shah, H. Bögge, M. Schmidtmann, S. Sarkar, P. Kögerler, B. Hauptfleisch, A. X. Trautwein and V. Schünemann, *Angew. Chemie Int. Ed.*, 1999, **38**, 3238–3241.