Electronic Supplementary Information

Green synthesis, optical and magnetic properties of a Mn^{II} metal-organic framework (MOF) that exhibits high heat of H_2 adsorption

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Scheme S1. Coordination modes of $[Mn_3(NDC)_3(DMA)_4]_n$

Fig. S1 PXRD patterns of compound **1** prepared by different routes (a) pattern calculated from the single crystal X-ray data (b) for as-synthesized sample by solvothermal route (c) for sample obtained by solvent assisted mechanochemical route (d) for sample obtained by sonochemical route.

Fig. S2 FT-IR spectrum of **1** synthesized by solvothermal route.

Fig. S3 FT-IR spectrum of **1** synthesized by sonochemical route.

Fig. S4 FT-IR spectrum of **1** synthesized by solvent assisted mechanochemical route.

Fig. S5 PXRD patterns of compound **1** (a) pattern calculated from the single crystal X-ray data (b) for as-synthesized sample by solvothermal route (c) for the sample heated at 250°C for 20h (d) for the degassed/desolvated sample (after adsorption studies) soaked in DMA for 3 days at room temperature.

Fig. S6 Nitrogen adsorption-desorption isotherms of **1'** at 77K.

Fig. S7 Hydrogen adsorption isotherm for **1'** at 77K. The solid line shows the best fit to the data using Langmuir- Freundlich Equation.

Fig. S8 Hydrogen adsorption isotherm for **1'** at 87K. The solid line shows the best fit to the data using Langmuir- Freundlich Equation.

Fig. S9 Enthalpy of hydrogen adsorption for **1'** using Clausius-Clapeyron Equation calculations.

Fig. S10 Carbon dioxide adsorption isotherm for **1'** at 273K. The solid line shows the best fit to the data using Langmuir- Freundlich Equation.

Fig. S11 Carbon dioxide adsorption isotherm for **1'** at 298K. The solid line shows the best fit to the data using Langmuir- Freundlich Equation.

Fig. S12 Enthalpy of carbon dioxide adsorption for **1'** using Clausius-Clapeyron Equation calculations.

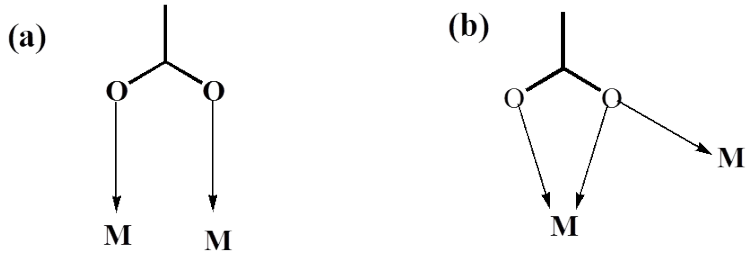
Fig. S13 Temperature dependence of χ_M^{-1} for **1** at 100 Oe.

Fig. S14 M vs H curve in **1** recorded at 2 K.

Fig. S15 Tauc plot for band gap calculation of **1** synthesized by solvothermal route.

Fig. S16 Tauc plot for band gap calculation of **1** synthesized by sonochemical route.

Fig. S17 Tauc plot for band gap calculation of **1** synthesized by mechanochemical route.



Scheme S1. Coordination modes of $[Mn_3(NDC)_3(DMA)_4]_n$

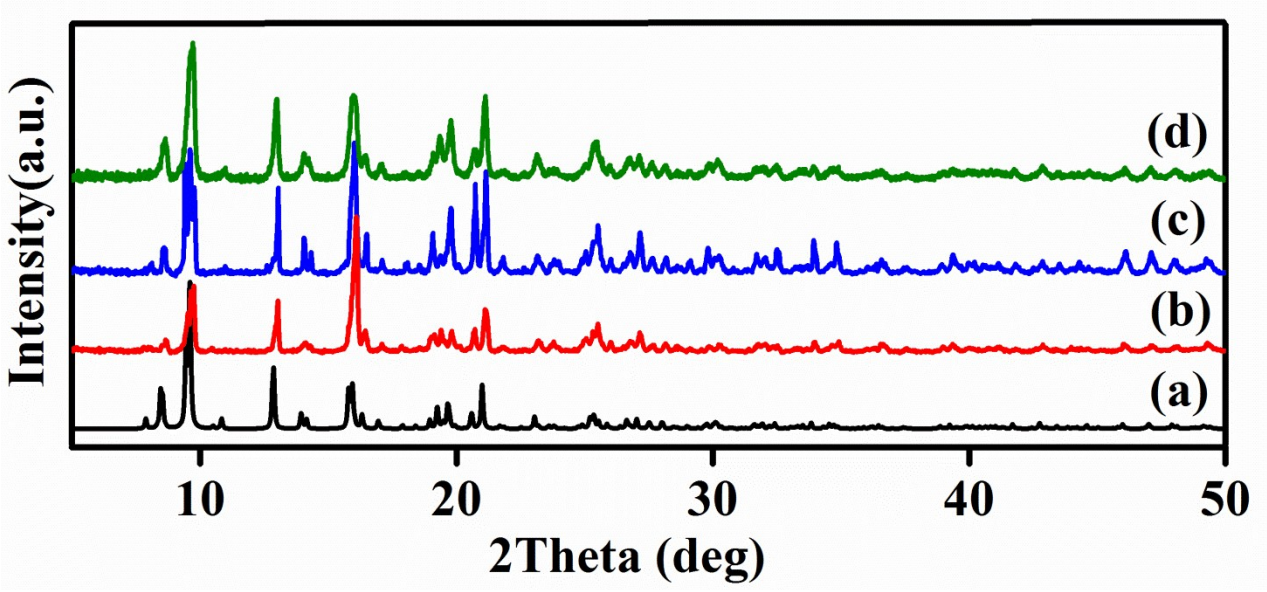


Fig. S1 PXRD patterns of compound **1** prepared by different routes (a) pattern calculated from the single crystal X-ray data (b) for as-synthesized sample by solvothermal route (c) for sample obtained by solvent assisted mechanochemical route (d) for sample obtained by sonochemical route.

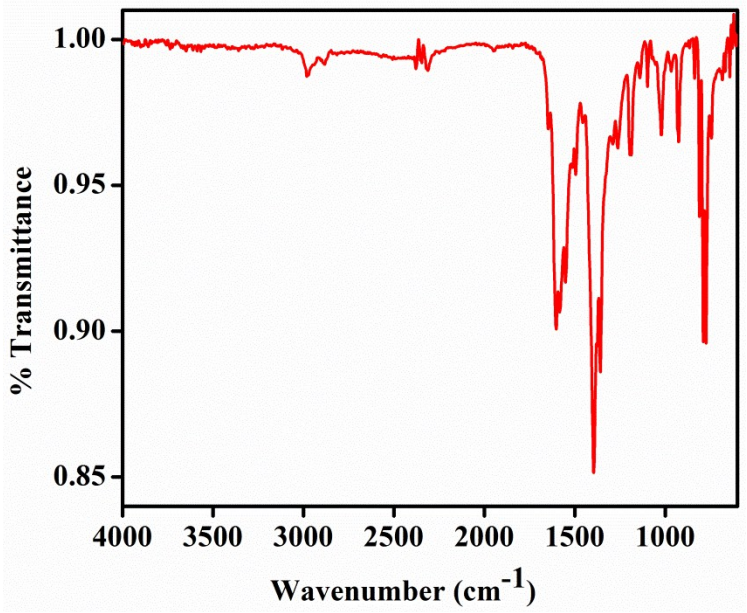


Fig. S2 FT-IR spectrum of **1** synthesized by solvothermal route.

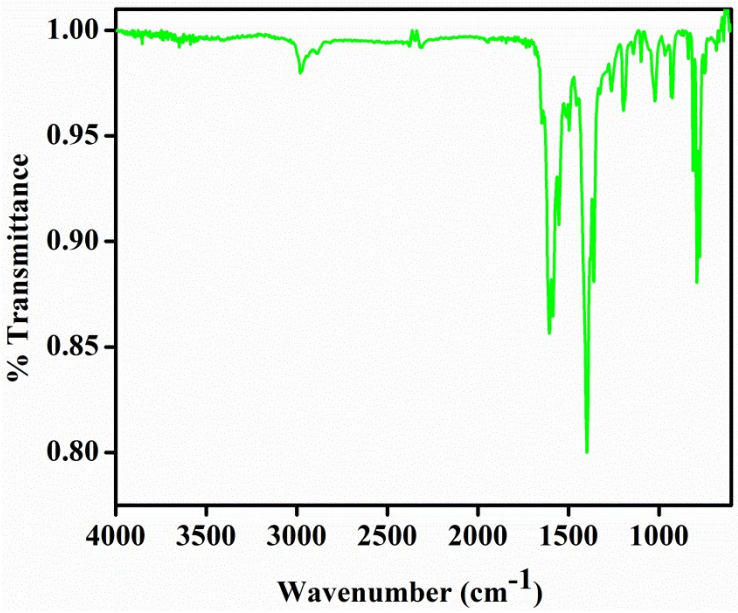


Fig. S3 FT-IR spectrum of **1** synthesized by sonochemical route.

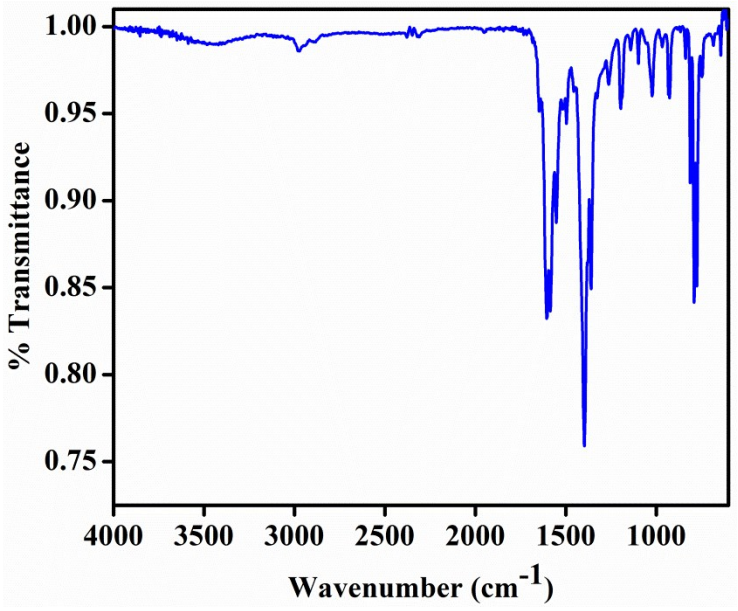


Fig. S4 FT-IR spectrum of **1** synthesized by solvent assisted mechanochemical route.

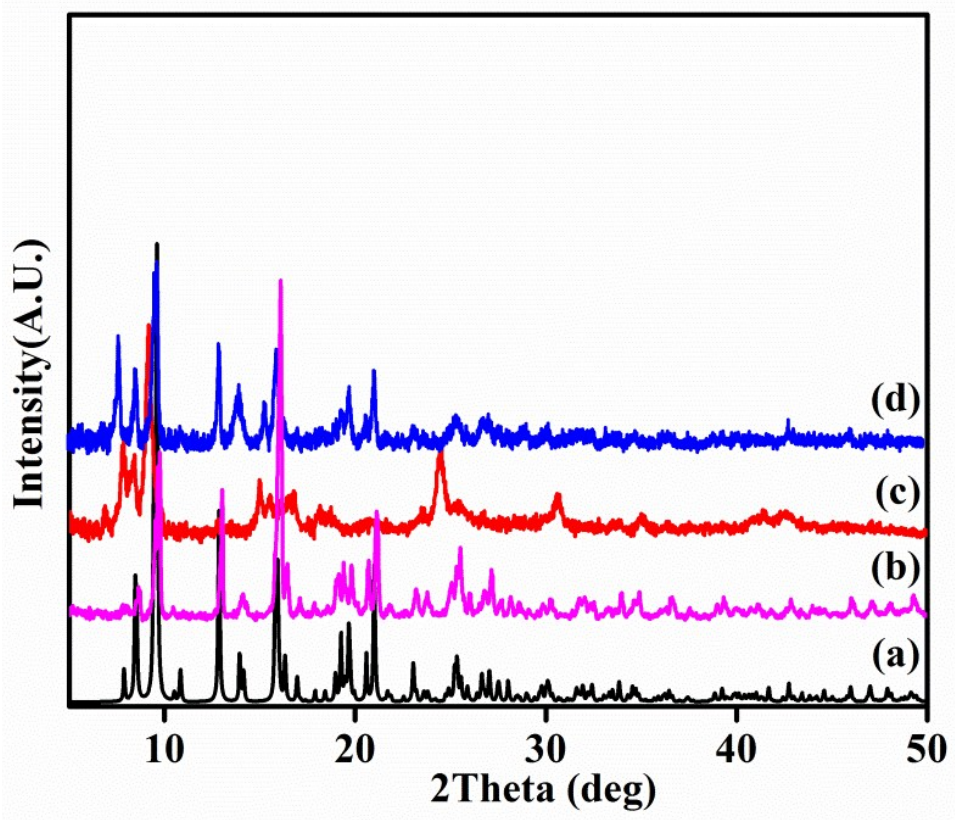


Fig. S5 PXRD patterns of compound **1** (a) pattern calculated from the single crystal X-ray data (b) for as-synthesized sample by solvothermal route (c) for the sample heated at 250^{o}C for 20h (d) for the degassed/desolvated sample (after adsorption studies) soaked in DMA for 3 days at room temperature.

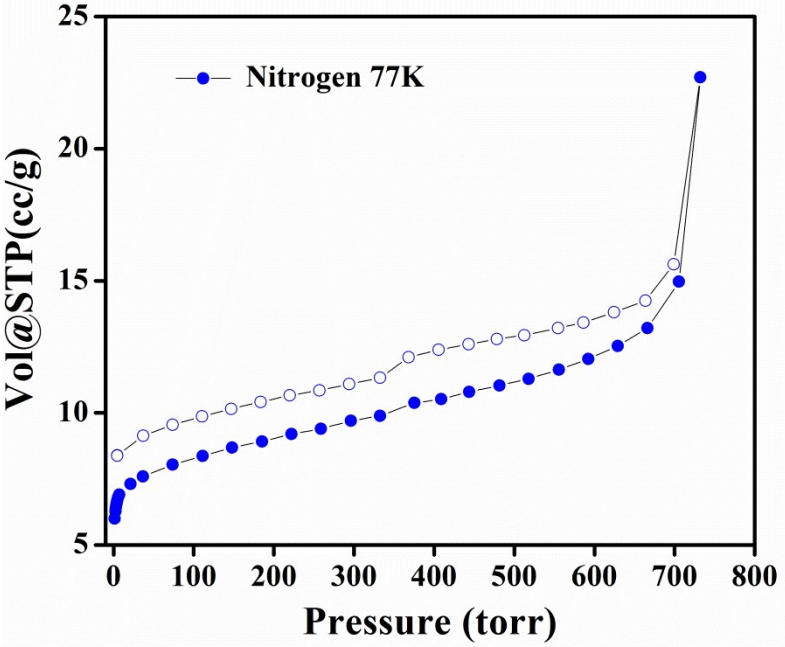


Fig. S6 Nitrogen adsorption-desorption isotherms of **1'** at 77K.

Analysis of Gas adsorption Isotherms

Clausius-Clapeyron Equation[1,2] was used to calculate the enthalpies of hydrogen adsorption. By using Langmuir Freundlich equation[3] an accurate fit was retrieved which gives a precise prediction of hydrogen adsorbed at saturation. A modification of Clausius-Clapeyron equation is used for calculations.

$$\ln\left[\frac{P_1}{P_2}\right] = \Delta H_{ads}\ X\left[\frac{T_2 - T_1}{R\ X\ T_2 T_1}\right] \qquad \text{------(i)}$$

where, P_1 and P_2 = pressures for isotherm at 77K and 87K respectively.

T_1 and T_2 = temperatures for isotherm at 77K and 87K respectively.

ΔH_{ads} = Enthalpy of adsorption.

R = Universal gas constant = 8.314 J/K/mol.

Pressure is a function of amount of gas adsorbed which was determined by using the Langmuir-Freundlich fit.

$$\frac{Q}{Q_m} = \frac{B\ X\ P^{(1/t)}}{1 + (B\ X\ P^{(1/t)})} \qquad \text{------(ii)}$$

where, Q = moles of gas adsorbed.

Q_m = moles of gas adsorbed at saturation.

B and t = constants.

P = Pressure.

By rearranging equation (ii) we get equation (iii)

$$P = \left[\frac{Q/Q_m}{B - (B\ X\ Q/Q_m)}\right]^t \qquad \text{------(iii)}$$

Substituting equation (iii) into equation (i) we get

$$\Delta H_{ads} = \frac{R \times T_1 \times T_2}{T_2 - T_1} \frac{\left[\frac{Q/Q_{m1}}{B - (B \times Q/Q_{m1})}\right]^{t1}}{\left[\frac{Q/Q_{m2}}{B - (B \times Q/Q_{m2})}\right]^{t2}} \quad \text{------(iv)}$$

In equation (iv), subscript 1 and 2 are representing data corresponding to 77K and 87K respectively in case of hydrogen gas and 273K and 298K in case of carbon dioxide gas.

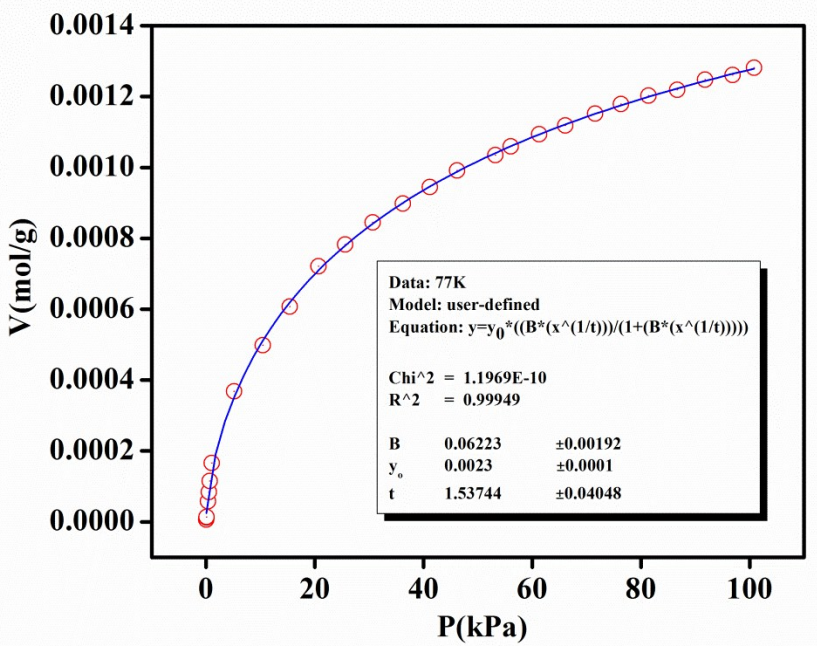


Fig. S7 Hydrogen adsorption isotherm for **1'** at 77K. The solid line shows the best fit to the data using Langmuir- Freundlich Equation.

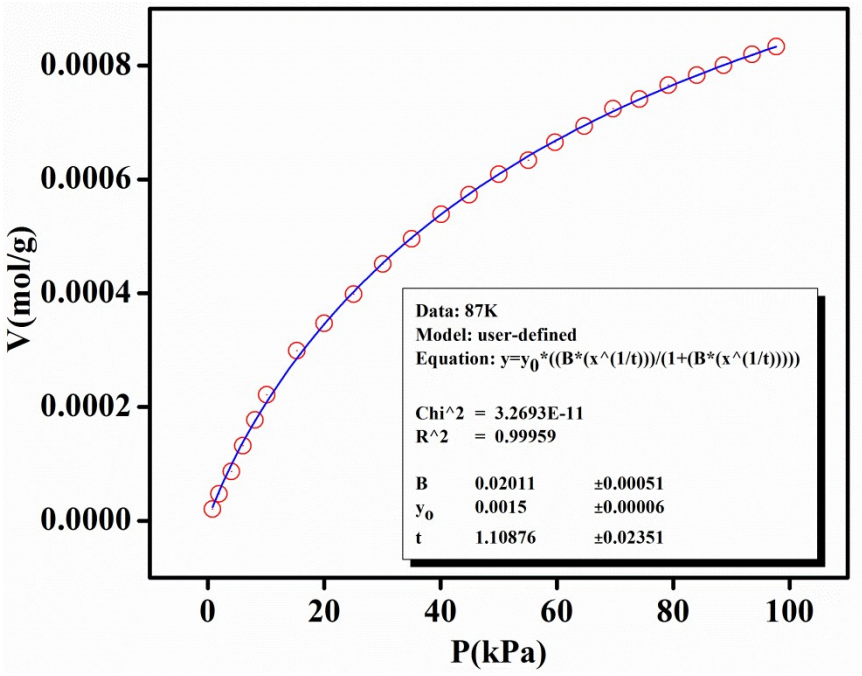


Fig. S8 Hydrogen adsorption isotherm for **1'** at 87K. The solid line shows the best fit to the data using Langmuir- Freundlich Equation.

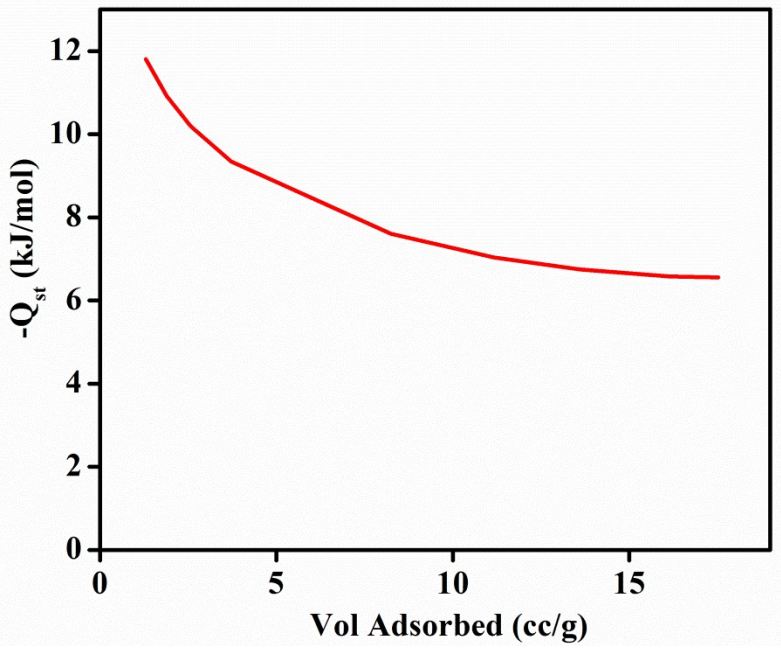


Fig. S9 Enthalpy of hydrogen adsorption for **1'** using Clausius-Clapeyron Equation calculations.

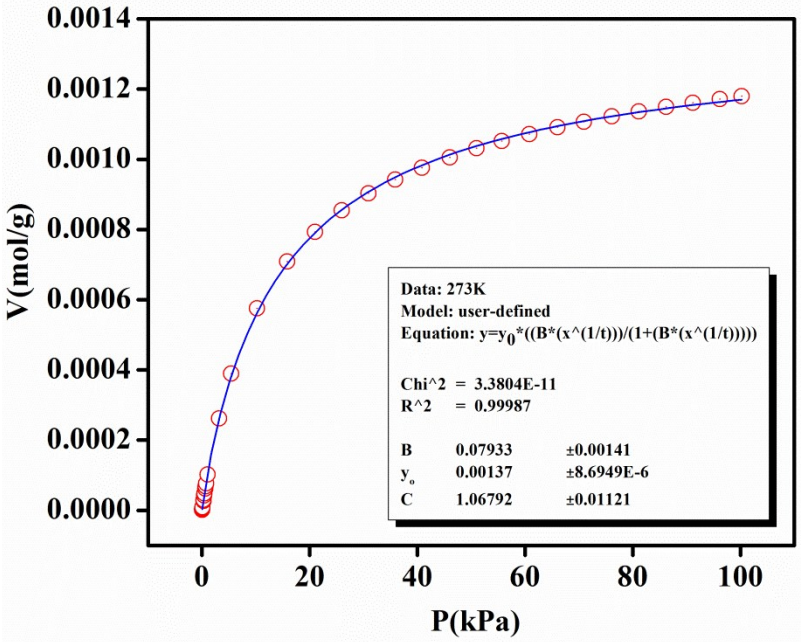


Fig. S10 Carbon dioxide adsorption isotherm for **1'** at 273K. The solid line shows the best fit to the data using Langmuir- Freundlich Equation.

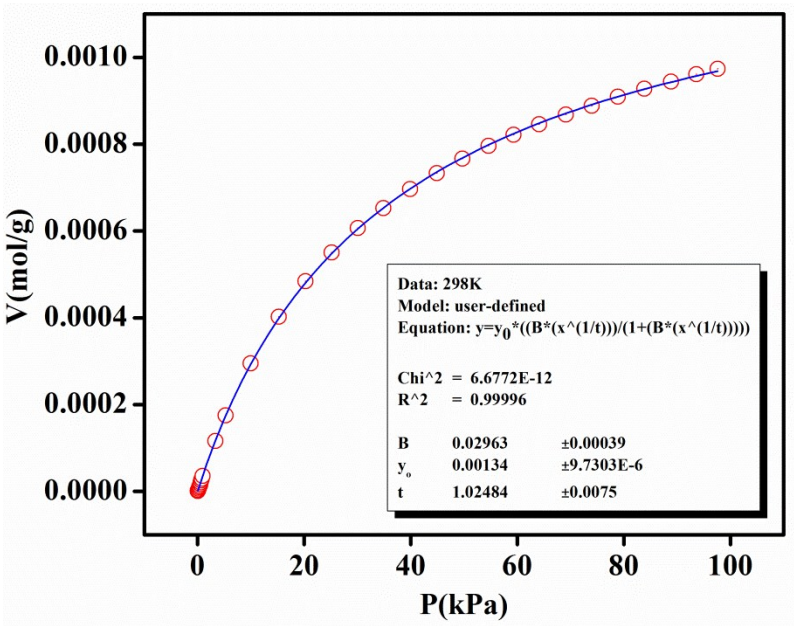


Fig. S11 Carbon dioxide adsorption isotherm for **1'** at 298K. The solid line shows the best fit to the data using Langmuir- Freundlich Equation.

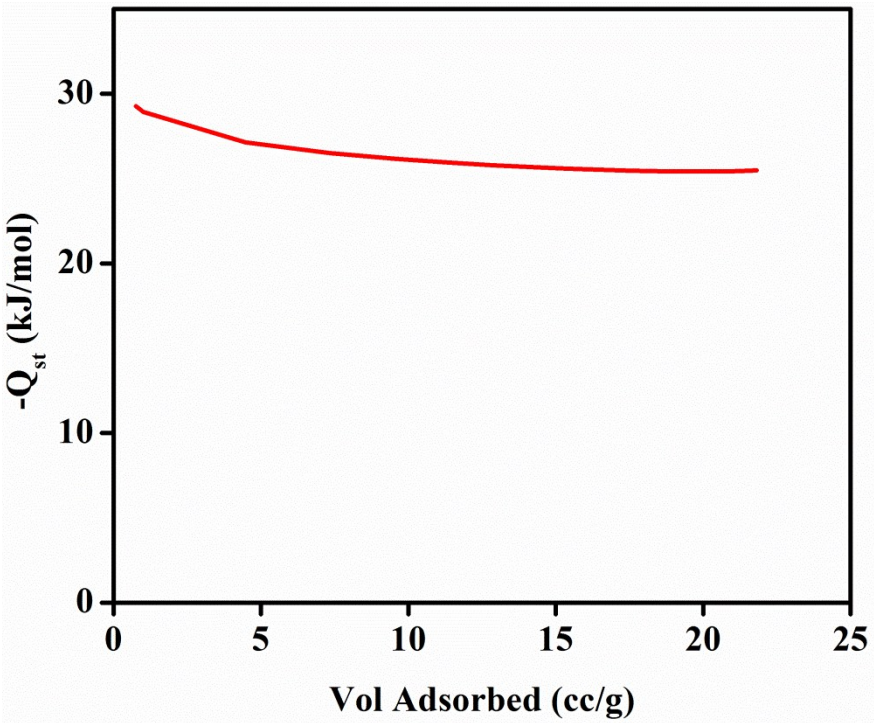


Fig. S12 Enthalpy of carbon dioxide adsorption for **1'** using Clausius-Clapeyron Equation calculations.

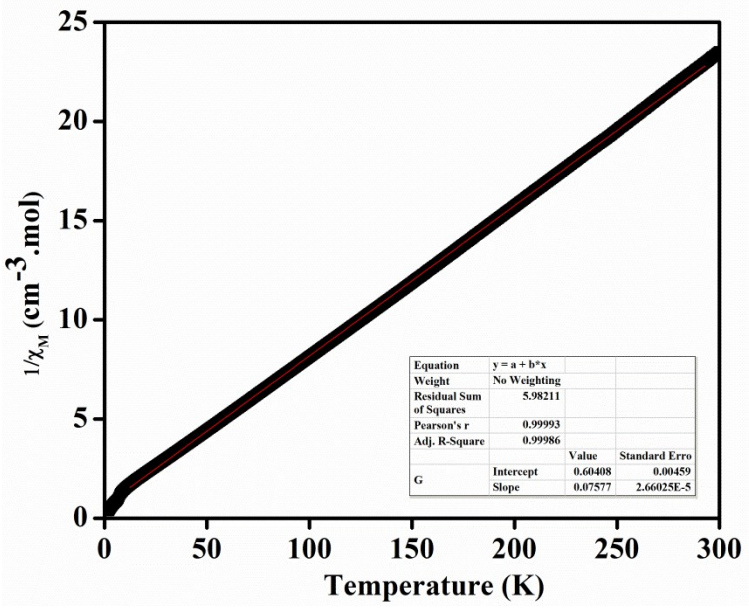


Fig. S13 Temperature dependence of χ_M^{-1} for **1** at 100 Oe.

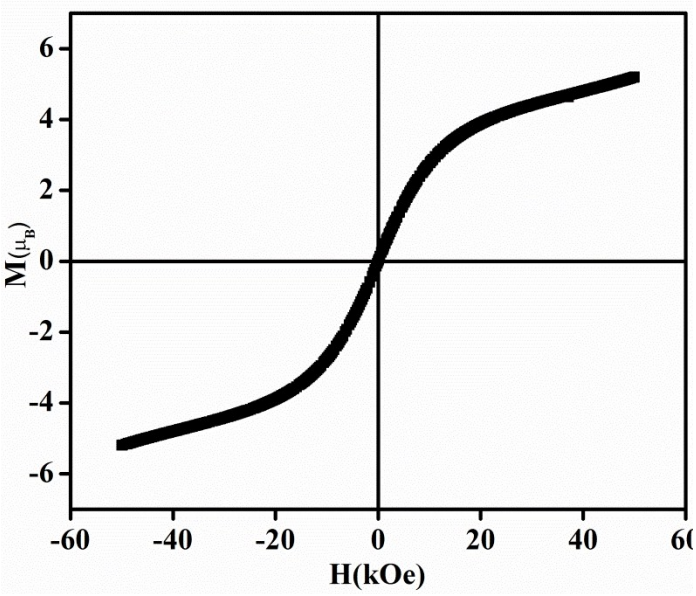


Fig. S14 M vs H curve in **1** recorded at 2 K.

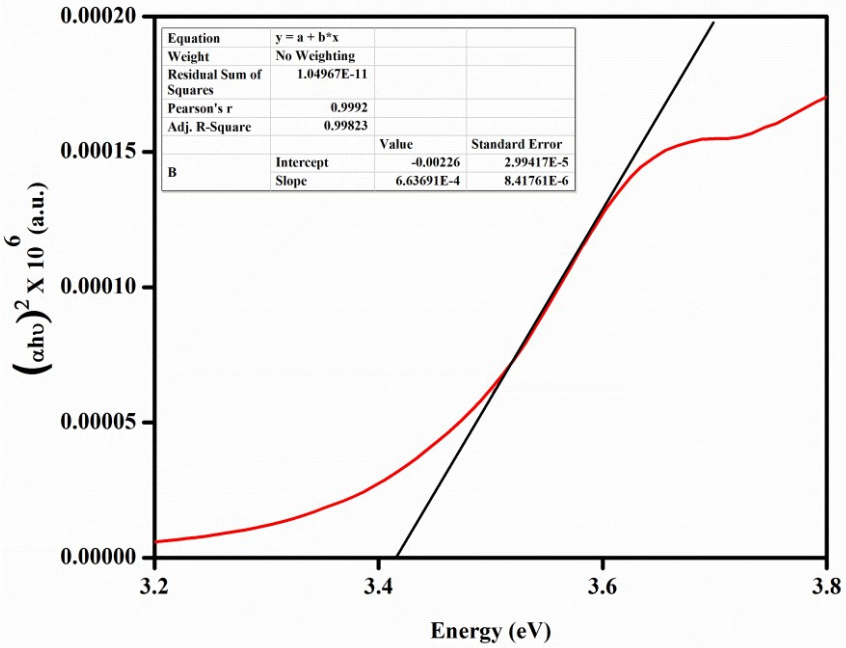


Fig. S15 Tauc plot for band gap calculation of **1** synthesized by solvothermal route.

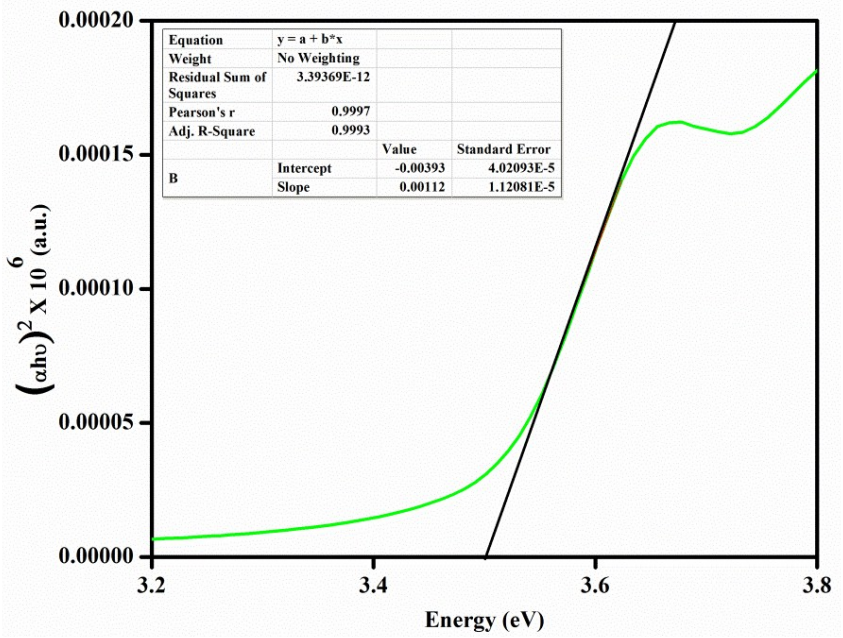


Fig. S16 Tauc plot for band gap calculation of **1** synthesized by sonochemical route.

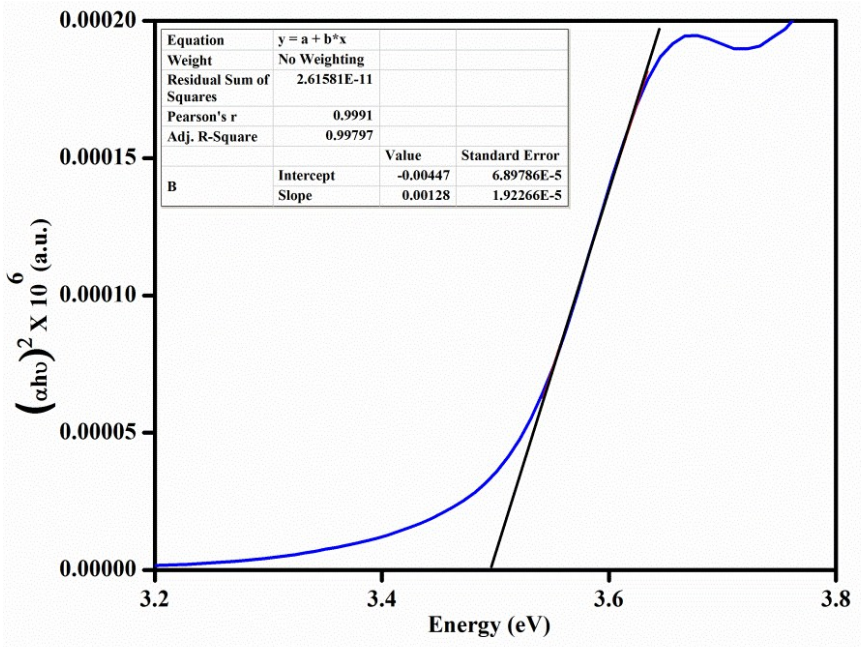


Fig. S17 Tauc plot for band gap calculation of **1** synthesized by mechanochemical route.

References

1. H. Pan, J. A. Ritter, P. B. Balbuena, *Langmuir*, 1998, **14**, 6323-6327.
2. N. Sikdar, A. Hazra, T. K. Maji, *Inorg. Chem.*, 2014, **53**, 5993-6002.
3. R. T. Yang, *Gas Separation by Adsorption Processes*, Butterworth, Boston, 1997.