Electronic Supplementary Information

Green synthesis, optical and magnetic properties of a Mn\textsuperscript{II} metal-organic framework (MOF) that exhibits high heat of H\textsubscript{2} adsorption

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Scheme S1. Coordination modes of [Mn\textsubscript{3}(NDC)\textsubscript{3}(DMA)\textsubscript{4}]\textsubscript{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 $\chi_{M^{-1}}$ 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.

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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.

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

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.

\(\Delta H_{ads}\) = 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.

\[
\frac{Q}{Q_m} = \frac{B \times P^{(1/t)}}{1 + (B \times P^{(1/t)})} \quad \text{(ii)}
\]

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)

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

Substituting equation (iii) into equation (i) we get
\[
\Delta H_{sd} = \frac{R \times T_1 \times T_2}{T_2 - T_1} \left[ \frac{Q/Q_{m1}}{B - (B \times Q/Q_{m1})} \right]^{1/2}
\]

---(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.

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References