Supporting Information

for

Polymer nanocomposites functionalised with nanocrystals of zeolitic imidazolate framework (ZIFs) as ethylene control agents

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[†]These authors contributed equally to the results.

Table of Contents

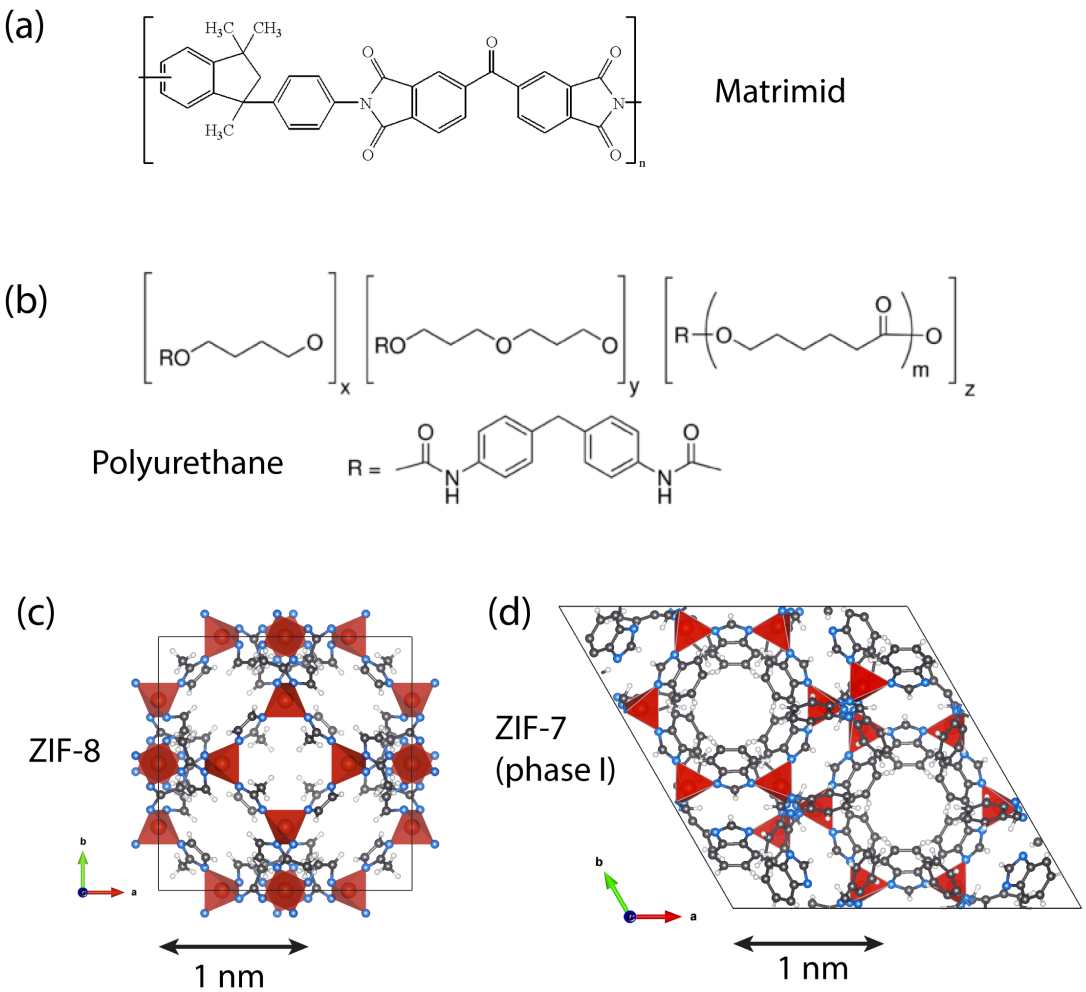

Fig. S1 (a) Chemical structure of the polyimide polymer matrix, termed Matrimid® 5218 (Huntsman Corporation). (b) Chemical structure of the polymer matrix polyurethane (PU) used in this study. It is a MDI (methylene diphenyl diisocyanate)-polyester/polyether polyurethane, whose exact composition is poly[4,4′-methylenebis (phenyl isocyanate)-*alt*-1,4-butanediol/di(propylene glycol)/polycaprolactone]. It is also evident from this figure that there are many sites that can serve as anchors for MOFs to bond with. Image taken from the manufacturer's website (Sigma Aldrich, CAS Number 68084-39-9). Unit cells showing the crystal structures of (c) ZIF-7 (phase I) and (d) ZIF-8, where red is zinc, blue is nitrogen, grey is carbon, white is hydrogen, and the red tetrahedra are ZnN_4. ZIF-8 has a cubic unit cell and its bridging linkers are 2-methylimidazolate (mIm). The unit cell of ZIF-7 (phase I) is hexagonal, and its bridging linkers are 2-benzimidazolate (bIm). Both of the ZIF structures have a sodalite topology[1]. It is anticipated that the ethylene adsorption sites in ZIFs are located in the vicinity of the imidazolate rings, due to favourable interactions with mIm and bIm linkers akin to other gasses reported [2,3].

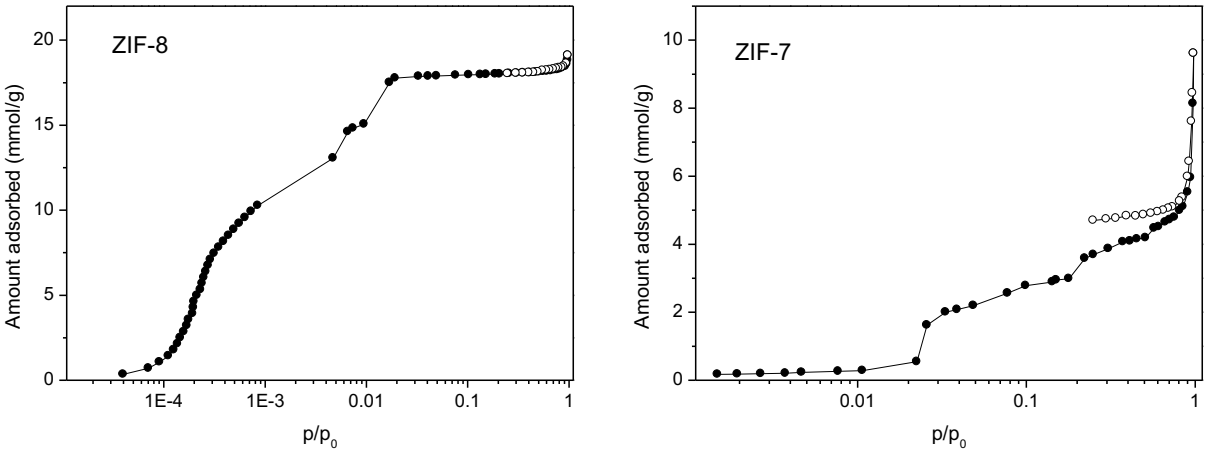

Fig. S2 N_2 adsorption (closed symbols) and desorption (open symbols) isotherms of the nanocrystals of ZIF-8 and ZIF-7 at 77 K. The gate-opening of ZIF-8 was detected at $p/p_0 \sim 0.005$-0.01 (i.e. 0.5-1 kPa) and at $p/p_0 \sim 0.01$-0.05 (i.e. 1-5 kPa), whereas the adsorption performance for ZIF-7, including the phase II to phase I transition, is more complex.

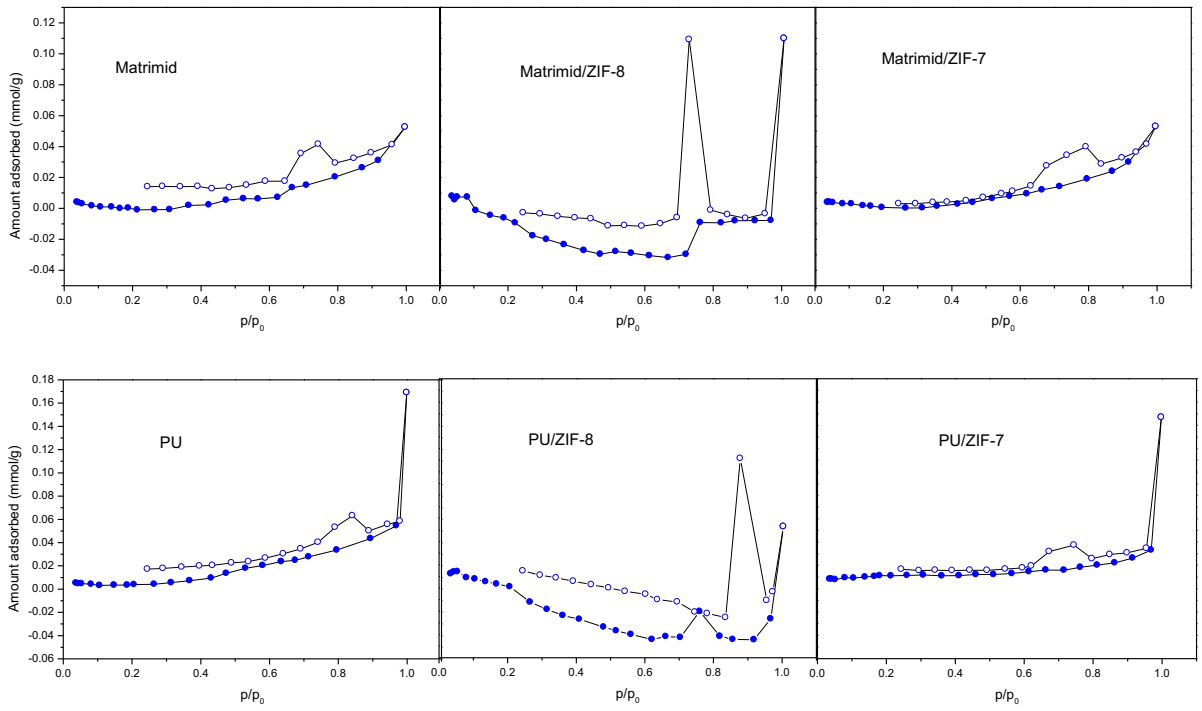

Fig. S3 N_2 adsorption (closed symbol) and desorption (open symbol) isotherms at 77 K of the different neat polymers and its nanocomposites. The data show that there is a negligible uptake of N_2 by the polymer matrix and its nanocomposites. The oscillations most probably due to small variations either in the liquid nitrogen bath level or in the manifold conditions. (Note: although these differences are not appreciable in a normal isotherm, the nearly zero adsorption capacity in these composites amplifies the deviations from high sensitivity of the manometric instrument employed in this study).

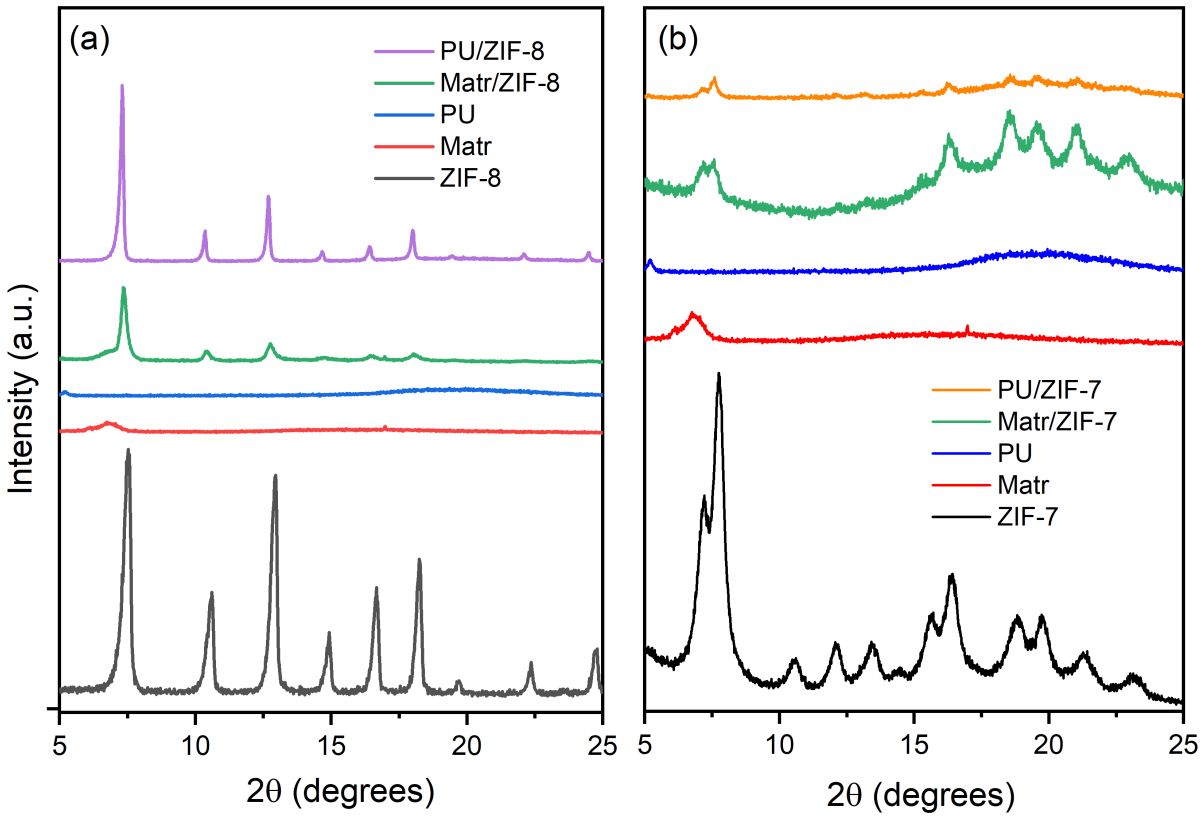

Fig. S4 XRD plots of the samples used in this study, with (a) ZIF-8 and its corresponding nanocomposites, and (b), ZIF-7 and its corresponding nanocomposites

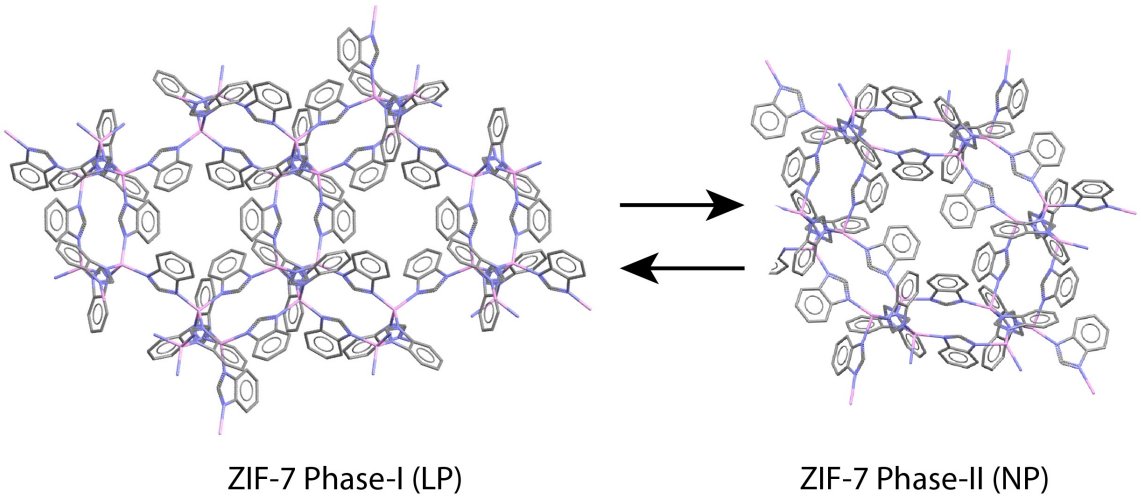

Fig. S5 Large-pore and narrow-pore phases of ZIF-7 denoted as phase-I and phase-II, respectively. Structures adapted from ref. [4].

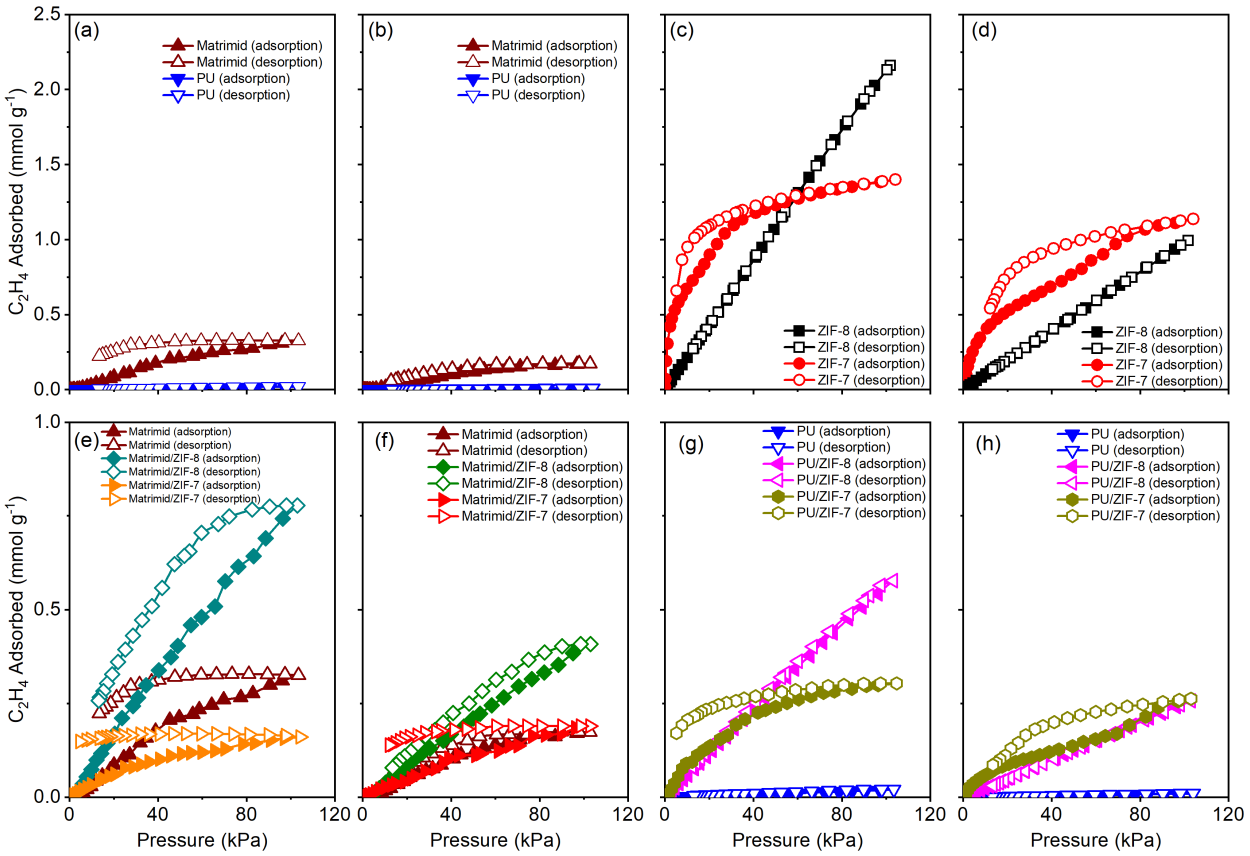

Fig. S6 Compilation of the adsorption/desorption curves for C_2H_4 at 5°C and 35°C, collated from Figures 3 to 5 reported in the main manuscript.

References

[1] Tan, J.C., Bennett, T.D. and Cheetham, A.K., Chemical structure, network topology, and porosity effects on the mechanical properties of Zeolitic Imidazolate Frameworks, *Proc. Natl. Acad. Sci. USA*, **107**, 9938 (2010).

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[4] Sun, Y., Li, Y. and Tan, J.C., Liquid Intrusion into Zeolitic Imidazolate Framework-7 Nanocrystals: Exposing the Roles of Phase Transition and Gate Opening to Enable Energy Absorption Applications, *ACS Appl. Mater. Interfaces*, **10**, 41831 (2018).