Supporting Information

Direct visualisation of supramolecular binding and separation of light hydrocarbons in MFM-300(In)

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1. Experimental

Synthesis of MFM-300(In). H$_2$L (330 mg, 1.00 mmol), In(NO$_3$)$_3$·5H$_2$O (585 mg, 1.50 mmol) were mixed in a DMF/MeCN mixture (30 ml, 2:1 v/v) with conc. HNO$_3$ (1.0 mL) in a 250 mL glass pressure reactor. Then the vessel sealed and heated at 80 °C for 48 h. The resultant flaky white precipitate was then washed with DMF and immersed in an excess of acetone for 3 days with frequent exchange of solvent.$^1$ Yield: 347 mg (42% yield based upon solvent content from microanalysis).

Gas Adsorption Isotherms and Breakthrough Experiments. Gravimetric isotherms (0-1000 mbar) were recorded at 273, 283, 293, 303, and 308 K (temperature controlled water-bath) for C$_2$H$_2$, C$_2$H$_4$, C$_2$H$_6$, C$_3$H$_4$, C$_3$H$_6$ and C$_3$H$_8$ and at 195 K (dry ice/acetone) for C$_2$H$_2$, C$_2$H$_4$, C$_2$H$_6$. Data were collected using an IGA-003 system (Hiden Isochema, Warrington, UK) equipped with a turbomolecular pumping system. Acetone exchanged samples were loaded into the system and degassed at 120 °C and 1 × 10$^{-6}$ mbar for 20 h to give a dry, desolvated material of typical mass ca. 50 mg. Ultra-pure research grade (99.99 %) gases were purchased from Air Liquide or BOC and used as received. C$_3$H$_2$ was purified by dual-stage cold trap systems operated at 195 K (dry ice) and an activated carbon filter before introduction to the IGA system. Dynamic breakthrough experiments were conducted on a Hiden Isochema IGA-003 with ABR attachments and a Hiden Analytical mass spectrometer by using a fixed-bed tube packed with 750 mg of MFM-300(In) powder. The sample was heated at 120 °C under a flow of dry He for 12h for activation, and then cooled to room temperature (293 K). Single-component gas breakthrough experiments with an inlet gas flow rate of 2 mL min$^{-1}$ diluted in a flow of He (total flow rate of 20 mL min$^{-1}$) were measured through a fixed-bed packed with MFM-300(In).

For equimolar mixtures of hydrocarbons, the flow rate of 2.0 mL min$^{-1}$/2.0 mL min$^{-1}$ diluted in He (total flow rate of 20 mL min$^{-1}$) was applied. Dynamic breakthrough experiments for 1:99 mixtures of C$_2$H$_2$/C$_2$H$_4$, C$_2$H$_2$/C$_2$H$_6$, and C$_2$H$_2$/C$_3$H$_4$ were conducted at the rate of 0.2 mL min$^{-1}$/19.8 mL min$^{-1}$. All breakthrough experiments were conducted at a total flow of 20 mL min$^{-1}$ at 293 K. The concentration of hydrocarbon gas at the outlet was determined by mass spectrometry and compared with the inlet concentration $C_0$, where $C/C_0 = 1$ indicates complete breakthrough.

Table S1. Physical parameters for C$_2$ and C$_3$ hydrocarbons.$^{2-8}$

| Gas     | Molecular size (Å$^3$) | Boiling point (K) | Kinetic diameter (Å) |
|---------|------------------------|-------------------|----------------------|
| C$_2$H$_2$ | 3.3 × 3.3 × 5.7 | 188.40 | 3.3 |
| C$_2$H$_4$ | 3.3 × 4.2 × 4.8 | 169.42 | 4.2 |
| C$_2$H$_6$ | 3.8 × 4.1 × 4.8 | 184.55 | 4.4 |
| C$_3$H$_4$ | 4.0 × 4.1 × 6.5 | 249.8 | 4.8 |
| C$_3$H$_6$ | 4.2 × 5.3 × 6.4 | 225.46 | 4.7 |
| C$_3$H$_8$ | 4.2 × 4.8 × 6.8 | 231.02 | 4.3-5.1 |
2. Powder X-ray Diffraction

![PXRD patterns](image)

Figure S1. PXRD patterns of as-synthesised, activated MFM-300(In), and sample after breakthrough experiments.

3. Thermogravimetric Analysis

The as-synthesised, acetone exchanged and activated MFM-300(In) were heated from room temperature to 510 °C at a rate of 5 °C min⁻¹ under a flow of air. The result shows that the MFM-300(In) can tolerate up to 400 °C confirming its high thermal stability.

![TGA curves](image)

Figure S2. TGA curves for as-synthesised, acetone-exchanged and activated MFM-300(In).
4. Characterisation of Porosity

Figure S3. $\text{N}_2$ adsorption/desorption isotherms for a) MFM-300(Al) and c) MFM-300(In) at 77 K. Micropore size distribution plots for b) MFM-300(Al) and d) MFM-300(In).

5. Additional Gas Adsorption Isotherms

Figure S4. Adsorption/desorption isotherms for acetylene in MFM-300(In).
Figure S5. Adsorption/desorption isotherms for ethylene in MFM-300(In).

Figure S6. Adsorption/desorption isotherms for ethane in MFM-300(In).
Figure S7. Adsorption/desorption isotherms for propyne in MFM-300(In).

Figure S8. Adsorption/desorption isotherms for propene in MFM-300(In).
Figure S9. Adsorption/desorption isotherms for propane in MFM-300(In).
6. Comparison of $\text{C}_2\text{H}_2$, $\text{C}_2\text{H}_4$, $\text{C}_2\text{H}_6$, $\text{C}_3\text{H}_4$, $\text{C}_3\text{H}_6$ and $\text{C}_3\text{H}_8$ isotherms

![Graph showing adsorption isotherms at 273 K for $\text{C}_2\text{H}_2$, $\text{C}_2\text{H}_4$, $\text{C}_2\text{H}_6$, $\text{C}_3\text{H}_4$, $\text{C}_3\text{H}_6$ and $\text{C}_3\text{H}_8$ in MFM-300(In) to a pressure of 1 bar. Desorption isotherms are omitted for clarity; the nature of reversible adsorption has been demonstrated above.]

**Figure S10.** Adsorption isotherms at 273 K of $\text{C}_2\text{H}_2$, $\text{C}_2\text{H}_4$, $\text{C}_2\text{H}_6$, $\text{C}_3\text{H}_4$, $\text{C}_3\text{H}_6$ and $\text{C}_3\text{H}_8$ in MFM-300(In) to a pressure of 1 bar. Desorption isotherms are omitted for clarity; the nature of reversible adsorption has been demonstrated above.

![Graph showing adsorption isotherms at 303 K for $\text{C}_2\text{H}_2$, $\text{C}_2\text{H}_4$, $\text{C}_2\text{H}_6$, $\text{C}_3\text{H}_4$, $\text{C}_3\text{H}_6$ and $\text{C}_3\text{H}_8$ in MFM-300(In) to a pressure of 1 bar. Desorption isotherms are omitted for clarity; the nature of reversible adsorption has been demonstrated above.]

**Figure S11.** Adsorption isotherms at 303 K of $\text{C}_2\text{H}_2$, $\text{C}_2\text{H}_4$, $\text{C}_2\text{H}_6$, $\text{C}_3\text{H}_4$, $\text{C}_3\text{H}_6$ and $\text{C}_3\text{H}_8$ in MFM-300(In) to a pressure of 1 bar. Desorption isotherms are omitted for clarity; the nature of reversible adsorption has been demonstrated above.
7. Analysis and Derivation of the Isoestic Heats of Adsorption

To estimate the isosteric enthalpies (ΔH) for adsorption of C₂H₂, C₂H₄, C₂H₆, C₃H₄, C₃H₆ and C₃H₈ isotherms between 273–308 K were fitted to the Van ’ Hoff equation;

\[
\ln P = \frac{\Delta H}{RT} - \frac{\Delta S}{R}
\]

(1)

where \( p \) is pressure in Pa, \( T \) is the temperature, and \( R \) is the ideal gas constant. All linear fittings show \( R^2 \) above 0.99 indicating the consistency of the isotherm data and of the fitting.

**Figure S12.** Linear fitting of 1/T vs LnP at intervals of 0.1 mmolg⁻¹ for substrates in MFM-300(In) to determine the isosteric heat of adsorption by the Van ’ Hoff method.
Figure S13. Entropy of adsorption for C\textsubscript{2} and C\textsubscript{3} hydrocarbons in MFM-300(In) calculated from isotherm data.
8. Calculation of IAST selectivity for gas adsorption.

To estimate the selectivity observed for each substrate isotherm data at 293 K were fitted using the dual-site Langmuir-Freundlich (DSLF) model (equation 2).

\[
N^*(f) = \frac{q_1 b_1 P^{n_1}}{1 + b_1 P^{n_1}} + \frac{q_2 b_2 P^{n_2}}{1 + b_2 P^{n_2}} \quad [2]
\]

where \( P \) is the pressure of the bulk gas at equilibrium with the adsorbed phase, \( q_i \) is the maximum adsorption amount, \( b_i \) is the affinity constant and \( n_i \) is the deviation from the simple Langmuir equation. Using this fitting, the IAST selectivity can be calculated by equation 3.

\[
S = \frac{x_1 / y_1}{x_2 / y_2} \quad [3]
\]

where \( x_i \) is the amount of each component adsorbed and \( y_i \) is the mole fraction of each component at equilibrium.
Figure S14. Selectivities as a function of pressure for C\textsubscript{2} and C\textsubscript{3} hydrocarbons in MFM-300(In) calculated by IAST from single component adsorption isotherms.
Figure S15. IAST fitting of isotherms for (a) C\textsubscript{2}H\textsubscript{2}, (b) C\textsubscript{2}H\textsubscript{4}, (c) C\textsubscript{2}H\textsubscript{6}, (d) C\textsubscript{3}H\textsubscript{4}, (e) C\textsubscript{3}H\textsubscript{6} and (f) C\textsubscript{3}H\textsubscript{8}-loaded MFM-300(In) at 293 K and up to 1 bar.
9. Dynamic Breakthrough Experiments

Calculation of dynamic adsorption capacity and productivity

To determine the dynamic adsorption capacity, the uptake of each component \( n_m \) was calculated based on the breakthrough curves by the equation described as follows:

\[
V_m = \frac{\int_0^t v_{gas\ out} \, dt - V_{dead}}{W_{MOF}}
\]

\[
n_m = \frac{PV_m}{RT}
\]

where \( v_{gas\ out} \) is the flow rate of the target gas with the unit of mL min\(^{-1}\); \( V_{dead} \) is the dead volume of the system (mL); \( W \) represents the mass of MFM-300(In) packed in the breakthrough bed (g); \( t \) is the retention time for the specific gas (min); \( P \) is atmospheric pressure (Kpa); \( R \) is Avogadro constant. \( T \) is the measurement temperature (K).

The productivity \( q_m \) of \( \text{C}_2\text{H}_4 \) and \( \text{C}_3\text{H}_8 \) was determined through the breakthrough amount of \( \text{C}_2\text{H}_4 \) and \( \text{C}_3\text{H}_8 \), which is calculated by integration of the breakthrough curves during a period from \( t_1 \) to \( t_2 \) during which the gas purity is greater than 99.9%:

\[
q_m = \frac{\int_{t_1}^{t_2} v_{gas\ out} \, dt - V_{dead}}{W_{MOF}}
\]

where \( v_{gas\ out} \) is the flow rate of target gas with the unit of mL min\(^{-1}\); \( V_{dead} \) is the dead volume of the system (mL); \( W \) represents the mass of MFM-300(In) packed in the breakthrough bed (g);

**Figure S16.** Breakthrough plots for single component (a) \( \text{C}_2\text{H}_2 \) and (b) \( \text{C}_3\text{H}_8 \) with an inlet gas flow rate of 2.0 mL min\(^{-1}\) diluted in He through MFM-300(In) at a total flow of 20 mL min\(^{-1}\) at 293 K.
Figure S17. Dynamic breakthrough plots for equimolar mixtures of (a) C$_2$H$_4$/C$_2$H$_2$, (b) C$_2$H$_6$/C$_2$H$_2$, (c) C$_3$H$_8$/C$_3$H$_4$ and (d) C$_3$H$_8$/C$_3$H$_6$ with an inlet gas flow rate of 2.0 mL min$^{-1}$/2.0 mL min$^{-1}$ diluted in He through a fixed-bed packed with MFM-300(In) at a total flow of 20 mL min$^{-1}$ at 293 K.

Figure S18. Dynamic breakthrough experiments for 1:99 mixtures of (a) C$_2$H$_2$/C$_2$H$_4$, (b) C$_2$H$_6$/C$_2$H$_4$, and (c) C$_2$H$_6$/C$_3$H$_6$ with an inlet gas flow rate of 0.2 mL min$^{-1}$/19.8 mL min$^{-1}$ through a fixed-bed packed with MFM-300(In) at a total flow rate of 20 mL min$^{-1}$ at 293 K.
Table S2. Dynamic adsorption of substrates on MFM-300(In) based on the breakthrough experiments.

| Substrate                  | Amount adsorbed (mmol g$^{-1}$) |
|----------------------------|----------------------------------|
| C$_2$H$_2$                 | 1.4                              |
| C$_3$H$_4$                 | 1.0                              |
| C$_3$H$_6$                 | 1.6                              |
| C$_3$H$_4$                 | 4.4                              |
| C$_3$H$_6$                 | 3.5                              |
| C$_3$H$_8$                 | 3.1                              |
| C$_2$H$_4$ in equimolar C$_2$H$_6$/C$_2$H$_4$ mixture | 0.7 |
| C$_3$H$_6$ in equimolar C$_2$H$_6$/C$_2$H$_4$ mixture | 1.4 |
| C$_3$H$_4$ in equimolar C$_3$H$_4$/C$_3$H$_6$ mixture | 4.6 |
| C$_3$H$_6$ in equimolar C$_3$H$_4$/C$_3$H$_6$ mixture | 3.1 |
Table S3. Comparison of separation performance for state-of-the-art MOFs.

| MOF         | Pore size (Å) | Pore volume (cm³ g⁻¹) | BET surface area (m² g⁻¹) | T (K) | Uptake (mmol g⁻¹) | Selectivity C₂H₆/C₂H₄ : 50/50 | Qst (KJ mol⁻¹) C₂H₆/C₂H₄ | C₂H₄ Productivity (L/kg) |
|-------------|---------------|------------------------|---------------------------|-------|-------------------|--------------------------------|-----------------------------|--------------------------|
| MFM-300(In) This work | 6.8           | 0.43                   | 1030                       | 293 K | 5.1/4.9           | 1.7                            | 30/28                       | 4.6 L/kg                 |
| MFM-300(Al)⁹ | 6.5           | 0.43                   | 1370                       | 293 K | 0.85/4.28         | /                              | /                          | /                        |
| JNU-2¹⁰     | 3.4, 4.6, 6.7 Å| 0.56                   | 1219                       | 298 K | 4.19/3.68         | 1.6                            | /                          | 21.2 L/kg                |
| TJT-100¹¹   | 8.7 × 11.6    | 0.39                   | 890                        | 298 K | ~3.66/3.4         | 1.2                            | 29/25                      | /                        |
| IRMOF-8¹²   | 17.5          | 0.69                   | 1360                       | 298 K | 2.16/1.25         | 1.8                            | 52.5/50                    | 2.5 L/kg                 |
| PCN-250¹³   | 5.9, 6.8, 9.3 | 0.56                   | 1470                       | 298 K | 5.21/4.22         | 1.9                            | 23/21                      | 10 L/kg                  |
| MUF-15¹⁴    | 8.5 × 3.5, 7 × 3.8, 3.2 × 1.2 | 0.51   | 1130                       | 293 K | 4.69/4.15         | 1.96                           | 28.2/29.2                  | 14 L/kg                  |
| Cu(Qc)₂¹⁵   | 3.3           | 0.11                   | 240                        | 298 K | 1.85/0.78         | 3.4                            | 29/25.4                    | 4.3 L/kg                 |
| Ni(bdc)(ted)₁₆ | 7.94       | 0.79                   | 1701                       | 298 K | 5.0/3.4           | 2                              | 21.5/18.2                  | /                        |
| PCN-245¹⁷   | 10            | 0.71                   | 1743                       | 298 K | 3.27/2.39         | 1.9                            | 20.5/23.0                  | 5.8 L/kg                 |
| Fe₂(O₂)dobdc²⁰ | /            | /                      | 1073                       | 298 K | 3.45/2.68         | 4.4                            | 19.3 L/kg                  | /                        |
| ZIF-4¹⁹     | /             | 0.38                   | 300                        | 293 K | 2.3/2.2           | 1.7                            | /                          | /                        |
| ZIF-8²₀     | 3.4           | 0.73                   | 1844                       | 293 K | 2.54/1.5          | 1.8                            | 17.2/16.1                  | /                        |
11. Neutron Powder Diffraction

Neutron powder diffraction experiments were undertaken at the WISH diffractometer at the ISIS Facility. MFM-300(In) was loaded into a 6 mm diameter vanadium sample can and outgassed at $1 \times 10^{-7}$ mbar and 100 °C for 1 day. The sample was loaded into a liquid helium cryostat and cooled to 7 K for data collection. C$_2$H$_2$, C$_2$H$_4$, C$_3$H$_6$, C$_4$H$_4$, C$_6$H$_6$ and C$_3$H$_8$ gas were introduced by warming the samples to 298 K and the gas dosed volumetrically from a calibrated volume. The gas-loaded sample was then cooled to 7 K over a period of 2 h to ensure good mobility of adsorbed species within the crystalline structure of MFM-300(In) and for a further 30 mins to ensure thermal equilibrium. Rietveld structural refinements were carried out on the NPD data using the TOPAS software package.21

![Rietveld fit profiles of the NPD data of MFM-300(In)·1.32(C$_2$D$_2$).](image)

Figure S19. Rietveld fit profiles of the NPD data of MFM-300(In)·1.32(C$_2$D$_2$).
Figure S20. Rietveld fit profiles of the NPD data of MFM-300(In)·1.66(C2D4)
Figure S21. Rietveld fit profiles of the NPD data of MFM-300(In):0.72(C$_2$D$_6$).
Figure S22. Rietveld fit profiles of the NPD data of MFM-300(In)\(0.2\)(C\(_3\)D\(_4\)).

Figure S23. Rietveld fit profiles of the NPD data of MFM-300(In)\(0.48\)(C\(_3\)D\(_4\)).
Figure S24. Rietveld fit profiles of the NPD data of MFM-300(\text{In})-0.46(\text{C}_3\text{D}_4).

Figure S25. NPD structure of MFM-300(\text{In})-0.2(\text{C}_3\text{D}_4).
**Figure S26.** NPD structure of MFM-300(In)-0.48(C_{3}D_{6}).

**Figure S27.** NPD structure of MFM-300(In)-0.46(C_{3}D_{6}).

**Table S4.** Host–Guest Interactions in MFM-300(In)-1.32(C_{2}D_{2}).

| Site | Interactions                        | Distances (Å) | Colour   |
|------|-------------------------------------|---------------|----------|
| Site I | H (HO-In)···C≡C (site I) | 2.52(1)       | Violet   |
|       | H (site I)···C≡C (site II)       | 3.73(1)       | Bright green |
|       | C≡C (site I)···phenyl groups     | 3.83(1)       | Orange   |
|       |                                    | 4.04(1)       |          |
| Site II | C≡C (site II)···H (site I)    | 3.73(2)       | Bright green |
Table S5. Host–Guest Interactions in MFM-300(In)·1.66(C₂H₄).

| Interactions                          | Distances (Å) | Colour   |
|---------------------------------------|---------------|----------|
| H (HO-In)···C=C (site I)              | 3.85(1)       | Violet   |
| H (site I)···C=C (site II)            | 3.91(1)       |          |
|                                       | 4.01(1)       | Bright green |
| H (site I)···phenyl groups            | 2.92(1)       | Orange   |
|                                       | 3.03(1)       |           |
|                                       | 3.73(2)       |           |
|                                       | 4.40(1)       |           |
| C=C (site II)···H (site I)            | 3.91(1)       | Bright green |
|                                       | 4.01(1)       |           |
| H (site II)···phenyl groups           | 4.27(1)       | Pink     |

Table S6. Host–Guest Interactions in MFM-300(In)·0.72(C₂H₆).

| Interactions                          | Distances (Å) | Colour   |
|---------------------------------------|---------------|----------|
| H (HO-In)···C (site I)                | 3.22(2)       | Violet   |
| H (site I)···C (site II)              | 2.99(4)       | Bright green |
| H (site I)···phenyl groups            | 2.65(2)       | Orange   |
|                                       | 3.30(2)       |           |
|                                       | 3.68(1)       |           |
|                                       | 4.18(2)       |           |
| C (site II)···H (site I)              | 2.99(4)       | Bright green |
Table S7. Host–Guest Interactions in MFM-300(In)∙0.2(C₃H₄).

| MFM-300(In)∙0.2(C₃H₄) | Interactions                   | Distances (Å) | Colour  |
|------------------------|--------------------------------|----------------|---------|
| Site I                 | H (HO-In)···C₃D₄              | 3.26(6)        | Violet  |
|                        | H (site I)···phenyl groups    | 3.18(6)        | Orange  |
|                        | C≡C (site I)···phenyl groups  | 3.56(1)        | Green   |

Table S8. Host–Guest Interactions in MFM-300(In)∙0.48(C₃H₆).

| MFM-300(In)∙0.48(C₃H₆) | Interactions                   | Distances (Å) | Colour  |
|------------------------|--------------------------------|----------------|---------|
| Site I                 | H (HO-In)···C≡C (site I)       | 3.37(1)        | Violet  |
|                        | H (site I)···phenyl groups     | 3.03(2)        | Orange  |
|                        |                                | 4.17(2)        |         |
|                        | C≡C (site I)···phenyl groups   | 3.89(1)        | Blue    |
| Site II                | C≡C (site II)···H (site I)     | 1.91(2)        | Bright green |
|                        | H (site II)···phenyl groups    | 4.07(1)        | Orange  |
### Table S9. Host–Guest Interactions in MFM-300(In)·0.46(C₃H₈).

| MFM-300(In)·0.46(C₃H₈) | Interactions | Distances (Å) | Colour |
|--------------------------|--------------|---------------|--------|
| Site I                   | H (HO-In)···C (site I) | 2.72(2) Å  | Violet |
|                          | H (site I)····C (site II) | 2.92(2)    | Bright green |
|                          | C (site I)···H (site II) | 3.19(2)    |         |
|                          | H (siteI)···phenyl groups |            | Orange |
|                          |                           | 3.17(2)    |        |
|                          |                           | 4.87(2)    |        |
|                          |                           | 4.02 (2)   |        |
|                          |                           | 3.37(2)    |        |
| Site II                  | C (site II)···H (site I) | 2.92(2)    | Bright green |
|                          | C (site I)···H (site II) | 3.19(2)    |         |
|                          | H (site II)··· phenyl groups | 3.35(1)  | Pink   |
|                          |                           | 3.02(1)    |        |

### 12. Inelastic Neutron Scattering Measurement

Inelastic neutron scattering (INS) experiments were undertaken using the TOSCA spectrometer at the ISIS Facility. MFM-300(In) was loaded into an 11 mm diameter vanadium sample can and outgassed at $1 \times 10^{-7}$ mbar and 100 °C for 1 day. The sample was loaded into a helium closed cycle refrigerator (CCR) cryostat and cooled to 11 K for data collection. C₂H₂, C₂H₄ and C₃H₆ gas were introduced by warming the sample to 298 K and the gas was dosed volumetrically from a calibrated volume. The gas-loaded sample was then cooled to 7 K over a period of 2 h to ensure good mobility of adsorbed species within the crystalline structure of MFM-300(In). The sample was kept at 7 K for an additional 30 mins before data collection to ensure the thermal equilibrium.
Figure S28. Comparison of bare and C$_2$H$_2$ loaded MFM-300(In).

Figure S29. Comparison of bare and C$_2$H$_4$ loaded MFM-300(In).
Figure S30. Comparison of bare and C$_2$H$_6$ loaded MFM-300(In).
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