

Understanding the Kinetic and Thermodynamic Origins of Xylene Separation in UiO-66(Zr) via Molecular Simulation

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SUPPORTING INFORMATION

- S1. Pore size distributions of UiO-66(Zr)
- S2. pX dimers in hydroxylated UiO-66(Zr)
- S3. Accessible adsorption sites in UiO-66(Zr)
- S4. Exploration of π - π stacking for xylenes in UiO-66(Zr)

S1 – PORE SIZE DISTRIBUTIONS OF UiO-66(Zr)

The pore size distribution (PSD) of hydroxylated and dehydroxylated UiO-66(Zr) were calculated following the method of Gelb and Gubbins¹, in which the largest sphere which may be successfully inserted into a cavity is determined. As in the other simulations undertaken in this work, the frameworks were described using a combination of the Universal² (for zirconium) and DREIDING³ (for all other atom types) force fields. In the determination of PSD, the frameworks were treated as rigid.

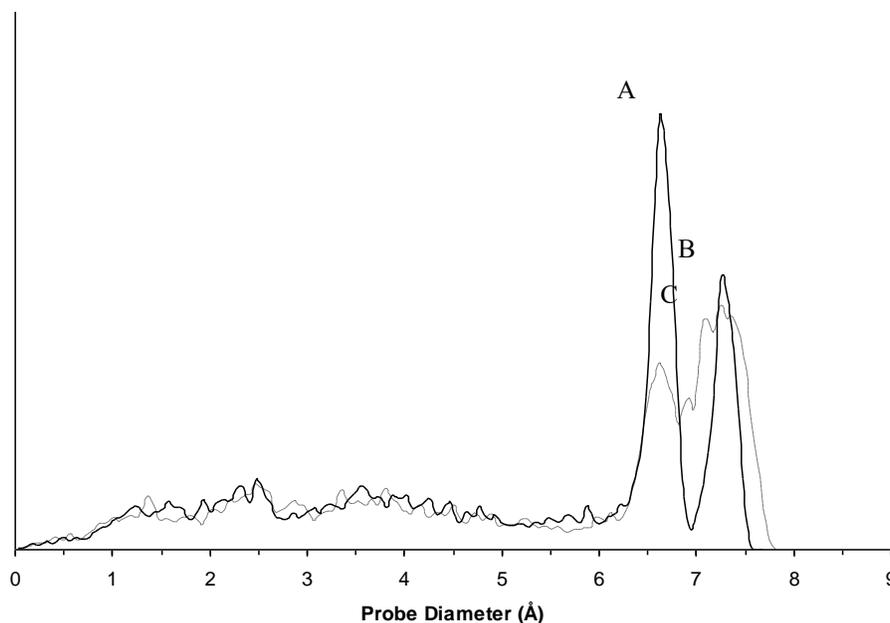


Figure S1 - Pore size distribution of hydroxylated (dashed line) and de-hydroxylated (solid line) UiO-66(Zr). Points A and B correspond to the smaller tetrahedral pore and the octahedral cavity, which are present in both forms of UiO-66(Zr). Point C corresponds to the intermediately sized tetrahedral cavity, which is present only in the hydroxylated form.

S2 – pX DIMERS IN UiO-66(Zr)

Single-component adsorption simulations in hydroxylated UiO-66(Zr) were further analyzed by tracking not only the number of molecules in the system as a function of pressure, but also which pore their centers of mass were located within. The adsorption isotherms per cavity (Figure S2), combined with simulation snapshots at higher pressures (Figure S3), demonstrate that the enhanced uptake of pX compared to the other two isomers is a result of the formation of pX dimers in one of the tetrahedral cavities. As there is no experimental evidence for increased capacity of the MOF for pX, this is likely to be an artefact of the GCMC simulation.

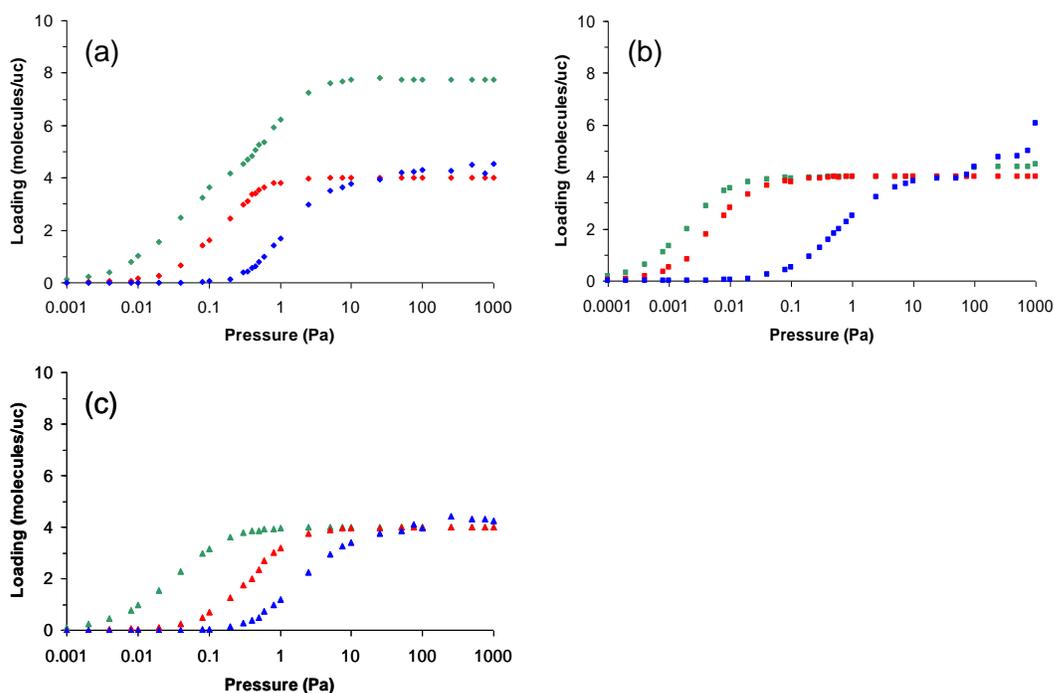


Figure S2 – Per-cavity single-component isotherms for pX (top-left), oX (top-right) and mX (bottom-left) in UiO-66(Zr). Adsorption isotherms are per pore type: small tetrahedral (red), intermediate tetrahedral (green) and larger octahedral (blue) pore.

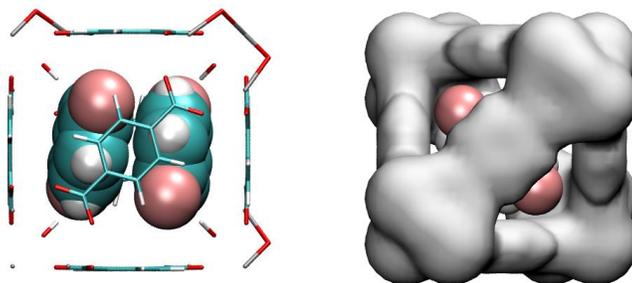


Figure S3 - In contrast to the other two isomers, two pX molecules may be adsorbed within the intermediate tetrahedral cavity, taking up a cruciform arrangement with their methyl groups (pink spheres) located within the pore windows. The framework is shown in stick representation, pX in spacefill. The van der Waals volume of the framework atoms, shown in grey in the right image, allows the location of the methyl groups within the windows to be clearly seen.

S3 – ACCESSIBLE ADSORPTION SITES IN UiO-66(Zr)

The total number of potential adsorption locations available to oX, mX and pX in the dehydroxylated form of UiO-66(Zr) was estimated using a modified version of the Poreblazer toolset⁴. The unit cell of the MOF was discretised on a 0.2 Å grid and an attempt was made to insert a xylene molecule at each point in turn. For each point, up to 1000 trial orientations were tested. The average Boltzmann factor for each isomer – to which the probability of observing a molecule during a GCMC simulation at a given pressure is directly correlated – depends on both the interaction energy and the total number of orientations/sites which do not result in an overlap with the framework. The relative number of available adsorption locations (Table S1) may thus be loosely termed an entropic driving force.

Table S1 – Number of accessible adsorption sites for each isomer per cavity type in dehydroxylated UiO-66(Zr)

	Number of Accessible Locations	
	Tetrahedral Cavity	Octahedral Cavity
pX	42,940	79,566
mX	41,022	93,746
oX	60,535	115,785

S4 – π - π STACKING FOR XYLENES IN UiO-66(Zr)

None of the GCMC simulation snapshots revealed any evidence of π - π stacking between the BDC ligands of the framework and adsorbed xylene molecules. Further investigation using a modified version of the Kh_d toolset⁵ showed that while none of the isomers are sterically restricted from accessing orientations which allow π - π interactions with the framework, these orientations are not energetically favourable. In these simulations, the pore space was discretised on a 0.2 Å grid and the interaction of the three xylene isomers with the framework at each point on the grid evaluated and averaged over 1000 trial orientations. The rotational freedom of the probe molecules was restricted so as the aromatic ring of the xylene molecule was kept parallel ($\pm 2.5^\circ$) to a plane corresponding to the BDC linkers which define one face of the tetrahedral pore type, mimicking π - π stacking. As the BDC linkers in the tetrahedral pores are arranged along the faces of a cube, all three primary π - π interaction geometries (Figure S4, following Martinez et al⁶) were explored in this manner.

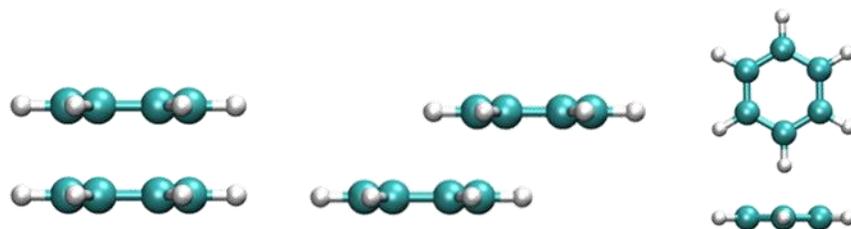


Figure S4- The three primary modes of π - π interactions⁶, demonstrated for benzene molecules: sandwich (left), parallel displaced (centre) and T-shaped (right).

While all three isomers are able to take up both sandwich and T-shaped geometries in the tetrahedral cavities, the strongest xylene-MOF interaction energy in these orientations (-38 to -45 kJ/mol) is considerably weaker than that observed in these pore types in NVT-MC simulations (-68 to -77 kJ/mol) where all possible orientations, including those which do not promote π - π interactions, are allowed. The limited pore space available to xylene molecules does not permit the formation of parallel displaced pairs, while the cubic arrangement of the BDC linkers means that if a molecule takes up an energetically favourable T-shaped arrangement with one linker, it must also be in an energetically unfavourable sandwich orientation with the neighbouring linkers, resulting in a comparatively low overall xylene-MOF interaction energy.

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