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Materials and Methods

1 Experimental and Computational Procedures

1.1 Ligand Synthesis

1,2,4,5-Tetrabromobenzene (product number 278343, 97 %) and tetrakis(triphenylphosphine)palladium (0) (product number 216666, 99 %) were purchased from Sigma-Aldrich. p-tolyl boronic acid was purchased from Fluorochem (product number 010854) and potassium carbonate (product number P/4080/53, >99 %), methanol (product number M/4056/17, >99.8 %) and toluene (product number T/2300/17, >99.8 %) were purchased from Fisher Scientific. All chemicals were used as received without further purification. H₄TCPB is a commercially available ligand which has been used to synthesise MOFs with large porosity and structural stability[1]. The rotational flexibility of the carboxyphenyl groups allows the ligand to form three-dimensional frameworks, and there are examples of this ligand being used to form stable porous 3D frameworks with gas storage and separation capabilities. The following reaction was run 6 times in parallel using a Radley's Carousel and all 6 reactions were combined for the work-up and isolation:

1,2,4,5-Tetrabromobenzene (3.15 g, 8 mmol), p-tolylboronic acid (6.53 g, 48 mmol) and potassium carbonate (8.85 g, 64 mmol) were charged to a round-bottomed flask followed by toluene (120 ml), methanol (40 ml) and deionised water (32 ml). Nitrogen was bubbled through the reaction mixture for 5 min then tetrakis(triphenylphosphine) palladium(0) (0.462 g, 0.4 mmol) was charged and the mixture was heated at reflux under a nitrogen atmosphere for 4 days. The 6 biphasic reaction mixtures were cooled to ambient temperature, combined and the layers separated. The organic layer was washed with 1M HCl (250 ml), water (2 × 250 ml), dried over MgSO₄ and filtered. The filtrate was concentrated on a rotary evaporator until approximately 50 ml of solvent remained. The suspension was diluted with 50 ml of acetone and filtered to afford 16.0 g of crude material. The solid was dissolved in hot toluene, a small amount of insoluble material was removed by filtration and the filtrate was concentrated to a volume of 50 ml. The suspension was allowed to cool to ambient temperature and the solid was collected by filtration. The cake was washed with toluene (10 ml) and dried under vacuum to afford 14.5 g (69 % yield) of 1,2,4,5-tetra-p-tolyl-benzene as a white solid. ¹H NMR (CDCl₃): 7.47 (2H, s, Ar-H), 7.12 (8H, d, Ar-H), 7.04 (8H, d, Ar-H), 2.32 (12H, s, 4 × CH₃). The ¹H NMR was consistent with the published data. This was then oxidised using the method of Farha et al.[1] to afford H₄TCPB.

1.2 Synthesis of 1

Ce(NO₃)₃.6H₂O (20 mg) and H₄TCPB (10 mg) were added to EtOH (3 ml) and H₂O (3 ml) in 12 mL borosilicate glass vial and the vials sealed. The mixture was sonicated for 10 minutes to form a white suspension, which is then heated at 2°C/min to 120°C for 48 hours and cooled at 0.2°C/min to room temperature (25°C). Large colourless single crystals are separated from the mother liquor by vacuum filtration and washed with EtOH and H₂O to yield pure compound with the formula Ce(HTCPB).0.28EtOH.2.75H₂O (Fig. S1, S2). These single crystals were used for the single crystal diffraction experiments. 1 can also be produced at 3x the scale (3x reagent in 3x solvent in 40 mL glass vial) which produces smaller particles of 1, with a more polydisperse particle size than from method A (Fig. S3). Samples produced by both methods were used in the liquid phase sorption experiments and produced identical results.
1 is stable on standing in water.

3 is synthesised by desolvation of 1 at 100°C and 10⁻³ mbar for 6 hours.

1.3 Analytical Data for 1 and 3

Phase purity of 1 was demonstrated by powder X-ray diffraction (PXRD) data collected in capillary transmission geometry on a Bruker D8 Advance with Cu Kα₁ radiation (Fig. S4(a)) at room temperature. 1 is stable on standing in water.

C and H analyses were obtained using a Thermo EA1112 Flash CHNS-O Analyzer. TGA was carried out using an SDT500 analyser with air as the carrier gas (Fig. S4(b)).

1: Ce(HTCPB)(H₂O)₂.₇₅(EtOH)₀.₂₈ Calculated % C: 54.76 H: 3.37. Found % C: 54.76 H: 3.48. Guest content from CH analysis 9.80%; Guest content measured by TGA 11.0%.

3: Ce(HTCPB): Calculated % C: 58.70 H: 2.75. Found %: C: 58.20 H: 2.66.

1.4 X-ray Single Crystal Data Collection and Analysis

All single crystal data collections were undertaken using a Rigaku AFC12K goniometer with Mo Kα radiation from a Rigaku 007-HF rotating anode microfocus X-ray source and collected using a Saturn 724+ CCD detector. Environmental control was achieved using a nitrogen stream from an Oxford Cryostat 700+. Crystal preparation, data collection, processing and refinement methods and structure analyses are described in the supplementary information. 3 was formed by heating 1 in-situ on the diffractometer. 3-Nd was formed by heating 1-Nd under Schlenk conditions and dynamic vacuum (section 3). The solvated structures 3P, 3M, 3P-Nd and 3M-Nd were formed by immersing 3 or 3-Nd in pX or mX under N₂, respectively. The Ce(HTCPB) and Nd(HTCPB) framework is completely ordered in 3P, 3M, 3P-Nd and 3M-Nd.

1.5 Gas Sorption

Isotherms on 3 were measured using the Intelligent Gravimetric Analyser (IGA) from Hiden. A sample of 1 was washed with water and EtOH and left to air-dry prior to use and was then outgassed at 100 °C under dynamic vacuum (10⁻⁵ mbar) until constant mass loss was reached. Data are described in supplementary information.

1.6 Computation

Docking and GCMC calculations were carried out with a fixed host using the COMPASS27 forcefield, supplied with Materials Studio 5.0 (Accelrys). Docking calculations were run with organic sorbates, geometry optimised with the COMPASS27 forcefield, using the Adsorption Locator module within Materials Studio with charges calculated using the QEq charge equilibration scheme¹⁴ and COMPASS27. Adsorption simulations were carried out using the Materials Studio 5.0 Sorption module. The configurational bias grand canonical Monte Carlo method (CB-GCMC) was used for more efficient sampling, with 1 million equilibration steps and 10 million production steps at 383 K. The maximum uptake was calculated at 10 bar, which can effectively be considered as the end point of the adsorption isotherms.
1.7 Selectivity of 3 Towards pX, mX and C₈ isomers

C₈ uptake experiments were carried out to study the uptake of C₈ isomers either singly or in equimolar mixtures by Ln(HTCPB) compounds (where Ln = La, Ce, Pr, Nd or Sm). 50 mg of 1 was activated at 100°C under vacuum overnight in a Schlenk tube to give 3. 1 ml of either a single C₈ isomer or equimolar solutions of two C₈ isomers were then added to 3 under N₂ and left for 24 hours after which time they were filtered and washed with DCM (10 ml).

The activation procedure used to produce 3 is effective in removing all sorbed molecules, hence any sorbed molecules present after this test will either be a C₈ compound, DCM introduced by the washing process, or adventitious water contamination in between washing and analysis.

Validation experiments were carried out to demonstrate that: (i) washing 3 with DCM did not alter it; (ii) mixing a simple mixture of C₈ compounds with DCM in the absence of 3 does not selectively remove certain C₈ compounds; and (iii) washing 3 loaded with C₈ compounds with DCM does not remove C₈ compounds from the pores of 3 (established by GC comparison of the pX/mX selectivity of samples dried overnight, rather than washed with DCM, with those washed with DCM); and (iv) 3 has no catalytic activity towards isomerisation of C₈ compounds.

TGA and CH microanalysis (Fig. S14) were used to calculate the formulas of the loaded frameworks, including the total C₈ compounds uptaken, DCM introduced by the washing process and water uptaken adventitiously in between washing and analysis.

In the cases where selectivity of isomer uptake from mixtures of C₈ compounds were studied (sections 6.1, 6.2, 6.5), gas chromatography was used to quantify the relative amounts of each isomer uptaken by 3. The analyses were conducted according to the following procedure. The loaded frameworks were broken down with 1 M NaOH solution and filtered, leaving an aqueous solution of the ligand (Na₄TCPB) and the C₈ compounds. The C₈ compounds were then extracted by washing three times with DCM, dried with MgSO₄ and filtered for GC analysis. GC measurements were carried out using a ZB-Wax capillary column using a Shimadzu GC-14B chromatogram. (Carrier Gas, 50 KPa He; Column Temp Program, isothermal at 40°C; Detector, 250°C; Injector, 250°C), calibrated against a standard equimolar solution of the two C₈ isomers under investigation. The selectivity αᵢⱼ = (Xᵢ / Xⱼ) / (Xᵢ₀ / Xⱼ₀) where Xᵢ and Xⱼ are mole fractions of the two C₈ isomers absorbed into solid 3 and Xᵢ₀ and Xⱼ₀ are mole fractions of the two isomers before exposure to 3.

2 Analytical Data

2.1 Microscopy

Optical Microscope (OM) and Scanning Electron Microscope (SEM) images show the large block morphology of single crystals of 1 (Fig. S1, S2) and reduction in particle size of the product when synthesised via the scaled up method B (Fig. S3).

2.2 Thermogravimetric Analysis of 1

For 1, the weight change of 11 % observed for the loss of the guest and coordinated EtOH and H₂O molecules before reaching a plateau at 120 °C is in good agreement with the values calculated from microanalysis. The observed final mass percentage of 20.1 % corresponds to
that calculated for the formation of 1 equivalent of CeO$_2$ after heating at 600 °C (Fig. S4(b)).

3 X-ray Single Crystal Data Collection and Analysis

3.1 Data Collection

A standard data collection comprising of 3x125° $\omega$-scans at 0, 120, 240° settings in $\varphi$ and common setting of -68° in $\kappa$ followed by a single 125° scan at $\kappa$ = -30° and $\varphi$ = 90° and final low angle 180° $\omega$-scan at $\kappa$ = $\varphi$ = 0° were employed for all samples. Data collection on compounds 1, 3, 3-Nd, 3P, 3P-Nd and 3M-Nd were undertaken at 1° and 3M 0.5° scan width in $\omega$.

3.2 Processing and Refinement

Method A: The data was integrated and reduced using FS_Process$^{[2]}$ with absorption and scaling correction being undertaken with the program ABSCOR$^{[3]}$. Using Olex2$^{[4]}$ the structure was solved with the olex2.solve structure solution program using Charge Flipping and refined with the ShelXL_ifc refinement package$^{[5]}$ using Least Squares minimisation.

Method B: The raw frames from the experiment were converted using FMD$^{[6]}$ and processed using APEXII$^{[7]}$. The converted data was integrated and reduced using SAINT$^{[8]}$ with absorption and scaling correction being undertaken with the program SADABS$^{[9]}$. Using Olex2, the structure was solved with SHELXS$^{[5]}$ using Direct Methods or Olex2.Solve and refined with ShelXL_ifc or ShelXL-2013/4 using Least Squares minimisation (see CIF for further details).

3.3 Compound 1: [Ce(HTCPB).$(\text{H}_2\text{O})_{2.5}(\text{EtOH})_2$]

A colourless prismatic crystal of 1 (0.055 × 0.055 × 0.044 mm) was selected in motherliquor, allowed to dry overnight on a glass slide and subsequently glue mounted to a 10 µm Mitegen tip with no oil and placed under the nitrogen flow on the diffractometer at 100 K. Data processing was undertaken as per section 3.2 method A. The crystal structure of 1 (Fig. S5) was found to have three unbound partial guest EtOH solvates, two located in channel 1 with common shared carbon atoms modelled using EXYZ, EADP (C11A, C12A and C11B, C12B) and split into PART 1 and PART 2 respectively. The disorder was refined using a free variable model of X and X-1 converging at X=58.2%. The third EtOH solvate (O1SB, C2SB, C3SB) was found to be disordered with a Ce bound EtOH (O1SA, C2SA, C3SA) which was also disordered with a bound water (O1WB) (Fig. S5C). All three components are located in channel 2 and were modelled together with the bound water and EtOH being modelled in PART 1 and PART 2 and due to the inversion symmetry the solvate EtOH in PART -1 with fixed occupancies of 0.5. DANG and DFIX restraints were applied to the disordered species for stability. All non-hydrogen atoms were refined anisotropically. Where possible hydrogen atoms were refined from the difference map with some hydrogen atoms being constrained using the appropriate AFIX for their geometry and occupancy and thermal parameter set based on the parent riding atom.

3.4 Compound 3: [Ce(HTCPB)]

The crystal of compound 1 was heated in situ on the diffractometer using CCVT$^{[10]}$ as part of a variable temperature experiment in 50 K steps at 330 K/hr from 100 to 250 K then a 70 K step to 320 K, followed by cooling to 100 K at 330 K/hr and subsequently heated from 100 to 340 K at 330 K/hr: a data collection was recorded at each temperature point of approximately 3 hours duration.
The crystal was cooled back to 100 K to undertake the final data collection of 3. The crystal structure of 3 is shown in Figure S7. Data processing was undertaken as per section 3.2 method B. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were constrained using the appropriate AFIX for their geometry and occupancy and thermal parameter set based on the parent riding atom.

The crystal structure of 3 was also determined directly from crystals prepared by heating 1 under a dynamic vacuum (10⁻² mbar) at 100 °C in a Schlenk tube overnight. After this time, the Schlenk was backfilled with N₂ and crystals isolated directly into fomblin Y-1800 oil. The same structure is found if 3 is generated ex-situ through desolvation in a Schlenk tube (as used in the single crystal xylene loading experiments described in 3.5).

3.5 Single Crystal Structure Determination of Ce(HTCPB)Xylene Loaded Crystals

For xylene loaded 3, single crystals were activated at 100 °C in a Schlenk tube under a vacuum of 10⁻² mbar overnight. Following activation the samples were back filled with N₂ and allowed to cool to room temperature after which time, pX (3P) and mX (3M) were added. The Schlenk tubes were sealed under N₂ and left for 24 hours before single crystal data was collected. The Ce(HTCPB) framework is completely ordered in both 3P and 3M.

3.5.1 Compound 3P: [Ce(HTCPB).pX]

Crystals of 3P were isolated under Schlenk conditions and placed under Fomblin Y-1800 oil on a glass side. A colourless prismatic crystal of 3P (0.079 × 0.05 × 0.031 mm) was then selected and mounted to a 10 µm Mitegen tip and placed under the nitrogen flow on the diffractometer at 100 K. Data processing was undertaken as per section 3.2 method B. All non-hydrogen atoms were refined anisotropically (Fig. S18). All hydrogen atoms were constrained using the appropriate AFIX for their geometry and occupancy and thermal parameter set based on the parent riding atom.

3.5.2 Compound 3M: [Ce(HTCPB).mX]

Crystals of 3M were isolated under Schlenk conditions and placed under Fomblin Y-1800 oil on a glass side. A colourless prismatic crystal of 3M (0.088 × 0.062 × 0.033 mm) was then selected, mounted on a 30 µm Mitegen tip and placed under the nitrogen flow on the diffractometer at 100 K. Data processing was undertaken as per section 3.2 method B. All non-hydrogen atoms were refined anisotropically (Fig. S19). All hydrogen atoms were constrained using the appropriate AFIX for their geometry and occupancy and thermal parameter set based on the parent riding atom. 3M contains two disordered sites of mX, one per channel. In channel 1 there are two partial overlapping mX moieties. On the application of symmetry the model grew over the symmetry operator producing two distinct overlapping mX units which are fully disordered when translational symmetry is applied. To make the final model the partial mX units were grown individually to produce the full mX molecules and the ring structure held using AFIX 66 constraints and FLAT restraint. The symmetry generated atoms were moved off their x,y,z coordinates and locked being placed in PART -2 and PART -3 for mXA and mXB respectively (blue and green shading respectively, Fig. S19B). The occupancy of each mX was set 0.5xX and 0.5xX-1 converging at X=41%. This produces 1 mX molecule in the grown structure for channel 1. In channel 2 a disordered partial single mX unit could be resolved which on the application of symmetry grew into two overlapping mX molecules. A single grown mX unit was isolated the symmetry generated...
atoms moved off their x,y,z coordinates and locked with a occupancy of the symmetry operator of 0.5 and placed in PART -1. The central mX ring was fixed using an AFIX 66 constraint. The methyl group angles were stabilised with DANG restraints from the neighbouring ring carbon atoms. This produced two overlapping mX molecules at an 0.5 occupancy giving 1 mX molecule in total in the grown structure for channel 2. As the disordered mX in channel 2 was significantly more resolved than in channel 1 a SAME restraint based on channel 2 mX was also applied to both mX molecules in channel 1. An ISOR restraint was applied to the disordered mX molecules in both channels.

3.6 Compound 1-Nd: [Nd(HTCPB)]

A colourless prismatic crystal of 1-Nd (0.265 × 0.147 × 0.047 mm) was selected in mother liquor and glue mounted to a 10 µm Mitegen tip with no oil and placed under the nitrogen flow on the diffractometer at 100 K. Data processing was undertaken as per section 3.2 method A. The crystal structure of 1-Nd (Fig. S33) was found to have one unbound guest EtOH solvate located in channel 1 modelled as disordered over three positions (O10A, C11A, C12A; O10B, C11B, C12B and O10C, C11C, C12C) split into PART 5, PART 6 and PART 7 with their occupancies refined with SUMP equal to 1, due to the degree of the disorder these atoms were refined isotropically and no hydrogen atoms were modelled. A partial Nd-bound EtOH disordered over two positions (O1S, C61A, C62A; O1S C61B C62B) which was also disordered with a bound water (O1WC) and two unbound waters each disordered over three positions (O1, O2, O3 and O2WA, O2WB and O2WC) were refined. All three components are located in channel 2 and were modelled together with the bound water and EtOH being modelled in PART 3, PART 2 and PART 1 with fixed occupancies of 0.5 for O1WC and O1S and 0.25 for C61A, C62A, C61B and C62B with the occupancies of O1, O2 and O3 and O2WA, O2WB and O2WC refined with SUMP equal to 1. Due to the level of disorder the unbound waters and ethanol carbon atoms were refined isotropically and no hydrogen atoms were modelled on the unbound water. DANG and DFIX restraints were applied to the disordered species for stability. All other non-hydrogen atoms were refined anisotropically. Where possible hydrogen atoms were refined from the difference map with some hydrogen atoms being constrained using the appropriate AFIX for their geometry and occupancy and thermal parameter set based on the parent riding atom.

3.7 Compound 3-Nd: [Nd(HTCPB)]

The crystal structure of 3-Nd was determined directly from crystals prepared by heating 1-Nd under a dynamic vacuum (10^{-3} mbar) at 100 °C in a Schlenk tube for six hours. After this time, the Schlenk was backfilled with N\textsubscript{2} and crystals isolated directly into Fomblin Y-1800 oil and placed under Fomblin Y-1800 oil on a glass side. A colourless prismatic crystal of 3-Nd (0.1 × 0.08 × 0.05 mm) was then selected and mounted on to a 50 µm Mitegen tip and placed under the nitrogen flow on the diffractometer at 100 K. Data processing was undertaken as per section 3.2 method B. All non-hydrogen atoms were refined anisotropically (Fig. S34). All hydrogen atoms were constrained using the appropriate AFIX for their geometry and occupancy and thermal parameter set based on the parent riding atom.

3.8 Single Crystal Structure Determination of Nd(HTCPB) Xylene Loaded Crystals
For xylene loaded 3-Nd, single crystals were activated at 100 °C in a Schlenk tube under a vacuum of 10^-3 mbar over six hours. Following activation the samples were back filled with N₂ and allowed to cool to room temperature after which time, pX (3P-Nd) and mX (3M-Nd) were added. The Schlenk tubes were sealed under N₂ and left for 24 hours before single crystal data was collected. The Nd(HTCPB) framework is completely ordered in both 3P-Nd and 3M-Nd.

3.8.1 Compound 3P-Nd: [Nd(HTCPB).pX]

Crystals of 3P-Nd were isolated under Schlenk conditions and placed under Fomblin Y-1800 oil on a glass side. A colourless prismatic crystal of 3P-Nd (0.079 × 0.052 × 0.033 mm) was then selected and mounted to a 30 µm Mitegen tip and placed under the nitrogen flow on the diffractometer at 100 K. Data processing was undertaken as per section 3.2 method B. All non-hydrogen atoms were refined anisotropically (Fig. S35). All hydrogen atoms were constrained using the appropriate AFIX for their geometry and occupancy and thermal parameter set based on the parent riding atom.

3.8.2 Compound 3M-Nd: [Nd(HTCPB).mX]

Crystals of 3M-Nd were isolated under Schlenk conditions and placed under Fomblin Y-1800 oil on a glass side. A colourless prismatic crystal of 3M-Nd (0.21 × 0.12 × 0.09 mm) was then selected, mounted on a 30 µm Mitegen tip and placed under the nitrogen flow on the diffractometer at 100 K. Data processing was undertaken as per section 3.2 method B. All non-hydrogen atoms were refined anisotropically (Fig. S36).

In both channel spaces mX could readily be resolved. For each channel to the crude mX model was determined and placed in PART -1, PART -3 (channel 1) and PART -2 (channel 2). To the crude mX model a Gaussian calculated fragment was fixed using AFIX 173 and allowed to refine. Then each fragment was moved to AFIX 6 and then locked after convergence back to AFIX 3. All hydrogen atoms were constrained using the appropriate AFIX for their geometry and occupancy and thermal parameter set based on the parent riding atom. The mX hydrogen positions were calculated using Olex2 hadd command and then removed from individual AFIXs and combined into the overall AFIX for the fragment. The occupancy of mX was set as 0.5 in channel 2 and 0.25 for both parts in channel 1. DELU and ISOR were both applied to the mX.

4 Gas Sorption

For the Brunauer-Emmett-Teller (BET) surface area measurement, the sample was cooled to 195 K by means of a Dewar vessel containing dry ice. The isotherm was measured to an absolute CO₂ pressure of 1 bar. For measurements at 273 K and 298 K, the sample was cooled using a Dewar vessel containing ice and water and water alone respectively. The samples in these cases were measured to a CO₂ pressure of 5 bar.

4.1 Porosity of 3

The porosity was investigated by collecting full isotherms following activation using conditions of 100°C under 10^-3 mbar overnight. In all cases an initial weight loss of 10 % was observed with the loss of coordinated and guest EtOH and H₂O, which is comparable with the solvent loss observed in the TGA data.
A reversible type 1 isotherm, characteristic of microporous materials\textsuperscript{[11]}, shows that 3 is permanently porous to CO\textsubscript{2} at 195 K and 1 bar. The Brunauer-Emmett-Teller (BET) surface area was calculated to be 378.95 m\textsuperscript{2} g\textsuperscript{-1} over the initial pressure ranges of p/p\textsubscript{0} = 0.02-0.2. The Dubinin–Radushkevich\textsuperscript{[12]} (DR) pore volume of 0.198 m\textsuperscript{3} g\textsuperscript{-1} was calculated from the CO\textsubscript{2} adsorption branch (Fig. S10).

A step isotherm shows that 3 is permanently porous to N\textsubscript{2} at 77 K and 1 bar (Fig. S11A). The isotherm shows a step in adsorption between 50 and 200 mbar which is also apparent in the desorption data over the same range, however some hysteresis is seen in the desorption. An H\textsubscript{2}O isotherm was also measured on 3 at 295 K. This produced a type I isotherm which showed that the material is permanently porous to H\textsubscript{2}O at 295 K and 25 mbar (Fig. S11B).

5 Computation

5.1 Docking Calculations

To test whether the xylene isomers were able to fit and therefore successfully dock within 3, docking calculations were carried out. Simulations were performed using a 2 × 2 × 2 supercell of the structure 3, with the framework held fixed. The COMPASS27 forcefield, supplied with Materials Studio 5.0 (Accelrys)\textsuperscript{[13]} was first used to geometry optimise the organic sorbate molecules, until the change in energy in successive steps was less than 0.01 kJ mol\textsuperscript{-1}. Docking calculations were then run using the Adsorption Locator module within Materials Studio with charges calculated using the QEq charge equilibration scheme\textsuperscript{[14]} and COMPASS27. Attempts were made to dock a single sorbate molecule into the rigid host structure within 100,000 insertion attempts. Any successful insertions were followed by a simulated annealing procedure involving 10 cycles of 100,000 steps with the sorbate geometry being optimised. This docking procedure was repeated 100 times for each sorbate molecule.

5.2 Sorption Simulations

To investigate the maximum possible uptake of the xylene isomers, adsorption simulations were carried out. 2 × 2 × 2 supercells of the structures 3, 3P and 3M were used with the framework held fixed and the xylene molecules deleted \textit{in silico} for the xylene-loaded structures. The COMPASS27 forcefield was used with the QEq charge equilibration method. We note that even with 10 million production steps the configurational space for the xylenes in this system is not perfectly sampled as the xylene molecules have dimensions similar to the magnitude of the pores. The simulations were repeated three times and the average uptake value calculated. The results we discuss here are consistent across all the simulations, with uptake values reported as a range where there was any significant difference between simulations. The uptakes were calculated both with single component pX or mX and dual component pX and mX guests, the latter simulations addressing competitive sorption between the two isomers. This allowed the selectivity ratio to be calculated as the ratio between the maximum uptakes of the two molecules in the simulations. The simulations were sampled every 25 steps to obtain information on the frequently visited sorption sites at this high loading.
6 Selectivity of 3 Towards C_8 compounds

The experimental protocols used for these studies are set out in section 1.7. The selectivity between C_8 isomers in competitive uptake experiments (sections 6.1, 6.2, 6.5) is established by GC analysis of the adsorbed C_8 molecules. Absolute C_8 uptake amounts are determined by CHN and TGA studies. Due to the experimental protocol used for the uptake and selectivity experiments (washing with DCM to accelerate removal of surface xylenes compared with air-drying of the samples) there is adventitious uptake of DCM and water by the samples which occurs after the experiments and is reflected in the stoichiometric calculations shown for the compositions of the materials: these compositions differ from those of the single crystals because the crystals are not washed with DCM or exposed to water after uptake of the C_8 isomers, and thus the structures of the crystals reveal how interaction solely with the pX and mX isomers produces the observed selectivity. Details are given in section 1.7 of the validation experiments used to ensure this did not affect either the total uptake of C_8 compounds or the selectivity measured.

6.1 Selective Sorption Experiments (equimolar mixtures)

\[ \alpha_{ij} = \frac{(X_i / X_j)}{(X_i^0 / X_j^0)} \]

**Equation S1**: Selectivity \( \alpha_{ij} \), where \( X_i \) and \( X_j \) are mole fractions of the two C_8 isomers absorbed into solid 3 and \( X_i^0 \) and \( X_j^0 \) are mole fractions of the two isomers before exposure to 3\textsuperscript{[15]}.

Equimolar binary mixtures of each combination of pX, mX, oX and EB were added to 3 according to the protocol described in section 1.7. The relative quantities of each isomer uptaken was measured by GC. The measurements show selectivity in the order pXoX > pXmX > EBmX = pXEB > oXmX >oXEB with values of \( \alpha_{pXmX} \) of 4.55, \( \alpha_{pXoX} \) of 5.65 and \( \alpha_{pXEB} \) of 2.38 (Table S8). These values can be compared to the best performing MOF and zeolite in xylene separation (Table S9). Example GC traces are given in Figure S16. Figure S16A shows a typical calibration curve for a 1:1 pXmX mixture used in the selectivity analysis, para-xylene elutes first. The detected ratio for the relevant starting mixture was used as the denominator for selectivity calculations in Equation S1. Figures S16B and S16C show example selectivity GC traces for Ce(HTCPB), exposed to a 1:1 pXmX mixture (initial isomer ratios \( X_i^o / X_j^o = 0.985 \) and 0.975 respectively) for 24 hours Figures S16D and S16E show example selectivity GC traces for Nd(HTCPB) exposed to a 1:1 pXmX mixture (\( X_i^o / X_j^o = 0.975 \) in both cases). In all cases it can be see that the pX content extracted from the MOF is greater than the mX content extracted from the MOF (Table S8 and S16).

Absolute values of C_8 uptaken in these experiments were quantified by CHN analysis and TGA weight loss:

Ce(HTCPB)·(pXEB)_{0.75}(DCM)_{0.22}(H_2O)_{0.16} Calc C: 60.63 H: 3.45; Observed C: 60.62 H: 3.32; TGA mass loss expected 12.70%; found 12.75%

Ce(HTCPB)·(pXmX)_{0.74}(DCM)_{0.16}(H_2O)_{0.11} Calc C: 60.95 H: 3.45; Observed C: 60.95 H: 3.36; TGA mass loss expected 11.92%; found 12.25%

Ce(HTCPB)·(pXoX)_{0.75}(DCM)_{0.13}(H_2O)_{0.10} Calc C: 61.16 H: 3.45; Observed C: 61.13 H: 3.39; TGA mass loss expected 11.73%; found 12.04%
6.2 Selective Sorption Experiments (variable mixtures)

The pX/mX selectivity of \(3\) was determined by GC using initial solutions with varying pX/mX ratios (\(X_i^o / X_j^o\) from 0.196 to 3.581). These experiments were carried out for 24 hours using 50 mg of \(3\) using the same protocol described in Section 1.7. The pX/mX ratio in the supernatant does not change during these experiments, confirmed by direct GC analysis. The selectivity, \(\alpha_{pXmX}\), dependence on pX/mX ratio is shown in Figure S17.

There is enhanced pX/mX selectivity for pX as more pX is loaded into \(3\). This agrees with the GCMC calculations which predict that \(3P\) is more selective than \(3M\), so as more pX is introduced to the framework, it becomes more selective to pX.

A similar effect has been observed with increasing the partial pressure of one gas in a binary mixture during separation using MOF-5 membranes: Increasing the partial pressure of CO\(_2\) in a CO\(_2\)/N\(_2\) mixture results in a higher CO\(_2\) selectivity\(^{16}\). Also, CO\(_2\) cooperative interactions between CO\(_2\) molecules and host amino groups on uptake increases the affinity of the Zn-Atz (Amino Triazole) MOF for CO\(_2\)\(^{17}\).

6.3 Uptake of Individual Xylene Isomers

mX uptake by \(3\) after 24 hours: Ce(HTCPB)\(\cdot\)(mX)\(_{0.42}\)(DCM)\(_{0.37}\)(H\(_2\)O)\(_{1.47}\) Calc C: 56.78 H: 3.39 Observed C: 56.76 H: 3.36 TGA mass loss expected 12.84% found 12.05% (Fig. S14)

pX uptake by \(3\) after 24 hours: Ce(HTCPB)\(\cdot\)(pX)\(_{0.65}\)(DCM)\(_{0.37}\)(H\(_2\)O)\(_{2.10}\) Calc C: 57.58 H: 3.73 Observed C: 57.59 H: 3.80 TGA mass loss expected 13.50% found 13.05% (Fig. S14)

6.4 Time Dependence Study

The effect of pXmX loading was investigated at different time periods. The same procedure as described in S1.7 was used.

TGA and CH microanalysis show that the pXmX loading of \(3\) increases over time, from 0.39 xylenes per formula unit after 1 minute to 0.7 after 7 days (Fig. S15B).

PXRD analysis of the loaded material over these time periods shows a change in structure compared to the original desolvated phase: Phase \(3\) is still present at around 30% after 1 minute alongside a ‘loaded’ phase, \(3PM\), which has a larger unit cell volume than \(3\), indexed against the single crystal structure of \(3\) loaded with an equimolar mixture of pX and mX (Fig. S15C). After 10 minutes, the amount of \(3\) has reduced to 20 % and has completely disappeared by 24 hours. The unit
cell volume of 3 increases slightly between 1 and 10 minutes due to loading of the material before conversion to 3PM. Phase 3PM is present at all times throughout the experiment, however the unit cell volume is decreasing with time. This may be due to ordering of the xylene molecules within the channels; initially at 1 minute there is a large amount of disorder so the structure has a larger unit cell volume, but as the xylenes become more ordered and form interactions with the channel walls, the unit cell volume decreases (Fig. S15D).

Absolute values of xylene uptaken in these experiments were quantified by CHN analysis and TGA weight loss:

1 minute Ce(HTCPB).(xylene)$_{0.39}$(DCM)$_{0.08}$(H$_2$O)$_{0.20}$ Calc: C: 56.33 H: 3.10; Obs: C: 56.33 H: 3.07; Expected TGA mass loss 9.0%; Observed TGA mass loss 7.5%

10 minutes Ce(HTCPB).(xylene)$_{0.46}$(DCM)$_{0.41}$(H$_2$O)$_{1.25}$Calc: C: 57.06 H: 3.38; Obs: C: 57.06 H: 3.35; Expected TGA mass loss 10.5%; Observed TGA mass loss 10.1%

24 hours Ce(HTCPB).(xylene)$_{0.65}$(DCM)$_{0.05}$(H$_2$O)$_{0.68}$ Calc: C: 60.36 H: 3.43; Obs: C: 60.35 H: 3.48; Expected TGA mass loss 13.9%; Observed TGA mass loss 13.5%

7 days Ce(HTCPB).(xylene)$_{0.70}$(H$_2$O)$_{0.61}$(DCM)$_{0.07}$ Calc: C: 60.55 H: 3.50; Obs: C: 60.51 H: 3.48; Expected TGA mass loss 13.6%; Observed TGA mass loss: 13.5%

6.5 Isostructural Ln(HTCPB) for Selective pX/mX Sorption

The pX/mX selectivity of a series of Ln(HTCPB) compounds (where Ln = La, Pr, Nd and Sm), isostructural to 3, were determined using the same batch liquid sorption procedure as described in section 1.7 after 24 hours. Figures S16D and S16E show example selectivity GC traces for Nd(HTCPB) exposed to a 1:1 pX:mX mixture (X$_i^o$ / X$_j^o$ = 0.975 in both cases). The selectivity (Table S16) is highest for 3-Nd, contrary to rigid lattice GCMC calculations (Table S17) which predict that 3-Ce should be more selective. Average selectivities for 3 and 3-Nd are 4.55(6) and 6.33(3) respectively.
Supplementary Data:

7 Structures of 1 and 3

On desolvation of the parent material 1, we can access crystallographically in-situ the intermediate state 2 in which a carboxylate bridge between Ce···Ce dimers has been formed and H2O has been removed but EtOH remains coordinated to Ce, which upon removal of EtOH leads to the fully desolvated material 3 (Fig. S7). The desolvation of the bound H2O and EtOH solvates in 1 is found to enable the Ce metal centre to form two new carboxylate bridges. This alters the parent material Ce environment from a dimeric array with no direct bridging groups to one of bridged dimers creating a fully bridged backbone with modulated short and long Ce separations. The Ce···Ce distances for the bridging Ce backbone in 3 are 3.9517(10) and 5.5491(11) Å compared to the isolated Ce dimers in 1 4.1713(5) and 7.7314(5) Å. The formation of the new bridges requires the reorientation of the linker with changes in ring 2 rotation particularly pronounced (136.3(2)° to 118.3(3)° change in ring normal with respect to the central ring, Table S2).

Each ligand (Fig. S8) in 3 coordinates to two Ce centres via a bridge on three of the four carboxylate groups (O2x, O4x, O5x, where x = 7 or 8). The fourth carbonyl group (O1x, where x = 7 or 8) binds to a single Ce centre (via O17), with the second oxygen environment (O18) protonated, which prevents this group from forming a carboxylate bridge. This results in two carboxylate groups (O4x and O5x) bridging directly across the short Ce···Ce distance of the dimeric unit (O58 forming a μ-O bridge) with O2x forming a carboxylate bridge which connects the Ce···Ce dimers to each other (Fig. S7C, S8). The rings at positions 4 and 5 on the central ring thus form dimers on one side of the channel in 3, giving this edge of the central ring a distinct structural role from that of the edge defined by positions 1 and 2 – both these carboxylate groups are found between the dimers, with 1 terminal and 2 bridging them. (Fig.3A,C, S21D) As the two sides of the linker have different roles (dimer forming for the 4,5 edge, dimer bridging for the 1,2 edge) on the two different Ce chains, the central ring slants across the channel direction to connect a dimer on one side to a dimer bridge on the other. The sequence of rings along a Ce chain runs (45)12(45)12 on one side of the channel, with ‘( )’ indicating rings that bridge pairs of dimers, and(54)21(54)21 on the other, with diagonal connection (45) to 21 representing a single HTCPB linker. It is interesting to note that all carbonyl groups are found to orient out of the plane of the parent phenyl ring with the smallest deviation belonging to the C=O of the protonated group (O18-C16-C13-C14 = -1.1(10)°).

The HTCPB ligand bridges at right angles to the dimers to connect four dimers forming a layer, with the bridge between pairs of dimers formed by the ring 2 carboxylate connecting these layers parallel to the channel axes. The ligand geometry itself, with two neighbouring phenyl groups followed by a single proton produces a rectangular spacer of approximately 7 × 12 Å in size. This produces two types of cavity. When viewed from a construct of centroids based on the pendant phenyl groups the two cavities can be observed to have square (channel 1) and rectangular (channel 2) topology (Fig. S9). The two channels have been colour coded magenta and blue for channel 1 and channel 2 respectively (Fig. 1D & G).
Pore dimensions measured from the single crystal structure of 3 show channels 1 and 2 have approximate dimensions of 5.10 × 4.66 Å and 4.91 × 4.40 Å respectively, when measuring across the channel perpendicular to the channel direction.

8 Computational Results

8.1 Docking

pX but not mX is able to dock into the rigid 3 host structure. The pX is able to dock at any point within channel 1 (the larger of the two channels), but the preferred orientation is with the pX along the length of the channel in the site that allows for two C-H⋯π interactions between the C-H of the host and the benzene ring of the pX (as shown in Fig 2A). This site is preferred over alternative locations along channel 1 by at least 28 kJ mol\(^{-1}\). The molecular axis (along its longest dimension) is tilted away from the channel axis by ~ 30º (Fig. S12). pX also docks in an energetically favourable site within the smaller channel 2, at the wide part of the channel such that the pX centre of mass is between the Ce atoms forming the dimer. This site is, however, infrequently sampled even over 1 million insertion steps, indicating a highly specific sorption site (i.e. the pX must be randomly inserted with the correct orientation and position within the channel). This contrasts with the large number of possible sorption sites within channel 1 for pX.

8.2 CB-GCMC Maximum Uptake Results

The results from the experimental measurements led us to investigate further the observed selectivity and the observation that mX could be absorbed into the 3 structure, in contrast to the preliminary docking results on 3. We carried out CB-GCMC simulations to calculate the maximum uptake for the xylene molecules in the 3, 3P and 3M structures. The maximum uptakes for the molecules in each of the different simulations are given in Table S4 and whether or not the molecules sorbed within each of the two channels for each of the simulations is summarised in Table S5.

Firstly, we used single component CB-GCMC simulations (i.e. only one molecule was in the reservoir for insertion during the simulation) to calculate the maximum possible uptake and preferred sorption sites at high loading levels for each of the molecules in the 3, 3P and 3M structures. We observed that mX could now be sorbed into both loaded structures (3P and 3M) and into both channels, with even a very small amount (0.2 xylene molecules per unit cell) being loaded under pressure (10 bar) into the empty host 3 in channel 1, because of the adaption and expansion of the channels from 3 to 3M. The 3P channels also expand, allowing the uptake of pX to double to 2 per unit cell from 3 to 3P. This demonstrates the importance of the framework flexibility in allowing these molecules to enter the structure, which is not accounted for in the simulations of the rigid host 3. The increase in the volume of the channels is clear from the calculated void measurements in Table S6; for channel 1 the void volume increases from 209.7 Å\(^3\) in 3 to 242.5 Å\(^3\) (3P) or 283.6 Å\(^3\) (3M) per unit cell and for channel 2 from 182.5 Å\(^3\) in 3 to 206.4 Å\(^3\) (3P) or 218.2 Å\(^3\) (3M) per unit cell. The consequence of these channel expansions is that for both of the molecules in their empty host structures (pX in 3P and mX in 3M), the maximum calculated uptakes are now approximately 2 molecules per unit cell (2.0 for pX and 1.9 for mX). This matches the uptake values determined from the single crystal X-ray diffraction (SC-XRD) structures and corresponds to one molecule sorbed in each of the 2 channels. For pX the doubling in uptake from 3
to 3P corresponds to channel 2 now being more easily sorbed into compared to 3, where the one possible sorption site was rarely sampled (hence the 1.1 to 2.0 per u.c. increase in uptake). For mX, both of the previously inaccessible channels in 3 are accessible for sorption in 3M.

The uptake values and preferred sorption sites agree well between the SC-XRD structures and the sorption simulations for the 3P and 3M hosts (Fig S13). For pX, the sampled sorption sites from the CB-GCMC simulations show specific, preferred, sorption sites in both channels (shown as green dots for the centre of mass of the molecule for each sampled sorption site in Fig S13A). In channel 1, pX prefers the sorption site that was also observed in the docking simulations, at the point in the channel where it can form C-H···π interactions with the host. A comparison between the simulation location in Fig S13A and the SC-XRD structure in Fig. S13B shows the good agreement between experiment and simulation. In channel 2, pX also has a specific, preferred, sorption site, in the pocket where the channel is wider, with the centre of mass of the sorbed molecule between the two cerium atoms of the cerium dimer. Again, this matches both the equivalent docking site in 3 and the SC-XRD structure and can be rationalised by the fact that the channel is wider at that point, creating an ideal size sorption ‘pocket’, of the same length as the pX molecule. Not only the location matches, with the molecular axis of both molecules running along the channel axis, but the relative orientation of the two pX molecules to each other (approximately perpendicular) matches to the experiment, as shown by a comparison of the orientations in Fig. 2A, 2B and Fig. S13B. Docking simulations for pX, as originally carried out in the 3 structure were repeated in the 3P structure. These found that the pX aligns parallel to the channel orientation, in contrast to the ~30° tilt of pX relative to the channel axis in 3. This difference, where channel 1 in 3P has an ideal sorption pocket for pX, whilst the channel is rather large for a good fit of pX in 3, is shown clearly in Fig. S12. The overall expansion of the channel volume is thus not homogeneous but involves enhancing the fit around the guest molecule by change in channel shape as well as size.

For mX, the simulations show that there is no preferred sorption site in channel 1 in 3M, with multiple sorption sites along the length of the channel being visited. This corresponds to the SC-XRD observation that the mX is disordered along channel 1 which has to expand homogeneously along the channel to a greater extent in 3M than 3P to allow mX access (as shown by the cyan colouring compared to yellow in Fig 2C), removing any ideal pocket location. In channel 2, the mX does have a specific sorption site in 3M, in the equivalent position to the pX in 3P, in the centre of the cerium dimer in the widest pocket of the channel. This matches the SC-XRD structure (compare Fig. S13C orange simulation sorption sites and S13D SC-XRD structure), with two adjacent sites separated by ≈ 0.8 Å visible in some of the sample pores, consistent with the structural disorder observed experimentally.

8.3 Differences Between pX and mX

The simulation results so far have indicated that the pX molecule can sorb more easily, and with less required adaption of the host when compared to mX. However, in isolation (i.e. single component GCMC simulations), the maximum uptake of the two molecules is the same, with 2 molecules per unit cell, one in each of the two channels; this would not suggest any selectivity by uptake between the molecules. However, dual component GCMC sorption simulations (Table S4) are able to give us a further insight into the competitive sorption and hence selectivity between the two molecules by the host framework. When the selectivity ratio for pX/mX is calculated as (maximum uptake)_{pX}/(maximum uptake)_{mX}, it is clear that there is a strong selectivity for pX over
mX. For the 3P structure, the selectivity ratio calculated from dual component simulations is 6-6.5. This selectivity for pX over mX is even the case for the 3M structure, with a selectivity ratio of 4.3. The selectivity ratios from the sorption experiments (4.5) are within the range of these two simulation results.

In the single component simulations mX enters either of the loaded structures, with uptake approaching that of the pX at 2 molecules per unit cell (1.9 in 3M and 1.5-1.7 in 3P). Docking simulations for pX in 3P and mX in 3M (carried out under the same conditions as the initial simulations with 3) show that the adsorption energies for pX in channel 1 of 3P are at least 30 kJ mol\(^{-1}\) more energetically favourable than for mX in channel 1 of 3M, in addition to the energy required to distort the host, both of which favour sorption of pX over mX competitively. The largest pore radii increase by ~0.2 Å for 3 to 3P (magenta to yellow), but slightly more, 0.3 Å, for 3 to 3M (magenta to cyan) (Fig. 2C) as the 3 to 3M channel expansion is greater (as is also clear from the channel volume changes Table S6). For channel 2, both the pX and mX adsorb in the equivalent sorption site, but again the channel in 3M has expanded more than in 3P for the xylene to sorb. This effect is not as striking as for channel 1 (difference in void volume per unit cell in the loaded 3P and 3M structures is 41.1 Å\(^3\) for channel 1 compared to 11.8 Å\(^3\) for channel 2).

8.4 Comment on Simulation Features

The COMPASS27 forcefield used was not specifically reparameterised for this system, and in particular uses an atom type for cerium in a Ce\(^{4+}\) oxide. As the host is treated as a rigid body and the cerium atoms are not near the surface of the pore channel (i.e. do not closely interact with any sorbates), we believed that this is a reasonable approximation. Also, to test that the electrostatic contributions were not key to the sorption and therefore not biased by the chosen partial charges, the key results were repeated with all partial charges set to 0, so as to “turn off” the electrostatic interactions. The selectivity results remain similar, as shown in Table S7, with slightly enhanced selectivity without charges, but with no noticeable differences in the sorption sites. These features of the simulations, combined with the accurate calculation of selectivity and sorption sites, suggest that the primary factor in determining the sorption sites are the van der Waals interactions between the organic components, such as C-H\(\cdots\pi\) interactions, which should be well parameterised in a transferable forcefield, such as COMPASS27. This corroborates our conclusions that rather than specific interactions with metal sites, which can produce selectivity in other materials,\(^{19}\) here it is the difference in molecular shape that results in a different “fit” of the molecules within the host framework and hence the observed strong selectivity.

9 Structural Changes from 3 on Xylene Loading

9.1 Exchange in Roles of Rings 2 and 5 from 3 to 3P/3M

The loading of xylene guests into 3 (Fig. S20) produces a collective change in the role of the rings in bridging the chains of Ce dimers which both leaves the environment of the Ce almost unchanged and adjusts the pore structure to maximise the capacity for xylenes. Differences in this relaxation between pX and mX produce the differences in the 3P and 3M structures which produce the high selectivity between the two xylene isomers. The complete crystallographic order of the Ce(HTCPB)
frameworks in both structures permits the detailed analysis of the atomic-scale reasons behind the high selectivity observed.

In 3, the 1,2 and 4,5 edges of the central ring of the HTCPB bear benzoate rings that are located either between (1,2 with ring 2 bridging the dimers) or forming (rings 4 and 5) the Ce₂ dimers, and thus have distinct structural roles. (Fig. 3A, C) Correlated motion of the benzoate rings upon loading of the xylene guests changes the role of two of the four rings through rotation of the central ring about an axis perpendicular to the channel direction coupled with relative displacement of successive dimer chains to move each benzoate in 3 one location along the Ce dimer chain, resulting in ring 2 participating in dimer formation and carboxyphenyl ring 5 in dimer bridging in 3P/3M and thus exchanging their structural roles. (Fig. 3B, D) This makes the two edges of the central ring equivalent in 3P and 3M – carboxyphenyl ring 1 is between whereas carboxyphenyl ring 2 forms dimers (these rings describe the 1,2 edge of the central ring), and carboxyphenyl ring 5 is between whereas carboxyphenyl ring 4 forms dimers (these two rings describe the 4,5 edge of the central ring).

In terms of the chain of aromatic rings used in section 7 above to describe the formation of dimers in 3, the sequence along two chains on opposite sides of a channel is now:

(24)51(24)51(2)
(42)15(42)15(4)

where the linker is now more perpendicular to the channel axis as its two edges play identical roles (forming and bridging/between dimers) in the two chains it connects. The pivoting of the linker about the central ring thus swaps the roles of two of the benzoates with only minor changes to the metal coordination environment – this process is eased by the low barriers associated with substitution reactions at lanthanide centres. This structural relaxation changes the nature of the sites accessible to the xylene guests and enhances the capacity of 3 by making them centrosymmetric and better matched to the benzene ring of the guest.

The exchange of benzoate bridging roles leaves the dimer chain and carboxylate bridges remarkably unchanged between 3 and 3P/3M (Fig. S21). Thus coordination to the metal in 3P and 3M is similar to 3 with the exception that the carboxylate bridging the Ce dimers to each other switches from O2x to O5x (Fig S7C, S18E, S19E).

Direct overlaying of the asymmetric units (RMSD 0.121 Å) of 3P and 3M (Fig. S22A) provides little indication of structural differences in itself implying that these changes must be small and cumulative in nature, i.e. the correlation between small positional changes of individual atoms.

The relaxation in the HTCPB ligand position associated with the changes in carboxylate roles discussed above alters the channel geometries from 3 to 3P. On examination of the packing in 3 it can be seen that there is an A-B layer motif with a subsequent small but observable lateral shift of the ligand per repeat coincident with the Ce···Ce dimer. However in 3P and 3M the shift is more diagonal in nature (Fig. S22 B-D). The change in this shift alters the topology of the channel and results in a pronounced deviation from the relatively straight and cylindrical channel surface form observed in 3.

9.2 Channel Geometries
Channel surfaces were calculated for 3, 3P and 3M using the program Hole2\textsuperscript{18}. In each case calculations were performed on the host framework with channel guests removed where appropriate. The hydrogen atom positions were maintained from the crystallographic refinement. For each structure the principal channel direction was determined using calcvoid in Olex2. Then the location of a coordinate within the two channel spaces was determined as the starting Hole2 probe position. This could be achieved by either constructing a pseudo-centroid at the centre of the xylene ring or the utilisation of calcsoolv in Olex2 (channel coordinated orthogonalised from the raw output): no significant difference was observed in the final Hole2 output. These two parameters were then used to construct a Hole2 input file utilising the Olex2 plugin olex2hole (Table S1). Element radii were defined from the CSD\textsuperscript{19}, sample 0.2, dotden 35, LINON, MCDISP 0.1, MCKT 0.1, MCSTEP 5000 and endrad 4 were used in all cases.

Examination of the channel metrics provided by Hole2 suggests a complex restructuring of the channels on guest loading. For the channel 1 surfaces 3<3P<3M in terms of minimum (min), mean and maximum (max) probe radius (Table S1), whereas for channel 2 we observe a trend of 3<3M<3P for both the min and mean parameters. However the delta (difference between minimum and maximum) and maximum parameters, with the trends of 3M<3P<3 and 3M<3<3P respectively, have smallest values for 3M. This suggests correlation between the maximum size and the shapes of channel 1 and channel 2, in contrast to simple homogeneous expansion on guest loading.

For channel 1 the surface generated from 3 appears to be the closest to a cylinder in morphology. For 3P there is a correlation between the channel radius and the pX location. The channel has a smaller probe radius (magenta) located near to the pX methyl groups with both cyan (the largest probe size) and yellow being dominant for the majority of the xylene location (Fig. 2C,D). The colour scheme is almost inverted when we examine the 3M channel 1 surface. In this case the surface is predominantly cyan with some yellow (~9 %) of the total surface area). This is in contrast to both 3P (~74 % yellow) and 3 (~18 %) and indicates homogeneous expansion of channel 1 in 3M. For mX, unlike the pX case, there is not an observable change in probe size encapsulating the guest i.e. there is no specific site defined for the guest within channel 1 in 3M. It is also apparent that the channel surface for 3M shows the greatest deviation from a true cylinder with a significant 'zig-zag' motif becoming observable.

In channel 2 the xylene is located in both 3M and 3P near the site of maximum probe radius, unlike in channel 1, where there is no direct correlation of probe radius and xylene length for mX in 3M. There is instead a larger area of surface with a smaller probe radius into which the pX methyls are observed to extend. The channel 2 surfaces for 3P and 3M are similar, with the most striking difference being an enlarged section of blue in 3M replacing a region of red in 3P (Fig. 2). This is consistent with the positional disorder of mX in this channel: the associated interactions were found to be longer and therefore weaker than in the 3P case, as demonstrated in the Hirshfeld surface analysis (Fig. S25 B,C).

In both 3M and 3P there is a noticeable 'dog leg' motif compared to the surface of 3 when viewed normal to the plane of the xylene guest. Viewing the surfaces parallel to the guest plane we observe a pocket which can be related to the dimension of the Ce dimer. The constriction defining this pocket is related to the location of the ligand-ligand carboxylic group hydrogen bond which terminates the dimers. This constriction is most noticeable in the surface of 3 probably due to its inherent cylindrical form. In 3P the nature of the groups producing the constriction (Fig. S23) offers
a possible mechanistic route for xylene transport via the rotation of the monodentate protonated carboxylate and parent phenyl ring 1 about the single Ce-O bond to become more parallel to the channel direction to open up the channel for xylene motion between pockets, and subsequent rotation back to obstruct the channel space.

9.3 Xylene Environments Including Hirshfeld Surfaces

Fig. S24 shows the C-H···π contacts present in channel 1 between pX and the framework in 3P (A, B) and mX and the framework in 3M (C, D). All the mX C-H···π interactions are longer than those for pX, and even formation of these more distant interactions requires rotation of the mX away from the pX orientation.

Hirshfeld surface analysis was undertaken along with 2D fingerprint plot generation to examine the local environment of each xylene (Fig. S25-28). The intermolecular interactions highlighted in these plots are listed in Tables S13-14.

The equidistant “T-shaped” C-H···π interaction of pX with the hydrogen of the central phenyl ring of the framework ligand (H3) shows as a prominent feature on the 2D fingerprint plot (Fig. S25A, yellow shading, & S26A). Examination of the equivalent depiction of channel 1 with mX shows that the ring is orientated away from this ideal alignment with a relative rotation of 16° from the pX ring plane. The resulting C-H···π interactions (Table S13) are asymmetric and all longer than those formed by pX. The two modelled mXs each have their own unique 2D fingerprint plot with similar characteristics (Fig. S25 B&C). The most outstanding features in both cases are the large area of diffuse interactions at large de/di (de is the distance from the Hirshfeld surface to the nearest nucleus outside the surface. di is the corresponding distance to the nearest nucleus inside the surface), characteristic of a poor fit of the guest into a cavity space that is too large and incorrectly shaped for it. The 3M framework 2D fingerprint plots for the mX are found at greater di and de values than found for pX, which suggests an inefficient fit to the mX molecular shape. We also observe a shift to shorter di/de distances which correlate to short H···H contacts in the mX-A plot, demonstrating remaining clashes in shape after the relaxation of the structure of 3 to accommodate the guest.

Longer non-bonded interactions are expected here than in simple molecular systems due to the pre-organised nature of the framework and the space limitations of the channel coupled to the guest sizes. For this reason we have used protein structural cut-offs as defined by Burley et al.(28) for C-H···π interactions and used parameterisations based on weak hydrogen bonding often observed in peptide structures. Classically in protein crystallography the edge-to-face type of interaction is often defined by the ring centroid to ring centroid distances between 4.5 and 7.0 Å with dihedral angles lying between 50° and 90°.

Examination of the C-H···π interactions between the pX and mX aromatic rings and the framework (ligand central aromatic ring C-H) in channel 2 suggests, as in channel 1, an edge-to-face interaction (Fig. S26C). Tsuzuki suggests that nature of the “T-shaped” or edge-to-face interactions is biased towards dispersive contributions with little to no electrostatic component. As such they are found to operate over greater distances and across a wider range of angles than classical hydrogen bonding would permit (dominated by electrostatic interactions). The weaker electrostatic component is only critical for alignment of the X-C direction along the phenyl ring plane normal.
However, unlike in channel 1 where the 2D fingerprint plot for 3P shows the characteristic “chicken wing”, we find no equivalent feature for 3P in channel 2 (Fig. S27A). This is because the angle of approach between the framework-H and the xylene-π changes significantly between channel 1 and channel 2. The framework-to-xylene and xylene-to-framework interactions for the mX in channel 2 of 3M are shown in Fig. S28 and Table S13&14.

The pX surface contributions in channel 1 and 2 are dominated by framework H atom to pX interactions as would be expected. However, unlike channel 1, the channel 2 surface also has a contribution from the framework O (17 %), Fig. S27C-F. The ability to access the framework O atoms in channel 2 produces a CH···O hydrogen bond from the xylene methyl to the framework OH moiety (Fig. 4, S27D), which itself is involved in an intramolecular hydrogen bond (Table S14), vide supra. The distances determined place this non-classical hydrogen bond within acceptable parameters for weak hydrogen bonding, comparable to those observed in many studies including peptidic systems[22].

There is only one C-H···O interaction formed by mX in channel 2 (Fig. S28) and the C-H···π contacts again favour one side of the ring only as in channel 1. Formation of these interactions requires relative rotation of the pX and mX molecules to each other both in yaw and pitch within the cavity space (Fig.S29).

The reasons for translational and orientational displacement of mX relative to pX can be appreciated by considering the location of the mX molecule coincident with the observed pX aromatic ring and one pX methyl position. This causes the second mX methyl position to puncture the wall of channel 2 of 3P in each case, Fig. S30. Therefore the mX molecule is forced to displace from the ideal pX location into two symmetry-related disordered positions, where it is as a result unable to align a single methyl into the central space of the channel as seen in pX: There are thus two non-ideal mX locations as opposed to one ideal pX location.

9.4 Guest-Free Expanded Region in 3M

The channel surfaces are dominated by the framework ligand phenyl rings (Fig. S31). Small alterations to the ring orientations relative to each other and to the channel allow for the formation of larger void spaces. To compare the ring orientations between 3P and 3M, a total of 64 parameters were defined for each structure based on three mean planes, two defined at the centre of each phenyl ring (planes parallel and normal to the central and pendant rings) and the third from a plane defined by the -CO₂ moiety (Fig. S32): Angle (plane-plane), Twist Angle (plane-plane), Fold Angle (plane-plane), Distance (plane centroid-plane centroid), Distance (plane[C1 C2 C3 C4 C5 C6]-centroid), Shift (plane [C1 C2 C3 C4 C5 C6]-plane), Distance (plane[Ox7 Ox8 Cx6]-centroid) and Shift (plane [Ox7 Ox8 Cx6]-plane) where x = 1, 2, 4, and 5 as per Fig. S7A, “Twist and Fold’ angles as defined in Olex2[4a] were calculated for each pair of mean planes and their associated centroids.

The guest-free expanded region in 3M is defined by H12, H51 and H52. We find that rings 1 and 5 of the framework ligand show differences between 3M and 3P, suggesting that it is relaxation of these rings which is involved in differentiating the framework response to pX and mX (Table S2). The structural relaxation from 3P to 3M to accommodate the mX guest through creation of the guest-free expanded region thus arises from repositioning of the two rings (1 and 5) that are in the
interdimer rather than dimer-forming positions in the xylene-loaded structures formed by relaxation of the carboxylate locations on sorption into 3. These two rings are thus less constrained by the requirement to form short bonds to two Ce centres, and able to relax to accommodate mX by the mechanisms discussed below.

The hydrogen at position 5 of the mX guest interdigitates into the space between rings 2 and 5. An equivalent short contact does not occur in the pX case. This short contact is evident in the Hirshfeld surface generated for mX in channel 2 (Fig. S27B, S28). Carboxyphenyl ring 2 (C20-C25) and Carboxyphenyl ring 5 (C50-C55) sit next to each other lining the opposing sides of the channel 2 (Fig. S31). Carboxyphenyl ring 5 is also close to the guest-free expanded region of the channel space observed in 3M. The centroid-centroid distances between carboxyphenyl ring 2 and 5 slightly increase from 3P to 3M (4.985 Å vs 5.170 Å). We also find a change in the torsion angle (O58-C56-C53-C52) of 4.16° of the carboxylate borne by carboxyphenyl ring 5. This torsion angle is linked to a bridging carboxylate group (O58-C56-O57) which bridges the longer interdimer Ce pair separation (Ce···Ce 5.6603(7) Å). There is only a shift of 0.77° for the equivalent carboxyphenyl ring 2 torsion (O28-C26-C23-C22, where the O28-C26-O27 group forms the short dimeric unit (Ce···Ce 4.0500(6) Å) itself. Carboxyphenyl ring 5 thus reorients from 3P to 3M.

H12 of carboxyphenyl ring 1 is also in close proximity to the guest-free expanded region in the mX channel 2 surface. In 3P the CO2H group of carboxyphenyl ring 1 hydrogen bonds to the methyl-H of the pX guest. This interaction is longer in the mX structure (O···C distances 3.442(6) vs 4.03(2) in 3P vs 3M) with the small rotation in carboxyphenyl ring 1 in 3M required to optimise this interaction increasing the void space over that in 3P where the closer match to the methyl positions does not require this extra displacement of carboxyphenyl ring 1.

9.5 Comparison of Ce(HTCPB) and Nd(HTCPB) Structures

The general trends of increasing unit cell volume as observed for the Ce(HTCPB) frameworks 3P<3M is maintained in the Nd(HTCPB) frameworks 3P<3M<Nd<3N<3M-Nd (Table S12). The Nd materials consistently show smaller unit cell volumes than the Ce equivalents. The expansion of 3-Nd to form 3P-Nd is 8Å³ greater (4.3% expansion from 3-Nd) than that for formation of 3P from 3 (3.8% expansion from 3), whereas the expansions of both Ce and Nd hosts to form the mX-loaded structures are the same (7.3%), suggesting greater ease of adapting the 3-Nd host structure to the pX rather than the mX isomer.

The percentage structure occupation shows the same trend as observed in Ce(HTCPB) 3>3P>3M (3-Nd >3P-Nd>3M-Nd). As with the Ce structures we find that the largest void spaces are observed for the 3M-Nd species. There is a greater difference of percentage solvent accessible volume per cell on going from 3-Nd to 3P-Nd than the equivalent 3 to 3P. This coupled to the changes in unit cell volume discussed above would suggest that 3-Nd is a slightly denser form than 3.

As with the Ce structures, we find that in 3P-Nd, pX loads into an ordered optimised location with mX in 3M-Nd showing a similar continuum of disorder in channel 1 and localised disorder in channel 2. With respect to the positions of the xylene guests in the frameworks 3M, 3M-Nd, 3P and 3P-Nd we find comparable C-H···π and C-H···O distances (Tables S13 and S14), consistent with the guest to framework response governing the guest location and the final structure of the guest-loaded
material. For 3M and 3M-Nd the minimum possible H–O contact distances to O18 for the methyl hydrogens of 3.342Å in 3M and 3.430Å in 3M-Nd were determined analytically as the minimum distance between the oxygen atom and a circle describing all possible hydrogen atom position due to rotation about C-C bond linking the methyl group to the aromatic ring of the xylene. This small difference results from the larger guest methyl carbon to O18 contact in the 3M-Nd case despite the smaller unit cell volume of 3M-Nd compared with 3M.

Examination of the relative alignment of the HTCPB moieties in the structure (Table S15) produces comparable results for 3P and 3P-Nd whereas we observe a greater asymmetry in the layer repeat in 3M-Nd compared to 3M, 3P or 3P-Nd. Examination of the core to pendant aryl ring torsion angles (Table S2) and the Nd dimers (Fig. S34, S35, S36) reveals that the ring-2 to ring-5 exchange observed in 3 to 3P and 3 to 3M is not present in 3-Nd which shows the ring-2 bridge from the start. The relaxations in the core to pendant torsion angles are larger in going from 3-Nd to 3P-Nd/3M-Nd than on going from 3 to 3P/3M, consistent with strong structural relaxation of 3-Nd on loading the xylene isomers, and also consistent with the comparable changes in unit cell volume upon guest loading to those seen in the Ce case.

A visual comparison of the six structures can be achieved by overlaying the asymmetric units of 3:3-Nd, 3P:3P-Nd and 3M:3M-Nd, Fig. S37. The greatest difference is observed for the 3 and 3-Nd structures with an alignment RMSD of 0.512 Å (cf. 0.221 and 0.239 Å for 3P:3P-Nd and 3M:3M-Nd respectively – RMSD calculated by superposing the framework non-hydrogen atoms only). There is good referencing in the location of the guests mX and pX in the Nd- and Ce-loaded materials.

The contraction in unit cell dimensions on moving from Ce to Nd would co-operatively amplify both favourable and unfavourable interactions between the guests and the framework, increasing the penalty of loading an unfavourable guest by increasing close framework to guest contacts while shortening the attractive contacts, consistent with enhanced guest selectivity for the Nd(HTCPB) material.
Tables

**Table S1:** Physical Properties of the C₈ aromatic isomers.

| C₈ Isomer | Boiling Point (°C) | Kinetic Diameter (Å) |
|-----------|--------------------|----------------------|
| pX        | 138.50             | 5.8                  |
| mX        | 139.10             | 6.4                  |
| oX        | 136.00             | 6.5                  |
| EB        | 144.40             | 6.0                  |

**Table S2:** Rotational changes in the HTCPB linker with formation of 3 from 1 and subsequent guest loading into 3. Central ring centroid plane normal to pendant ring plane normal angle (°) as defined in Fig. S32B where 1, 2, 4 and 5 refer to ring number. The rotational differences between 3M and 3P are discussed in 9.4. Subsequently this is indicated as (9.4) at the end of a Table or Figure caption. 3 is Ce(HTCPB), 3-Nd is Nd(HTCPB), P and M indicate structures loaded with pX and mX respectively.

| Compound | 1       | 2       | 4       | 5       |
|----------|---------|---------|---------|---------|
| 1        | 132.69(15) | 136.30(15) | 131.97(15) | 135.46(15) |
| 3        | 146.1(3) | 118.3(3) | 138.7(3) | 130.8(3) |
| 3P       | 143.66(13) | 117.00(15) | 139.32(13) | 126.45(15) |
| 3M       | 137.99(19) | 120.1(2) | 138.49(18) | 127.7(2) |
| 3-Nd     | 139.5(3) | 128.7(2) | 146.9(3) | 117.9(2) |
| 3P-Nd    | 143.8(4) | 117.0(9) | 139.10(12) | 127.40(13) |
| 3M-Nd    | 138.24(12) | 119.80(13) | 138.74(12) | 129.04(13) |
Table S3: Ln dimer and central HTCPB ring orientation changes associated with the transformation from 1 to 3 and guest loading into 3. C1 > C6 mean plane normal to (100) plane normal angle (°), C1 > C6 mean plane normal to Ln-Ln vector and Ln-Ln vector to (100) plane normal angles (°). The (100) plane normal is the channel direction.

| Compound | (C1-C6) Plane- (Ln-Ln)Vector Angle (°) | Ln-Ln Vector to (100) Plane Normal Angle (°) | C1 > C6 [Mean Plane Normal to (100) Plane Normal Angle (°)] |
|----------|----------------------------------------|-----------------------------------------------|-------------------------------------------------|
| 1        | 7.27(10)                               | 54.09(10)                                     | 52.14(11)                                      |
| 3        | 15.00(10)                              | 11.85(10)                                     | 22.33(17)                                      |
| 3P       | 14.83(10)                              | 29.17(10)                                     | 18.22(10)                                      |
| 3M       | 15.47(14)                              | 30.20(14)                                     | 15.86(14)                                      |
| 3-Nd     | 15.62(19)                              | 36.868(10)                                    | 43.25(19)                                      |
| 3P-Nd    | 14.26(9)                               | 28.583(7)                                     | 17.82(10)                                      |
| 3M-Nd    | 14.99(9)                               | 29.620(6)                                     | 15.60(9)                                       |

Table S4: Maximum uptake calculated from CB-GCMC simulations (8.2) with one (pX or mX sorbed separately) or two (competitive sorption of both pX and mX) guest species at 383 K and 10 bar in the 3, 3P and 3M structures. The values are quoted per unit cell (equivalent to per two Ce(HTCPB) units) and are averaged over three repeats of the simulations.

| Host | Components | pX  | mX  | ratio   |
|------|------------|-----|-----|---------|
| 3    | 1          | 1.13| 0.22| 5.11    |
| 3    | 2          | 0.9-1.0| 0.02| 45-50   |
| 3M   | 1          | 1.82| 1.88| 0.97    |
| 3M   | 2          | 1.63| 0.38| 4.33    |
| 3P   | 1          | 2.00| 1.48-1.70| 1.18-1.36|
| 3P   | 2          | 1.50-1.63| 0.25| 6.0-6.5 |
Table S5: Occupation of each of the two channels by the xylene guests across all the simulations (8.2). [a] Note: these sites were sampled infrequently even over millions of insertion steps.

| Host | Simulation                      | pX channel 1 | mX channel 1 | pX channel 2 | mX channel 2 |
|------|--------------------------------|--------------|--------------|--------------|--------------|
| 3    | Docking                        | YES          | NO           | YES[a]       | NO           |
| 3    | CB-GCMC single component       | YES          | YES[a]       | YES          | NO           |
| 3    | CB-GCMC dual component         | YES          | YES[a]       | YES[a]       | NO           |
| 3M   | CB-GCMC single component       | YES          | YES          | YES          | YES          |
| 3M   | CB-GCMC dual component         | YES          | YES          | YES          | YES          |
| 3P   | CB-GCMC single component       | YES          | YES          | YES          | YES          |
| 3P   | CB-GCMC dual component         | YES          | YES          | YES          | YES          |

Table S6: Channel volumes, solvent accessible volumes and channel radius at narrowest points for 1, 3, 3P, 3M, 3-Nd, 3P-Nd and 3M-Nd.

| ID | Volume/cell | Total solvent accessible | Cell Volume | Radius Largest Probe | Structure Occupies |
|----|-------------|--------------------------|-------------|----------------------|--------------------|
|    | (Å³) (%)    | Channel 1 Channel 2      | (Å³) (%)     | (Å)                  | (%)                |
| 1* | 274.10      | 16.10                    | 242.60 14.2 | 15.8 0.9             | 1702.79 2.20       | 1036.66 60.88      |
| 3  | 392.20      | 24.30                    | 209.70 13.0 | 182.50 11.30         | 1611.72 2.20       | 914.45 56.74       |
| 3P | 448.90      | 26.80                    | 242.50 14.5 | 206.40 12.30         | 1673.27 2.40       | 917.67 54.84       |
| 3M | 501.80      | 29.00                    | 283.60 16.4 | 218.20 12.60         | 1729.02 2.50       | 917.70 53.08       |
| 3-Nd | 415.1      | 26.0                     | 219.5 13.8  | 195.6 12.3           | 1594.39 2.20       | 914.99 57.39       |
| 3P-Nd | 485.7     | 29.2                     | 268.2 16.1  | 217.5 13.1           | 1663.42 2.40       | 915.28 55.02       |
| 3M-Nd | 535.6     | 31.3                     | 307.6 18.0  | 228.1 13.3           | 1711.72 2.50       | 915.62 53.49       |

*Calculations based on Ce-EtOH solvate (PART 0 & 2) with all unbound guests removed from channel space. Void 3 15.8 Å³ 0.9 % located in channel 2 shifted down x from Void 2. Void volumes calculated using calcsolv(1.2, 0.2) in Olex2. Largest probe radius and penetration direction using calcvoid –p –r=0.1 in Olex2. Standard CSD element radii used for all calculations.\(^{[19]}\).
**Table S7:** Results for the maximum uptake calculated from CB-GCMC simulations at 383 K and 10 bar for the 3P structure, with (QEq) and without (None) the inclusion of partial charges in the simulation. The values are quoted per unit cell and are averaged over three repeats of the simulations.

| Charges | Components | pX    | mX        | Ratio |
|---------|------------|-------|-----------|-------|
| QEq     | 1          | 2.00  | 1.48-1.70 | 1.2-1.4 |
| QEq     | 2          | 1.50-1.63 | 0.25 | 6-6.5 |
| None    | 1          | 2.00  | 1.38      | 1.46  |
| None    | 2          | 1.53  | 0.00      | ∞     |

**Table S8:** Selectivity of 3 towards equimolar mixtures of the C₈ aromatic isomers. Selectivities ($α_{ij}$) calculated using equation S1. Errors calculated from repeat experiments.

| C₈ isomer j | oX  | mX  | pX  | EB  |
|-------------|-----|-----|-----|-----|
| C₈ isomer i | oX  | mX  | pX  | EB  |
| oX          | -   | 1.22 (2) | 0.18 (3) | 0.64 (5) |
| mX          | 0.81 (2) | -    | 0.22 (6) | 0.42 (2) |
| pX          | 5.65 (3) | 4.55 (6) | -    | 2.38 (2) |
| EB          | 1.56 (5) | 2.38 (2) | 0.42 (2) | -    |

**Table S9:** Xylene selectivity ($α_{ij}$) reported for porous materials.

| MOF            | Selectivity ($α_{ij}$) | $α_{pXmX}$ | $α_{pXoX}$ | $α_{pXEB}$ |
|----------------|------------------------|------------|------------|------------|
| MIL-125(Ti)-NH₂ [25] | 4.4                    |            |            |            |
| CAU-1(Al)-NH₂ [25]  | 2.8                    |            |            |            |
| MIL-125(Ti) [25]    | 3.5                    | 2.2        |            |            |
| MIL-47 [26]         | 2.9                    | 0.7        | 9.7        |            |
| MIL-53(Al)ht [26]   | 0.8                    | 0.3        | 3.1        |            |
| HKUST-1 [26]        | 0.9                    | 1.4        | 1.2        |            |
| MOF-1 [27]          | 0.5                    |            |            |            |
| UiO-66 [28]         | 0.4                    |            |            |            |
| Zeolite KBaY [15]   | 4.0                    |            |            | 2.1        |
| Zeolite KY [29]     | 4.5                    |            |            |            |
| ZSM-5 membrane [30] | 4.3                    | 4.4        |            |            |
Table S10: Selectivity of 3 towards an equimolar mixture of pX and mX after the period of time shown. Errors calculated from repeat experiments.

| Time     | Selectivity, $\alpha_{pXmX}$ |
|----------|-----------------------------|
| 1 minute | 3.28 (3)                     |
| 10 minutes | 3.72 (7)                   |
| 24 hours | 4.55 (6)                     |
| 7 days   | 4.91 (5)                     |

Table S11: Minimum, Maximum, Difference (Delta) and Mean Probe Radius (Å) determined by Hole2 for the channels in 3, 3P and 3M.

| Compound | Channel 1 | Channel 2 |
|----------|-----------|-----------|
|          | Min | Max | Delta | Mean | Min | Max | Delta | Mean |
| 3        | 2.05 | 2.25 | 0.20  | 2.15 | 1.66 | 2.27 | 0.61  | 1.97 |
| 3P       | 2.18 | 2.42 | 0.24  | 2.30 | 1.95 | 2.33 | 0.38  | 2.14 |
| 3M       | 2.30 | 2.54 | 0.24  | 2.42 | 1.93 | 2.26 | 0.33  | 2.10 |

Table S12: Unit cell dimensions of 3, 3P, 3M, 3-Nd, 3P-Nd and 3M-Nd (100 K).

|          | a /Å   | b /Å    | c /Å   | α /°   | β /°    | γ /°   | V / Å³ |
|----------|--------|---------|--------|--------|---------|--------|--------|
| 3        | 9.9890(11) | 11.4163(13) | 15.2492(17) | 93.756(5) | 90.263(6) | 93.814(6) | 1611.70(3) |
| 3P       | 9.5603(4)  | 12.1386(5)  | 15.9458(10)  | 88.455(10) | 74.417(10) | 70.233(10) | 1673.27(12)  |
| 3M       | 9.7441(6)  | 12.3318(7)  | 15.7737(9)   | 88.979(2)   | 77.299(2)   | 69.498(2)   | 1729.02(18)  |
| 3-Nd     | 9.3093(11) | 11.9578(14) | 15.8071(19)  | 81.178(4)   | 73.671(4)   | 71.162(4)   | 1594.4(3)    |
| 3P-Nd    | 9.5256(5)  | 12.1272(6)  | 15.8886(8)   | 88.508(2)   | 74.677(2)   | 70.379(2)   | 1663.42(15)  |
| 3M-Nd    | 9.6812(6)  | 12.2892(7)  | 15.7406(10)  | 88.977(2)   | 77.463(2)   | 69.750(2)   | 1711.72(18)  |
Table S13: C-H⋯π Interactions from the framework to the xylene guests in 3P, 3M, 3P-Nd and 3M-Nd\textsuperscript{[24]}.

| Compound | Channel | Xylene | Donor | Centroid-Centroid Distance (Å) | Dihedral Angle between aromatic rings (°)* | No./Xylene |
|----------|---------|--------|-------|-----------------------------|------------------------------------------|------------|
| 3P       | 1       | pX     | H3    | 5.658                       | 92.097                                   | 2          |
| 3P       | 2       | pX     | H44   | 5.561                       | 143.23                                   | 2          |
| 3M       | 1       | mXA    | H3    | 5.811                       | 93.75                                    | 1          |
| 3M       | 1       | mXA    | H3    | 6.026                       | 93.75                                    | 1          |
| 3M       | 1       | mXB    | H6    | 6.184                       | 90.93                                    | 1          |
| 3M       | 1       | mXB    | H6    | 5.961                       | 90.93                                    | 1          |
| 3M       | 2       | mX     | H44   | 5.938                       | 142.14                                   | 1          |
| 3M       | 2       | mX     | H44   | 4.931                       | 142.14                                   | 1          |
| 3P-Nd    | 1       | pX     | H3    | 5.658                       | 92.50                                    | 2          |
| 3P-Nd    | 2       | pX     | H44   | 5.470                       | 142.54                                   | 2          |
| 3M-Nd    | 1       | mXA    | H3    | 5.791                       | 89.5                                     | 1          |
| 3M-Nd    | 1       | mXA    | H3    | 6.011                       | 89.5                                     | 1          |
| 3M-Nd    | 1       | mXB    | H6    | 6.183                       | 89.2                                     | 1          |
| 3M-Nd    | 1       | mXB    | H6    | 5.955                       | 89.2                                     | 1          |
| 3M-Nd    | 2       | mX     | H44   | 5.851                       | 142.34                                   | 1          |
| 3M-Nd    | 2       | mX     | H44   | 4.923                       | 142.34                                   | 1          |

*The dihedral angle is defined from the normal of a mean plane generated for each aromatic ring and the angle between them.
Table S14: C-H···O Hydrogen Bonds from the xylene methyl to the carboxyphenyl ring 1 OH (first two rows 3P, 3M, 3P-Nd and 3M-Nd), and classical hydrogen bonds[^22] (final five rows).

| Compound | D   | H   | A   | d(D-H)/ Å | d(H-A)/ Å | d(D-A)/ Å | D-H-A/ ° | No./Xylene |
|----------|-----|-----|-----|-----------|-----------|-----------|----------|------------|
| **C-H···O** |     |     |     |           |           |           |          |            |
| 3P       | C20X | H20C| O18 | 0.98(5)   | 2.583(3)  | 3.442(6)  | 146.3(4) | 2          |
| 3M       | C10X | H10A| O18 | 0.978(17) | 3.351(5)  | 4.03(2)   | 128.2(14)| 1          |
| 3P-Nd    | C20X | H20A| O18 | 0.979(5)  | 2.563(2)  | 3.431(6)  | 147.6(4) | 2          |
| 3M-Nd    | C7C  | H7CC| O18 | 0.959(6)  | 3.818(2)  | 4.092(6)  | 99.8(4)  | 1          |

| **O-H···O** |     |     |     |           |           |           |          |            |
| 1          | O1WB | H1WC| O28S2| 0.869(10)| 2.59(19)  | 2.721(4)  | 89(12)   | -          |
| 1          | O17  | H17 | O28S2| 0.61(6)  | 1.90(6)   | 2.507(4)  | 171(8)   | -          |
| 3          | O18  | H18 | O27S1| 0.84     | 1.82      | 2.642(7)  | 167.3    | -          |
| 3P         | O18  | H18 | O58S4| 0.84     | 1.82      | 2.661(4)  | 173.2    | -          |
| 3M         | O18  | H18 | O58S5| 0.84(5)  | 1.840(3)  | 2.672(6)  | 170.4(3) | -          |
| 3-Nd       | O18  | H18 | O58S5| 0.84     | 1.82      | 2.658(6)  | 172.3    | -          |
| 3P-Nd      | O18  | H18 | O58S5| 0.84     | 1.82      | 2.645(4)  | 167.7    | -          |
| 3M-Nd      | O18  | H18 | O58S5| 0.84     | 1.8468(1) | 2.6606(1)| 162.71   | -          |

[^22]: Distance represented by dark blue double headed arrow Fig. S32A: there are two distinct distances in the structure, both of which are tabulated. #Light blue double headed arrow Fig. S32A represented as before.

Table S15: Parameters showing the largest deviations between 3M, 3P, 3M-Nd and 3P-Nd in terms of changes to rings 2 and 5 and the associated carboxylate torsions (parameters shown in Fig. S32).

| Parameter                                | 3M     | 3P     | 3M-Nd  | 3P-Nd  |
|------------------------------------------|--------|--------|--------|--------|
| Plane-plane angle (RING5-CO_{2}(5)-plane)° | 147.242| 151.911| 150.170| 146.135|
| Plane-plane angle (Central RING-CO_{2}(5)-plane)° | 95.268 | 101.172| 100.896| 95.052 |
| Plane-plane angle (Central RING-CO_{2}(2)-plane)° | 110.357| 112.952| 110.941| 108.559|
| Plane-plane angle (RING2-CO_{2}(2)-plane)° | 8.113  | 8.563  | 10.650 | 9.589  |
| Torsion angle (O58-C56-C53-C52)° | 26.876 | 31.031 | 28.711 | 31.749 |
| Torsion angle (O28-C26-C23-C22)° | 6.342  | 5.576  | 7.546  | 8.207  |
| Torsion angle (C25-C20-C2-C1)° | -122.176| -117.979| -122.272| -118.082|
| Distance (central ring plane to central ring centroid) of next layer + 1Å | 9.418  | 9.023  | 9.373  | 9.021  |
| Distance (central ring centroid to central ring centroid) [next repeat] Å | 5.170 [4.684] | 4.998 [4.615] | 4.924 [4.835] | 4.975 [4.610] |
| Distance (plane[RING2]-centroid)-(plane[_RING5]-centroid) [next repeat] Å | 4.858 [4.954] | 4.683 [4.984] | 4.666 [5.131] | 4.675 [4.961] |
**Table S16:** $\alpha_{pXmX}$ selectivities of a series of isostructural Ln(HTCPB) compounds denoted 3-Ln. Errors calculated from repeat experiments.

| Ln   | Selectivity $\alpha_{pXmX}$ |
|------|-----------------------------|
| 3-La | 4.48 (7)                    |
| 3-Ce (3) | 4.55 (6)            |
| 3-Pr | 6.15 (3)                    |
| 3-Nd | 6.33 (3)                    |
| 3-Sm | 6.08 (4)                    |

**Table S17:** Maximum uptake calculated from CB-GCMC simulations at 383 K and 10 bar in the 3-Nd structure. The values are quoted per unit cell (equivalent to per two Nd(HTCPB) units) and are averaged over three repeats of the simulations. The outcome of equivalent calculations on rigid 3-Ce from Table S4 are shown to enable comparison of the predicted selectivities based on rigid host structures which do not relax.

| Host  | Components | pX    | mX    | Ratio |
|-------|------------|-------|-------|-------|
| 3-Nd  | 1          | 1.54  | 0.07  | 22    |
| 3-Nd  | 2          | 1.25  | 0.11  | 11.36 |
| 3-Ce  | 1          | 1.13  | 0.22  | 5.11  |
| 3-Ce  | 2          | 0.9-1.0 | 0.02 | 45-50 |
Table S18: Crystal data and refinement parameters for parent structures 1,1-Nd,3 and 3-Nd.

| Identification code | fs_100KT | snt100K-3 | B00098 | C00119C3 |
|---------------------|----------|-----------|---------|-----------|
| Sample Code         | 1        | 3         | 1-Nd    | 3-Nd      |
| CCDC                | 920427   | 920428    | 977993  | 975279    |
| Empirical formula   | C37.5H34.| 75CeO12.5 | C34H19CeO8 | C37.3H24.5Nd O12.8 |
|                     | C34H19NdO8 |         |         | C34H19NdO8 |
| Formula weight      | 825.52   | 695.61    | 822.53  | 699.73    |
| Temperature/K       | 100(2)   | 100(2)    | 100(2)  | 100(2)    |
| Crystal system      | triclinic| triclinic | triclinic| triclinic |
| Space group         | P-1      | P-1       | P-1     | P-1       |
| a/Å                  | 10.57830(10) | 9.2989(11) | 10.55610(10) | 9.3093(11) |
| b/Å                  | 10.42710(10) | 11.4163(13) | 10.53780(10) | 11.9578(14) |
| c/Å                  | 16.9210(11) | 15.2492(17) | 16.8962(11) | 15.8071(19) |
| α/°                  | 83.158(6) | 93.756(5) | 83.205(6) | 81.178(4) |
| β/°                  | 76.314(5) | 90.263(6) | 76.425(5) | 73.671(4) |
| γ/°                  | 70.023(5) | 93.814(6) | 69.971(5) | 71.162(4) |
| Volume/Å³            | 1702.80(11) | 1611.7(3) | 1715.02(13) | 1594.4(3) |
| Z                    | 2        | 2         | 2       | 2         |
| pcalc mg/mm³         | 1.61     | 1.433     | 1.593   | 1.458     |
| m/mm³                | 1.405    | 1.46      | 1.582   | 1.676     |
| F(000)               | 836      | 690       | 822.0   | 694       |
| Crystal size/mm³     | 0.055 x 0.055 x 0.044 | 0.055 x 0.055 x 0.044 | 0.269 x 0.147 x 0.047 | 0.1 x 0.08 x 0.05 |
| 2Θ range for data collection | 6.14 to 61.02° | 3.58 to 49.42° | 6.132 to 54.958° | 3.608 to 50.7° |
| Index ranges         | -15 ≤ h ≤ 12, -14 ≤ k ≤ 14, -23 ≤ l ≤ 24 | -10 ≤ h ≤ 10, -13 ≤ k ≤ 13, -17 ≤ l ≤ 17 | -13 ≤ h ≤ 13, -13 ≤ k ≤ 13, -17 ≤ l ≤ 21 | -11 ≤ h ≤ 11, -14 ≤ k ≤ 14, -19 ≤ l ≤ 18 |
| Reflections collected | 34351    | 18718     | 30270   | 24593     |
| Independent reflections | 10336[R(int) = 0.0768] | 5476[R(int) = 0.1273] | 7846 [Rint = 0.0689] | 5819 [Rint = 0.1064] |
| Data/restraints/Parameters | 10336/60/5 | 476/0/389 | 7846/15/476 | 5819/0/389 |
| Goodness-of-fit on F2 | 1.04     | 0.935     | 1.076   | 0.999     |
| Final R indexes [I>=2σ (I)] | R1 = 0.0511, wR2 = 0.0975 | R1 = 0.0832, wR2 = 0.1872 | R1 = 0.0441, wR2 = 0.0938 | R1 = 0.0532, wR2 = 0.1159 |
| Final R indexes [all data] | R1 = 0.0726, wR2 = 0.1056 | R1 = 0.1224, wR2 = 0.2072 | R1 = 0.0546, wR2 = 0.0982 | R1 = 0.0808, wR2 = 0.1281 |
| Largest diff. peak/hole / e Å-3 | 1.07/-0.99 | 6.167/-1.316 | 1.35/-0.78 | 1.53/-1.73 |
Table S19: Crystal data and structure refinement parameters for reported xylene loaded structures 3P,3M, 3P-Nd and 3M-Nd.

| Identification code | sntB00106C1 | sntB00131C2 | C00158C2 | sntc00161c5 |
|---------------------|-------------|-------------|----------|-------------|
| Sample Code         | 3P          | 3M          | 3P-Nd    | 3M-Nd       |
| CCDC                | 920429      | 920430      | 975280   | 975281      |
| Empirical formula   | C42H29CeO8  | C42H29CeO8  | C42H29NdO8 | C42H29NdO8  |
| Formula weight      | 801.77      | 801.77      | 805.89   | 805.89      |
| Temperature/K       | 100         | 100         | 100(2)   | 100(2)      |
| Crystal system      | triclinic   | triclinic   | triclinic | triclinic   |
| Space group         | P-1         | P-1         | P-1      | P-1         |
| a/Å                 | 9.5603(4)   | 9.7441(6)   | 9.5256(5)| 9.6812(6)   |
| b/Å                 | 12.1386(5)  | 12.3318(7)  | 12.1272(6)| 12.2892(7)  |
| c/Å                 | 15.9458(6)  | 15.7737(9)  | 15.8868(8)| 15.7406(10) |
| α°                  | 88.4550(10) | 88.979(2)   | 88.508(2)| 88.977(2)   |
| β°                  | 74.4170(10) | 77.399(2)   | 74.677(2)| 77.463(2)   |
| γ°                  | 70.2330(10) | 69.498(2)   | 70.379(2)| 69.750(2)   |
| Volume/Å³           | 1673.27(12) | 1729.02(18) | 1663.42(15)| 1711.72(18)|
| Z                   | 2           | 2           | 2        | 2           |
| \(P_{\text{calc}}\)mg/mm³ | 1.591   | 1.54        | 1.609    | 1.564       |
| m/mm⁻¹              | 1.418       | 1.372       | 1.618    | 1.573       |
| F(000)              | 806         | 806         | 810      | 810         |
| Crystal size/mm³    | 0.179 × 0.05 × 0.031 | 0.088 × 0.061 × 0.033 | 0.079 × 0.052 × 0.033 | 0.21 × 0.12 × 0.09 |
| 2Θ range for data collection | 3.58 to 52.88° | 4.28 to 47.76° | 4.308 to 56.562° | 4.29 to 56.156° |
| Index ranges        | -11 ≤ h ≤ 11, -15 ≤ k ≤ 15, -19 ≤ l ≤ 15 | -11 ≤ h ≤ 11, -14 ≤ k ≤ 14, -16 ≤ l ≤ 17 | -12 ≤ h ≤ 12, -16 ≤ k ≤ 16, -21 ≤ l ≤ 16 | -11 ≤ h ≤ 12, -13 ≤ k ≤ 16, -19 ≤ l ≤ 20 |
| Reflections collected | 26198   | 30736       | 28075    | 27051       |
| Independent reflections | 6878[R(int) = 0.0681] | 5326[R(int) = 0.0657] | 8248 [R(int) = 0.0609] | 8300[R(int) = 0.0901] |
| Data/restraints/parameters | 6878/0/463 | 5326/236/570 | 8248/0/463 | 8300/198/542 |
| Goodness-of-fit on \(F²\) | 1.034 | 1.098 | 1.038 | 1.012 |
| Final R indexes [l>2\(σ(l)\)] | R1 = 0.0416, wR2 = 0.0945 | R1 = 0.0443, wR2 = 0.1085 | R1 = 0.0421, wR2 = 0.0941 | R1 = 0.0500, wR2 = 0.1020 |
| Final R indexes [all data] | R1 = 0.0535, wR2 = 0.1001 | R1 = 0.0588, wR2 = 0.1185 | R1 = 0.0554, wR2 = 0.0996 | R1 = 0.0796, wR2 = 0.1124 |
| Largest diff. peak/hole / e Å⁻³ | 1.866/-1.966 | 2.499/-1.014 | 1.57/-2.07 | 1.57/-2.07 |
Figures

Figure S1: Optical microscope images of 1 at 11.25 × magnification - synthesised using method A.

Figure S2: SEM images of large particle 1 prepared using synthesis method A with particle size of ca. 50 μm.
Figure S3: SEM images of a small particle (2-20 μm) sample of 1 prepared using method B.

Figure S4: Bulk characterisation of 1. A: PXRD profile of 1. Final observed (black), calculated (red) and difference (grey) X-ray powder diffraction profile measured in transmission geometry using Bruker D8 Advance with Cu Kα₁ radiation in a sealed 0.5mm capillary for the Le Bail refinement of 1 ($R_{wp} = 4.51\%$, $R_{exp} = 2.94\%$, $R_p = 3.36\%$, $\chi^2 = 2.35$; $a = 10.81826(97)$, $b = 10.65732(70)$, $c = 16.96384(152)$ Å, $\alpha = 76.92450(49)$, $\beta = 83.27133(65)$, $\gamma = 68.36294 (48)$, $V = 1769.64575\text{Å}^3 (P\bar{1})$. Reflection positions are marked. B: TGA profile of 1.
**Figure S5**: Single crystal structure of 1. **A**: Asymmetric unit; **B**: Both PART 1 and PART 2 disordered channel EtOH; **C**: PART -1, PART 1 and PART 2 disorder in coordinated EtOH, channel EtOH and associated H$_2$O; **D**: Ce coordination single disordered component shown for clarity; **E**: Ce dimer with carboxylate and solvent coordination shown. Ce (purple), O (red) C (grey), H (white). $1$ 1-X,1-Y,2-Z, $2$ 2-X,1-Y,1-Z, $3$ -1+X,1+Y,1+Z, $4$ 1-X,2-Y,1-Z, $5$ +X,+Y,1+Z, $6$ 1-X,2-Y,2-Z, $7$ +X,1+Y,+Z.

**Figure S6**: HTCPB ligand orientation in 1. **A**: along and **B**: normal to the central ring plane. Bound water and ethanol shown in cyan and green respectively. Carboxyphenyl ring 2 carboxylate shown in orange.
Figure S7: Single crystal structure of 3. A: Asymmetric unit; B: Ce coordination; C: Ce dimer with carboxylate shown. Ce (purple), O (red) C (grey), H (white). $1 -X,-Y,2-Z$, $2 +X,-1+Y,+Z$, $3 1-X,1-Y,2-Z$, $4 -X,1-Y,1-Z$, $5 +X,-1+Y,1+Z$, $6 -X,-Y,1-Z$, $7 +X,+Y,1+Z$, $8 -X,1-Y,2-Z$, $9 -1+X,-1+Y,+Z$.

Figure S8: HTCPB ligand in 3 viewed along the central ring plane: carboxyphenyl ring 2 carboxylate shown in orange.
**Figure S9**: A: Ring naming convention and colour coding for the HTCPB linker. B and C: Two cavities within 1 and 3 respectively. Square channel 1 (magenta) and rectangular channel 2 (blue).

**Figure S10**: Sorption measurements on 3. A: CO$_2$ isotherm of 3 collected at 195 K B: BET plot for surface area determination; C: Dubinin-Radushkevich plot for calculation of pore volume based on 195 K isotherm.

**Figure S11**: A: N$_2$ isotherm of 3 collected at 77 K and B: H$_2$O isotherm of 3 collected at 295 K.
**Figure S12:** Structural relaxation and xylene orientation in channel 1. Comparison of an energetically favourable docking site in channel 1 for A: pX in 3 and B: pX in 3P. The pX molecule is tilted relative to the axis of channel 1 in the rigid host 3, but is orientated with its molecular axis along the channel axis in rigid host 3P. This demonstrates how the structural rearrangement from 3 to 3P creates an optimal binding site for the pX molecule, with the channel distorting to provide an enhanced fit to the guest (8.1).

**Figure S13:** Comparison of the sampled sorption sites (shown as green spheres for pX and orange spheres for mX) from CB-GCMC simulations in the loaded host structures (A,C) and the SC-XRD structures (B, D) for 3P (top) and 3M (bottom). The channels are labelled with white numbers. The pinch points in channel 2 for the 3P structure are shown by white arrows surrounding the sorption pocket for one site – the structural origin of these constrictions is shown in Figure S23. Note that (C) is an indicative example for the 2 channels in the 3M supercell, but a range of other sites are observed in other channels (which are obscured in this view by the two visible channels) and in repeats of the simulation (i.e. with improved sampling) (8.2).
**Figure S14**: TGA characterisation of xylene-loaded 3. **A**: TGA profiles of loaded 3 with pX (3P) and mX (3M) individually (6.1). **B**: TGA profiles for mixed xylene loaded samples of 3 (6.2).

**Figure S15**: Powder X-ray diffraction measurements during sorption of a 1:1 pX:mX mixture by 3. **A**: Time dependence of powder X-ray diffraction profiles of loaded material during xylene uptake experiments on 3; **B**: TGA profiles of loaded material following xylene uptake experiments on 3. **C** Analysis of the relative amounts of 3 (blue) and xylene loaded 3PM (red) and **D**: Unit cell volume of 3 (blue) and 3PM (red) over the time course of the pXMX selectivity experiments (6.3).
Figure S16: Scanned GC traces for selectivity experiments. **A:** calibration trace for a typical 1:1 $pXmX$ mixture used in the selectivity experiments, para-xylene elutes at 11.805 minutes, meta-xylene elutes at 12.275 minutes. In this example $X_i^o/X_j^o = 0.985$ **B:** example scanned GC trace of selectivity experiments for Ce(HTCPB), measured concentrations $pX$ (11.815 minutes) = 0.081%, $mX$ (12.273 minutes) = 0.0185%; $X_i^o/X_j^o = 0.985$; $\alpha_{pXmX} = 4.44$; **C:** example scanned GC trace of selectivity experiments for Ce(HTCPB), measured concentrations $pX$ (10.923 minutes) = 0.006%, $mX$ (11.347 minutes) = 0.0013%; $X_i^o/X_j^o = 0.975$; $\alpha_{pXmX} = 4.73$; **D:** example scanned GC trace of selectivity experiments for Nd(HTCPB), measured concentrations $pX$ (11.548 minutes) = 0.0127%, $mX$ (12.000 minutes) = 0.0021%; $X_i^o/X_j^o = 0.975$; $\alpha_{pXmX} = 6.20$; **E:** example scanned GC trace of selectivity experiments for Nd(HTCPB), measured concentrations $pX$ (11.540 minutes) = 0.013%, $mX$ (11.990 minutes) = 0.0021%; $X_i^o/X_j^o = 0.975$; $\alpha_{pXmX} = 6.35$; (6.1)
Figure S17: Selectivity, $\alpha_{pXmX}$, of 3 with increasing pX uptake. (6.4)

Figure S18: Single crystal structure of 3P. A: Asymmetric unit; B: pX1 in channel 1; C: pX2 in channel 2; D: Ce coordination; E: Ce dimer with carboxylate coordination shown. Ce (purple), O (red) C (grey), H (white). $1 +X,1+Y,+Z, 2 -1-X,1-Y,-Z, 3 1-X,1-Y,1-Z, 4 +X,1+Y,-1+Z, 5 +X,+Y,-1+Z, 6 -X,-2-Y,1-Z, 7 1-X,2-Y,-Z, 8 1-X,2-Y,1-Z, 9 1+X,+Y,-1+Z.$
Figure S19: Single crystal structure of 3M. A: Asymmetric unit; B: mX disorder in channel 1; C: mX in channel 2; D: Ce coordination sphere; E: Ce dimer with carboxylate shown. Ce (purple), O (red), C (grey), H (white). $1$ 2-X,1-Y,1-Z, $2$ +X,1+Y,+Z, $3$ 2-X,1-Y,1-Z, $4$ 2-X,1-Y,1-Z, $5$ +X,1+Y,1+Z, $6$ +X,1+Y,1+Z, $7$ 1-X,1-Y,1-Z, $8$ 2-X,1-Y,1-Z, $9$ 1+X,+Y,1+Z.
Figure S20: Views of the crystal structures of 3P and 3M along the different crystallographic axes. A, B, C: View of 3P along [100], [010] and [001] directions as packing diagram showing the pX guest (faded green channel 1, dark green channel 2) in spacefill against the framework as ball and stick. D, E, F: [100], [010] and [001] directions of 3M as packing diagram showing the mX guest (disordered shown in yellow and orange colouring for both channels: the overlapping mX positions in channel 1 form a continuum whereas the mX in channel 2 is confined to the pockets defined by the Ce₂ dimer) in spacefill against the framework as ball and stick. One of the two symmetry-related mX disordered positions is shown in Fig. 2-4 for clarity (9.1).
Figure S21: The structural effect of the changes in pendant carboxylate roles from 3 to 3P. A: The exchange of roles of rings 2 and 5 from 3 to 3P produces a very similar Ce environment and distribution of carboxylate groups around Ce in 3 (green) and the xylene-loaded 3M (red) B: HTCPB ligand in 3P viewed normal to the central ring plane and C: parallel to the central ring plane. D: Interchange of carboxylates from rings 2 (green) and 5 (blue) from 3 (bottom) to 3P (top). Carboxyphenyl ring 1 (magenta) and carboxyphenyl ring 4 (yellow) remain unchanged. (9.1) Hydrogen bonds shown as red dashed lines.
Figure S22: Structural differences between 3P and 3M appear small but are significant: both phases involve displacement of successive layers from 3. A: Overlay of asymmetric units of 3P (pink) and 3M (green). View down [100] of B: 3; C: 3P and D: 3M. Area of layer slippage from 3 to 3P/M highlighted in blue (9.1).
**Figure S23**: Depiction of 3P channel 2 surface in the vicinity of the constriction between the pockets containing the pX guest (9.2). The Ce dimers (polyhedral purple) define the limits of the pockets. The carboxylate bridges with O2x in green and O4x in orange form the dimers, O5x in blue bridges the dimers while O1x (carbon gray, oxygen red and hydrogen white) is uniquely bonds to only one Ce and is located between rather than forming the dimers. The pX location is shown in the channel. In A the carboxylic acid group (carboxyphenyl ring 1) is shown in the van der Waals depiction with its parent phenyl ring in CPK to show the relative orientation of the groups to the surface, and in particular the role of the free carboxyl oxygen in the O1x group in defining the constriction between the pockets. In B as per A but with the entire carboxyphenyl ring 1 group shown in CPK for clarity. C is a rotated view further emphasising how the protonated carboxylic group defines the channel space around the pX. Rotation about the Ce-O bond formed by the second oxygen in the O1x carboxyl would open the channel to permit transport of the guests between pockets.
Figure S24: The xylene guests in channel 1 (9.3). C-H⋯π interactions from framework to xylene are shown in purple. A: View down [100] direction for pX in 3P and C: mX in 3M. B: View normal to the xylene plane 3P and D: mX in 3M. To aid with alignment for 3M two C-H⋯π interactions are shown even though they exceed the cut-off parameters (Table S13).

Figure S25: Hirshfeld surface 2D fingerprint plots for A: pX in channel 1 of 3P with 'T-shaped' C-H⋯π feature “chicken wing” highlighted in yellow; B: mX position 1 in channel 1 of 3M, short de/di shown by * and long de/di, signifying a poor spatial fit to the host highlighted in gray and C: mX in position 2 of channel 1 in 3M (long de/di highlighted in gray) (9.3).
Figure S26: **A**: Breakdown of the Hirshfeld surfaces for channel 1 pX in 3P. Top: The coloured regions of the Hirshfeld surface and the associated extrapolated 2D fingerprint plot showing all the internal to external hydrogen contacts (iAll-eH) only. The grey regions correspond to contacts to external non-hydrogen atoms. Bottom: The same figure with only the internal carbon to external hydrogen interactions depicted (iC-eH). This clearly highlights the “chicken wing” motif and its relationship to the two C-H⋯π interactions. **B**: Channel 1 mX A and B positions (top) and pX (bottom) showing the degree of offset in the edge-face-interaction in the case of mX (lengths greater than accepted interaction distances have been shown (broken purple lines) to highlight the interaction difference between mX and pX). **C**: Channel 2 alignments of mX (left - lengths greater than accepted interaction distances have been used to highlight the interaction difference between mX and pX) and pX (right). Orientations chosen to emphasise possible C-H⋯π alignment (9.3).
Figure S27: Hirshfeld surface 2D fingerprint plots for A: pX in channel 2 of 3P (9.3); B: mX in channel 2 of 3M (9.4). Hirshfeld surfaces and 2D fingerprint plots for pX in channel 2 of 3P, coloured to show specific interactions. C: (iAll-eH); D: (iAll-eO) E: (iH-eH) and F: (iC-eH); where i = internal and e = external to the Hirshfeld surface.
**Figure S28:** Hirshfeld surfaces and 2D fingerprint plots for mX in channel 2 of 3M coloured to show specific interactions. **A:** (iAll-eH); **B:** (iH-eH); **C:** (iAll-eO) and **D:** (iC-eH) where i = internal and e = external to the Hirshfeld surface (9.3, 9.4).

**Figure S29:** Overlay of pX (green) from 3P with both symmetry-disordered mX components from 3M (yellow, orange) in channel 2 viewed normal **A** and parallel **B** to the aromatic ring. It can be observed that there is a rotation in the ring plane normal, the longest axis direction and the phenyl ring orientation of mX compared to pX (9.3).
**Figure S30:** The mX displacement and reorientation from the pX position in channel 2 occurs to minimise clashes with the channel surface. The solid surface represents channel 2 in 3P, crosses represent the surface generated for 3M channel 2. Four pseudo mX molecules generated from the pX core (blue) shown in yellow, grey, orange and red to simulate the effect of locating an mX molecule at the position occupied by pX in the 3P channel. In all cases one of the two methyl groups punches through the channel wall. It is not possible to put mX in the symmetrical position occupied by pX; it needs to occupy an asymmetric location in order to fit into channel 2 (9.3).
Figure S31: The structure of the channel 1 and 2 surfaces in 3P and 3M. A: pX (green) in channel 1 in 3P; B: pX in channel 2 of 3P C: mX (yellow) in channel 1 of 3M; D: mX in channel 2 of 3M. C-H···π interactions between xylenes and the framework shown in purple. The components of the HTCPB ligand defining the framework are shown as: Carboxyphenyl ring 1 (magenta), carboxyphenyl ring 2 (green), carboxyphenyl ring 4 (orange), carboxyphenyl ring 5 (blue), with the carbons from the central ring shown in grey. Xylenes at either end of the channel space have been retained to aid visualisation, all other xylenes and disorder removed for clarity. C-H contacts to the xylenes come from the central ring in channel 1 and the pendant rings in channel 2 (9.4).
Figure S32: Ring numbering, torsions and displacements to account for structural changes between 3P and 3M. A: Generic model showing atom labels, plane to plane definitions and carboxyphenyl ring 2 (green) and carboxyphenyl ring 5 (pink) to carboxylate torsions, and carboxyphenyl ring 2 (yellow) and carboxyphenyl ring 5 (orange) to central ring torsion angles. Central ring mean plane [C1 C2 C3 C4 C5 C6]-centroid to central mean plane ring [C1 C2 C3 C4 C5 C6]-centroid distance between neighbouring sheets shown in light blue. Carboxyphenyl ring 2 mean plane centroid to carboxyphenyl ring 5 mean plane centroid distance shown with dark blue arrows. B: Mean planes used to define 64 parameters for structural changes between 3, 3P and 3M, along with mean planes and ring atom numbering for all ring system. C1 > C6 = central ring as used in Table S15 (9.4).
**Figure S33**: Single crystal structure of 1-Nd. **A**: Asymmetric unit; **B**: Nd coordination single disordered component shown for clarity; **C**: Nd dimer with carboxylate and solvent coordination shown. Nd (green), O (red) C (grey), H (white). $1$ $+X, +Y, 1+Z$, $2$ $1-X, 2-Y, -Z$, $3$ $1-X, 1-Y, 1-Z$, $4$ $1+X, -1+Y, Z$, $5$ $-X,2-Y,1+Z$, $6$ $+X, -1+Y,1+Z$, $7$ $1-X, 1-Y, -Z$. 
Figure S34: Single crystal structure of 3-Nd. A: Asymmetric unit; B: Nd coordination sphere ($1 \begin{array}{c} +X, -1+Y, -Z, \end{array}$ $2 \begin{array}{c} 2-X, 1-Y, -Z, \end{array}$ $3 \begin{array}{c} 1+X, -1+Y, -1+Z, \end{array}$ $4 \begin{array}{c} 1-X, 1-Y, 1-Z, \end{array}$ $5 \begin{array}{c} 1+X, +Y, -1+Z, \end{array}$ $6 \begin{array}{c} 2-X, -Y, 1-Z; \end{array}$ C: Nd dimer with carboxylate shown ($1 \begin{array}{c} +X, -1+Y, +Z, \end{array}$ $2 \begin{array}{c} 2-X, 1-Y, -Z, \end{array}$ $3 \begin{array}{c} 1+X, -1+Y, -1+Z, \end{array}$ $4 \begin{array}{c} 1-X, 1-Y, 1-Z, \end{array}$ $5 \begin{array}{c} 1+X, +Y, -1+Z, \end{array}$ $6 \begin{array}{c} 2-X, -Y, 1-Z, \end{array}$ $7 \begin{array}{c} 2-X, -Y, -Z, \end{array}$ $8 \begin{array}{c} 1-X, -Y, -Z, \end{array}$ $9 \begin{array}{c} +X, +Y, -1+Z \end{array}$). Nd (dark blue), O (red) C (grey), H (white). (9.5)
Figure S35: Single crystal structure of 3P-Nd. A: Asymmetric unit; B: Nd coordination ($S1 +X,1+Y,+Z$, $S2$ 1-X,1-Y,-Z, $S3$ 1-X,1-Y,1-Z $S4$ +X,1+Y,-1+Z, $S5$ +X,+Y,-1+Z, $S6$ -X,2-Y,1-Z); C: Nd dimer with carboxylate coordination shown ($S1$ 1-X,2-Y,-Z, $S2$ +X,1+Y,+Z, $S3$ 1-X,1-Y,-Z, $S4$ 1-X,1-Y,1-Z, $S5$ +X,1+Y,-1+Z, $S6$ +X,+Y,-1+Z, $S7$ -X,2-Y,1-Z, $S8$ 1-X,2-Y,1-Z, $S9$ 1+X,+Y,-1+Z); D: pX1 in channel 1; E: pX2 in channel 2;Nd (dark blue), O (red) C (grey), H (white). (9.5)

Figure S36: Single crystal structure of 3M-Nd. A: Asymmetric unit; B: mX disorder in channel 1; C: mX in channel 2; D: Nd coordination sphere ($S1$ +X,1+Y,+Z, $S2$ 1-X,1-Y,1-Z, $S3$ +X,1+Y,-1+Z, $S4$ 1-X,1-Y,2-Z, $S5$ +X,+Y,-1+Z, $S6$ -X,2-Y,2-Z); E: Nd dimer with carboxylate shown ($S1$
$+X,1+Y,+Z, \S 2 \ 1-X,1-Y,1-Z, \S 3 \ +X,1+Y,-1+Z, \S 4 \ 1-X,1-Y,2-Z, \S 5 \ +X,+Y,-1+Z, \S 6 \ -X,2-Y,2-Z, \S 7 \ 1-X,2-Y,1-Z, \S 8 \ 1-X,2-Y,2-Z, \S 9 \ 1+X,+Y,-1+Z)$. Nd (dark blue), O (red) C (grey), H (white). (9.5)

**Figure S37**: Overlay of Ce (violet) and Nd (blue) single crystal structures for A: 3 and 3-Nd, B: 3P and 3P-Nd and C: 3M and 3M-Nd. (9.5)

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