

Supporting information for:

Computational Screening of Porous Organic
Molecules for Xenon/Krypton Separation

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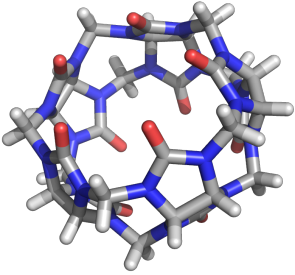
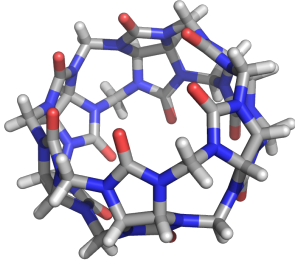
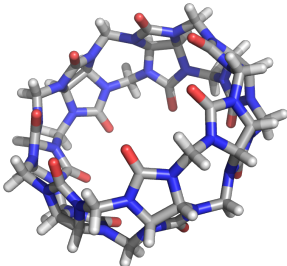
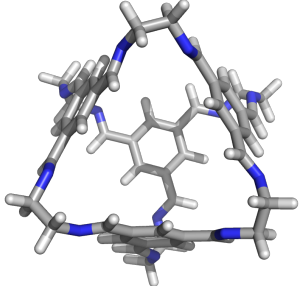
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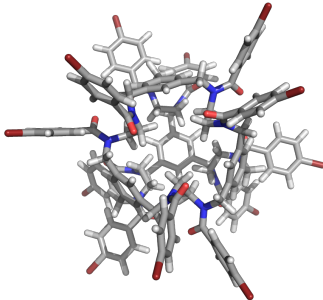
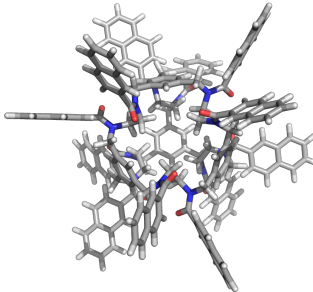
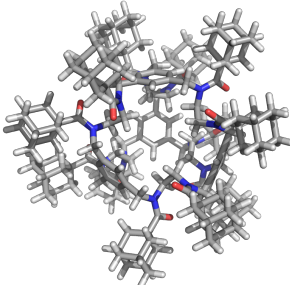
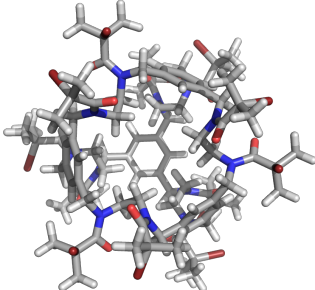
1 Cage Database (*CDB*)

Table S1: A List of Porous Organic Molecules in *CDB41*.

<i>CDB</i> identifier	alternative literature names	image ^a	reference no. ^b / CSD refcode
CB5	cucurbit[5]uril		S1, S2 FUYHEN
CB6	cucurbit[6]uril		S3, S4 BATVUP
CB7	cucurbit[7]uril		S1, S2 FUYHIR
CC1			S5 PUDWUH

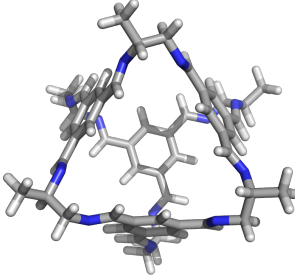
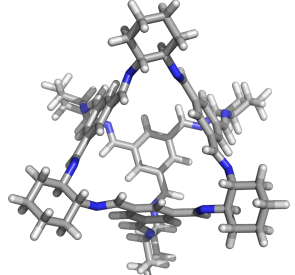
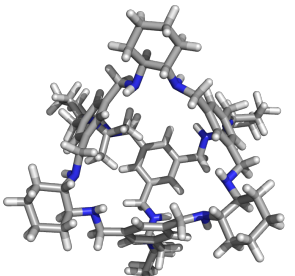
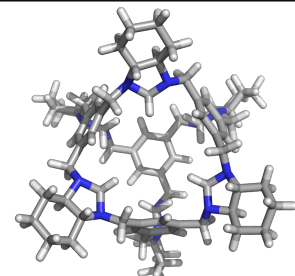
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<i>CDB</i> identifier	alternative literature names	image ^a	reference no. ^b / CSD refcode
RCC1a			S6 FIFTAR
RCC1b			S6 FIFTEV
RCC1c			S6 FIFTIZ
RCC1d			S6 FIFTOF

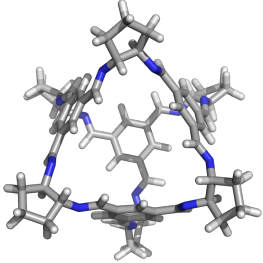
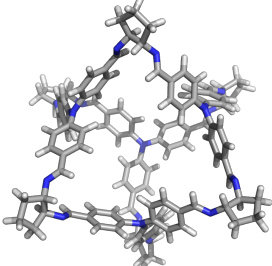
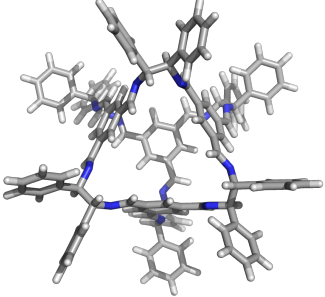
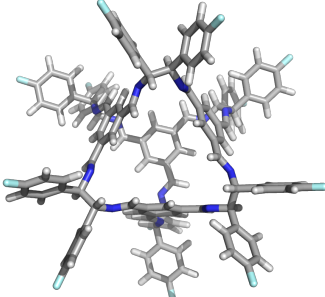
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<i>CDB</i> identifier	alternative literature names	image ^a	reference no. ^b / CSD refcode
CC2			S5 PUDXAO
CC3			S7, S5 PUDXES
RCC3a	AT-RCC3		S8 VOLZON
RCC3b	FT-RCC3		S8 VOMPAQ

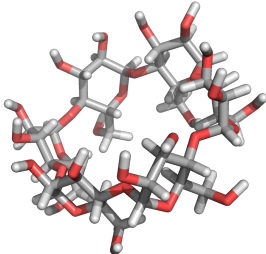
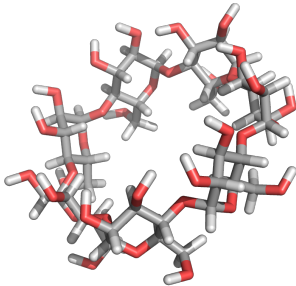
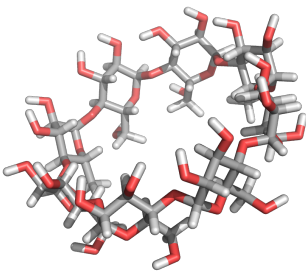
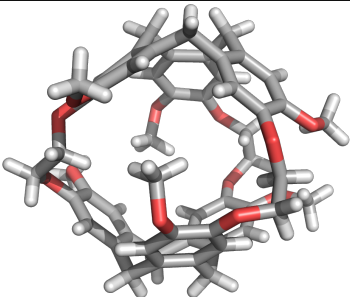
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<i>CDB</i> identifier	alternative literature names	image ^a	reference no. ^b / CSD refcode
CC4			S9 OZECAY
CC5			S10 UTEVOF
CC9			S11 GANDAC
CC10			S11 GANDUW

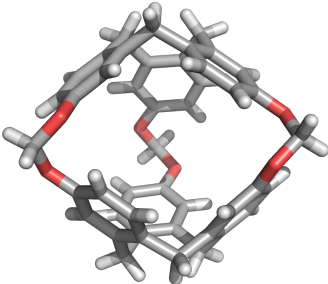
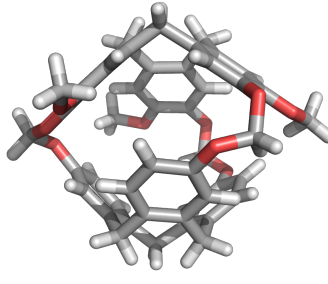
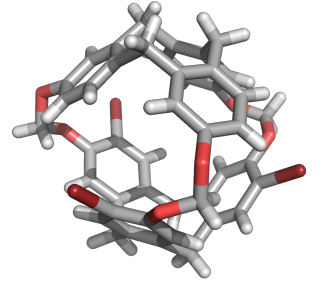
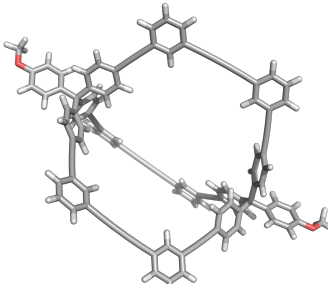
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<i>CDB</i> identifier	alternative literature names	image ^a	reference no. ^b / CSD refcode
CD1	α -cyclodextrin		S12, S13 ACDMFM
CD2	β -cyclodextrin		S12, S14 DUCMUL
CD3	γ -cyclodextrin		S12, S15 NUNRIX
CP1	cryptophane-A		S16, S17 OJITOR

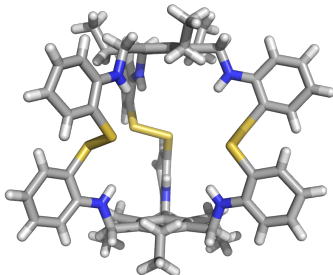
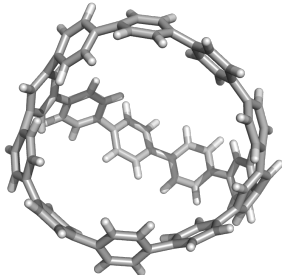
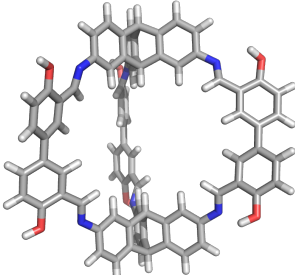
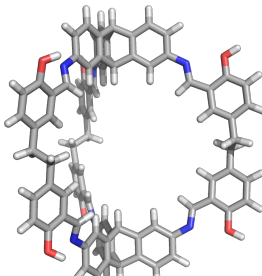
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<i>CDB</i> identifier	alternative literature names	image ^a	reference no. ^b / CSD refcode
CP3	111 (cryptophane-111)		S16, S18 NOVNAP
CP4	(MeO) ₃ -111 (cryptophane-111)		S16, S19 FOQTOW
CP5	Br ₃ -111 (cryptophane-111)		S16, S19 FOQTEM
DC1	C1		S20 REQXES

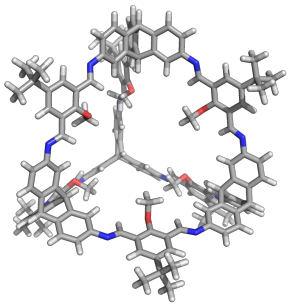
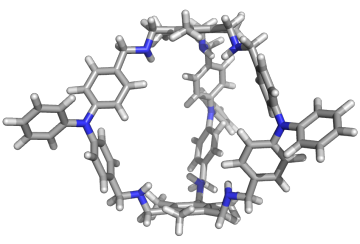
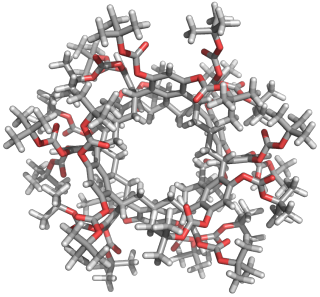
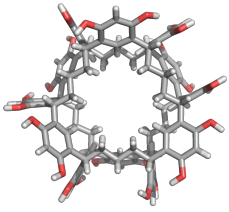
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<i>CDB</i> identifier	alternative literature names	image ^a	reference no. ^b / CSD refcode
HC1			S21 MAVVAI
IC2	carbon nanocage		S22 NUXHIZ
MC3			S23 SATJAA
MC4			S23 SATJEE

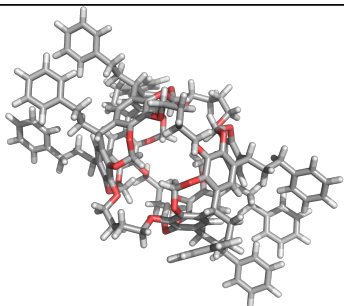
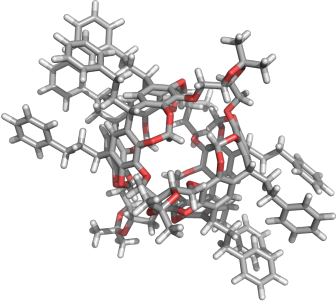
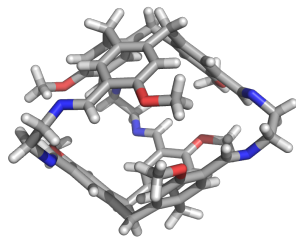
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<i>CDB</i> identifier	alternative literature names	image ^a	reference no. ^b / CSD refcode
MC5			S24 FEQXAC
MC7			S25 FOMLUQ
NC1	noria-Boc		S26 MESTUA
NC2	noria		S26, S27 GUMCIB

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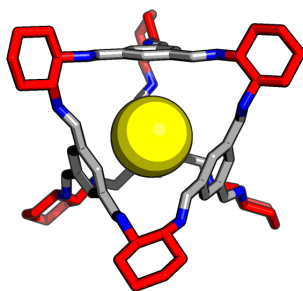
<i>CDB</i> identifier	alternative literature names	image ^a	reference no. ^b / CSD refcode
WC2	hemicarcerand		S28 LUXVAB
WC3	hemicarceplex		S29 PAQFES
WC4	hexaimine cryptophane		S30 EPIRUR

^a The molecules are not shown to scale. Atom coloring: C, grey; H, white; O, red; N, blue; S, yellow; Br, brown; F, pale blue. ^b The references are typically for the work where the molecule was first reported, however, when it is not the source of the X-ray diffraction crystal structure used in this work, an additional reference as well as the Cambridge Structural Database (CSD) refcode.

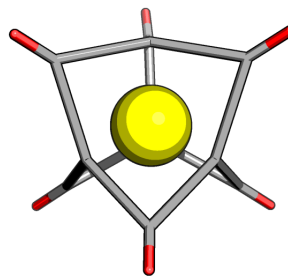
2 Molecular dynamics simulations on solid state structures of CC3

Table S2: Polymorph Analysis

Polymorph	Supercell ($a \times b \times c$)	Supercell dimensions ($\text{\AA}$)	Cell symmetry	Ref.
CC3 α - <i>R</i>	2 x 2 x 2	49.6 x 49.6 x 49.6	cubic	S5 PUDXES
CC3 α -(<i>R,S</i>)	2 x 2 x 2	49.2 x 49.2 x 49.2	cubic	S31
CC3 β - <i>R</i>	2 x 2 x 4	50.3 x 50.3 x 44.1	trigonal	S32 PUDXES02



(a)



(b)

Figure S1: a) A **CC3** cage molecule structure, hydrogens omitted for clarity, with the intrinsic cavity shown as the yellow sphere. The vertices are coloured red, imine bonds blue and the rest of the molecule in gray. b) the simplified wireframe model of **CC3**, where vertices are colored red and rest of the molecule gray.

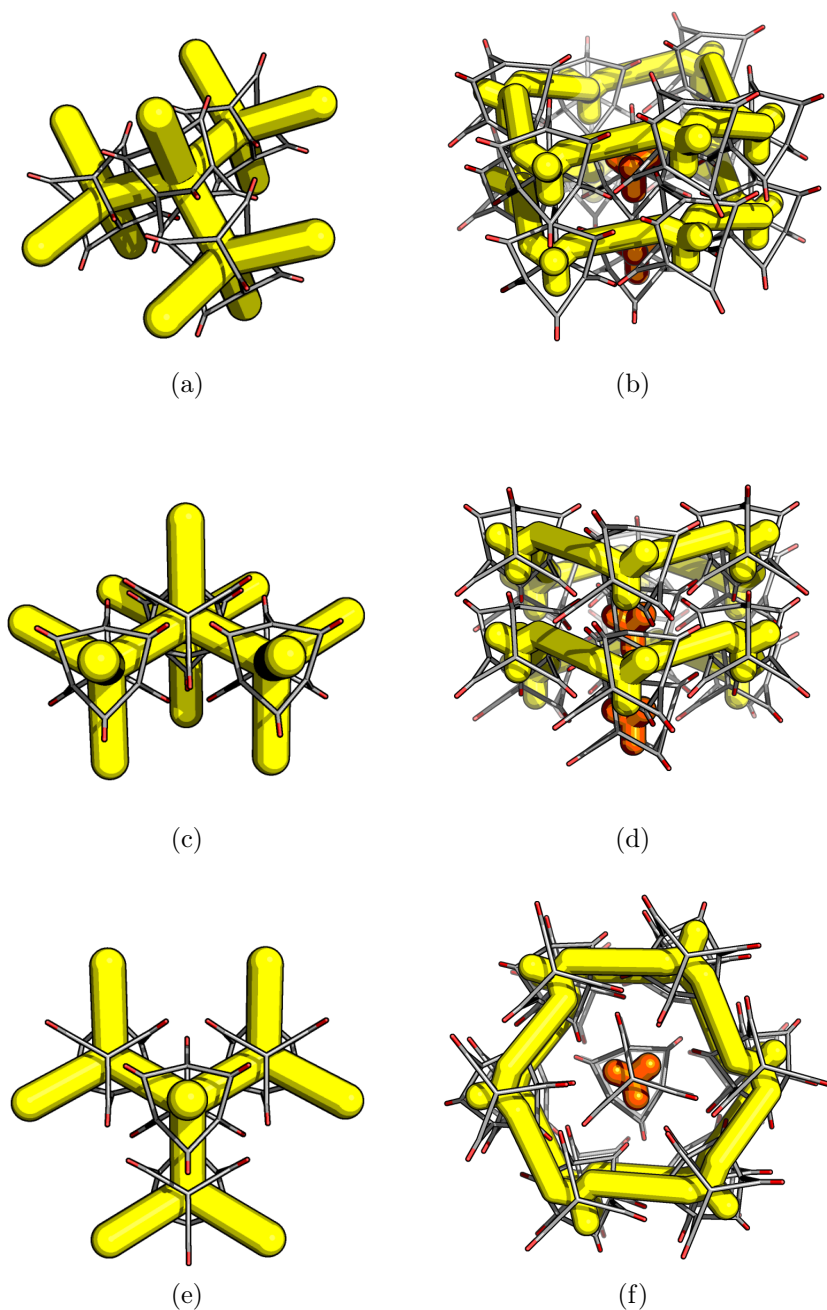


Figure S2: The figures on the left hand side (a, c, e) show $\text{CC3}\alpha\text{-}R$ and $\text{CC3}\alpha\text{-}R,S$ crystal packing from different perspectives, with the diamondoid shaped pore network shown as yellow tubes and CC3 replaced with the simplified wireframe model shown in Figure S1b. The figures on the right hand side (b, d, f) show $\text{CC3}\beta\text{-}R$ crystal packing with the honey-comb shaped interconnected porous network considered as ‘accessible’ showed as yellow tubes and the intrinsic excluded intrinsic voids in orange that are considered as ‘non-accessible’.

3 Structural analysis with pyWINDOW

The maximum diameter of a molecule (d_{max}) and the intrinsic void diameter (d_{void}) were calculated using XYZ coordinates and the euclidean distance matrix as implemented in the scikit-learn package.³³ d_{max} is defined as the distance between the two furthest atoms in the molecule and is then corrected for the appropriate van der Waals (vdW) radii. d_{void} is defined as the distance between the centre of mass (COM) of the molecule and the closest atom, corrected for the appropriate vdW radii and multiplied by 2. The spherical void volume (V_{void}) is then derived from the d_{void} value. The Diameter Fractions for Kr (DF_{Kr}) and Xe (DF_{Xe}) are then the vdW diameters of Kr (3.69 Å) and Xe (4.10 Å) divided by the appropriate d_{void} . Accordingly, the pore fractions for Kr (PF_{Kr}) and Xe (PF_{Xe}) are the vdW volumes of Kr (26.31 Å³) and Xe (36.09 Å³) derived from their vdW diameters divided by the appropriate V_{void} .

The window sizes were calculated by the Python pyWINDOW package³⁴ developed in our group, which works as follows:

1. From the XYZ coordinates of a cage, d_{max} is calculated as described above.
2. A sphere, with the diameter equal to d_{max} and the centre of the sphere positioned at COM of the cage is then defined. Using Vogel’s method for a spiral distribution of points on a disc with the “golden angle” approach, adapted for a sphere using cylindrical coordinates,³⁵ a set of evenly distributed sampling points is projected on the sphere’s surface. The number of sampling points is dependent on the sampling sphere’s surface area and is estimated according to this equation:

$$\log_{10}(sphere_surface_area) * 250 \tag{1}$$

The initial number of point is multiplied by 250 as it proved to give sufficient sampling.

3. For each sampling point distributed on the sphere, a vector connecting COM of the cage and the point is defined. The largest included sphere, which corresponds to the distance between a point on the vector and the closest atom from the cage molecule corrected by an appropriate vdW radius, is calculated. This procedure is repeated for points along the vector in 0.1 Å increments and results in a set of the largest included spheres along the vector path.
4. The vectors with a set of the largest included spheres that do not cross any atom of the molecule are clustered by using the density-based spatial clustering algorithm from the scikit-learn package. The number of distinct clusters determines the number of windows found in the cage molecule.
5. Next, for each cluster, a single sampling vector with the set of the largest diameters for the largest included spheres along its path is chosen and a circular plane perpendicular to this vector is generated. The diameter of this plane is defined and it corresponds to the necking of a cage’s window (d_{window}).
6. The point at which the sampling vector passes through this spherical plane of a window is a rough estimate of the window centre. Next, an optimisation of the centre of the window plane is performed using minimize feature of SciPy package.³⁶ The XYZ coordinates of the window centre are used as variables and d_{window} is the output of a two step minimization function, resulting in more accurate XYZ coordinates for the centre of the window plane.
7. As a result the number of molecular windows in the molecule along with d_{window} are obtained.

3.1 Structural properties for *CDB41*

Table S3: Analysis of *CDB41* for Structural Properties in Comparison to the Size of Xenon and Krypton.

<i>CDB41</i>	d_{max} (Å)	d_{void} (Å) ^a	V_{void} (Å ³)	DF_{Kr}	DF_{Xe}	PF_{Kr}	PF_{Xe}
RCC3a	22.6	3.33	19.3	1.11	1.23	1.36	1.87
CP4	14.8	3.40	20.5	1.09	1.21	1.28	1.76
CP5	14.2	3.69	26.4	1.00	1.11	1.00	1.37
CD1	16.0	3.84	29.5	0.96	1.07	0.89	1.22
CB5	12.8	3.95	32.2	0.93	1.04	0.82	1.12
RCC1c	25.8	4.06	35.0	0.91	1.01	0.75	1.03
RCC1a	28.3	4.09	35.9	0.90	1.00	0.73	1.01
WC2	29.4	4.11	36.4	0.90	1.00	0.72	0.99
RCC1b	29.8	4.23	39.7	0.87	0.97	0.66	0.91
CP3	13.3	4.38	44.1	0.84	0.94	0.60	0.82
HC1	19.1	4.52	48.4	0.82	0.91	0.54	0.74
RCC1d	22.2	4.53	48.6	0.82	0.91	0.54	0.74
WC3	28.8	4.63	52.0	0.80	0.89	0.51	0.69
CP1	15.8	4.64	52.3	0.80	0.88	0.50	0.69
NC2	20.5	4.66	53.1	0.79	0.88	0.50	0.68
NC1	29.6	4.79	57.4	0.77	0.86	0.46	0.63
CB6	14.8	4.84	59.3	0.76	0.85	0.44	0.61
MC3	21.5	5.23	74.7	0.71	0.78	0.35	0.48
WC4	16.0	5.30	78.0	0.70	0.77	0.34	0.46
CC2	20.1	5.40	82.6	0.68	0.76	0.32	0.44
CC10	26.7	5.42	83.6	0.68	0.76	0.31	0.43
CC9	25.4	5.43	83.7	0.68	0.76	0.31	0.43
CC3	22.6	5.47	85.9	0.67	0.75	0.31	0.42
CC1	17.6	5.52	88.2	0.67	0.74	0.30	0.41
RCC3b	22.5	5.71	97.5	0.65	0.72	0.27	0.37
CD2	18.0	5.77	100	0.64	0.71	0.26	0.36
CC4	21.6	6.09	118	0.61	0.67	0.22	0.30
CB7	16.0	6.26	128	0.59	0.66	0.21	0.28
MC4	22.2	7.00	180	0.53	0.59	0.15	0.20
CD3	19.1	7.32	205	0.50	0.56	0.13	0.18
MC7	25.3	7.43	215	0.50	0.55	0.12	0.17
IC2	18.9	7.66	235	0.48	0.54	0.11	0.15
MC5	31.1	7.95	263	0.46	0.52	0.10	0.14
CC5	28.3	8.43	313	0.44	0.49	0.084	0.12
DC1	34.4	9.63	468	0.38	0.43	0.056	0.077

^a The table is sorted in ascending void diameter order.

4 Electronic structure calculations for *CDB26*

Table S4: The binding energies for Kr ($E_{b,Kr}$) and Xe ($E_{b,Xe}$) and relative binding ($E_{b,rel}$) calculated using *DFT* for *CDB26* as described in the calculating binding energies methods section of the main paper. The table is sorted in order of ascending relative binding energy.

<i>CDB26</i>	$E_{b,Kr} (kJ mol^{-1})$	$E_{b,Xe} (kJ mol^{-1})$	$E_{b,rel} = E_{b,Kr} - E_{b,Xe} (kJ mol^{-1})$
WC3	-25.7	-23.4	-2.3
RCC1b	-21.5	-23.9	2.4
MC3	-12.6	-15.2	2.6
CD3	-11.2	-14.3	3.0
MC7	-14.7	-17.9	3.2
MC4	-11.9	-15.9	4.0
CP3	-29.1	-33.9	4.7
HC1	-11.2	-16.6	5.4
WC2	-27.7	-33.2	5.5
CB7	-17.7	-23.5	5.8
RCC1c	-25.1	-31.1	6.0
CC10	-23.4	-29.4	6.0
RCC1d	-24.8	-31.2	6.4
RCC1a	-21.6	-28.6	7.0
CD2	-13.1	-20.5	7.5
CC9	-21.9	-29.4	7.5
CC1	-19.5	-27.0	7.6
CC2	-20.2	-27.8	7.6
NC2	-24.3	-31.9	7.6
CC4	-18.3	-26.0	7.7
CC3	-20.3	-28.1	7.7
CP1	-30.2	-39.0	8.8
RCC3b	-22.5	-31.9	9.4
WC4	-27.7	-37.7	10.0
CB6	-23.1	-33.5	10.4
NC1	-17.9	-31.5	13.6

4.1 DFT binding energies compared to void diameters

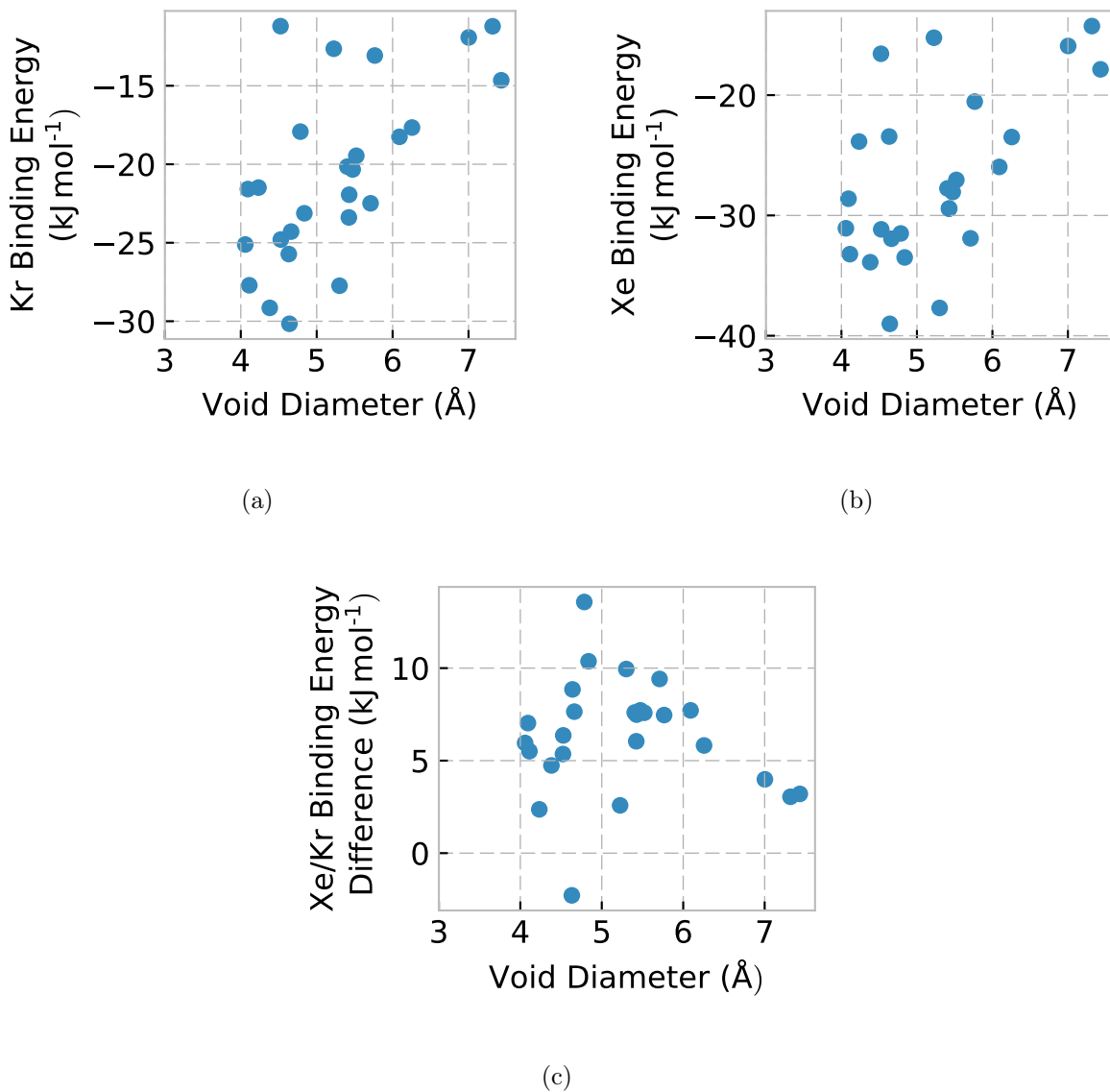


Figure S3: Scatter plots of the measured void diameters (X-axis) against the calculated (Y-axis) a) DFT Kr binding energies b) DFT Xe binding energies c) Binding energy differences between the host-guest complex with Kr and Xe.

5 NC1 and NC2 structural overlays

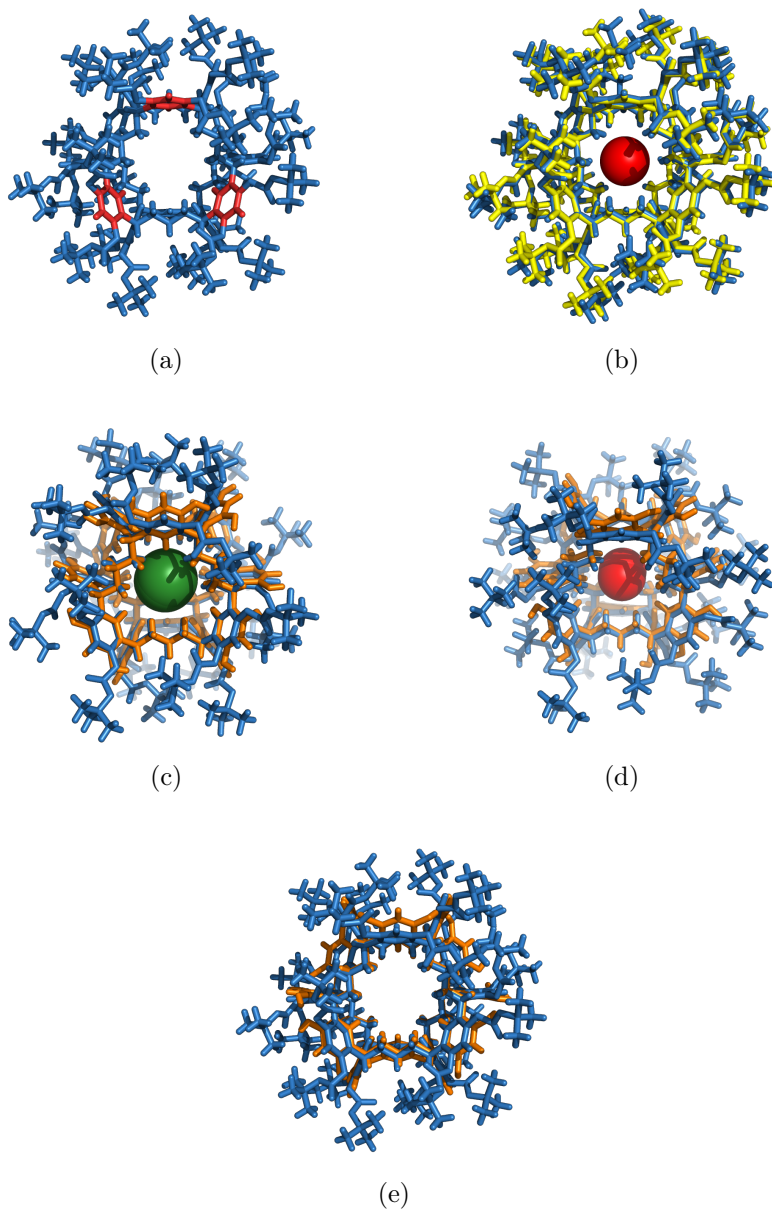


Figure S4: a) The structure of DFT optimised **NC1** in blue with the benzene rings that are used to compare the structural differences to **NC2** in red; b) the overlay of the empty DFT optimised **NC1** in blue and **NC1-Kr** in yellow, with Kr colored red; c) DFT optimised **NC1-Xe** in blue with Xe in green and **NC2-Xe** in orange; d) DFT optimised **NC1-Kr** in blue and **NC2-Kr** in orange; e) the overlay of DFT optimised empty structures of **NC1** in blue and **NC2** in orange.

6 Experimental and DFT void diameters for *CDB12*

Table S5: The void diameters for molecules calculated for: as extracted from X-ray crystal structure ($d_{void,cryst.}$), for the DFT-D3 geometry-optimised empty molecule ($d_{void,DFT-empty}$), for the DFT-D3 geometry-optimised complex with Kr ($d_{void,DFT-Kr}$) and for the DFT-D3 geometry-optimised complex with Xe ($d_{void,DFT-Xe}$).

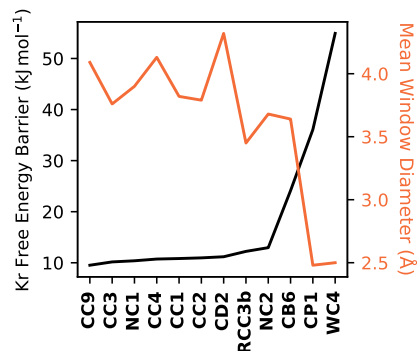
<i>CDB12</i>	$d_{void,cryst.} (\text{\AA})$	$d_{void,DFT-empty} (\text{\AA})$	$d_{void,DFT-Kr} (\text{\AA})$	$d_{void,DFT-Xe} (\text{\AA})$
CB6	4.84	5.15	5.12	5.15
CC1	5.23	5.60	5.48	5.48
CC2	5.31	5.50	5.38	5.38
CC3	5.40	5.54	5.52	5.53
RCC3b	5.74	5.61	5.61	5.61
CC4	5.26	5.78	5.69	5.66
CC9	4.93	5.26	5.19	5.20
CD2	5.60	5.67	5.68	5.56
CP1	4.64	4.71	4.70	4.71
NC1	5.14	4.87	4.88	4.88
NC2	5.04	4.55	4.52	4.61
WC4	5.30	5.33	5.30	5.32

7 Free energy barriers for *CDB12*

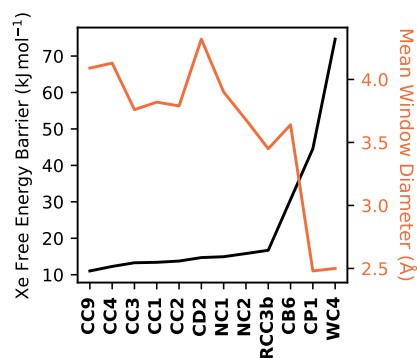
Table S6: The free energy barriers for a Kr molecule (FEB_{Kr}) or a Xe molecule (FEB_{Xe}) diffusing through windows calculated using metadynamics simulations. The relative difference (*diff*) and the production run simulation times (*sim. time*) for Kr and Xe are also provided.

<i>CDB12</i>	FEB_{Kr} ($kJ\ mol^{-1}$)	FEB_{Xe} ($kJ\ mol^{-1}$)	<i>diff</i> ($kJ\ mol^{-1}$)	<i>sim. time</i> Kr / Xe (ns)
CB6	24.13 ± 0.04	30.64 ± 0.05	6.51	300 / 300
CC1	10.83 ± 0.03	13.40 ± 0.03	2.57	300 / 300
CC2	10.96 ± 0.02	13.75 ± 0.04	2.79	300 / 300
CC3	10.17 ± 0.02	13.28 ± 0.03	3.11	300 / 300
RCC3b	12.23 ± 0.03	16.70 ± 0.04	4.47	300 / 300
CC4	10.73 ± 0.02	12.27 ± 0.02	1.54	300 / 300
CC9	9.52 ± 0.02	11.03 ± 0.03	1.51	300 / 300
CD2	11.18 ± 0.02	14.70 ± 0.03	3.52	400 / 400
CP1	36.08 ± 0.04	44.58 ± 0.07	8.50	400 / 400
NC1	10.39 ± 0.04	14.94 ± 0.03	4.55	700 / 1100
NC2	12.96 ± 0.02	15.81 ± 0.02	2.85	800 / 1100
WC4	54.91 ± 0.16	74.64 ± 0.18	19.73	300 / 400

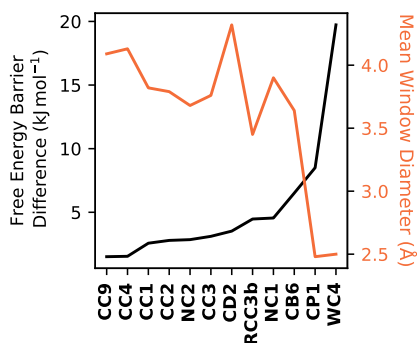
7.1 Free energy barriers *vs.* void diameters



(a)



(b)



(c)

Figure S5: a) Kr free energy barriers (left-hand side Y-axis) plotted against the mean window diameter (right-hand side Y-axis in orange) for *CDB12* b) Xe free energy barriers (left-hand side Y-axis) plotted against the mean window diameter (right-hand side Y-axis in orange) for *CDB12* c) free energy barriers difference (left-hand side Y-axis) plotted against the mean window diameter (right-hand side Y-axis in orange) for *CDB12*.

8 Experimental analysis of aNC1, aNC2 and aCC3

8.1 NMR spectroscopy

Solution ^1H NMR spectra were recorded at 400.13 MHz using a Bruker Avance 400 NMR spectrometer.

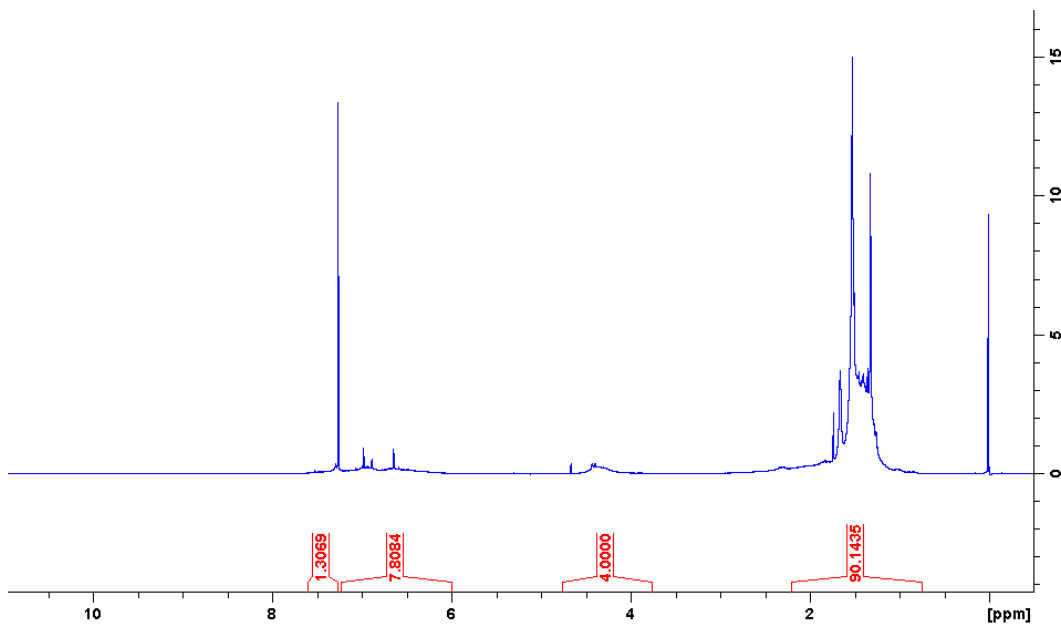


Figure S6: ^1H NMR (CDCl_3) of **NC1** after vacuum drying at 90 °C.

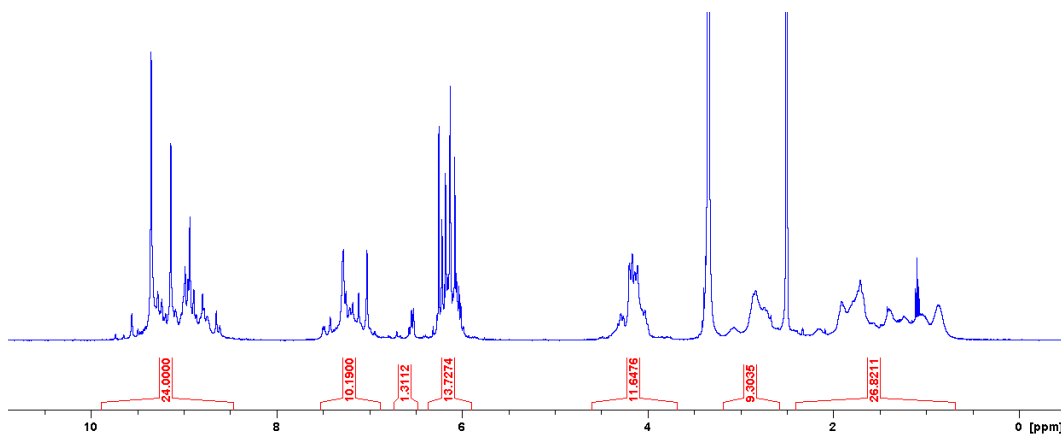


Figure S7: ^1H NMR (DMSO) of **NC2** after vacuum drying at 90 °C.

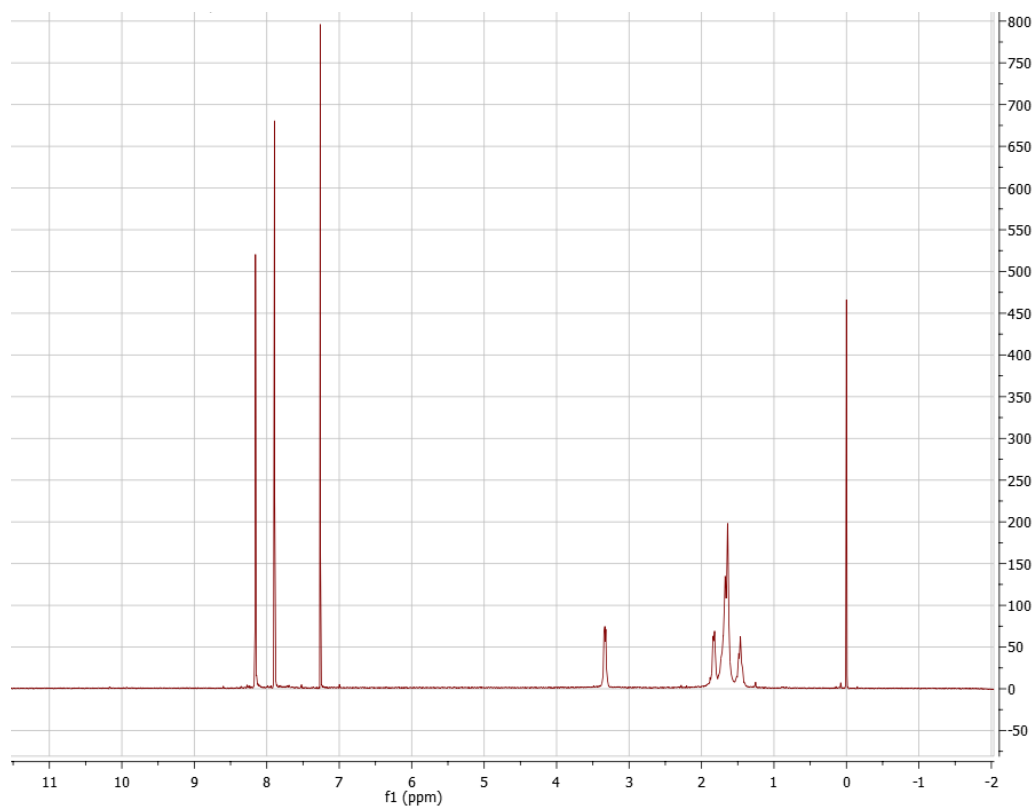


Figure S8: ^1H NMR (CDCl_3) of **aCC3** after freeze drying.

8.2 PXRD data

Powder X-ray diffraction (PXRD) data were collected in transmission mode on loose powder samples held on thin Mylar film in aluminum well plates on a Panalytical X'Pert PRO MPD equipped with a high throughput screening (HTS) XYZ stage, X-ray focusing mirror, and PIXcel detector, using $\text{Cu K}\alpha$ radiation.

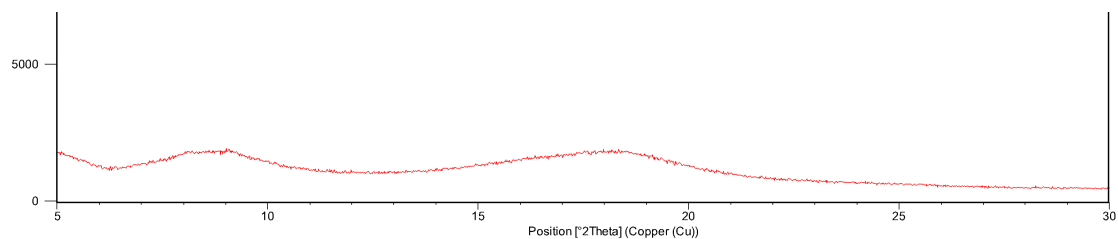


Figure S9: PXRD of **NC1** after vacuum drying at 90 °C.

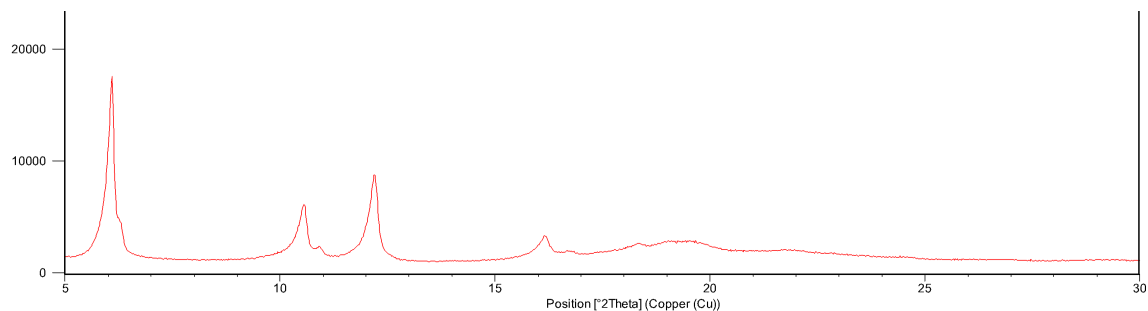


Figure S10: PXRD of **NC2** after vacuum drying at 90 °C.

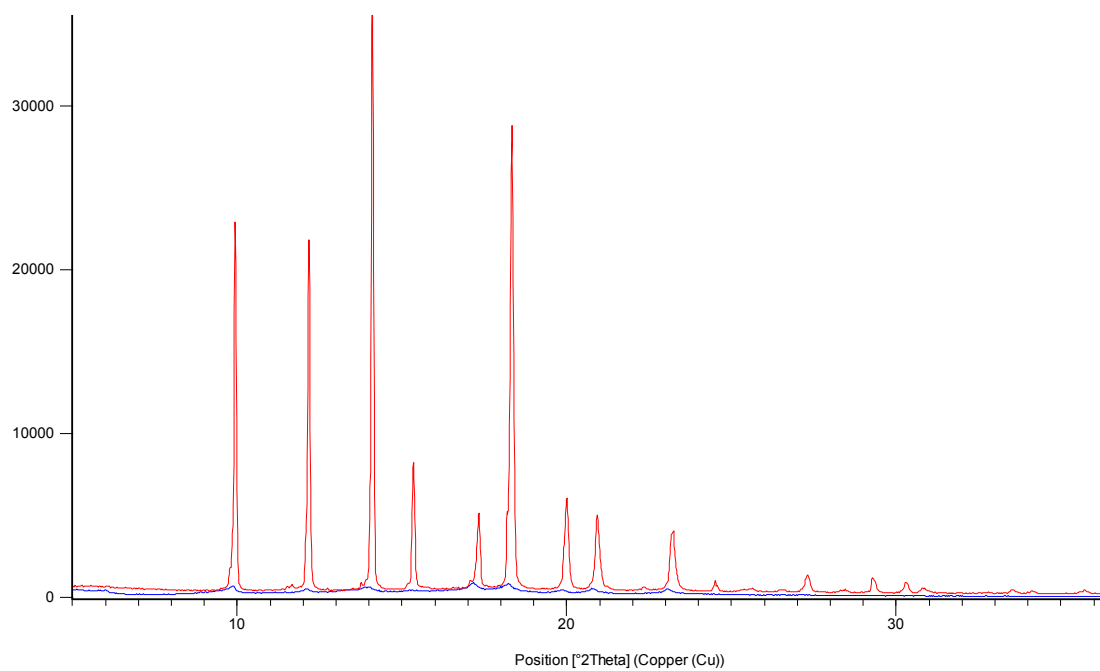


Figure S11: PXRD of **CC3 α** (red) isolated from synthesis and **aCC3** (blue) isolated after freeze drying.

8.3 Gas adsorption measurements

Kr and Xe adsorption and desorption isotherms were measured at 298 K up to 1 bar using a Micromeritics 2020 volumetric adsorption analyser. Powder samples were degassed offline at 90 °C under dynamic vacuum (10^{-5} bar) before analysis.

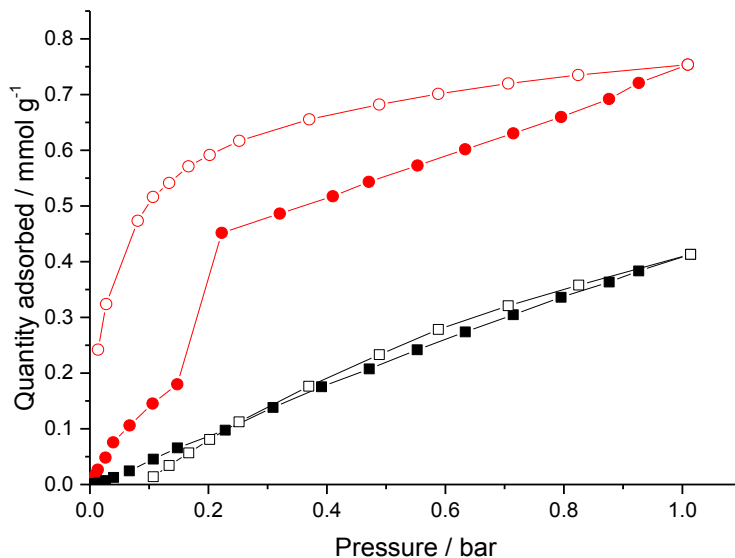


Figure S12: Gas sorption isotherms for the uptake of Kr (black squares) and Xe (red circles) in **aNC1**. Closed and open symbols represent adsorption and desorption, respectively.

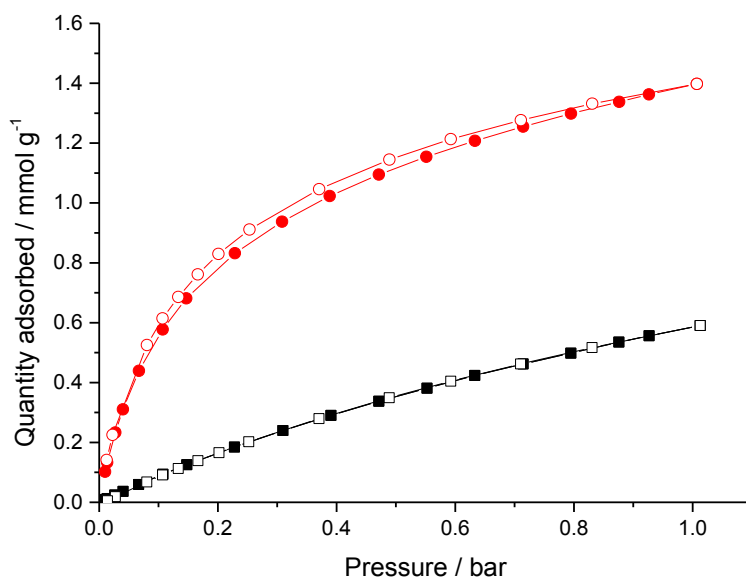


Figure S13: Gas sorption isotherms for the uptake of Kr (black squares) and Xe (red circles) in **aNC2**. Closed and open symbols represent adsorption and desorption, respectively.

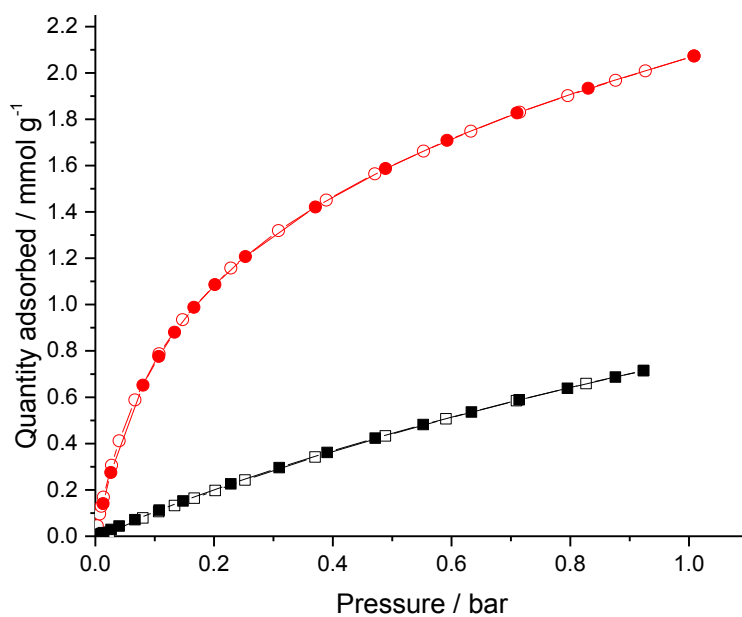


Figure S14: Gas sorption isotherms for the uptake of Kr (black squares) and Xe (red circles) in **aCC3**. Closed and open symbols represent adsorption and desorption, respectively.

9 pyIAST adsorption isotherms fitting

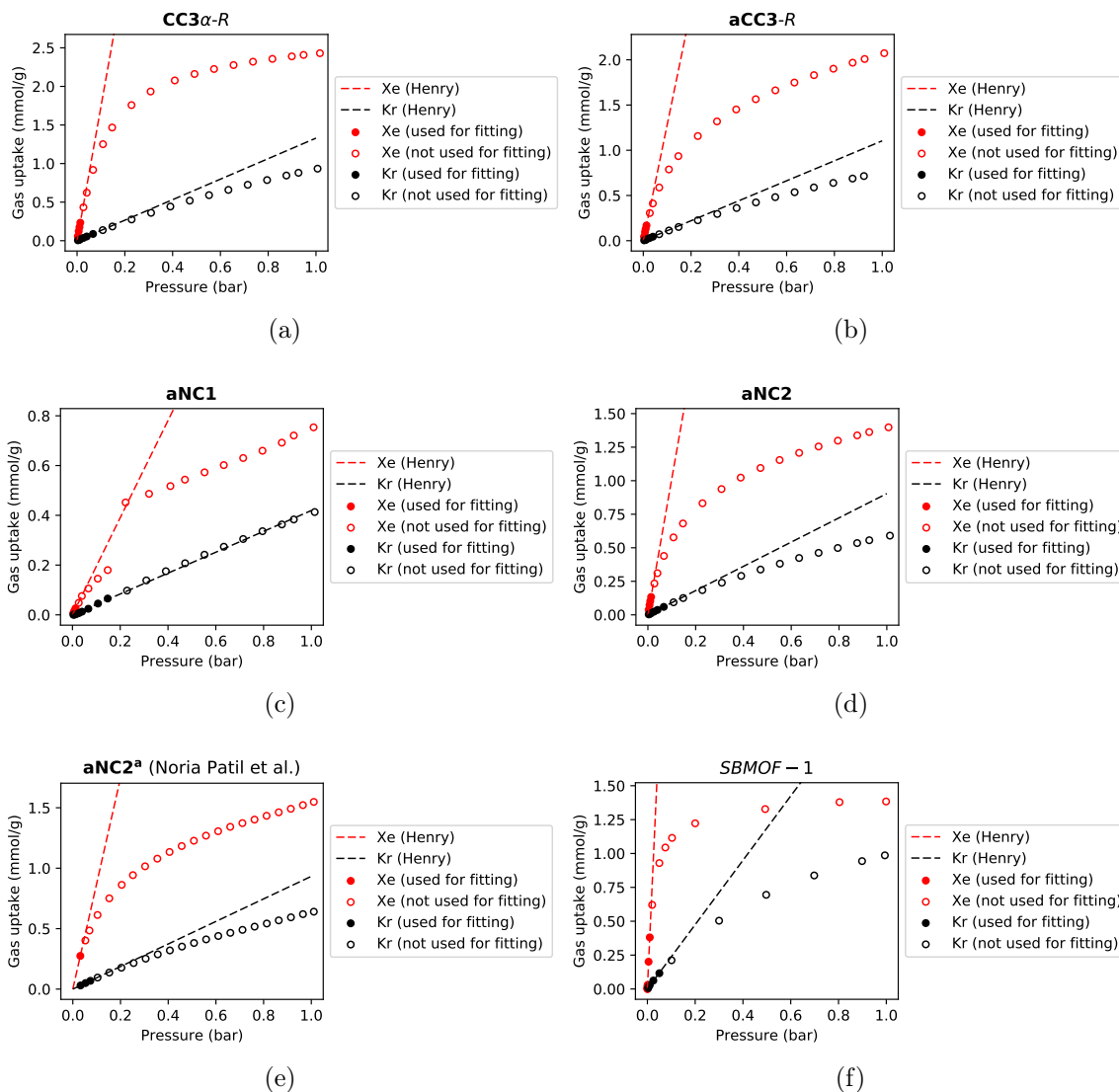


Figure S15: Points in Henry's region of the linear adsorption increase phase used for the fitting and calculating the Henry's constants. The Kr and Xe adsorption isotherms data were taken from the literature for **CC3 α -R**³⁷ (plot a), **aNC2^a** (Noria molecule as synthesised by Patil *et al.*³⁸ in plot e) and SBMOF-1³⁹ (plot f). Single component adsorption isotherms data for **aCC3-R** (plot b), **aNC1** (plot c) and **aNC2** (plot d) are from this work.

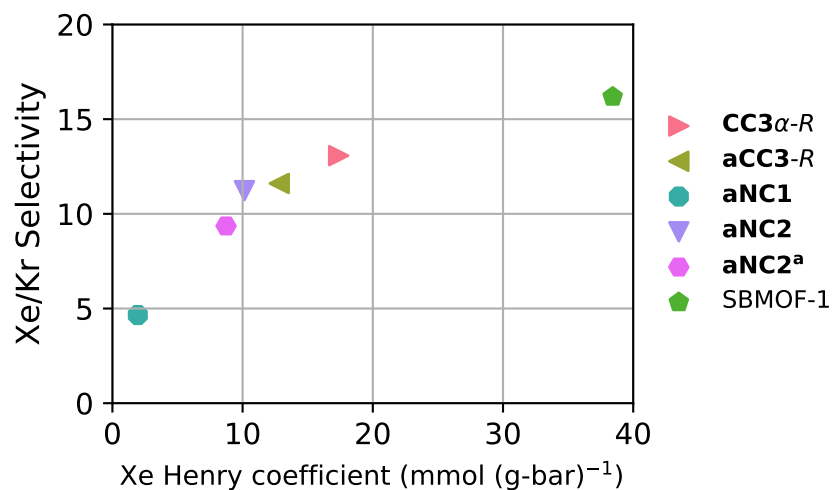


Figure S16: The calculated Xe/Kr selectivities for Henry's region (infinite dilution) for Xe and Kr at 298 K against the Xe Henry's coefficients at such conditions for literature data for SBMOF-1,³⁹ **CC3 α -R**³⁷ and **aNC2^a** (Noria molecule as synthesised by Patil *et al.*³⁸) and as reported here for **aCC3-R**, **aNC1** and **aNC2**.

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