Supplementary material: The origin of the measured chemical shift of ¹²⁹Xe in UiO-66 and UiO-67 revealed by DFT investigations

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A1 Synthesis

For UiO-66, ZrCl₄ (1.58 g, 6.8 mmol) was dissolved in DMF (390 ml) by ultrasonication for 10 minutes. Afterwards, 1,4benzenedicarboxylic acid (1.02 g, 6.15 mmol) was added and the mixture was sonicated again for 5 minutes. Then benzoic acid (24.9 g, 200 mmol) was added and the resulting mixture was placed into an oven at 393 K for 96 h. The white precipitate was collected, washed several times with DMF and ethanol. The powder was dried in vacuum at 393 K.

For UiO-67, ZrCl₄ (1 g, 4.35 mmol) was dissolved in DMF (400 ml) by ultrasonication for 10 minutes. Afterwards, 4,4'biphenyldicarboxylic acid (1g, 4.13 mmol) was added to the resulting solution and the mixture was sonicated for five more minutes. Acetic acid (18.6 ml, 325 mmol) was added and the resulting mixture was placed into an oven for three days at 393 K. The resulting powder was collected, washed several times with DMF and ethanol and dried under vacuum at 393 K.

A2 Materials and methods

ZrCl₄ (98 % purity, Sigma Aldrich), *N*,*N*-dimethylformamide (DMF) (p.a. purity, ABCR LTD), acetic acid (tech. grade, Biesterfeld), ethanol (99.0 %, ABCR LTD), 4,4'-biphenyldicarboxylic acid (>97 %, TCl), benzene-1,4-dicarboxylic acid (99 %, Acros Organics) and benzoic acid (99 %, Acros Organics) were used as received. Powder X-ray diffraction (PXRD) patterns were collected on a STOE STADI P diffractometer operated at 40 kV and 30 mA with monochromated Cu-K α 1 (λ = 0.15405 nm) radiation. Adsorption experiments were carried out on a Belsorpmax apparatus (MICROTRACBEL, Japan). High purity nitrogen (99.999 %) was used. Prior to the adsorption experiments the samples were activated at 423 K for 16 h. The BET area was calculated from multi-point BET plot, in the region of minimum deviation from consistency criteria.

A3 Powder XRD patterns



Figure A1 Powder XRD patterns for UiO-66. Calculated from the crystal structure (black) and measured (red).



Figure A2 Powder XRD patterns for UiO-67. Calculated from the crystal structure (black) and measured (red).

A4 Adsorption experiments



Figure A3 Nitrogen adsorption isotherms for UiO-66 and UiO-67 at T = 77 K with $p_0 = 101325$ Pa. From experimental measurements (denoted with EXP) as well as calculated with the RASPA code (referred to as MC).

Table A1 Calculated and measured BET surface area and pore volume. The simulated BET surface is $S_{\text{BET,sim}}^{1}$, the geometrically calculated pore volume is $V_{\text{calc,pore}}$ (calculated with Poreblazer^{2,3}), the experimental BET surface area is $S_{\text{BET,exp}}$ and the experimental pore volume is $V_{\text{exp,pore}}$. The experimental BET surface areas are in good agreement with simulated ones and the pore volumes are in good agreement with⁴.

Compound	S _{BET,sim} [m ² /g]	V _{calc,pore} [cm ³ /g]	S _{BET,exp} [m ² /g]	V _{exp,pore} [cm ³ /g]
UiO-66	1290	0.41	1309	0.54
UiO-67	2892	1.01	2450	0.96

A5 Pore dimension and pore size analysis

Pore dimensions

The pore dimensions $d_{\rm PD}$ can be approximated from the analysis of the void volume per structure, see table A5. One can estimate the pore dimension by the diameter of a sphere with the same volume as the respective pores, thus d = 2r with $r = \sqrt[3]{\frac{3V_{\rm pores}}{4\pi}}$. This leads, considering that $V_{\rm Op} \approx 4V_{\rm Tp}$, to the presented values of the pore dimensions. In this analysis, $T_{\rm p,1}$ and $T_{\rm p,2}$ are assumed to be equal in size. Thus, the average for the $T_{\rm p}$ is given. The results are summarized in table A2. A good agreement to literature values⁴ is found. The only difference occurs for the $O_{\rm p}$ in UiO-67, where we find a smaller dimension in comparison to the $T_{\rm p}$ in UiO-66. According to⁴, these pores have equal dimensions.

Table A2 Pore dimensions d_{PD} evaluated from the void volumes.

		V _{pores} [Å ³]	$d_{\rm PD}$ [Å]	$d_{\rm PD,lit}$ [Å] ⁴
150.66	Tp	229	7.59	7.5
010-00	Op	916	12.05	12
11:0 67	Tp	601	10.47	12
010-07	Op	2404	16.62	16

Pore sizes

The maximum pore size diameter d_{PS} , which can be obtained from a given pore size distribution (PSD), is in general defined as the maximum diameter of a sphere which can be placed inside a pore. With that, one can explicitly calculate the pore sizes for UiO-66 and UiO-67. For this purpose, the middle of each pore has been taken as a starting point. Afterwards, the maximum radius of a sphere which can be placed inside the three pores (T_{p,1}, T_{p,2} and O_p) was calculated. This was done taking the vdW radii of all surrounding atoms into account. Following this ansatz, the pore sizes of UiO-66 and UiO-67 were obtained as shown in table A3.

Table A3 Pore sizes d_{PS} calculated from the maximum radius of a sphere which can be placed inside each pore.

		$d_{\rm PS}$ [Å]
	T _{p,1}	7.19
UiO-66	T _{p,2}	7.71
	Op	8.45
	T _{p,1}	9.63
UiO-67	$T_{p,2}$	10.42
	Ôp	12.75
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Furthermore, the PSDs were calculated with Poreblazer² and RASPA^{5,6}. The PSD calculations are based on Monte-Carlo (MC) simulations using a force field description to model the interatomic interactions. All RASPA calculations were performed with the so called "CrystalGenerator" force field while for Poreblazer simulations we used the universal force field (UFF)⁷. A critical parameter for a typical MC simulation is the number of MC cycles. This number needs to be varied until the results of the MC run are converged. Another point is that the PSDs are evaluated from histograms. With that, the key properties of the histogram (number of bins or bins width) have to be analyzed for numerical stable results (see table A4). For the evaluation of the calculated PSD we interpolated and

smoothed the PSD to determine the most intensive peaks. The post-processing was done within Python using the numpy package for interpolation, the scipy package for convolution/ smoothing by applying the hanning window convolution kernel as de-

Program	MC	bins		UiO-66	UiO-67
	1000	100	$d_{\mathrm{PS},1}$ [Å]	7.43	11.62
			$d_{\mathrm{PS},2}$ [Å]	6.86	8.89
			$d_{\mathrm{PS},3}$ [Å]	4.91	4.88
		400	$d_{\mathrm{PS},1}$ [Å]	7.72	11.94
RASPA ^{5,6}	4000		$d_{\mathrm{PS},2}$ [Å]	7.37	10.02
			$d_{\mathrm{PS},3}$ [Å]	6.89	9.19
			$d_{\mathrm{PS},1}$ [Å]	7.76	12.01
	8000	800	$d_{\mathrm{PS},2}$ [Å]	7.41	10.06
			$d_{\mathrm{PS},3}$ [Å]	6.89	9.24
	1000	0.25	$d_{\mathrm{PS},1}$ [Å]	8.01	12.30
Poreblazer ²			$d_{\mathrm{PS},2}$ [Å]	7.22	10.24
			$d_{\mathrm{PS},3}$ [Å]		9.24
	1000 0		$d_{\mathrm{PS},1}$ [Å]	8.00	12.24
		0.20	$d_{\mathrm{PS},2}$ [Å]	7.40	10.19
			$d_{\mathrm{PS},3}$ [Å]	6.79	9.40
	8000		$d_{\mathrm{PS},1}$ [Å]	8.00	12.24
		0.20	$d_{\mathrm{PS},2}$ [Å]	7.40	10.19
			$d_{\mathrm{PS},3}$ [Å]	6.79	9.40

Table A4 Pore sizes d_{PS} calculated with RASPA and Poreblazer. The number of MC steps is denoted with MC while the number of bins (for RASPA) or the bin width (for Poreblazer) is given as bins.

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$$w(n) = 0.5 - 0.5 \cos\left(\frac{2\pi n}{M-1}\right) \qquad 0 \le n \le M-1,$$
 (1)

where the number of points in the output window M was set to 21, and the peakutils package for peak detecting. For all calculations with RASPA we used the primitive cells, whereas for the Poreblazer calculation the conventional cells were used. The resulting PSDs are shown in figure A4.

Void and accessible volume

The void volume V_{void} is the volume which is not occupied within a given system. Thus, it represents the volume in which no atom exists, according to its vdW radius. This strictly leads to the porosity like $\Phi_{\text{void}} = V_{\text{void}}/V_{\text{total}}$, where V_{total} refers to the total volume of the system (usually the conventional cell or primitve cell volume). On the other hand, the accessible volume V_{acc} is the volume which can be reached by a certain species. With that, one takes a probe radius r_{probe} in addition to the vdW radii of the atoms into account. Commonly, the probe radius is either 1.2 Å (vdW radius of H) or 1.4 Å (vdW radius of He). However, any other radius can be used, e.g. the vdW radius of Xe with 2.16 Å. The probe cannot be closer to



Figure A4 Theoretical PSD investigations using the codes RASPA and Poreblazer.

any atom than $r_{vdW} + r_{probe}$. This gives rise to another property, the accessible porosity $\Phi_{acc} = V_{acc}/V_{total}$. Unlike the void volume, the accessible volume depends on the probe radius, thus $V_{acc} = V_{acc}(r_{probe})$. Furthermore, the geometrical pore volume can be calculated as $V_{pore} = V_{acc}/m_{total}$, where m_{total} is the mass of the investigated system. As can be easily seen, this quantity depends on the probe radius as well.

Consequently, one has to be careful when calculating and comparing porosities and geometrical pore volumes to literature values. Clearly, the void porosity will always be greater than the accessible one. We calculated all mentioned quantities with several available Monte-Carlo/ Molecular dynamics programs to give an insight into the occurring differences, see therefore table A5. Additionally, we used our own python script, labelled as calcMOFpy, to calculate the properties and to ensure a consistent evaluation.

			UiO-66	UiO-67
Program	V _{total}	[Å ³]	2308	4972
	m _{total}	$[10^{-24} \text{ kg}]$	2.763	3.521
	Vvoid	[Å ³]	1366	3595
PLATON ⁸	Φ_{void}	[%]	59	72
	$V_{\rm acc}$	[Å ³]	1223	3431
$r_{\rm probe} = 1.20$ Å	$\Phi_{ m acc}$	[%]	53	69
	Vpore	$[cm^3/g]$	0.443	0.974
	$V_{\rm acc}$	[Å ³]	969	3182
$r_{\rm probe} = 2.16 \text{ Å}$	$\Phi_{ m acc}$	[%]	42	64
	Vpore	$[cm^3/g]$	0.351	0.904
	Vvoid	[Å ³]		_
RASPA ^{5,6}	$\Phi_{ m void}$	[%]		_
	$V_{\rm acc}$	[Å ³]	1204	3481
$r_{\rm probe} = 1.40$ Å	$\Phi_{ m acc}$	[%]	52	70
	Vpore	[cm ³ /g]	0.436	0.989
	Vvoid	[Å ³]	1339	3626
Poreblazer ²	Φ_{void}	[%]	58	73
	$V_{\rm acc}$	[Å ³]	1269	3559
$r_{\rm probe} = 1.40 \text{ Å}$	$\Phi_{ m acc}$	[%]	55	72
	Vpore	$[cm^3/g]$	0.459	1.011
	Vvoid	[Å ³]	1365	3598
calcMOFpy	Φ_{void}	[%]	59	72
	$V_{\rm acc}$	[Å ³]	1180	3378
$r_{\rm probe} = 1.20 \text{ Å}$	$\Phi_{ m acc}$	[%]	51	68
	Vpore	$[cm^3/g]$	0.427	0.959
	$V_{\rm acc}$	[Å ³]	924	3129
$r_{\rm probe} = 2.16 \text{ Å}$	Φ_{acc}	[%]	40	63
	Vpore	$[cm^3/g]$	0.334	0.889

Table A5 Porosities Φ_{void} and Φ_{acc} as well as geometrical pore volumes V_{pore} for UiO-66 and UiO-67. All corresponding values for the primitive cells are presented as well.

A6 NMR spectrum of UiO-66



Figure A5 *In situ* ¹²⁹Xe NMR spectrum of UiO-66 measured at 237 K and a relative pressure of 1 with signal assignments.

A7 Energetically favourable sites

To visualize the energetically most favourable sites, the following approach was carried out. A Xe atom is placed at the middle of each pore within a MOF. Afterwards, the Xe atom is stepwise moved towards either the SBU or the linker in the pore. The maximum distance is chosen to be smaller than the sum of the vdW radii of the involved atoms, thus $d_{\text{max}} \leq \sum r_{\text{vdW}}$. Given this constraint, the maximum distance per pore is sampled. For all considered movements, the total energy of the system is calculated. This energy is used to evaluate the energy difference ΔE with respect to the global minimum energy of the considered MOF

$$\Delta E = E_{\text{Xe-site}} - E_{\min}, \qquad (2)$$

where $E_{Xe-site}$ is the total energy of the system with Xe being at a specific position within the MOF. The minimum energy E_{min} refers to the MOF with Xe at its most favourable position.

A comparison of these calculated energy differences (see table 6) leads to the following two main conclusions.

First of all, the most favourable site in each pore is characterized by the smallest difference to the global energy minimum. For both MOFs and all considered pores, it can be seen that the positions close to the SBU are energetically more favourable than any other position (regarding the smallest possible distance to the structure elements). Given this fact, the conclusion can be drawn that Xe atoms tend to go towards the corners of the pores, even in situations where the pores are not completely filled.

Secondly, the energetically most favourable site within the MOF can be determined. As can be seen from the table, for UiO-66

Table 6 Energy differences for various positions of Xe inside the pores ($T_{p,1}$, $T_{p,2}$ and O_p) for UiO-66 and UiO-67. The calculated total energy at a specific position was subtracted by the global minimum for the respective MOF. The reference energies are given by $E_{UiO-66} \approx -4691.487979$ Ry and $E_{UiO-67} = -5383.602073$ Ry. The positions labelled with 'to linker' describe a movement from the middle of the pore directly towards the linker while the label 'to SBU' specifies a movement towards the SBU.

System	nosition	$\Delta E_{\mathrm{T}_{\mathrm{p},1}}$	$\Delta E_{T_{p,2}}$	ΔE_{O_p}
System	position	[meV]	[meV]	[meV]
	middle	+73	+149	+205
	+1 Å to SBU	—	—	+180
UiO 66	+2 Å to SBU	_	_	+84
010-00	+2.5 Å to SBU	_	_	± 0
	+1 Å to linker	—	—	+182
	+2 Å to linker			+88
	middle	+353	+404	+443
	+1 Å to SBU	+342	+397	+434
	+2 Å to SBU	+284	+352	+420
	+3 Å to SBU	+175	+273	+382
UiO-67	+4 Å to SBU	± 0	+122	+317
010-07	+5 Å to SBU	—	—	+195
	+1 Å to linker	+338	+393	+435
	+2 Å to linker	+266	+344	+417
	+3 Å to linker			+382
	+4 Å to linker			+294

the global minimum is found inside the O_p . Here, it is necessary to note again that there is only space for one Xe atom in the tetrahedral pores of UiO-66. Given the constraints of the vdW radii of all atoms and the chosen step size, only the value for the energy difference in the middle of the pore is presented. This at least allows a comparison between $T_{p,1}$ and $T_{p,2}$. On the other hand for UiO-67, the global minimum occurs within $T_{p,1}$.

A8 Chemical shifts for the model systems

Regarding the tabulations of all values for the model systems, certain points need to be clarified. Taking all model calculations for the Xe-Xe pair model, the linker as well as the Zr cluster model into account, there are approximately 6000 values. To display all of these values in a tabulated form is not feasible. As already done in the main document, the Xe-Xe contribution has been completely displayed, as it only depends on the distance between two Xe atoms. In the following, a more detailed description about the contributions of the Zr cluster, i.e. the SBU, shall be carried out. With that, a somewhat deeper insight into the obtained shifts for the different pores will be derived. In the end, a visual summary for the chemical shifts around the linker

model will be given.

First of all, the analysis of the model systems shall be explained in more detail. To calculate the chemical shift depending on a given chemical environment, a Xe atom has been placed at several positions around a given model. Afterwards, the resulting magnetic shielding and correspondingly the chemical shift for this relative position to the model has been calculated. To visualize where the Xe atom has been placed relative to the models, see figures 6 and 7.

With this approach, several thousand positions have been evaluated. This ensures a thorough evaluation of the chemical shift at any position relative to the models. Given the equilibrated Xe positions from molecular dynamics simulations, an extrapolation between the tabulated shifts corresponding to the nearest adjacent positions can be carried out. Based on the mentioned rigorous sampling, the resulting error from these extrapolations will be small.

For a more detailed description of the resulting chemical shifts, some results for the shift around the SBU (Zr cluster) are presented in table 7. There, for each site, i.e. each individual corner for $T_{p,1}$ (μ_3 -O), $T_{p,2}$ (μ_3 -OH) and O_p (blank Zr), the shift for an increase in distance to the respective site $\Delta d_{Xe-site}$ has been displayed. Only the values for the distances which point directly away from the sites and thus directly into the pores are given. In other words, if the atom slightly shifts away from this path, a new sampling is needed or the value has to be extrapolated. The starting values of the distance to the sites vary, because the minimum has been chosen to be slightly smaller than the sum of the van der Waals (vdW) radii of the involved atoms. Correspondingly, the initial distances are 3.8 Å for $T_{p,1}$, 3.1 Å for $T_{p,2}$ and 3.9 Å for O_p .

Table 7 Chemical shifts for three different sites of the Zr cluster, representing the three corners of the individual pores $T_{p,1}$, $T_{p,2}$ and O_p (see figure 6 for further explanations).

$\Delta d_{\rm Xe-site}$	$\delta_{\mathrm{T}_{\mathrm{p},1}}$	$\delta_{\mathrm{T}_{\mathrm{p},2}}$	$\delta_{\mathrm{O}_{\mathrm{p}}}$
[Å]	[ppm]	[ppm]	[ppm]
0.0	491	106	256
0.3	299	63	146
0.6	177	37	83
0.9	103	21	47
1.2	60	11	26
1.5	34	7	14
1.8	17	5	8
2.1	8	3	5

Given these values, exponential behaviors of the chemical shift



Figure 6 The Zr cluster, a SBU with coordinated CO₂. The directions to the specific pores are illustrated.



Figure 7 The linker model, where the directions of the sampling paths (abbreviated with p) are illustrated. P1 and p3 have been distinguished to average contributions which occur if xenon is close to the oxygen atoms within the MOFs (where they are not saturated in the same way as implied in this model system). In between the paths p4 and p5, several more values have been sampled, denoted as p6. The positions above the H atoms were analyzed with a benzene model (the corresponding paths are denoted as p7 and p8). This can be done based on the fact that this specific influence does not change for the linker. Additionally for all paths, the height per path has been increased by several steps to include several distances to this structure unit. The initial value for the height was chosen according to the vdW radii of C and Xe. With that, values in an area (path \cdot height) are sampled for each path.

at Xe-site distance d,

$$\begin{split} &\delta_{\mathrm{T}_{\mathrm{p},1}}(d) = 548 \cdot e^{-1.930(d-3.8 \mathrm{\AA})} \\ &\delta_{\mathrm{T}_{\mathrm{p},2}}(d) = 101 \cdot e^{-1.717(d-3.1 \mathrm{\AA})} \\ &\delta_{\mathrm{O}_{\mathrm{p}}}(d) = 252 \cdot e^{-1.878(d-3.9 \mathrm{\AA})}, \end{split}$$



Figure 8 Chemical shifts for three different sites of the Zr cluster.

can be determined (see figure 8).

Accordingly, the shifts for each different site and with that for each individual pore are significantly different. It can be seen that the shift due to the influence of the SBU in $T_{p,2}$ is smaller than in $T_{p,1}$ (see figure 8), which was already discussed in the main document.

In order to illustrate the influence of the linker on the chemical shift, the values for different sampling paths (see figure 7) have been plotted (see figure 9). Under the condition that Xe is very close to the linker, very high shifts are induced (see red colors in figure 9), which rapidly decrease once the height (i.e. the distance to the molecular plane) increases. This is identified by the presented color code, where blue values represent small chemical shifts while green and yellow values refer to intermediate shifts considering the maximum of the shift scale. This behavior is found for the other paths (p4, p5, p6, p7 and p8) as well. The initial heights represent very small Xe-surface distances. These distances do not occur in the MOF, based on structural limitations. Thus, the chemical shift introduced by the linker, which is part of the MOF, will be smaller than the maximum shifts presented in figure 9. It should be considered that each corner in the T_p is created by one SBU and three linkers. On the other hand, each corner in the Op consists of a SBU and four linkers. Thus, even if the individual contributions per linker are small, the total shift can be rather large. These multiple contributions have to be taken into account when analyzing the final shifts.

For more information regarding all values which have been generated with the model systems, please contact the corresponding author.



Figure 9 3D visualization of the chemical shift paths (p1, p2 and p3) of the linker model. The color code indicates the magnitude of the chemical shift. Gray values denote small, negative shifts. The paths are displayed as arrows within the molecule in analogy to figure 7. The atoms of the linker model are illustrated with C in red, O in green and H in blue.

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