Electronic Supporting Information (ESI) to the article

NMR relaxation and modelling study of the dynamics of SF6 and Xe in porous organic cages

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Note on cage nomenclature and chirality. Helicity, or axial chirality, is an intrinsic property of the organic cage CC3. In this study, a homochiral diamine, (R, R)-1,2-cyclohexanediamine was used in the cage synthesis. The cage used throughout the gas study was therefore the homochiral form, CC3-R. Identical results would, presumably, be obtained with the opposite enantiomer, CC3-S. Gas adsorption measurements suggested that the racemic equivalent, CC3-(R, S), also has similar properties with respect to gas adsorption. This latter cage would be less expensive to produce on a large scale because it can be prepared from the racemic cyclohexanediamine. However, the chiral forms, CC3-R and CC3-S, can form large single crystals with enhanced long-range order with respect to the less expensive racemic cage, CC3-(R, S). This is because the racemic form is much less soluble than the homochiral form and precipitates rapidly, preventing the growth of large, high-quality single crystals. For this reason, the homochiral form of CC3 was used for these fundamental studies, in particular because it allows direct analysis of a highly crystal structure with fewer defects.

S1 NMR observations

S1.1 Loading effect on the chemical shift of SF6

19F NMR spectra of the LL and ML samples were measured using spectrometer with 14.1 T magnetic field (resonance frequency of 19F is 564 MHz). The complete set of recorded relaxation and diffusion data are provided in Section S4 and Tables S3-S4. The chemical shift (Fig. S1A) varied slightly with loading ratio and temperature 250-370K. T1 relaxation (Fig. S1B) varied significantly between the samples (less than 100 ms at LL and close to 500 ms at ML). T2 relaxation behaved similarly in both samples (Fig. S1C). A plausible explanation of the large change in T1 is that at ML a portion of gas molecules are outside the cages. This scenario provides an increased fraction of long T1 seen in ML sample (Figure S1B). The T2 in Fig S1C is similar in ML and LL, however, the linewidth is larger for ML as is discussed in the main paper. This increased linewidth may be explained with additional broadening also from a fraction of free or almost free SF6 in ML sample. The chemical shift is larger for ML sample (see Figure S1A). Considering the QC estimates in Tables S5 and S6, it is seen that the chemical shift is a few ppm larger in gas phase. Hence, the concentration trend for ML in Fig S1A is consistent with a fraction of free-gas SF6. These observations motivates quantitative study of only the LL sample, as it is complicated to take the effect of free gas into account.

![Figure S1](image_url)

**Figure S1** (A) Chemical shift, as well as (B) T1 and (C) T2 relaxation times of 19F in SF6 molecule absorbed to CC3-R material measured at 14.1 T magnetic field.
S1.2 Diffusion of SF6
Translational diffusion measurement of SF6 is displayed in Figure S2, together with HL Xe data. The SF6 measurement is in the high temperature region in comparison to the relaxation study and the two loadings (LL and ML) samples show similar magnitude of diffusion constants. Considering the hypothesis in Section S1.1, that a fraction of the ML gas is not fully incorporated in the CC3-R structure, the slightly steeper slope for ML SF6 is explained by a change in fraction of CC3-R incorporated gas.

Figure S2 Diffusion coefficients of the ML and LL SF6 samples and the HL xenon sample.

S2 Relaxation model
The individual relaxation rate contributions are given by: 1

\[
R_{\text{1,inter}}^{\text{AH}}(\omega_A) = - \frac{1}{2} K_{\text{DD}}^{\text{AH}} [J_{\text{inter}}^{\text{AH}}(\omega_A - \omega_H) + 3 J_{\text{inter}}^{\text{AH}}(\omega_A) + 6 J_{\text{inter}}^{\text{AH}}(\omega_A + \omega_H)],
\]

\[
R_{\text{2,inter}}^{\text{AH}}(\omega_A) = \frac{1}{2} K_{\text{DD}}^{\text{AH}} [3 J_{\text{inter}}^{\text{AH}}(0) + 4 J_{\text{inter}}^{\text{AH}}(\omega_A - \omega_H) + 3 J_{\text{inter}}^{\text{AH}}(\omega_A) + 6 J_{\text{inter}}^{\text{AH}}(\omega_A + \omega_H) + 6 J_{\text{inter}}^{\text{AH}}(\omega_A + \omega_H)],
\]

\[
R_{\text{1, intra}}^{\text{AH}}(\omega_A) = \frac{3}{20} b_{\text{AH}}^{\text{2}} [3 J_{\text{intra}}(0) + 5 J_{\text{intra}}(\omega_A) + 2 J_{\text{intra}}(2 \omega_A)],
\]

\[
R_{\text{2, intra}}^{\text{AH}}(\omega_A) = \frac{3}{20} b_{\text{AH}}^{\text{2}} [3 J_{\text{intra}}(0) + 5 J_{\text{intra}}(\omega_A) + 2 J_{\text{intra}}(2 \omega_A)],
\]

\[
R_{\text{1, Y Y}}^{\text{AH}}(\omega_A) = \frac{1}{10} b_{\text{AH}}^{\text{2}} [4 J_{Y}(\omega_A - \omega_H) + 3 J_{Y}(\omega_A) + 6 J_{Y}(\omega_A + \omega_H)], \quad Y = \{R, L, ex\},
\]

\[
R_{\text{2, Y Y}}^{\text{AH}}(\omega_A) = \frac{1}{15} b_{\text{AH}}^{\text{2}} [3 J_{Y}(0) + 5 J_{Y}(\omega_A) + 6 J_{Y}(\omega_A)], \quad Y = \{R, L\},
\]

\[
R_{\text{2,ex}}(\omega_A) = \omega_A \Delta \delta \frac{1}{2} X_{c} X_{W} \frac{X_{\text{ex}}(0)}{X_{W} - (1 - X_{C})},
\]

\[
R_{1}^{\text{SR}} = R_{2}^{\text{SR}} = \frac{2 b_{\text{DD}}^{\text{A}}}{3 h \tau} \left[ t r \left[ C_{\text{SR}} \right] \right]^{2} \tau_{j}; \quad \tau_{j} = \frac{1}{6 k_{B} T},
\]

\[
K_{\text{DD}}^{\text{A}}(\omega_A) = - \frac{1}{10} N_{H} \left( \frac{\mu_{A}}{4 \pi} \gamma_{A} \gamma_{H} \hbar \right)^{2},
\]

\[
b_{\text{AH}} = \left( - \frac{\mu_{0} Y_{A} Y_{H} \hbar}{4 \pi r_{c}^{2} f} \right),
\]

where \( h \) is the Planck constant in angular units, \( \mu_{0} \) is the vacuum permeability and the intra-DD constant \( b_{\text{DD}}^{\text{A}} \) depends on the effective spin distance \( r_{c}^{2} \) (see Sections 3.3.1 and 3.3.3 for 129Xe and SF6 respectively). The close-contact distances of proton and nuclear spin A=\{129Xe, F\} is given by \( d_{\text{DD}}^{\text{A}} \) and \( N_{H} \) is the proton spin density in CC3-R. Note that \( N_{H} \) is the number of spins per unit sphere. Hence, the number of proton spins per unit volume, known for the CC3-R structure (5.7337-1028 per m3), is multiplied with \( (4 \pi /3) \). The DDinter interaction is assuming spins located at the centre of the SF6-sphere (see figure 3 of the main paper). The second rank chemical shielding anisotropy \( \gamma_{A} \) is given.
by $\Delta \sigma$ in parts per million (ppm) with contribution from local rotation and C-W exchange respectively. The calculation of chemical shielding anisotropy from quantum chemistry is discussed in the main paper. The C-W chemical shift difference in angular units is given by $\omega_A \Delta \delta$, where the Larmor frequency is given by $\omega_A = \gamma_A B_0$ and $B_0$ is the static magnetic field and $\gamma_A$ is the gyromagnetic ratio for spin A = {129Xe, F}. The exchange rate is given by $k_{ex}$. The site molar fractions are $X_C$ and $X_W$ for cage and window cavity respectively. The nuclear spin-rotation contribution for SF6 contain the SF6 moment of inertia (I), nuclear spin-rotation tensor ($CSA$, computed by quantum chemistry, see the main text) and depends on inverse of fitted rotational correlation time $\tau_R$. The relaxation rates are given by linear combination of spectral densities ($f(\omega)$, eqs S1-S10, see also section 3.2.3 of main paper).

S2.1 Notation for SF6 relaxation model

In Figure 6 of main paper the mechanisms contributions for SF6 are displayed and the corresponding formulas are translational diffusion modulated dipole-dipole DDinter (Eqs. S1 and S2), intra molecular dipole-dipole DDFF-R (Eqs. S3 and S4 with $\tau_R$ dependent spectral density), cavity intermolecular dipole-dipole DDFH-R (Eqs. S5 and S6, with $\tau_R$ dependent spectral density), chemical shift anisotropy CSA-R (Eqs. S7, S8 with $\tau_R$ dependent spectral density) and nuclear spin-rotation SR (Eq. S10). The DDHF-ex (Eqs. S5 and S6) and shift-ex (Eq. S9) are modeled with correlation time $1/k_{ex}$ approximated with $\tau_D = d_{HF}^2 / D$ ($D$: F-diffusion constant).

Potential cross-correlation to consider is between CSA-R and DDFF-R (or DDFH-R). Given the angle of approximately $\pi/2$ between the dominant CSA-R principal component and the shortest FF dipole-dipole vector in SF6, a scale-down of the contribution is expected. It is noted that this will be a $1/T_1$ contribution since $\tau_R$ is too short to significantly influence $1/T_2$ (considering the model results). The potential cross-correlation between CSA-R and DDFH-R or DDFH-R and DDFF-R, the stochastic process of reference-frames are, within the proposed model, significantly different not leading to significant cross-correlation. The cross-correlations are not expected to alter the trends determined in this study and are omitted.

S2.2 Notation for 129Xe relaxation model

In Figure 4 of main paper the mechanisms for 129Xe are shown with shift-ex (Eq. 9 relaxation modulation by C-W site exchange), local intermolecular dipole-dipole DDHXe-L (Eqs. S5 and S6, with $\tau_L$ dependent spectral density), DDHXe-ex (Eqs. S5 and S6, with $1/k_{ex}$ dependent spectral density), CSA-L (Eqs. S7, S8 with $\tau_L$ dependent spectral density).

S3 Estimated parameter distribution from MCMC-Bayesian method

Bayes theorem is here used to relate conditional probability distribution, $P(x|EXP,I)$, of the model parametrization $x$ given the experimental data EXP and the prior assumptions $I$ to the experimental likelihood $P(EXP|x,I)$:

$$P(x|EXP,I) = \frac{P(EXP|x,I)P(x|I)}{Z},$$

(S13)

where $P(x|I)$ is the prior assumption on $x$ and $Z$ is a normalization factor. In this work the “uninformed” prior is used where prior to data processing, the variables in $x$ are assumed to be uniform random variables with the boundaries dictated by Table S1 and S2 for the xenon and SF6 study respectively. The experimental likelihood takes the form $P(EXP|x,I) = \exp(-\chi^2)$ where $\chi^2$ is the sum of square cost-function of Eq. 10 in the main paper. The probability distribution of the parametrization $x$ is sampled by Markov Chain Monte Carlo (MCMC, see main paper section 3.4),
where we may sample \( P(x|\text{EXP}, I) \propto P(\text{EXP}|x, I)P(x|I) \) by MCMC.\(^{5,6}\) Hence, the normalization \( Z \) is not required to arrive at the \( x \) parameter distributions.

Table S1: Parameter boundaries in the MCMC simulation for \(^{129}\)Xe relaxation of HL, ML and LL samples. The parameters \( \tau_{0:1} \) and \( E_{\text{ex}} \) represent Arrhenius model for cage and window exchange rate and \( \tau_{L:1} \) \( E_{L} \) corresponding parameters for local site dynamics. The posteriori model estimation of the parameters given in table 3 of the main paper.

| Boundary | \( \tau_{0:1} \) (10\(^{10}\) s\(^{-1}\)) | \( E_{\text{ex}} \) (kJ/mol) | \( \tau_{L:1} \) (10\(^{10}\) s\(^{-1}\)) | \( E_{L} \) (kJ/mol) |
|----------|---------------------------------|----------------|----------------|----------------|
| Min      | 0.05                            | 0.1            | 2              | 1              |
| Max      | 260                             | 35             | 500            | 50             |

Table S2: Parameter boundaries in the MCMC simulation for LL-SF6 relaxation and diffusion data. The DDFF amplitude (\( b_{\text{FF}} \)) is estimated to 1.22e5 s\(^{-1}\) from energy minimized quantum structure F-F distances.

| Boundary | \( d_{\text{FH}} \) (Å) | \( \tau_{0:1} \) (10\(^{10}\) s\(^{-1}\)) | \( E_{\text{R}} \) (kJ/mol) | \( X_{c} \) scaleR | \( D_{0} \) (10\(^{-10}\) m\(^{2}\)s\(^{-1}\)) | \( E_{D} \) (kJ/mol) |
|----------|------------------------|---------------------------------|----------------|-----------------|----------------|----------------|
| Min      | 2.2                    | 0.01                            | 1              | 0.7             | 0.5            | 0.1            | 13             |
| Max      | 7                      | 10000                           | 40             | 1.0             | 5              | 10             | 25             |

S3.1 Parametrization of xenon model

In Figures S3-S5 the MCMC sampled values in histogram form of the exchange rate and local cavity correlation times are given. It is observed that these distributions are relatively narrow with corresponding 95% confidence intervals estimated in Table 3 of main article. In particular it is seen that the distributions are centered around a single value even though MCMC trajectories where started from 50 random initial configurations in parameter space (with boundary of Table S1). The single centered values point to a unique parametrization in the sense that we do not have obvious multiple distributions of values in the xenon relaxation model.

The diffusion constants entering the DDinter mechanism are obtained from Arrhenius model of experimental data displayed in Fig. S6. The Arrhenius parameters (activation energy kJ/mol, amplitude m\(^{2}\)/s) are for HL: (33\(\pm\)1, 6e-6), ML (11\(\pm\)0.5, 2.5e-8) and LL (19\(\pm\)4, 8.5e-7).

![Histograms](image1.png)

**Figure S3** Parameters for the HL-Xe sample, MCMC histograms of cavity exchange rate \( (k_{\text{ex}}) \) and local cavity correlation time \( (\tau_{L}) \) in panel a and b respectively.
Figure S4 Parameters for the ML-Xe sample, MCMC histograms of cavity exchange rate ($k_{ex}$) and local cavity correlation time ($\tau_L$) in panel a and b respectively.

Figure S5 Parameters for the LL-Xe sample, MCMC histograms of cavity exchange rate ($k_{ex}$) and local cavity correlation time ($\tau_L$) in panel a and b respectively.
Arrhenius model fitted to diffusion experiments, top left panels HL, ML and lower panel LL sample.

S3.2 parametrization of SF₆ model
In Figures S7 and S8 parameter histograms for LL-SF₆ data. In Figure S7 panel a the rescale parameter (scaleR) of the dipole-dipole interaction is given. The scaleR is the factor of rescale that the static spin-spin distance (computed from optimized quantum chemistry structure) of F-H and F-F dipole-dipole interaction. The panel b-d show the SF₆ rotational correlation time at two temperatures, the close contact distance (entering DDinter mechanism) and the molar fraction of cage population respectively. In Figure S8 the Arrhenius parameters of rotational correlation time and translational diffusion are displayed in panels a and b respectively. It is noted from Figure S7 that parameters are not in distinctly separated distributions in spite starting MCMC trajectories from random starting configurations. Hence, no obvious multiple parametrization. This is also true for the Arrhenius parameters in Figure S8.
Figure S7 Parameter histograms for LL-SF6 sample, generated by MCMC, showing the dipole-dipole distance scale factor, site reorientation correlation time (computed from Arrhenius parameters in figure S7), the close contact F-H spin distance and the cage molar fraction in panels a-d respectively.

Figure S8 Arrhenius parameter histogram for LL-SF6 sample, generated by MCMC for rotational correlation time and translational diffusion constant in panel a and b respectively.

S4 Experimental data and uncertainty
The experimental relaxation rates and diffusion constants are listed in tables S3a-S3c. The experimental uncertainties were estimated from the fits of experimental data with exponentially dependent function (in case of T1, T2) and extracting the standard error reported in origin 2018 software. The experimental uncertainty in SF6 relaxation rates were estimated from the repeated
measurements in a temperature cycle (see Table S4). The uncertainty in diffusion data where deduced by taking the difference of measured data with realistic Arrhenius models.

Table S3a: $^{129}$Xe 1/T$_1$, 1/T$_2$ and Diff experimental data HL-sample.

| T (K) | T$_{1:1}$ 10$^3$ (s$^{-1}$) 7T | 1/T$_2$ (s$^{-1}$) 7T | T (K) | T$_{1:1}$ 10$^3$ (s$^{-1}$) 14T | 1/T$_2$ (s$^{-1}$) 14T | T (K) | Diff 10$^{-10}$ (m$^2$s$^{-1}$) |
|-------|-------------------------------|-----------------------|-------|-------------------------------|-----------------------|-------|-----------------------------|
| 295.5 | 22±0.4                        | 57±4                  | 296.5 | 17±0.25                       | 97±6                  | 312   | 0.2±0.02                    |
| 301.2 | 24±0.4                        | 52±4                  | 302   | 18±0.28                       | 86±6                  | 324   | 0.28±0.03                   |
| 312.5 | 30±0.6                        | 45±4                  | 313   | 22±0.29                       | 71±5                  | 335   | 0.41±0.04                   |
| 323.9 | 38±0.8                        | 38±4                  | 324   | 27±0.45                       | 60±4.6                | 346   | 0.57±0.05                   |
| 335.2 | 46±1                          | 35±3                  | 335   | 33±0.42                       | 53±4.1                | 357   | 0.89±0.11                   |
| 346.6 | 53±1.3                        | 32±3.6                | 346   | 40±0.68                       | 48±4.0                | 368   | 1.16±0.13                   |
| 358.0 | 61±1.9                        | 28±3.2                | 356   | 47±0.7                        | 46±4.1                | 379   | 1.77±0.22                   |
| 369.3 | 65±1.8                        | 25±3                  | 368   | 53±1.2                        | 42±4.0                | -     | -                           |
| 380.7 | 68±1.4                        | 24±3                  | 378.5 | 57±1.1                        | 41±4.1                | -     | -                           |

Table S3b: $^{129}$Xe 1/T$_1$, 1/T$_2$ and Diff experimental data ML-sample.

| T (K) | T$_{1:1}$ 10$^3$ (s$^{-1}$) 14T | I/T$_2$ (s$^{-1}$) 14T | Diff 10$^{-10}$ (m$^2$s$^{-1}$) |
|-------|--------------------------------|-----------------------|---------------------------------|
| 255   | 79.7±0.8                       | 19±2                  | 1.42±0.04                       |
| 266   | 74.5±0.7                       | 20±2                  | 1.78±0.06                       |
| 278   | 69.4±0.7                       | 22±2                  | 1.2±0.1                         |
| 289   | 63.3±1.3                       | 24±2                  | 2.6±0.1                         |
| 298   | 60.3±1.4                       | 27±2                  | 2.8±0.1                         |
Table S3c: $^{129}\text{Xe}$ 1/T$_1$, 1/T$_2$ and Diff experimental data LL-sample.

| T (K) | T$_{1-1}$ 10$^3$ (s$^{-1}$) | 1/T$_2$ (s) | Diff 10$^{-10}$ (m2s$^{-1}$) |
|-------|----------------|---------------|-------------------|
|       | 14T            | 14T           |                   |
| 255   | 112±15         | 34±2          | 1.1±0.6           |
| 266   | 89±6           | 32±3          | 3.2±0.8           |
| 278   | 86±7           | 30±2          | 3.8±0.6           |
| 289   | 78±8           | 30±2          | 3.5±2             |
| 298   | 73±10          | 30±3          | 5.5±0.9           |

Table S4: SF$_6$ 1/T$_1$, 1/T$_2$ and Diff experimental data LL-sample, the standard deviations in experimental relaxation rates are obtained from temperature cycle.

| T (K) | T$_{1-1}$ (s$^{-1}$) | T$_{2-1}$ (s$^{-1}$) | T (K) | T$_{1-1}$ (s$^{-1}$) | T$_{2-1}$ (s$^{-1}$) | T (K) | Diff 10$^{-13}$ (m2s$^{-1}$) |
|-------|-------------------|-------------------|-------|-------------------|-------------------|-------|-------------------|
|       | 7T                | 7T                |       | 14T               | 14T               |       |                   |
| 255   | 9.1±0.05         | 1630±430         | 255   | 11±0.08           | 1680±418          | 335   | 5±1.8            |
| 266   | 7.9±0.04         | 1610±55          | 266   | 9.2±0.04          | 1553±120          | 345   | 6.4±1            |
| 278   | 7.0±0.07         | 1150±10          | 278   | 8.1±0.04          | 1137±88           | 357   | 8.1±0.4          |
| 289   | 6.1±0.01         | 750±11           | 289   | 7.1±0.014         | 766±18            | 368   | 8.4±0.5          |
| 298   | 5.6±0.002        | 546±5            | 298   | 6.5±0.012         | 548±22            | 379   | 8.9±1.0          |
| 304   | 5.3±0.04         | 436±16           | 304   | 6.1±0.005         | 460±4             |       |                   |
| 315   | 4.9±0.002        | 301±10           | 315   | 5.6±0.02          | 318±12            |       |                   |
| 323   | 4.6±0.002        | 231±10           | 323   | 5.3±0.02          | 248±12            |       |                   |

S5 Structures used in DFT modeling of SF$_6$ NMR parameters

The cage/window cavity models for DFT modeling of $^{19}$F NMR parameters of SF$_6$ are here attached as CC3-R_Xe Cage.xyz and CC3-R_Xe Window.xyz files. These are copied from the crystal structure optimized in the previous study and attached here as CC3-R_Xe_PBE-TS_FULLOPT.cif file. The 3D periodic crystal model all cage and window cavities were occupied by a Xe atom and the structure was fully optimized, i.e. both ion positions and lattice parameters (symmetry preserved) were changed, using CASTEP code. The optimization was carried out using PBE0 DFT functional with Tkatchenko-Scheffler (TS)$_{10}$ dispersion correction. We used the “fine” level (Energy: 1E-5 eV/atom, Max. gradient: 0.03 eV/Å, Max. stress: 0.05 GPa, Max. displacement: 0.001 Å) of geometry optimization with gamma-centered 2x2x2 Monkhorst-Pack grid (ca. 0.035 1/Å spacing in each reciprocal direction) of the Brillouin zone and 280 eV cut-off energy.

The chemical shielding for SF$_6$ were calculated for DFT energy minimized structure in the cavities (see section 3.3.2 of main article), with results reported in table S5. In the relaxation an average value of chemical shift difference ($\Delta \delta = 10.7$ ppm) and shielding anisotropy in cage ($\Delta \sigma_c = 390$ ppm) are used.
Table S5: SF₆ chemical shielding ($\sigma_X$), shielding anisotropy ($\Delta\sigma_X$) and asymmetry ($\eta_X$) computed in the crystal frame of CC3-R for Cage and Window cavity ($X = C, W$) respectively (see section 3.3.2 of main article).

| # | $\sigma_C$ (ppm) | $\Delta\sigma_C$ (ppm) | $\eta_C$ | $\sigma_W$ (ppm) | $\Delta\sigma_W$ (ppm) | $\eta_W$ |
|---|------------------|-----------------------|--------|------------------|-----------------------|--------|
| 1 | 73.6             | 406.8                 | 0.067  | 60.1             | 405.2                 | 0.011  |
| 2 | 85.9             | 395.4                 | 0.038  | 78.6             | 391.8                 | 0.012  |
| 3 | 93.2             | 379.0                 | 0.079  | 66.0             | 397.4                 | 0.024  |
| 4 | 80.3             | 395.3                 | 0.013  | 84.1             | 409.4                 | 0.004  |
| 5 | 90.8             | 383.2                 | 0.015  | 68.9             | 390.2                 | 0.015  |
| 6 | 75.2             | 406.8                 | 0.015  | 77.2             | 395.6                 | 0.014  |

The nuclear spin-rotation (SR) and shielding tensor was computed with Dalton code for SF₆ molecule with energy minimized structure in vacuum. Hence, mimicking a gas phase SF₆. The level of calculation was the same, nonrelativistic B3LYP/co-r(F)/def2-TZVP(S) as above shielding calculation. This gave SR constant (mean of the tensor trace) of -5.96 kHz used as fixed parameter in SR relaxation of SF₆ in the cage cavity. The shielding data is listed in Table S6. It is noted that average chemical shielding in cage is 83 ppm and the corresponding vacuum value is 80 ppm and thus a decrease in chemical shielding. Hence, cage to vacuum corresponds to a 3 ppm increase in the chemical shift scale. Thus, in accordance with the observed spectral broadening for ML-sample discussed in section S1.1 and the main paper.

Table S6: Chemical shielding ($\sigma$), shielding anisotropy ($\Delta\sigma$) and asymmetry ($\eta$) computed for vacuum structure.

| #  | $\sigma$ (ppm) | $\Delta\sigma$ (ppm) | $\eta$ |
|----|----------------|----------------------|-------|
| 1-6| 79.6           | 406.6                | 0.0   |

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