

A close view to the organic linker in a MOF: structural insights from a combined ^1H NMR relaxometry and computational investigation

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Fig. S2. Representative configuration of *NH₂-MIL-125* extracted from the molecular dynamics simulations at the 25 °C used to predict the EFG PAS orientation (yellow lines) on the different nitrogen sites. In this structure, the -CNH₂ moieties are planar. The tensor is perpendicular to the CHH plane and the N lone pair in the planar moiety is essentially a slightly polarized p_z atomic orbital. Thus, it should have a contribution to V_{zz} larger than the lone pair in a pyramidal nitrogen. The periodic replicas are represented with grey lines.

Fig. S3. ¹³C-¹H LG-CP spectrum of *NH₂-MIL-125*. The ¹H-¹³C dipolar splitting of carbon atoms 3, 5, 6, which are bound to a hydrogen, is about 10 kHz, which compares with 13 kHz, the value expected on the basis of the formula $-\frac{\mu_0}{4\pi} \frac{\gamma_{1H}\gamma_{13C}\hbar^2}{r_{HC}^3} \cos\theta_m$,³ where γ_{1H} and γ_{13C} represent the gyromagnetic ratios of ¹H and ¹³C nuclei, respectively, μ_0 is the vacuum permeability, \hbar is the Planck constant, r_{HC} is the distance C-H, with $r_{HC}=1.1 \text{ \AA}$ and $\theta_m=54.7^\circ$. On the contrary, the ¹H-¹³C dipolar splitting of carbon atoms 1, 2, 4, 7, 8, which are not bound to a hydrogen, is much smaller.

Fig. S4. Evolution of the hydrogen bond distance during the first 300 ps of the dynamics at T=110 °C.

Fig. S5. Principal components of the ¹⁴N EFG tensor (blue lines) in two different local structures of the BDC-NH₂ unit of *NH₂-MIL-125*. **a)** sp² nitrogen hybridization, NH₂ on the molecular plane; **b)** sp³ nitrogen hybridization, NH₂ perpendicular to the molecular plane (extracted from the MD trajectory at 110 °C). In both cases the V_{zz} component of the EFG tensor is along the lone pair direction.

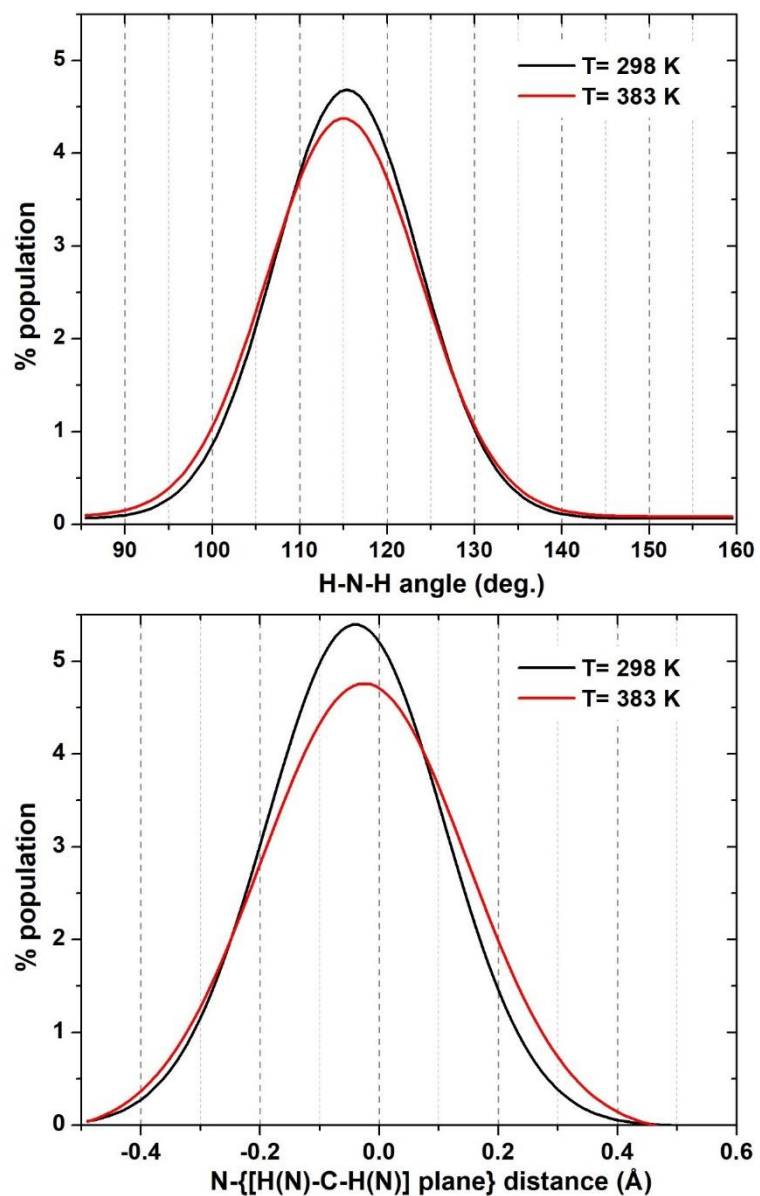


Fig. S1. Distributions of H-N-H angle (**top**) and N distance to the plane of the its ligands (**bottom**) obtained from sampled configurations extracted from the molecular dynamics simulations at the indicated temperatures.

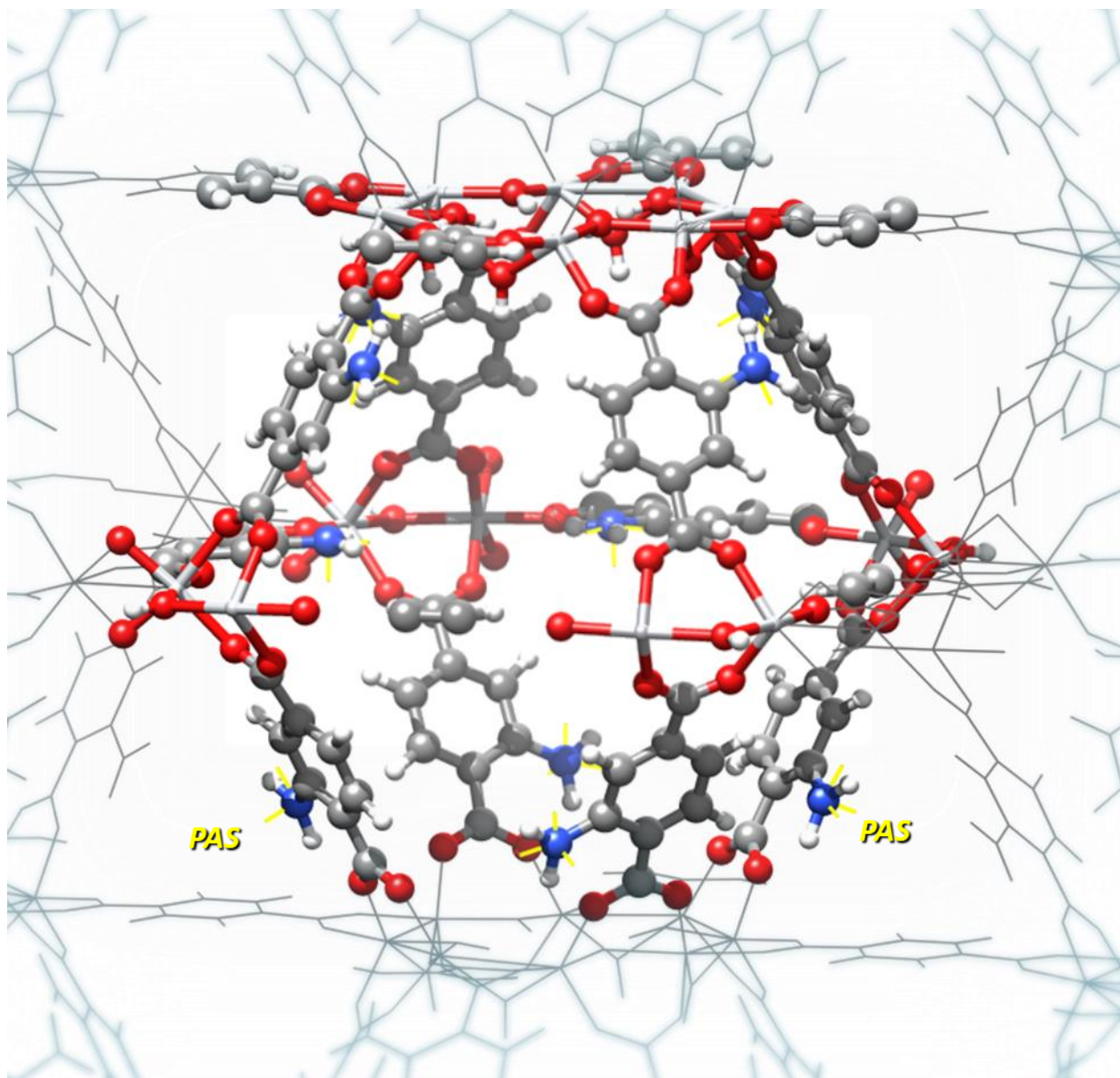


Fig. S2. Representative configuration of NH_2 -MIL-125 extracted from the molecular dynamics simulations at the 25 °C used to predict the EFG PAS orientation (yellow lines) on the different nitrogen sites. In this structure, the $-CNH_2$ moieties are planar. The tensor is perpendicular to the CHH plane and the N lone pair in the planar moiety is essentially a slightly polarized p_z atomic orbital. Thus, it should have a contribution to V_{zz} larger than the lone pair in a pyramidal nitrogen. The periodic replicas are represented with grey lines.

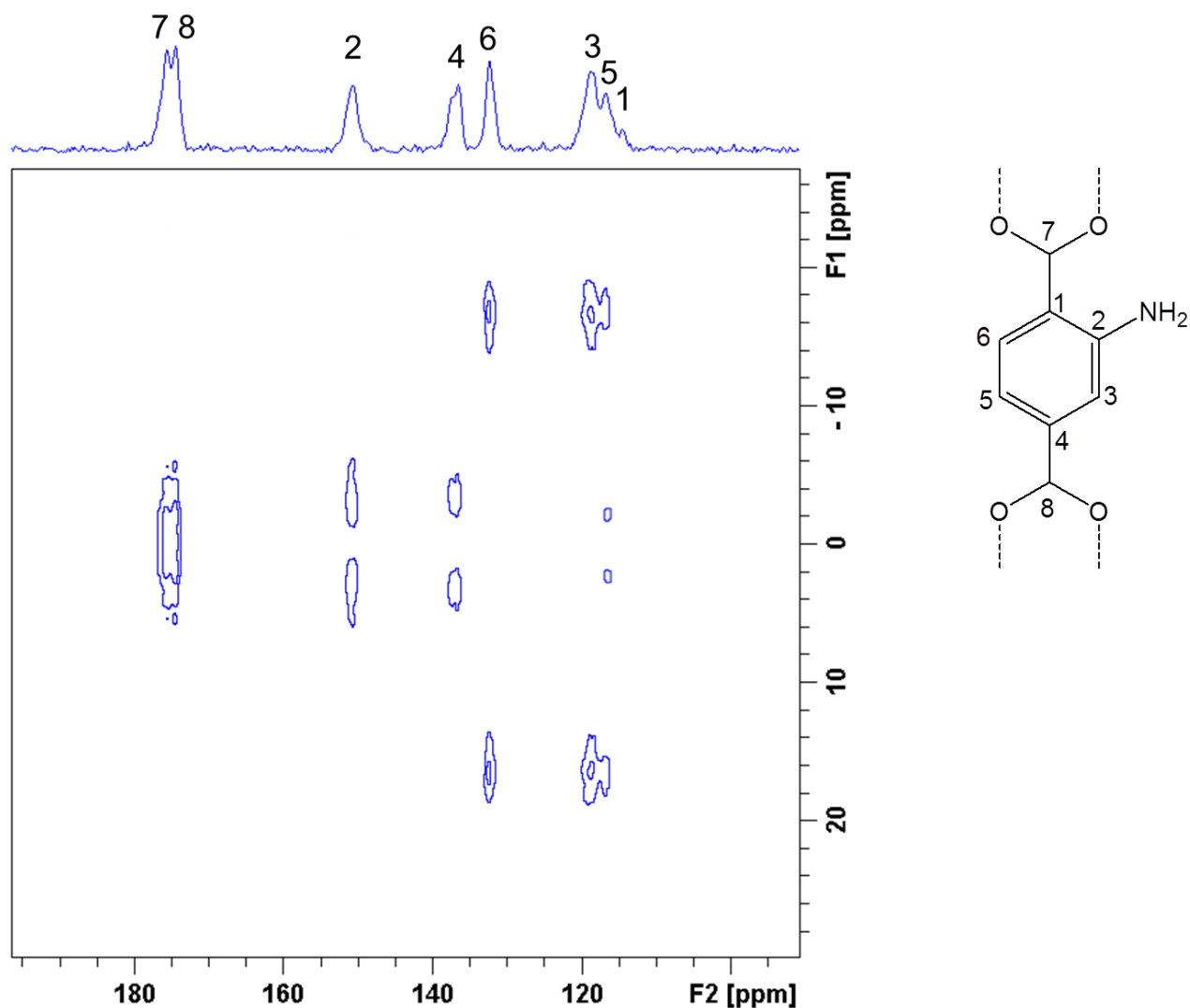


Fig. S3. ^{13}C - ^1H LG-CP spectrum of $\text{NH}_2\text{-MIL-125}$. The ^1H - ^{13}C dipolar splitting and the isotropic ^{13}C chemical shift appear on F1 and F2 dimensions, respectively. The assignment of the ^{13}C signals is based on that reported for IRMOF-3 in ref. 1.

The ^1H - ^{13}C dipolar splitting of carbon atoms 3, 5, 6, which are bound to a hydrogen, is about 10 kHz, which compares with 13 kHz, the value expected on the basis of the formula

$$-\frac{\mu_0}{4\pi} \frac{\gamma_{^1\text{H}} \gamma_{^{13}\text{C}} \hbar^2}{r_{\text{HC}}^3} \cos\theta_m,$$

where $\gamma_{^1\text{H}}$ and $\gamma_{^{13}\text{C}}$ represent the gyromagnetic ratios of ^1H and ^{13}C nuclei, respectively, μ_0 is the vacuum permeability, \hbar is the Planck constant, r_{HC} is the distance C-H, with $r_{\text{HC}} = 1.1 \text{ \AA}$ and $\theta_m = 54.7^\circ$.

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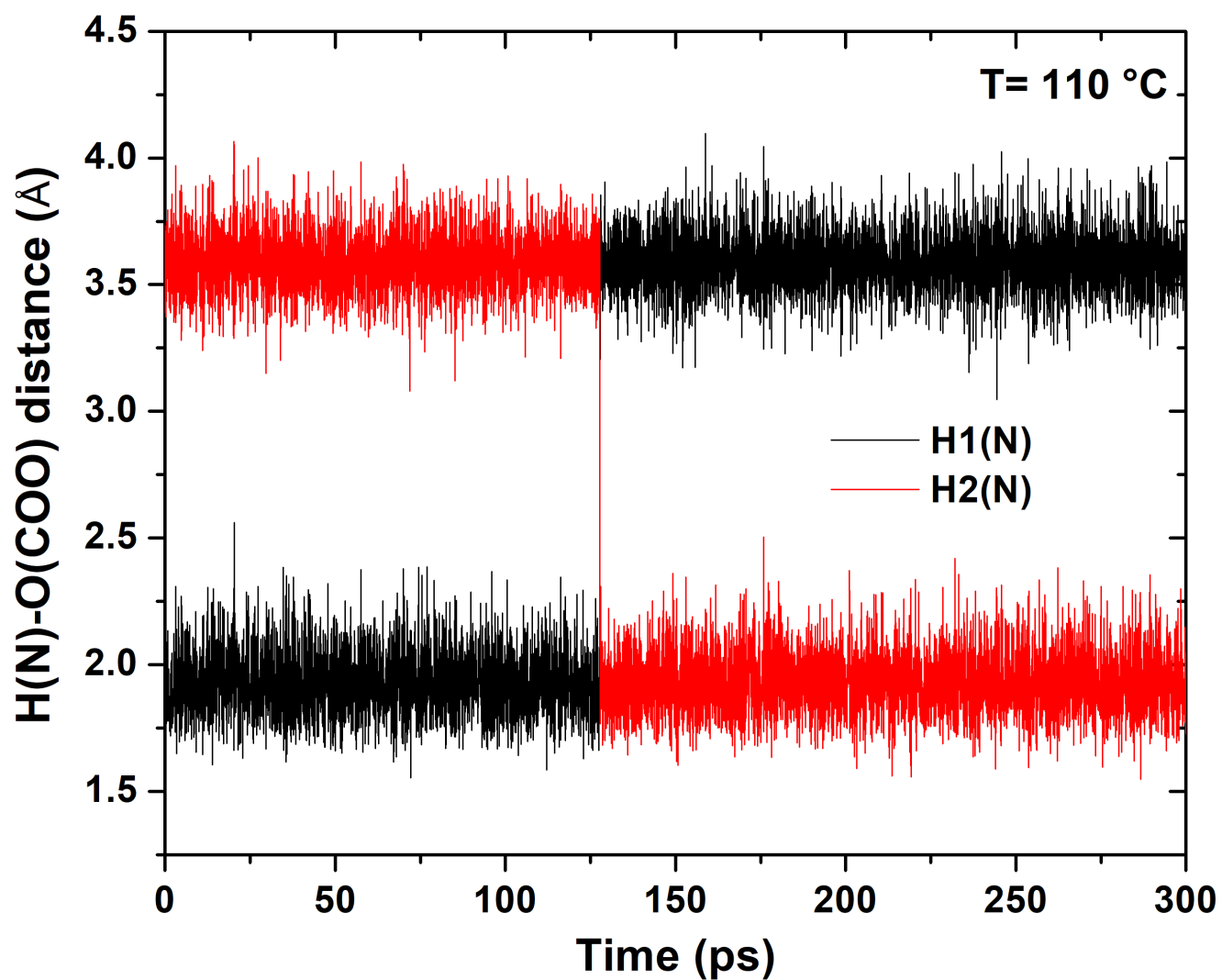


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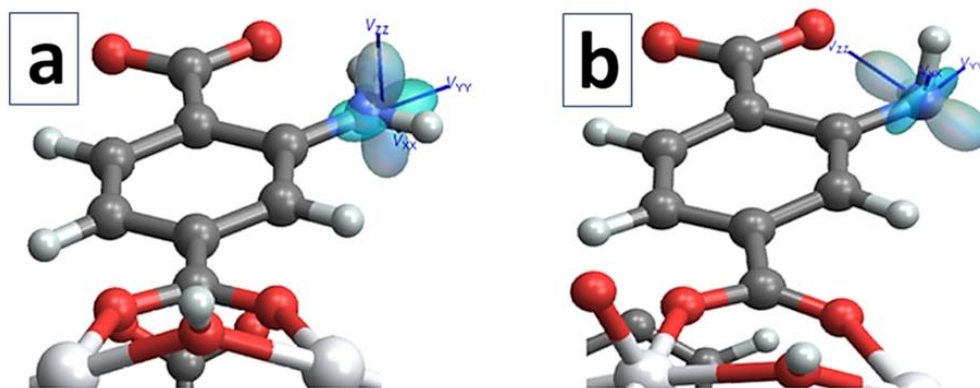


Fig. S5. Principal components of the ^{14}N EFG tensor (blue lines) in two different local structures of the BDC- NH_2 unit of $\text{NH}_2\text{-MIL-125}$. **a)** sp^2 nitrogen hybridization, NH_2 on the molecular plane; **b)** sp^3 nitrogen hybridization, NH_2 perpendicular to the molecular plane (extracted from the MD trajectory at $110\text{ }^\circ\text{C}$). In both cases the V_{zz} component of the EFG tensor is along the lone pair direction. The representation of EFG tensors as surfaces obtained by means of TensorView is shown.³

¹ Morris, W.; Taylor, R. E.; Dybowski, C.; Yaghi, O. M.; Garcia-Garibay, M. A. Framework mobility in the metal–organic framework crystal IRMOF-3: Evidence for aromatic ring and amine rotation. *J. Mol. Struct.* **2011**, *1004*, 94-101.

² van Rossum, B.-J.; de Groot, C. P.; Ladizhansky, V.; Vega, S.; de Groot, H. J. M. A Method for Measuring Heteronuclear (¹H-¹³C) Distances in High Speed MAS NMR *J. Am. Chem. Soc.* **2000**, *122*, 3465-3472.

³ R. P. Young, C. R. Lewis, C. Yang, L. Wang, J. K. Harper, L. J. Mueller “TensorView: A software tool for displaying NMR tensors” *Magn. Reson. Chem.* **2019**, *57*, 211–223.