

Unusual Room Temperature CO₂ Uptake in a Fluoro-Functionalized MOF: Insights from Raman Spectroscopy and Theoretical Studies

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Experimental Section:

Materials and methods: All the reagents and solvents employed were commercially available and used as supplied without further purification. ZnSiF₆·xH₂O and pyrazine were obtained from Sigma Aldrich Chemical Co. The elemental analysis was carried out using a Thermo Fischer Flash 2000 Elemental Analyzer. Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 Discover instrument using Cu-K α radiation. Raman spectra were recorded using custom built Raman spectrometer with a HeNe red laser as the excitation source (632.8 nm).^{*} For temperature dependent Raman, a Linkam THMS 600 heating-cooling stage was used. The spectra obtained were smoothened using 5 point FFT and baseline correction was done to remove the background.

^{*} G. V. P.Kumar and C.Narayana, *Current Science*, 2007, **93**, 778.

Gas adsorption measurements: CO₂ adsorption-desorption isotherm measurements at 195, 273 and 298 K with the dehydrated sample of compound **1** prepared at 393 K under high vacuum were carried out using QUANTACHROME QUADRASORB-SI analyzer. The carbon dioxide gas used for the measurements is of scientific/research grade with 99.999% purity. For the

measurements, approximately 100 mg of sample was taken in a sample holder and degassed at 393 K under 10^{-1} pa vacuum for about 12 hours. Dead volume of the sample cell was measured using helium gas of 99.999% purity. During all the measurements, extra care was taken so that samples do not get exposed to moisture.

CO₂ adsorption measurements at 195 and 298 K have been carried out several times to validate experimental findings. As-synthesized compound was evacuated at 393 K and at 195 K measurement was carried out. After measurement same sample was again activated and used for 298 K measurement. For both measurements extra care has been taken for the activation of the compound.

Computational details:

Periodic density functional theory (DFT) calculations were performed using the CP2K package.¹ Geometry optimizations as well as molecular dynamics simulations were carried out using the QUICKSTEP module of CP2K. Simulations were carried out in a super cell of size $2 \times 2 \times 2$ of the experimental unit cell. CP2K uses a mixed basis set in which the Kohn-Sham orbitals are expanded in an atom centered Gaussian basis set while the electronic charge density is described using an auxiliary plane wave basis set. Valence electrons were treated with the BLYP functional in the double-zeta single polarized basis set.²⁻⁴ In addition, empirical van der Waals corrections prescribed by Grimme were employed.⁵ Electron density was described with an energy cutoff of 280 Ry and the effect of core electrons and nuclei were represented using norm-conserving pseudopotentials of Goedecker-Teter-Hutter.⁶ During the geometry optimization, component of forces on every atom were less than 10^{-4} a. u. To calculate the binding energy of CO₂ molecule with the MOF, first, geometry optimization of MOF and of one CO₂ adsorbed in the MOF (in the ratio of one CO₂ per formula unit of MOF) was carried out with CP2K package until the forces were converged. The energy of a geometry optimized, free CO₂ was also calculated. Binding energy was calculated using the following formula,

$$\Delta E = E(\text{MOF}+\text{CO}_2) - E(\text{MOF}) - E(\text{CO}_2)$$

where $E(\text{MOF}+\text{CO}_2)$, $E(\text{MOF})$ and $E(\text{CO}_2)$ represent the total energy of MOF with CO₂, MOF and CO₂ molecule respectively.

Born-Oppenheimer molecular dynamics calculations were carried out using the hybrid Gaussian and plane wave basis as implemented in CP2K. Simulations were run at two temperatures, 195 and 300 K. Nose-Hoover thermostat was used to maintain the temperature of the system at these values.⁷ A time step of 0.5 fs was used to integrate the equations of motion. At each temperature, a 10 ps trajectory was generated of which the last 7 ps trajectory was used for analysis. Trajectory was visualized using VMD.⁸

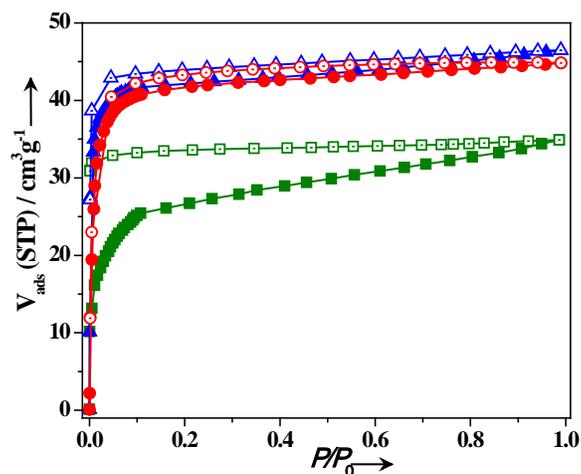


Fig. S1: CO₂ adsorption-desorption isotherms of compound **1'** measured at 195 (green), 273 (red) and 298 K (blue). Close symbols indicate adsorption and open symbols desorption. P_0 is the saturated vapour pressure of CO₂ at the measurement temperatures.

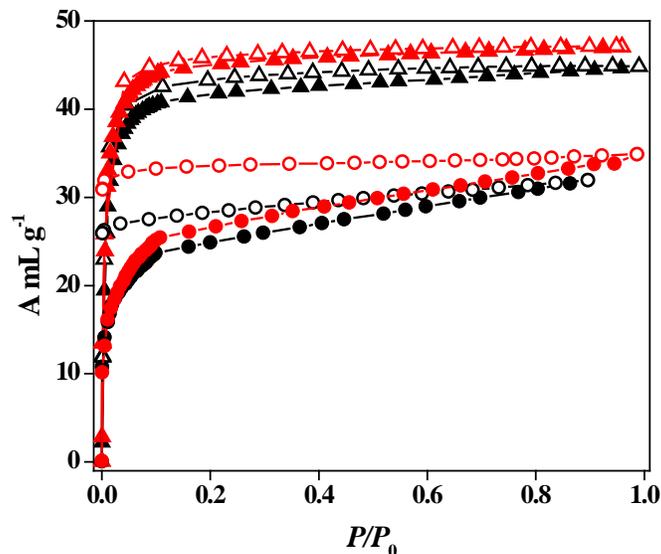


Fig. S2: CO₂ adsorption-desorption isotherms of compound **1'** measured at 195 (circle), and 298 K (triangle) using the same sample. Closed symbols indicate adsorption and open symbols desorption. P_0 is the saturated vapour pressure of CO₂ at the measurement temperatures. The first cycle is in red and the second in black colour. The same sample (0.100 g) was used for all the measurements conducted with similar conditions. Prior to every adsorption-desorption experiment, the sample was activated by heating at 393 K for 8 h under 10⁻¹ Pa vacuum.

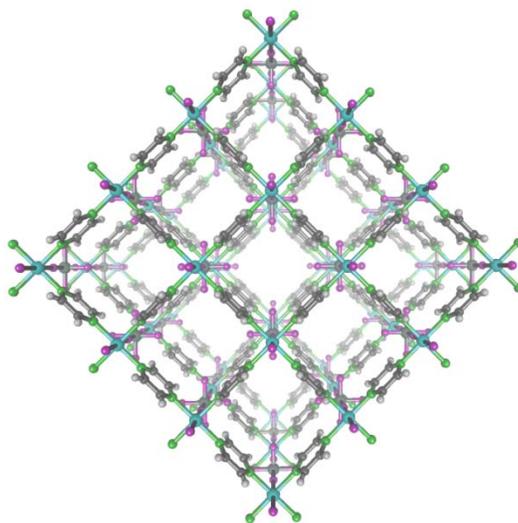


Fig. S3: 3D view of compound **1** show 1D channels along the *c*-direction.

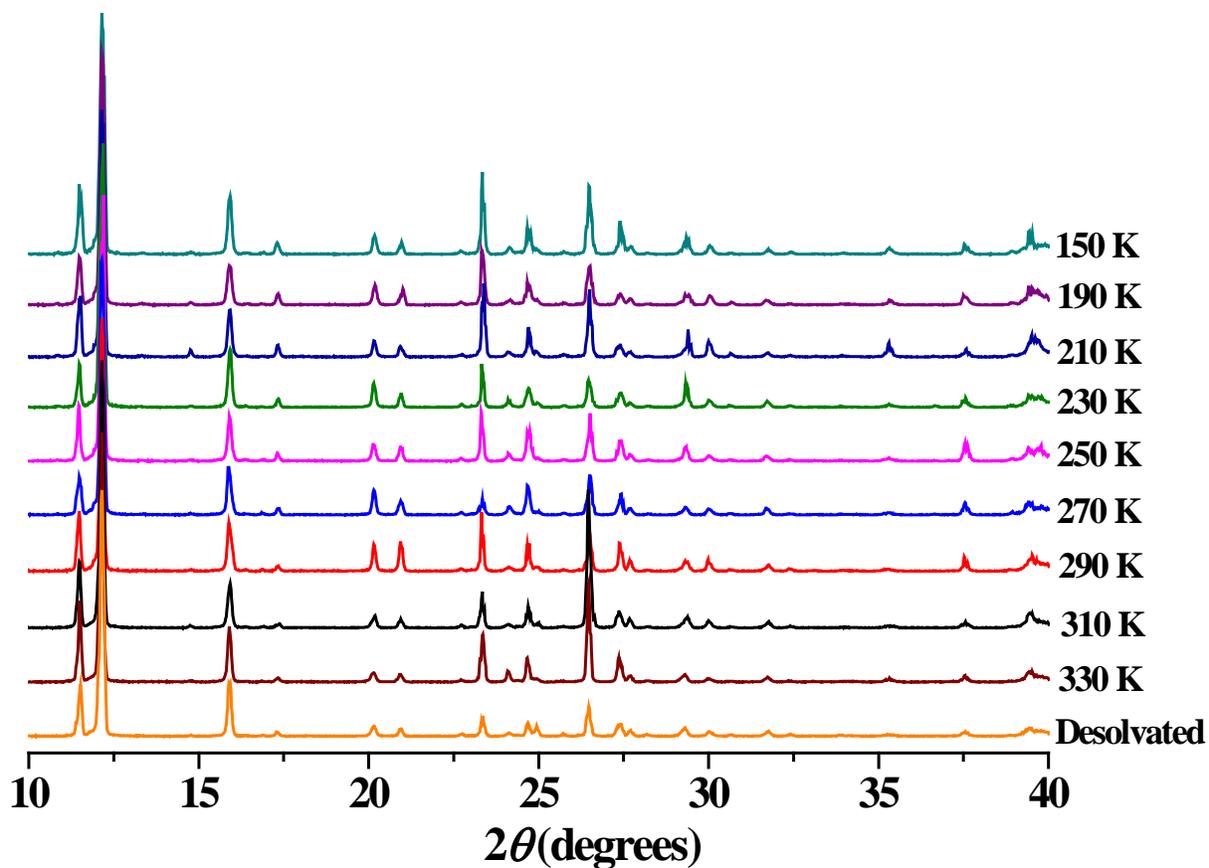


Fig. S4: Temperature dependent PXRD of compound 1.

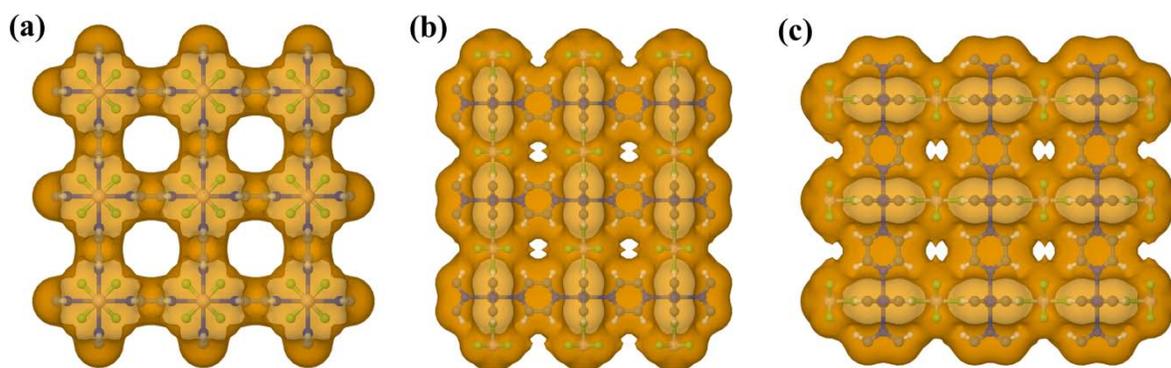


Fig. S5: Solvent accessible surface mapped on to MOF in three crystallographic directions. One dimensional channel is along the *c*-direction, as seen in Panel (a).

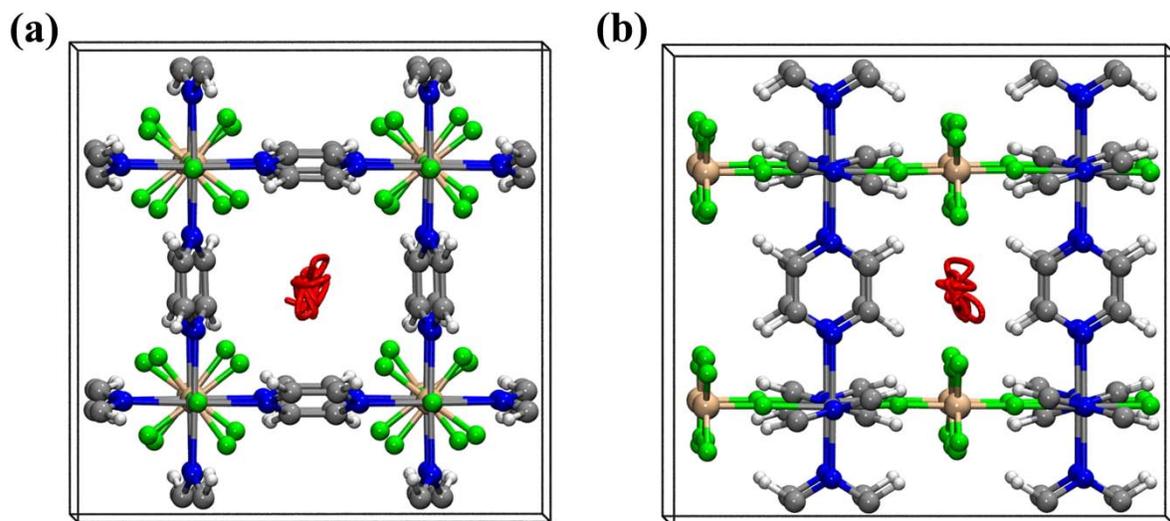


Fig. S6: Trajectory of center of mass of CO₂ within MOF, shown in two crystallographic directions, obtained from ab initio molecular dynamics simulation at 195 K. Panel (a) shows view along crystallographic *c*-axis. Adjacent pyrazine rings along the *c*-axis are not coplanar, (b) shows view along *b*-axis. Coordinates of the MOF shown here are those obtained from geometry optimization at zero Kelvin.

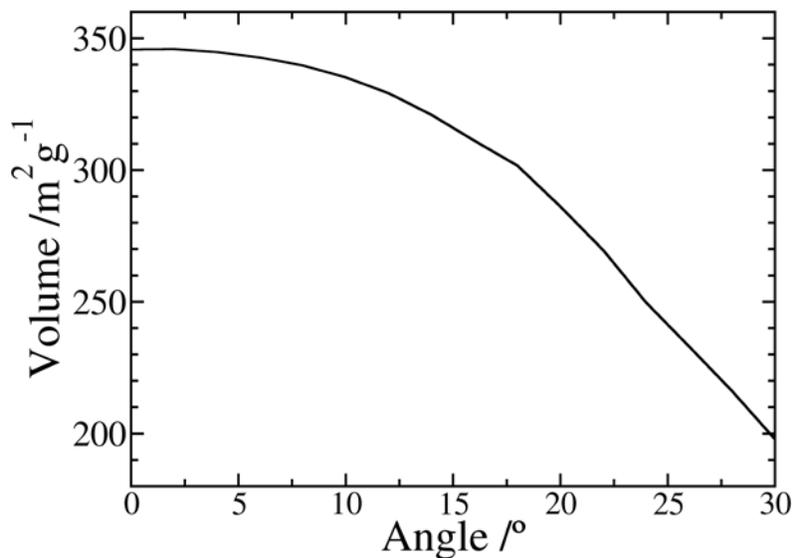


Fig. S7: Calculated accessible surface area for CO₂ molecule as a function of the angle between planes of adjacent pyrazine rings and that formed by Si-Zn-Si atoms.¹⁰

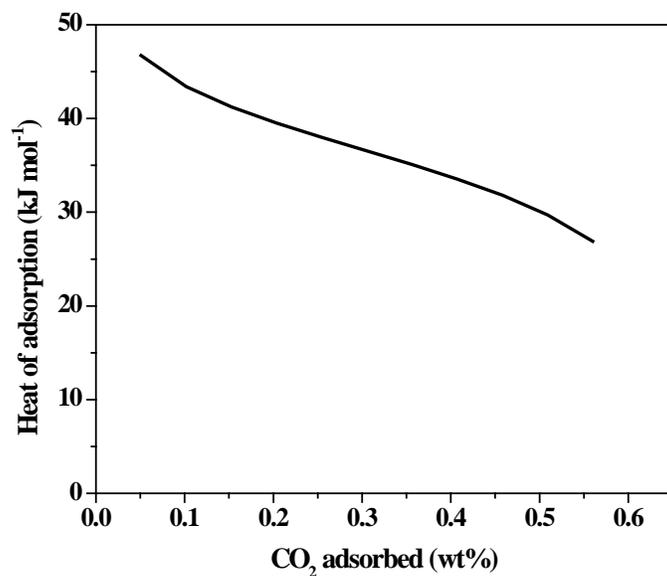


Fig. S8: Enthalpy of CO₂ adsorption for **1'** calculated using Clausius-Clapeyron equation based on the adsorption profile at 273 K and 298 K.

Table S1: Raman Band assignment of MOF

Raman frequency (cm ⁻¹)	Assignment
145	δ N-Zn-N ¹¹
197	δ F-Zn-N ¹¹
649	Pyz ring ν_4 ¹²
663	Si-F ¹³
707	Str Si-F ₆ + ν_{10} B _{2g} (Pz) ¹⁴
757	Pz H bend ν_{10a} ¹² , Zn-F,
1025	ν Pz ring ¹²
1036	ν Pz ring
1236	Pz H bend ν_{9a} ¹²
1525, 1529	ν Pz ring ¹²
1620	Pyz (609+1015) ¹²
3071	C-H str
3081	C-H str
3096	C-H str

References :

1. J. VandeVondele, M. Krack, F. Mohamed, M. Parrinello, T. Chassaing, X. Hutter, *J. Compt. Phys. Commun.*, 2005, **167**, 103.
2. J. VandeVondele, J. Hutter, *J. Chem. Phys.*, 2007, **127**, 114105.
3. A. D. Becke, *Phys. Rev. A.*, 1988, **38**, 3098.
4. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B.*, 1988, **37**, 785.
5. S. Grimme, *J. Comp. Chem.*, 2006, **27**, 1787.
6. C. Hartwigsen, S. Goedecker, J. Hutter, *Phys. Rev. B.*, **1998**, 58, 3641.
7. G. J. Martyna, M. L. Klein, M. Tuckerman, *J. Chem. Phys.*, 1992, **97**, 2635.
8. W. Humphrey, A. Dalke, K. Schulten, *J. Molec. Graphics.*, 1996, **14**, 33.
9. C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. Van de Streek, P.A. Wood, *J. Appl. Crystallogr.*, 2008, **41**, 466.
10. Accessible surface area code, Copyright (C) 2007, T. Duren, L. Sarkisov, R. Q. Snurr, http://www.see.ed.ac.uk/~tduren/research/surface_area/ortho/
11. Y. Saito, M. Cordes, K. Nakamoto, *Spectrochim. Acta* 1972, **28A**, 1459.
12. R. C. Lord, A. L. Marston, F. A. Millers, *Spectrochim. Acta.*, 1957, **9**, 113.
13. G. M. Begun, A. C. Rutexberg, *Inorg. Chem.* 1967, **6**, 2212.
14. G. Sbrana, V. Schettino, R. Righini, *J. Chem., Phys.* 1973, **59**, 2441.