Supporting Information for

Prediction of Flexibility of Metal–Organic Frameworks CAU-13 and NOTT-300 by First Principles Molecular Simulations

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Details of quantum chemical calculations

We performed first principles calculations in the density functional theory approach with periodic unit cell, full use of the crystals' symmetry elements and localized basis sets as implemented in the CRYSTAL09 code.[1] We used the B3LYP hybrid exchange-correlation functional,[2] with empirical correction for the dispersive interactions following the "D2" scheme of Grimme.[3] All electron basis sets were used for H, C, O, Al.[4] The accuracy of this methodology is now well established for the calculation of MOF structures, both rigid[5] and flexible.[6] It is fully detailed in our earlier work.[7]

In a first step, the structures of CAU-13 and NOTT-300 were fully relaxed (energy minimized) in the absence of mechanical pressure by optimizing both atomic positions and unit cell parameters, starting from the experimental crystallographic structure. In both cases, we found a good agreement with the original experimental structures, and the small differences in unit cell parameters observed could be ascribed to the removal of the solvent within the pores of the experimental structures.

In a second step, we characterized the mechanical properties of these relaxed structures in the elastic regime, by calculating their full tensor of second-order elastic constants (21 terms for triclinic CAU-13, 6 for quadratic NOTT-300). We then followed the methodology outlined in refs. 7 and 8 to perform a tensorial analysis of this stiffness matrix, obtaining directional information about the elastic moduli of the two materials.

In a third step, we imposed mechanical stress on the materials: isotropic pressure on CAU-13, and tetragonal [1 –1 0] shear on NOTT-300. In the latter case, the symmetry of the system was lowered from the original tetragonal group ($I4_122$) into a orthorhombic subgroup ($I2_12_12_1$), consistent with the nature of the deformation applied. Starting from the relaxed structures, we performed series of consecutive enthalpy minimization for each value of stress, obtaining the evolution of unit cell parameters as a function of stress. The structures obtained were all checked for possible higher symmetries, using the PLATON tool.[9] Indeed, for CAU-13 we found that at pressures lower than –1 GPa, we find a transition to higher symmetry (from *P –1* to *I 2/m*).

Finally, the structures identified as "large pore" and "narrow pore" form for each material were checked for accessible porosity, using PLATON's CALC SOLV tool, with the standard probe radius of 1.2 Å.

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Details of first principles molecular dynamics simulations

The first principles molecular dynamics (FPMD) simulations of NOTT-300 were performed with the CP2K package[10] in the framework of density functional theory (DFT) as implemented in the QUICKSTEP module:[11] the Kohn-Sham orbitals are developed on atom-centred Gaussian basis sets, while the electronic density is represented in an plane-wave basis. Since we performed constant-pressure simulations, which require a high precision in the evaluation of atomic forces to converge the resultant stress on the unit cell, we used TZV2P basis sets for all atoms (Al, O, C, H), and a relatively high cut-off energy of 600 Ry. The interactions between ionic cores and valence electrons were represented by GTH pseudopotentials,[12] and the exchange and correlation energies were approximated by the PBE functional.[13] Similarly to our static quantum chemical detailed above, we used an empirical correction for the dispersive interactions following the "D2" scheme of Grimme.[3]

A single unit cell of NOTT-300 was simulated, due to its relatively large size. The deformation of the material was studied through FPMD simulations in the (N, σ, T) ensemble, with all lattice parameters and angles were free to move (in particular, this does not restrict the shape of the unit cell to quadratic or orthorhombic structures). The time step for the integration of the equations of motion was 0.5 fs, and the hydrogen atoms were deuterated. The temperature was controlled by a CSVR thermostat[14] with a time constant of 0.1 ps. A barostat with a time constant of 0.2 ps was used in order to impose the various values of isotropic pressure chosen (0 MPa, 500 MPa, 700 MPa, and 1 GPa). All four systems were simulated for a total duration of 6 ps.

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	CAU-13		NOTT-300	
	Narrow pore	**Large pore**	**Large pore**	**Narrow pore**
Constraints	Relaxed	Isotropic tension	Relaxed	Tetragonal shear
Stress	0 GPa	−1 GPa	0 GPa	1 GPa
Space group	*P −1*	*I 2/m*	*I* 4_1 *2 2*	*I* 2_1 2_1 2_1
a	6.646 Å	13.442 Å	14.839 Å	9.423 Å
b	8.550 Å	6.715 Å	14.839 Å	11.680 Å
c	9.226 Å	15.411 Å	11.882 Å	17.818 Å
α	102.06°	90°	90°	90°
β	108.79°	95.98°	90°	90°
γ	92.11°	90°	90°	90°
Cell volume	482.3 $Å^3$	1383.5 $Å^3$ = 2 × 691.7 $Å^3$	2616.5 $Å^3$	1961.1 $Å^3$
Pore volume	70.5 $Å^3$ (15%)	485.2 $Å^3$ (35%)	1183.4 $Å^3$ (45%)	457.7 $Å^3$ (23%)

Table S1. Unit cell parameters of the structures of CAU-13 and NOTT-300, in both "narrow pore" and "large pore" form, obtained by quantum chemical calculations.

103.29	13.89	23.55	4.22	1.46	0.85
	24.93	38.57	17.49	0.50	7.31
		114.94	34.82	−1.05	−2.44
			32.85	3.20	0.50
				13.20	1.61
					10.53

Table S2. Full stiffness matrix of CAU-13, whose components are the second-order elastic constants C_{ij} in units of GPa. The matrix is symmetric, but only the upper triangular half is shown for reasons of clarity.

49.34	47.71	25.64	0	0	0
	49.34	25.64	0	0	0
		133.60	0	0	0
			26.16	0	0
				26.16	0
					20.394

Table S3. Full stiffness matrix of NOTT-300, whose components are the second-order elastic constants C_{ij} in units of GPa. The matrix is symmetric, but only the upper triangular half is shown for reasons of clarity.

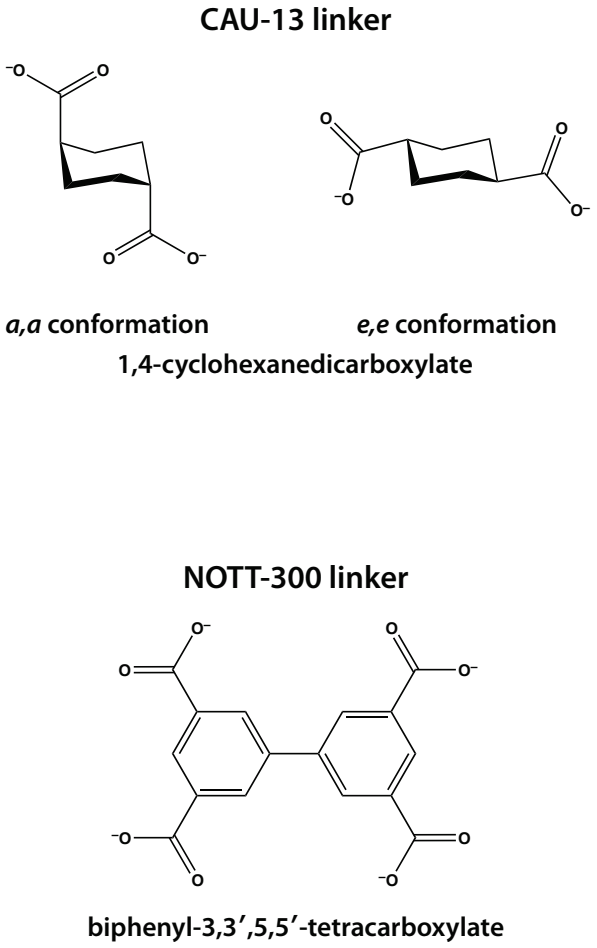

Figure S1. Structure of the organic linkers of CAU-13 and NOTT-300. Both the *a*,*a* and *e*,*e* conformations of CDC are shown.