

Supporting Information

Designing 3-D COFs with enhanced hydrogen storage capacity.

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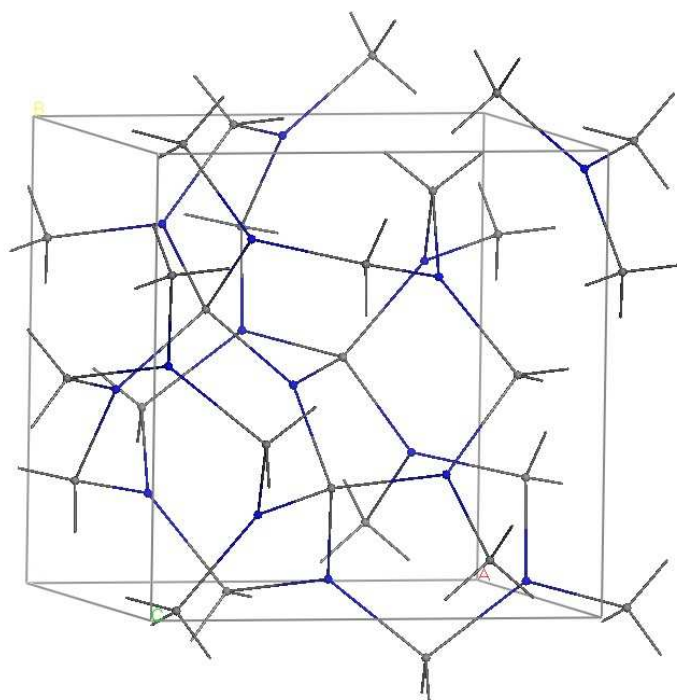
- 1. Design methodology of the proposed 3D-COF structures.**
- 2. Optimization procedure of the periodic COF structures.**
- 3. Excess gravimetric and volumetric adsorption isotherms.**

1. Design methodology of the proposed 3D-COF structures.

The crystal structure of COF-102 has been based on the ctn net¹ (Figure S1), which was constructed by appropriately linked molecular building units that had tetrahedral and trigonal shapes. In the case of COF-102, each trigonal unit (N atoms) was replaced by a B3O3 ring and each C-N bond was replaced by the corresponding organic molecule (a phenyl ring in the case of COF-102).

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Figure S1. The ctn periodic network that was used for the construction of the periodic COFs.



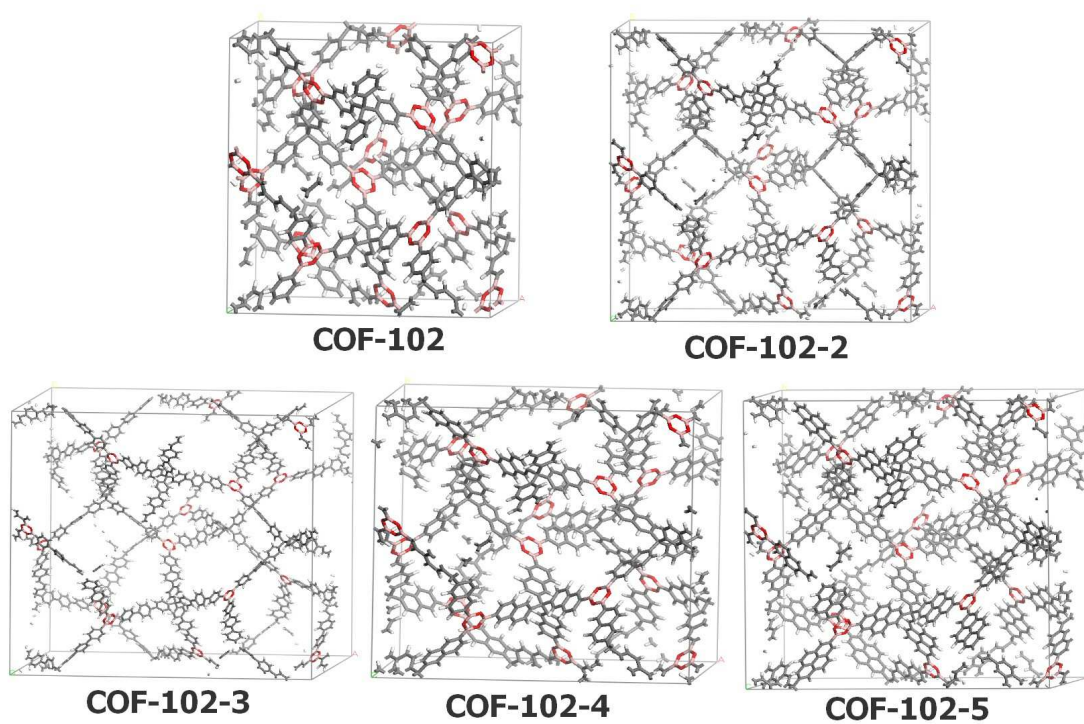
2. Optimization procedure of the periodic COF structures.

After the preparation of the periodic COF structures, we optimized the periodic structures by using molecular mechanics calculations as implemented in Tinker program package². All the initial periodic structures were minimized in energy with respect to all degrees of freedom in P1 space group with the program *minimize* and then were minimized in energy with respect of all degrees of freedom and the lattice parameters with program *xtalmin*. We used an explicitly parametrized MM3 forcefield on the basis of Density Functional Theory (DFT) calculations that was created by Schmid et al³. Additionally, we have inserted some more explicitly parameters that were taken from the work of Amirjalayer et al⁴ in order to treat the C-C bonds between adjacent phenyl rings in the cases of COF-102-2 and COF-120-3. The cutoffs for the dipole-dipole and van der Waals interactions was set at 10 Å and 12 Å and the threshold in the rms gradient of 0,001 Kcal·mol⁻¹·Å⁻¹ was used for the minimizations in energy. In table S1 we have summarized the lattice parameters for the optimized periodic structures and the optimized COF cells are demonstrated in Figure S2.

Table S1. Cell parameters fro the periodic COF structures. All the parameters were obtained from the minimization of the energy in a periodic cell in P1 space group. Cell lengths a, b, c are in Å and α , β , γ cell angles are in degrees.

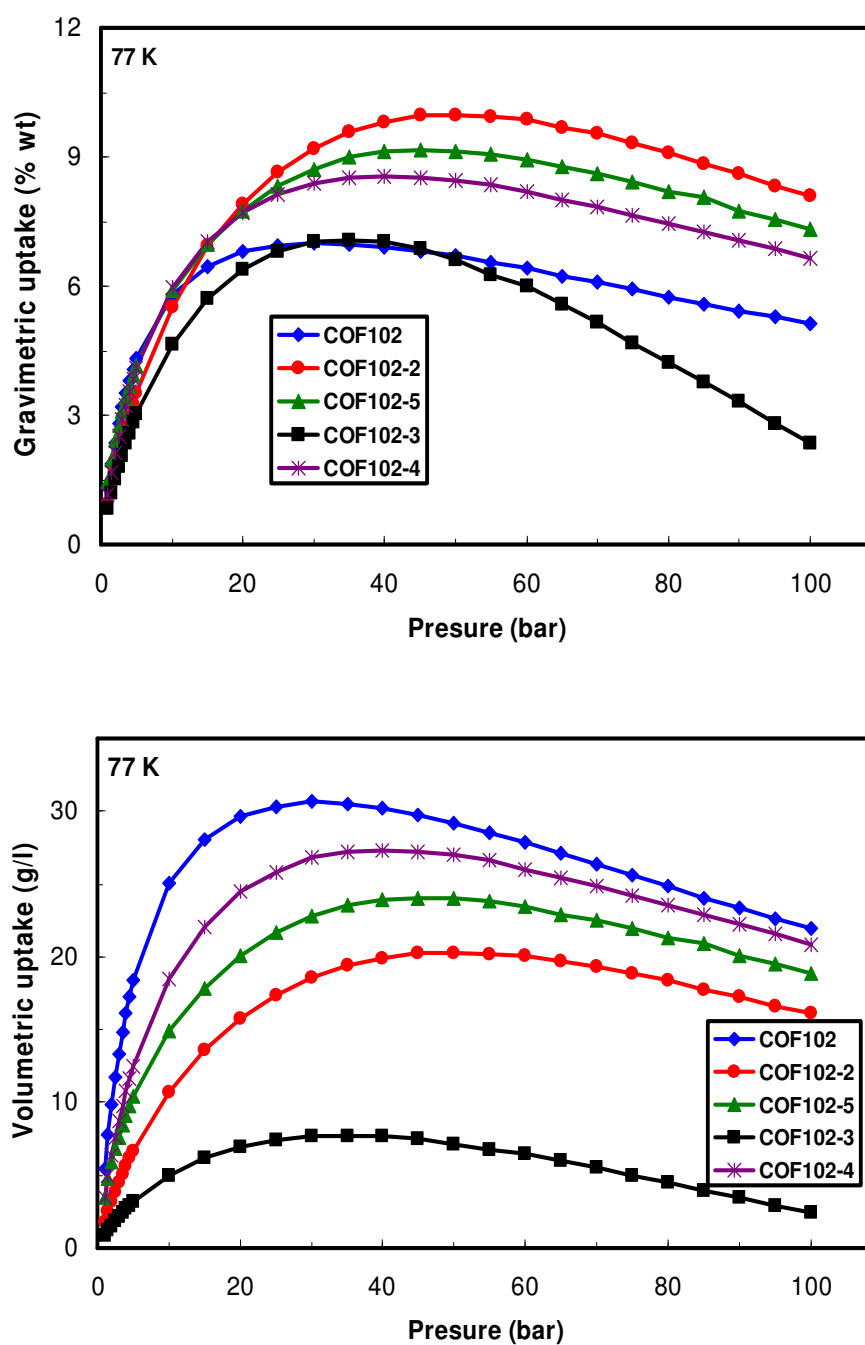
	a	b	c	α	β	γ
COF-102	27,026501	27,026501	27,026501	90,0	90,0	90,0
COF-102-2	42,941002	42,941002	42,941002	90,0	90,0	90,0
COF-102-3	58,787601	58,787601	58,787601	90,0	90,0	90,0
COF-102-4	34,963799	34,963799	34,963799	90,0	90,0	90,0
COF-102-5	42,512199	42,512199	42,512199	90,0	90,0	90,0

Figure S2. The optimized periodic COF cells.



3. Excess gravimetric and volumetric adsorption isotherms.

Figure S3. Calculated excess gravimetric and volumetric adsorption isotherms at 77K for COF-102, COF-102-2, COF-102-3, COF-102-4 and COF-102-5.



¹ <http://epinet.anu.edu.au/home>

² Ponder, J. W.; Richards, F. M. J. *Comput. Chem.*, 1987, 8, 1016. tinker version 4.2, June 2004; <http://dasher.wustl.edu/tinker/>.

³ Schmid, R.; Tafipolsky, M. *J. Am. Chem. Soc.* **130**, 2008, 12600.

⁴ Amirjalayer, S.; Schmid, R. *J. Phys. Chem. C* **112**, 2008, 14980.