Supplementary Material (ESI) for CrystEngCom
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Supporting Information

Selective binding in different adsorption sites of a 2D covalent organic framework

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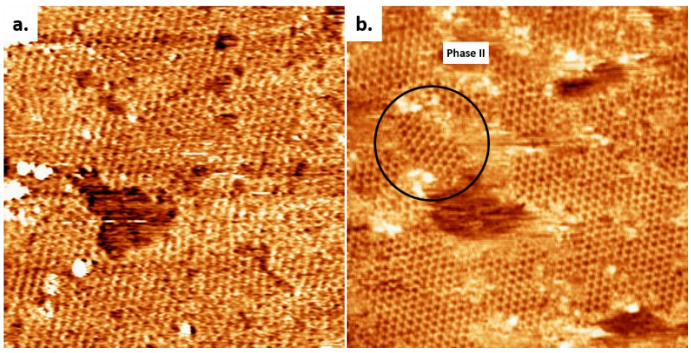

Figure S1. **(a)** STM image of COF-1 synthesized in 1,2,4-trichlorobenzene (TCB), collected at the air/solid interface. Image width: 60 nm. Scanning conditions: V= -1000 mV, I= 100 pA. **(b)** STM image of COF-1 synthesized in heptanoic acid, collected at the interface of heptanoic acid and HOPG. A small domain of Phase II is marked by black circle. Image width: 60 nm. Scanning conditions: V= -800 mV, I=100 pA.

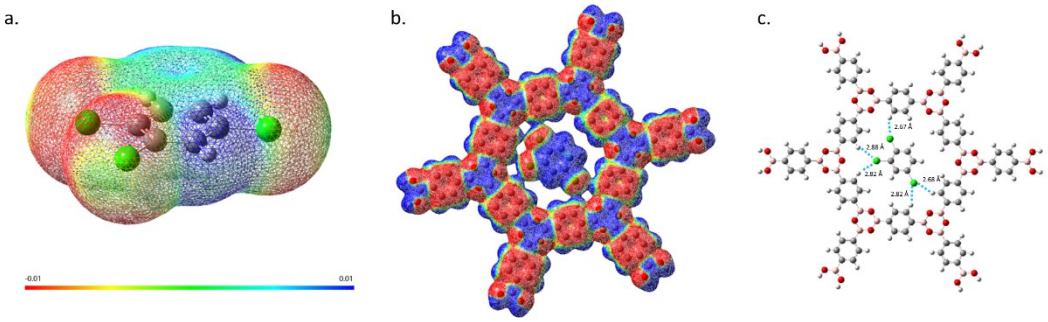

Figure S2. **(a)** Molecular electrostatic potential (ESP) map (M06-2X/LANL2DZ) for isolated TCB in the gas phase (3D view). **(b)** Molecular ESP map of optimized geometry (M06-2X/LANL2DZ) for TCB in COF-1 hexagonal pore. The ESP maps for a and b are expressed in atomic units (a.u., Rydberg/e) on 0.0004 e/Bohr^3 and 0.004 e/Bohr^3 isodensity surfaces, respectively. The color scale from blue (+ve) to red (−ve) spans the following ranges: ±0.01 a.u. for both a and b. **(c)** Optimized geometry of one TCB in hexagonal pore (M06-2X/LANL2DZ), with marking the distances of Cl…H (dashed blue line) interatomic contacts. (Only showing the distances less than the sum of the vdW radii for Cl…H contacts)

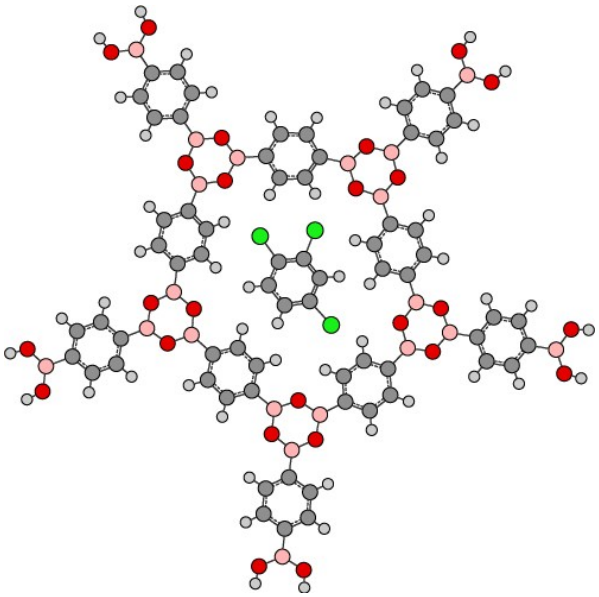

Figure S3. Indicative geometry for TCB in pentagonal pore. All H…H distances between hydrogens on the TCB molecule and hydrogens on the COF-1 pore are below 2 vdW radii for hydrogen ($2r_H$=2.4 Å),[1] suggesting that the TCB molecule cannot be accommodated in a planar adsorption geometry in the pentagonal pore.

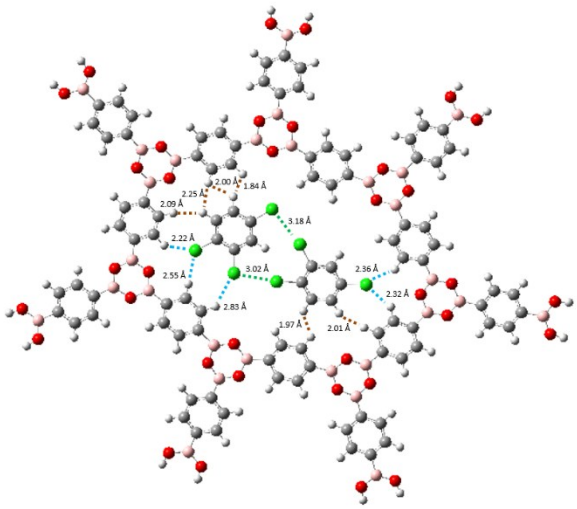

Figure S4. Optimized geometry for two TCB molecules in a heptagonal pore. This geometry allows for Cl…H (dashed blue line) interactions between the TCB and the COF-1 pore as well as Cl…Cl (dashed green line) interactions between the two TCB molecules. However, bond distances for Cl…H interactions are shorter than expected (i.e., shorter than the optimized distances found for a single TCB in a hexagonal pore, see table 1), and unfavourably short H…H (dashed brown line) interactions exist between hydrogen atoms on the TCB molecules and the COF-1 pore (i.e., distances shorter than $2r_H$=2.4 Å). These closer interactions suggest that perhaps the epitaxial heptagonal pore is expanded somewhat from the gas-phase dimensions reflected in this geometry. The inter-atom distances for Cl…Cl, Cl…H and H…H are marked accordingly. (Only showing those less than the sum of the vdW radii)

Table 1. Van der Waals radii[1] and calculated inter-atom distance*

	Van der Waals radii					Calculated inter-atom distance		
	r_H	r_{Cl}	$2r_H$	$r_H + r_{Cl}$	$2r_{Cl}$	d_{H-H}	d_{H-Cl}	d_{Cl-Cl}
TCB/hexagon	1.20 Å	1.75 Å	2.40 Å	2.95 Å	3.50 Å	N/A	2.67 Å	N/A
TCB/heptagon						1.84 Å	2.22 Å	3.02 Å

*The inter-atom distances in table 1 are reported by selecting smallest value in calculation for each case. For detailed data list, please check corresponding calculated graphics.

Reference

1. Bondi, A., *van der Waals Volumes and Radii.* The Journal of Physical Chemistry, 1964. **68** (3): p. 441-451.