# **Flexible Porous Molecular Materials**

# Responsive to CO<sub>2</sub>, CH<sub>4</sub> and Xe Stimuli

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#### 1. Synthesis and Preparation

#### **1.1 General Remarks**

All reagents and solvents were commercially available, except for tetrakis(4-bromophenyl)methane, 1,3,5,7tetrakis(4-bromophenyl)adamantane and tetrakis(4-bromophenyl)silane which were prepared as reported elsewhere[S1]. Methanetetrabenzoic acid (MTB) and adamantane-1,3,5,7-tetrayl)tetrabenzoic acid (ATB) have been prepared following the procedure reported for silanetetrabenzoic acid (STB) [S2].

#### 1.2 Synthesis of MTB

Under inert atmosphere, at -78°C, to a solution of tetrakis(4-bromophenyl)methane (890mg, 1,39 mmol) in dry THF (dry ml), Buli (3ml, 2.5M, 7,50 mmol) was slowly added. The solution was stirred at room temperature for 1 hour and then, at room temperature, gaseous CO<sub>2</sub> was bubbled and stirred for 4 hours, then the solution was stirred overnight. HCl (12ml, 6M) was dropped in the solution and stirred for 30 min. The solvent was concentrated and the solid was filtrated, washed with water (10ml) and vacuum dried. The crude was recrystallized in THF/Hexane affording a white solid (250mg, yield 36%). IR (cm<sup>-1</sup>): 3024w, 2951m, 2922m, 2849m, 2854m, 2673w, 2553w, 1648s, 1603m, 1569w, 1503m, 1432w, 1411s, 1375w, 1299m, 1279s, 1186m, 1019s, 803m, 771m, 763s, 701w, 616w. <sup>1</sup>H NMR (400 MHz, DMSO):  $\delta$ , 7.32 (d, J= 8.4 Hz, 8H, CH(Ph)), 7.88 (d, J= 8.4 Hz, 8H, CH(Ph)), 12.95 (sbr, 1H, OH(CO)). Anal.Calc. for C<sub>17</sub>H<sub>12</sub>OS (264.34): C, 77.24; H, 4.58. Found: C, 77.19; H, 4.62%.

#### 1.3 Synthesis of STB

Under inert atmosphere, at -78°C, to a solution of tetrakis(4-bromophenyl)silane (900 mg, 1,38 mmol) in dry THF (dry ml), BuLi (2,8ml, 2.5M, 6,90 mmol) was slowly added. The crude then was recrystallized in THF/hexane affording a white solid (425mg, yield 50%). IR (cm<sup>-1</sup>): 2878 br, 2628w, 2508w, 1682vs, 1558m, 1552m, 1479w, 1379m, 1389s, 1302m, 1242s, 1221s, 1182m, 1109w, 1088s, 1018m, 847m, 766m, 758s, 692vs, 643m, 534vs, 465m.<sup>1</sup>H NMR (400 MHz, DMSO):  $\delta$ , 7.62 (d, J= 10.8 Hz, 8H, CH(Ph)), 8.00 (d, J= 10.8 Hz, 8H, CH(Ph)), 13.40 (sbr, 1H, OH(CO)).Anal.Calc. for C<sub>17</sub>H<sub>12</sub>OS (264.34): C, 77.24; H, 4.58. Found: C, 77.19; H, 4.62%.

#### 1.4 Synthesis of ATB

The same procedure used for MTB was used. Under inert atmosphere, at -78°C, to a solution of 1,3,5,7-tetrakis(4-bromophenyl)adamantane (900 mg, 1,19 mmol) in dry THF (dry ml), Buli (2,5ml, 2.5M, 6,25 mmol) was slowly added. The crude then was recrystallized in THF/hexane affording a white solid (300mg, yield 41%). IR (cm<sup>-1</sup>): 3062br, 2923m, 2901m, 2850m, 2660w, 2543w, 1685vs, 1606s, 1571m, 1505w, 1501w, 1448w, 1413s, 1356m, 1327m, 1267s, 1245s, 1185s, 1109m, 1017m, 890w, 855m, 764vs, 700s, 656m. <sup>1</sup>H NMR (400 MHz, DMSO):  $\delta$ , 2.13 (s, 12H, CH<sub>2</sub>), 7.70 (d, J= 8.0 Hz, 8H, CH(Ph)), 7.90 (d, J= 8.0 Hz, 8H,

CH(Ph)), 12.80 (sbr, 1H, OH(CO)). Anal.Calc. for C<sub>17</sub>H<sub>12</sub>OS (264.34): C, 77.24; H, 4.58. Found: C, 77.19; H, 4.62%.

#### 1.5 Preparation of TCF-1, TCF-2 and TCF-3

Crystals suitable for single crystal XRD were obtained stratifying hexane over a solution of MTB, STB or adamantanetetrabenzoic acid ATB in THF, yielding guest-containing tetracarboxylic-based frameworks (TCF-1, TCF-2 and TCF-3, respectively). The porous frameworks were obtained by removal of the guest under mild conditions of temperature and vacuum.

#### 2. Experimental

#### 2.1 Solution NMR and FTIR spectroscopies

<sup>1</sup>H NMR spectra were recorded on a Bruker Advance 300 and 400 spectrometer using standard Bruker pulse sequences. Chemical shifts ( $\delta$ ) for <sup>1</sup>H and <sup>13</sup>C spectra were referenced using internal solvent resonances and are reported relative to tetramethylsilane (TMS).

FTIR spectra (4000-700 cm<sup>-1</sup>) on a Perkin-Elmer FT-IR Nexus spectrometer equipped with a Thermo-Nicolet microscope.

#### 2.2 Calorimetric Analysis

Thermogravimetric (TG) analysis was performed on Mettler Toledo TGA/DSC 1 with N<sub>2</sub> gasflow (50 mL/min) from 30 to 500 °C at a heating rate of 10 °C min<sup>-1</sup>.

Differential Scanning Calorimetry (DSC) data were recorded on a Mettler Toledo Stare DSC1 analysis system equipped with  $N_2$  low temperature apparatus. The experiments were run under nitrogen atmosphere in standard 40 µl Al pans. The samples were heated from 25°C to 400°C, at 10°C/min.

#### 2.3 Adsorption Isotherms and Isosteric Heat of Adsorption

 $CO_2$  adsorption/desorption isotherms were acquired at 195K (dry ice and acetone bath) up to 1 bar, using Micromeritics analyzer ASAP2020 HD. Porous TCF-1 sample was previously outgassed at 50°C for 22 hours while close-packed TCF-1 sample was outgassed at 140°C for a few hours. TCF-2 sample was previously outgassed at 95°C overnight. N<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub> isotherms at different temperatures (298K, 273K and 195K for methane) and up to 10 bar were collected using Micromeritics Analyzer ASAP 2050. The isotherms were fitted using Langmuir model as follows:

$$Ads = Ads_{MAX} \frac{KP}{1 + KP}$$

Isosteric heats of adsorption have been calculated both for  $CO_2$  and  $CH_4$  using Vant'Hoff equation and adsorption isotherms at 298K and 273K.

#### 2.4 Single Crystal X-ray Diffraction by Synchrotron Radiation

Data collection for TCF-1/guest, TCF-1/CO<sub>2</sub>, TCF1/Xe and TCF-3 were performed at the X-ray diffraction beamline (XRD1) of the Elettra Synchrotron, Trieste (Italy)[S3]. TCF-1/guest and TCF-3 were collected at 100 K (nitrogen stream supplied by an Oxford Cryostream 700). TCF-1/CO<sub>2</sub> and TCF-1/Xe crystals were inserted into quartz capillaries loaded, respectively, with CO<sub>2</sub> and Xe under pressure and sealed. Datasets were collected at 220 K to avoid CO<sub>2</sub> condensation in the sealed tube. The datasets were collected through the rotating crystal method and using a monochromatic wavelength of 0.700 Å on a Pilatus 2M hybrid-pixel area detector. The diffraction data were indexed and integrated using XDS [S4]. Scaling have been done using CCP4-Aimless code [S5,S6]. The structures were solved by the dual space algorithm implemented in the SHELXT code [S7]. Fourier analysis and refinement were performed by the full-matrix least-squares methods based on F2 implemented in SHELXL-2014 [S8]. The assignment of the residual electron density in the cavities was performed as follows: the CO<sub>2</sub> molecules were modelled using the constraint of 1.16 Å C=O bond distance and linearity.

#### 2.5 Single Crystal X-ray Diffraction

Data collection for TCF-2 was performed on a Bruker Smart APEXII area detector diffractometer, Mo K $\alpha$ :  $\lambda$  = 0.71073 Å, at 200 K. The intensity data were integrated from several series of exposures frames (0.3° width) covering the sphere of reciprocal space. An absorption correction was applied using the program SADABS [S9]. The structures were solved with SHELXT code and Fourier analysis, and refinement were performed with SHELXL-2014. The WingX [S10] and Olex2 [S11] packages were used.

#### 2.6 Powder X-ray diffraction

X-ray Powder Diffraction (XRPD) data of porous TCF-1, TCF-1/hexane and close-packed TCF-1 were collected on a Thermo Scientific<sup>TM</sup> ARL<sup>TM</sup> X'TRA diffractometer in theta-theta Bragg Brentano geometry with CuK $\alpha_1$  radiation. In order to improve the signal-to-background ratio and limit the effect of X-ray transparency for structural solution purposed, the sample was prepared on a silicon zero-background sample holder. Data were collected with Variable Counting Time (VCT) scheme in order to improve S/N ratio at higher 2theta values. Data were then merged and normalized to counting time. In-situ non-ambient data were collected on the same instrument with an Anton-Paar non-ambient chamber. A modest vacuum (10<sup>-2</sup> mbar) was applied during the measurement in order to push towards the formation of porous TCF-1 from TCF-1 with hexane guest; the temperature was then increased by 10 °C per step up to 160 °C until close-packed TCF-1 was formed. The crystal structure of the close-packed TCF-1 was solved from X-ray powder diffraction data by means of a simulated annealing algorithm [S12] while the porous TCF-1 was determined by tuning the structure of guest-containing TCF-1 derived from the single crystal X-ray analysis in order to fit the experimental data. The close-packed TCF-1 crystallized in I-4 space group while the porous TCF-1 preserves the same space-group of TCF-1/guest. All structures were refined by Rietveld refinements [S13]. Multi-phase Rietveld refinement was performed to refine the crystal structure of TCF-1: we took into account the slight content of

TCF-1/guest and clos-packed TCF-1 phases. The porous TCF-1 was described with a rigid body: the sp<sup>3</sup> C atom was located on the 4-fold axis while the rotations were free to vary [S14].

#### 2.7 Solid State NMR

Quantitative solid-state <sup>1</sup>H MAS NMR spectra (single-pulse excitation SPE) were performed with a Bruker Avance III 600 MHz instrument operating at 14.1 T, using a recycle delay of 20 s. A MAS Bruker probe head was used with 2.5 mm  $ZrO_2$  rotors spinning at 30 kHz. The 90° pulse for proton was 2.9 µs. The <sup>1</sup>H chemical shift was referenced to adamantane. Spectral profiles were fit by Lorentzian line shapes.

Solid-state NMR spectra were run at 75.5 MHz for <sup>13</sup>C and at 83.02 MHz for <sup>129</sup>Xe on a Bruker Avance 300 instrument operating at a static field of 7.04 T equipped with high-power amplifiers (1 kW), a 4 mm double resonance MAS probe and a 5 mm wide-line probe.

 $^{13}C{^{1}H}$  ramped-amplitude cross polarization (CP) MAS experiments were performed at room temperature at a spinning speed of 12.5 kHz, using a contact time of 2 ms. The 90° pulse used for proton was 2.9 µs. Crystalline polyethylene was taken as an external reference at 32.8 ppm from TMS.

A MAS NMR 4mm rotor containing porous TFC-1 was capped with an home-made apparatus under a controlled atmosphere of <sup>13</sup>C-enriched CO<sub>2</sub>. The CO<sub>2</sub> adsorption has been performed at a constant pressure of 100 torr at 195K for 3 h. <sup>13</sup>C SPE-MAS NMR spectrum of TCF-1 sample loaded with <sup>13</sup>C-enriched CO<sub>2</sub> was collected at 235 K at a spinning speed of 8 kHz with a recycle delay of 10 s. At 235K the CO<sub>2</sub> loading was estimated to be 3 mmol/g (4 CO<sub>2</sub> molecules per unit cell).

For the thermally polarized <sup>129</sup>Xe experiments, xenon was adsorbed at room temperature for 30 minutes at 820 torr than it was condense and the system was flame sealed in a glass vial. The system was allowed to equilibrate overnight. <sup>129</sup>Xe SPE spectra were collected at variable temperature in the range 193 – 293 K using a recycle delay of 20 s and a 90° pulse of 7  $\mu$ s. The <sup>129</sup>Xe NMR spectra were simulated by NMR Weblab software[S15] applying the following main components of the chemical shift tensor  $\delta_{11}$ =295 ppm,  $\delta_{22}$ =223 ppm,  $\delta_{33}$ =218 ppm with a progressive upfield shift from low to high temperature. The isotropic chemical shifts vs temperature are the following 213, 213, 220, 221, 232, 239, 247 and 263 ppm vs 293K, 291K, 294K, 278K, 265K, 248K, 233K and 193K. A two-site jump of  $\phi$ =90° and a cone angle of  $\theta$ =90° were used. The exchange rates varied from 3000 to 14000 Hz. A Lorentzian line shape with a broadening of 2÷4 ppm was applied, except for the spectrum at 193K that required a larger line broadening of 10 ppm.

## 3. Theoretical calculations

#### **3.1 Difference MAPS**

All the difference maps were generated using the WINGX v2014.1 software package. The 3D Fourier (Beevers-Lipson) was used with a resolution of 0.1 Å for the crystallographic *a*- and *b*-axes and 0.05 Å for the *c*-axis. The Z axis (crystallographic *c*-axis) projection was used in order to generate slice (162 slices) along

the c-axis and therefore the channel axis. By multiplying the fractional c-axis coordinated with the number slices it is possible to identify the exact slice for the 2-D difference map projections [S16].

#### **3.2 Computational Details**

Atomic coordinates were imported from the refined crystal structures. Only the hydrogen atoms in the frameworks were optimized as part of a periodic system using the CASTEP module of the Materials Studio software suite. The optimizations were performed using the GGA PBE functional with Grimme's DFT-D dispersion correction, and thresholds for geometry optimization and SCF convergence were chosen as  $2 \times 10^{-6}$  eV. Single point energy calculations using the DMol<sup>3</sup> module of the Materials Studio software suite were performed using the GGA PBE functional with Grimme's DFT-D dispersion correction, and threshold for SCF convergence were chosen as  $1 \times 10^{-6}$  eV. The electron density data obtained from the DMol<sup>3</sup> calculations were used to construct the three-dimensional 0.01 e<sup>-/</sup>Å<sup>3</sup> electron density contour used for the molecular electrostatic potential map.

#### 3.3 Molecular Electrostatic maps

The electrostatic potentials were calculated using the VAMP module of the Materials Studio Software suite as a single point energy calculation using the NDDO Hamiltonian type and the AM1\* Hamiltonian. An SCF convergence threshold of  $5 \times 10^{-7}$  kcal/mol was used and the grid size for the imported electrostatic potential was set to 0.1 Å. The electron density data obtained from DMol<sup>3</sup> calculations were used to construct the three-dimensional 0.01 e<sup>-/</sup>Å<sup>3</sup> electron density contours of the CO<sub>2</sub> molecules. The molecular electrostatic potential calculated for TCF-1 was then mapped onto the electron density contours of the CO<sub>2</sub> molecules.

#### 3.4 Molecular Mechanics (MM) and Molecular Dynamics (MD) Simulations

All MM and MD calculations were performed using the Forcite-Plus module within the Biovia Materials Studio software suite. The Quench Dynamics (QD, Combination of MD and MM optimizations) protocol was used to perform a configurational search for the possible guest positions and arrangements. The Sorption module was used to determine the Forcite energy parameters by comparing the simulated sorption isotherm and density distribution of the guest with experimental data (Sorption measurements and SCXRD difference maps of guest loaded structures).

#### 3.5 Atomic charges for MM and MD calculations

Single point calculations were carried out using a crystal structure with optimized hydrogen atoms. These calculations were performed using the GGA PBE functional with Grimme's DFT-D dispersion correction; thresholds for SCF convergence were chosen as  $1 \times 10^{-6}$  eV. The Milliken charges were calculated at the end of the SCF cycle (this is given as an option in the properties tab of the calculation setup). These atomic charges were used in all the molecular mechanics and molecular dynamics calculations.

#### 3.6 Simulations for determination of the CO<sub>2</sub> arrangements and interaction energies

Possible arrangements were determined using QD simulations for one unit-cell. DFT optimizations (CASTEP) were performed to obtain the energies used for the final determination of the most probable guest arrangements. The optimizations were performed using the GGA PBE functional with Grimme's DFT-D dispersion correction, and thresholds for geometry optimization and SCF convergence were chosen as  $2 \times 10^{-6}$  eV.

Forcite energy parameters. Quality: Fine; Force field: COMPASS; Charges: Current (obtained from CASTEP); Electrostatic: Group based; van der Waals: Group based; Ewald accuracy: 1.0e<sup>-5</sup> kcal/mol.

Forcite Geometry optimization parameters. Algorithm: Quasi-Newton; Energy tolerance: 1.0e<sup>-4</sup> kcal/mol; Force: 0.005 kcal/mol/Å; Max iterations: 500.

Forcite Quench Dynamics parameters. Ensemble: NVT (constant V and T); Temperature: 298 K; Time step: 1 fs; Simulation time: 100 ps; Thermostat: Velocity scale (2 K); Quench: Every 1000 frames.

Single point energies, calculated using CASTEP, were used to determine the interaction energies and theywere calculated as follows:

E(host + guest): The full crystal structure with the guest included hydrogens and the guest molecules. E(host): The guest molecules are removed from the periodic model. E(guest): The host molecules are removed from the periodic model.  $E_{int}(host-guest) = E(host + guest) - (E(host) - E(guest))$ 

#### 3.7 Simulations for determination of the Xenon arrangements and interaction energies.

The computational model used is a super cell consisting of 5 unit-cells along the channel axis (crystallographic *c*-axis) to produce 10 sorption sites along the channel. Since the crystallographic occupation factor is 0.6, the super-cell was then occupied with 6 Xe atoms. Xe configurations were determined using QD simulations which matches the 16 only possible unique configurations for 6 Xe atoms with 10 available sites. These configurations can be extracted from the QD simulation or constructed manually. DFT optimizations (CASTEP) were performed to obtain the energies used for the final determination of the most probable guest arrangement. The optimizations were performed using the GGA PBE functional with Grimme's DFT-D dispersion correction, and thresholds for geometry optimization and SCF convergence were chosen as  $2 \times 10^{-6}$  eV.

Forcite energy parameters. Quality: Ultrafine; Force field: COMPASS; Charges: Current (obtained from CASTEP); Electrostatic: Ewald; van der Waals: Ewald; Ewald accuracy: 1.0e<sup>-5</sup> kcal/mol.

Forcite Geometry optimization parameters. Algorithm: Quasi-Newton; Energy tolerance: 1.0e<sup>-5</sup> kcal/mol; Force: 0.001 kcal/mol/Å; Max iterations: 1000.

Forcite Quench Dynamics parameters. Ensemble: NVT (constant V and T); Temperature: 220 K; Time step: 1 fs; Simulation time: 100 ns; Thermostat: Velocity scale (2 K); Quench: Every 1000 frames.

Single point energies, calculated using CASTEP, were used to determine the interaction energies. They were calculated as follows:

E(host + guest): The full crystal structure with the guest included with hydrogens and the guest molecules. E(host): The guest molecules are removed from the periodic model. E(guest): The host molecules are removed from the periodic model.  $E_{int}(host-guest) = E(host + guest) - (E(host) - E(guest))$ 

#### 3.8 Energy barrier for the diffusion of a Xe atom from one site to another

The CASTEP module in Materials Studio was used for this DFT calculation by performing a transition state (TS) search using the "Complete LST/QST" search protocol available in this software package. The level of theory for the calculation was set using the quality settings of the setup and was chosen as "medium". The maximizations were performed using the GGA PBE functional with Grimme's DFT-D dispersion correction. The SCF convergence threshold were chosen as  $2 \times 10^{-6}$  eV using the "All Bands/EDFT" electronic minimizer. The TS calculation protocol does not allow the host molecules to move during the entire calculation.

The host molecules for the minimum and selected positions including the transition state were optimized, with the fractional coordinates of the Xe atoms fixed using a quality setting of "Fine" (SCF convergence of  $1 \times 10^{-6}$  eV and "Density Mixing" electronic minimizer). This is followed by a single point calculation using a very strict quality setting of "Ultra-Fine" (SCF convergence of  $5 \times 10^{-7}$  eV "Density Mixing" electronic minimizer). The energy barrier is then calculated by the difference between the energy of minimum and the transition state.

## **3.9 GCMC Simulation**

Grand Canonical Monte Carlo method was used to simulate the adsorption behaviour of the porous crystals. We have applied Metropolis method and COMPASS force field. The Lennard-Jones cut-off distance was set to 14 Å. The simulation box was a supercell of 2 x 2 x 3 crystallographic units and the atom positions were fixed. The simulations at 298 K and 273 K include a 2 x  $10^6$  cycle equilibration period and 1 x  $10^7$  cycles of production for each pressure. The number of cycles of the simulations at 195 K was doubled to increase the accuracy. The Ewald sum technique was used to compute the electrostatic interactions.

## 4. FT-IR Spectra



**Figure S1.** FT-IR Spectra of A) TCF-1/guest and B) the close-packed phase obtained treating the sample at 140°C for 1 hour.

IR H<sub>4</sub>MTB-*guest* (cm<sup>-1</sup>): 3024w, 2951m, 2922m, 2849m, 2854m, 1648s, 1603m, 1569w, 1503m, 1432w, 1411s, 1375w, 1299m, 1279s, 1186m, 1019s, 803m, 771m, 763s, 701w, 616w.

IR H<sub>4</sub>MTB-*closed* (cm<sup>-1</sup>): 3069br, 2651w, 2502w, 1658vs, 1602m, 1571w, 1502w, 1416s, 1359s, 1318w, 1255vs, 1192s, 1123m, 1019m, 966w, 850m, 788s, 761vs, 658m.





IR TCF-2-*guest* (cm<sup>-1</sup>): 2906wbr, 2620wbr, 2505wbr, 1679vs, 1598m, 15554w, 1469w, 1378m, 1388s, 1301m, 1240s, 1220s, 1180s, 1087vs, 1018m, 844m, 765m, 757m, 682vs, 530vs.



Figure S3. FT-IR Spectra of TCF-3/guest.

IR TCF-3 (cm<sup>-1</sup>): 3149wbr, 2919m, 2893m, 2845m, 1678vs, 1603vs, 1567m, 1505w, 1405s, 1321m, 1236s, 1178s, 1103m, 1013m, 847m, 747vs, 697s, 647m, 520m.

## 5. Thermogravimetric analysis TGA



Figure S4. Thermogravimetric analysis of the TCF-1/guest (dark blue) and the close-packed phase (light blue).



## 6. Differential Scanning Calorimetry

Figure S5. DSC traces of TCF-1/hexane compound.

	TCF-1/guest	TCF-1/CO <sub>2</sub>	TCF-1/Xe	TCF-3	TCF-2
Empirical formula	$C_{29}H_{20}O_8$	$C_{30}H_{20}O_{10}$	C29 H20 O8 Xe0.60	$C_{56}H_{64}O_{13}$	$C_{28}H_{20}O_8Si$
Formula weight	496.45	540.46	575.23	945.07	512.53
Temperature/K	100(2)	220(2)	220(2)	100(2)	200
Crystal system	tetragonal	tetragonal	tetragonal	tetragonal	tetragonal
Space group	P4 <sub>2</sub> /n	$P4_2/n$	$P4_2/n$	P4/n	I4 <sub>1</sub> cd
a/Å	13.2038(4)	13.105(2)	13.2479(1)	18.9552(3)	26.190(4)
b/Å	13.2038(4)	13.105(2)	13.2479(1)	18.9552(3)	26.190
c/Å	8.0331(3)	8.079(2)	8.0336(1)	7.07520(10)	37.413(6)
$\alpha/^{\circ}$	90	90	90	90	90
β/°	90	90	90	90	90
$\gamma/^{\circ}$	90	90	90	90	90
Volume/A <sup>3</sup>	1400.5(1)	1387.5(5)	1409.95(3)	2542.12(9)	25662(9)
Z	2	2	2	2	24
$\rho_{calc}g/cm^3$	1.177	1.294	1.355	1.235	0.796
$\mu/\text{mm}^{-1}$	0.084	0.095	0.793	0.084	0.085
F(000)	516	560	581	1008.0	6384.0
Crystal size/mm <sup>3</sup>	0.17 x 0.08 x 0.08	0.16 x 0.07 x 0.06	0.21 x 0.09 x 0.04	$0.17 \times 0.09 \times 0.08$	$0.32 \times 0.28 \times 0.19$
Radiation	synchrotron ( $\lambda = 0.700$ )	synchrotron ( $\lambda = 0.700$ )	synchrotron ( $\lambda = 0.700$ )	synchrotron ( $\lambda = 0.700$ )	MoKa ( $\lambda = 0.71073$ )
$\Theta$ range for data collection/°	2.148 to 25.970	2.917 to 29.995	2.141 to 29.994	2.835 to 27.029	1.547 to 19.92
Index ranges	-16<=h<=16, - 16<=k<=16, -10<=l<=10	0<=h<=18, 0<=k<=18, 0<=l<=11	-18<=h<=18, - 18<=k<=18, -11<=l<=10	$\begin{array}{l} \text{-}24 \leq h \leq 24,  \text{-}24 \leq k \leq \\ 24,  \text{-}9 \leq l \leq 9 \end{array}$	$\begin{array}{l} -25 \leq h \leq 23,  -24 \leq k \leq \\ 25,  -35 \leq l \leq 35 \end{array}$
Reflections collected	17397	42528	25863	35340	54438
Independent reflections	1440 [R(int) = 0.0671]	2103 [R(int) = 0.0449]	2144 [R(int) = 0.0596]	2908 [ $R_{int} = 0.0576$ ]	5903 [R <sub>int</sub> = 0.1156]
Data/restraints/parameters	1440 / 3 / 88	2103 / 11 / 108	2144 / 4 / 111	2908/90/222	5903/13/254
Goodness-of-fit on F <sup>2</sup>	1.008	1.007	1.015	1.002	1.011
Final R indexes [I>= $2\sigma$ (I)]	R1 = 0.0611, wR2 = 0.1815	R1 = 0.0606, wR2 = 0.1796	R1 = 0.0828, wR2 = 0.1971	$R_1 = 0.0893, wR_2 = 0.2833$	$R_1 = 0.0571, wR_2 = 0.1436$
Largest diff. peak/hole / e $Å^{-3}$	0.300 and -0.293	0.454 and -0.255	0.493 and -0.813	0.37/-0.40	0.26/-0.18
Flack parameter	-	-	-	-	0.18(13)

**Table S1.** Single crystal data and structure refinement for TCF-1/guest, TCF-1/CO<sub>2</sub>, TCF-1/Xe, TCF-2, TCF-3.

Table S2. X-ray Powder diffraction data and structure refinement for porous TCF-1 and close-packed TCF-1.

Name	Porous TCF-1	TCF-1/closed
Empirical Formula	$C_{29}H_{20}O_8$	$C_{29}H_{20}O_8$
Formula weight	496.45	496.45
Temperature/K	295	295
Crystal System	Tetragonal	Tetragonal
Space Group	P4 <sub>2</sub> /n	I-4
Z	2	2
a/Å	12.760(4)	12.533(3)
c /Å	8.173(2)	7.530(2)
$V/Å^3$	1330.7(8)	1182.8(5)
Radiation $\lambda/Å$	1.54056	1.54056
Colour	white	white
2θ range	5 - 60	5 - 70
R <sub>p</sub>	5.02	3.80
$\mathbf{R}_{wp}$	6.36	4.90
Goodness-of-Fit	0.28	0.11

## 8. Powder X-ray diffraction



**Figure S6.** Experimental patterns of A) porous TCF-1 and B) TCF-1/guest at starting point. C) Calculated pattern of TCF-1/guest.



**Figure S7.** Rietveld refinement of the porous TCF-1 against experimental data (blue dots).  $Y_{calc}-Y_{obs}$  residual curve is reported in grey. Range 40°-60° is zoomed 4x to appreciate the agreement between the calculated and experimental patterns.

## 9. Phase transformations

<sup>1</sup>H NMR spectra exhibit a difference between the porous structure and the close-packed one: namely, the carboxylic hydrogen signals resonate at 13.0 ppm compared with 10.8 ppm, respectively, showing a large 2.2 ppm downfield shift. A universal calibration of chemical shift *vs* oxygen distances of carboxylic acid dimers yields a distance of 2.6-2.7 Å for the porous structure. This result is in full agreement with the short O...H-O distance of 2.7 Å observed by XRD in the channel-like structure *vs* 3.0/3.2 Å in the close-packed architecture, that displays looser interactions.

<sup>13</sup>C CP MAS NMR spectra of the channel structures show a 3 ppm downfield shift of the carboxylic group with respect to that of the close-packed form, owing to occurrence of stronger hydrogen bond formation.



**Figure S8.** <sup>1</sup>H MAS (30 kHz) NMR spectra of A) porous TCF-1 and B) close-packed TCF-1 structures. The simulated profiles correspond to the carboxylic hydrogen resonances. C) Carboxylic region of <sup>13</sup>C CP MAS NMR spectra of TCF-1 forms.



Figure S9. Topological representation of the diamandoid framework as built by connecting tetrahedral carbons.



**Figure S10.** <sup>13</sup>C CP MAS NMR spectrum of close-packed TCF-1 (above) and of regenerated channel-like TCF-1 form (below). Spinning speeds of 12.5 KHz and 8 KHz were applied (above and below, respectively). The asterisks indicate the spinning side bands of the aromatic carbons (spinning speed of 8 KHz). A contact time of 2 ms was applied.



**Figure S11.** Rietveld refinement of the close-packed TCF-1 (red line) against experimental data (blue dots).  $Y_{calc}-Y_{obs}$  residual curve is reported in grey. Range 40°-70° is zoomed 4x to appreciate the agreement between the calculated and experimental patterns.

![](_page_16_Figure_2.jpeg)

**Figure S12.** A) Conformational change of the molecular entities in the TCF-1/hexane (left), porous TCF-1 (middle) and close-packed TCF-1 (right). B) Hydrogen bond interactions between symmetry related molecules in the unit cell of TCF-1/hexane (left), porous TCF-1 (middle) and close-packed TCF-1 (right).

![](_page_17_Figure_0.jpeg)

**Figure S13.** PXRD patterns of the close-packed form (orange line) and the regenerated channel-like structure (blue line).

## 10. CO<sub>2</sub> Adsorption Isotherms, Fitting and Heat of adsorption

![](_page_17_Figure_3.jpeg)

Figure S14. CO<sub>2</sub> adsorption isotherms of porous TCF-1 at 298K (red) up to 10 bar.

![](_page_18_Figure_0.jpeg)

**Figure S15.** Isosteric Heat of Adsorption calculated on CO<sub>2</sub> adsorption isotherms at 195K, 273K and 298K using Van't Hoff equation.

## 11. Simulation Results: CO2 Configurations in the Channels

![](_page_18_Figure_3.jpeg)

**Figure S16.** Density difference map for the crystal structure of TFC-1 loaded with  $CO_2$  viewed along the crystallographic *c*-axis (A) and *b*-axis (B). The simulated  $CO_2$  density distribution, calculated using the Sorption module in Materials Studio, viewed along the crystallographic *c*-axis (C) and *b*-axis (D).

![](_page_19_Figure_0.jpeg)

**Figure S17.** The simulated positions of CO<sub>2</sub> molecules within the channels of TCF-1. (A and B) The two lowest energy CO<sub>2</sub> configurations 1 (green) and 2 (blue) including all the symmetry generated molecules. (C and D) Configuration 1 with the symmetry related CO<sub>2</sub> molecules included in pink and indicated with the arrows. The inclusion of the symmetry related CO<sub>2</sub> molecules for configuration 1 shows that each guest site contains 4 positions with an occupancy factor of 0.25 with respect to the total probability of configurations 1 (i.e. 0.78). (E and F) The main configuration 1 without symmetry related CO<sub>2</sub> molecules and the two unique CO<sub>2</sub> molecules indicated. The host is shown in stick representation and the CO<sub>2</sub> molecules in space-filling representation. The hydrogen atoms have been omitted for clarity.

#### 12. CH<sub>4</sub> Adsorption Isotherms, Fitting and Isosteric Heat of Adsorption

![](_page_19_Figure_3.jpeg)

**Figure S18.** Experimental CH<sub>4</sub> adsorption isotherm, collected at 298K (black spots) compared to calculated Langmuir isotherm (blue line). The curve was fitted with a Langmuir model  $Ads_{max}$ = 42.45 cm<sup>3</sup>/g and K= 0.24 bar<sup>-1</sup>.

![](_page_20_Figure_0.jpeg)

**Figure S19.** Experimental CH<sub>4</sub> adsorption isotherm, collected at 273K (black spots) compared to calculated Langmuir isotherm (blue line). The curve was fitted with a Langmuir model  $Ads_{max}$ = 43.70 cm<sup>3</sup>/g and K= 0.54 bar<sup>-1</sup>.

![](_page_20_Figure_2.jpeg)

**Figure S20.** Isosteric Heat of Adsorption calculated on CH<sub>4</sub> adsorption isotherms at 273 and 298K using Van't Hoff equation.

![](_page_21_Figure_0.jpeg)

![](_page_21_Figure_1.jpeg)

**Figure S21.** Xe adsorption isotherm of porous TCF-1 at 195K up to 110 torr (above). GCMC simulation of Xe adsorption isotherm in porous TCF-1 at 298K and up to 10 bar (below).

![](_page_22_Figure_0.jpeg)

**Figure S22.** A) and B) Experimental Xe crystal structure of TCF-1/Xe as compared to C) and D) Xe probability distribution calculated by GCMC method and using the maximum uptake at 195K.

![](_page_22_Figure_2.jpeg)

**Figure S23.** (TOP) The relative energy plot for the CASTEP transition state calculation. (BOTTOM) The volume occupied by the probe center-of-mass calculated using a probe radius of 2.1 Å (Xe vdW radius is 2.16 Å). The fractional *c*-axis coordinate of the transition state is indicated for both.

![](_page_23_Figure_0.jpeg)

Figure S24. The 16 possible Xe configurations for a 10-site channel occupied by 6 Xe atoms.

![](_page_23_Figure_2.jpeg)

Figure S25. The QD energy plot with the bands for the different number of groupings indicated.

![](_page_24_Figure_0.jpeg)

**Figure S26.** An energy plot for the different groupings to highlight the presence of all 16 configurations. The bottom-left figure illustrates the codes used to describe the configurations.

![](_page_24_Figure_2.jpeg)

**Figure S27.** A chart representation of the relative energies and corresponding Boltzmann distribution for all the Xe configurations.

![](_page_25_Figure_0.jpeg)

**Figure S28.** The Y axis represents the probabilities calculated from the Boltzmann distribution calculated for 220 K using the ab initio derived energies. Calculated using configurations of **ALL GROUPS**.

![](_page_25_Figure_2.jpeg)

**Figure S29.** The Y axis represents the probabilities calculated from the Boltzmann distribution calculated for 220 K using the ab initio derived energies. Calculated using only configurations of **2 GROUPS**.

Table S	53.	The	relative	energies	and	corres	ponding	Boltzn	nann di	stributi	ion for	all th	e Xe	config	urations
Lance	<i>J</i> <b>J</b> ••	1 IIC	101utive	energies	unu	conco	ponuing	DOILT	nunn un	Surouu	1011 101	un un	$10 \pm 10$	comis	uration

Configurations	Rel. Potential Energy (kJ/mol)	Boltzmann Distribution @ 220K (%)
1B1B1B3B	6.64	0.8
1B1B2B2B	6.68	0.8
1B2B1B2B	6.68	0.8
1B1B4BB	4.48	2.6
1BB1B4B	4.48	2.6
1B2B3BB	4.53	2.6
1B2BB3B	4.54	2.6
1BB2B3B	4.53	2.6
2B2B2BB	4.58	2.5
1B5BBB	2.24	9.0
1BB5BB	2.32	8.6
2B4BBB	2.30	8.7
2BB4BB	2.39	8.3
3B3BBB	2.31	8.7
3BB3BB	2.39	8.3
6BBBB	0.00	30.6

	Energy of unit cell (eV)	Fractional coordinate along the c-axis (Å)	Relative energy (kJ/mol)	Relative energy (kcal/mol)
Initial Minimum	-34526.39683	0.1936	0.00	0.00
	-34526.3762	0.2869	1.99	0.47
	-34526.3067	0.3881	8.70	2.08
Transition State	-34526.0826	0.4413	9.30	2.22
	-34526.31872	0.4618	7.54	1.80
	-34526.3934	0.4951	0.33	0.08
	-34526.3928	0.5995	0.39	0.09
	-34526.39683	0.6936	0.00	0.00

**Table S4.** The energies calculated to determine the energy barrier for a Xe atom moving from one site to the neighbouring site.

## 14. CO<sub>2</sub> Adsorption Isotherm and Calorimetry of TCF-2

![](_page_27_Figure_1.jpeg)

**Figure S30.** DSC profiles of A) guest-containing TCF-2, B) porous TCF-2 and C) close-packed TCF-2 compounds. TCF-2/guest underwent guest removal by thermal treatment at 95°C overnight and vacuum at 10<sup>-3</sup> torr yielding the porous TCF-2.

![](_page_27_Figure_3.jpeg)

Figure S31. Experimental CO<sub>2</sub> adsorption isotherm on TCF-2, collected at 195K (blue circle).

#### 15. Crystal Structure of TCF-3

![](_page_28_Figure_1.jpeg)

**Figure S32.** Molecular structure and crystal packing of TCF-3. Molecular unit with THF molecules (A); Interaction mediated by THF, distance are a reported in Å (B); Packings of supramolecular pillars (C); Packing projected along the *c*-axis with THF molecule in spacefill mode (D).

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