# Electronic Supplementary Information

## Discovery of a novel, second large pore phase in a bimetallic Al/V metal-organic framework

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## Synthesis of the COMOC-2-$V_x$-$Al_{1-x}$ materials

The synthesis of **COMOC-2(V)** is performed as previously reported.[1] In brief, an amount of 0.5 g of vanadyl(IV)sulfate hydrate ($VOSO_4 \bullet H_2O$), 1.02 g of 4,4'-biphenyl dicarboxylate ($H_2$bpdc) and 70 mL of N,N-dimethylformamide (DMF) are transferred into a 100 mL round-bottom flask equipped with a magnetic stirrer. The reaction vessel is sealed, slowly heated to 421 K under stirring and kept at this temperature for 16 h. Afterwards, the yellow-green powder is collected over a membrane filter and washed thoroughly with DMF, methanol and acetone to remove unreacted starting materials. In a final step the material is activated under vacuum for 2 h at 393 K.

**DUT-5(Al)** is synthesized and activated according to a previously reported procedure.[2] In a typical synthesis, 0.26 g of $H_2$bpdc, 0.52 g of aluminium(III)nitrate nonahydrate ($Al(NO_3)_3 \bullet 9H_2O$), and 30 mL of DMF are mixed in a 50 mL round-bottom flask equipped with a magnetic stirrer. The flask is sealed, slowly heated to 421 K under stirring, and kept at this temperature for 16 h. The white powder is filtered and washed with DMF, methanol and acetone. All solvents are removed by an activation step at 393 K under vacuum for 2 h.

Synthesis of the **mixed-metal COMOC-2-$V_x$-$Al_{1-x}$ series**: the mixed-metal MOFs are all synthesized via a direct one-pot synthesis and labelled from **1 (V=81%)** to **8 (V=1%)**. The mol% vanadium of compound **1** is **81 %** while compound **8** contains **1 %**. These values are experimentally determined via ICP analysis. In this supplementary information only the experimental metal concentrations will be used. All the different concentrations of the starting reagents are listed up in Table S1. whereas the sample characteristics and Al/V ratios are presented in Table S2. To obtain these frameworks, a mixture of organic $H_2$bpdc linker, different ratios of metal salts $VOSO_4 \bullet H_2O$/$Al(NO_3)_3 \bullet 9H_2O$ and DMF are added in a 50 mL round-bottom flask equipped with a magnetic stirring bar. The reaction mixture is slowly heated to 421 K and kept at this temperature for 16 h. Subsequently the obtained crystalline material is filtrated at synthesis temperature and washed with DMF, methanol and acetone. All compounds are in a final step activated at 393 K for 2 h.

## Materials and methods

**General procedures:** All chemicals were bought from Sigma-Aldrich or TCI Europe and used as received without further purification. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements were recorded in the region between 4000-750 $cm^{-1}$ on a Thermo Nicolet 6700 spectrometer, equipped with a nitrogen-cooled MCTA detector and a KBr beam splitter at 393 K under vacuum, using a Graseby Specac diffuse reflectance cell. Raman spectra were obtained on an RXN1 Raman spectrometer (Kaiser Optical Systems) equipped with a 532 nm laser operating at 40 mW using an optical probe. XRPD patterns were collected on a Thermo Scientific ARL X'Tra diffractometer, operated at 40 keV and 40 mA using a Cu anode (Cu-$K_\alpha$, $\lambda$ = 1.5406 Å). Thermogravimetric analyses (TGA) were performed on a Netzsch STA 449 F3 Jupiter-simultaneous TG-DSC (thermogravimetric - differential scanning calorimetry) analyzer in the temperature range of 25-800 °C under air and with a heating rate of 2 °C $min^{-1}$. Nitrogen sorption measurements were done on a Belsorp Mini (Bel Japan, Inc.) apparatus. Before the sorption measurements, the samples were degassed at 353 K for 2 hours. The vanadium content was determined by using an ICP-MS (inductively coupled plasma mass spectroscopy) Perkin Elmer Elan DRC 6000, whereas the Al content was obtained on an ICP-OES (ICP optical emission spectroscopy) Varian Vista MPX setup. For both elements, argon was used to create the plasma. To avoid interference with $ClO^-$ anions during the analysis of vanadium, methane was added as a reaction gas. Before the analysis, the MOF powders were completely dissolved in an acidic medium. Equilibrium isotherms of $CO_2$ and $C_2H_4$ were measured by means of the static volumetric method using an Isorb-HP1 device from Quantachrome. The measurements were performed in a temperature range from 228 K-303 K. Approximately 150 mg of sample was loaded in the stainless-steel sample holder. Before each measurement, the powder was degassed at a heating rate of 2 K $min^{-1}$ to 363 K and kept at this temperature for 2 hours. High-resolution *in-situ* synchrotron XRPD data were collected at beamline I11 at the Diamond Light source synchrotron facilities (UK, Didcot) using a monochromatic X-ray beam ($\lambda$ = 0.82696 Å) and a Mythen position sensitive detector, with a total scan time of 5 s. The samples were packed into a 0.5 mm quartz glass capillary and held in place by a quartz wool plug. The capillary was sealed, mounted onto a motorized goniometer head and connected to the high-pressure system. To ensure the complete removal of entrapped gas-molecules, the sample was evacuated under a dynamic vacuum with a turbo pump to $10^{-6}$ bar and heated for 30 min at 353 K with a heating rate of 2 K $min^{-1}$ which was controlled by a $N_2$-cryostream and a hot gas blower. Prior to the analysis, the sample was cooled down to 233 K and a gas dosing system was used to increase the $CO_2$ pressure from vacuum to 17.5 bar.[1] Bright-field scanning transmission electron microscopy (BF-STEM) and energy dispersive X-ray spectroscopy (EDX) was performed on a JEOL JEM-2200FS high resolution scanning transmission electron microscope equipped with an EDX spectrometer with a spatial resolution of 0.13 nm, image lens spherical aberration corrector, electron energy loss spectrometer (filter) and an emission field gun (FEG) operating at 200 KeV.

The X-band setup was a Bruker ESP300E spectrometer equipped with an ER 4102ST standard resonator, a HP5350 B frequency counter and a Bruker ER 035M Gaussmeter. The magnetic fields were calibrated by using the spectrum of diphenyl picrylhydrazyl (DPPH; g=2.0036). The EPR spectra were recorded at approximately 5 mW microwave power (avoiding saturation) and 100 kHz modulation. Rietveld refinement for powder pattern fitting was performed for all samples by using Topas Academic3. The refined parameters were the measurement specific or global zero error and cosine Chebyshev function of 12 polynomial terms and the phase specific scale factors and the unit cell parameters.

**Table S1 Solvent, linker and metal ratio of reported samples.**

| Sample name | Dimethyl-formamide [DMF] | | 4,4'-biphenyl-dicarboxylic acid [$H_2bpdc$] | | Vanadyl(IV)sulfate hydrate [$VO(SO_4).H_2O$] | | Aluminium (III)nitrate nonahydrate [$Al(NO_3)_3.9H_2O$] | |
|---|---|---|---|---|---|---|---|---|
| | mL | mmol | g | mmol | g | mmol | g | mmol |
| **COMOC-2(V)*** | 70 | 908 | 1.0200 | 4.21 | 0.5000 | 2.76 | 0 | 0 |
| **COMOC-$V_xAl_{1-x}$-1 (V=81%)** | 25 | 324 | 0.2572 | 1.06 | 0.1800 | 0.99 | 0.0200 | 0.05 |
| **COMOC-$V_xAl_{1-x}$-2 (V=66%)** | 25 | 324 | 0.2572 | 1.06 | 0.1700 | 0.94 | 0.0400 | 0.11 |
| **COMOC-$V_xAl_{1-x}$-3 (V=46%)** | 30 | 389 | 0.3500 | 1.44 | 0.2850 | 1.57 | 0.1520 | 0.41 |
| **COMOC-$V_xAl_{1-x}$-4 (V=23%)** | 30 | 389 | 0.3500 | 1.44 | 0.2167 | 1.20 | 0.2972 | 0.79 |
| **COMOC-$V_xAl_{1-x}$-5 (V=9%)** | 30 | 389 | 0.3500 | 1.44 | 0.1430 | 0.79 | 0.4464 | 1.19 |
| **COMOC-$V_xAl_{1-x}$-6 (V=7%)** | 30 | 389 | 0.3500 | 1.44 | 0.0716 | 0.40 | 0.5936 | 1.58 |
| **COMOC-$V_xAl_{1-x}$-7 (V=3%)** | 30 | 389 | 0.3500 | 1.44 | 0.0180 | 0.10 | 0.7049 | 1.88 |
| **COMOC-$V_xAl_{1-x}$-8 ( (V=1%))** | 30 | 389 | 0.3500 | 1.44 | 0.0070 | 0.04 | 0.7272 | 1.94 |
| **DUT-5(Al)*** | 30 | 389 | 0.2600 | 1.07 | 0 | 0 | 0.52 | 1.39 |

*COMOC-2(V) and DUT-5(Al) are synthesized according to literature recipes.[1,2]

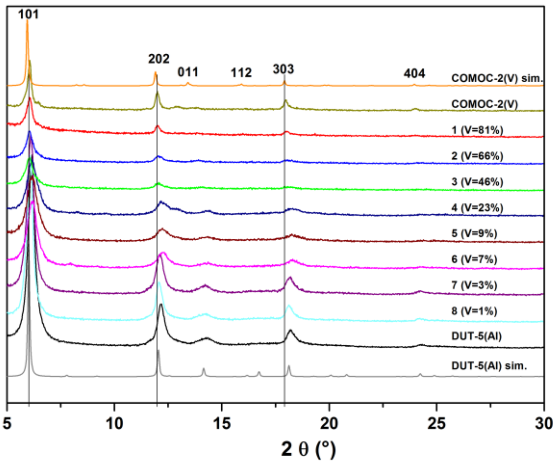



**Fig. S1 XRPD of the pristine COMOC-2(V), pristine DUT-5(Al) and the mixed-metal COMOC-2-$V_x$-$Al_{1-x}$ series. Simulated diffractograms of the pristine materials are also represented and indicated with sim.**

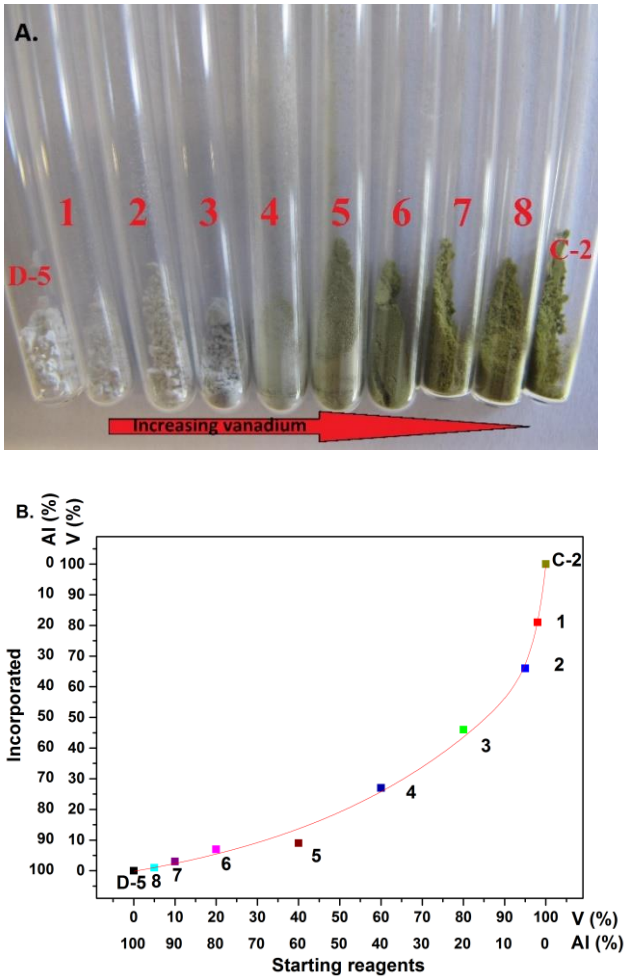



**Fig. S2 (A) Visual representation of the powder samples in a quartz tube. The two extremes are D-5 for DUT-5(Al), a completely white crystalline powder and C-2 for COMOC-2(V) a yellow-green powder. From (1-8): 1 (V=81%) to 8 (V=1%) with increasing number, the aluminium content increases. (B) ICP analysis of the Al/V ratio in the monometallic COMOC-2(V) (C-2), DUT-5(Al) (D-5) and mixed-metal COMOC-2-$V_x$-$Al_{1-x}$ series. The plotted line is a guide for the eye.**

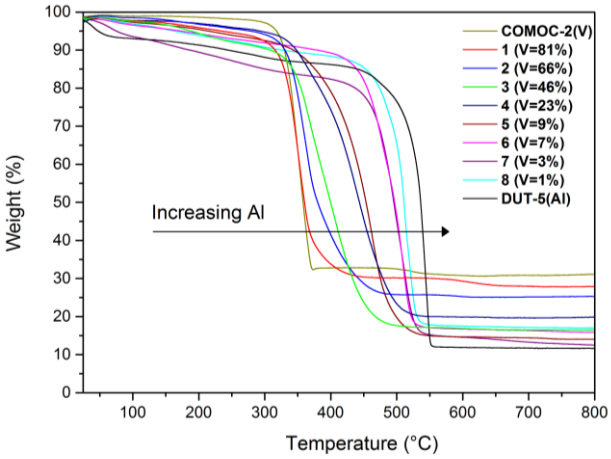



**Fig. S3 TGA data of the monometallic frameworks COMOC-2(V), DUT-5(Al) and the MM COMOC-2-$V_x$-$Al_{1-x}$ series.**

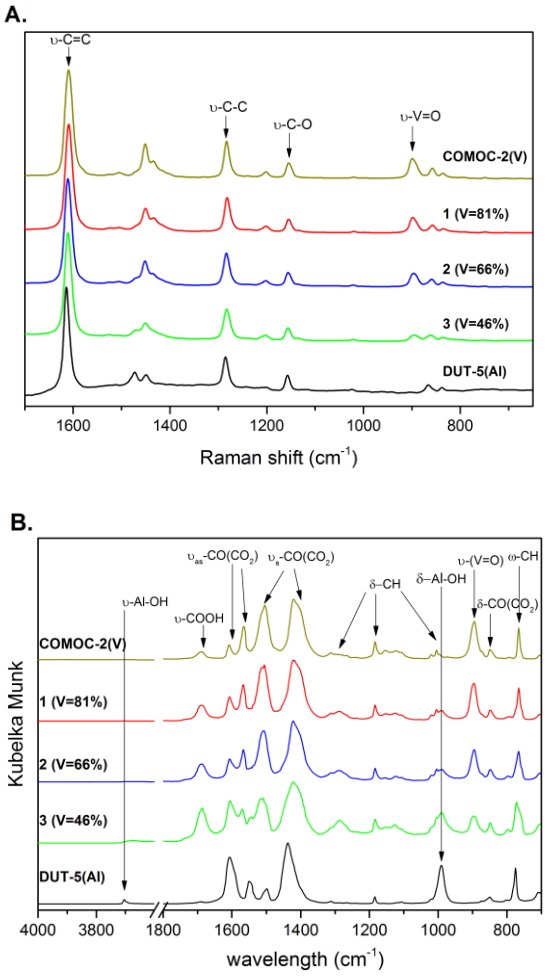



**Fig. S4 (A) Raman spectra in the region between 1700-750 $cm^{-1}$. (B) DRIFTS spectra in the region between 4000-3600 $cm^{-1}$ and 1800-750 $cm^{-1}$ both of compounds COMOC-2(V), 1 (V=81%), 2 (V=66%), 3 (V=46%) and DUT-5(Al).**

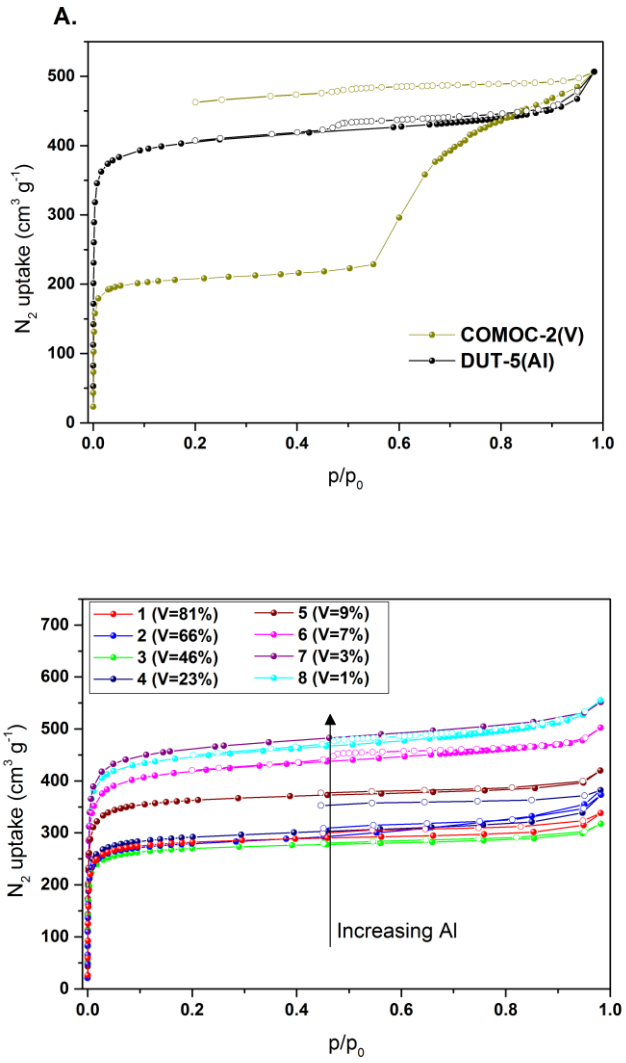



**Fig. S5 Nitrogen sorption isotherms of (A) DUT-5(Al) and COMOC-2(V), (B) mixed-metal COMOC-2-$V_x$-$Al_{1-x}$ structures from 1 (V=81%) to 8 (V=1%).**

**Table S2 Theoretical and experimental vanadium and aluminium composition, Langmuir Surface Area and isosteric heat of adsorption of the synthesized samples.**

| Sample | Theoretical[a] | | Experimental[b] | | $S_{Langmuir}$ ($m^2\ g^{-1}$) | $^{c}CO_2$-$Q_{st}^0$ (kJ $mol^{-1}$) | $^{c}C_2H_4$-$Q_{st}^0$ (kJ $mol^{-1}$) |
|---|---|---|---|---|---|---|---|
| | V(x) | Al(1-x) | V(x) | Al(1-x) | | | |
| **COMOC-2(V)** | 1 | 0 | 1 | 0 | 958 | -24.2 | -20.4 |
| **1 (V=81%)** | 0.95 | 0.05 | 0.81 | 0.19 | 1280 | -23.7 | -21.9 |
| **2 (V=66%)** | 0.90 | 0.10 | 0.66 | 0.34 | 1264 | -23.3 | -21.7 |
| **3 (V=46%)** | 0.80 | 0.20 | 0.46 | 0.54 | 1238 | -22.9 | -23.6 |
| **4 (V=23%)** | 0.60 | 0.40 | 0.23 | 0.77 | 1339 | - | - |
| **5 (V=9%)** | 0.40 | 0.60 | 0.09 | 0.91 | 1648 | - | - |
| **6 (V=7%)** | 0.20 | 0.80 | 0.07 | 0.93 | 1965 | - | - |
| **7 (V=3%)** | 0.05 | 0.95 | 0.03 | 0.97 | 2203 | - | - |
| **8 (V=1%)** | 0.02 | 0.98 | 0.01 | 0.99 | 2147 | - | - |
| **DUT-5(Al)** | 0 | 1 | 0 | 1 | 1958 | -22.1 | -22.5 |

[a] Theoretical molar ratio of vanadium and aluminium added in the synthesis of the samples.
[b] The experimental molar ratio of vanadium and aluminium in all samples are determined with ICP analysis. Prior to the analysis, the samples are destructed under acid conditions and diluted to fit the detection range of the equipment.
[c] Isosteric heat of adsorption obtained by fitting adsorption data collected at 228 K and 303 K.

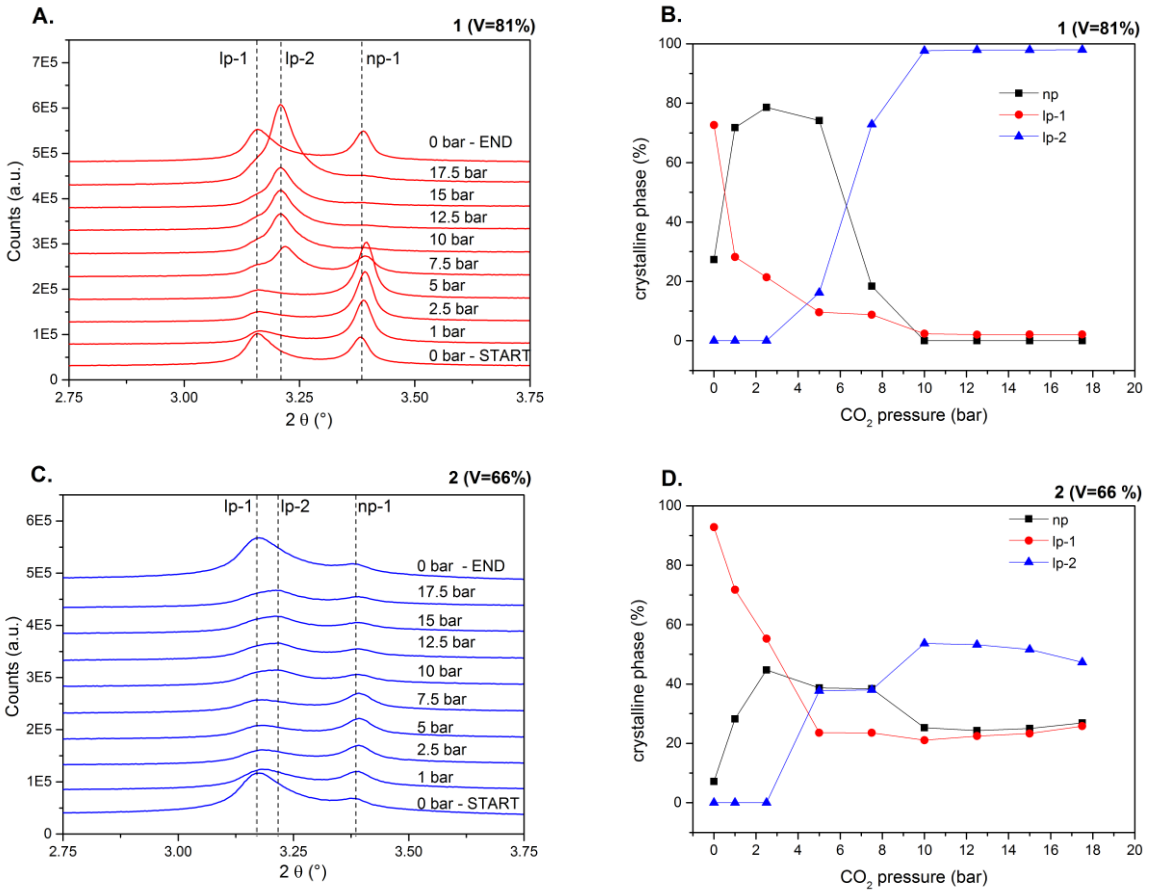



**Fig. S6 High pressure $CO_2$-XRPD analysis between 0-17.5 bar at 233 K and Rietveld refinements of: (1=81 % (A, B); 2V = 66 % (C, D). Three fractions are identified np (■), lp-1 (●) and lp-2 (▲).**

**Tab. S3 Calculated and empirically determined lattice parameters for the different forms of COMOC-2(V)[1] and DUT-5(Al)[2].**

| Phase | Crystal system | a (Å) | b (Å) | c (Å) | α | β | γ | V(Å$^3$) |
|---|---|---|---|---|---|---|---|---|
| **COMOC-2(V)** | | | | | | | | |
| **np (exp)[a]** | Monoclinic | 6.651(4) | 27.94(4) | 10.735(13) | 97.06(8) | 90 | 90 | 1979.4(47) |
| **np (calc)** | Orthorhombic | 6.991 | 28.111 | 6.809 | 90 | 90 | 90 | 1338.13 |
| **lp (exp)[b]** | Orthorhombic | 6.776(3) | 23.087(19) | 18.897(9) | 90 | 90 | 90 | 2956.1(32) |
| **lp (calc)** | Orthorhombic | 6.927 | 21.642 | 20.498 | 90 | 90 | 90 | 3073.00 |
| **lp (exp)[c]** | Orthorhombic | 6.957(4) | 21.443(3) | 20.570(2) | 90 | 90 | 90 | 3069(5) |
| **DUT-5(Al)** | | | | | | | | |
| **lp[b]** | Orthorhombic | 6.60721(14) | 22.698(2) | 19.2398(13) | 90 | 90 | 90 | 2885.4(5) |

[a] Determined based on synchrotron XRPD pattern with 7.5 bar $CO_2$ pressure at 233 K.

[b] Crystal data obtained from Rietveld structure refinement on laboratory XRPD pattern of COMOC-2 at 293 K.

[c] Determined based on synchrotron XRPD pattern with 15 bar $CO_2$ pressure at 233 K.

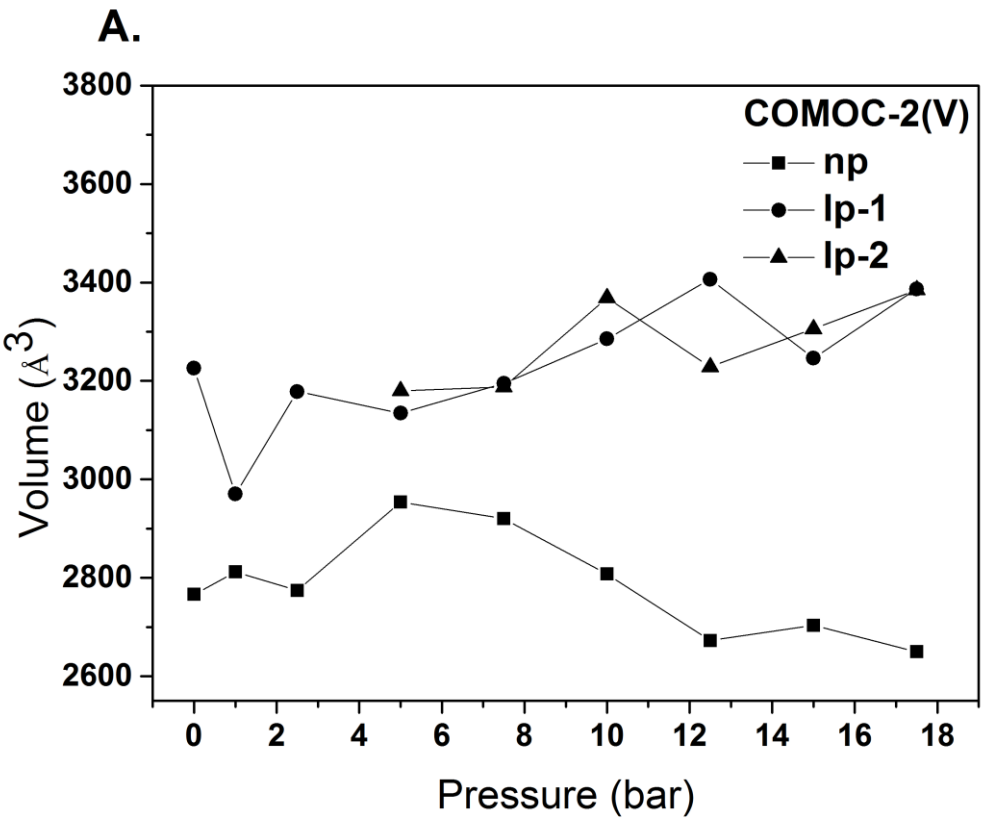
**Table S4 Fractions (%) of the np, lp-1 and lp-2 obtained via high-pressure XRPD measurements in the range 0-17.5 bar $CO_2$ at 228 K for compounds COMOC-2(V), 1 (V=81%), 2 (V=66%), 3 (V=46%).**

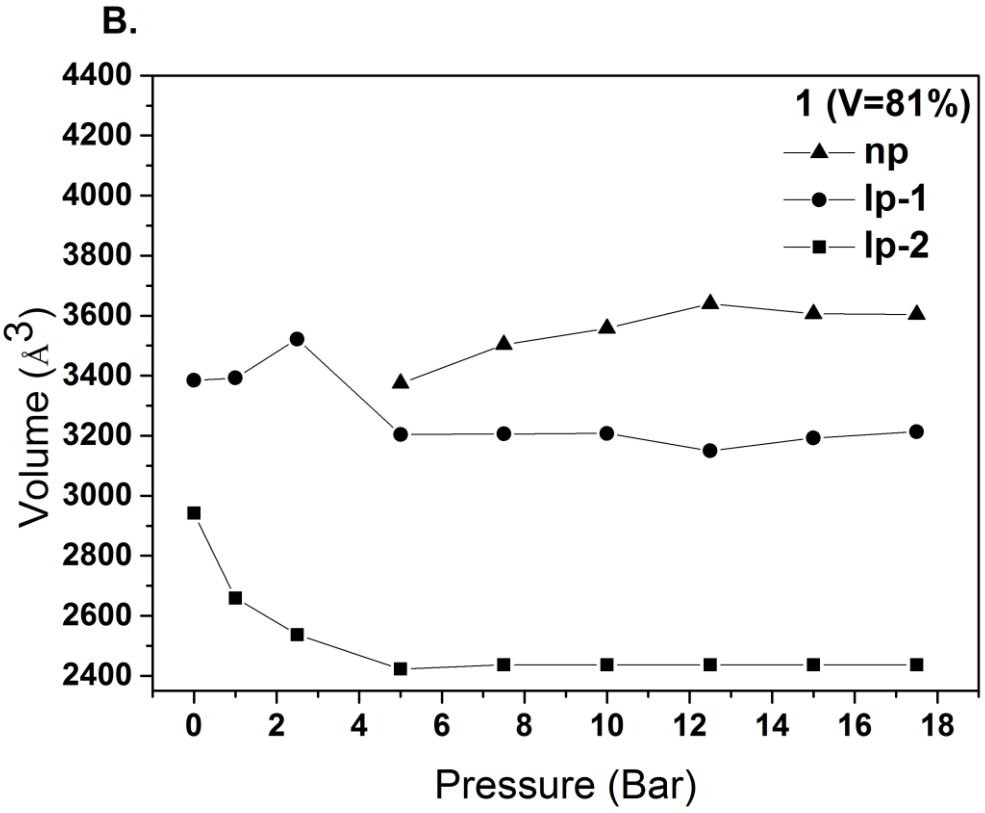
| COMOC-2(V) | | | |
|---|---|---|---|
| **Pressure (bar)** | **np (%)** | **lp-1 (%)** | **lp-2 (%)** |
| **0-Start** | 4.40 | 95.60 | 0 |
| **1** | 14.43 | 85.57 | 0 |
| **2.5** | 28.67 | 71.33 | 0 |
| **5** | 39.71 | 42.81 | 17.48 |
| **7.5** | 25.2 | 47.32 | 27.50 |
| **10** | 7.73 | 38.66 | 53.60 |
| **12.5** | 8.10 | 38.85 | 53.06 |
| **15** | 7.82 | 36.81 | 55.36 |
| **17.5** | 7.45 | 37.34 | 55.21 |
| **0-End** | 5.12 | 94.89 | 0 |

| 1 (V=81%) | | | |
|---|---|---|---|
| **Pressure (bar)** | **np (%)** | **lp-1 (%)** | **lp-2 (%)** |
| **0-Start** | 27.32 | 72.68 | 0 |
| **1** | 71.79 | 28.20 | 0 |
| **2.5** | 78.62 | 21.39 | 0 |
| **5** | 74.16 | 9.61 | 16.22 |
| **7.5** | 18.35 | 8.78 | 72.88 |
| **10** | 0 | 2.35 | 97.65 |
| **12.5** | 0 | 2.06 | 97.94 |
| **15** | 0 | 2.09 | 97.91 |
| **17.5** | 0 | 2.11 | 97.98 |
| **0-End** | 26.91 | 73.09 | 0 |

| 2 (V=66%) | | | |
|---|---|---|---|
| **Pressure (bar)** | **np (%)** | **lp-1 (%)** | **lp-2 (%)** |
| **0-Start** | 7.20 | 92.80 | 0 |
| **1** | 28.23 | 71.77 | 0 |
| **2.5** | 44.74 | 55.26 | 0 |
| **5** | 38.69 | 23.59 | 37.75 |
| **7.5** | 38.44 | 23.54 | 38.02 |
| **10** | 25.25 | 21.07 | 53.69 |
| **12.5** | 24.30 | 22.44 | 53.25 |
| **15** | 25.04 | 23.33 | 51.63 |
| **17.5** | 26.87 | 25.80 | 47.33 |
| **0-End** | 7.98 | 92.02 | 0 |

| 3 (V=46%) | | | |
|---|---|---|---|
| **Pressure (bar)** | **np (%)** | **lp-1 (%)** | **lp-2 (%)** |
| **0-Start** | 27.32 | 72.68 | 0 |
| **1** | 71.79 | 28.20 | 0 |
| **2.5** | 78.62 | 21.39 | 0 |
| **5** | 74.16 | 9.61 | 16.22 |
| **7.5** | 18.35 | 8.78 | 72.88 |
| **10** | 0 | 2.35 | 97.65 |
| **12.5** | 0 | 2.06 | 97.94 |
| **15** | 0 | 2.09 | 97.91 |
| **17.5** | 0 | 2.11 | 97.98 |
| **0-End** | 26.91 | 73.09 | 0 |


A.
COMOC-2(V)
np
lp-1
lp-2
Volume (Å3)
Pressure (bar)
3800
3600
3400
3200
3000
2800
2600
0
2
4
6
8
10
12
14
16
18


B.
1 (V=81%)
np
lp-1
lp-2
Volume (Å3)
Pressure (Bar)
4400
4200
4000
3800
3600
3400
3200
3000
2800
2600
2400
0
2
4
6
8
10
12
14
16
18

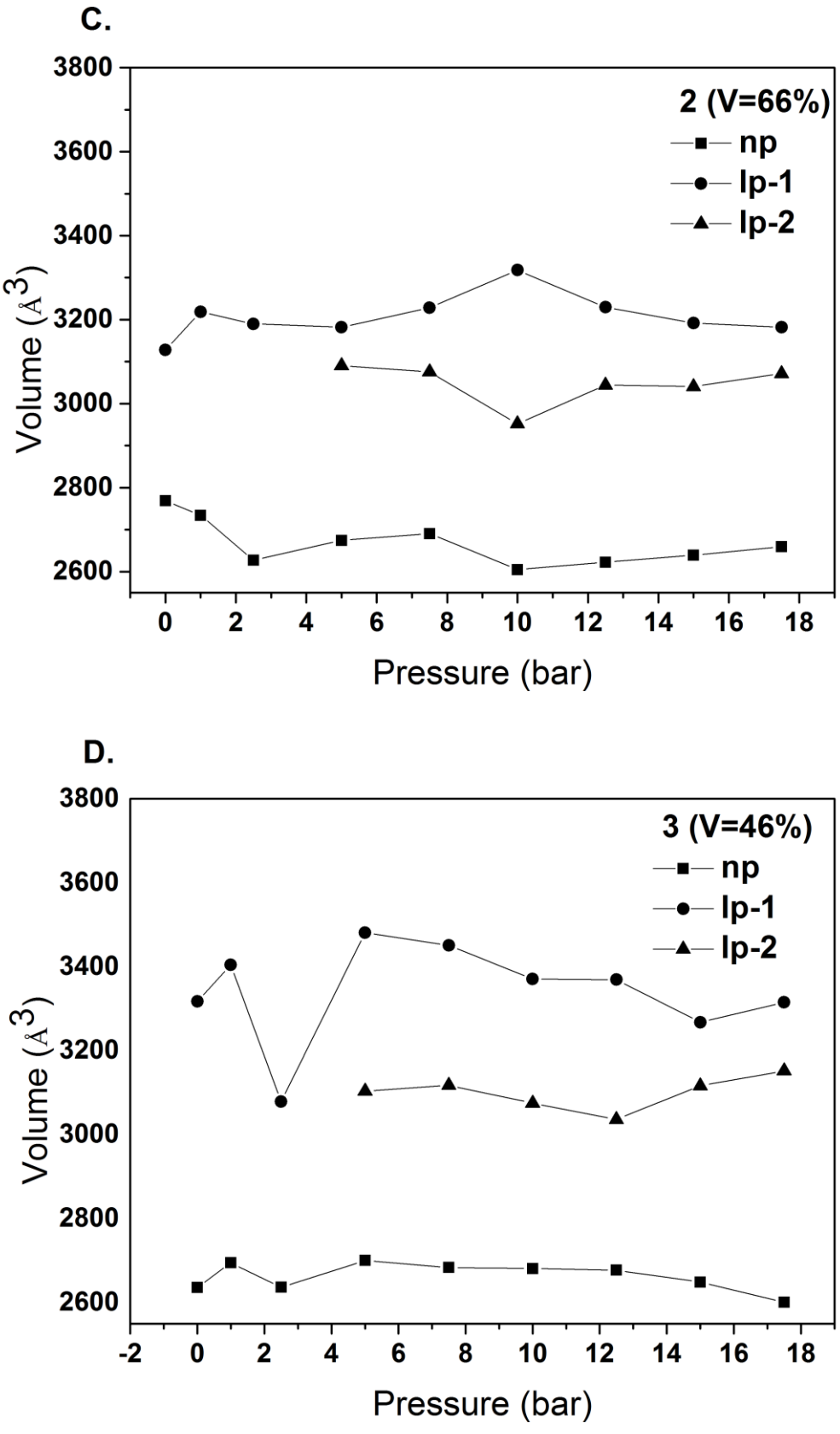



**Fig. S7 Evolution of the volume upon induced pressure for COMOC-2(V) in the three states: np, lp-1 and lp-2 for compounds (A) COMOC-2(V), (B) 1 (V=81%), (C) 2 (V=66%), (D) 3 (V=46%).**

**Table S5 Empirically determined lattice parameters for COMOC-2(V) at variable pressure for the three states (np, lp-1 and lp-2).**

| **np** | **COMOC-2(V)** | | | |
|---|---|---|---|---|
| Pressure (bar) | a(Å) | b(Å) | c(Å) | Volume (Å$^3$) |
| 0 | 21.26076 | 6.94049 | 18.7464 | 2766.2188 |
| 1 | 21.31003 | 7.20581 | 18.77984 | 2811.72213 |
| 2.5 | 21.51677 | 6.81396 | 18.92336 | 2774.43526 |
| 5 | 21.39871 | 7.32613 | 18.84329 | 2954.05672 |
| 7.5 | 21.40149 | 7.2396 | 18.8452 | 2919.84307 |
| 10 | 21.15791 | 7.11148 | 18.65899 | 2807.50955 |
| 12.5 | 21.16035 | 6.77265 | 18.6473 | 2672.37543 |
| 15 | 21.14909 | 6.85673 | 18.64139 | 2703.25432 |
| 17.5 | 21.13104 | 6.73041 | 18.63156 | 2649.7914 |
| 0 | 21.45219 | 6.98295 | 18.87741 | 2827.82582 |

| **lp-1** | **COMOC-2(V)** | | | |
|---|---|---|---|---|
| Pressure (bar) | a(Å) | b(Å) | c(Å) | Volume (Å$^3$) |
| 0 | 24.81274 | 6.85609 | 18.96316 | 3225.98309 |
| 1 | 24.92118 | 6.27611 | 18.98926 | 2970.07226 |
| 2.5 | 25.36087 | 6.52118 | 19.21855 | 3178.41864 |
| 5 | 25.23822 | 6.48038 | 19.16507 | 3134.50822 |
| 7.5 | 25.23969 | 6.60439 | 19.16683 | 3194.88172 |
| 10 | 24.892 | 6.941 | 19.01602 | 3285.50092 |
| 12.5 | 24.89255 | 7.19671 | 19.01626 | 3406.65788 |
| 15 | 24.89541 | 6.85651 | 19.01753 | 3246.20848 |
| 17.5 | 24.8952 | 7.15383 | 19.01744 | 3386.93053 |
| 0 | 25.1972 | 6.51932 | 19.15056 | 3145.8356 |

| **lp-2** | **COMOC-2(V)** | | | |
|---|---|---|---|---|
| Pressure (bar) | a(Å) | b(Å) | c(Å) | Volume (Å$^3$) |
| 0 | - | - | - | - |
| 1 | - | - | - | - |
| 2.5 | - | - | - | - |
| 5 | 25.03082 | 6.68856 | 18.99256 | 3179.73839 |
| 7.5 | 24.72185 | 6.85618 | 18.80828 | 3187.95555 |
| 10 | 24.32859 | 7.45649 | 18.56974 | 3368.65989 |
| 12.5 | 24.235 | 7.15328 | 18.62305 | 3228.48792 |
| 15 | 24.1958 | 7.326 | 18.64658 | 3305.61829 |
| 17.5 | 24.19832 | 7.49979 | 18.64974 | 3384.5981 |
| 0 | - | - | - | - |

**Table S6 Empirically determined lattice parameters for compound 1 (V=81%) at variable pressure for the three states (np, lp-1 and lp-2).**

| **np** | **1 (V=81%)** | | | |
|---|---|---|---|---|
| Pressure bBar) | a(Å) | b(Å) | c(Å) | Volume (Å$^3$) |
| 0 | 24.36559 | 7.23967 | 18.85828 | 3326.58065 |
| 1 | 24.09406 | 7.02418 | 18.73145 | 3170.13085 |
| 2.5 | 24.08016 | 6.68667 | 18.72494 | 3015.01532 |
| 5 | 24.08018 | 6.85448 | 18.72497 | 3090.68719 |
| 7.5 | 24.09787 | 6.81234 | 18.73329 | 3075.31224 |
| 10 | 24.14143 | 6.5196 | 18.75493 | 2951.88622 |
| 12.5 | 24.13205 | 6.72776 | 18.75053 | 3044.23506 |
| 15 | 24.11402 | 6.72797 | 18.74205 | 3040.67823 |
| 17.5 | 24.08003 | 6.81213 | 18.72492 | 3071.56635 |
| 0 | 24.20635 | 6.4329 | 18.62095 | 2994.09542 |

| **lp-1** | **1 (V=81%)** | | | |
|---|---|---|---|---|
| Pressure (bar) | a(Å) | b(Å) | c(Å) | Volume (Å$^3$) |
| 0 | 24.40585 | 7.18915 | 19.28844 | 3384.29579 |
| 1 | 24.73239 | 7.27758 | 18.84977 | 3392.8092 |
| 2.5 | 24.84442 | 7.49507 | 18.91306 | 3521.8144 |
| 5 | 24.83104 | 6.81069 | 18.94865 | 3204.5285 |
| 7.5 | 24.84032 | 6.81079 | 18.94972 | 3205.95548 |
| 10 | 24.8489 | 6.81068 | 18.95353 | 3207.65871 |
| 12.5 | 24.85663 | 6.6847 | 18.95696 | 3149.87389 |
| 15 | 24.8723 | 6.76813 | 18.96391 | 3192.3644 |
| 17.5 | 24.90486 | 6.80995 | 18.94745 | 3213.50095 |
| 0 | 24.78835 | 7.1942 | 19.0547 | 3398.06993 |

| **lp-2** | **1 (V=81%)** | | | |
|---|---|---|---|---|
| Pressure (bar) | a(Å) | b(Å) | c(Å) | Volume (Å$^3$) |
| 0 | - | - | - | - |
| 1 | - | - | - | - |
| 2.5 | - | - | - | - |
| 5 | 24.4933 | 7.36473 | 18.70872 | 3374.80053 |
| 7.5 | 24.37484 | 7.71365 | 18.63387 | 3503.52091 |
| 10 | 24.59738 | 7.8021 | 18.53873 | 3557.79312 |
| 12.5 | 24.59982 | 7.98057 | 18.53977 | 3639.73686 |
| 15 | 24.66804 | 7.89078 | 18.52633 | 3606.15083 |
| 17.5 | 24.66091 | 7.89067 | 18.52324 | 3604.45658 |
| 0 | - | - | - | - |

**Table S7 Empirically determined lattice parameters for compound 2 (V=66%) at variable pressure for the three states (np, lp-1 and lp-2).**

| **np** | **2 (V=66%)** | | | |
|---|---|---|---|---|
| Pressure (bar) | a(Å) | b(Å) | c(Å) | Volume (Å$^3$) |
| 0 | 21.24984 | 6.98274 | 18.66214 | 2769.12827 |
| 1 | 21.21767 | 6.89761 | 18.68024 | 2733.87524 |
| 2.5 | 21.17478 | 6.64604 | 18.66931 | 2627.30346 |
| 5 | 21.16352 | 6.7714 | 18.66157 | 2674.32879 |
| 7.5 | 21.1617 | 6.81333 | 18.66032 | 2690.47442 |
| 10 | 21.14769 | 6.60401 | 18.65079 | 2604.75878 |
| 12.5 | 21.15202 | 6.64572 | 18.65381 | 2622.17404 |
| 15 | 21.1548 | 6.68744 | 18.65603 | 2639.29555 |
| 17.5 | 21.1693 | 6.72937 | 18.66553 | 2659.01793 |
| 0 | 21.42646 | 6.51996 | 18.63665 | 2603.53221 |

| **lp-1** | **2 (V=66%)** | | | |
|---|---|---|---|---|
| Pressure (bar) | a(Å) | b(Å) | c(Å) | Volume (Å$^3$) |
| 0 | 24.6778 | 6.72915 | 18.86866 | 3128.2576 |
| 1 | 24.51629 | 6.98186 | 18.80235 | 3218.38701 |
| 2.5 | 24.56766 | 6.89748 | 18.82551 | 3190.07546 |
| 5 | 24.59724 | 6.85545 | 18.87203 | 3182.30163 |
| 7.5 | 24.63164 | 6.93983 | 18.88757 | 3228.63081 |
| 10 | 24.68159 | 7.10911 | 18.9101 | 3318.04365 |
| 12.5 | 24.63737 | 6.93919 | 18.89018 | 3229.53057 |
| 15 | 24.64438 | 6.85492 | 18.89334 | 3191.75319 |
| 17.5 | 24.59614 | 6.85524 | 18.87157 | 3181.97955 |
| 0 | 24.62285 | 7.02271 | 18.99525 | 3284.64171 |

| **lp-2** | **2 (V=66%)** | | | |
|---|---|---|---|---|
| Pressure (bar) | a(Å) | b(Å) | c(Å) | Volume (Å$^3$) |
| 0 | - | - | - | - |
| 1 | - | - | - | - |
| 2.5 | - | - | - | - |
| 5 | 24.08018 | 6.85448 | 18.72497 | 3090.68719 |
| 7.5 | 24.09787 | 6.81234 | 18.73329 | 3075.31224 |
| 10 | 24.14143 | 6.5196 | 18.75493 | 2951.88622 |
| 12.5 | 24.13205 | 6.72776 | 18.75053 | 3044.23506 |
| 15 | 24.11402 | 6.72797 | 18.74205 | 3040.67823 |
| 17.5 | 24.08003 | 6.81213 | 18.72492 | 3071.56635 |
| 0 | - | - | - | - |

**Table S8 Empirically determined lattice parameters for compound 3 (V=46%) at variable pressure for the three states (np, lp-1 and lp-2).**

| **np** | **3 (V=46%)** | | | |
|---|---|---|---|---|
| Pressure (bar) | a(Å) | b(Å) | c(Å) | Volume (Å$^3$) |
| 0 | 21.20742 | 6.64416 | 18.71067 | 2636.43729 |
| 1 | 21.04715 | 6.89759 | 18.56368 | 2694.97665 |
| 2.5 | 21.2187 | 6.64553 | 18.69943 | 2636.79766 |
| 5 | 21.20633 | 6.81314 | 18.69093 | 2700.49629 |
| 7.5 | 21.20514 | 6.77121 | 18.69011 | 2683.60884 |
| 10 | 21.19527 | 6.77121 | 18.68334 | 2681.38916 |
| 12.5 | 21.17781 | 6.77121 | 18.67137 | 2677.46259 |
| 15 | 21.12342 | 6.72949 | 18.63403 | 2648.82242 |
| 17.5 | 21.12837 | 6.60464 | 18.63743 | 2600.76311 |
| 0 | 21.20642 | 6.68598 | 18.7101 | 2652.82731 |

| **lp-1** | **3 (V=46%)** | | | |
|---|---|---|---|---|
| Pressure (bar) | a(Å) | b(Å) | c(Å) | Volume (Å$^3$) |
| 0 | 24.36544 | 7.23697 | 18.8127 | 3317.28109 |
| 1 | 24.26094 | 7.45472 | 18.82313 | 3404.32259 |
| 2.5 | 24.29706 | 6.79616 | 18.71967 | 3078.83696 |
| 5 | 25.80337 | 6.81216 | 19.8038 | 3481.04856 |
| 7.5 | 25.50821 | 6.89654 | 19.61647 | 3450.89914 |
| 10 | 25.42682 | 6.77045 | 19.57973 | 3370.66843 |
| 12.5 | 25.42015 | 6.77055 | 19.57648 | 3369.27381 |
| 15 | 25.18666 | 6.68711 | 19.40302 | 3267.97137 |
| 17.5 | 25.21635 | 6.77086 | 19.41817 | 3315.38926 |
| 0 | 24.37585 | 7.32359 | 18.81695 | 3359.17936 |

| **lp-2** | **3 (V=46%)** | | | |
|---|---|---|---|---|
| Pressure (bar) | a(Å) | b(Å) | c(Å) | Volume (Å$^3$) |
| 0 | - | - | - | - |
| 1 | - | - | - | - |
| 2.5 | - | - | - | - |
| 5 | 24.39725 | 6.76937 | 18.79152 | 3103.49368 |
| 7.5 | 24.27785 | 6.85374 | 18.73669 | 3117.67446 |
| 10 | 24.21992 | 6.76989 | 18.75443 | 3075.09055 |
| 12.5 | 24.21733 | 6.68635 | 18.75316 | 3036.61664 |
| 15 | 24.30298 | 6.81213 | 18.82503 | 3116.57946 |
| 17.5 | 24.28733 | 6.89672 | 18.81799 | 3152.06553 |
| 0 | - | - | - | - |

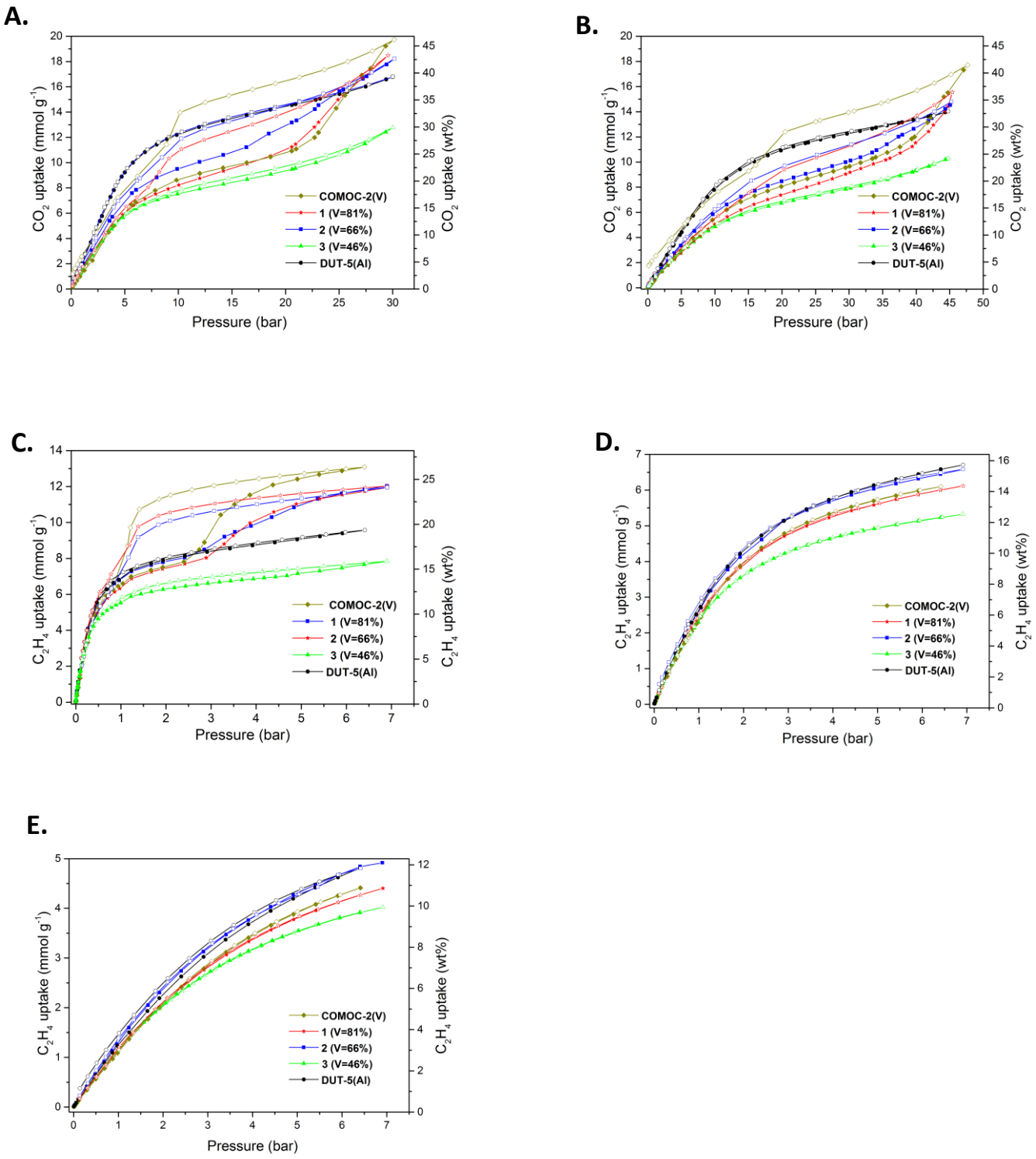



**Fig. S8 High-pressure carbon dioxide sorption measurement at (A) 273 K from 0-35 bar;(B) 303 K from 0-45 bar; high-pressure ethylene sorption measurements at (C) 228 K from 0-7 bar; (D) 273 K from 0-7 bar; (E) 303 K from 0-7 bar; for the compounds COMOC-2(V),DUT-5(Al), 1 (V=81%), 2 (V=66%) , 3 (V=46%). Infrared measurements show a higher amount of linker leftover also explaining the lower adsorption capacity for sample 3 (V=46%).**

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