Supporting Information

Porous dipeptide crystals as selective CO_2 adsorbents: experimental isotherms vs Grand Canonical Monte Carlo simulations and MAS NMR spectroscopy

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Experimental conditions

Materials. L-alanyl-L-valine (Ala-Val), L-valyl-L-alanine (Val-Ala), L-isoleucyl-L-valine (Ile-Val) and L-valyl-L-isoleucine (Val-Ile), L-alanyl-L-isoleucine (Ala-Iso), L-Isoleucyl-L-valine (Ile-Val), L-valyl-L-valine (Val-Val) and L-leucyl-L-serine (Leu-Ser) were purchased from Bachem (Switzerland). The samples underwent thermal treatment at 60°C under vacuum (10^{-3} mmHg) and the porous crystal structures of dipeptides were tested by powder X-ray diffraction. Carbon dioxide, methane and nitrogen adsorption-desorption isotherms for the porous materials were performed at 195K and room temperature using a Micromeritics analyzer ASAP 2050 (up to 10 atm) and a Micromeritics analyzer ASAP HD 2020 (up to 1 atm). The samples were previously outgassed overnight *in vacuo* (10^{-3} mmHg) at 70°C in a glass oven.

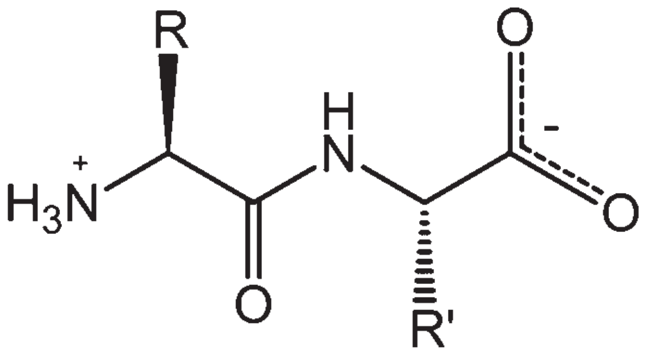
Solid-state two-dimensional (2D) $^{13}C\{^{1}H\}$ HETeronuclear chemical shift CORrelation (HETCOR) NMR experiments were performed on a Bruker Avance 300 MHz instrument operating at a static field of 7.04 T. Experiments were conducted at 240 K temperature under magic-angle spinning (MAS) conditions at 3 kHz by using a Bruker $^{1}H/X$ double-resonance MAS probehead with 7 mm zirconia rotors. 90° pulse for proton was 3.4 μs. Cross-polarization times of 5 ms were applied. ^{13}C MAS NMR measurements were performed by using a recycle delay of 3 s.

Computational. The Quantum Mechanical code CRYSTAL09 [1] was used to optimize the structure of the crystal models, at the DFT level with a medium-size basis set, 6-31G (d,p) [2]. Materials Studio package [3] was used for the simulation of adsorption isotherms and the calculation of isosteric heats, within the Grand Canonical Monte Carlo [4] method. The COMPASS Force Field [5] was chosen to match QM energy scan in model systems (vede infra); $2*10^{6}$ and $1*10^{7}$ steps were used for equilibration and production jobs, respectively.

Choice of the force field for Grand Canonical Monte Carlo simulations. Different FF implemented in Materials Studio package have been tested against high level Quantum Mechanical calculations. The most suitable was COMPASS as shown for instance in the following energy scans, referred to N_2 and CO_2 and a single Val-Ala dipeptide (Figure S5).

Models and simulations. Models of the eight crystal structures were created starting from single crystal diffraction data (CIF files) and optimizing the structures with CRYSTAL09, including periodic boundary conditions .

Some details of the structural properties are summarized in Table S1, where the crystal density (ρCRYST) and the total free volume (V_{FREE}) of each crystalline dipeptides are estimated using the suitable functions in the Materials Studio package: the density is compared to the experimental values reported in ref. 7.



Ala-Val	R=methyl	R'=isopropyl
Val-Ala	R=isopropyl	R'=methyl
Ile-Val	R=sec-butyl	R'=isopropyl
Val-Ile	R=isopropyl	R'=sec-butyl
Ile-Ala	R= sec-butyl	R'=methyl
Ala-Ile	R=methyl	R'=sec-butyl
Val-Val	R= sec-butyl	R'= sec-butyl
Leu-Ser	R=isobutyl	R'=hydroxymethyl

Scheme S1. Chemical formulas of the dipeptides.

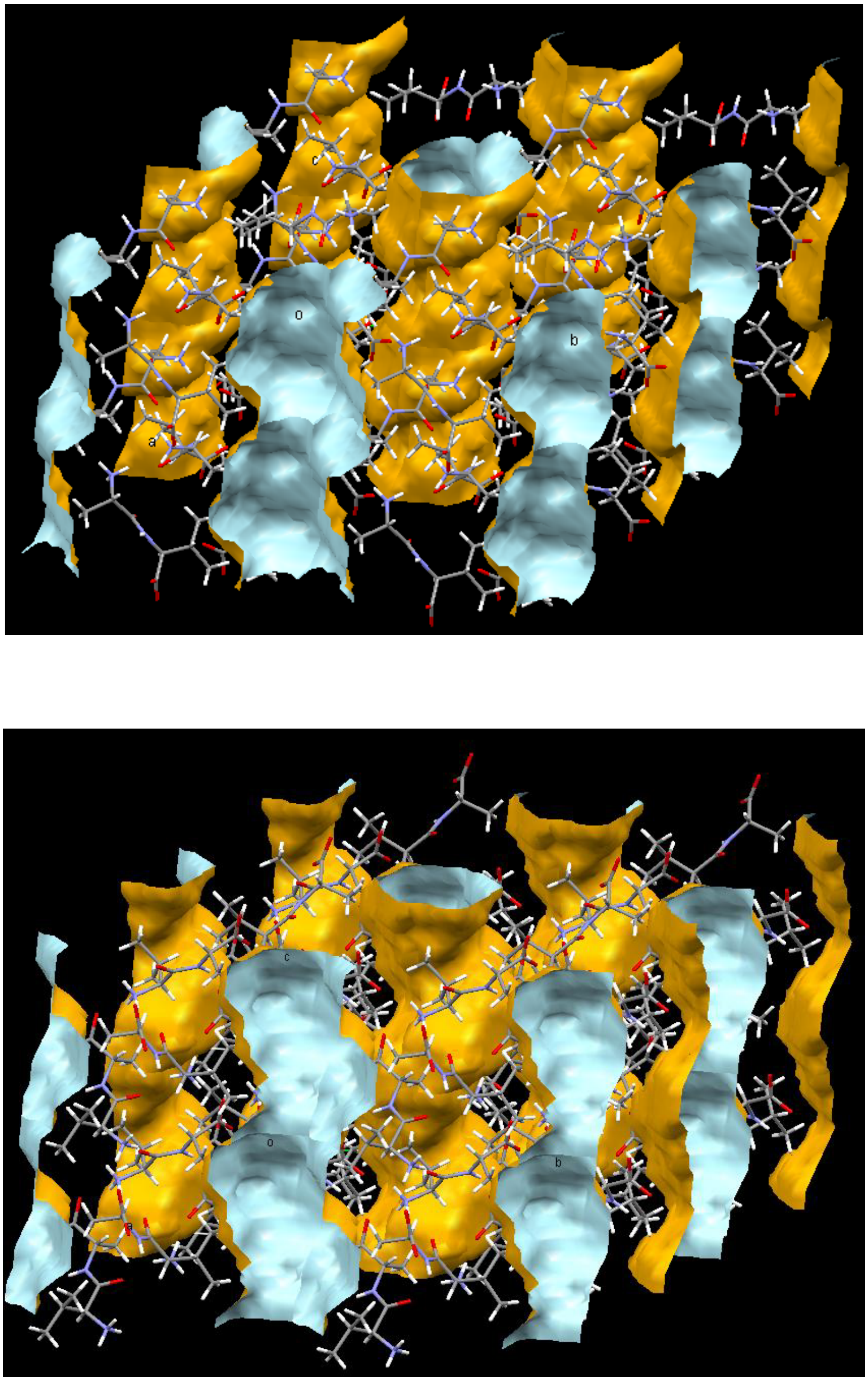


Figure S1. Crystal structures of porous Ala-Val (above) and Val-Ala (below) compounds showing the empty channels along the *c*-axis. The channels correspond to the space described a sphere with a radius of 1.2 Å and a grid spacing of 0.5 Å.

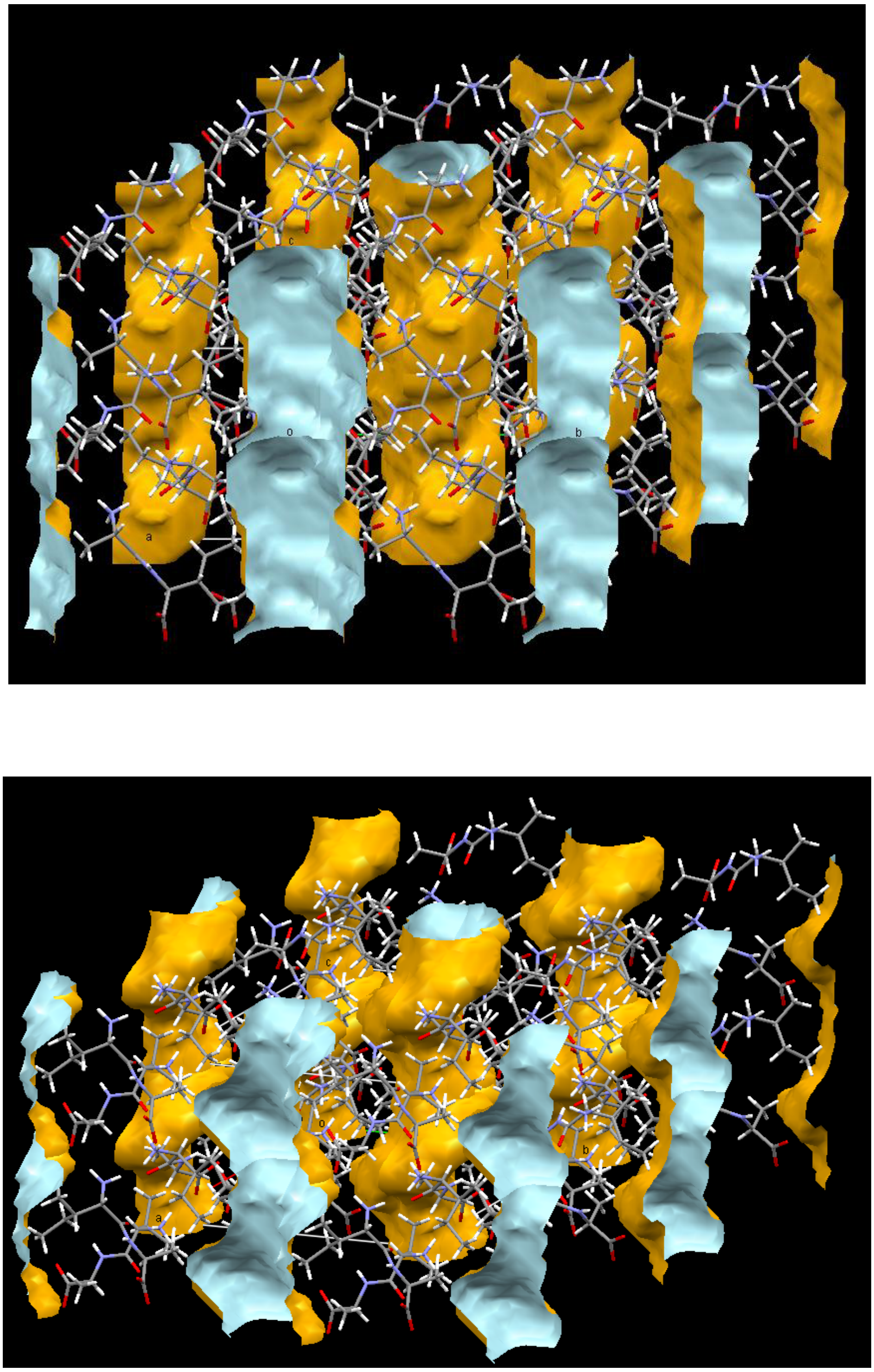


Figure S2. Crystal structures of porous Ala-Ile (above) and Ile-Ala (below) compounds showing the empty channels along the *c*-axis. The channels correspond to the space described a sphere with a radius of 1.2 Å and a grid spacing of 0.5 Å.

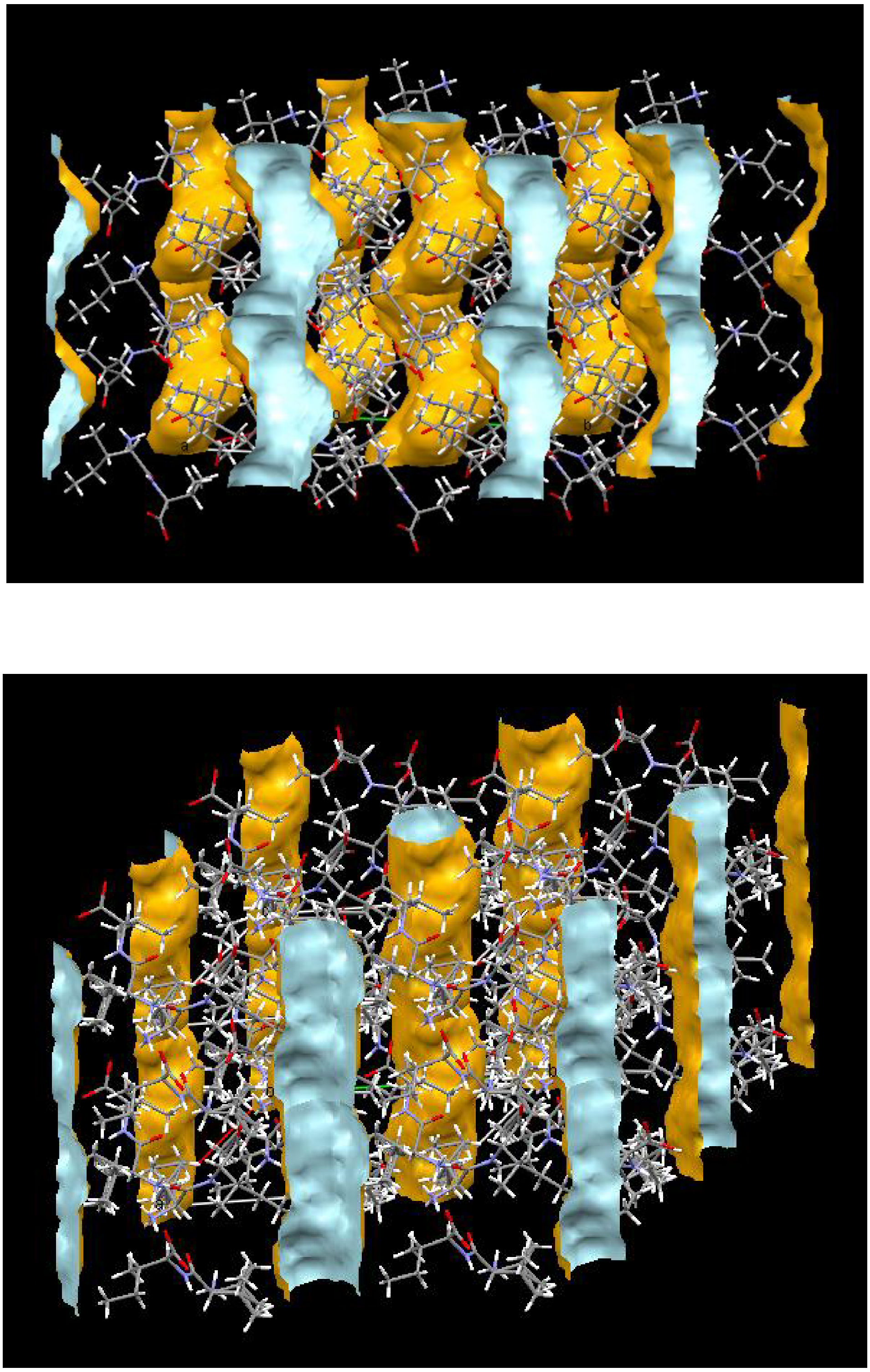


Figure S3. Crystal structures of porous Ile-Val (above) and Val-Ile (below) compounds showing the empty channels along the *c*-axis. The channels correspond to the space described a sphere with a radius of 1.2 Å and a grid spacing of 0.5 Å.

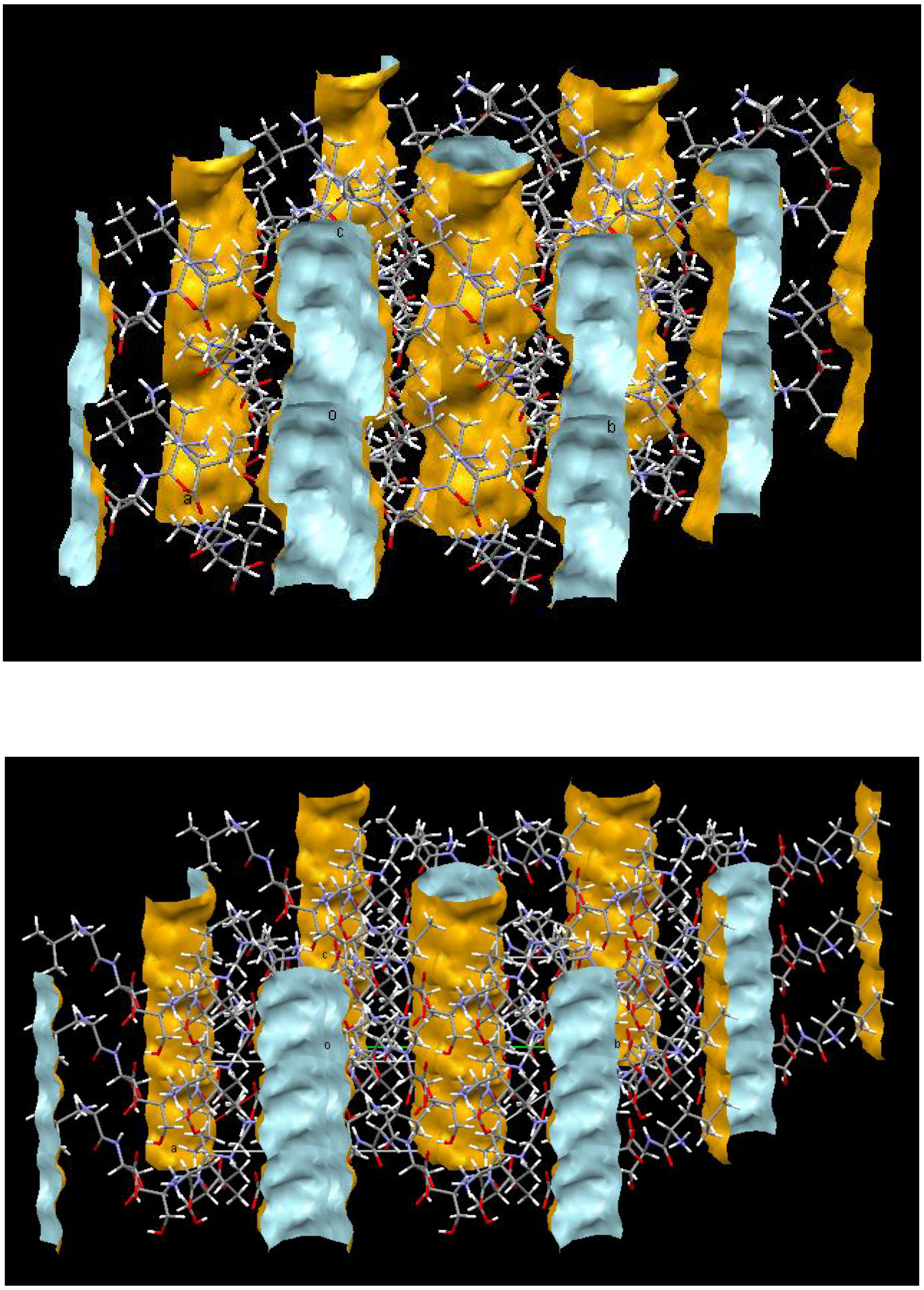


Figure S4. Crystal structures of porous Val-Val (above) and Leu-Ser (below) compounds showing the empty channels along the *c*-axis. The channels correspond to the space described a sphere with a radius of 1.2 Å and a grid spacing of 0.5 Å.

The crystal structures reported in Figures S1-S4 have been reported in the following references: S. A. Moggach, C. H. Gorbitz, J. E. Warren CrystEngComm 2010, 12, 2322; C. H. Gorbitz, E. Gundersen Acta Crystallogr., Sect. C: Cryst.Struct. Commun. 1996, 52, 1764; C. H. Gorbitz New J. Chem. 2003, 27, 1789; D. V. Soldatov, I. L. Moudrakovski, E. V. Grachev, J. A. Ripmeester J. Am. Chem. Soc. 2006, 128, 6737; Leu- Ser C. H. Gorbitz, N. Nilsen, K. Szeto, L. W. Tangen Chem. Commun. 2005, 4288.

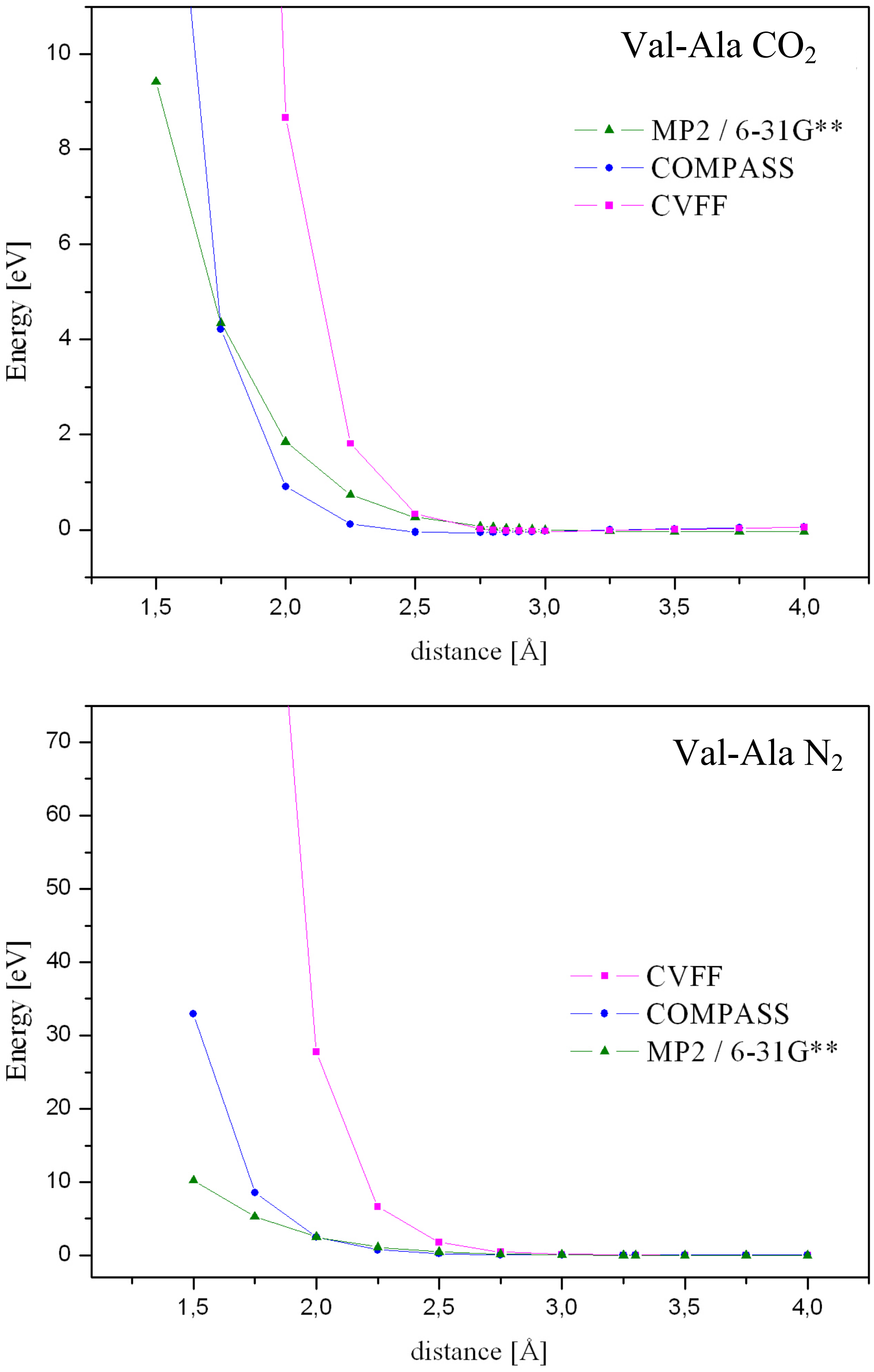


Figure S5. Energy scan for CO_2 (above) and N_2 (below) with Val-Ala dipeptide computed at MP2 level and with different force fields.

Table S1.

COMPOUNDS	ρ_{CRYS} (g/cm^3)^a	ρ_{CRYS} (g/cm^3)	V_{FREE} (cm^3/g)
Ala-Val	1.033	1.027	0.235
Val-Ala	1.027	0.972	0.292
Ala-Ile	1.119	1.079	0.165
Ile-Ala	1.106	1.041	0.214
Ile-Val	1.163	1.112	0.125
Val-Ile	1.176	1.129	0.113
Val-Val	1.132	1.076	0.168
Leu-Ser	1.238	1.171	0.100

a) from ref. n. 7

Adsorption isotherms were simulated with the Sorption module from the Materials Studio program with the COMPASS force field. The crystallographic cell, reduced to P_1 symmetry, was used as simulation box, using periodic boundary conditions to produce a homogeneous solid.

The simulated isotherms for N_2 are illustrated below, see text for CO_2 compared to experiments. In the case of CO_2 adsorption for Val-Ala, the comparison between calculated and measured isotherms has been extended up to 40 bar (Figure S6), to check the reliability of the simulation method, which results in excellent agreement with the experiment over all the pressure range.

[1] R. Dovesi, V.R. Saunders, C. Roetti, R. Orlando, C. M. Zicovich-Wilson, F. Pascale, B. Civalleri, K. Doll, N.M. Harrison, I.J. Bush, Ph. D'Arco, M. Llunell, *CRYSTAL09 User's Manual*, University of Torino, Torino, 2010.
[2] J.S. Binkley, J.A. Pople, W.J. Hehre, *J. Am. Chem. Soc*, 102, 1980.
[3] Materials Studio, 6.0 V; Accelrys, Inc., San Diego, CA, 2010
[4] D. Frenkel and B. Smith, Understanding Molecular Simulations, Academic Press, New York (2002).
[5] H. Sun, J. Phys. Chem. B, 1998, **102**, 7338.

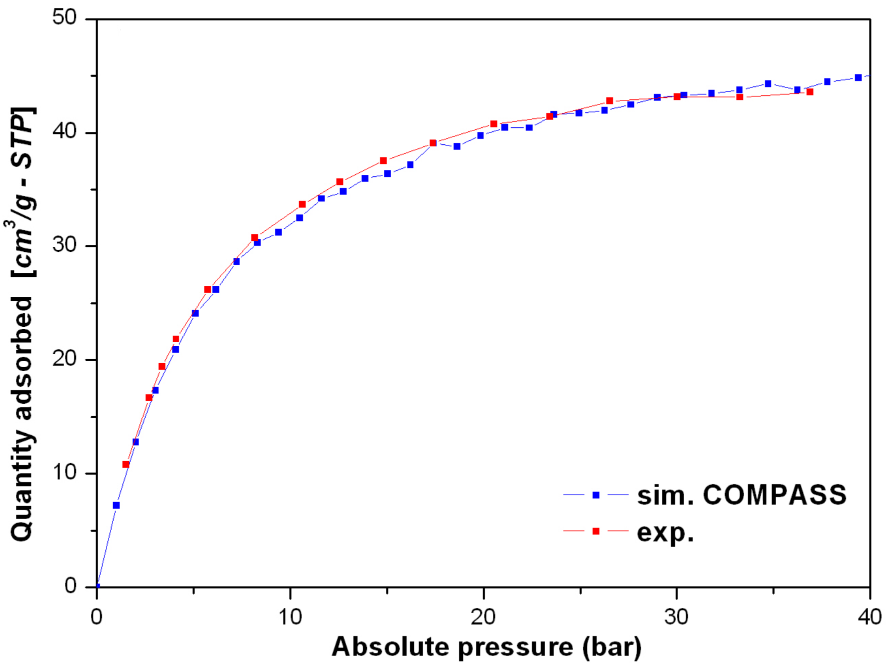


Figure S6. Experimental and GCMC CO_2 adsorption isotherms of Val-Ala at room temperature up to 40 bar.

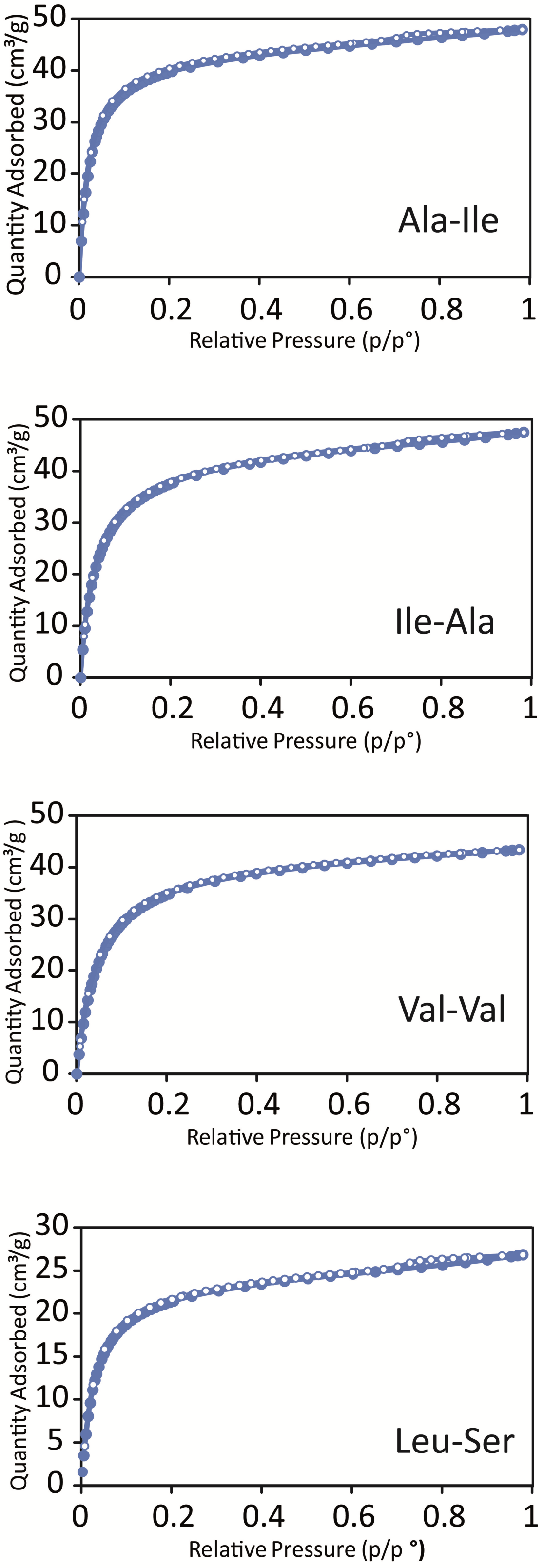


Figure S7. CO_2 adsorption isotherms of dipeptide crystals at 195K.

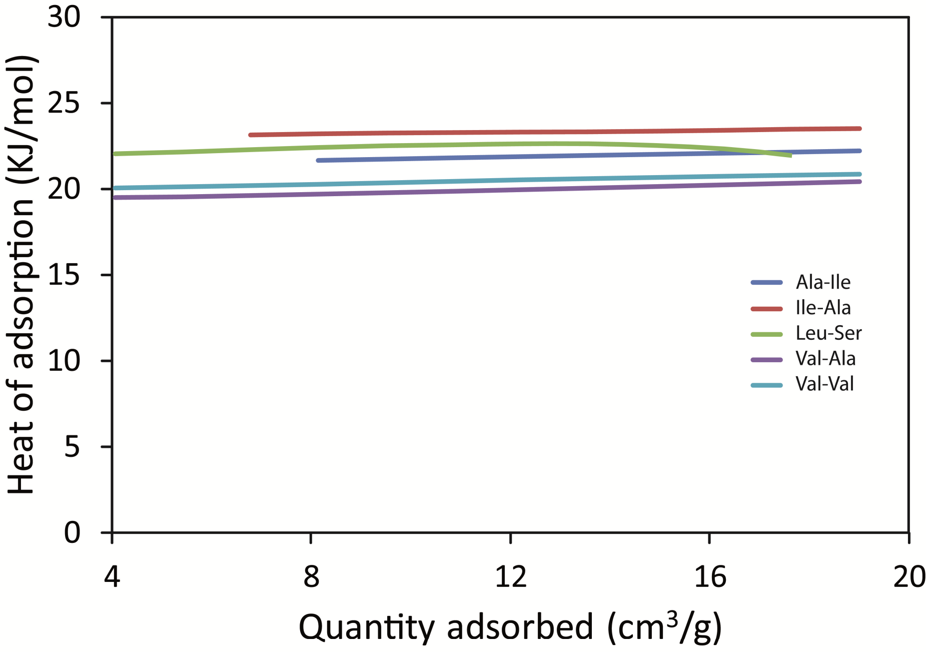


Figure S8. Isosteric heat of adsorption of CO_2 in porous dipeptide crystals.

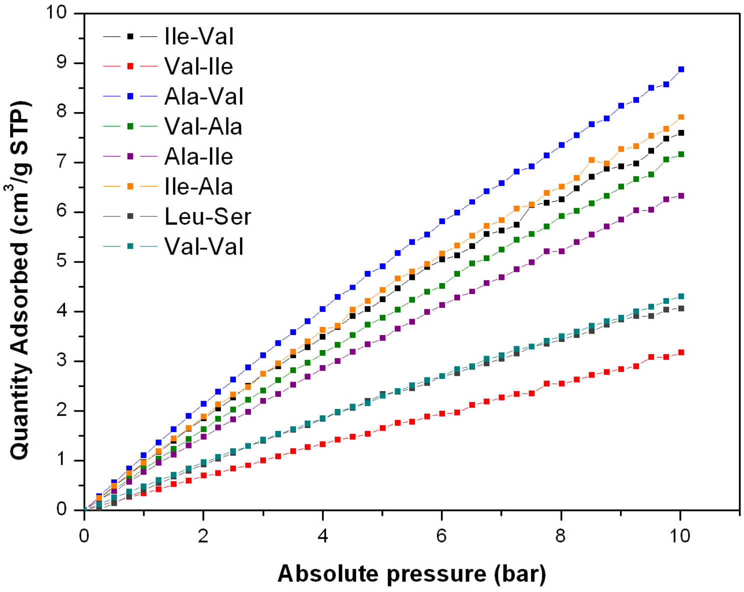


Figure S9. N_2 adsorption isotherms at room temperature and up to 10 bar as calculated by Grand Canonical Monte Carlo simulations.

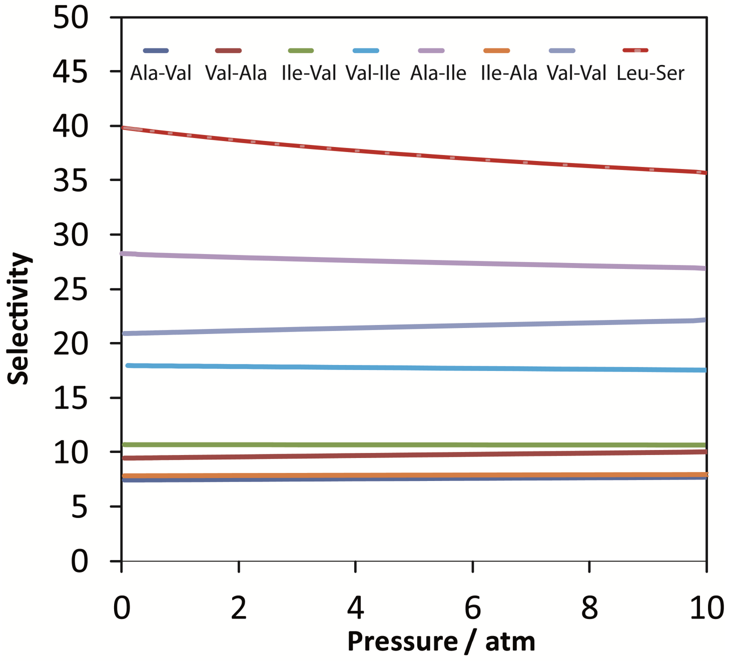


Figure S10. IAST selectivities of CO_2 over N_2 for 15:85 molar mixtures as determined from Grand Canonical Monte Carlo adsorption isotherms.

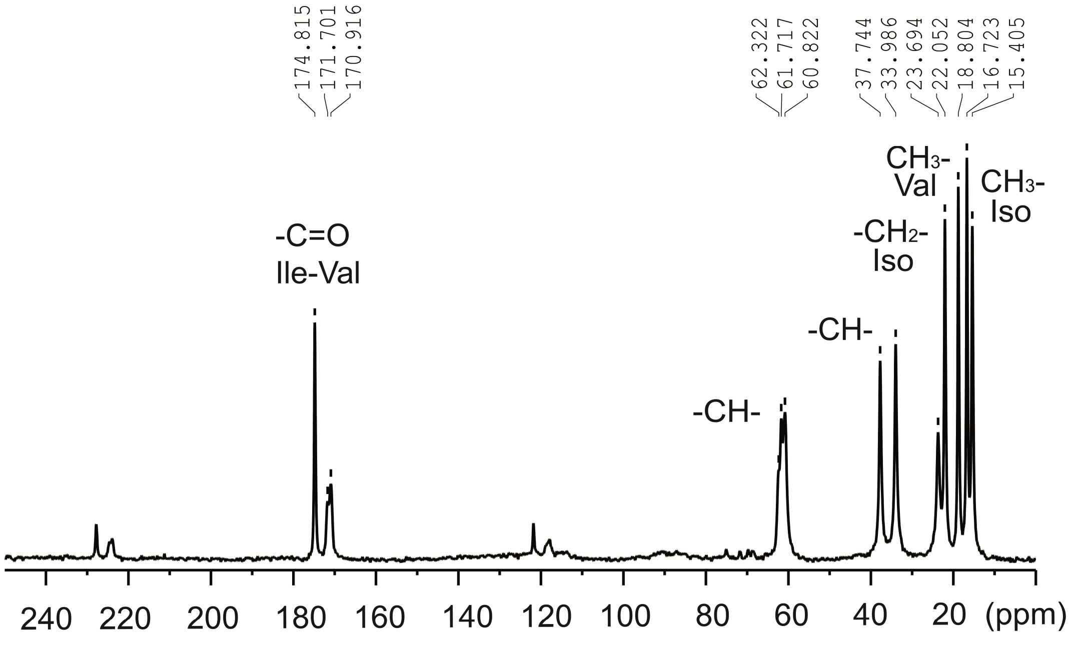


Figure S11. ^{13}C MAS NMR spectrum of porous Ile-Val compound (4 kHz spinning speed).

Breakthrough Experiments

Separation experiments were performed using a home-made “breakthrough” apparatus. The breakthrough apparatus (Figure S12) consists in:

- three gas lines for CO_2, CH_4 and He whose gas pressure and flow were controlled by pressure reducers and electronic controllers (Figure S12a);
- a mixing chamber (about 5 l) in which the gases were dosed to desired composition and pressure (Figure S12b);
- a rotary vacuum pump connected to the mixing chamber (Figure S12c);
- a glass column (10 cm height, 1 cm diameter) in which dipeptides are packed. It was connected to the mixing chamber and the gas cromatograph. The column can be by-passed (Figure S12d)
- a PC-operated gas chromatograph (Figure S12e).

In a typical experiment, 1-2 g of activated dipeptide (evacuated at 60 °C and 10^{-3} torr overnight) was packed in the glass column which was then connected to the system. Mixing chamber, gas lines and glass column were thoroughly evacuated (10^{-3} torr). In a first series of experiments, the activated microporous material was purged with helium and kept under a helium atmosphere (1.3-2 atm) before being invested by the CO_2/CH_4 gas mixture. Then, a second series of experiments were carried out without He gas, i.e. microporous material was kept *in vacuo* before absorption. In both cases, the column containing the dipeptide bed was isolated and CO_2 and CH_4 were allowed to enter the mixing chamber up to the desired composition (e.g. 1 : 1 equimolar composition at 2 atm) which was continuously monitored by the gas chromatograph. Then the gas was deviated through the column containing the peptide sorbent and the superincumbent gas phase was analyzed along with time to assess changes in composition with respect to gas feed. For comparison, the behavior of the separation system without the sorbent material (blank experiments) was tested. As expected, since no sorbent is present in the system, the relative amount of methane and carbon dioxide did not change throughout the entire experiment (Figure S13).

After performing the “breakthrough” experiments, the cartridge containing the saturated microporous crystals was purged with a stream of pure helium; carbon dioxide and methane contained in the micropores were released in a mixture with helium which acted as a carrier. In this case, the content of carbon dioxide was higher than methane, in agreement with preferential CO_2 sequestration during the previous selective adsorption step.

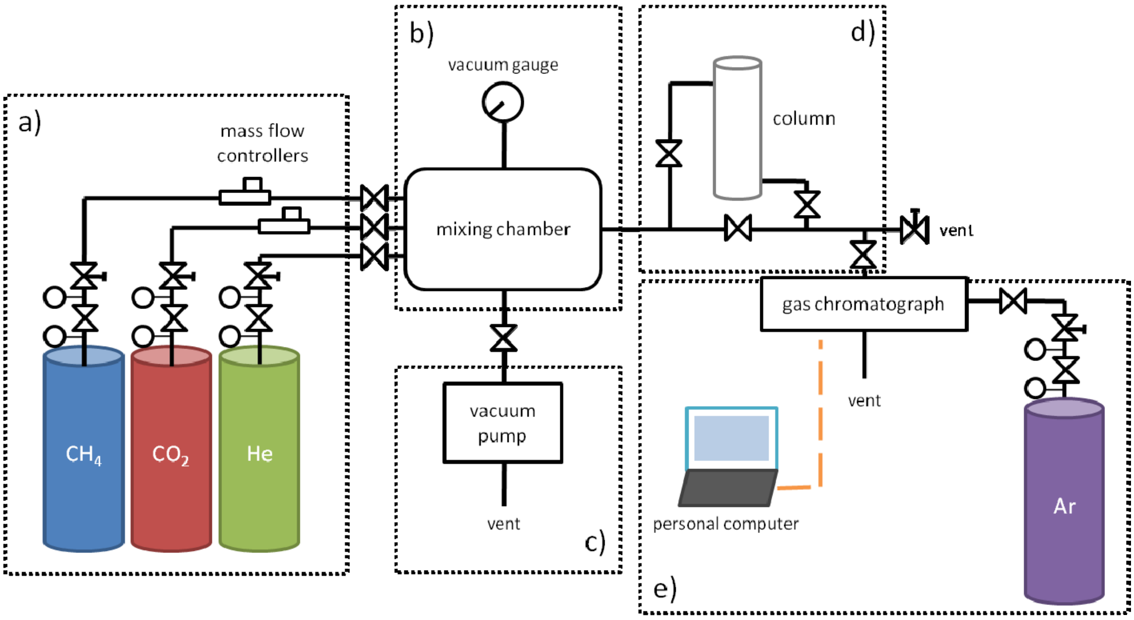


Figure S12. Scheme of “breakthrough” apparatus. a) methane, cabon dioxide and helium gas lines provided with pressure reducers and mass flow controllers, b) mixing chamber, c) vacuum pump, d) glass column holding microporous sorbent and e) gas analyzer (gas chromatograph, PC, carrier line)

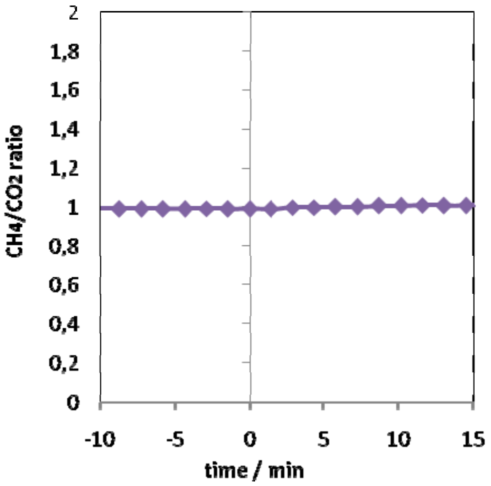


Figure S13. “Breakthrough” blank run without helium. Methane (blue diamonds) and carbon dioxide (red squares) percentage composition is plotted against time. Methane/carbon dioxide molar ratio is unchanged.

The whole separation process is sketched in Figure S14. At the beginning of the experiment the nanoporous material was either held in a “inert” gas atmosphere or in vacuum (Figure S14a); then the material was invested by the gas mixture flow and carbon dioxide was selectively physiadsorbed in the porous dipeptide while methane remained preferentially in the gas phase (Figure S14c). During the desorption process, a helium stream was passed through the dipeptide bed, and an excess of carbon dioxide was detected.

The reversibility of the process was maintained over all the experiments and the dipeptide crystals tolerated more than fifty cycles of gas exposure followed either by helium purge or vacuum treatment without losing appreciably their sorption capabilities.

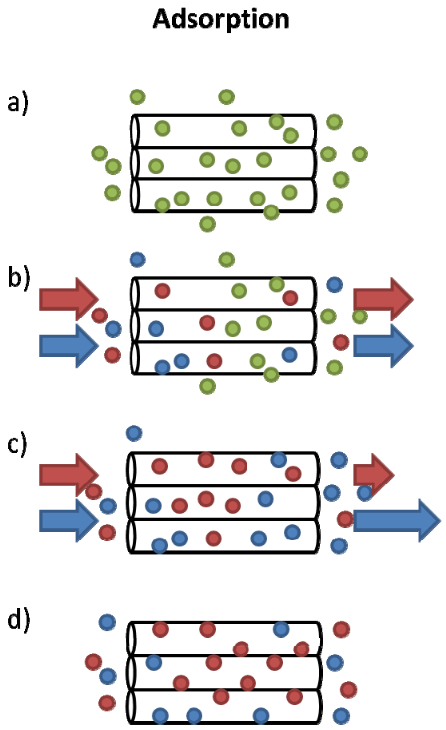


Figure S14. Adsorption process: a) dipeptide crystalline powders in He atmosphere, b) equimolar CO_2/CH_4 stream passing through the dipeptide-containing bed, c) preferential sorption of CO_2 over CH_4 and enrichment of outlet gas in methane, d) dipeptide crystalline powder containing larger amount of CO_2 in the nanopores.