

# Methane, carbon dioxide and hydrogen storage in nanoporous dipeptide-based materials†

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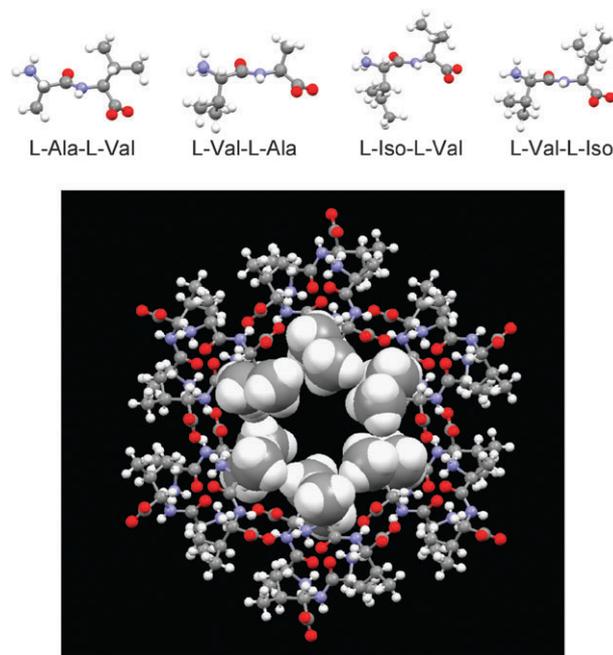
**Dipeptide crystals containing nanochannels of various sizes show remarkable and selective absorption of methane, carbon dioxide and hydrogen.**

Increasing toxic gas emissions and energy demand are dramatic issues today for the planet. Thus, the absorption of important gases, like carbon dioxide, methane and hydrogen, in porous materials for energetic and environmental reasons is a challenging research field which can lead to benefits for the future.<sup>1</sup> A large variety of strategies exploiting materials of widely differing nature and structure have been used. Among the most traditional examples we can enumerate zeolites and clays, as well as carbonaceous derivatives.<sup>2</sup> Recently, metal-organic frameworks, mesoporous metal oxides, porous organosilicas, organic polymers and crystals<sup>3</sup> have emerged as valid alternatives for ameliorating storage capacity and selectivity. Each class presents significant prototypes with relevant advantages towards specific achievements. However, new strategies are necessary for future breakthroughs. Biological molecules (or biological building blocks) are promising tools for constructing a variety of unrealized structures in porous materials. In principle, they offer the possibility of exploiting targeted interactions and are readily available, biocompatible and biodegradable.<sup>4</sup> Biological systems containing permanent pores in the form of nanochannels can offer a multiplicity of specific functions but their exploitation as materials is still rare.<sup>5</sup> Recently, permanent porosity has been recognized in dipeptide architectures.<sup>6</sup> The high number of peptide monomers, together with their sequential arrangement, has enabled the setting up of an efficient strategy aimed at forming robust porous materials with channels of tunable size, shape and helicity.<sup>7</sup> Herein, we propose, for the first time, the use of channel-forming dipeptides for the absorption of environmentally and energetically relevant gases such as carbon dioxide, methane and hydrogen. Although the crystalline scaffold is held together by a network of hydrogen bonds, stable nanochannel pores with internal hydrophobic surfaces are generated there. The hydrophobicity combined with the suitable cross-section makes them excellent candidates for creating an ideal cradle that encapsulates, efficiently and selectively, guest gases. For this reason, L-alanyl-L-valine (AV), L-valyl-L-alanine (VA), L-isoleucyl-L-valine (IV) and

L-valyl-L-isoleucine (VI) were chosen with the expectation that they could raise selectivity and gas storage ability. The soft nature of the interactions guarantees reversibility of the process and triggered delivery simply by reducing gas pressure.

The four crystalline dipeptides (AV, VA, IV and VI) present a hexagonal crystalline arrangement (space group  $P6_1$ ) forming one-dimensional chiral channels (Fig. 1) (ESI†).<sup>6,7</sup> The key feature is the presence of channels with distinct diameters of 5.0, 4.7, 3.9 and 3.7 Å (for AV, VA, IV and VI, respectively) and highly hydrophobic walls, as the methyl groups point towards the axes of the channels.

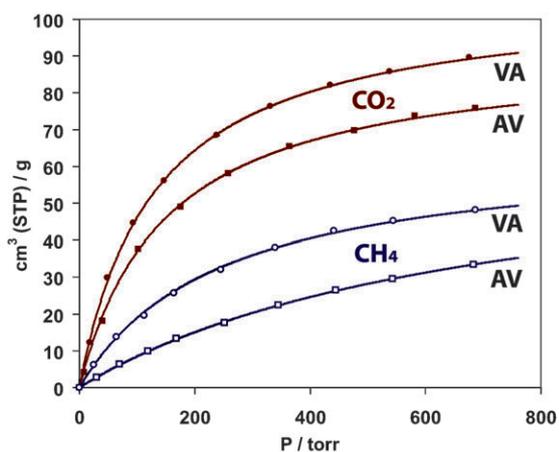
The adsorption isotherms of CO<sub>2</sub> and CH<sub>4</sub> for AV and VA at 195 K and 1 atm are presented in Fig. 2. The curves can be fitted by a type I Langmuir equation that is typical of microporous systems. The storage capacity of VA to absorb carbon dioxide is already remarkable at 250 torr and reaches a value of 91 cm<sup>3</sup> (STP) g<sup>-1</sup> at 1 atm. This corresponds to 4.6 molecules of gas per unit cell, indicating the virtually complete filling of the available volume in the structure. The measured capacity of 18%wt and the estimated maximum filling of 20%wt exceed the capacity reported for silicalite.<sup>8</sup> The carbon dioxide isotherm for AV follows a parallel



**Fig. 1** Chemical structures of L-alanyl-L-valine (AV), L-valyl-L-alanine (VA), L-isoleucyl-L-valine (IV) and L-valyl-L-isoleucine (VI) (above). Crystal structure of AV showing the open hydrophobic channel of 5 Å (below).<sup>6</sup>

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**Fig. 2** Adsorption isotherms of carbon dioxide (full circles and squares) and methane (open circles and squares) at 195 K for AV and VA. Experimental data are fitted by a Langmuir type I curve.

behavior with a slightly lower sorption capacity that reaches  $78 \text{ cm}^3 \text{ (STP) g}^{-1}$  (15%wt). The higher capacity of VA over AV is consistent with the larger volume available for VA, realized by the channel helicity that develops in the crystalline structure albeit its narrower channel cross-section.

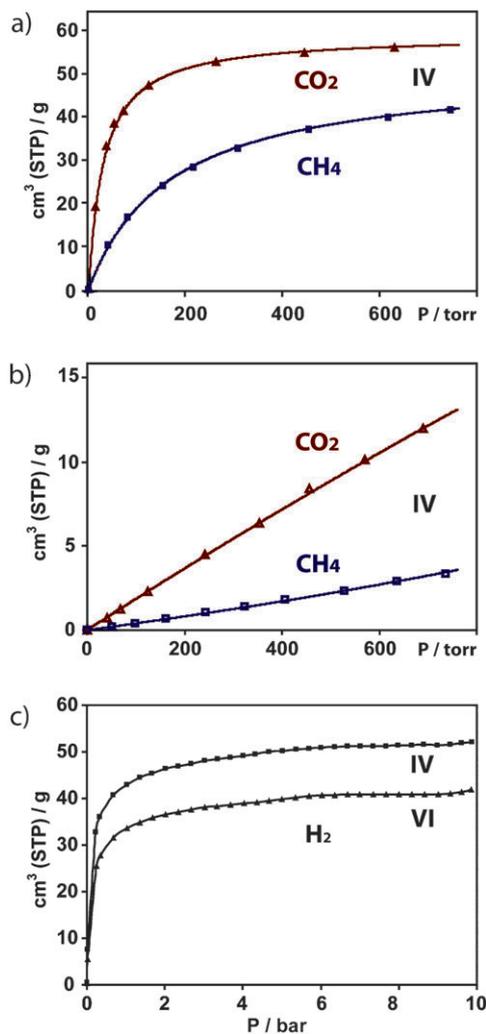
On the basis of a storage limit beyond which close van der Waals contacts lead to direct interaction among the gas molecules within the nanochannels, we can conclude that most of the space available for guests is occupied, indicating high storage capacity and large host-guest interaction. Furthermore, the absorption values of  $\text{CO}_2$  are even remarkable under the extremely mild conditions of ambient temperature and pressure, reaching, in the case of VA, 30 litres of  $\text{CO}_2$  per litre of host ( $\text{ESI}^\dagger$ ),<sup>9</sup> which exceeds the outstanding performance of the recently proposed ZIF-100 (28 L/L).<sup>10</sup> Also, methane is efficiently stored in dipeptide-based nanoporous systems, and up to 50 and  $35 \text{ cm}^3 \text{ (STP) g}^{-1}$  at 195 K and 1 atm are exhibited for VA and AV, respectively (Fig. 2). In other terms, 2.4 methane molecules per unit cell of VA (0.6 mol/mol) are captured by the porous crystal already at 1 atm, and a full loading of 2.8 molecules per unit cell can be reached at 5 atm. The value of  $50 \text{ cm}^3 \text{ g}^{-1}$  for VA is comparable with or exceeds the values for inorganic zeolites containing 1D channels with a similar diameter and is attractive for methane storage even at the moderate pressure of 1 atm.<sup>2,11</sup> The full capacity value, obtained by using the Langmuir equation to fit  $\text{CH}_4$  adsorption data, reaches 4.6%wt for VA ( $63 \text{ cm}^3 \text{ g}^{-1}$ ). In addition, the methane storage value of VA nanoporous material under mild conditions of room temperature and pressure ( $\text{ESI}^\dagger$ ) is particularly high compared with that of inorganic zeolites, organic zeolites and a few MOFs.<sup>11,12</sup>

The evaluated adsorption energies at low coverage (0.1 mol/mol) for  $\text{CO}_2$  and  $\text{CH}_4$  are 13 and  $9 \text{ kJ mol}^{-1}$ , respectively (for both VA and AV). This suggests that a selective  $\text{CO}_2$  over  $\text{CH}_4$  absorption can occur, as shown by  $\text{CO}_2/\text{CH}_4$  absorption ratios of 2–2.5 at 195 K. However, a higher degree of selectivity and milder temperature conditions are desirable. This is particularly critical for the prominent industrial process of separating  $\text{CO}_2$  from  $\text{CH}_4$ . Higher selectivity could, in principle, be achieved by using tighter

channels, which would result in a more efficient discrimination between the two gases. Indeed, the dipeptide-based biozeolite family offers a large variety of porous materials with channels of tailored cross-sections. The small channel diameter of IV (3.9 Å) was successfully used for the target. Fig. 3 shows the adsorption isotherms of  $\text{CO}_2$  and  $\text{CH}_4$ : at 195 K and already at 250 torr the  $\text{CO}_2$  absorption reaches the value of  $53 \text{ cm}^3 \text{ (STP) g}^{-1}$  (90% maximum loading), but even at pressures as low as 50 torr the absorption is extremely efficient. Instead,  $\text{CH}_4$  sorption with increasing pressure presents a slower slope, therefore the  $\text{CO}_2/\text{CH}_4$  ratio becomes greatly advantageous below 50 torr, reaching values as high as 3.5–5.

Such a high selectivity ratio is realized even at room temperature and is retained up to atmospheric pressure (Fig. 3b), indicating that this porous system could be useful for practical applications in methane purification. This selectivity is competitive with that of recently proposed porous materials.<sup>10,13</sup>

Moreover, the high isosteric energies determined here for IV, namely 23 and  $19 \text{ kJ mol}^{-1}$  for  $\text{CO}_2$  and  $\text{CH}_4$  respectively, guarantee a strong capture of the individual molecules due to



**Fig. 3** Adsorption isotherms of carbon dioxide and methane in IV at (a) 195 K and (b) 298 K. (c) Hydrogen adsorption isotherms at 77 K of IV and VI up to 10 bar.

the tight fit between the gas size (kinetic ratios of 3.6 Å for CO<sub>2</sub> and 3.9 Å for CH<sub>4</sub>) and the channel cross-section of 3.9 Å, supporting the predictions that narrow channels can lead to higher affinity.<sup>14</sup> Multiple van der Waals interactions between the hydrophobic walls and the gas result in overall stabilization. The adsorption energy for CH<sub>4</sub> is one of the highest values reported so far (microporous polymers 22 kJ mol<sup>-1</sup> and MOFs with entatic metal centers 23 kJ mol<sup>-1</sup>)<sup>3,15</sup> and exceeds those of other porous materials (IRMOF-6 12.1 kJ mol<sup>-1</sup> and MIL53 17 kJ mol<sup>-1</sup>).<sup>16</sup> It falls within the range considered optimal for the reversible storage and release process.

The above results prompted us to tackle the challenging issue of hydrogen storage in dipeptide-based materials. Hydrogen showed a particular affinity for the IV and VI as shown by the adsorption isotherms run up to 10 atm (Fig. 3c). The type I Langmuir profile at 77 K reached maximum loading already at pressures close to 1 atm, and an absorption capacity of 52 cm<sup>3</sup> (STP) g<sup>-1</sup> for IV that corresponds to 0.5 mol/mol. Thus IV absorbs as many moles of hydrogen as it does of methane (0.5 mol/mol at 195 K and 1 atm), indicating a remarkable affinity for this light gas. This is a particular achievement given the absence of metal sites,<sup>1</sup> and the overall hydrophobic nature of the narrow-channel walls that are lined with methyl groups, thus providing a suitable environment for molecular hydrogen to be hosted. The isosteric heat of adsorption is 5.0 kJ mol<sup>-1</sup> for both IV and VI, which is competitive with the values measured for recently proposed microporous carbons (3.9–5.2 kJ mol<sup>-1</sup>), zeolite-like MOFs (5.1 kJ mol<sup>-1</sup>) and IRMOF-1 (5.1 kJ mol<sup>-1</sup>).<sup>12,17</sup> The complete overlapping of the adsorption/desorption curves demonstrates the fully reversible behavior.

In conclusion, our findings revealed the application of nanoporous dipeptides for adsorption, separation and storage of gases, such as methane, carbon dioxide and hydrogen. This is the first time that the strategy of using crystals of biomolecules showing permanent porosity has been proposed to capture relevant gases for energetic applications. The proper fit of the crystalline nanochannels to the size of the gases of interest makes them an efficient alternative to other porous materials, especially molecular crystals and zeolites. With L-isoleucyl-L-valine we were able to attain remarkable selectivity even at atmospheric pressure, supporting the idea that this crystalline powder can find application in methane purification from carbon dioxide. The present approach suggests challenging perspectives for the use of biomaterials in novel applications.

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