A double helix of opposite charges to form channels with unique CO₂ selectivity and dynamics†

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Porous molecular materials represent a new front in the endeavor to achieve high-performance sorptive properties and gas transport. Self-assembly of polyfunctional molecules containing multiple charges, namely, tetrahedral tetra-sulfonate anions and bifunctional linear cations, resulted in a permanently porous crystalline material exhibiting tailored sub-nanometer channels with double helices of electrostatic charges that governed the association and transport of CO₂ molecules. The charged channels were consolidated by robust hydrogen bonds. Guest recognition by electrostatic interactions remind us of the role played by the dipolar helical channels in regulatory biological membranes. The systematic electrostatic sites provided the perfectly fitting loci of complementary charges in the channels that proved to be extremely selective with respect to N₂ (S = 690), a benchmark in the field of porous molecular materials. The unique screwing dynamics of CO₂ travelling along the ultramicropores with a step-wise reorientation mechanism was driven by specific host–guest interactions encountered along the helical track. The unusual dynamics with a single-file transport rate of more than 10⁶ steps per second and an energy barrier for the jump to the next site as low as 2.9 kcal mol⁻¹ was revealed unconventionally by complementing in situ C¹³ NMR anisotropic line-shape analysis with DFT modelling of CO₂ diffusing in the crystal channels. The peculiar sorption performances and the extraordinary thermal stability up to 450 °C, combined with the ease of preparation and regeneration, highlight the perspective of applying these materials for selective removal of CO₂ from other gases.

Introduction

The manufacture of materials with permanent porosity is one of the major challenges in current research. This goal can be achieved through various strategies that promote the formation of covalent and metal–organic frameworks as well as molecular architectures. They are diversified by their greater or lesser tendency to form stable structures and their degree of crystalline periodicity. Highly crystalline porous molecular materials can be constructed easily by spontaneous assembly of precursor molecules, provided that their shapes and functionalities are adequately designed. Indeed, fully organic porous materials can be assembled by means of soft and reversible interactions enabling the highest modularity, processability and large single-crystal formation. Their excellent performances in gas capture and interaction with chemical and physical stimuli have been explored in recent years.

Organic functions of opposite charges on complementary molecules promote intense attractive interactions, and reciprocal recognition such as positively charged ammonium groups with carboxylic and sulfonic anions; thus, electrostatic interactions can be exploited to sustain robust molecular frameworks. Additionally, electrostatic charges can be exposed to the pores, making it possible to expand research towards unexplored developments.

In our approach, multiple-charged functional groups protruding in the space produce directional interactions, favourable to the design of porous molecular architectures, forming programmable charged channels. In general, the shape and symmetry of the building blocks to construct porous frameworks must be taken into account: specifically, highly symmetric and rigid tetrahedral struts (S₄ point group) constitute a primary element, which sustained permanently porous materials and yielded very high surface areas.

Biological systems are promising sources for the formation of sub-nanometer channels for the transport of molecules and
ions, wherein the electrostatic distribution of charges on the channel walls and steric factors play a strategic role for building useful functions. By analogy, we have engineered a permanently porous 3D molecular architecture containing sub-nm channels formed by a double helix with two intertwined and alternatively charged ribbons, characteristic of transmembrane channels. It was generated by the assembly of tetrahedral and tetrafunctional \(4,4',4'',4'''\)-methane tetrabenzenesulfonate (TBS) anions and a bifunctional cation \(1,4\)-diamidiniumbenzene (DAB) and was found to be highly stable. The porous structure was capable of reversibly absorbing relevant gases such as \(\text{CO}_2\) and \(\text{CH}_4\) with an exceptional \(\text{CO}_2/\text{N}_2\) selectivity of 690 owing to the tight fitting and the complementary electrostatic pattern of the sub-nm channels. The direct detection of \(\text{CO}_2\) pervading the porous molecular framework was provided by multinuclear 2D MAS NMR spectra, depicting the exceptional \(\text{CO}_2\)-matrix association in the properly fitting pockets. Furthermore, the anisotropic \(^{13}\text{C}\) NMR variable-temperature lineshapes unveiled the unique coordinated rotation and translation dynamics of \(\text{CO}_2\) while it jumps from one site to the next, following the helical charge patterning of the channel. Intriguingly, \(\text{CO}_2\) molecules receive the orientational encoding from the nanochannel sites at each diffusion turn of the screwing motion. Thus, by this unconventional means, we could establish the transport rate of a single gas molecule that is as fast as a million steps per second, corresponding to guest diffusion rates observed in biological channels. DFT calculations and Molecular Dynamics (MD) supported the NMR determination of the preferred arrangement and the energy landscape perceived by \(\text{CO}_2\) exploring the channels.

Results and discussion
Fabrication of charged sub-nanometer channels
The organotetrasulfonate TBS self-assembled with organo-diamidinium DAB to form needlelike single crystals suitable for X-ray analysis (ESI†). After guest removal by thermal treatment under vacuum at 150 °C, the 3D architecture is maintained, yielding a new crystalline porous organosulfonate–amidinium salt (CPOS-5) (Fig. 1). It crystallizes in the tetragonal \(I4_1\alpha\) space group, which contains a quarter of TBS (a phenyl-SO\(_3\)-group) and half of DAB in the asymmetric unit (molecular formula equal to TBS[DAB]\(_2\)). A 4-fold rotoinversion axis crosses the central carbon (C1), which orients four sulphonate groups along the vertices of a tetrahedron. Hence, organosulfonate anions and organoamidinium cations, driven by hydrogen bonds,
assemble in a double helix of electrically charged ribbons (Fig. 1C). Both negatively and positively charged moieties draw alternatively charged helices that lead to the formation of 1D-channels (Fig. 1D), running parallel to the c-axis. The empty channels with a cross-section of $5.3 \times 6.8 \, \text{Å}^2$ generate a porosity of 743.03 $\text{Å}^3$ per cell corresponding to 14.6% of the cell volume (radius of the rolling sphere = 1.2 Å). The $^{13}$C MAS NMR spectrum confirmed the absence of guests in the cavities (ESI†). The porous compound exhibits high stability to water and temperature (up to 400 °C) owing to the connection of four organosulfonate anions to DAB monomers through charge-assisted hydrogen bonds in all directions.

**Gas capture and CO$_2$ selectivity**

CO$_2$ adsorption isotherms were collected on CPOS-5 to demonstrate its permanent porosity (Fig. 2). Interestingly, at 273 K the CO$_2$ adsorption isotherm displayed a Langmuir profile, which at 1 bar reached the value of 48 cm$^3$ g$^{-1}$, representing 8 CO$_2$ molecules per unit cell (Fig. 2A). Notably, CO$_2$ uptake was already extremely high at low pressure and exhibited a loading as high as 59 mg g$^{-1}$ (273 K) at 0.1 bar, suggesting excellent affinity of the quadrupolar gas molecules with charge-decorated pore surfaces. At 0.1 bar and at room temperature, typical conditions of CO$_2$ pressure in flue gas from power plants, CPOS-5 adsorbs 39 mg g$^{-1}$, outperforming many well-known MOFs with greater surface areas such as HKUST-1, UMCN-150(N2), MIL-47, IRMOF-3 and ZIF-8, and porous hydrogen-bonded and supramolecular organic frameworks such as SOF-1, SOF-7, HOF-3 (ref. 27) and CB6 (ref. 17) and its absorption value is comparable to that of the best performing HOF-5.44

The isosteric heat of adsorption $Q_{st}$ calculated using the van’t Hoff equation accounted for 34.5 kJ mol$^{-1}$, which is in agreement with the binding energy determined by DFT calculations $\Delta E = 33.8$ kJ mol$^{-1}$ (ESI†). The $Q_{st}$ value is comparable to those of some high-performance porous crystalline materials such as SOF-1, MIL-53, HKUST-1 (ref. 19) and NaX zeolites, which contain channels decorated with charged moieties.

The prominent difference in the CO$_2$ uptake with respect to N$_2$ under the same pressure and temperature conditions prompted us to calculate the CO$_2$/N$_2$ selectivity using Ideal Adsorbed Solution Theory (IAST) applied to single-component isotherms starting from a 15 : 85 (CO$_2$ : N$_2$) mixture in order to simulate the flue gas conditions (Fig. 2B). The CO$_2$/N$_2$ selectivity at 273 K exhibited values in the 320–690 range at low

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**Fig. 3** CPOS-5 loaded with $^{13}$C-enriched CO$_2$ (0.75 bar at RT): (A) $^{13}$C MAS NMR spectrum; (B) 2D $^1$H–$^{13}$C HETCOR MAS NMR spectra collected at room temperature and at two distinct contact times (ct). The host–CO$_2$ cross peaks are highlighted in red. Chemical structures of TBS and DAB with labels (below). (C) Electrostatic potential projected on CO$_2$ molecules by the DAB and TBS host moieties. The CO$_2$ molecules were localized by DFT calculations.
pressures (<0.1 bar) and 110 at 1 bar. The CO$_2$/N$_2$ selectivity at room temperature was 540, as calculated using the ratio of Henry’s constants (ESI†). This is one of the highest selectivities shown to date in porous molecular materials.$^{19,20,24,47}$ Furthermore, the isosteric heat of adsorption calculated for methane is 21.0 kJ mol$^{-1}$, which is remarkably high compared to those of typical 3D frameworks with open metal sites or higher surface areas (Fig. 2C). It is comparable to SOF-1 ($\Delta H = 20.8$ kJ mol$^{-1}$) and one of the highest reported values in microporous polymers and crystals.$^{23,51–53}$

Screwing dynamics and diffusion rate of CO$_2$ in the channels

The remarkable CO$_2$-matrix association allowed direct observation of the gas exploring the nanochannels by NMR spectroscopy. The $^{13}$C MAS NMR spectrum showed two dominant signals at $\delta_c = 125.5$ and 125.8 ppm for $^{13}$C-enriched CO$_2$: the former identifying free CO$_2$ and the latter CO$_2$ housed in the confined space of the crystal (Fig. 3A). The downfield signal is generated by the magnetic susceptibility effect experienced by CO$_2$ molecules embedded in the polar environment of the crystal. In the cross-polarization (CP) spectrum, the $\delta_c = 125.8$ ppm signal is largely dominating, for the fast magnetization transfer even at room temperature, from the matrix hydrogens to the CO$_2$ carbons lying a short distance away (<1 nm),$^{54}$ proving that the gas is exceptionally well-retained (ESI†). This is a remarkable result given the well-known difficulty of transferring nuclear polarization in conventional systems from a solid towards a gas, because of the short gas residence time, especially at room temperature.

The surprising efficiency of gas–solid CP was exploited for the success of 2D $^1$H–$^{13}$C CP NMR, which allowed for both in situ spectroscopic detection of CO$_2$ and the identification of the specific interaction sites (Fig. 3B).$^{33,55,56}$ Even at a contact time as short as 0.5 ms and room temperature, CO$_2$ carbon nuclei receive magnetization from the amidinium hydrogens (at $\delta_H = 7.4$ ppm), showing the short distances of the gas from these
species lining the channel walls. The short internuclear
distances were confirmed by ab initio DFT calculations, which
pointed out the CO₂ location and a distance of 3.24 Å between
the N–H hydrogen and CO₂ carbon. The close proximity of
the CO₂ carbon with the N–H group is imposed by the interaction
of one of the CO₂ oxygens with the amidinium cation. Also the
aromatic C–H group of DAB undergoes favorable interactions
with CO₂ oxygens as demonstrated by the highly positive elec-
 trostatic potentials (Fig. 3C: the red regions on the oxygen atom
of CO₂). Actually, at a longer contact time of 1 ms the 2D NMR
spectrum highlights the correlation between the aromatic C–H
d of DAB and CO₂ carbon (distance of 4.18 Å). With regard to the
organosulfonate anions, DFT calculations show CO₂ molecules
clamped in between the oxygens of two TBS sulfonate groups
(Fig. 3C: the blue regions on the carbon atom of CO₂), keeping the
C–H hydrogens of TBS far apart from the CO₂ carbon (distance of 5.75 Å), consistent with the absence of NMR cross-
correlations. From the combined NMR and modelling
approach, we can conclude that the charge distribution of the
host complements the charges on the CO₂ molecule and
determines the stabilization of the gas in the channels.

Remarkably, multiple aspects of the dynamics of the CO₂
molecules in the channels came to light from variable tempera-
ture ¹³C NMR spectra recorded in the static mode (Fig. 4A).
Actually, the spectra depicted axial chemical shift anisotropy
(CSA) restricted to a fraction of the total spectral width of solid
CO₂ in the bulk.⁵⁷,⁵⁸ From the NMR lineshape simulation we
were able to determine the mechanism of motion, the dynamics
and the inclination of CO₂ molecules in the channels. The lineshape
at room temperature describes a rapid 4-site re-orientation of CO₂
molecules by a 90° jump mechanism (Fig. 4B). Nonetheless, the
CO₂ main axis maintains an inclination angle equal to \( \theta = 56.7° \)
with respect to the rotation axis. By lowering the temperature
to 215 K, the inclination increases to 58.1° due to the increased
loading and the larger contribution of CO₂–CO₂ interactions
(ESI†). Notably, by the spectral analysis at variable temperature, it
was possible to measure the 90° jump rates (k) that are higher
than \( 10^{15} \) Hz at room temperature and still over \( 10^{9} \) Hz at 215 K.

To understand in-depth the NMR determinations of the gas
diffusing in the tight-fitting channels, molecular dynamics
combined with ab initio calculations provided a model for the
energy profile and interaction sites perceived by CO₂ travelling in
the channels. Each site accommodates a CO₂ molecule at a time
and imparts to the CO₂ molecule an average inclination angle \( \theta \)
of \( 57°–58° \), in perfect agreement (±0.7°) with the NMR data (ESI†).
Regarding the fast 90° re-orientation, it cannot occur within the
same site without a very high energy cost, for steric and electro-
static reasons. In contrast, the next site along the channel
(symmetry related by a four-fold screw axis, \( 4_1 \)) can host CO₂ after
its 90° turn (Fig. 4C). Thus, CO₂ reorientation, observed by NMR,
implies rotation correlated with sliding motion to the next site
within a rate of \( 10^{8} \) steps per second (Fig. 4D). Indeed, the unique
feature of this diffusion phenomenon is the concerted roto-
translational mechanism (i.e. simultaneous rotation and trans-
lation along the \( c \) axis) occurring with extremely rapid dynamics
of the confined CO₂, which follows a helical trajectory by a
scrwing path along a single file (Fig. 4E). From the NMR jump
rates (k) vs. temperature, an Arrhenius plot can be derived,
establishing a small activation energy of 2.9 kcal mol⁻¹ (Fig. 4F),
in excellent agreement with the energy barrier of 2.1 kcal mol⁻¹
for a diffusion step of CO₂ molecules, during the helical trans-
port, as calculated by DFT analysis (Fig. 4G).

Conclusions

Multifunctional tetra-anionic and di-cationic molecules combine
together to form frameworks with the property of being perma-
nently porous. The crystalline framework was designed by the use
of intrinsically rigid molecules as constructive elements and ionic
interactions between sulfonate anions and amidinium cations.
The ionic patterning of the crystalline channels allows the
establishment of high interactions of 35 kJ mol⁻¹, ideal for CO₂
capture/release cycles. This high energy value stably retains the
quadrupolar molecules of CO₂. Such CO₂ sequestration was so
efficient that the CO₂/N₂ selectivity values at low pressures (<0.1
bar) range from 320 to 690.
The interaction strength of the CO₂ with the host was
recognized by the striking capability of CO₂ to receive nuclear
polarization from the framework at room temperature and to
develop the anisotropic patterns in the static ¹³C NMR spectra.
A unique screwing mechanism of CO₂, which follows the helical
track of the charges on the channel walls, was observed. The
rate of a single step (>10⁸ steps per second) in the diffusion
trajectory along the tunnel could be unconventionally estab-
lished by NMR. The orientational and dynamical features
are enforced by the computational models of gas–framework
interactions. The contribution of the charges patterning the
channel walls is of paramount importance for directing the
association of a gas, such as CO₂, with the host. These pieces of
evidence encourage the use of multiple charge molecules of
opposite polarity to spontaneously self-organize into functional
materials endowed with high thermal stability and exploit the
rich modularity of polyanions and polycations to design struc-
tures tailored to a specific gas for capture and sequestration.

Moreover, the fabrication of artificial charged channels in
crystalline materials with a high degree of order and uniformity
as well as a controllable structure promotes the understanding
of the role of electrostatic interactions in the transport prop-
ties of transmembrane channels of biological systems.⁵⁵,⁵⁹
Indeed, the CO₂ diffusion in helical narrow channels, such as in
aquaporins, plays a strategic role in the selection and concen-
tration of gases in plant cells.⁵⁹ Our newly fabricated crystalline
channels share helical and sub-nanometric structural features,
and transport properties in a single file through the polar
environment, thus achieving high selectivity.

Conflicts of interest

There are no conflicts to declare.

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