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Ultra-fast molecular rotors and their CO_2 tuning in MOFs with rod-like ligands

Silvia Bracco,[a] Fabio Castiglioni,[a] Angiolina Comotti,[a,*] Simona Galli,[b] Mattia Negroni,[a] Angelo Maspero[b,*], Piero Sozzani[a]

Abstract: A metal organic framework (MOF) engineered to contain in its scaffold rod-like struts featuring ultra-fast molecular rotors showed extremely rapid 180° flip reorientation with rotational rates of 10^{11} Hz at 150 K. Crystal-pore accessibility of the MOF allowed the CO_2 molecules to enter the cavities and control the rotor spinning speed down to 10^5 Hz at 150K. Rotor dynamics, as modulated by CO_2 loading/unloading in the porous crystals, was described by ^1H T_1 and ^2H NMR spectroscopy. This strategy enabled the regulation of rotary motion by the diffusion of the gas within the channels and the determination of the energetics of rotary dynamics in the presence of CO_2.

Molecular rotors and motors have become an important issue today, being a prominent challenge to present-day research where the target is to reorganize molecular motion from a chaotic to a coherent state.[1] When opportunely governed, molecular motion can be exploited for its response to electric-field stimuli in optical devices, switches and sensors.[2] To date, light energy has aided the promotion of unidirectional propulsion for the fabrication of nano-robots and nanomachines.[3] Artificial molecular pumps have been fabricated, mimicking rotary machines that, in nature, perform fundamental functions such as proton pumps.[4] Thus solid state structures, periodically organized in 2D and 3D, have the potential to offer a reliable venue for the controlled motion of molecular rotors, though they often suffer from a tendency towards close-packing inducing reciprocal interference among rotors.[5]

However, crystalline porous materials with their low density and structural order can overcome this limitation, and are excellent candidates for the fabrication of molecular rotors in the solid state.[6] Furthermore, porosity allows rotor exposure to diffusing species through adsorption, this occurrence enlarging the application perspectives.[7] Indeed, the easy rotor accessibility results in an active manipulation of rotary motion through interaction with guests,[6] revealing the feasibility of molecular rotors as responsive elements sensitive to chemical perturbation. The architecture of porous materials can be realized by a variety of chemical bonds and supramolecular interactions.[8] Specifically, in metal-organic frameworks (MOFs) metal organic nodes and proper organic struts ensure both crystallinity and robustness.[9]

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The large variety of MOFs offers a valid platform to build solid state molecular rotors in a porous environment, providing, in principle, the free volume needed for motion to occur. However, in the MOFs presented in literature, the typically-adopted chemical bonds on which molecular rotors are pivoted are rather inadequate to ensure a low barrier for rotation.[6,10] Attempts to lower this energy barrier have been carried out by destabilizing the ground state through the introduction of lateral substituents on *p*-phenylene units in the struts, although this causes the molecular mass of the rotor and its inertia momentum to increase, leading to relatively slow rotational frequencies.[11] To increase the rotational spinning speed, an alternative strategy adopted in porous molecular crystals is to insert into the struts triple bonds as pivots for the molecular rotor, thus for lowering the energy barrier for rotation.[5,7]

In the present paper we show extremely fast rotor dynamics, already 10^{11} Hz at 150 K, comparable to liquid matter, in a bis(pyrazolate)-based MOF architecture. Moreover, the CO_2 entering the porous material could actively tune the spinning speed and govern the mechanics of motion (Figure 1). This opens up the perspective of actively manipulating rotor response in a robust framework, simply by the adsorption of a gas.

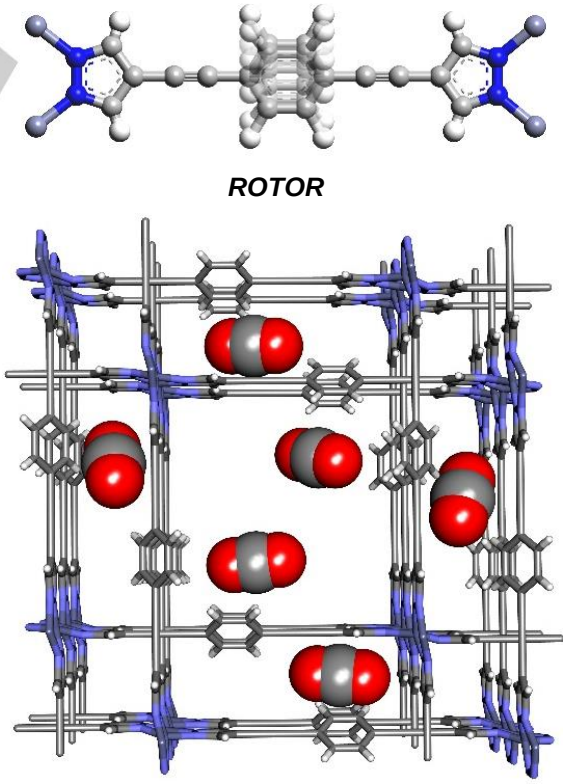

Figure 1. 1,4-bis(1H-pyrazol-4-ylethynyl)benzene linker (above) and Zn-BPEB showing CO_2 molecules diffusing in both small and large cavities (below).

The porous and absorptive architecture was realized through the robustness of metal-organic bonds and the use of rigid molecular rods bearing the rotors. We selected a suitable rod-like strut that contains a central *p*-phenylene unit (the rotor) connected through ethynyl groups to two pyrazole moieties 1,4-bis(1H-pyrazol-4-ylethynyl)benzene (BPEB) which interacts with Zn(II) ions to fabricate the microporous MOF Zn-BPEB (Figure S3).[12] The isostructural MOF *d*$_4$-Zn-BPEB selectively deuterated on the central *p*-phenylene moiety was prepared to investigate the rotor dynamics. Straightforward evidence of the dynamics in the presence and the absence of CO_2 within the pores was provided by ^{13}C and ^{1}H T_1 relaxation times as well as ^{2}H solid-state NMR spectroscopy, which is a unique method to understand the motional trajectories and reveal the mechanism of reorientation of the C-D vectors.[13]

The crystal structure of Zn-BPEB features 1D square channels with 10 Å × 10 Å cross section and small pores with aperture of 4.3 Å diameter connecting the large channels (Figure S3), accounting, respectively, for an empty volume of 1356 Å^3 and 696 Å^3 *per* unit cell, (calculated through an exploring sphere of 1.2 Å radius and the contact surface model). Each *p*-phenylene unit, which constitutes the mobile element capable of rotating, is exposed to both channels. The tetrahedral metal node plays a key role in the separation of the rod-like ligands, providing the molecular rotor with enough room to rotate. The robustness of the MOF structure is guaranteed by the coordination of pyrazolate rings at the end of the rods with metal node (Zn^{+2}). The crystal and molecular structure was confirmed by solid state NMR multiplicity of signals (Figures S6), compared with PXRD structural refinement. The channels are empty and no residual solvent is included. The porous materials exhibit a BET surface area of 1214 m^2 g^{-1} (Langmuir SA=1366 m^2 g^{-1}) and pore volume of 0.64 cm^3 g^{-1} (Figure S10).

Structure analysis reveals that the minimum distance between adjacent axes of central *p*-phenylene rings is 7.3 Å along the *c*-axis (Figures S4). On the other hand, being an interpenetrated network, in the *ab* plane each *p*-phenylene ring faces both the ethynyl and the pyrazolate groups of the adjacent linker. The pyrazolate plane is at a distance of 5.2 Å and does not interfere with the rotor. Such a relatively large distance allows for the rotation of the *p*-phenylene ring and, considering the low rotation barrier about Csp^2-Csp bonds (as the *p*-phenylene-ethynyl bond), the *p*-phenylene moieties are expected to be efficient as fast molecular rotors.

This was demonstrated by wide-line ^{2}H NMR spectroscopy of selectively deuterated d$_4$-Zn-BPEP, on the central *p*-phenylene ring of MOF. At room temperature the spectrum exhibits a restricted spectral profile (with singularities separated by 27.7 kHz), which does not change appreciably down to 150 K, except for a minor increase of the spectral shoulders. The simulated line-shapes show that the mechanism of motion consists of a rapid two-site 180° flip reorentation of the *p*-phenylene moieties about their main axis, passing through the pivotal ethynyl groups, and extremely fast reorientation (k > 10^8 Hz) of the aromatic C-D bonds (Figure 2a). Rapid librations of the *p*-phenylene ring about the energy minimum, witnessed by the weakening of the spectral shoulder, must also be taken into account, together with the 180° flip mechanism that is preserved in the strut. Surprisingly, rates in the fast exchange limit (>10^8 Hz) and libration amplitudes of more than ± 20° occur even down to 150K.

These results are consistent with ^{1}H T_1 spin-lattice relaxation times, as measured in Zn-BPEB, because they provide information on the rotary frequency at each temperature following, the master curve generated by Kubo-Tomita relation. When spin-lattice relaxation times increase with temperature, the system is exploring the extreme narrowing limit and the dynamics are faster than the observation frequencies (typically from 10^8 to 10^{12} Hz), complementing ^{2}H NMR data. This was the case in Zn-BPEB in the ^{1}H domain, in which Ln(T_1) proved to be inversely proportional to 1/T (Figure 2b and Supporting Information). The activation energy was calculated to be 0.5 kcal mol^{-1}. The *p*-phenylene dynamics discovered in this MOF is orders of magnitude faster than those observed in MOFs, which are still in slow exchange regimes at room temperature.[10,14] The extremely fast dynamics and the low energy barrier we observed are a benchmark in the class of MOFs, and overcome the best molecular rotation value recently published for non-porous crystalline compounds.[15]

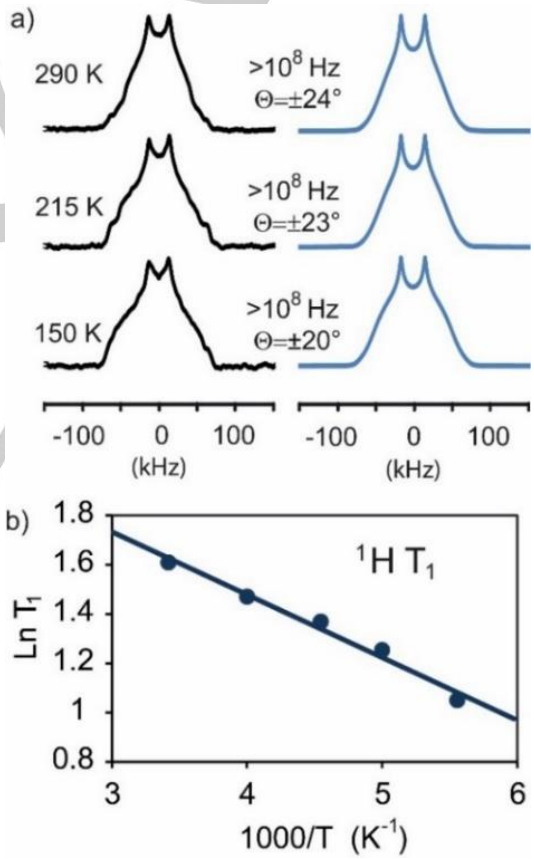

Figure 2. a) Experimental (left) and simulated (right) ^{2}H NMR spectra of d$_4$-Zn-BPEB. K corresponds to reorentational rates and θ to libration amplitude. b) ^{1}H T_1 relaxation times versus the reciprocal of temperature for Zn-BPEB.

Moreover, the permanent porosity of the crystals enables CO_2 control of the molecular rotor dynamics while exploring the MOF nanochannels. As a matter of fact, CO_2 adsorption isotherms, run at various temperatures from 298 K down to 195 K (Figures S11 and S12), enabled us to assess the loading of the material at each temperature, and the adsorption energy at low coverage. The interaction energy, as evaluated by the van't Hoff equation, is 25

kJ mol^{-1}, indicating a good interaction of CO_2 with the channel walls. ^{1}H T_1 and ^{2}H NMR made it possible to investigate the rotor dynamics in the presence of the gas into the channels. At variance with the empty MOF, ^{1}H relaxation times of Zn-PBEB loaded with CO_2 increase with temperature and fall in the regime of motion of solids, on the contrary of the empty structure. *d*$_4$-Zn-BPEB was sealed under pressurized CO_2 at 9 bar and room temperature (denoted as *d*$_4$-Zn-BPEB/CO_2) and ^{2}H NMR spectra were collected at variable temperature (Figure 3). The dramatic change of the spectral series with respect to that of the empty matrix in the same range of temperatures from 150 K to 290 K, is apparent. At 150 K the spin-echo ^{2}H NMR spectrum exhibits a dominant profile associated with a rotation rate *k* of 10^5 Hz and a two-site 180°-flip reorientation mechanism (Figure 3, blue profile). Thus, the rotation rate is slowed by more than 6 orders of magnitude compared to the empty MOF (in the order of 10^{11} Hz at 150 K), owing to the hampering effect of CO_2 molecules filling the channels. At this temperature virtually complete loading of the channels occurs.[16] These hampered rotors progressively increase their rotational rates on increasing the temperature. The measured energy barrier is 4.5 kcal mol^{-1}, i.e. 4 kcal mol^{-1} higher than that recorded in the empty sample. These results clearly show that CO_2 controls the rotor dynamics, yet without changing the main two-fold flip mechanism.

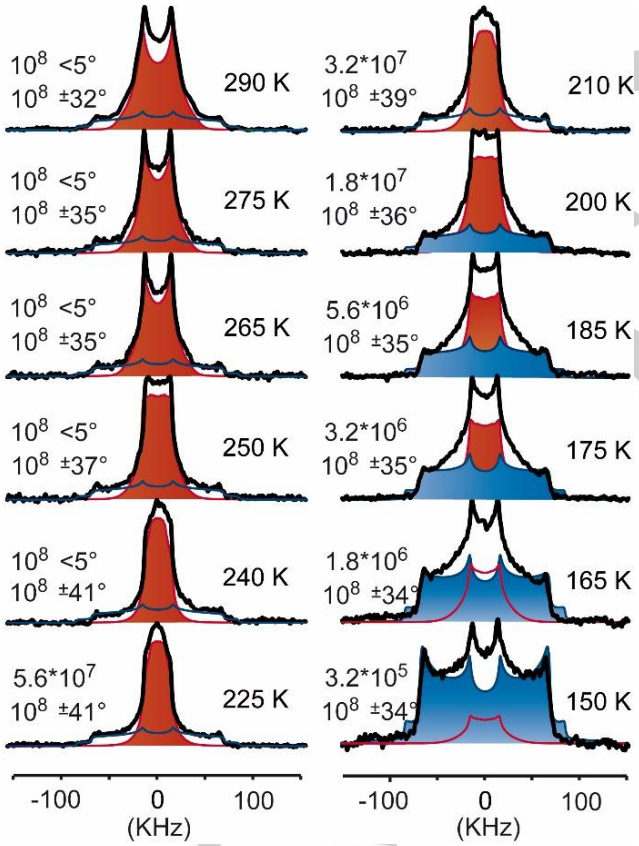

Figure 3. Experimental ^{2}H NMR spectra (black lines) of d$_4$-Zn-BPEB at variable temperature. Blue and red areas represent the slow and fast components. Rotational frequencies *k* and libration amplitudes θ for the two components are expressed in Hz and degrees, respectively.

At high temperatures (> 200 K) a narrower profile, representing a motional dynamics faster than 10^8 Hz, clearly emerges and dominates progressively evolving with temperature (Figure 3, red profile). This profile was simulated with the occurrence of large librations from θ=±32° to ±41° in addition to the 180° flip reorientation. Characteristic tower-shaped profiles are produced by this mechanism when large librations take place and, to date, they have only been observed at much higher temperatures in rotor-containing porous materials.[7b] Grand Canonical Monte Carlo simulations established the number, partition and location of CO_2 molecules between the small pores and large channels as a function of loading (Figure 4 and Figures S16-S19). At high temperature and low loading, CO_2 occupies only the small cavities (Figure 4c, configuration I), while on decreasing the temperature the system reaches its full loading and CO_2 molecules also fill the main channels (Figure 4d, configuration II). In the latter configuration, each rotor is surrounded by 3 CO_2 molecules simultaneously: two in the small pores (one on either side of the rotor) and one in the large channels (facing the rotor at the short distance of 3.4 Å). Thus, the CO_2 molecules wrap the rotor and slow down its motion (Figure 3: blue profile). On increasing the temperature, the probability of 3 CO_2 molecules surrounding simultaneously a single rotor decreases progressively, and CO_2 molecules leave the wider channels, reducing the constriction on the rotors that gain mobility. Consequently, in the ^{2}H NMR spectra the component with faster dynamics and large librations prevails (Figure 3: red profile). Moreover, the profiles of both components evolve progressively with temperature according to the recovery of dynamics due to increased thermal energy.[17]

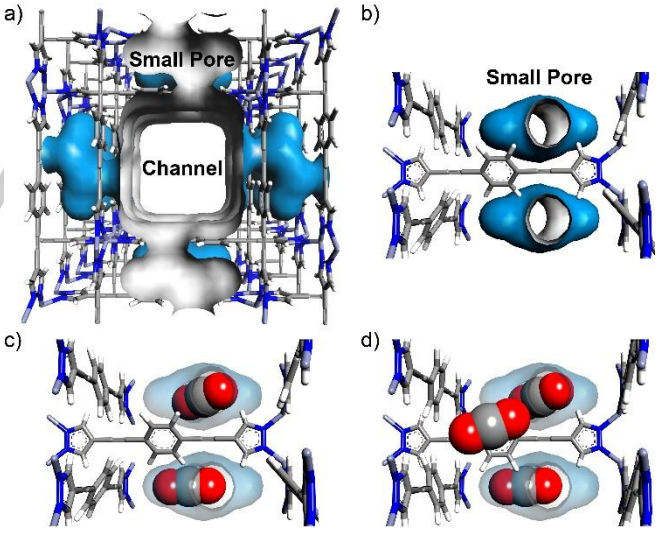

Figure 4. a) The small pores and the large channel in Zn-BPEB described by a sphere of 1.6 Å radius. b) The molecular rotor surrounded by the small pores in the channel walls. Exploration of the cavities by CO_2: c) low and d) high loadings (configuration I and II, respectively).

In conclusion, in our search for fast molecular rotors in porous solids we discovered the fastest dynamics of molecular rotors in MOFs and achieved a benchmark in the field of fast molecular rotors in general. This was made possible by rod-like ligands endowed with virtually barrierless pivotal bonds, which keep the

rotors in register. The large empty space, isolating the individual rotors, ensures that there is no interference from one rotor to another. These features render the material an ideal candidate to detect the effects on the rotation frequencies of a gas flowing into the pores. Indeed, CO_2 adsorbed by the material could play an active role in modulating the dynamics of the rotors. Indeed, a few solid-state NMR parameters were sensitive to the presence of CO_2 inside the channels. Moreover, molecular modeling reproduced adsorption-isotherms and portrayed the progressive loading of pores of distinct size and shape, entailing distinct CO_2 clustering around individual rotors.

This challenging project of having realized dynamics in crystals as fast as in liquids opens new perspectives such as the control of molecular dynamics by the influence of mild chemical stimuli, i.e. gas loading. The rapid reorientation of mobile elements in crystals enables the activation of switchable ferroelectric properties that can be used in opto-electronic devices. This unique response of the materials to a gas is of great importance for the environment, enlarging perspectives in the field of sensors and gas detection.

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Keywords: Crystal Engineering · Porous Materials · Molecular Rotors · CO_2 Adsorption · Solid State NMR Spectroscopy

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[16] At low temperature there occurs high loading of 8.5 mmol g^{-1}, corresponding to 95% of full loading. Above 200K there is a progressive decrease in loading (5.6 mmol g^{-1} at 290 K, 62% of full loading).

[17] The activation energy of 4.5 kcal mol^{-1} was calculated for the most crowded configuration (configuration I: 3 CO_2 molecules around the rotor).

Table of Contents

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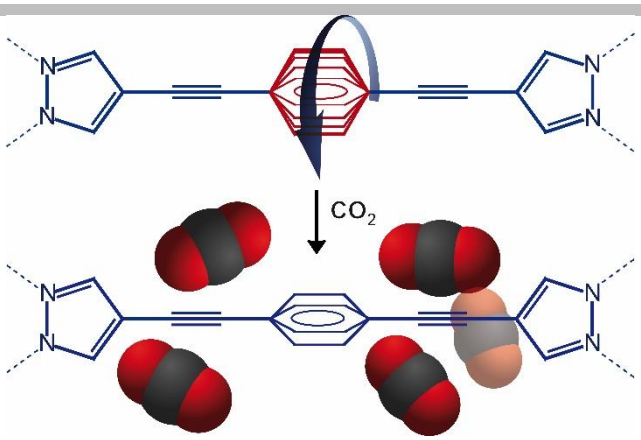

S. Bracco, F. Castiglioni, A. Comotti, S. Galli, M. Negroni, A. Maspero*, P. Sozzani*

Ultra-fast Molecular Rotors and their CO_2 Tuning in MOFs with Rod-like Ligands

CO_2 gas flows into the Zn-based MOF which sustains ultra-fast rotors and intervenes actively in the motional mechanics, increasing reversibly the energy barrier for rotation and allowing active manipulation of molecular rotor dynamics.

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