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Dynamic Porous Materials | Hot Paper

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Molecular Rotors in Porous Organic Frameworks**

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Abstract: *Porous organic frameworks perform a variety of functions, owing to their extremely large surface areas, but the dynamics of the structural elements have never been explored. Our discovery of ultra-fast molecular rotors (10^6 Hz at 225 K) in their architectures allows us to look at them from a new perspective. The constructive elements are robust struts and rapid rotors, resulting in a dynamic material whose motion can be frozen or released at will. The rotational motion can be actively regulated in response to guests. As the temperature is increased, the rotors spin ever faster, approaching free-rotational diffusion at 550 K. The unusual combination of remarkable nanoporosity with fast dynamics is intriguing for engineering oscillating dipoles and producing responsive materials with switchable ferroelectricity, and for applications spanning from sensors to actuators, which capture and release chemicals on command.*

The attainment of extremely high surface areas and pore capacities in recently developed porous materials has opened up new perspectives for gas storage, catalysis, photochemistry and confined reactions.[1] The constructive principles for building frameworks of the highest porosity exploit a diversified range of interactions and chemical bonds. Covalent bonds are certainly the most energetic and directional bonds, ensuring robustness of low-density architecture because of their low conformational flexibility. Therefore, extended 3D networks containing carbon–carbon and carbon–silicon bonds have become very promising in recent years.[2] Their thermal and chemical stability virtually guarantees infinite storing/delivery cycles with gases, qualifying them as ideal media for thermal reactions and confined polymerization.[3] On the other hand, the rigidity of the covalent network is not necessarily in contrast with local rotational freedom, allowing selected groups to reorient as molecular rotors. Molecular rotors built in porous materials[4,5] have recently raised considerable interest for the intriguing perspectives of realizing actuators, sensors, and materials endowed with switchable dielectric properties.[6] However, the systems proposed up to now, constructed by the use of metal–organic and siloxane bonds,[4,5] are still rare, and are limited to porous materials with moderate sorption capacities and relatively slow dynamics.

These considerations stimulated us to investigate rotor-containing porous materials of covalently fabricated frameworks, endowed with robustness and extremely high surface area and pore capacity (typically $S_{BET} > 5000\ m^2 g^{-1}$ and $S_{Langmuir} > 7000\ m^2 g^{-1}$). In fact, we discovered a completely novel aspect of porous organic frameworks, namely the extraordinarily fast dynamics of molecular rotors, which are displayed even at very low temperatures; we also described the interaction of molecular rotors with other species, exploring the large available space in the high-capacity porous materials. Actually, the extreme intimacy between the matrix and guests diffusing inside the galleries promotes effective interactions between the exposed rotors and selected absorbed molecules at the single-rotor level. The exposure to low-pressure vapors, such as those of I_2, is sufficient to regulate the rotor response, or even to hamper their thermally activated motion. Guest removal by vacuum treatment resulted in the complete reinstatement of rotor dynamics.

Prominent examples of the family of polyaromatic frameworks PAFs, namely polytetraphenylmethane-based (PAF1) and polytetraphenylsilane-based (PAF3) frameworks (Figure 1), were prepared by the Yamamoto homocoupling reaction, as reported by Ben et al.[2a] Moreover, the latter

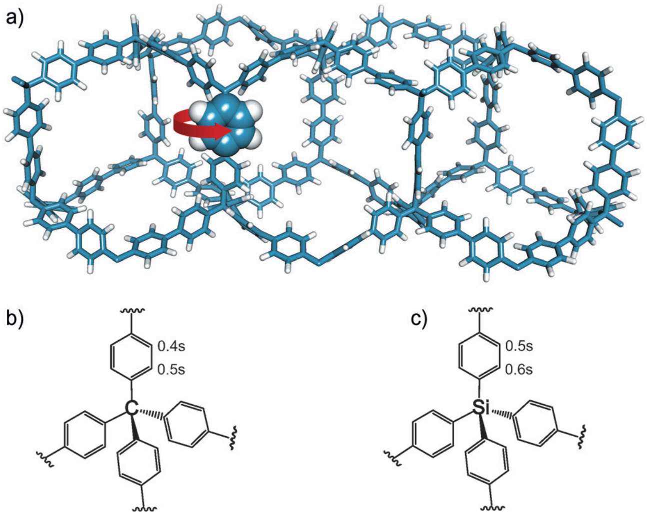

Figure 1. a) Idealized structure of porous aromatic frameworks (PAFs); C light blue, H white; a representative *p*-phenylene rotor is highlighted with van der Waals radii, and the red arrow indicates fast rotary motion. b,c) Structure of the monomer units of PAF1 (b) and PAF3 (c). Room temperature ^{13}C spin-lattice relaxation times of the mobile CH aromatic elements are reported.

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compound was synthesized as a perdeutero compound for ^{2}H NMR analysis of the dynamics ([D$_4$]PAF3). Surface areas are remarkable, and reach the BET and Langmuir values of 5002 and 6586 m^{2}g^{-1} for PAF1 and 2927 and 3781 m^{2}g^{-1} for [D$_4$]PAF3, (Supporting Information, Figure S1). The pore distribution, obtained by NLDFT analysis of the sorption isotherms, is centered at 14.2 and 13.2 Å for PAF1 and [D$_4$]PAF3, respectively. The high thermal stability to temperatures above 450 °C, which is guaranteed by covalent bonds, was ascertained by thermogravimetric analysis (TGA; see the Supporting Information).

Spin-lattice relaxation times (T$_1$(^{13}C)) and spin-echo deuterium NMR are the most powerful methods for describing the reorientation frequencies and the trajectories travelled by the mobile elements in solids.[7,8] Variable-temperature measurements of ^{13}C spin-lattice relaxation rates of both PAF1 and PAF3 enabled us to establish the correlation times associated with the distinct carbon atoms. Specifically, T$_1$ values as short as 0.5 s, measured at ambient temperature for CH carbons on the aromatic rings, demonstrate the occurrence of extremely efficient relaxations and fast molecular motion of the phenylene groups about their principal axes (Figure 1). Such motion corresponds to correlation times (τ_c) close to 10^{-8} s, which match the observation frequencies. This was the first quantitative indication of the remarkable dynamics of the porous organic frameworks at room temperature. On the other hand, the motional mechanism could only be obtained by deuterium NMR measurements. ^{2}H spin-echo NMR spectral profiles vary progressively with increasing temperature from 200 to 250 K, exploring, even at low temperatures, high motional frequencies (Figure 2). The spectra were simulated successfully by considering reorientation rates that are in the characteristic timescale of wide-line ^{2}H NMR.[8]

Line-shape analysis indicates that the mechanism of motion is consistent with a rapid two-site 180° flip reorientation of *p*-phenylene moieties about their *para* axis. Already at temperatures as low as 225 K, the spectral profiles show exchange rates (k) in the MHz regime and at 200 K, the line shape is consistent with exchange rates as rapid as 10^5 Hz. To the best of our knowledge, this compound exhibits the fastest dynamics of *p*-phenylene molecular rotors in porous materials reported thus far. The energy barrier for rotation can be calculated by an Arrhenius plot reporting log (k) as a function of the inverse absolute temperature (Figure 2c), showing an activation energy E$_a$ of 28 kJ mol^{-1} and a motional frequency extrapolated at infinite temperature (k_0) of 4×10^{12} Hz. The k_0 value is consistent with the moment of inertia of a *p*-phenylene ring rotating about its main axis.[9] Remarkably, the activation energy is the lowest found in porous materials with the same inertia mass and k_0 of about 10^{12} s^{-1}.[4,5] In a few examples of porous materials containing rotors with larger inertial masses, the activation energy is lower, but motional rates are slower by several orders of magnitude at any temperature.[10]

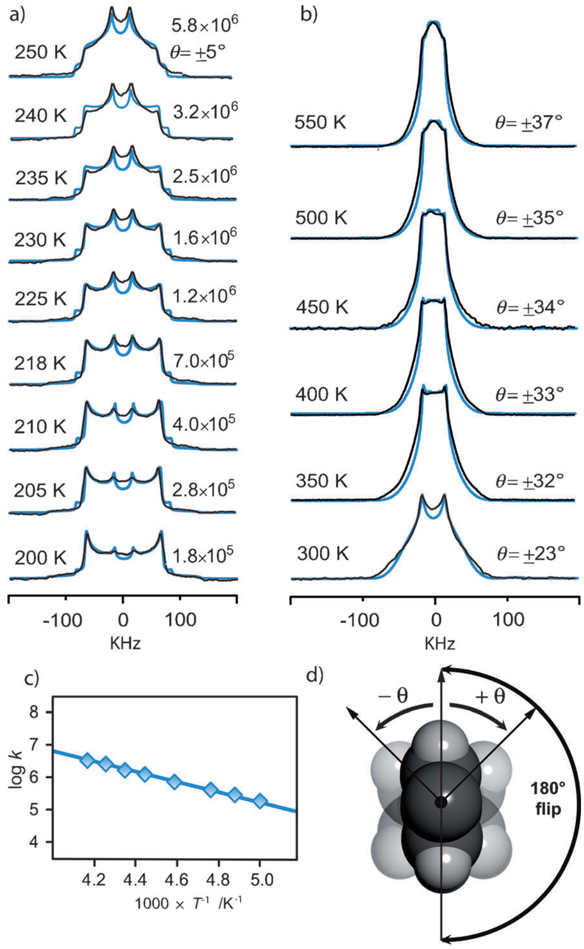

Figure 2. a,b) Experimental (black) and calculated (blue) ^{2}H spin-echo NMR spectra of [D$_4$]PAF3 in the low temperature range (a) and in the high temperature range up to 550 K (b). The rotational rates (in Hz) and the librational amplitude in the fast exchange limit ($>10^8$ Hz) are reported. c) Arrhenius plot of the rotational rates of the *p*-phenylene rotors inserted in the framework. d) A single rotor, as viewed along the rotational axis undergoing 180° flip and 2θ amplitude librations.

Above room temperature (Figure 2b) the weakening of the spectral shoulders are apparent, indicating that further averaging processes, that is, librations of the C–D vector about the rotational minimum, are added to the dominant 180° flip mechanism and the flipping rates are in the fast limit of solid deuterium NMR ($>10^8$ Hz). Indeed, the rotational mechanism is ensured at high spinning speeds, because the rotors are pivoted on the robust covalent architecture. The high rotational frequencies ($k>10^8$ Hz) measured by ^{2}H NMR spectroscopy are consistent with T$_1$(^{13}C) values that showed, as anticipated, the maximum relaxation efficiency at a frequency of 7.5×10^7 Hz at about room temperature. In the upper temperature limit (up to 550 K) a gradual filling of the central region of the spectrum occurs and the line shapes are accurately simulated considering, aside from the 180° flip mechanism, large amplitude librations about the main axis increasing up to $\theta = \pm37°$ at 550 K with jump rates over 10^8 Hz (Figure 2b). The line shapes and the θ oscillation angles evolve smoothly as a function of temperature and, despite the thermal energy provided at these temperatures, the rotational mechanism is fully preserved in the rigid adamantoid structure. This is a rare example of a frame that supports the extremely fast internal dynamics of the linkers with a defined motional mechanism maintained over a few hundred degrees Celsius, approaching free diffusional rotation in the temperature limit. After thermal treatment at 550 K and cooling to any lower measurement temperature, the spectral profile reverts back to the original one, confirming the thermal stability of the framework on which the rotors are mounted.

In this highly porous system, in which *p*-phenylene rotors are accessible from any direction normal to their rotational axis, we can expect that the rotor dynamics could be regulated by molecules entering the galleries. Actually, the relevant exposure of the rotors entails the possibility of installing direct interactions with guests, such as CH⋯π interactions. The compounds *n*-dodecane (C_{12}) and *n*-eicosane (C_{20}) were diffused from the molten phase in the evacuated pores of $[D_4]$PAF3 ($[D_4]$PAF3/C_{12} and $[D_4]$PAF3/C_{20}) and the rotor dynamics were investigated (Figure 3). At 230 K, the *p*-phenylene dynamics were reduced to values compatible with the static Pake spectrum, and in both cases spectra with reorientational rates in the 10^3 Hz regime occurred. Remarkably, at the same temperature, the empty matrix fell in the highly dynamic regime of 10^6 Hz, which is about three orders of magnitude higher than the loaded samples (Figure 3c). This result supports, in an unconventional way, that linear alkanes are massively adsorbed within the pores and can actively interact by weak interactions with the entire population of phenyl rings. Indeed, CH⋯π interactions are established with the aromatic rings of the matrix, as demonstrated by short average distances revealed by effective ^{1}H-^{13}C cross-polarization from the alkane hydrogen nuclei to the hydrogen-depleted aromatic carbons (see the Supporting Information). Interestingly, cross polarization itself is modulated by the molecular dynamics, in fact it is effective at low temperature, whereas at room temperature the high mobility of aromatic units prevents polarization transfer.[11] The interaction energy between the hydrocarbon methylenes and *p*-phenylene groups was estimated by the rotational rates at low temperature derived from ^{2}H NMR to be 8 kJ mol^{-1}, which is in accordance with the values reported in the literature for CH⋯π intermolecular interactions.[12]

Surprisingly, a large portion of the rotational freedom was recovered by a small temperature increase of only 10 degrees (from 240 K to 250 K) for $[D_4]$PAF3/C_{12} (Figure 3a): in this temperature range, the energy and the pre-exponential factor calculated by an Arrhenius plot would be unreasonably high. This evidence suggests the occurrence of a transition in the host–guest adducts, likely due to the competition of thermal energy with CH⋯π interactions between the two components. Similar observations apply to C_{20}-laoded $[D_4]$PAF3 (Figure 3b), although the transition is shifted to the higher temperature of 260 K. At temperatures below the transition the motion is hampered, but above the transition the material switches back to motional regimes as fast as in the pure matrix (Figure 3c). At room temperature and above, the spectra can be simulated by considering a motional regime in the fast limit of $>10^8$ Hz and large-amplitude librations of up to $\theta = 36°$, as in the empty matrix, which suggests that the nanofluidity of the alkanes in the galleries increases considerably at these temperatures.

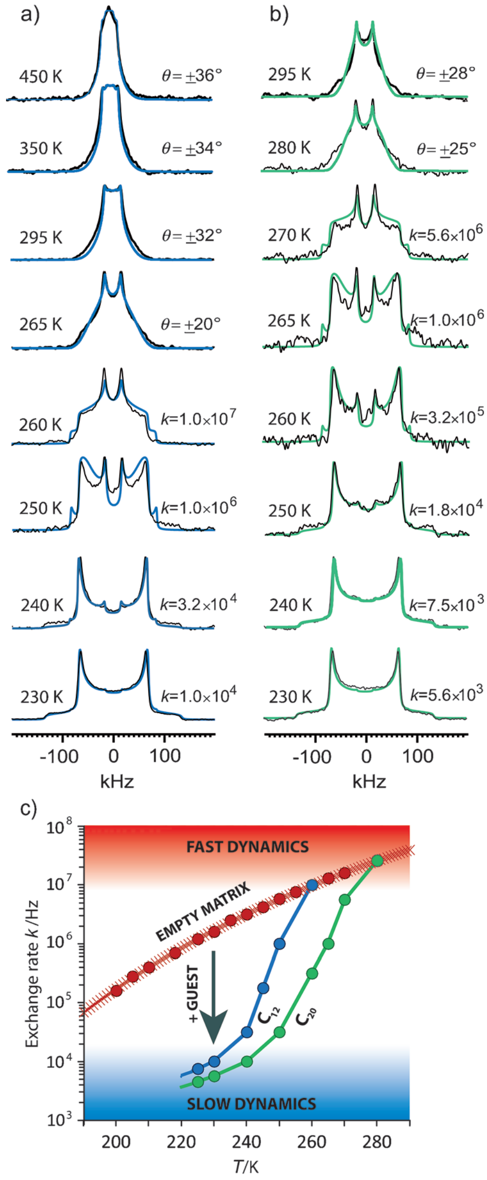

Figure 3. a,b) Variable temperature ^{2}H spin-echo NMR spectra of $[D_4]$PAF3/C_{12} (a) and $[D_4]$PAF3/C_{20} (b); experimental values (black), calculated (blue/green). c) Rotational rates (k) of empty $[D_4]$PAF3 (red), and C_{12}- (blue) and C_{20}-loaded (green) $[D_4]$PAF3 as a function of temperature. The red- and blue-shaded areas indicate the fast and slow exchange limits, respectively. The arrow shows the rotor-hampering effect of the included guests.

Moreover, even the uptake of vapors at very low pressure could regulate rotor motion: the phenomenon was induced by I_2 vapors at room temperature with an I_2 vapor pressure of 0.4 mbar at 298 K (Figure 4). The guest-induced motional changes were followed in situ by the modification of ^{2}H spin-echo spectral profiles of porous $[D_4]$PAF3 exposed to the vapors of solid iodine (see the Supporting Information). The deuterium NMR powder pattern of the rotors in the framework changed progressively as I_2 diffused into the sample pores. The reduction of overall dynamics was drastic and, at room temperature, the rotational rate (k) slowed from 10^8 to 10^5 Hz after the I_2 loading of the $[D_4]$PAF3; therefore, the

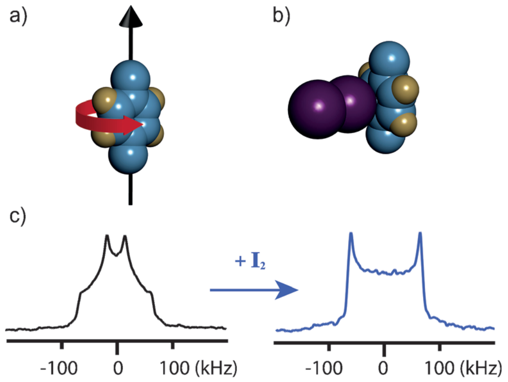

Figure 4. a,b) A single molecular rotor under rotation in the empty matrix (a) and hampered by the absorbed I_2 molecule in the porous framework (b). c) ^{2}H spin-echo NMR spectra at 250 K of porous [D$_4$]PAF3 (black) and I_2-loaded [D$_4$]PAF3 (violet).

correlation times span a few orders of magnitude, namely from times as short as nanoseconds to tens of microseconds.

Also, $T_1(^{13}C)$ relaxation times of I_2-loaded PAF1 and PAF3 become considerably longer at room temperature (about 10 s), as compared to the pristine empty matrices (less than 500 ms), confirming the braking action of I_2 molecules on the molecular rotors (see the Supporting Information). Iodine desorption, obtained by simple use of vacuum, yielded the reestablishment of ultrafast motion, thus showing the reversibility of rotor dynamics following guest absorption and desorption. The effectiveness of I_2 in individually regulating the rotor speed is superior to that of alkanes: as an example, the same k value of 10^5 Hz is reached in I_2-, C_{20}- and C_{12}-loaded samples at 298, 260, and 245 K, respectively, as compared to the empty sample in which the rotational rate of 10^5 Hz occurs at the much lower temperature of 210 K. Remarkably, in the I_2-loaded matrix a fully static spectrum is obtained at 250 K, whereas the empty sample still exhibits a mobile spectrum at the same temperature (Figure 4c). The increment of activation energy from included I_2, as compared to the empty matrix, was 12 kJ mol^{-1}, which suggests the formation of favorable I_2–phenylene interactions, as described in I_2–benzene complexes.[13] These results are a direct microscopic demonstration that I_2 can be absorbed in the organic covalent framework. Independently, I_2 uptake was measured by weight increase at room temperature after exposure of the porous matrix to I_2 vapors and resulted in a weight fraction of 0.30 for [D$_4$]PAF3 and 0.62 for PAF1. The latter value corresponds to 163 % of I_2 adsorbed per matrix weight, which is among the highest uptake values in porous materials.[14] The massive iodine permeation in the pores provides a rationale for the extensive influence on the rotor dynamics over the whole covalent framework.

In conclusion, our insight into the structure of porous aromatic frameworks of the highest surface area led us to discover the fast and pervasive dynamics of their elements. The robust yet light architecture made of *p*-phenylene groups is subjected to intense dynamics, even at temperatures as low as 200 K. This is explained by the fact that the rotors are isolated from the next neighbors in the sponge-like material, but they are nevertheless reachable by liquids or vapors. Thus, the material perceives the presence of diffused-in guests (*n*-alkanes and iodine), by which the rotors are hampered. Fast rotation is recovered after guest removal, generating a switchable dynamic porous material. These results suggest a strategy for the fabrication of sensing devices that, after suitable engineering, can detect the presence of adsorbates and would ensure selective recognition of pollutants or contaminants, such as radioactive iodine in the environment.

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