Porous Dynamical Materials

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Fast Molecular Rotor Dynamics Modulated by Guest Inclusion in a Highly Organized Nanoporous Organosilica**

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Rotary motion is the key feature of numerous molecular machines that carry out fundamental biological functions, and it constitutes the constructive motif for designing artificial molecular motors.[1] Research towards the fabrication of materials containing rotors mounted on surfaces or arranged in ordered 3D arrays is presently very intense.[2] Indeed, the organization of individual rotors into ordered arrays in solids can provide the necessary juxtaposition to make them operate as devices and to realize materials that could express useful functions in the fields of electronics, optoelectronics, and nanofluidics.[3]

Molecular rotors in bulk materials require both a large free volume and low energy barriers that allow rotation about the pivotal bonds. Fulfillment of these criteria has been accomplished in low-density organic crystals by reducing the interactions of the mobile elements and protecting them in closed molecular capsules.[4] However, one of the most intriguing perspectives is the achievement of an effective communication with the external environment by inserting rotors in porous nanostructures, making the rotors responsive to chemical stimuli. Thus, properties such as rotor accessibility from the gas phase could enable external regulation of the rotor dynamics. Furthermore, robustness and thermal stability of the framework could expand rotor operating conditions.

Apart from these considerations, a substantial breakthrough could be the fabrication of next-generation materials comprising both ultrafast molecular rotors and robust porous frameworks. This idea prompted us to address porous covalent materials of extremely low density and high surface area that have the advantage of being easily accessible from the surrounding space through the open pores. We selected periodic mesoporous organosilicas (PMOs) containing large nanochannels and ordered arrays of organic elements covalently linked to a robust siloxane framework.[5] Connection of the organic elements to the siloxane layers through a virtually barrierless C–Si bond dictates their regularity, separating them one from the other and creating the premise for realizing highly mobile organic rotors in the low-density mesoporous organosilica. In this context we found an architecture of aligned molecular rotors with ultrafast motion that can interact actively with guest molecules. Thanks to the extremely high surface area of the easily accessible and interactive honeycomb structure, the dynamics of the molecular rotors in the thin nanochannel walls could be fine tuned by the chemical influence of guest molecules in the channels. As these molecules communicate with the exposed rotors by weak host–guest interactions, their effect is completely reversible, and the rotor rate can be regulated at will by chemical interactions.

p-Phenylenesilica (PPS),[6] comprising ordered arrays of *p*-phenylene units connecting two adjacent siloxane layers (Figure 1), presents an intriguing periodic architecture that is hierarchically organized both on the molecular scale and the mesoscale. The aromatic elements are aligned in the 1.7 nm walls surrounding 3.8 nm wide nanochannels (see the Supporting Information). The properties of this low-density architecture prompted us to synthesize a deuterated $[D_4]p$-phenylenesilica ($[D_4]$PPS) to study the dynamics of the *p*-phenylene rotors by ^{2}H solid-state NMR spectroscopy. The spin–echo spectra provide the mechanism of reorientation of the C–D vectors and are sensitive to motional averaging for frequencies that overcome the MHz regime.[7] Consequently, variable-temperature solid-state ^{2}H spin–echo NMR spectra were recorded to determine the reorientation rate and the mechanism of motion of *p*-phenylene rings in the porous material.

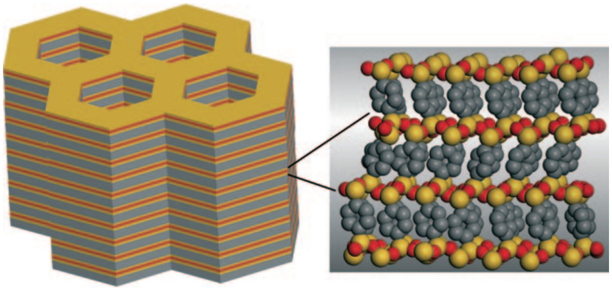

Figure 1. Schematic representation of the mesoporous *p*-phenylenesilica. Each *p*-phenylene rotor pivots on two silicon atoms through C–Si bonds that are inserted in inorganic siloxane layers. Rotors are aligned along the channel axes and exposed to the internal free volume of the empty channels.

The ^{2}H NMR spectral profiles of the deuterated mesoporous *p*-phenylenesilica vary progressively with increasing temperature from 216 to 300 K (Figure 2 a) and were simulated successfully by considering reorientation rates that are intermediate (10^3–10^7 Hz) or fast (above 10^7 Hz) on the timescale of ^{2}H NMR spectroscopy (Figure 2 b). At room temperature, the spectrum shows a profile with singularities separated by 33.4 kHz, which corresponds to about one-fourth of the 135 kHz splitting of the static pattern (Pake spectrum). The 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; exchange rates k as high as 5.6×10^7 Hz were obtained at room temperature.[8] This extremely rapid regime of motion in a crystalline solid exceeds the exchange rates of *p*-phenylene groups in most organic materials and solid polymers.[9] Notably, the dynamics detected in this case are orders of magnitude faster than those recently detected in the metal–organic framework MOF-5, which are still in the slow exchange regime at room temperature.[10] The molecular

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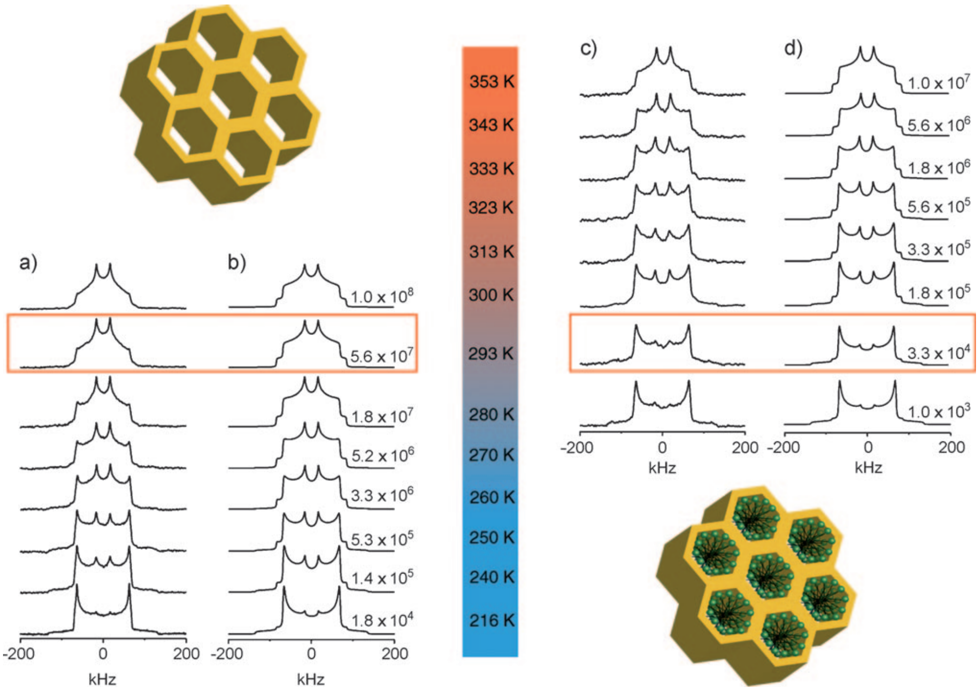

Figure 2. a,b) Deuterium NMR spectra from 216 to 300 K of the mesoporous [D_4]PSS (a) compared to the simulated spectra (b). The spectrum at room temperature shows singularities separated by 33.4 kHz (highlighted with a rectangle), thus indicating the fast dynamics that occur in the porous hybrid material. c,d) Deuterium NMR spectra from 280 to 353 K of the mesoporous [D_4]PSS with the nanochannels filled with OTMA (c) compared to the simulated spectra (d). The spectrum at room temperature is highlighted with a rectangle. Below room temperature the spectral profiles indicate a slow motional regime. The exchange rates *k* (in Hz) for each spectrum are given.

motion in [D_4]PPS also persists at low temperatures, and exchange rates are slowed down to 1.8×10^4 Hz only at 216 K, showing a Pake spectrum with singularities separated by 127.7 kHz.

The sample was subjected to repeated cooling/heating cycles, and the rotor rates associated with specific temperatures are precisely reproduced without hysteresis, thus demonstrating that the phenomenon is reversible and tunable by temperature. Furthermore, the thermal stability of the covalent architecture of PPS widened the accessible temperature range for molecular rotors up to 750–800 K; these temperatures are normally unattainable for porous molecular crystals, polymers, and MOFs.[11] Thanks to this high stability, extremely fast regimes can be reached at high temperatures (above 10^{10} Hz, see the Supporting Information). To account for the further restriction of the linewidths together with the weakening of the spectral shoulders, fast fluctuations of the phenyl rings within each jump site must be included in the 180° flip mechanism. The spectra can be simulated with a distribution of fluctuations with increasing amplitude ($\pm 15°$ at 320 K up to $\pm 35°$ at 420 K). Nevertheless, the mechanism of diffusional reorientation of the elements about their axes is substantially retained, owing to the robust scaffold that ensures the stable support of molecular rotors for the accomplishment of even ultrafast motional frequencies. In fact, the rapid motion is feasible because the aligned rotors are held at a minimum distance of 4.4 Å, which is much greater than that of a face-to-face stacking of two benzene rings (ca. 3.4 Å). Thus, to experience fast regimes, the molecular rotors benefit not only from the nanochannel voids but also from the free volume made available by the framework in the thin pore walls. Moreover, the nature of the C–Si single bonds connecting the rotors to the siloxane framework is particularly favorable for promoting rotational motion, as we ascertained by ab initio calculations.[12] Essentially negligible torsional barriers of less than 0.5 kcal mol^{-1} have been found. Therefore structural design plays an important role in promoting both stability and mobility.

As anticipated, the extremely high surface area and the open framework of the mesoporous material allow easy diffusion of chemical species that upon penetrating the nanochannels interact directly with the aromatic groups on the pore walls and can, in principle, affect their motion. We were able to fine tune the collective dynamics of the entire population of rotors by the active use of included molecules, thus enabling the external regulation of the motional regime through weak intermolecular interactions produced at the extended interfaces. The ^{2}H NMR spectra recorded at variable temperatures for the sample with the nanochannels filled with octadecyltrimethylammonium bromide (OTMA, Figure 2c) and their simulations (Figure 2d) show mobility only above room temperature. At lower temperatures, the spectral profiles display a “static” pattern typical of a slow exchange regime. The rotational speed of the *p*-phenylene moieties at any temperature was reduced by three orders of magnitude with respect to that observed in the walls of the empty nanochannels (see spectra in Figure 2 and those in the Supporting Information). This finding reveals unprecedented chemical control of the molecular rotor rates by soft interactions.

To establish the energy barrier for rotation of the mobile elements in the empty and the occupied nanochannels, we report the rotational rates versus 1/*T* as an Arrhenius plot (Figure 3). In the guest-free mesoporous material, the activation energy is as low as 13.2 kcal mol^{-1}, while a value of 17.8 kcal mol^{-1} is obtained when guest molecules occupy the channels. At very high temperatures the least-squares fitting lines for the empty and loaded matrices converge. As the rotating elements inserted into identical architectures have the same inertial mass, the rotors in both samples achieve fast

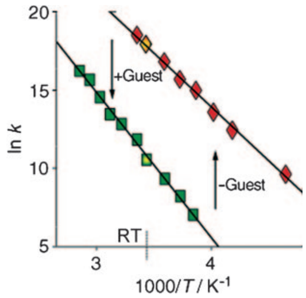

Figure 3. Arrhenius plot of the motional rates of the rotors inserted in the nanochannel walls as a function of temperature for the [D$_4$]PSS mesoporous matrix (diamonds) and for the sample loaded with OTMA guest (squares). The highlighted symbols represent the k values for the spectral profiles of the samples at room temperature. The cycle of guest uptake/removal (+Guest/−Guest) is illustrated by down and up arrows.

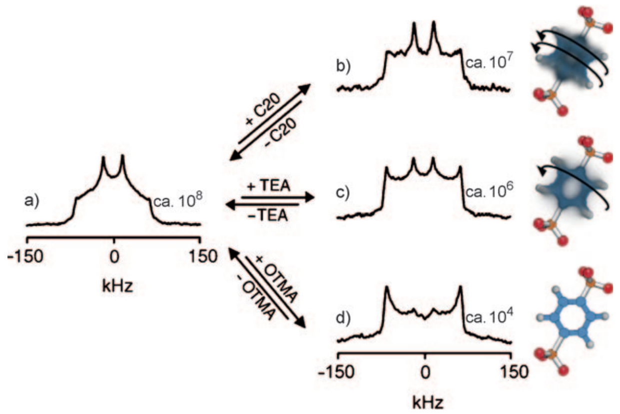

Figure 4. Deuterium NMR spectra of mesoporous [D$_4$]PSS with b) C20, c) TEA, and d) OTMA guests compared to the empty matrix (a). The samples containing C20 (b) and TEA (c) show mobility intermediate between the two extreme cases (a, d). The exchange rates (k in Hz) for each spectrum are given.

rotation in the terahertz regime. Indeed, in the high-temperature limit, the energy profiles of the mobile elements during their rotation becomes irrelevant to the rotor dynamics.

Notably, the difference between the energy barriers to rotation in the empty and guest-filled samples is only 4.6 kcal mol^{-1}, and this value is consistent with weak interactions occurring at the extended interfaces between the rotor elements in the host walls and the guest.[13] This is a rare observation of host–guest interactions, revealed by the change in the host properties. As depicted in Figure 3, it is possible to drastically reduce the molecular mobility of the empty material by diffusing a guest inside the channels (+Guest); removing it (−Guest) causes reversion to the initial value.

Control over the rotor dynamics was also achieved by a variety of guest molecules diffused into the nanochannels from solution or from the melt. The screening of guests with varied polarity and molecular masses, such as *n*-eicosane (C20), tetraethylammonium chloride (TEA), and water, showed the modulated response of the rotor dynamics in the host framework, which resemble the active switching of molecular motion in engineered molecular machines.[14] The limiting case of high mobility of the empty [D$_4$]PPS (Figure 4a) is compared with three intermediate cases of curbed motion obtained by the inclusion of C20, TEA, and OTMA in the nanochannels. Additional cases of intermediate motional regimes obtained by guest inclusion are presented in the Supporting Information.

Repeated cycles of guest uptake and removal illustrate the fine-tuned reversible switching, from rapidly mobile to slower rates of molecular motion and back. Collectively, these results provide robust evidence that included guest molecules act efficiently as brakes to the entire population of the host molecular rotors, showing the unprecedented tunability of the molecular dynamics under chemical stimulus. This braking effect can be accomplished or dosed at will. In fact, the proper choice of selected guests allowed us to control the mobility over a wide range of motional regimes at a given temperature.[15]

In conclusion, the unique combination of ultrafast molecular rotors and structural porosity, demonstrated herein for mesoporous hybrid materials, enabled the active speed regulation of ordered 3D arrays of individual rotors. Owing to the extremely high surface area of the materials, the rotary elements inserted in the pore walls of the nanochannels are easily accessible and interact with the environment. On the basis of these results, the fine tuning of molecular dynamics can be programmed to respond to guest molecules. The absorption ability, fast dynamics, and crystalline order of these materials are extremely attractive for the creation of molecular machines and devices engineered for specialized functions. We believe that the possibility to modulate the mobility of rotors by guest interaction in organosilica materials can be generalized to other porous molecular materials by exploiting the adsorption of gases and vapors as chemical stimuli.

Experimental Section

[D$_4$]*p*-Phenylenesilica was prepared by a template synthesis in which the organic–inorganic building blocks [D$_4$]1,4-bis(triethoxysilyl)benzene ([D$_4$]BTEB) self-organize around amphiphilic molecules of octadecyltrimethylammonium bromide in aqueous NaOH (molar ratio OTMA/[D$_4$]BTEB/NaOH/H$_2$O 0.96:1.00:4.03:559.23) as reported elsewhere.[6] To prepare the *n*-eicosane [D$_4$]PSS material, *n*-eicosane (1.5 g) and the empty mesoporous material (1 g) were degassed together at 120 °C under vacuum. The mixture was heated at 80 °C, and the melted guest was left to diffuse into the mesoporous host for a few hours. In the case of water-soluble guests, such as tetraethylammonium chloride, concentrated solutions were left in the presence of the empty matrix after its evacuation. Guests were easily removed by stirring the powder in an appropriate solvent and recovering the empty mesoporous material.

Solid-state ^{2}H NMR spectroscopy experiments were performed on a Bruker 300 Avance spectrometer operating at a frequency of 46.07 MHz under a static magnetic field of 7.04 T, using a Bruker 5 mm widelines probe. Fully relaxed spectra (15 s recycle delay) were acquired with the quadrupolar echo pulse sequence,[7] $(\pi/2)_x$–τ_1–$(\pi/2)_y$–τ_2, with a $\pi/2$ pulse of 2.1 µs and a pulse spacing of $\tau_1 = \tau_2 = 50$ µs. Spectra obtained with pulse spacing between 30 and 70 µs have the same line shapes. The stability and accuracy of the temperature controller (Bruker B-VT2000) were approximately ±1 K.

Theoretical simulation of ^{2}H NMR spectra for a two-site 180° jump model was performed by the program Express 1.0,[8a] with a quadrupole coupling constant of 180 kHz and an asymmetry parameter of 0.02. Simulations are obtained for a log-Gaussian distribution of jump rates by superposition of 61 spectra for different jump rates. A single distribution width of $\sigma = 1.5$ was used.

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[15] The arrays of phenylene units in the channel walls reside for longer in the face-to-face configuration with C–D vectors pointing to the channels. The phenyl reorientation mechanism implies that C–D dipoles reorient as well; it can be suggested that the braking effect is due to the occurrence of favorable weak interactions between C–D bonds and the guest species, which can further stabilize this configuration, thus slowing down the motion. Our observations support the conclusions that the hydrocarbons affect the rotor dynamics less strongly than polar guests, which present larger interactions with reorienting dipoles.