

Molecular rotors in hierarchically ordered mesoporous organosilica frameworks†

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Diphenylene moieties, molecularly ordered in the framework of periodic mesoporous organosilicas, behave as molecular rotors and show a mobility with correlation times as short as a few nanoseconds.

Periodic mesoporous organosilicas (PMOs)¹ are an emerging class of materials that offer new possibilities to tailor the macroscopic properties of porous solids. By incorporating organic moieties into high-surface-area siliceous frameworks, their structural features and interfacial interactions can be modified to enhance their adsorption, catalytic, molecular recognition, confinement, luminescence, or photochemical properties. Furthermore, the composition and structure of these hybrid materials can be adjusted over a hierarchy of molecular and mesoscopic length scales, providing additional possibilities for controlling their properties. Separately, the construction of novel molecular motors and rotors is attracting growing attention, and constitutes a new stimulating research field.^{2,3} It has opened up a variety of perspectives for creating anisotropic and correlated motions in solids and, as a consequence, novel macroscopic properties. Such molecular rotors have been fabricated in solution, in monoliths, or on surfaces,^{2,3} but have not been demonstrated in self-assembled mesoporous materials. In mesoporous organosilicas with crystalline-like order in their walls,⁴ organosiloxane elements are organized into ordered arrays, and align their molecular axes parallel to the mesochannel axis, enabling the fabrication of belt-like layers of alternating organic and inorganic moieties lining the mesochannel walls. A representative example of this class of materials is diphenylenesilica as presented in Fig. 1. Organic groups, commonly aromatics, are pivoted between two silicon atoms, each of which are cross-linked within the mesostructured organosilica framework and hinder close-packing of the organic moieties because of the constraints imposed by the inorganic layers. Thus, in these materials the available free volume can be exploited, permitting the aromatic moieties to experience rotational motions.

Herein we report, for the first time, the remarkable dynamic behavior of highly ordered hexagonal mesoporous *p*-diphenylenesilicas, and recognize the presence of parallel and aligned molecular rotors in their pore walls. This results in an effectively ‘amphidynamic’ structure of the mobile hydrophobic diphenylene groups (rotors), which pivot on the more rigid hydrophilic silica species through covalent C–Si bonds.⁴ The structure is such that the diphenylene moieties are exposed to the interior pore spaces of the mesochannels. The intra-framework structure and motional behaviors of mesoporous diphenylene-silica are elucidated by solid-state multinuclear experiments and fast magic-angle spinning (MAS) ¹H, ¹³C, and ²⁹Si nuclear magnetic resonance (NMR) spectroscopy.⁵ Hexagonal mesostructured diphenylenesilicas were examined as-synthesized and after removing the structure-directing alkylammonium (C₁₈TMA⁺Br[−]) surfactant species. Nitrogen adsorption analyses at 77 K of mesoporous diphenylene-silica establish a surface area of 745 m² g^{−1}, pore volume of 0.73 cm³ g^{−1}, and mean pore diameter of 3.74 nm (ESI†). Characterization by X-ray diffraction shows a high degree of hexagonal mesoscale order (*d*-spacing of 4.48 nm) and molecular periodicity (001) along the channel axes of 1.17 nm, with higher-order reflections at 0.59, 0.39, 0.29 and 0.24 nm (Fig. 1 and ESI†).

Two-dimensional (2D) solid-state NMR spectroscopy is sensitive to local composition and structure of the diphenylene-silica hybrid materials, including interatomic distances and dynamics. The molecular proximity of the silicon- and hydrogen-containing moieties can be unambiguously established by measuring and correlating the extent of their heteronuclear ²⁹Si–¹H dipole–dipole interactions in 2D heteronuclear chemical shift correlation (HETCOR) spectra.⁵ The different relative intensities in the contour spectrum reflect the different relative strengths of the dipole–dipole couplings; the more intense

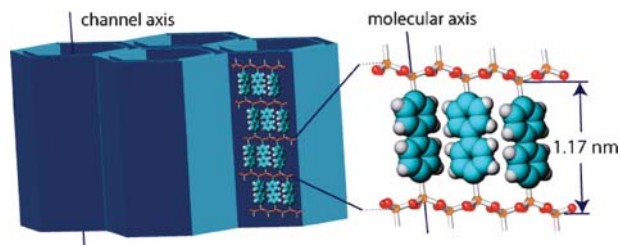


Fig. 1 Schematic representation of the mesochannels in hexagonal mesoporous diphenylene-organosilica. An expanded region shows diphenylene molecular moieties with their molecular axes parallel to the mesochannel axes.

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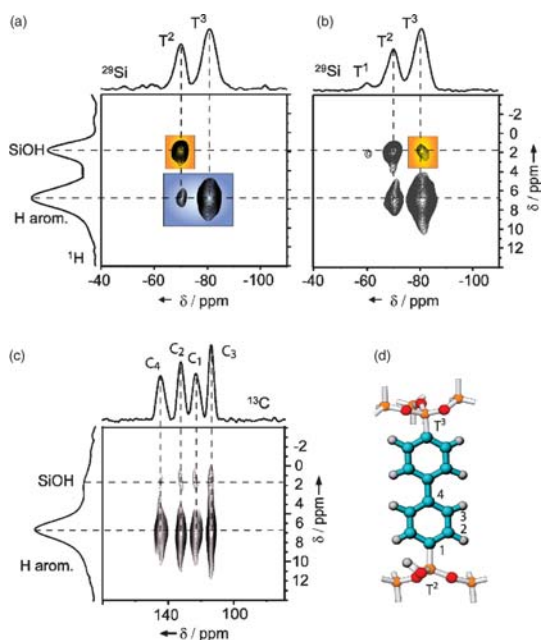


Fig. 2 (a,b) 2D $^{29}\text{Si}\{^1\text{H}\}$ HETCOR MAS NMR spectra of mesoporous diphenylene-silica recorded at 11.7 T, a spinning frequency of 15 kHz, and contact times of (a) 2 ms and (b) 8 ms. 1D projections are shown along the corresponding ^1H and ^{29}Si axes. (c) A 2D $^{13}\text{C}\{^1\text{H}\}$ HETCOR MAS NMR spectrum using an 8 ms contact time. A quantitative single-pulse 1D ^{13}C MAS NMR spectrum, recorded with a recycle delay of 100 s, is reported. (d) Schematic diagram of a diphenylene-silica moiety showing the different types of ^{29}Si and ^{13}C nuclei.

correlations point to more strongly coupled species (nearer in space and with lower mobilities). Comparisons of correlated signal intensities in 2D $^{29}\text{Si}\{^1\text{H}\}$ HETCOR spectra of mesoporous diphenylene-organosilica acquired at short (2 ms) and longer (8 ms) contact times allow strongly and weakly coupled species, respectively, to be distinguished. For the short 2 ms contact time, the 2D $^{29}\text{Si}\{^1\text{H}\}$ HETCOR spectrum in Fig. 2a shows strong correlated signal intensity between the silanol protons ($\delta_{\text{H}} = 1.8$ ppm) and the T^2 ^{29}Si species to which they are bonded (hydrogen-to-silicon distance of *ca.* 0.25 nm). In contrast, the aromatic hydrogen atoms ($\delta_{\text{H}} = 6.9$ ppm) correlate with both T^2 and T^3 ^{29}Si species ($\delta_{\text{Si}} = -70.3$ and -80.4 ppm, respectively), since each silicon atom is bonded to an organic group and is separated by the same distance of *ca.* 0.3 nm from the aromatic hydrogen atoms. This is a direct demonstration of the intimate molecular proximity of the organic and inorganic layers in these materials.

At longer contact times (8 ms), the silanol protons interact with the covalently bonded T^2 species and also more distant T^3 ^{29}Si sites, which therefore must be within *ca.* 0.5 nm (Fig. 2b). These results indicate that T^2 and T^3 ^{29}Si species are proximate to each other within the same hybrid network and not segregated into defect regions of the material. ^{29}Si T_1 spin-lattice relaxation times of the condensed species T^2 and T^3 are long, 41 s and 108 s, respectively, consistent with the rigid structure of the silica moieties in the framework about which the molecular rotors pivot. The longer relaxation time of the T^3 ^{29}Si sites is due to less efficient nuclear spin relaxation

mechanisms, due to their lower mobilities and the absence of bonded silanol protons.

The 1D ^{13}C MAS spectrum in Fig. 2c of mesoporous diphenylene-organosilica shows four narrow signals, out of the twelve carbon atoms present in the diphenylene moieties, suggesting a highly symmetric arrangement or significant dynamical behavior of these groups within the organosilica framework. The 2D $^{13}\text{C}\{^1\text{H}\}$ HETCOR spectrum of Fig. 2c shows strong intensity correlations between all of the aromatic ^{13}C atoms and nearby aromatic hydrogen atoms and weaker correlations with the silanol protons. In particular, the correlations with silanols are consistent with the expected proximities of the different phenyl ^{13}C atoms to the silanol protons ($\delta_{\text{H}} = 1.8$ ppm). The relative strengths of the intensity correlations associated with ^{13}C sites C_1 , C_2 , and C_3 ($\delta_{\text{C}} = 131.0$, 135.6 and 126.2 ppm, respectively), which are nearer to the silica framework, are significantly stronger than that of the diphenylene-bridging C_4 sites ($\delta_{\text{C}} = 141.6$ ppm), which are more distant at *ca.* 0.5 nm (Fig. 2d). These results demonstrate the high extent of local ordering of the rod-like diphenylene moieties in the organic layers of the ordered hybrid material.

The motional behaviors of the molecular moieties in the mesoporous diphenylene-organosilica are established by ^1H and ^{13}C spin-lattice relaxation measurements that are sensitive to regimes of motion over the range of frequencies from 30 to 300 MHz. Measurements of ^1H and ^{13}C spin-lattice relaxation rates (at 30, 75 and 300 MHz) are shown in Fig. 3a, as functions of temperature from 175 to 450 K. These enable correlation times to be established, as well as apparent activation energies of the motional processes. The most efficient relaxation is obtained when the motional frequencies match the Larmor frequency of the

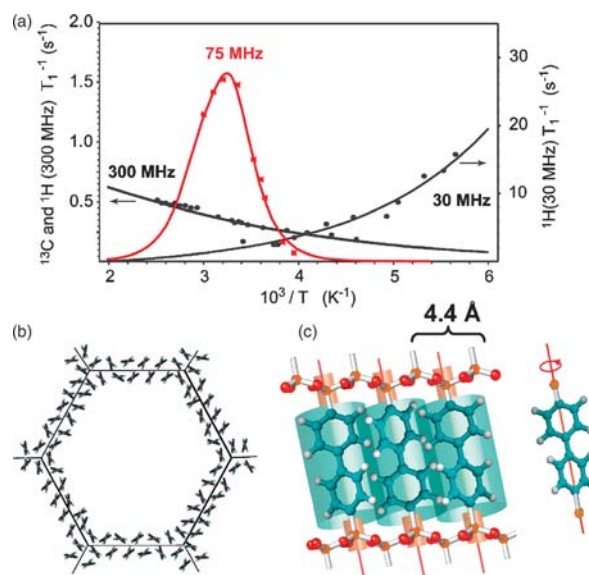


Fig. 3 (a) Temperature-dependent ^1H $1/T_1$ relaxation rates at 30 and 300 MHz and ^{13}C $1/T_1$ relaxation rates at 75 MHz (for C_2 carbon) measured for mesoporous diphenylene-silica. Schematic diagrams of hexagonal mesoporous diphenylene-silica showing (b) a cross-section of a single mesochannel, with *ca.* 1 nm-thick walls that comprise two rows of diphenylene rotors, viewed along their main axes; and (c) a single row constituted by the rod-like diphenylene rotors that are vertically aligned along the channel axis and exposed to the mesochannels.

observed nuclei. The experimental results can be fitted, using a non-linear least-squares analysis, by applying the Kubo–Tomita equation that describes the relaxation rates as a function of temperature.⁶

The hydrogen atoms of both the aromatic rings and the silanols relax collectively, due to their mutual interactions *via* homonuclear dipole–dipole couplings. The relaxation results at 30 MHz indicate a motional behavior typical of the liquid regime with a weak temperature dependence and low apparent activation energy (6.4 kJ mol⁻¹), due to conformational mobility about the central bond of diphenylene moieties in agreement with theoretical calculations⁷ (the same activation energy is measured by the best fitting of the hydrogen relaxation rates at 300 MHz). ¹³C relaxation rates at 75 MHz can be used to assess the different motional characteristics of the ¹³C nuclei in the diphenylene-silica frameworks of the mesoporous material. The ¹³C relaxation rates at 75 MHz for the C₂ and C₃ carbon atoms show maximum values at 310 K (Fig. 3a), consistent with fast molecular motions of the phenyl-ring moieties about their molecular rotation axes with a mean correlation time τ_c of 13 ns.⁸ Analyses of the temperature dependence of the relaxation rates yield an apparent activation energy of 39 kJ mol⁻¹, which corresponds to the energy value reported in the literature for a 180° flip process of the *para*-substituted phenyl rings about their central axes, as reported for polycarbonate and poly-*p*-phenylene.⁹ Each aromatic ring possesses a lateral van der Waals steric hindrance of *ca.* 0.34 nm (each π -electron cloud accounts for 0.17 nm), and the distance between adjacent axes of the diphenylene moieties imposed by the framework is *ca.* 0.44 nm, as established by XRD. Consequently, there is more space available than that of a face-to-face close-packed configuration, permitting facile rotational motion to occur. In addition, the thickness of the framework walls separating adjacent pairs of mesochannels is *ca.* 1 nm, so that the walls are comprised of two rows of adjacent and parallel diphenylene molecular rotors (Fig. 3b), each of them facing neighboring mesochannels. The rod-like diphenylene groups can be envisaged as molecular rotors (Fig. 3c), each pivoted about two silicon atoms that are 1.1 nm apart.^{4a} The *ca.* 10⁻⁸ s correlation times are much shorter than those typically observed in conventional crystalline materials, reflecting a framework structure with unusual internal molecular mobility, similar to liquid-crystalline materials. The mobility is as high as that of molecular gyroscopes recently proposed in organic crystals.³ In addition, our assembly of rotors presents the unique feature of being easily accessible in these porous and high-surface-area materials.

The large interface of the rotors to species that may occupy the mesochannels is apparent in the as-synthesized diphenylene-silica with the structure-directing C₁₈TMA⁺ surfactant molecules residing in the mesochannels and interacting with the anionic charges on the silica regions of the framework. This is established by 2D ²⁹Si{¹H} HETCOR NMR results (8 ms contact time, ESI†), which show strong correlated signal intensity in the ¹H dimension at $\delta_H = 2.7$ ppm, associated with the polar surfactant head groups of the methylammonium moieties, with T² and T³ ²⁹Si sites in the ²⁹Si dimension. Such correlated NMR signal intensity indicates that the framework species face the mesopore channels and are accessible to guest molecules.

In conclusion, multinuclear NMR results from magnetic fields ranging from 0.7 to 11.7 T have, for the first time,

established the unusual dynamic character of molecularly ordered diphenylene moieties in the siliceous framework of the ordered mesoporous hybrid system. The 3D periodic structure contains layers of diphenylene groups that line the mesochannel walls, and that have high rotational mobilities with extremely short correlation times in the liquid-like regime. The molecular rotation axes of diphenylene moieties are parallel and are aligned along the mesochannel axes, yielding an unusual anisotropic arrangement of surface-exposed molecular rotors in the rigid 3D scaffold. The observation of such rapid molecular motions, juxtaposed alongside rigid silica layers in the hybrid framework, establishes its amphidynamic character, which is to the best of our knowledge the first such example in mesoporous hybrid materials. It can be expected that the new-found motional properties of PMOs will open new opportunities in the design and chemical syntheses of multifunctional responsive materials, *e.g.* dipolar rotors inserted in the mesochannel walls that reorient upon external stimulation, such as electrical fields, to modulate or switch optical or sorption properties.

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