Supporting Information

Molecular Rotors in Hierarchically-ordered Mesoporous Organosilica Frameworks

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Synthesis of the diphenylenesilica

Mesostructured diphenylene-silica was synthesized by self-assembly of amphiphilic octadecyltrimethylammonium bromide ($C_{18}TMA^+Br^-$) surfactant species in an aqueous sodium hydroxide (NaOH) solution in the presence of 4,4'-bis(triethoxysilyl)diphenyl (BTEDP). The following molar ratios were used in a typical synthesis: 1.28 $C_{18}TMA^+Br^-$: 1.00 BTEDP : 12.16 NaOH / 1320 H_2O. $C_{18}TMA^+Br^-$ was dissolved in aqueous NaOH at 60-70 °C, after which BTEDP was added dropwise to the solution under vigorous stirring at room temperature. The mixture was stirred at room temperature for 20 h, then kept at 95 °C for 22 h under static conditions. A white precipitate was recovered by filtration and dried to yield the as-synthesized mesostructured diphenylene-silica material still containing the structure-directing surfactant molecules **1**. The surfactant was subsequently solvent-extracted by stirring 1 g of the as-synthesized product in 200 ml of ethanol and 0.8 g of 36% hydrochloride aqueous solution at room temperature for 8 h, yielding mesoporous diphenylene-silica. Thermogravimetric analyses are reported in the Supplementary Information.

Experimental

Mesostructured diphenylene-silica was synthesized as reported in Supporting Information. Solid-state two-dimensional (2D) $^{13}C\{^1H\}$ and $^{29}Si\{^1H\}$ HETeronuclear chemical shift CORrelation (HETCOR) NMR experiments were performed on a Bruker AVANCE-500 NMR spectrometer operating at 500.13 MHz, 125.76 MHz, and 99.35 MHz for ^1H, ^{13}C, and ^{29}Si, respectively. Experiments were conducted at room temperature under magic-angle spinning (MAS) conditions at 15 kHz by using a Bruker ^1H/X double-resonance MAS probehead with 4.0-mm zirconia rotors. For the $^{13}C\{^1H\}$ HETCOR experiments, a 4.2 μs 90° pulse was used for cross-polarization. 20ms acquisitions with a 4s recycle delay were collected for 72 t_1 increments. For the $^{29}Si\{^1H\}$ HETCOR experiments, a 4.2 μs 90° pulse was used for cross-polarization. 10 ms acquisitions with a 4s recycle delay were collected for 64 t_1 increments. The ^1H MAS spectra were collected at 34kHz with a Bruker ^1H/X double-resonance MAS probehead with 2.5-mm zirconia rotors. The ^1H and ^{29}Si chemical shifts were referenced to tetrakis(trimethylsilyl)silane $[(CH_3)_3Si]_4Si$, and the ^{13}C chemical shift was referenced to adamantane ($C_{10}H_{16}$). ^{13}C spin-lattice relaxation times were measured at 75 MHz by applying the CP T_1 sequence and ^1H spin-lattice relaxation times by an inversion recovery sequence on a Bruker AVANCE-300 NMR spectrometer operating at 300 MHz, respectively. The proton relaxation rates at 30 MHz were measured using a Stelar Spinmaster-FFC field-cycling relaxometer that operates at variable magnetic field strength up to 1 T.

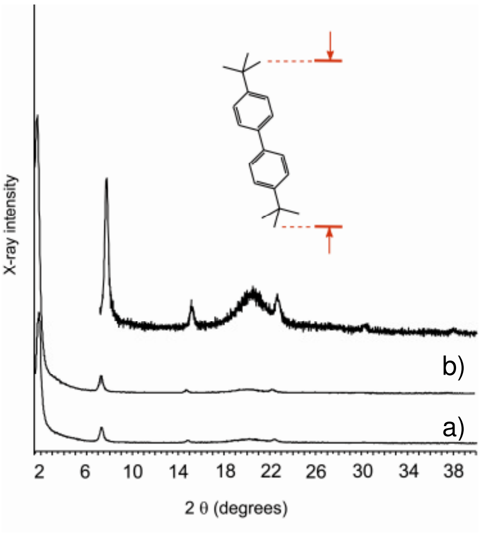

Figure S1. Powder X-ray diffraction of the diphenylene-silica materials a) as-synthesized, containing alkylammonium (C_{18}TMABr) templating agent and b) freed from the guest.

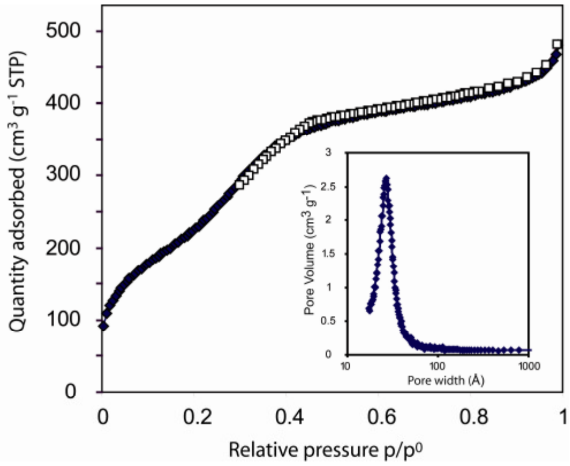

Figure S2. Nitrogen adsorption measurements at 77K of the guest-free organosilica and the BJH pore size distribution.

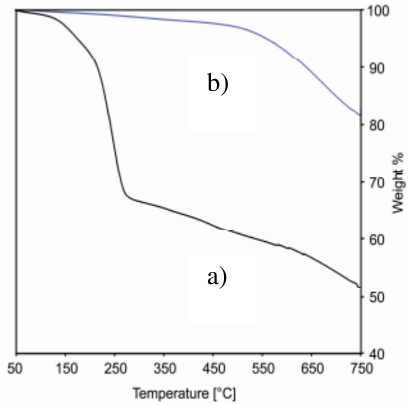

Figure S3. Thermogravimetric analysis of diphenylene-silica materials: a) as-synthesized, containing alkylammonium (C_{18}TMABr) templating agent and b) freed from the guest.

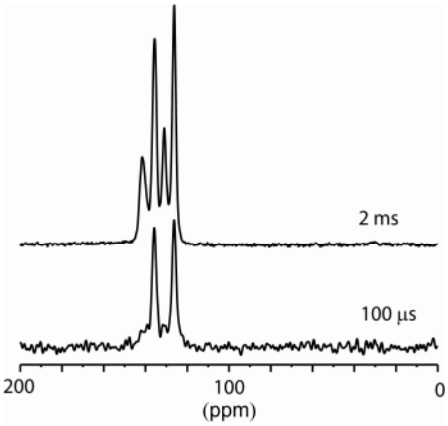

Figure S4. ^{13}C CP MAS NMR spectra of the guest-free sample at two different contact times. The spectra enable ^{13}C signals from the aromatic carbon atoms that are covalently bonded to hydrogen atoms to be distinguished from unprotonated carbon atoms C-Si (C_1 and C_4). Rakita, L. S. Worsham *J. Organometallics Chemistry* **1977**, *137*, 145.

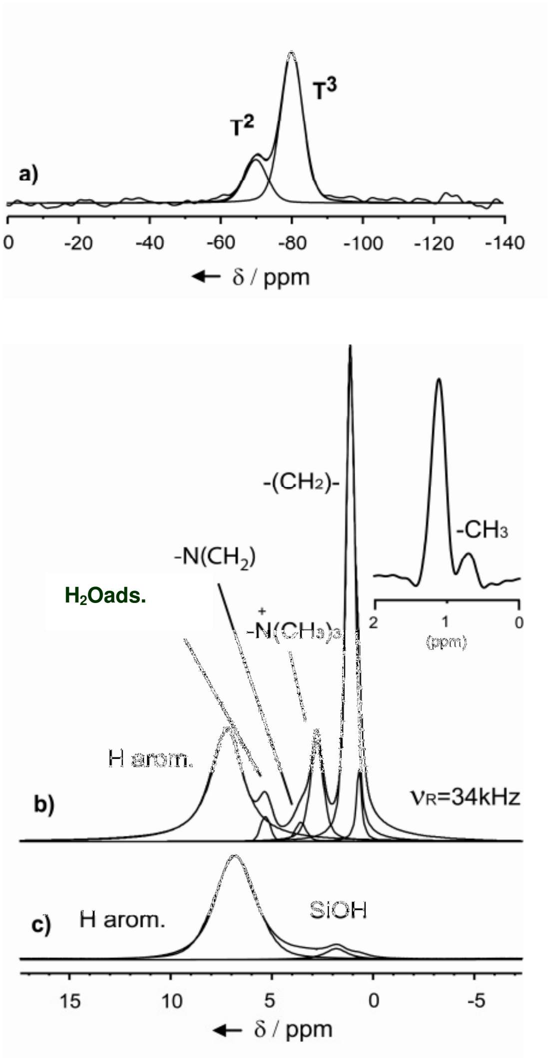

Figure S5. a) A single-pulse ^{29}Si magic-angle spinning (MAS) NMR spectrum recorded with 500 s recycle delay of mesoporous diphenylene-organosilica. The single-pulse ^{29}Si MAS NMR spectrum shows resonances at δ_{Si}=-80.4 and -70.3 ppm, associated with condensed T^3 and T^2 ^{29}Si species, respectively. Quantitative analysis of their integrated signal intensities yields a T^3/T^2 ratio of 3:1. Single-pulse ^{1}H MAS NMR spectra acquired at 34 kHz MAS of mesoporous diphenylene-organosilica b) with and c) following removal of the surfactant species. In (b), methylammonium and alkyl proton moieties associated with the structure-directing surfactant species resonate at 2.7 and 1.1 ppm, respectively, ^{1}H signals at δ_H = 5.2 ppm are assigned to hydrogen-bonded adsorbed water. Deconvolution of the signals allow the ^{1}H signals from the methylene-ammonium and chain-end methyl moieties to be inferred at 3.5 and 0.7 ppm, respectively. Diphenylene groups and hydroxyl groups associated with framework silanol species resonate at δ_H=6.9 ppm and δ_H = 1.8 ppm, respectively. Upon removal of the surfactant species and thermal treatment at 150 °C, the ^{1}H spectrum in (c) shows ^{1}H signals at 6.9 ppm and 1.8 ppm associated with the diphenylene-organosilica framework ($H_{arom.}$) and the silanol hydrogens (SiOH), respectively (B. Grünberg, T. Emmler, E. Gedat, I. Shenderovich, G. H. Findenegg, H.-H. Limbach and Buntkowsky, *Chem. Eur. J.* **2004**, *10*, 5689). The integrated intensity ratio of 1:16 (SiOH:$H_{arom.}$) corresponds to a distribution of one -OH group out for every four aromatic rings in the structure, in excellent agreement with the relative distribution of silanol and phenylene proton species estimated from Figure S5a above.

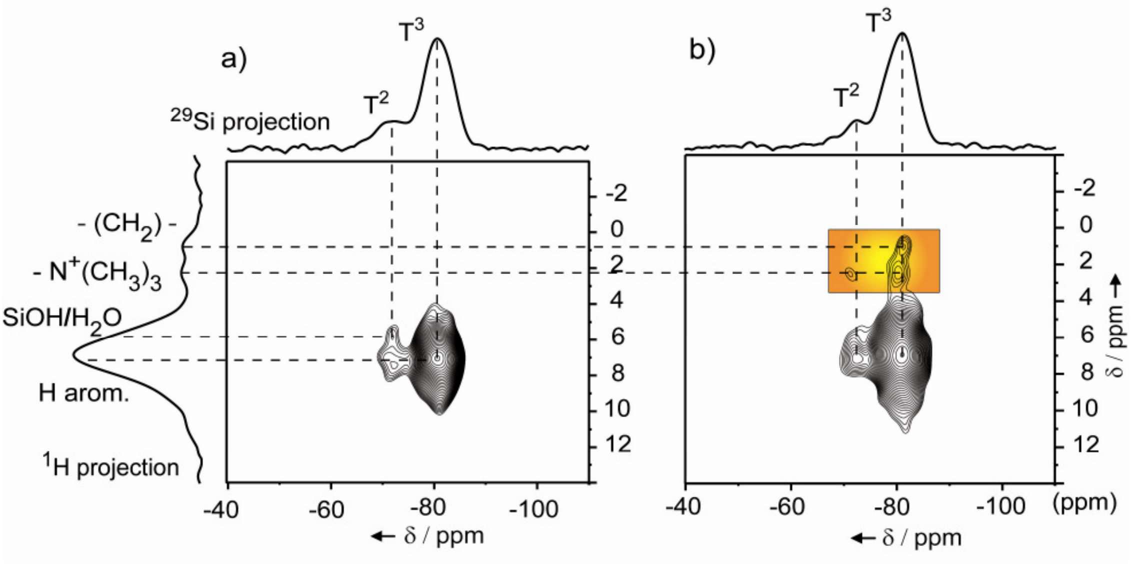

Figure S6. 2D ^{1}H-^{29}Si HETCOR MAS NMR spectra of the hybrid mesoporous material with surfactant with contact time of a) 2 ms and b) 8 ms. Due to the presence of water, silanol hydrogens resonate at 5.2 ppm and fall below the aromatic signal.