Supporting Information

Dynamics in Amine-Functionalized Mesoporous Hybrid Materials Probed through Deuterium Magic Angle Spinning NMR and Molecular Dynamic Simulations

V. S. Veena^a, I. Kavya^{b,d}, A. Lazar^{c,d}, C. P. Vinod^{c,d}, T. G. Ajithkumar^{b,d} and S. Jayanthi^{a*}

 ^aDepartment of Physics, Indian Institute of Space Science and Technology, Valiamala, Thiruvananthapuram 695 547, Kerala, India.
 ^bCentral NMR Facility and Physical and Materials Chemistry Division, CSIR-National Chemical Laboratory, Pune 411008, Maharashtra, India.
 ^cCatalysis and Inorganic Chemistry Division, CSIR-National Chemical Laboratory, Pune 411008, Maharashtra, India.
 ^dAcademy of Scientific and Innovative Research, Campus: CSIR- National

Chemical Laboratory, Pune 411008, India

*Author for correspondence: jayanthi.s@iist.ac.in; mssjayanthi@gmail.com Phone number: +91 471 2568658; Fax No. +91 471 2568542

CONTENTS

1. Relative Integrated intensity from ²⁹ Si CPMAS NMR Spectra.	S 3
2. Room temperature ¹ H MAS NMR spectra with deconvoluted components-	C 4
3 Room temperature ¹ H MAS NMR spectra with deconvoluted components-	54
diamine-MATMS.	S 5
4 . ² H MAS NMR spectra and best fit of diamine-GPTMS recorded at 273 and 298 K.	S6
5 . Room temperature ² H MAS NMR spectra with deconvoluted components- diamine –GPTMS (wet).	S7
6 . Room temperature ¹ H MAS NMR spectra with deconvoluted components- diamine –GPTMS (dry).	S 8
 Plot showing the variation of relative percentages of deconvoluted components from ²H MAS NMR spectra for diamine-GPTMS. 	S9
8 . ² H MAS NMR spectra and the best fit of diamine-MATMS recorded at 273 and 298 K.	S10
 Room temperature ²H MAS NMR spectra with deconvoluted components- diamine –MATMS (wet). 	S11
 Room temperature ²H MAS NMR spectra with deconvoluted components- diamine –MATMS (dry). 	S12
 Plot showing the variation of relative percentages of deconvoluted components from ²H MAS NMR spectra for diamine-MATMS. 	S13
12 . MD Calculation with diamine-GPTMS in T_3 conformation and four hydroxyls.	S14
13 . MD Calculation with diamine -MATMS in T_2 conformation and four silanols.	S15
14 . MD Calculation with diamine -MATMS in T ₃ conformation – more hydroxyls.	S16
15 . MD Calculation with diamine -MATMS in T ₂ conformation– more hydroxyls.	S17
16 . MD Calculation with diamine Diamine-MATMS in T ₃ conformation – Rigid.	S18
17. Variation of polar angle – diamine-GPTMS.	S19
18. Variation of polar angle – diamine-MATMS.	S20

²⁹ Si groups in	Diamine-GPTMS	Diamine-MATMS
modified SBA-15	(%)	(%)
Q ₂	11.64	4.99
Q ₃	50.93	47.04
Q4	25.31	27.07
T ₂	4.59	8.3
T ₃	7.54	12.6

Table S1: Relative percentages of various resonances extracted using DMFIT from²⁹Si CPMAS spectra of diamine-GPTMS and diamine-MATMS.



Figure S1: Diamine-GPTMS ¹H MAS spectra recorded at 298 K and their best fit, for the wet and dry states. The spectra correspond to **Figure 2(a)** in the main text. (*) denotes an impurity peak with relative integrated intensity < 1%. Ratio of the total integrated intensities for the dry and wet samples is 0.58.



Figure S2: Diamine-MATMS ¹H MAS spectra recorded at 298 K and their best fit, for the wet and dry states. The spectra correspond to **Figure 2(e)** in the main text. (*) denote impurity peaks with relative integrated intensity < 1%. The peak observed at 0.6 ppm and denoted by (x) has a constant relative integrated intensity of 5 % in both wet and dry states and is excluded from the dynamic discussion. Ratio of the total integrated intensities for the dry and wet samples is 0.6.



Figure S3: Diamine-GPTMS ²H MAS NMR spectra recorded at 6666 Hz MAS, for temperatures 273 and 298 K, along with their best fit are shown for the wet and dry states of the sample. Best fit spectra are obtained by summing the individual deconvoluted components.



Figure S4: Diamine-GPTMS ²H MAS NMR spectra recorded at 6666 Hz MAS, and 298 K for the wet state. The relative percentage of integrated intensity and the averaged quadrupolar parameters of the deconvoluted components are shown in the plot.



Figure S5: Diamine-GPTMS ²H MAS NMR spectra recorded at 6666 Hz MAS, and 298 K for the dry state. The relative percentage of integrated intensity and the averaged quadrupolar parameters of the deconvoluted components are shown in the plot. The large amplitude dynamic component contributes very little to the best fit.



Figure S6: Percentage of rigid (\blacksquare) and sum of intermediate and large amplitude dynamic components (\Box) as function of temperature for the dry and wet states of diamine-GPTMS. The total sum (\blacktriangle) is shown at the top of the plot.

Diamine-MATMS (Dry)

Diamine-MATMS (Wet)



Figure S7: Diamine-MATMS ²H MAS NMR spectra recorded at 6666 Hz MAS, for temperatures 273 and 298 K, along with their best fit are shown for the wet and dry states of the sample. Best fit spectra are obtained by summing the individual deconvoluted components.



Figure S8: Diamine- MATMS ²H MAS NMR spectra recorded at 6666 Hz MAS, and 298 K for the wet state. The relative percentage of integrated intensity and the averaged quadrupolar parameters of the deconvoluted components are shown in the plot.



Figure S9: Diamine-MATMS ²H MAS NMR spectra recorded at 6666 Hz MAS, and 298 K for the dry state. The relative percentage of integrated intensity and the averaged quadrupolar parameters of the deconvoluted components are shown in the plot. The large amplitude dynamic component contributes very little to the best fit.



Figure S10: Percentage of rigid (\blacksquare) and sum of intermediate and large amplitude dynamic components (\Box) as function of temperature for the dry and wet states of diamine-MATMS. The total sum (\blacktriangle) is shown at the top of the plot.



Figure S11: MD calculations for diamine-GPTMS in T_3 configuration and three hydroxyls positioned at 4.468, 4.713 and 5.043 Å from the anchoring silicon atom (model (4) in Table 4 (main text)). Time dependence of dihedral angles (left), spatial variation of C⁻²H vectors (middle), and molecular conformations (right) derived from MD. Averaged quadrupolar parameters are shown nearby. Yellow (Si), red(O), grey(C), blue (N), and white (H) are the colour codes for the respective atoms.



Figure S12: MD calculations for diamine-MATMS in T₂ configuration and four hydroxyls positioned at a distance of 3.022, 3.811, 3.511, and 4.673 Å from the anchoring silicon atom (model (3) in Table 5 (main text)). Time dependence of dihedral angles (left), spatial variation of $C^{-2}H$ vectors (middle), and molecular conformations (right) derived from MD. Averaged quadrupolar parameters are shown nearby. The time dependence of dihedral angles shows very limited dynamics along the chain except for the end group. Dynamics of $-C_2^{-2}H_2$ -NH₂ provides an averaged quadrupolar coupling of 74 and 76 kHz, whereas for =N- $C_1^{-2}H_2$ - it is 80 and 82 kHz. Yellow (Si), red(O), grey(C), blue (N), and white (H) are the colour codes for the respective atoms.



Figure S13: MD calculations for diamine-MATMS in T₃ configuration and two silanols positioned at 4.763 and 6.467 Å from the anchoring silicon atom (model (2) in Table V (main text)). Time dependence of dihedral angles (left), spatial variation of C⁻²H vectors (middle), and molecular conformations (right) derived from MD. Averaged quadrupolar parameters are shown nearby. The time dependence of dihedral angles shows very limited dynamics along the chain except for the end group. Dynamics of $-C_2-^2H_2-NH_2$ provides an averaged quadrupolar coupling of 44 kHz, whereas for =N- $C_1-^2H_2$ - it is 77 and 79 kHz. Yellow (Si), red(O), grey(C), blue (N), and white (H) are the colour codes for the respective atoms.



Figure S14: MD calculations for diamine-MATMS in T_2 configuration and four hydroxyls positioned at 2.771, 3.509, 3.911, and 3.751 Å from the anchoring silicon atom (model (5) in Table 5 (main text)). Time dependence of dihedral angles (left), spatial variation of C $-^2$ H vectors (right), and molecular conformations (bottom) derived from MD. Averaged quadrupolar parameters are shown nearby. The time dependence of dihedral angles shows very limited dynamics along the chain except for the end group. Dynamics of $-C_2-^2H_2-NH_2$ provides an averaged quadrupolar coupling of 43 and 48 kHz, whereas for =N- $C_1-^2H_2$ - it is 77 and 80 kHz. Yellow (Si), red(O), grey(C), blue (N), and white (H) are the colour codes for the respective atoms.



Figure S15: MD calculations for diamine-MATMS in T₃ configuration and four hydroxyls positioned at 4.358, 4.598, 6.744 and 8.649 Å from the anchoring silicon atom (model (7) in Table 5 (main text)). Time dependence of dihedral angles (left), spatial variation of $C-^{2}H$ vectors (right), and molecular conformations (bottom) derived from MD. Averaged quadrupolar parameters are shown nearby. The time dependence of dihedral angles shows very limited dynamics along the chain. The molecule got almost stabilised through NH₂---OH-Si and (H₂)C-O---HO-Si hydrogen bonding resulting in averaged quadrupolar couplings in the 153-156 kHz range in agreement with the rigid component for the wet sample at 298K. Yellow(Si), red(O), grey(C), blue (N) and white (H) are the colour codes for the respective atoms.



Figure S16: Time dependence of the polar angle θ for C₁-²H_{1,2} (a,b) and C₂-²H_{3,4} (c,d) for diamine-GPTMS and the model described in Figure 7(main text).



Figure S17: Time dependence of the polar angle θ for C₁-²H_{1,2} (a,b) and C₂-²H_{3,4} (c,d) for diamine-MATMS and the model (6) given in Table 5. Molecular conformations are shown nearby.