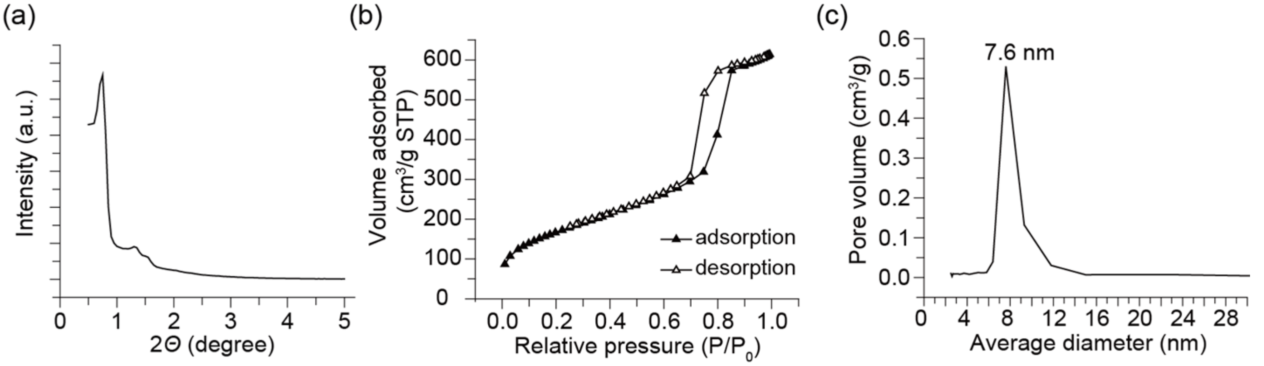
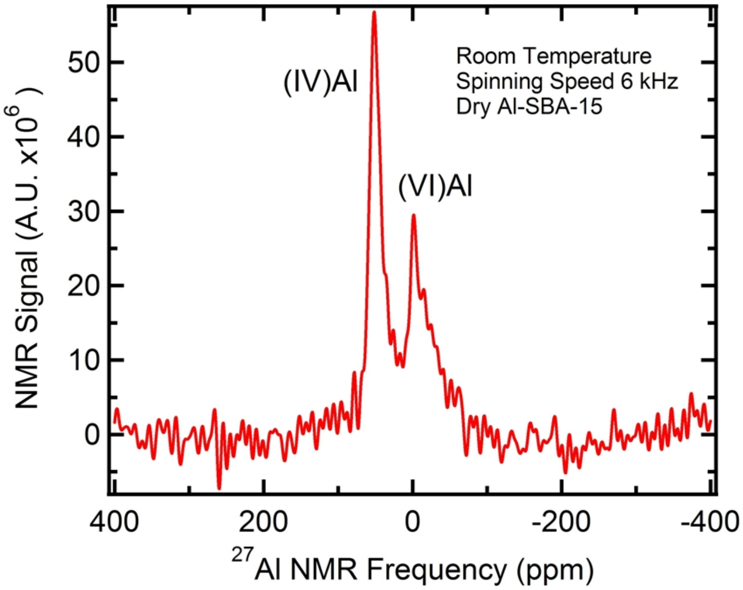
## Supporting Information

**Synthesis of Al-SBA-15.** The synthesis composition, conditions, and procedure followed the direct Al-SBA-15 synthesis reported by Ying *et al.*[1] Specifically, 2.00 g of nonionic triblock copolymer surfactant $EO_{20}PO_{70}EO_{20}$ (P123, BASF) was dissolved in 75 mL of hydrochloric acid solution (HCl, pH = 1.5 prepared from 1N $HCl_{(aq)}$, Fisher) to form solution A. Additionally, 3.27 g of tetramethyl orthosilicate (TMOS, 98 %, Sigma-Aldrich) and 0.22 g of aluminum isopropoxide (≥ 98 %, Sigma-Alrdich) were added to 5 mL of $HCl_{(aq)}$ at pH = 1.5 to yield solution B with Si/Al = 20, which was vigorously stirred at room temperature for 3 h. Then, solution B was added dropwise into solution A under vigorously stirring condition, and the mixture was further stirred at 40 ºC for 20 h. Subsequently, the whole mixture was transferred into an autoclave (poly(tetrafluoroethylene) (PTFE)-lined stainless steel Parr™) heated at 100 ºC for 24 h. After hydrothermal synthesis, the product (designated as as-synthesized Al-SBA-15) was filtered, washed using excess deionized water, and dried at room temperature. Calcination of as-synthesized Al-SBA-15 was performed in thin beds under static air condition and followed the profile: room temperature ramp to 550 ºC at 1 ºC/min; hold at 550 ºC for 12 h; then cool to room temperature. The resultant material was referred to as calcined Al-SBA-15.

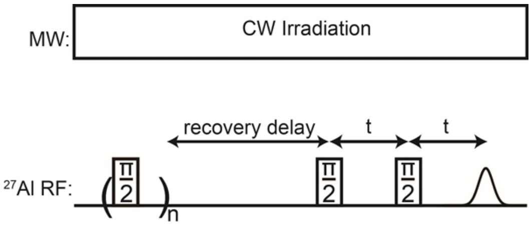
**Al-SBA-15 Characterization.** The long-range order of calcined Al-SBA-15 was characterized using small-angle X-ray scattering (SAXS). The SAXS pattern (S.I. Figure 1a) was collected using a Riguku SMART lab diffractometer and a Cu Kα radiation ($\lambda = 1.5405$ Å) generated at 44 kV and 40 mA. The scanning angle range of a SAXS pattern was from 0.5 to 5.0° $2\Theta$ and the step size was set to 0.5 °/min. Elemental analysis was performed using Thermo jCAP 6300 model in Materials Research Laboratory (MRL) at UCSB, before calcined Al-SBA-15 materials were dissolved in *ca*. 2 wt % hydrofluoric acid (HF) and *ca*. 3 wt % nitric acid ($HNO_3$) solution at room temperature for several days. Nitrogen ($N_2$) adsorption/desorption isotherms (S.I. Figure 1b) were collected using the TriStar 3000 instrument. Calcined Al-SBA-15 samples were degassed under continuous $N_2$ flow at 200 °C overnight before the $N_2$ adsorption/desorption measurements. The pore size distribution curve (S.I. Figure 1c) was established using the Barrett-Joyner-Halenda (BJH) method based on the desorption isotherm.



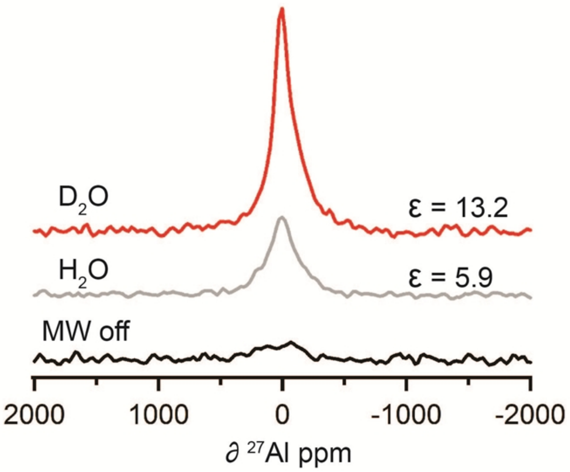
**SI Figure 1.** (a) Powder small-angle X-ray scattering pattern, (b) $N_2$ adsorption-desorption isotherms, and (c) pore size distribution of calcined Al-SBA-15.



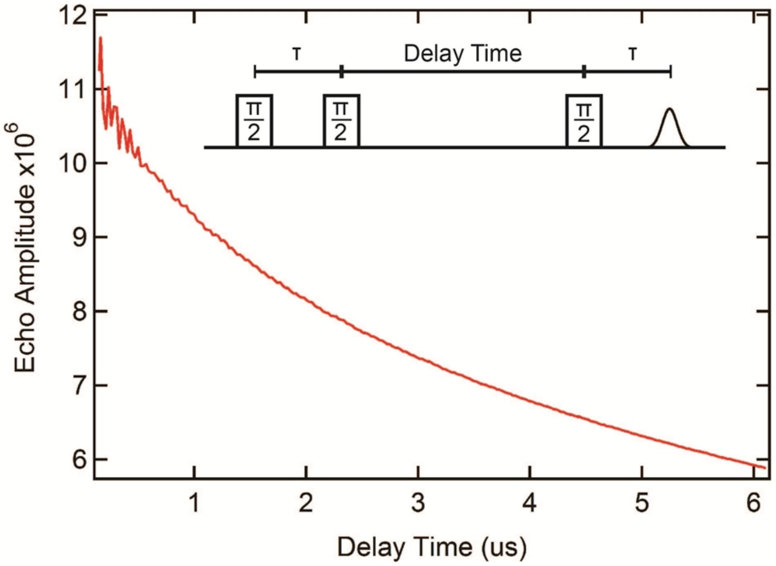
**SI Figure 2.** 27Al MAS NMR measured at 7 T with a custom Revolution NMR LLC MAS probe. This spectrum was measured with a one π/2 pulse measurement, with a recycle delay of 10 s using a Bruker Avance solid state spectrometer.



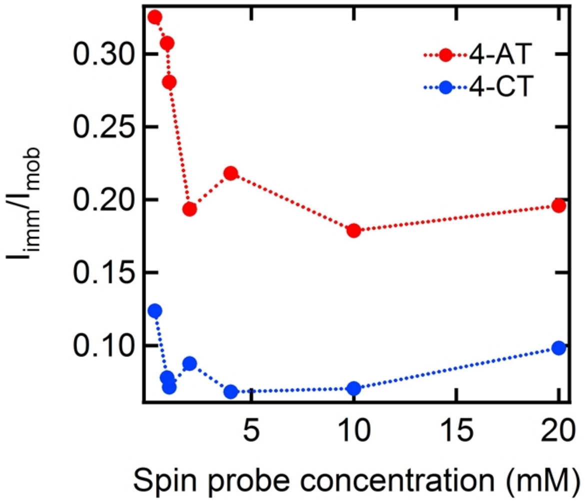
**SI Figure 3.** DNP/NMR saturation solid echo pulse sequence. t=20 µs, n=100, with a recovery delay of 60 s.



**SI Figure 4**. $^{27}$Al Direct DNP spectra of Al-SBA-15 embedded with 10 mM 4-amino TEMPO solutions using $D_2O$ (red) and $H_2O$ (grey) as the solvent.



**SI Figure 5**. Electron Spin echo decay for three pulse ESEEM. The insert shows the pulse sequence for the 3 pulse ESEEM experiment. For this experiment the π/2 pulse was 16 ns, τ=140 ns, and the Delay time was varied from 40 ns to 6000 ns in increments of 32 ns.



**SI Figure 6**. Ratio of immobile and mobile population for 4-AT and 4-CT determined from the room temperature cw EPR spectrum for the given spin probe concentration.

**9.5 GHz cw EPR Instrument and Measurements.** To qualitatively determine the strength of the adsorbed spin probe population of 4-AT and 4-CT the total concentration of imbibed spin probe to the Al-SBA-15 sample was varied and the $I_{imm}/I_{mob}$ determined as described in the text. S.I Figure 4 shows the $I_{imm}/I_{mob}$ dependence on total imbibed spin concentration for 4-AT and 4-CT. Most importantly, we observe an increase in $I_{imm}/I_{mob}$ with decreasing concentration of 4-AT, strongly suggesting that $I_{imm}/I_{mob}$ is a measure of relative adsorbed population that is maximal at low spin probe concentration, and whose fraction proportionally decreases with increasing 4-AT concentration that increases the fraction of free 4-AT.

**240 GHz cw EPR Instrument and Measurement.** To obtain the high field cw EPR spectrum the technique of rapid passage cw EPR was employed on a non-commercial EPR spectrometer operating at 8.56 T, as detailed in a previous publication.[2] The EPR measurements are performed in induction mode with superheterodyne detection. [3] The rapid passage method allows one to directly measure the undistorted absorption spectrum of the nitroxide line at liquid helium temperatures. Rapid passage conditions were achieved with a 8 μL sample of 10 mM 4-amino TEMPO in a 50:40:10 v/v% d-glycerol:$D_2O$:$H_2O$ solvent placed at the end of a 240 GHz waveguide at 8.56 T. A $B_0$ field modulation of 20 kHz, $B_0$ field sweep rate of 0.2 mT/s, and sweep width of 120 mT was used to directly measure the absorption cw EPR spectrum at 4 K. The frequency axis of the spectrum was linearly scaled with the gyromagnetic ration for 4-amino TEMPO.

## References

[1] Y. Li, W. Zhang, L. Zhang, Q. Yang, Z. Wei, Z. Feng, C. Li, *J. Phys. Chem. B* **2004**, *108*, 9739–9744.

[2] M. Weger, *Bell Syst. Tech. J.* **1960**, *39*, 1013–1112.

[3] S. Takahashi, L.-C. Brunel, D. T. Edwards, J. van Tol, G. Ramian, S. Han, M. S. Sherwin, *Nature* **2012**, *489*, 409–413.