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-Aldrich) 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 °C for 20 h. Subsequently, the whole mixture was transferred into an autoclave (poly(tetrafluoroethylene) (PTFE)-lined stainless steel Parr™) heated at 100 °C 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 °C at 1 °C/min; hold at 550 °C 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 Rigaku SMART lab diffractometer and a Cu Kα radiation (λ = 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° 2Θ 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 (HNO₃) solution at room temperature for several days. Nitrogen (N₂) adsorption/desorption isotherms (S.I. Figure 1b) were collected using the TriStar 3000 instrument. Calcined Al-SBA-15 samples were degassed under continuous N₂ flow at 200 °C overnight before the N₂ 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) N₂ adsorption-desorption isotherms, and (c) pore size distribution of calcined Al-SBA-15.
**SI Figure 2.** $^{27}$Al MAS NMR measured at 7 T with a custom Revolution NMR LLC MAS probe. This spectrum was measured with a one $\pi/2$ 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$_2$O (red) and H$_2$O (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 $\pi/2$ pulse was 16 ns, $\tau=140$ ns, and the Delay time was varied from 40 ns to 6000 ns in increments of 32 ns.
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 \( \frac{I_{\text{imm}}}{I_{\text{mob}}} \) determined as described in the text. S.I Figure 4 shows the \( \frac{I_{\text{imm}}}{I_{\text{mob}}} \) dependence on total imbibed spin concentration for 4-AT and 4-CT. Most importantly, we observe an increase in \( \frac{I_{\text{imm}}}{I_{\text{mob}}} \) with decreasing concentration of 4-AT, strongly suggesting that \( \frac{I_{\text{imm}}}{I_{\text{mob}}} \) 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.

**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.
**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\(_2\)O:H\(_2\)O 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 ratio for 4-amino TEMPO.

**References**

