

Supporting Information

Sample preparation

Cu(II)(DL-alanine)₂·H₂O, Cu(II)(L-alanine)₂, and Cu(II)(8-quinolinol)₂ were prepared following the methods described in references by Liu et al.,⁹ Calvo et al.,^{s1} and Fanning et al.,^{s2} respectively. 8-quinolinol (8-hydroxyquinoline or oxine) was purchased from Fisher Scientific Co. (Hanover Park, IL). All other materials required for the syntheses such as non-labeled DL-alanine and L-alanine, CuSO₄·5H₂O, Ba(OH)₂·8H₂O, and CuCO₃·Cu(OH)₂ were purchased from Sigma-Aldrich Co. (St. Louis, MO).

Experiments

Solid-state NMR (SSNMR) spectra were recorded at 9.4 T (¹H frequency 400.2 MHz) with a Varian Infinityplus 400 NMR spectrometer using a home-build 2.5 mm double-resonance MAS probe, which provides stable spinning up to 30 kHz. All the data were processed with Varian Spinsight software. Experimental ¹H shifts were referenced to TMS at 0 ppm using the secondary external standard H₂O at 4.7 ppm. Because paramagnetic isotropic shifts have 1/T dependence (Curie's law), spinning speed and an RF-duty factor were found to affect observed shift positions. To avoid line broadening due to temperature distribution over the sample, the flow rate of cooling air was set to 140-160 (ft)²/hour. For experimental simplicity, we indicated the temperature of the cooling air rather than that of a sample. Typical temperature difference between the sample and the cooling air was 4, 24, 47 °C at $\omega_R/2\pi$ of 10, 20, 28 kHz, respectively. All the spectra in Figs. 1-3 were recorded with a rotor-synchronous echo sequence. After the initial magnetization was prepared along the y-axis in the rotating frame by a ($\pi/2$)-pulse, a π -pulse was applied along the y-axis at the middle of two rotor cycles. The signals were acquired with 1 μ s sampling intervals from the end of the second rotor cycle. Recycle delays or intervals between two scans were adjusted to three times of ¹H T₁ values.

For the ¹H SSNMR NMR experiments in Fig. 1, the carrier frequencies for the ¹H channel for (a-c) and (d-f) were set to 12.8 and 16.0 ppm, respectively. The pulse widths for $\pi/2$ - and π -pulses are 2.5 μ s and 5 μ s for (a-c), respectively, while the former and the latter for (d-f) are 1.8 μ s and 3.6 μ s, respectively. The recycle delays were 4.5 and 3.0 ms for (a-c) and (d-f), respectively. The signals were acquired during acquisition periods of 1 ms, which were used as a part of the recycle delays for each spectra. The temperature was set at 24 and -15 °C for (a-c) and (d-f), respectively. Each spectrum was observed with signal acquisition of 4 scans with 2 dummy scans. The inset in (d) displays an expanded center line region for clarity of the signal assignment.

For the ¹H SSNMR micro analysis shown in Figs. 2 and 3, each sample was center packed in a 2.5-mm zirconia rotor using powdered NaCl as spacer. NaCl was also used to dilute the sample in order to accurately weigh a nano-mole-scale sample at a standard analytical balance as follow. A paramagnetic sample of 1.0 mg was mixed with 19.0 mg of a dry NaCl powder, and then ground well; 1.0 mg of the mixture was mixed with 9.0 mg of the NaCl powder to adjust the final concentration at 5.0 μ g of the sample in 1.0 mg of the mixture. For the control sample, L-Alanine, the final concentration of 2.5 μ g in 1 mg was used by mixing 19.0 mg of NaCl in the second step. The obtained mixture of 1.0-1.4 mg was packed in a rotor. A shorter Torlon cap (4mm in length) and no plastic spacers were used to reduce the background signal. The remaining background signal was separately collected under the same condition with no sample (only NaCl). Then, the background signal was subtracted from the spectra acquired with a sample to obtain the spectra in Figs. 2 and 3. The indicated experimental time does not include that for the background signal. In Fig. 2, the carrier frequencies for the ¹H channel for (a), (b), and (c) were set to 40, 0 and 0 ppm, respectively. The ¹H $\pi/2$ - and π -pulse widths were set to 1.75 and 3.5 μ s respectively. Figure 2(a, b) and (c) were obtained with 16 and 2 dummy scans, respectively. The temperature was set at 25 °C for all the experiments in Fig. 2. The spectra in Fig. 2(a), (b) and (c) were processed by a Gaussian broadening function of 800, 900 and 550 Hz, respectively. The line widths for Cu(L-Ala)₂, Cu(DL-Ala)₂, and L-Ala without broadening functions are approximately 1600, 1800, and 1100 Hz, respectively. The acquisition period for each sample was set to the period inversely proportional to the line width so that artifacts due to signal truncation were suppressed. The signal to noise ratios (S/N) were obtained using a macro in Varian Spinsight software ("s2n_best_20"). To obtain a common noise level, the spectra in Fig. 2 (a, b) were scaled. The scaling factors were calculated on the basis of a theoretical prediction that the noise level is proportional to the square root of the number of scan and acquisition length. We also experimentally confirmed that a common noise level was obtained in Fig. 2 after scaling by the theoretical factors. In Fig. 3, the carrier frequency for the ¹H channel was set to 27.6 ppm, and the ¹H $\pi/2$ - and π -pulse widths were set to 1.67 and 3.34 μ s respectively. The temperature was set to -5 °C for the experiments in Fig. 3.

Comparison of sensitivity between paramagnetic and diamagnetic solids under VFMAS

Sensitivity of FT NMR with a matched window function is generally given by^{s3}

$$\xi \equiv S/\sigma_N = \langle s(t)^2 \rangle^{1/2} (t_{\max}/T)^{1/2} / \rho_N, \quad [1]$$

where S is the peak height, σ_N is the r.m.s noise amplitude in the spectral domain, $s(t)$ is an envelope function of a FID, t_{\max} is an acquisition period of a FID, T is a recycle time or an interval between two scans, and ρ_N is the r.m.s. noise per a unit band width in the time domain. The factor $\langle s(t)^2 \rangle$ is the average signal power. For simplicity, we assumed that $s(t)$ is given by an exponential decay as $s(t) = \exp(-t/T_2)$. When t_{\max} is matched to T_2 , as $t_{\max} = cT_2$, where c is a constant, $\langle s^2 \rangle$ is independent of T_2 . Thus, the sensitivity, ξ depends only on the receiver duty factor (t_{\max}/T). In SSNMR experiments, T is usually adjusted to $3T_1$, and hence, $t_{\max}/T = (c/3)T_2/T_1$. For ^1H SSNMR of diamagnetic systems, t_{\max}/T is only about 0.03-0.1 % ($t_{\max} \sim 1$ ms and $T \sim 1$ -3 s). In contrast, t_{\max}/T for paramagnetic systems is as large as 10-30 % ($t_{\max} \sim 0.5$ -1 ms and $T \sim 3$ -5 ms). Hence, based on the assumption that sidebands are sufficiently suppressed by VFMAS, the theoretical sensitivity of ^1H SSNMR for paramagnetic systems is greater than that for diamagnetic systems by a factor of 10-30 with VFMAS.

References:

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