Figure S1. 2D proton detected $^{15}$N-$^1$H correlation spectrum of the SH3-domain of $\alpha$-spectrin, with assignment labels. All signals that have been observed to undergo slow exchange are marked in red (the decays of these peaks are shown in the Figures S4 and S5 below). Most of the unlabeled peaks in this spectrum are the spinning side bands that fold into the main spectrum area due to the narrow spectral width in the indirect ($^{15}$N) dimension. The second side chain peak of Q50 overlaps with the backbone R21 peak. However, the intensity of R21 is much lower than that of Q50 and thus can be neglected. The peak N35δ(a) partially overlaps with D40 peak, it has much smaller intensity and thus the data for this peak could be determined reliably. X1 and X2 are two unassigned peaks. They do not undergo exchange and thus the data for these peaks are not shown in the paper.
The spectrum shown in Fig. S1 was obtained with the pulse sequence described in ref. 11. Experimental parameters: resonance frequency for protons 600 MHz, MAS rate 10 kHz, $T = 14$ °C, repetition delay 2 s, indirect dimension spectral width 1550 Hz, indirect time domain 55 ms, number of scans 64. CODEX 2D exchange spectra were acquired using the same parameters, except for a higher number of scans (128). The acquisition of one CODEX 2D spectrum took from 11 h to one day depending on the mixing time (1 ms to 2.5 s). Side chain amide resonance assignments were obtained using standard HNCACB type experiments [R. Linser, U. Fink, B. Reif. J. Magn. Reson. 193 (2008) 89-93]. In this experiment, asparagines are readily assigned by identifying correlations from backbone and side chain amide proton resonances to resonances with identical $\text{C}\alpha$/C$\beta$ chemical shifts. Similarly glutamines are assigned. Differentiation among different glutamine side chains relies uniquely on C$\beta$ chemical shift dispersion.

Fig. S2 shows the details of the $T_1$-correction of the CODEX decays and $^{15}\text{N}$ spin-lattice relaxation rates ($R_1 = 1/T_1$) as a function of a residue number. In Fig. S3, we show examples for the fitting quality of the relaxation data, where the error intervals associated with $R_1$ are smaller than 10% in the shown cases (i.e., for residues for which $T_1$ is on the order of or not significantly longer than the typical slow-motion correlation time range). As can be seen on the right hand side, the uncertainty of the corrected CODEX data caused by $R_1$ uncertainty is much smaller than the internal experimental error of the CODEX experiment. Since the relaxation experiments were only conducted up to relaxation delays of 4 s, the error for those residues with very long $T_1$ (on the order of 10s and more) is larger, up to 15-25%. However, this long timescale is sufficiently separated from the timescale of the CODEX experiments, thus not introducing any substantial error.

In Fig. S4, exchange decays and fits are plotted for all peaks with the upper limit of the error margin below 0.95 in Fig. 2a (black circles). For comparison, Fig. S5 shows several noisier exchange decays for signals corresponding to the ratio values (regardless of the error bars) in Fig. 2a below 0.95 (grey circles).
Figure S2. (a) Examples of raw (solid symbols) and corrected (open symbols) CODEX mixing time dependencies of peaks undergoing (top) and not undergoing (bottom) slow exchange. Dashed lines are the fits to spin-lattice relaxation data measured as described in ref. 5. The corrected data were obtained by dividing the peak intensity obtained in the CODEX experiment by spin-lattice relaxation decays:

\[ I^* (\tau_m) = I(\tau_m) / \exp(-R_1 \tau_m) , \]

where \( I^* (\tau_m) \) and \( I(\tau_m) \) are the corrected and raw CODEX intensities, respectively; (b) \(^{15}\)N spin-lattice relaxation rates \( R_1 = 1/T_1 \) as a function of residue number.
Figure S3. Examples demonstrating the fitting quality and the typical errors associated with the $R_1$ determination (left), and the robustness of the corrected CODEX data when using the fitted $R_1$ or the upper/lower ends of the error interval ($R_1 \pm \Delta R_1$) for correction (right). Red lines on the left are the exponential fits of the relaxation decays. Solid and (up and down) open circles on the right are the $R_1$-corrected CODEX decays corresponding to the average $R_1$ and ($R_1 \pm \Delta R_1$), respectively.
Figure S4 (a). $T_1$-corrected CODEX exchange decays and exponential fits according to $I(\tau_m)\cdot f + (1-f)\cdot \exp(-\tau_m/\tau_c)$ for backbone signals that show exchange decay beyond experimental error (the upper limit of the error bar in Fig 2a is below 0.95, black circles). The solid symbols (black: short $\tau_m$, red: long $\tau_m$) denote the points which were averaged and used to calculate the ratio plotted in Fig. 2a of the paper. Because of the experimental error and relatively short range of $\tau_m$ in some cases the fitting could only provide upper limits for $f$ and lower limits for $\tau_c$. 

Leu 10

$f < 0.9$
$\tau_c > 1$ s

Ala 11

$f = 0.7 \pm 0.08$
$\tau_c = 1.6 \pm 0.8$ s

Lys 27

$f < 0.85$
$\tau_c > 1.5$ s

Ser 36

$f = 0.3 \pm 0.06$
$\tau_c = 0.1 \pm 0.04$ s

Asp 40

$f < 0.8$
$\tau_c > 1$ s

Trp 41

$f = 0.83 \pm 0.06$
$\tau_c = 0.8 \pm 0.85$ s

Trp 42

$f = 0.75 \pm 0.05$
$\tau_c = 0.9 \pm 0.4$ s

Val 44

$f < 0.75$
$\tau_c > 1.5$ s

Lys 60

$f = 0.44 \pm 0.28$
$\tau_c = 4.3 \pm 3$ s

Leu 61

$f = 0.8 \pm 0.17$
$\tau_c = 2.5 \pm 3.5$ s

mixing time / s
Figure S4 (b). Exchange decays and fits for the side chain peaks undergoing exchange beyond experimental error.
Figure S5. CODEX decays for the peaks corresponding to the intensities ratio below 0.95 in Fig 2a (grey circles). Because of the high experimental uncertainty, fitting of these data provides too ambiguous results and thus was not performed.