Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Signal enhancement of *J*-HMQC experiments in solid state NMR involving half-integer quadrupolar nuclei.

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Experimental conditions

All experiments were performed on a Bruker Avance-II 400 MHz spectrometer using a 4-mm triple-resonance MAS probe at a spinning rate of ν_R = 12.5 kHz. The WURST-80[1] irradiation had a sweep range of 12.5 kHz (equal to ν_R), a length of ca. $3T_R$ = 240 μs, and a maximal rf-field of ca. 15 kHz. The offset was optimized with the "(WURST)$_N$ – $(\pi/2)_{sel}$ – Acquire" experiment, by maximizing the CT signal, and its value was of ±300 kHz for our sample, and the WURST parameters were the same as those in simulations.

In case of ^{31}P-{^{27}Al} PT-*J*-HMQC experiments, a contact time of 3 ms in the ^{1}H → ^{31}P initial CP was used. The ^{31}P rf-fields were of $\nu_{31P,CP} \approx$ 40 kHz, $\nu_{1H,CP} \approx$ 52 kHz (ramped) and $\nu_{31P,\pi} \approx$ 52 kHz. The ^{31}P resolution was enhanced with simultaneous ^{1}H and ^{27}Al decouplings. A SPINAL-64 ^{1}H decoupling[2] with a rf field of 75 kHz was applied at the end of the CP transfer, whereas during t_2 acquisition, ^{27}Al rotor-asynchronized multiple-pulse (RA-MP) decoupling,[3] was also applied. RA-MP decoupling consisted of ^{27}Al pulses with rf-field strength of 40 kHz, lasting 5 μs each, and separated by windows of 83 μs. The two CT selective π/2 pulse-lengths on ^{27}Al channel were of 7.5 μs. The conventional *J*-HMQC experiment is obtained by setting the WURST shape pulse amplitude to zero. The 2D ^{31}P-{^{27}Al} HETCOR spectra were obtained by averaging 32 transients for each of the 200 t_1 increments with $\Delta t_1 = 1/\nu_R$ = 80 μs, and a recycle delay of 3 s.

AlPO-Mu-4

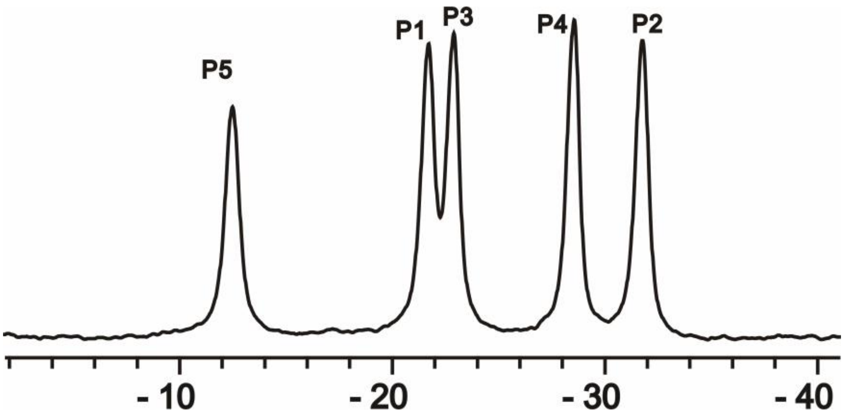

Fig.S1. ^{31}P spectrum of Mu-4 layered aluminophosphate observed by ^{1}H → ^{31}P CP with B_0 = 9.4 T, ν_R = 12.5 kHz, and ^{1}H/^{27}Al simultaneous decouplings.

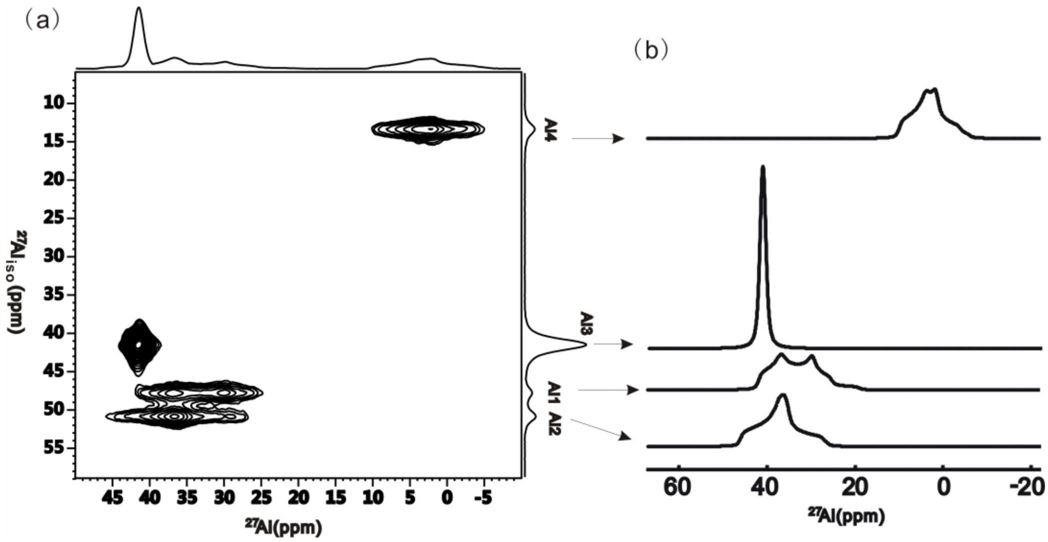

Fig.S2. (a) 2D ^{27}Al sheared 3QMAS spectrum of Mu-4 observed with B_0 = 9.4 T, ν_R = 12.5 kHz with 3Q z-filtering pulse sequence:[4] p1 - t_1 - p2 - τ - p3 – Acq. (b) Fits of the slices of 3QMAS spectrum. The p1 and p2 pulse lengths were set at 7 and 2 μs, respectively, with an rf-field of 65 kHz. The soft π/2-pulse p3 was set to 7.5 μs with a rf-field of 11.1 kHz. The 2D spectrum was obtained by averaging 12 transients for each of 280 t_1 increment with Δt_1= 40 μs, and a recycle delay of 0.5 s.

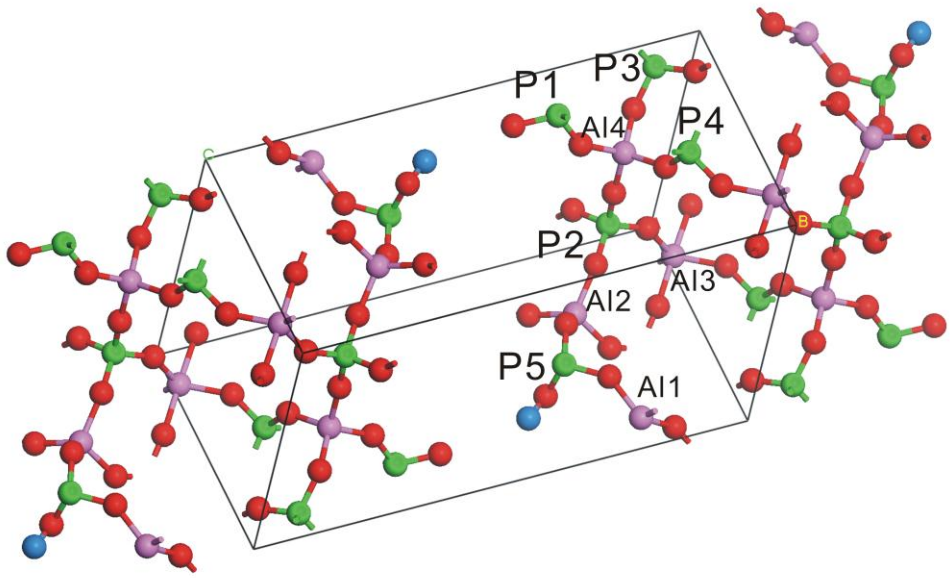

Fig.S3. the crystal structure of Mu-4. Green: P, Purple: Al, Red: O, Blue: H.

Table S1. ^{27}Al quadrupolar interaction parameters obtained by fitting with the dmFIT program each slice from 2D ^{27}Al 3QMAS spectrum of Mu-4.

Site	Al1	Al2	Al3	Al4
δ_{cs} (ppm)	43.4	46.3	42.1	10.3
C_Q (MHz)	~4.1	~3.6	< 0.1	~3.3
η_Q	0.37	0.89	~	0.71

Table S2. Al-O-P connectivities between aluminum and phosphorus atoms in the structure of Mu-4 according to its crystallographic data.[5,6]

	P1	P2	P3	P4	P5
Al1	○	○	○		○
Al2	○	○		○	○
Al3	○	○	○	○	
Al4		○	○	○	

Representation of the S = 5/2 spin operator S_z, C_z , T_z and F_z in the basis set of the spin wave functions |5/2>, |3/2>, |1/2>, |-1/2>, |-3/2>, |-5/2>,

$$S_z = \frac{1}{2}\begin{pmatrix} 5 & 0 & 0 & 0 & 0 & 0 \\ 0 & 3 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -3 & 0 \\ 0 & 0 & 0 & 0 & 0 & -5 \end{pmatrix}$$

$$C_z = \frac{1}{2}\begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad T_z = \frac{1}{2}\begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad F_z = \frac{1}{2}\begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 \end{pmatrix}$$

Reference:

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