Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information for:

Natural abundance solid-state ^{67}Zn NMR characterization of microporous zinc phosphites and zinc phosphates at ultrahigh magnetic field

by Andre Sutrisno, Li Liu, Jun Xu and Yining Huang*

Contribution from:

Department of Chemistry, The University of Western Ontario, London, Ontario, Canada N6A 5B7.

Experimental details for ^{31}P, ^{13}C, ^{19}F, ^{27}Al and $^{6/7}$Li MAS NMR experiments acquired at 9.4 T.

All the ^{31}P, ^{13}C, ^{19}F, ^{27}Al and $^{6/7}$Li MAS NMR spectra of all the materials studied were acquired at 9.4 T on a Varian Infinity Plus 400 WB spectrometer using either a 4-mm HXY or a 5-mm HFXY T3 MAS probe [ν_0 = 161.7, 100.4, 375.8, 104.1, 58.8 and 155.3 MHz for ^{31}P, ^{13}C, ^{19}F, ^{27}Al, ^{6}Li and ^{7}Li respectively]. Standard samples used for pulse calibration and chemical shift referencing were ADP ($NH_4H_2PO_4$, solid, δ_{iso} = 0.0 ppm), adamantane ($C_{10}H_{16}$, solid, δ_{iso} = 38.5 ppm for higher frequency resonance), TFT ($C_6H_5CF_3$, 1 M solution, δ_{iso} = -65.4 ppm), $Al(NO_3)_3$ (1 M solution, δ_{iso} = 0.0 ppm) and LiCl (1 M solution, δ_{iso} = 0.0 ppm) for ^{31}P, ^{13}C, ^{19}F, ^{27}Al, $^{6/7}$Li respectively. A single pulse with proton decoupling was used in all experiments, applying small (< 30°) tip angle.

Table S1. Detailed ^{67}Zn SSNMR experimental conditions.

Sample	Type of experiment	B_0 (T)	pulse length (µs)	SW (kHz)	recycle delay (s)	τ_a (µs)	M (# of loops)	τ_1 (µs)	τ_2 (µs)	τ_3 (µs)	τ_4 (µs)	# scans
$ZnHPO_3$-CJ1	MAS 8 kHz	21.1	4.0	100	2	---	---	---	---	---	---	27132
	static WURST-QCPMG	21.1	50	500	2	500	32	39	40	40	40	7200
	static QCPMG	9.4	2.3	250	4	200	19	25	26	26	27	21664
NTHU-5	static WURST-QCPMG	21.1	50	500	1	200	32	29	30	30	30	83000
$ZnHPO_3$-CN_3H_6	static WURST-QCPMG	21.1	50	500	2	500	32	39	40	40	40	10800
$ZnHPO_3$-PIP	static WURST-QCPMG	21.1	50	500	1	200	32	29	30	30	30	6680
$ZnHPO_3$-DMPIP	static WURST-QCPMG	21.1	50	500	1	200	32	29	30	30	30	3000
ZnPO-Li-ABW	static WURST-QCPMG	21.1	50	500	2	500	32	39	40	40	40	3600
	static QCPMG	9.4	2.3	250	2	200	19	25	26	26	27	2 × 167104

Table S2. Bond distances and angles for the Zn-based materials investigated.

Compound	Zn–O bond distances (Å)	Average Zn–O bond distances (Å)	O–Zn–O bond angles (degrees)	Average O–Zn–O bond angles ± standard deviation (degrees)
$ZnHPO_3$-CJ1 site 1	1.810, 1.850, 1.929, 2.015	1.901	73.8, 106.5, 108.2, 114.6, 119.2, 123.8	107.68 ± 17.83
site 2	1.925(×2), 1.967 (×2)	1.946	105.2, 107.3 (×2), 110.5 (×2), 115.5	109.38 ± 3.64
NTHU-5	1.902, 1.913, 1.935, 1.953	1.926	104.8, 106.6, 106.8, 109.8, 112.2, 115.9	109.35 ± 4.15
$ZnHPO_3$-CN_3H_6	1.937 (×2), 1.952 (×2)	1.945	96.4, 108.6 (×2), 108.7, 117.3 (×2)	109.48 ± 7.69
$ZnHPO_3$-PIP site 1	1.913, 1.922, 1.942, 1.949	1.932	97.6, 105.3, 111.1, 111.4, 112.9, 117.4	109.28 ± 6.92
CASTEP-optimized	1.936, 1.948, 1.961, 1.980	1.956	95.5, 104.7, 109. 9, 111.8, 114.2, 119.0	109.18 ± 8.20
site 2	1.910, 1.925, 1.926, 1.954	1.929	96.4, 103.1, 107.1, 114.3, 115.5, 119.9	109.38 ± 8.78
CASTEP-optimized	1.927, 1.950, 1.952, 1.983	1.953	94.1, 102.9, 105.5, 115.8, 116.3, 122.0	109.43 ± 10.38
$ZnHPO_3$-DMPIP	1.929, 1.933, 1.951, 1.953	1.941	104.1, 105.5, 107.4, 109.2, 110.9, 119.1	109.37 ± 5.36
CASTEP-optimized	1.940, 1.947, 1.967, 1.969	1.956	102.6, 104.3, 108.3, 109.1, 112.3, 119.5	109.35 ± 6.06
ZnPO-Li-ABW	1.845, 1.966, 1.975, 1.983	1.942	99.5, 100.6, 109.2, 113.7, 114.9, 116.2	109.02 ± 7.34
CASTEP-optimized	1.921, 1.964, 1.965, 1.978	1.957	102.3,107.5, 107.6, 108.8, 114.7, 115.6	109.42 ± 4.98

Table S3. Calculated ^{67}Zn C_Q values of zinc phosphite model cluster

Figure 5a data		*Figure 5b* data		*Figure 5c* data		*Figure 5d* data	
one Zn–O bond (Å)	**$\|C_Q\|$ (MHz)**	**average Zn–O bond (Å)**	**$\|C_Q\|$ (MHz)**	**one O–Zn–O bond angle (deg.)**	**$\|C_Q\|$ (MHz)**	**one P–O–Zn bond angle (deg.)**	**$\|C_Q\|$ (MHz)**
1.71	28.32			101	7.77	105	2.84
1.73	25.66			102	7.22	110	3.22
1.75	23.12			103	6.68	115	3.59
1.77	20.69			104	6.16	120	3.90
1.79	18.37			105	5.67	125	4.18
1.81	16.16			106	5.22	130	4.43
1.83	14.06	1.83	5.23	107	4.80	135	4.65
1.85	12.05	1.85	5.03	108	4.47	140	4.84
1.87	10.16	1.87	4.84	109	4.22	145	5.01
1.89	8.40	1.89	4.64	110	4.07	150	5.14
1.91	6.81	1.91	4.46	111	4.02	155	5.23
1.93	5.95	1.93	4.30	112	4.09	160	5.28
1.95	5.14	1.95	4.14	113	4.26	165	5.27
1.97	4.36	1.97	3.99	114	4.53		
1.99	4.39	1.99	3.85	115	4.88		
2.01	4.87			116	5.31		
2.03	5.44			117	5.78		
2.05	6.00			118	6.31		
2.07	6.55			119	6.85		
2.09	7.10			120	7.42		

Table S4. Summary of all experimental and calculated CSA parameters for ZnPO-Li-ABW

Method[a]	**Ω (ppm)**[b]	**κ**[c]
Experimental	**50**	**1.00**
CASTEP	*220*	*0.85*
CASTEP-optimized	*111*	*-0.30*
Cluster I ($ZnO_4P_4O_{12}^{10-}$)	238	-0.26
Cluster II ($ZnO_4P_4O_{12}Li_9^{-}$)	254	-0.11

[a] Basis set used for Gaussian cluster calculations: 6-311G* for Zn atoms, 6-311+G* for O atoms bonded directly to Zn, and 6-31G* for other atoms. The chemical shift tensor is described by three principal components (δ_{11}, δ_{22}, δ_{33}) such that: [b] $\Omega = \delta_{11} - \delta_{33}$; [c] $\kappa = 3(\delta_{22} - \delta_{iso})/\Omega$.

Figure S1. Powder XRD spectra of the materials studied

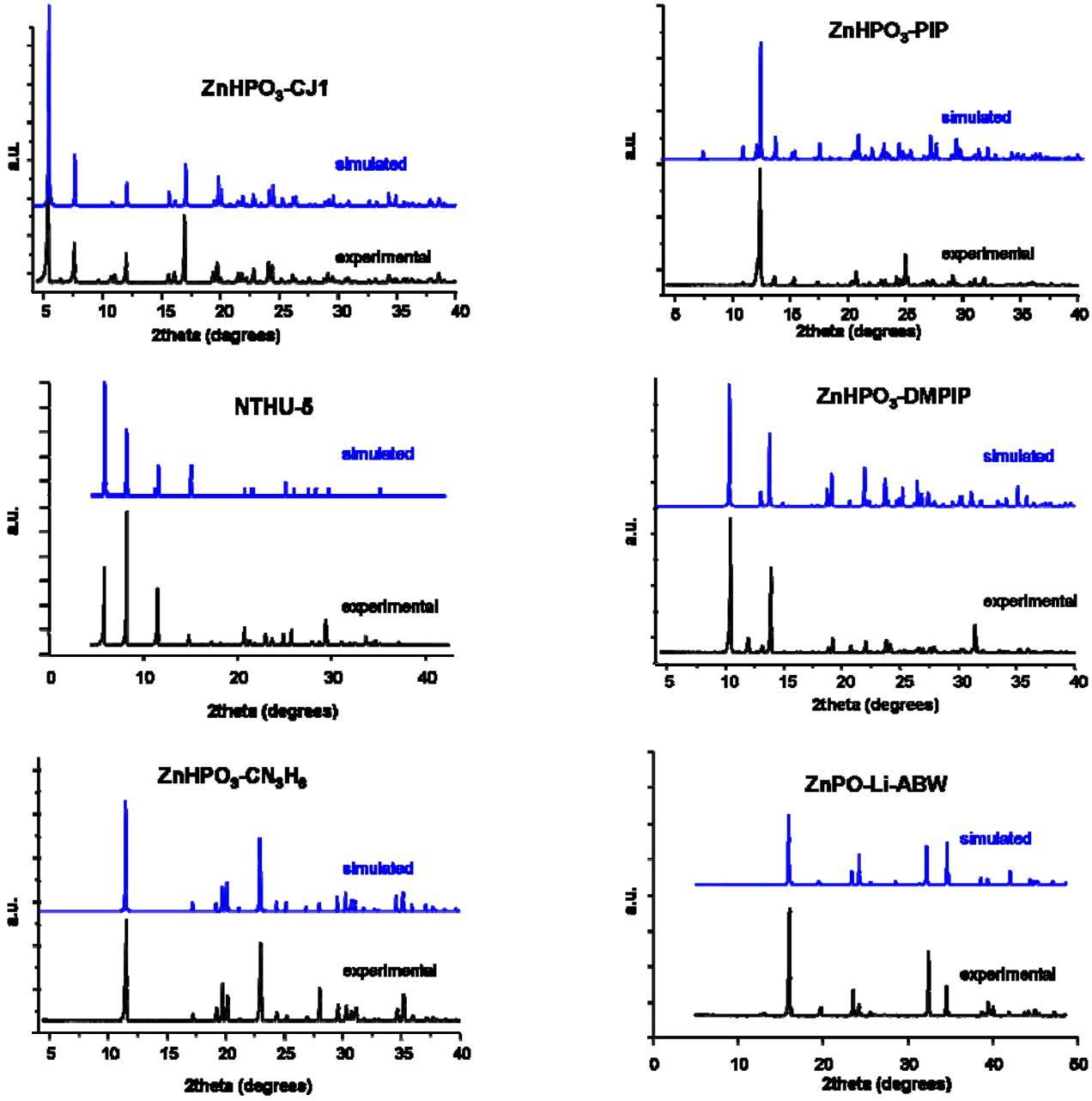


Figure S2. ^{31}P MAS NMR spectra of the materials studied at 8 kHz. Asterisks (*) indicate spinning sidebands, while number signs (#) indicate impurities present.

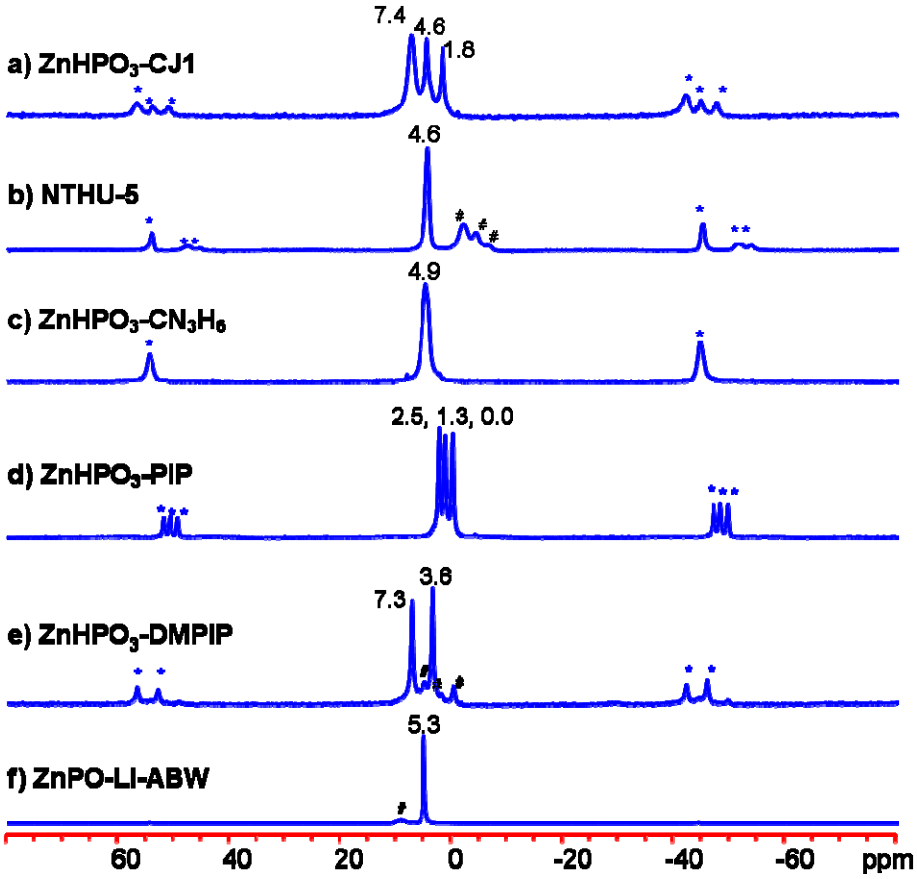
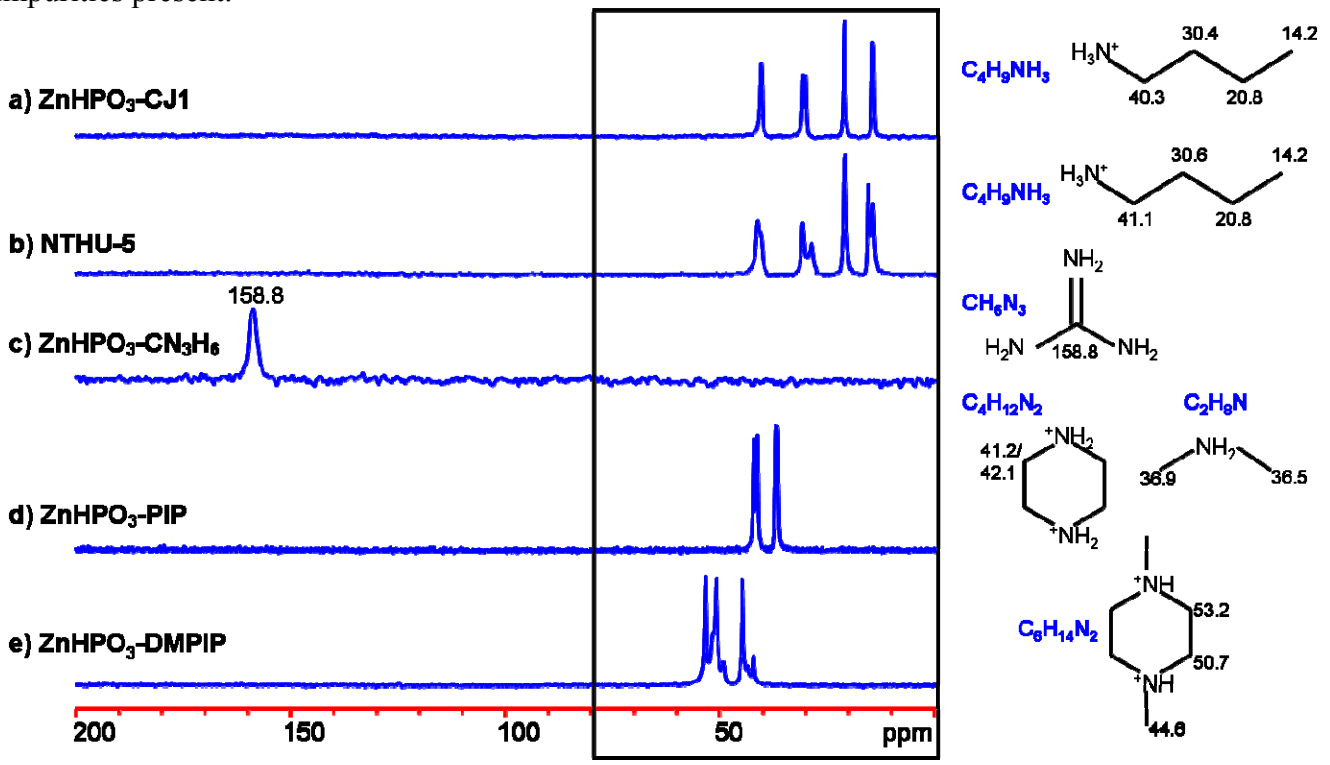
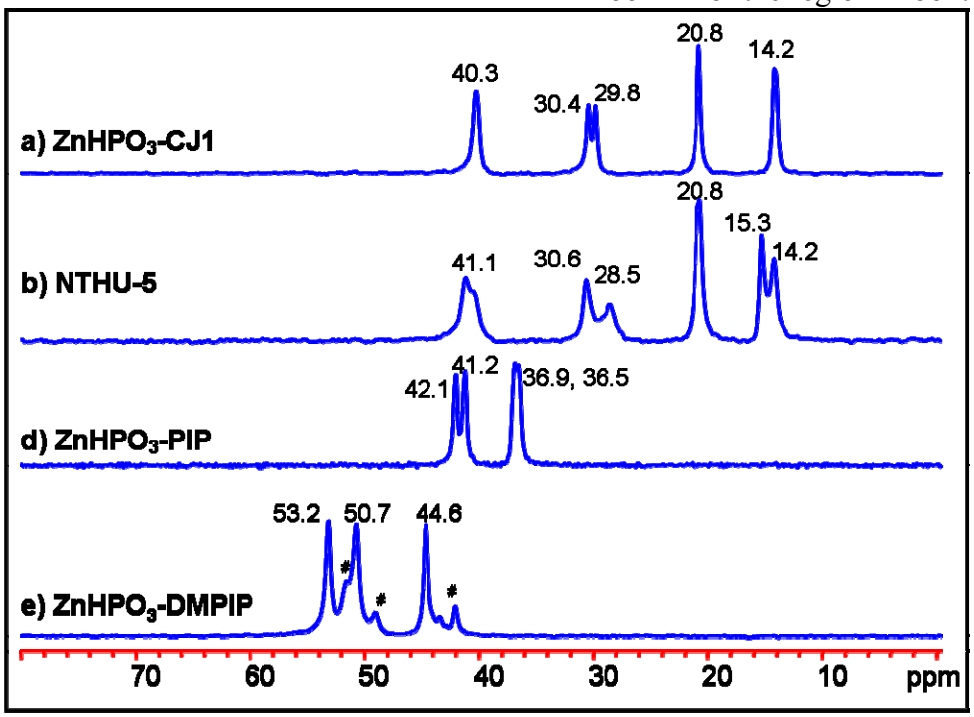


Figure S3. ^{13}C MAS NMR spectra of the materials studied at 10 kHz. Number signs (#) indicate impurities present.



Zoom-in of the region in box:



References for C-13 NMR chemical shifts assignments:
Acyclic and aliphatic amines (a, b and d): H. Eggert and C. Djerassi, *J. Am. Chem. Soc.*, 1973, **95**, 3710-3718.
Guanidines (c): L. M. Jackman and T. Jen, *J. Am. Chem. Soc.*, 1975, **97**, 2811-2818.
Piperidines (similar to d and e): E. L. Eliel, D. Kandasamy, C.-Y. Yen and K. D. Hargrave, *J. Am. Chem. Soc.*, 1980, **102**, 3698-3707.

Figure S4. ^{19}F MAS NMR spectrum of NTHU-5 at 8 kHz. Asterisks (*) indicate spinning sidebands.

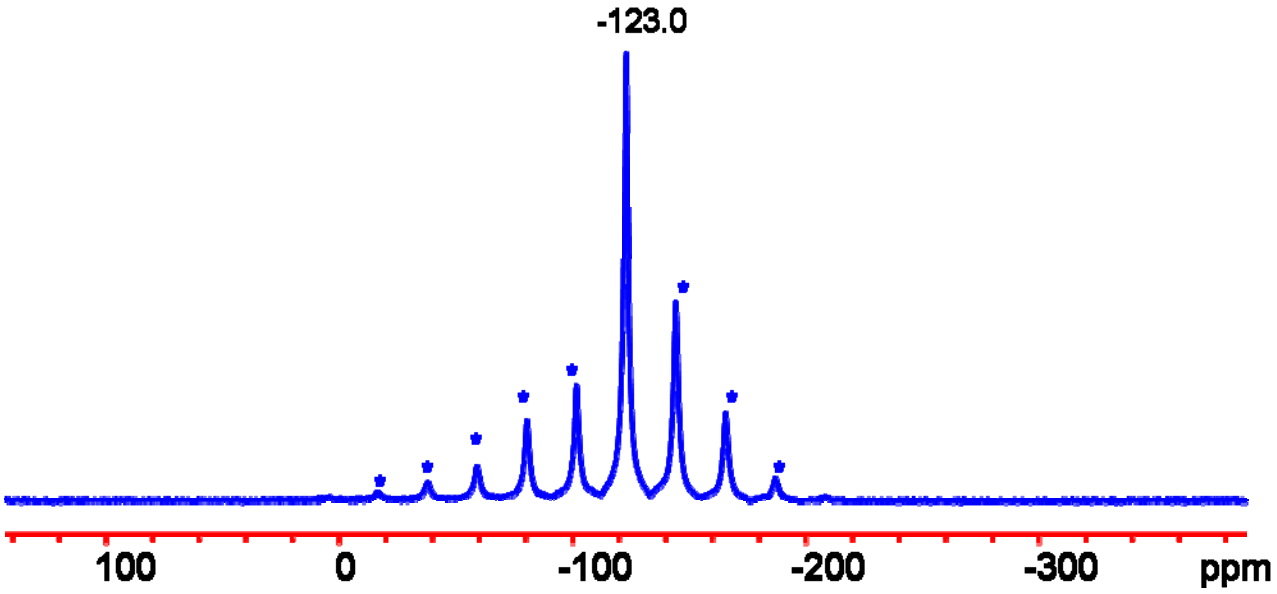


Figure S5. ^{27}Al MAS NMR spectrum of NTHU-5 at 8 kHz. Asterisks (*) indicate spinning sidebands.

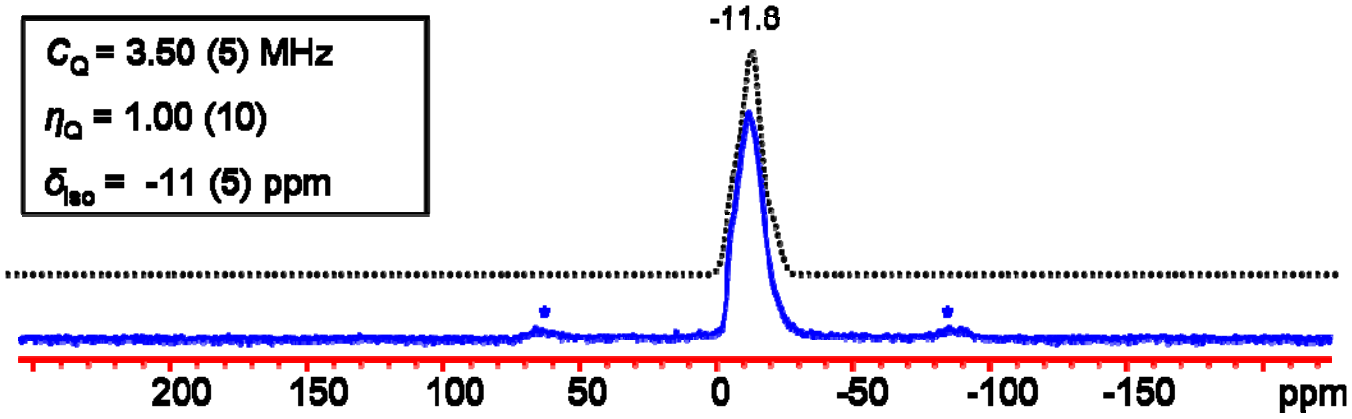


Figure S6. a) ^{6}Li MAS NMR spectrum of ZnPO-Li-ABW at 6 kHz. b) ^{7}Li MAS NMR spectrum of ZnPO-Li-ABW at 8 kHz. Asterisks (*) indicate spinning sidebands.

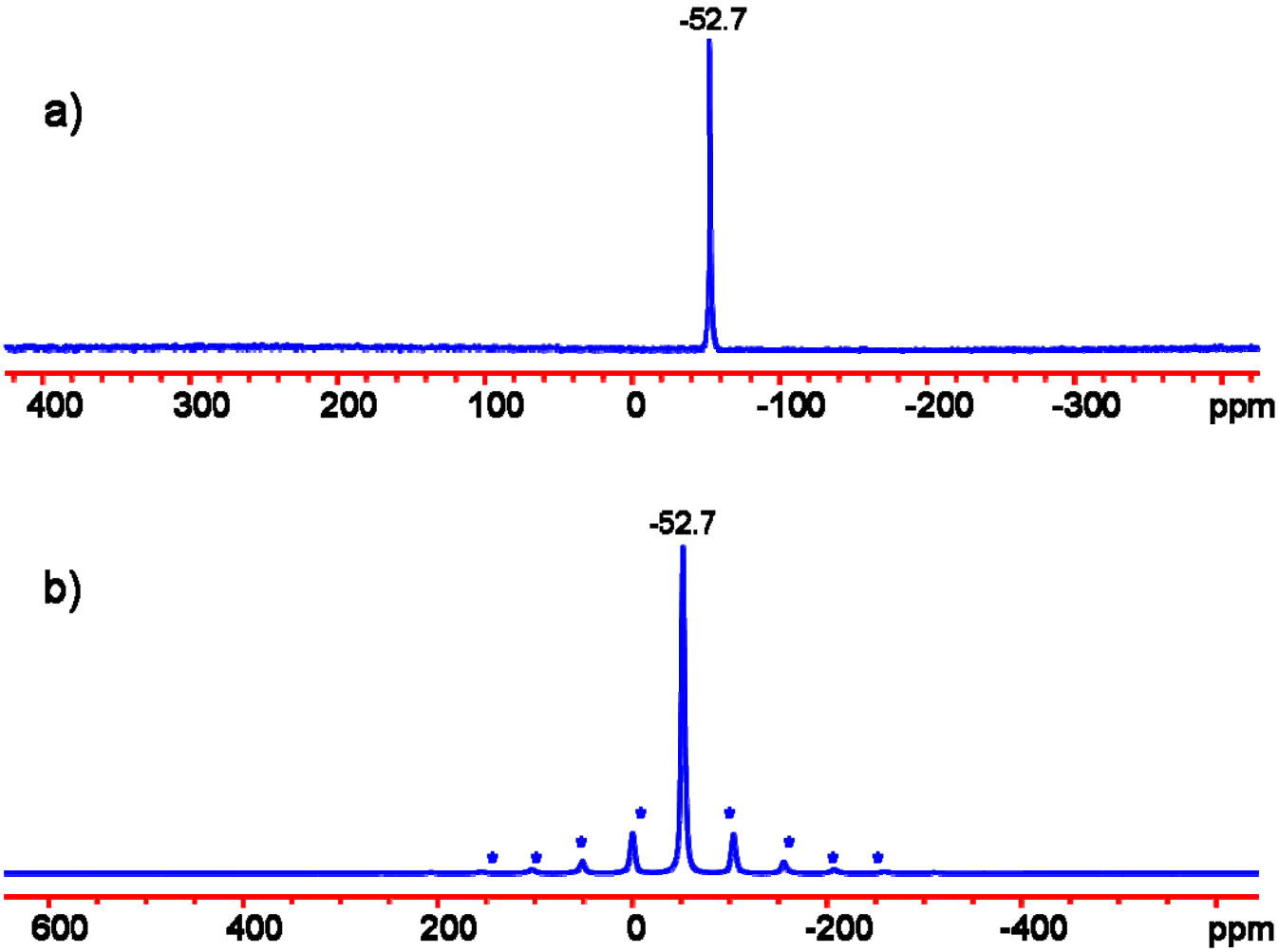


Figure S7. ^{67}Zn MAS NMR spectrum of $ZnHPO_3$-CJ1 at 21.1 T at 8 kHz.

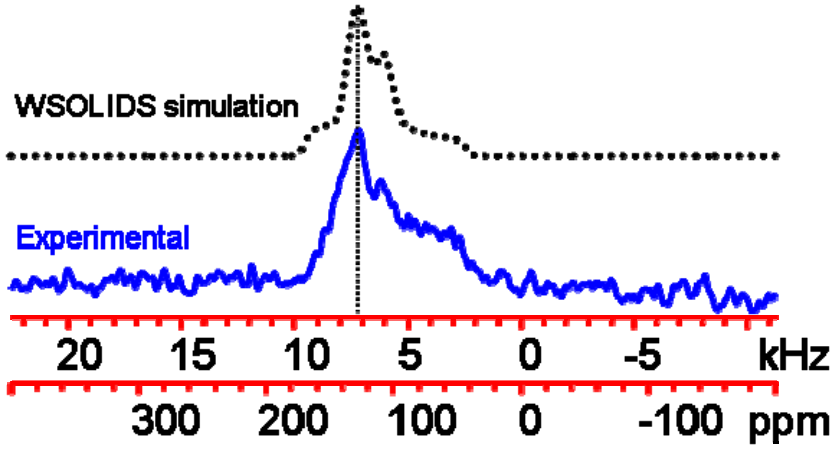


Figure S8. Static ^{67}Zn QCPMG NMR spectrum of $ZnHPO_3$-CJ1 at 9.4 T.

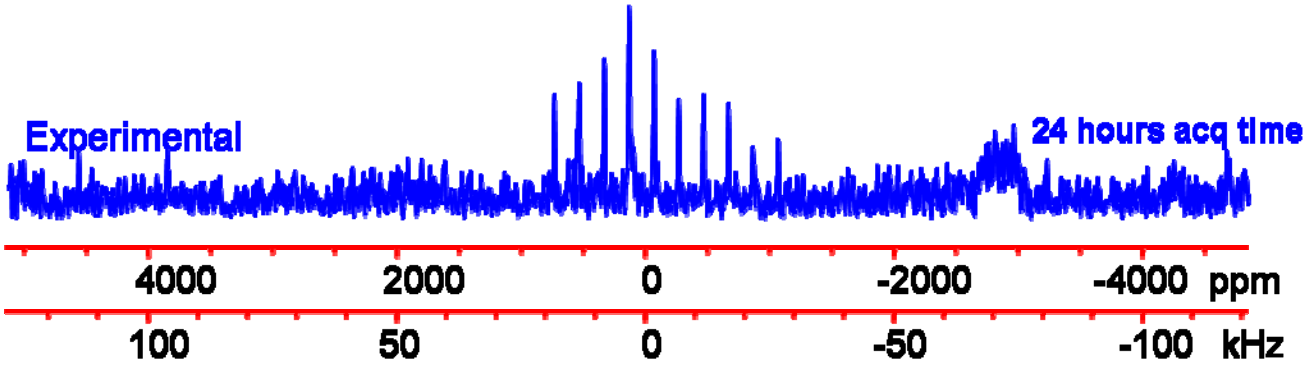


Figure S9. Static ^{67}Zn QCPMG NMR spectra of ZnPO-Li-ABW at 9.4 T

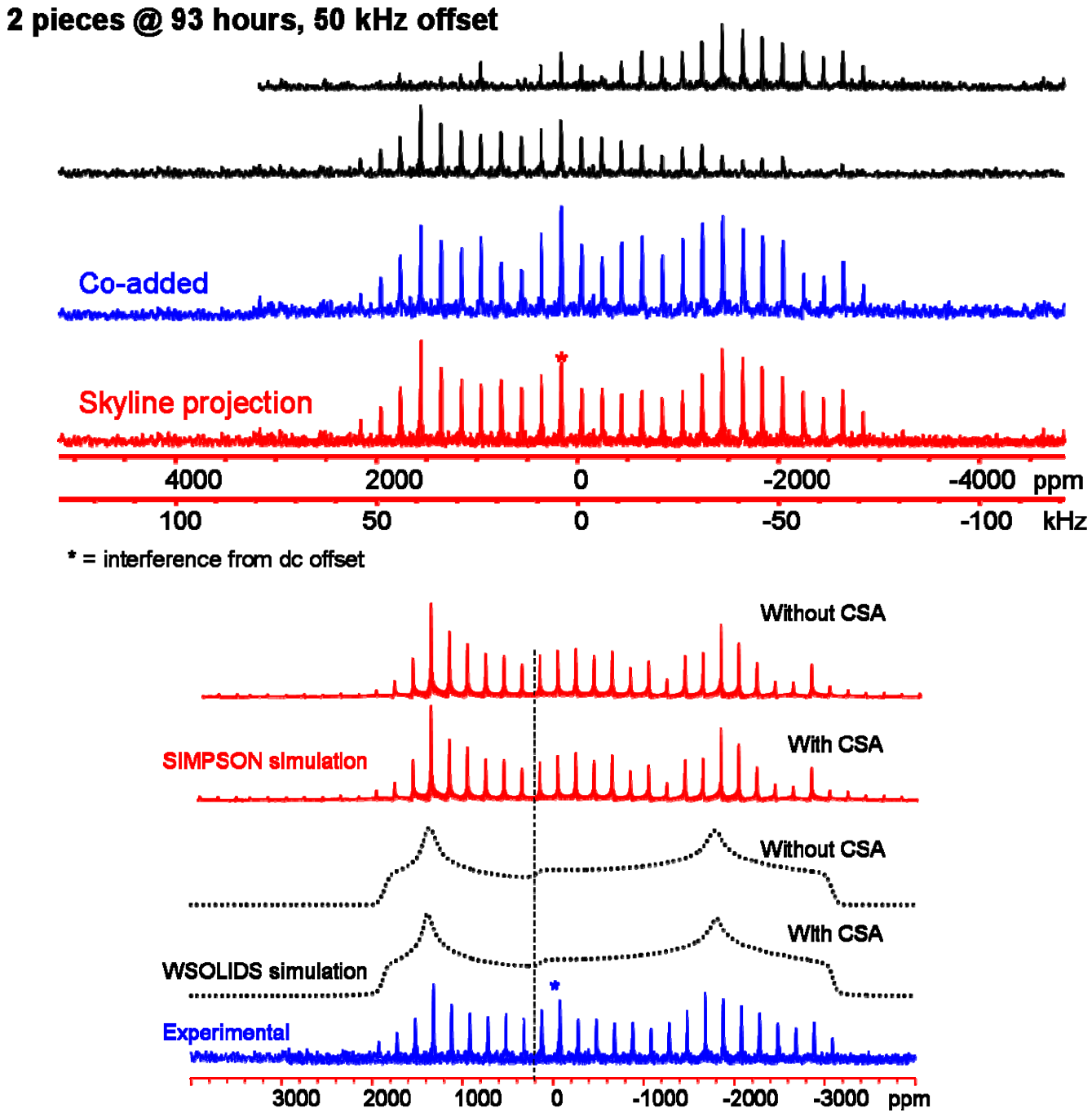


Figure S10. Simulation of static spectra acquired at 21.1 T for ZnPO-Li-ABW.