

Supporting Information for:

Solid-state ^{91}Zr NMR Characterization of Layered and Three-dimensional Framework Zirconium Phosphates

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Sample Preparation

The ion-exchanged phases of α -ZrP were prepared according to the following previously reported procedures. **Preparation of initial α -ZrP gel.** 8.05 g of zirconium oxychloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) was added into a 200 mL of 3 M HCl solution. Then, a mixture of 115.2 mL of 3.32 M H_3PO_4 , 50 mL of concentrated HCl and 35 mL of water was added slowly to the zirconium oxychloride solution with stirring and the gelatinous precipitates were allowed to stand overnight. They were then filtered, washed with 2% H_3PO_4 until free of chloride ion and given a final wash with distilled, deionized water multiple times. **Synthesis of α -ZrP.** 7.5 g of wet ZrP gel was added into 105 mL of 8.4 M H_3PO_4 solution. The precipitates were then heated with constant stirring and refluxing for 4 days. They were then washed with distilled water several times. After separation of the solids by centrifugation, the product was dried in air at room temperature. **Preparation of K- and Li-ZrP ion-exchange.**¹⁻³ 0.6 g of α -ZrP was dissolved in 120 mL of water. A solution of 0.1 M KOH/LiOH was added drop wise with stirring (pH = 10-12) and the solution was allowed to sit for one day. They were then filtered, washed three times with distilled water, and air-dried. **Preparation of Co-ZrP intercalation.**⁴ 0.5 g of α -ZrP was dissolved in 100 mL of water. A solution of 0.025 M $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ was added to the mixture, and were stirred under a reflux condenser for an hour at 75°C (pH = 2.8-3.5). They were then filtered, washed three times with distilled water, and air-dried.

All the other samples were also prepared according to the previously reported procedures. **ZrPO₄-DES8.**⁵ A Teflon-lined autoclave (total volume 23 mL) was charged with deep eutectic solvent (DES) made from oxalic acid (1.0 g, 7.94 mmol) and TPABr (3.2 g, 12.01 mmol), ZrOCl_2 (250 mg, 0.76 mmol), H_3PO_4 (177 mg, 1.54 mmol), HF (66 μL , 1.52 mmol) and 1,4-dimethylpiperazine (175 mg, 1.53 mmol). The autoclave was then heated at 180 °C for 3 days. After cooling the autoclave to room temperature, the solid product was recovered by dissolving the eutectic mixture in distilled water and subsequent filtration. The white solid was then washed thoroughly acetone, and dried at room temperature. **ZrPO₄-DES1 and ZrPO₄-DES2.**⁶ A typical synthesis procedure was as follows: a Teflon-

lined autoclave (volume 23 mL) was charged with appropriate quantities of deep eutectic solvent, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, H_3PO_4 and HF. The autoclave was then heated in an oven to the required temperature (180°C for 3 days for all phases). For $\text{ZrPO}_4\text{-DES1}$: The DES consisted of urea (2.9 g, 48.3 mmol) and tetramethyl ammonium chloride (2.4 g, 21.9 mmol), $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (250 mg, 0.76 mmol), HF (0.102 mL, 2.10 mmol) and H_3PO_4 (179 mg, 1.55 mmol). For $\text{ZrPO}_4\text{-DES2}$: The DES consisted of urea (2.8 g, 46.6 mmol) and tetramethyl ammonium chloride (2.4 g, 21.9 mmol), $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (250 mg, 0.76 mmol), HF (0.025 mL, 0.52 mmol) and H_3PO_4 (181 mg, 1.57 mmol). **ZrPOF-pyr.**⁷ The hydrothermal reactions were carried out under autogenous pressure in Teflon-lined stainless steel autoclaves (25 mL) with a filling of approximately 60%. First, the hydrogen fluoride was added to an aqueous solution of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and the mixture was stirred for about 10 min. Then phosphoric acid, followed by pyridine was added to the solution while continuing to stir. This produced a white gel. The molar ratios of the starting reactants used for a typical synthesis were 3 HF : 1 ZrO_2 : 0.5 P_2O_5 : 3 pyridine : 100 H_2O . The charged autoclaves were then placed in an oven at 180°C for 7 days. The crystalline products were filtered, washed with distilled water, and finally dried at 60°C overnight. **ZrPOF-Q1.**⁸ The typical synthesis process as follows: First, the hydrogen fluoride was added to an aqueous solution of ZrOCl_2 and the mixture was stirred for about 10 min. Then phosphoric acid, followed by quinoline was added to the solution while continuing to stir. The molar ratios of the starting reactants was 2 HF : 1 ZrO_2 : 1 P_2O_5 : 3 quinoline : 100 H_2O . The mixture was sealed in a 30 mL Teflon-lined stainless steel autoclave with a filling capacity of approximately 70% and heated at 180°C for 7 days under autogenous pressure. The crystalline products were separated by centrifugation, washed with distilled water, then washed with ethanol, and dried at room temperature in air. **ZrPOF-EA.**⁹ A Teflon-lined autoclave (total volume 23 mL) was charged with deep eutectic solvent made from oxalic acid dihydrate (2.0 g, 15.88 mmol) and ethyl ammonium chloride (2 g, 24.50 mmol), $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (250 mg, 0.76 mmol), H_3PO_4 (177 mg, 1.54 mmol) and HF (75 μL , 1.73 mmol). The autoclave was then heated at 180°C for 4 days and then cooled to room temperature. The solid product was washed thoroughly with acetone and water, and dried at

room temperature. **ZrPOF-DEA**. The synthesis for ZrPOF-DEA is similar to that of ZrPOF-EA but ethyl ammonium chloride was replaced by diethyl ammonium chloride in deep eutectic solvent. A Teflon-lined autoclave (total volume 23 mL) was charged with deep eutectic solvent made from oxalic acid dihydrate (2.0 g, 15.88 mmol) and diethyl ammonium chloride (2.7 g, 24.64 mmol), $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (250 mg, 0.76 mmol), H_3PO_4 (180 mg, 1.57 mmol) and HF (90 μL , 2.08 mmol). The autoclave was then heated at 180 °C for 4 days and then cooled to room temperature. The solid product was washed thoroughly with acetone and water, and dried at room temperature.

Experimental details for additional ^{31}P , ^{13}C , ^{19}F and $^6/7\text{Li}$ MAS NMR experiments acquired at 9.4 T. All the ^{31}P , ^{13}C , ^{19}F and $^6/7\text{Li}$ MAS NMR spectra of all the materials studied in this work were acquired at 9.4 T on a Varian Infinity Plus 400 WB spectrometer using either a 4-mm HXY or a 5-mm HFX T3 MAS probe [$\nu_0 = 161.7, 100.4, 375.8, 58.8$ and 155.3 MHz for ^{31}P , ^{13}C , ^{19}F and ^6Li and ^7Li respectively]. Standard samples used for pulse calibration and chemical shift referencing were ADP ($\text{NH}_4\text{H}_2\text{PO}_4$, solid, $\delta_{\text{iso}} = 1.33$ ppm, relative to 85% H_3PO_4 in H_2O), adamantane ($\text{C}_{10}\text{H}_{16}$, solid, $\delta_{\text{iso}} = 38.5$ ppm for higher frequency resonance, relative to TMS in CDCl_3), TFT ($\text{C}_6\text{H}_5\text{CF}_3$, 1 M solution, $\delta_{\text{iso}} = -65.4$ ppm, relative to CFCl_3) and LiCl (1 M solution, $\delta_{\text{iso}} = 0.0$ ppm) for ^{31}P , ^{13}C , ^{19}F and $^6/7\text{Li}$ respectively. A single-pulse with proton decoupling was used in all experiments, applying small ($< 30^\circ$) tip angle. The pulse delays used were 60, 5, 5, 5 and 1 second(s) for ^{31}P , ^{13}C , ^{19}F , ^6Li and ^7Li respectively.

Table S1. Detailed ^{91}Zr SSNMR experimental conditions.

Sample	Type of experiment	pulse length (μs)	SW (kHz)	τ_a (μs)	M (# of loops)	τ_1 (μs)	τ_2 (μs)	τ_3 (μs)	τ_4 (μs)	# scans
K-ZrP	MAS echo 12.5kHz	3	500	---	---	77	---	---	---	10240
	static echo	3	250	---	---	97	---	---	---	65536
	static WURST-QCPMG	50	200	1000	32	69	70	70	70	4096
Li-ZrP	MAS echo 12.5kHz	3	500	---	---	77	---	---	---	49820
	static echo	3	250	---	---	97	---	---	---	77824
	static WURST-QCPMG	50	200	1000	32	69	70	70	70	8192
Co-ZrP	MAS echo 12.5kHz	3	500	---	---	77	---	---	---	10240
	static echo	3	250	---	---	97	---	---	---	16384
	static WURST-QCPMG	50	200	1000	32	69	70	70	70	2048
ZrPO ₄ -DES8	MAS echo 20kHz	2	500	---	---	48	---	---	---	56108
	static echo	2	250	---	---	97	---	---	---	6600
	static WURST-QCPMG	50	500	200	32	29	30	30	30	256
ZrPO ₄ -DES1	MAS 1 pulse 20kHz	2	50	---	---	---	---	---	---	4096
	static echo	2	250	---	---	97	---	---	---	989
	static echo (14.1 T)	1.2	200	---	---	97	---	---	---	160960
ZrPO ₄ -DES2	MAS 1 echo 20kHz	2	500	---	---	48	---	---	---	49152
	static echo	2	250	---	---	97	---	---	---	4096
	static WURST-QCPMG	50	500	500	32	29	30	30	30	6550
ZrPOF-pyr	static echo	2	500	---	---	97	---	---	---	43400
	static WURST-QCPMG	50	500	200	32	29	30	30	30	7200
ZrPOF-Q1	static echo	2	500	---	---	97	---	---	---	45861
	static WURST-QCPMG	50	500	200	32	29	30	30	30	512
ZrPOF-EA	MAS echo 20kHz	2	500	---	---	48	---	---	---	83968
	static echo	2	500	---	---	97	---	---	---	12900
	static WURST-QCPMG	50	500	200	32	29	30	30	30	6239
ZrPOF-DEA	static WURST-QCPMG	50	500	200	32	29	30	30	30	2520

Table S2. Comparison of α -ZrP and its derivatives with their interlayer spacings.

Sample	$d_{\text{(this work)}} (\text{\AA})$	$d_{\text{(previous work)}} (\text{\AA})$	Ref.	% of ion-exchanged
α -ZrP	7.52	7.56	a	N/A
Li-ZrP	10.25	10.1	b, c	100
K-ZrP	10.72	10.8	a, d	100
Co-ZrP	11.31	11.16	e	~30

List of references: (a) Clearfield, A.; Stynes, J. A. *J. Inorg. Nucl. Chem.* **1964**, 26, 117; (b) Clearfield, A.; Troup, J. J. *Phys. Chem.* **1970**, 74, 314; (c) Alberti, G.; Constantino, U.; Allulli, S.; Massucci, M. A.; Pelliccioni, M. *J. Inorg. Nucl. Chem.* **1973**, 35, 1347; (d) Clearfield, A.; Duax, W. L.; Garces, J. M.; Medina, A. S. *J. Inorg. Nucl. Chem.* **1972**, 34, 329; (e) Hasegawa, Y.; Kizaki, S.; Amekura, H. *Bull. Chem. Soc. Jpn.* **1983**, 56, 734.

Table S3. Summary of relevant bond distances and angles for the Zr-based materials.

Compound	Zr–O bond distances (Å)	O–Zr–O bond angles (degrees)
α -ZrP (ZrO ₆)	2.049, 2.054, 2.065, 2.071, 2.074, 2.075	88.9, 89.0, 89.4, 89.5, 89.8, 89.9, ($\times 2$), 90.0, 90.5, 91.1 ($\times 2$), 91.2
K-ZrP (ZrO ₆)	1.912, 2.012, 2.082, 2.123, 2.144, 2.213	81.0, 81.4, 83.1, 85.1, 88.8, 90.7, 92.4 ($\times 2$), 93.0, 94.4, 95.5, 102.8
K-ZrP (ZrO ₆) – CASTEP-opt	2.035, 2.052, 2.067, 2.075, 2.098, 2.099	83.0, 83.1, 85.9, 87.2, 87.7, 89.7, 90.6, 90.9, 91.9, 94.1, 98.6, 99.3
ZrPO ₄ -DES8 (ZrO ₆)	2.035, 2.048, 2.050, 2.069 ($\times 2$), 2.109	87.4, 87.6, 88.4, 88.8, 89.6, 90.3 ($\times 2$), 90.4, 91.0, 91.7, 91.8, 92.8
ZrPO ₄ -DES1 (ZrF ₂ O _{4-trans})	2.052 ($\times 2$), 2.068 ($\times 2$); <i>2.009 ($\times 2$)^a</i>	88.5($\times 2$), 91.5($\times 2$); <i>87.9($\times 2$), 89.5($\times 2$), 90.5($\times 2$), 92.1($\times 2$)</i>
ZrPO ₄ -DES2 (ZrFO ₅)	2.047, 2.048, 2.056, 2.065 ($\times 2$); <i>2.016</i>	88.7, 89.1, 89.3, 89.6, 90.3, 90.5, 90.7, 95.2; <i>86.8, 88.9, 89.9, 91.2</i>
ZrPOF-pyr – site 1 (ZrO ₆)	1.923, 2.009, 2.014, 2.046, 2.092 ($\times 2$)	86.2, 86.8, 87.1 ($\times 2$), 89.0 ($\times 2$), 89.2, 91.4 ($\times 2$), 92.8 ($\times 2$), 97.8
ZrPOF-pyr – site 2 (ZrF ₂ O _{4-cis})	2.007, 2.060 ($\times 2$), 2.111; <i>1.947, 2.127</i>	90.5 ($\times 2$), 93.2 ($\times 2$), 94.3; <i>81.7,</i> <i>86.9 ($\times 2$), 88.6 ($\times 2$), 101.1; 82.9^b</i>
ZrPOF-pyr – site 3 (ZrFO ₅)	2.030, 2.066, 2.076 ($\times 2$), 2.161; <i>2.141</i>	86.9 ($\times 2$), 91.2 ($\times 2$), 92.1, 92.9, ($\times 2$), 98.3; <i>82.9, 86.8, 89.1 ($\times 2$)</i>
ZrPOF-Q1 – site 1 (ZrO ₆)	2.030, 2.044, 2.050, 2.055, 2.057, 2.071	87.4, 87.9, 88.4, 88.5, 88.9, 90.0, 90.6, 90.7, 91.1 ($\times 2$), 92.1, 93.6
ZrPOF-Q1 – site 2 (ZrO ₆)	2.048, 2.054 ($\times 3$), 2.056, 2.087	86.0, 87.3 ($\times 2$), 87.9, 88.8, 89.8, 90.9 ($\times 2$), 91.9, 92.2, 93.0, 94.1
ZrPOF-Q1 – site 3 (ZrO ₆)	2.032, 2.043, 2.046, 2.051 ($\times 2$), 2.067	86.5, 87.9, 88.8, 88.9 ($\times 2$), 89.0, 89.9, 90.0, 90.2, 92.1, 93.2, 94.4
ZrPOF-Q1 – site 4 (ZrF ₄ O ₂)	2.067, 2.085; <i>2.032, 2.042</i> <i>($\times 2$), 2.050</i>	95.2; <i>85.8, 87.4, 89.2, 90.1, 90.2</i> <i>($\times 2$); 84.6, 88.5, 91.8, 93.5, 94.4</i>

^aThe numbers in italicized and blue indicate one F atom is involved instead of one O atom. ^bThe numbers in italicized and red indicate two F atoms are involved instead of two O atoms.

Table S4. Structural data for all the ZrP/ZrPOF materials investigated in this study.

Compound	Ref.	# of Zr sites; Zr coordination (site symmetry)	# of P, F sites	Space group	Unit cell volume (Å ³)
ZrPO ₄ -DES8	5	1; ZrO ₆ (C ₁)	2, 0	<i>P</i> 2 ₁ /c (no. 14)	1,060
ZrPO ₄ -DES1	6	1; ZrF ₂ O ₄ (C _i)	1, 1	<i>P</i> -1 (no. 2)	315
ZrPO ₄ -DES2	6	1; ZrFO ₅ (C ₁)	2, 1	<i>C</i> 2 (no. 5)	1,035
ZrPOF-pyr	7	3; 1 ZrO ₆ , 1 ZrFO ₅ , 1 ZrF ₂ O ₄ (C _s)	4, 2	<i>P n n m</i> (no. 58)	1,920
ZrPOF-Q1	8	4; 3 ZrO ₆ , 1 ZrF ₄ O ₂ (C ₁)	6, 4	<i>P</i> -1 (no. 2)	1,980
ZrPOF-EA	9	8; 4 ZrO ₆ , 4 ZrFO ₅ (C _s)	12, 2	<i>P b a m</i> (no. 55)	4,895

Table S5. Calculated ⁹¹Zr C_Q values of zirconium phosphate model cluster for ZrPO₄-DES1.

<i>Figure 9a data</i>		<i>Figure 9b data</i>		<i>Figure 9c data</i>		<i>Figure 9d data</i>	
two Zr-F bond (Å)	C _Q (MHz)	two Zr-O bond (Å)	C _Q (MHz)	two F-Zr-O angle (deg.)	C _Q (MHz)	two O-Zr-O angle (deg.)	C _Q (MHz)
1.900	46.21	1.900	75.29	80	48.15	80	31.09
1.940	25.93	1.920	64.13	82	40.88	82	24.94
1.969	13.10	1.940	53.54	84	33.59	84	18.83
1.980	10.12	1.960	43.35	86	26.31	86	13.04
1.985	9.05	1.980	33.62	88	19.06	86.7	9.08
1.990	8.00	2.000	24.35	90	11.85	88.5*	8.48
1.995	6.95	2.020	15.53	90.3	9.81	90	9.87
1.996	6.75	2.027	3.28	92.1*	8.48	90.3	8.59
1.997	6.54	2.040	9.58	93.9	7.90	92	15.04
1.998*	6.34	2.050	5.50	94	11.27	94	21.17
1.999	6.50	2.060	7.12	96	18.71	96	27.52
2.000	6.71	2.068*	8.48	98	26.13	98	33.87
2.009	8.48	2.070	8.72	100	33.50	100	40.14
2.015	9.74	2.080	10.87	102	40.81	102	46.27
2.020	10.73	2.100	15.98				
2.060	23.63	2.109	14.56				
2.100	36.98	2.120	22.94				
2.140	49.05	2.140	29.59				
2.180	59.98	2.160	35.92				
		2.180	41.96				

*The asterisk sign indicates a minimum point on the curve; while the numbers in blue indicate crystallographic values.

Figure S1. Powder XRD patterns of ion-exchanged ZrP studied in this work. Asterisks (*) indicate reflections from the initial α -ZrP phase.

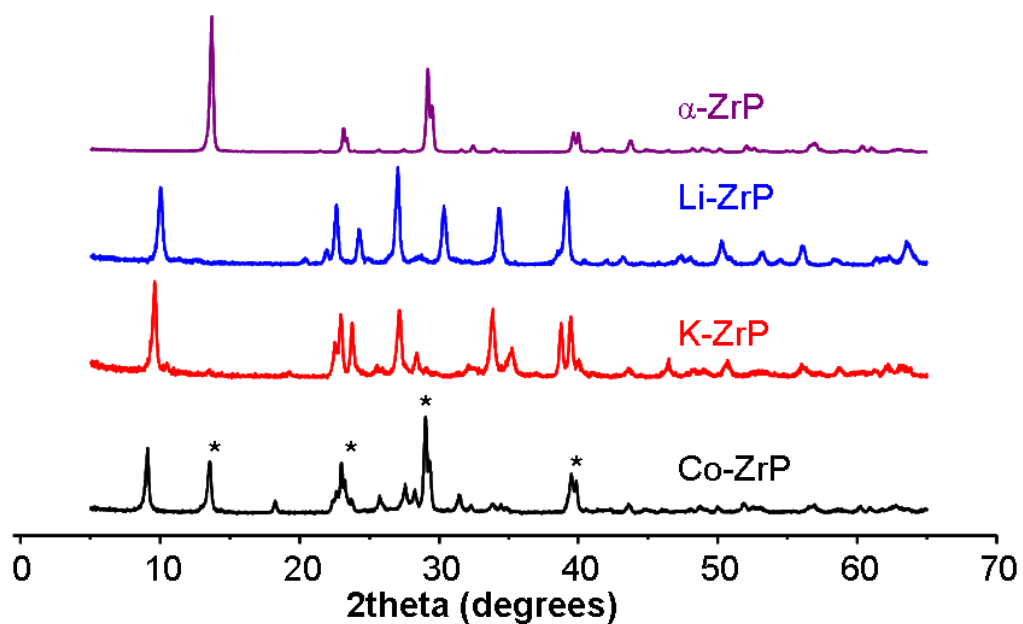


Figure S2. ^{31}P MAS NMR spectra of ion-exchanged ZrP derivatives at 9.4 T.

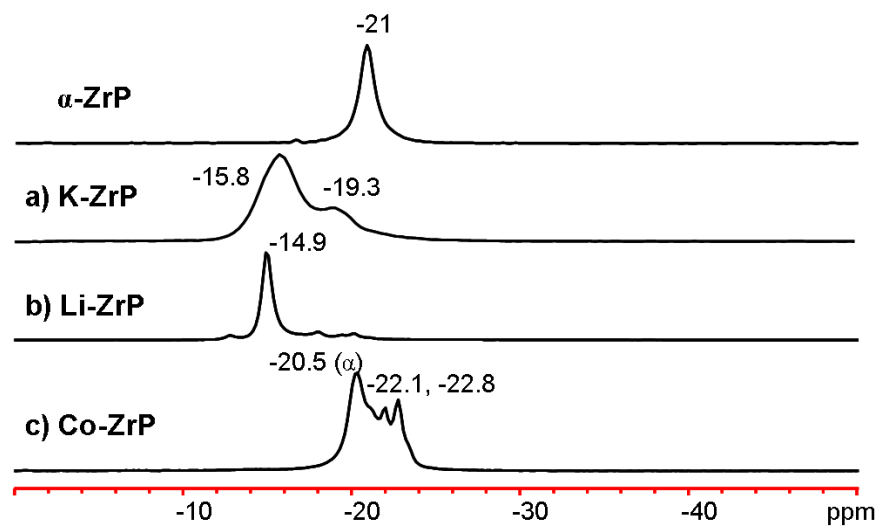


Figure S3. (a) ^6Li and (b) ^7Li MAS NMR spectra of Li-ZrP at 9.4 T spinning at 8 kHz. Asterisks (*) indicate spinning sidebands from the satellite transition (ST).

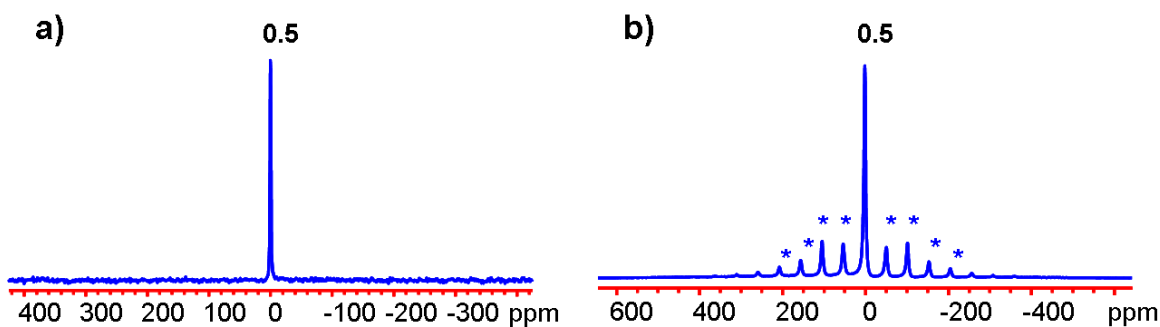


Figure S4. ^{91}Zr static QCPMG NMR spectra of α -ZrP and its ion-exchanged derivatives at 21.1T. For $\text{NH}_4\text{-ZrP}$, no experimental QCPMG spectrum was available at 21.1T. The spectrum shown was simulated using experimental NMR parameters obtained at lower fields reported earlier. Blue spectra indicate the new ones acquired in this work.

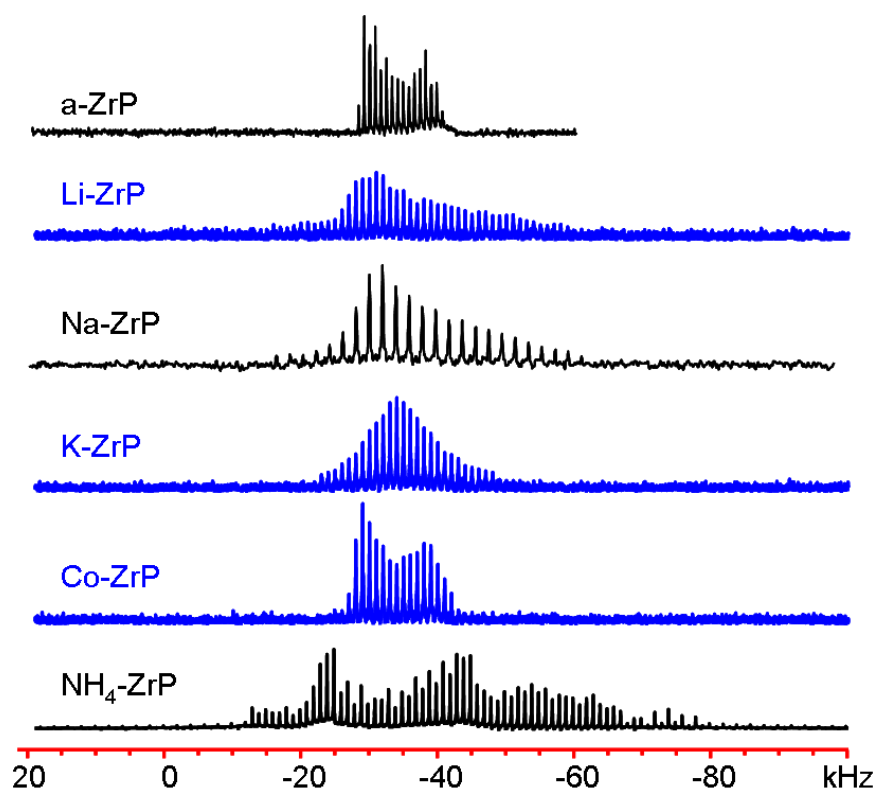


Figure S5. Correlation between various experimental ^{91}Zr NMR and structural parameters. The five data points in solid blue were taken from the following paper: Yan, Z.; Kirby, C. W.; Huang, Y. *J. Phys. Chem. C* **2008**, *112*, 8575.

The definitions of each distortion parameter ($|\Psi|$ and $|\alpha|$) are as follows: $|\Psi|$ or shear strain = $(\sum |\tan(\theta_i - 90)|)$, where θ_i is the actual O–Zr–O angle and the sum runs over 12 angles; $|\alpha|$ or longitudinal strain = $(\sum |\ln(l_i - l_{\text{ave}})|)$, where l_i is the actual Zr–O length and the sum runs over 6 bond lengths; for further details, see *Am. Mineral.* **1973**, *58*, 748.

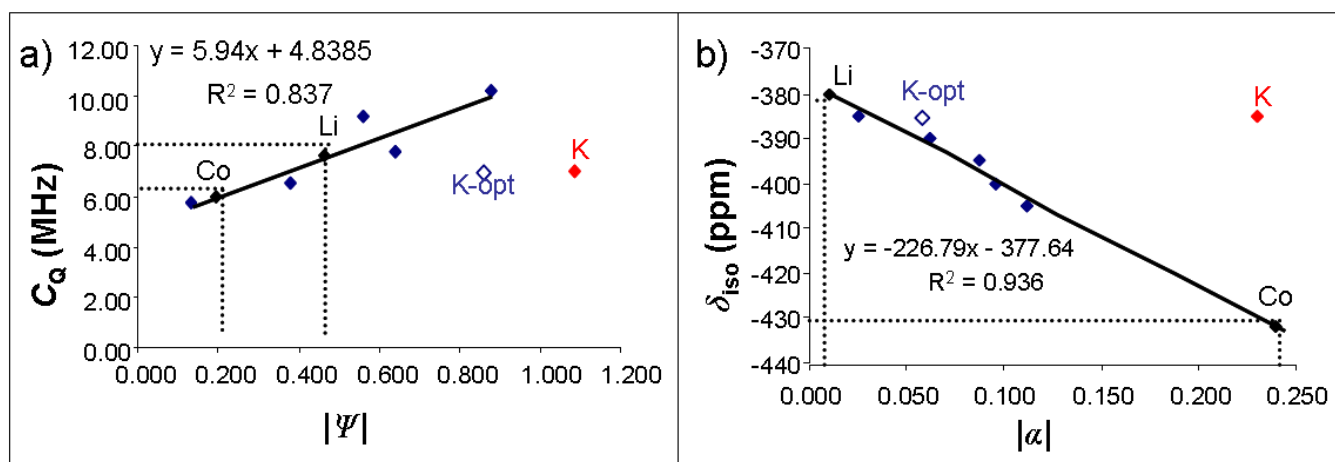


Figure S6. Powder XRD patterns of all the ZrP/ZrPOF materials studied in this work.

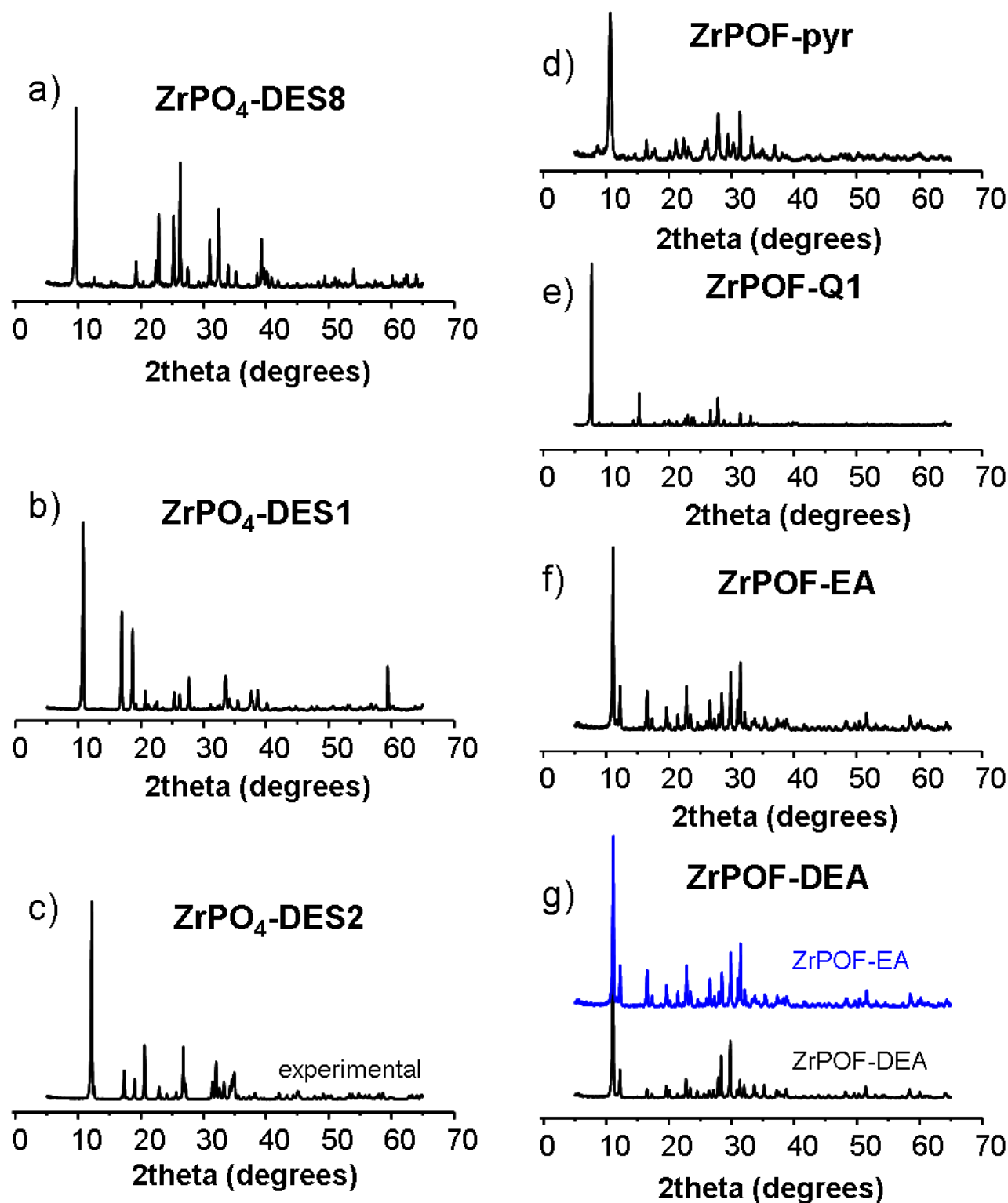


Figure S7. ^{31}P MAS NMR spectra of all the ZrP/ZrPOF materials studied in this work at 7 or 8 kHz. Number signs (#) indicate impurities present.

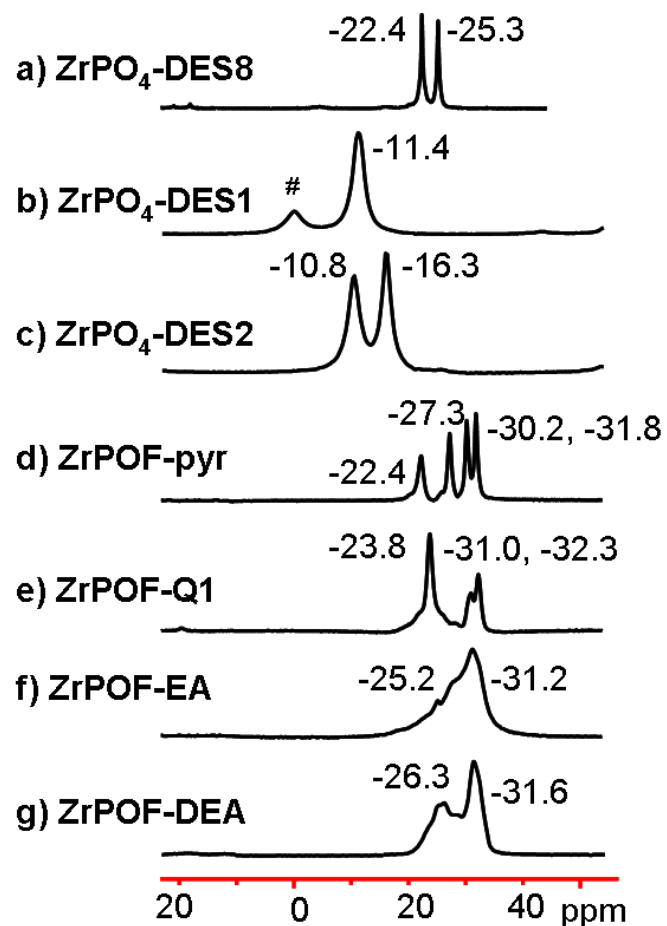


Figure S8. ^{13}C MAS NMR spectra of all the materials studied in this work at 9.4 T. Asterisks (*) indicate spinning sidebands. References for ^{13}C NMR chemical shifts assignments: Piperidines (DMPIP in a): *J. Am. Chem. Soc.*, 1980, **102**, 3698-3707; Pyridine and Quinoline (b and c): Spectral Database for Organic Compounds (SDBS), http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/cre_index.cgi; Acyclic and aliphatic amines (EA and DEA in d and e): *J. Am. Chem. Soc.*, 1973, **95**, 3710-3718.

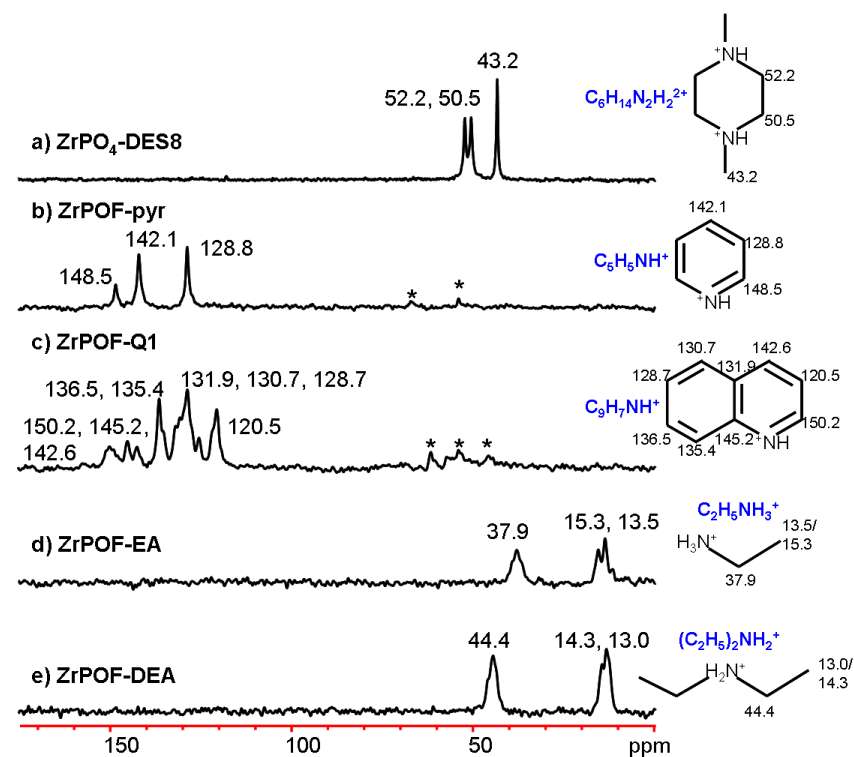


Figure S9. ^{91}Zr MAS NMR spectra of $\text{ZrPO}_4\text{-DES8}$ at 21.1 T, showing signal from ZrO_2 rotor.

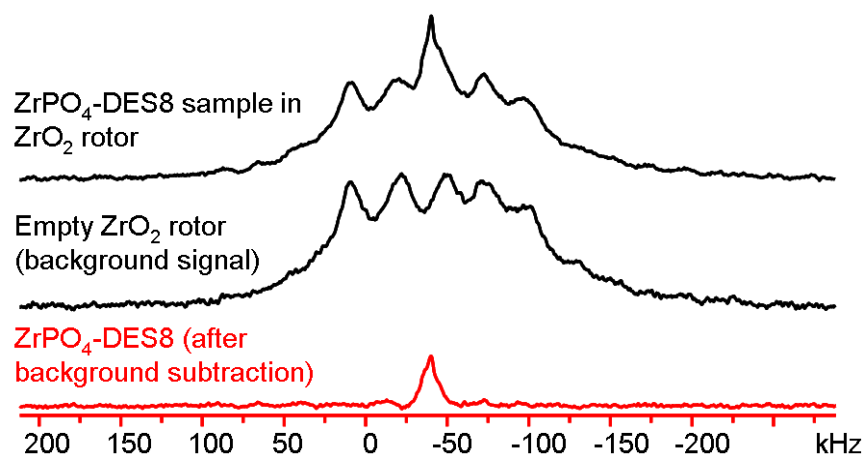
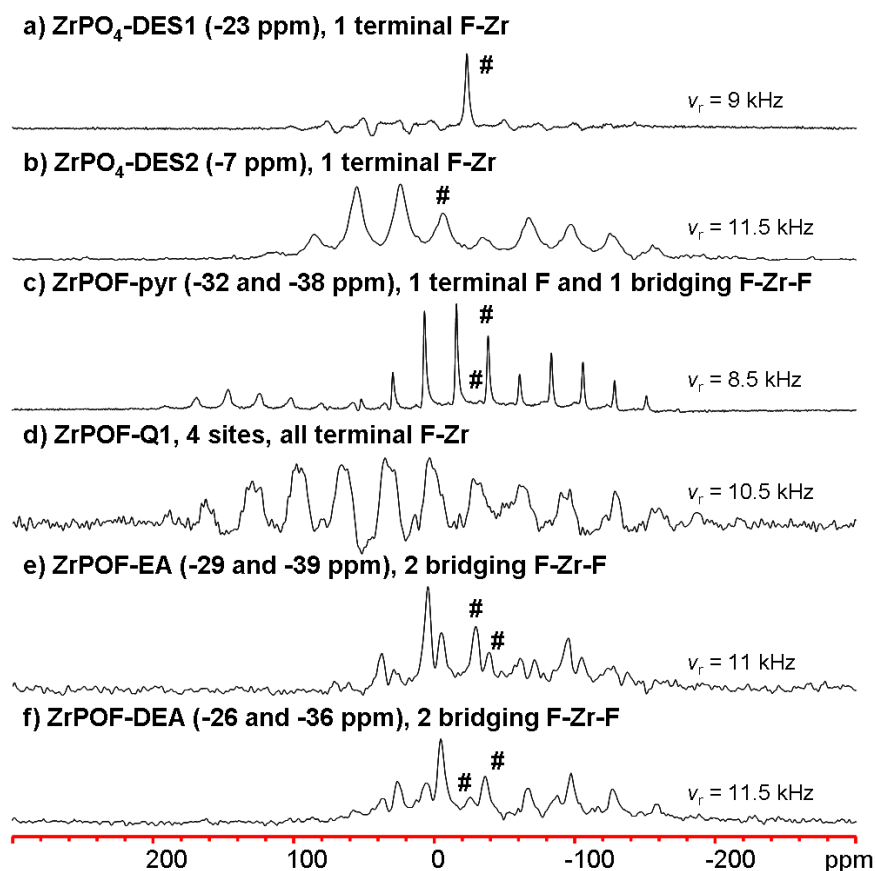


Figure S10. ^{19}F MAS NMR spectra of all the materials studied in this work at 9.4 T, spinning at various speed (ν_r) indicated. Number signs (#) indicate isotropic chemical shifts, while the other unlabeled peaks are spinning sidebands. For each compound, at least two spectra were acquired at different spinning speeds in order to extract the isotropic chemical shifts. For (d), the individual F site can not be resolved due to band overlapping.



References:

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