

Exfoliation of zirconium aminophosphonates: investigation on the electronic properties by *ab initio* calculations.

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Supporting Information

Geometry Optimization

Table S1: Simulated unit cell parameters of *bulk* and 2D structures with their respective relative errors calculated by the vdW-DF2-C09 functional.

Functional	vdW-DF2-C09 - bulk			vdW-DF2-C09 - exfoliated		
	α -ZrP	ZAMPAOX	ZAEPACI	α -ZrP	ZAMPAOX	ZAEPACI
a (Å)	8.83/-2.52%	23.80/-3.55%	9.24/-1.14%	8.91	-	9.25
b (Å)	5.11/-3.49%	7.89/0.83%	5.37/-0.27%	5.20	7.99	5.33
c (Å)	15.36/-0.32%	11.83/-3.30%	29.05/-1.81%	-	11.11	-
Basal Spacing (Å)	7.52/-1.69%	10.44/-2.80%	13.98/-2.98%	-	-	-
α (°)	90.00/0.00%	89.94/0.07%	90.29/-0.32%	90.00	88.97	90.15
β (°)	101.23/0.47%	118.06/0.45%	105.72/-2.65%	97.62	120.97	102.79
γ (°)	90.00/0.00%	89.78/0.25%	91.23/-1.37%	90.00	90.30	90.01

Table S2: Simulated unit cell parameters of the dehydrated 2D structures calculated by the PBE functional.

Parameters	α -ZrP	ZAMPAOX
<i>a</i> (Å)	9.11	-
<i>b</i> (Å)	5.30	7.87
<i>c</i> (Å)	-	12.02
α (°)	90.00	88.99
β (°)	97.78	117.38
γ (°)	90.00	90.26

Vibrational Analysis

Vibrational calculations were carried out to characterize optimized structures as either minimum or maximum. The vibrational modes were obtained from phonon calculations, which were based on the harmonic approximation by density functional perturbation theory (DFPT)^[1,2], at the Γ *q* point, and the convergence threshold was 10^{-16} . The infrared absorption spectra were

simulated using a Lorentzian distribution curve with a full width at half-maximum of 10 cm^{-1} . Experimental data of α -ZrP^[3-5]; ZAMPAOX and ZAEPACl^[6] were reported in recent studies.

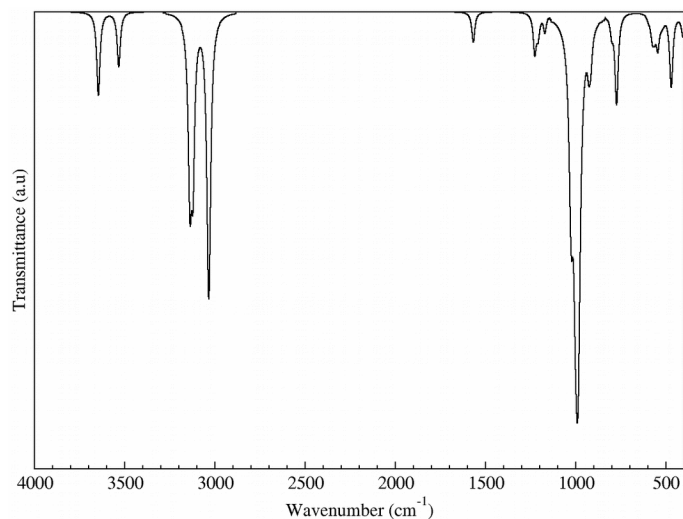


Figure S1: Simulated infrared spectrum of α -ZrP.

Table S3: Assignments of the simulated vibrational modes of α -ZrP.

Wavenumber (cm^{-1})	Assignments
470	$\delta(\text{O-Zr-O} + \text{O-P-O}) + \text{Libration}(\text{H}_2\text{O})$
544, 771	$\text{Libration}(\text{H}_2\text{O} + \text{-OH})$
992	$\delta(\text{H-O-P}) + \nu(\text{O-P-O})$
1229	$\delta(\text{H-O-P})$
1568	$\delta(\text{H}_2\text{O scissor})$
3036, 3142	$\nu(\text{-OH})$
3531	$\nu_{\text{symmetric}}(\text{H}_2\text{O})$
3644	$\nu_{\text{antisymmetric}}(\text{H}_2\text{O})$

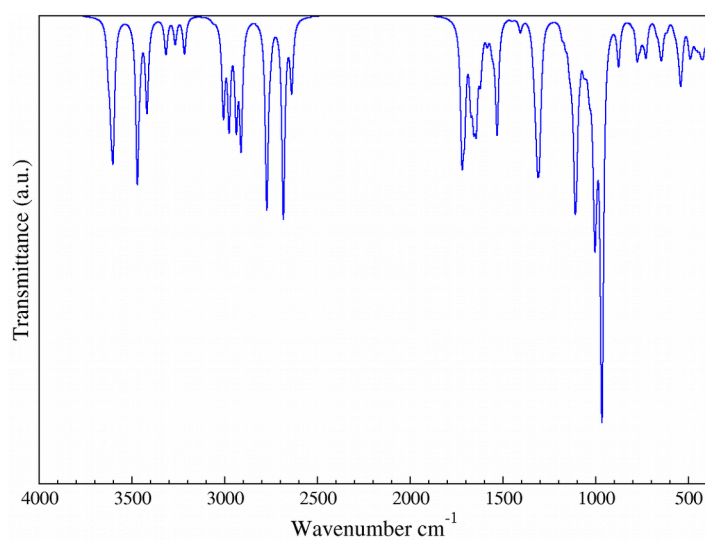
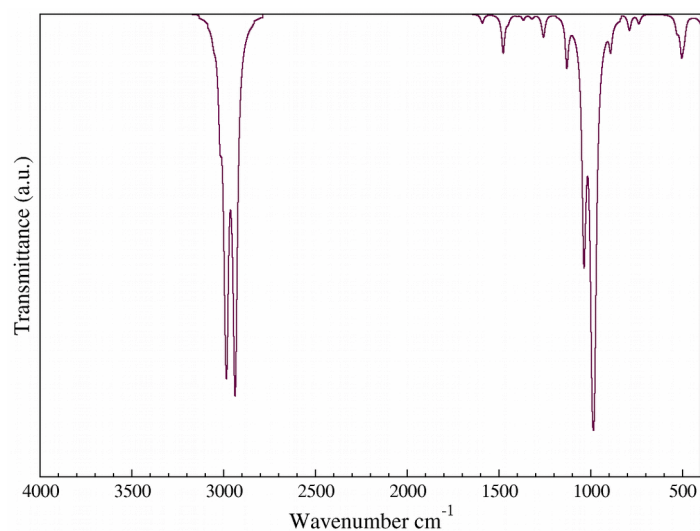


Figure S2: Simulated infrared spectrum of ZAMPAOX.

Table S4: Assignments of the simulated vibrational modes of ZAMPAOX.

Wavenumber (cm ⁻¹)	Assignments
538	$\delta(\text{O-Zr-O} + \text{O-P-O}) + \text{Libration}(\text{H}_2\text{O} + \text{-NH}_3)$
640	$\delta(\text{O-Zr-O} + \text{O-P-O}) + \text{Libration}(\text{H}_2\text{O})$
724	$\nu(\text{P-C}) + \text{Libration}(\text{H}_2\text{O} + \text{-NH}_3)$
767	$\delta(\text{O-C-O}) + \text{Libration}(\text{H}_2\text{O})$
876	$\delta(\text{O-C-O}) + \nu(\text{C=C})$
970, 1003	$\delta(\text{O-P-O})$
1112	$\delta(\text{O-P-O} + \text{-CH}_2\text{-NH}_3)$
1313	$\delta(\text{O-C-O}) + \nu(\text{C=C}) + \delta(\text{O-P-O} + \text{-CH}_2\text{-NH}_3)$
1409	$\delta(\text{-CH}_2 \text{ scissor})$
1530	$\delta(\text{O-C-O}) + \delta(\text{-NH}_3) + \delta(\text{H}_2\text{O})$
1640, 1717	$\delta(\text{O-C-O}) + \delta(\text{-NH}_3)$
2639, 2683, 2772, 2911, 2937, 2976, 3216, 3266, 3315	$\nu(\text{-NH}_3)$
3006	$\nu(\text{-NH}_3) + \nu_{\text{symmetric}}(\text{-CH}_2)$
3418, 3470, 3612	$\nu(\text{H}_2\text{O})_{(\text{sym and anti})}$

**Figure S3:** Simulated infrared spectrum of ZAEPACI.**Table S5:** Assignments of the simulated vibrational modes of ZAEPACI

Wavenumber (cm ⁻¹)	Assignments
503	$\delta(\text{-NH}_3 + \text{-CH}_2 + \text{O-P-O})$
737	$\text{R}(\text{-CH}_2)$
788	$\delta(\text{H-N-C}) + \nu(\text{P-C})$
890	$\text{R}(\text{-CH}_2) + \delta(\text{H-N-C})$
985	$\nu_{\text{antisymmetric}}(\text{O-P-O})$
1035	$\nu_{\text{symmetric}}(\text{-PO}_3)$
1130	$\nu(\text{C-C}) + \delta(\text{H}_3\text{N-CH}_2\text{-CH}_2\text{-})$
1264, 1320, 1366	$\text{Twisting}(\text{H}_3\text{N-CH}_2\text{-CH}_2\text{-})$
1476	$\delta_{\text{symmetric}}(\text{-NH}_3)$
1590	$\delta_{\text{antisymmetric}}(\text{-NH}_3)$
2937, 2984	$\nu(\text{-NH}_3)$

NMR Simulation

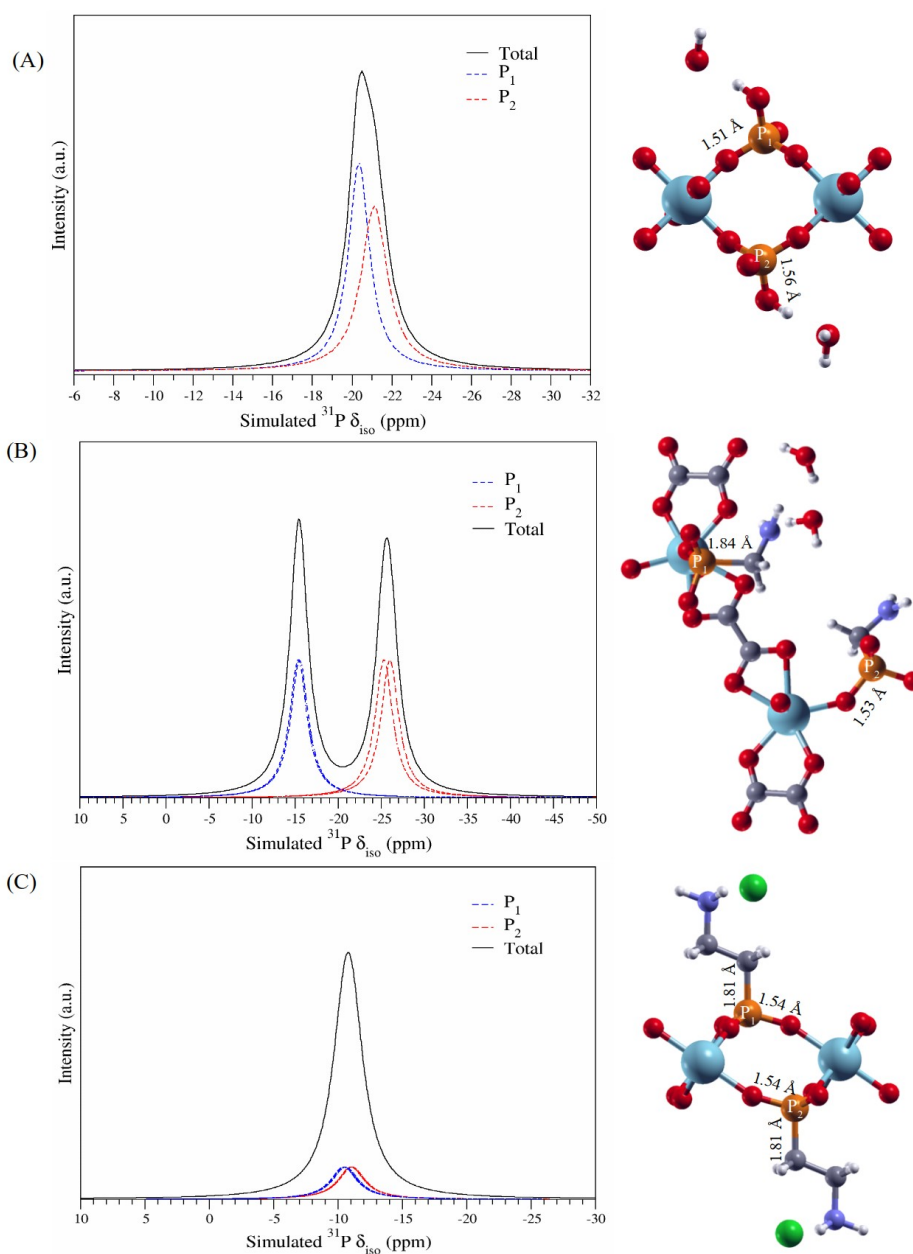
The chemical shielding tensors (σ) of ^{31}P and ^{13}C were calculated using gauge-including projector augmented waves (GIPAW). These magnetic resonance properties were calculated at the DFT level, exploiting the full translational symmetry of crystals [7,8]. The interaction of the valence electrons with the nuclei and the core electrons was treated by the projector augmented-wave (PAW) method. The chemical shifts of the nucleus ^{31}P were calculated by the following equation: $\delta_{\text{iso}} = (\sigma_{\text{ref}} - \sigma_{\text{iso}}) - \delta_{\text{ref}}$, where σ_{ref} and σ_{iso} are the calculated chemical shielding of the reference ($\sigma_{\text{ref}} = 269.44$) and the chemical shieldings of the studied compounds (Table S6), respectively. δ_{ref} is the experimental chemical shift of a secondary reference ($\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$, $\delta_{\text{ref}} = 2.3$ ppm) reported by some NMR works of α -ZrP [9,10]. Thereby, the simulation of NMR spectra was done based on some experimental conditions known from the α -ZrP NMR analysis, such as the Larmor frequency adopted by Clayden *et al.* [10]. Afterwards, the NMR spectra of ZAMPAOX and ZAEPACl were simulated in this work (Figure S4), though the experimental data were not reported yet. The QUADFIT program was used for the generation of the simulated NMR spectra [11] and a Lorentzian broadening of 300 Hz was used for each spectrum. In the case of ^{13}C nucleus, the calculations of the chemical shifts were obtained from the linear regression: $\delta_{\text{iso}} = 164.94 - 0.985316 \times \sigma_{\text{iso}}$ [12].

As can be noted in Figure S4, the δ_{iso} value and simulated NMR spectra for α -ZrP showed a good agreement with some experimental works [9,10]. In addition, the calculated chemical shifts of ^{31}P nucleus confirmed the symmetry of phosphates and phosphonates groups for the α -ZrP and ZAEPACl structures, because the signals for each structure were very close and both convoluted to a single peak in the spectra. On the other hand, the NMR spectrum of ZAMPAOX presents different types of phosphorus shielding, caused by the different positions of the phosphonate groups on the layer: some groups adopt a perpendicular orientation to the oxalate groups (P_1), while the other ones remain on the same oxalate plane (P_2).

For the ^{13}C nucleus, the calculated chemical shifts of ZAMPAOX were easily assigned to alkyl (27.15 ppm) and oxalate (150-161 ppm) groups. The two simulated ^{13}C chemical shifts of ZAEPACl were also assigned in terms of the connectivity of the carbon atoms: CH_2 (bonded to P) (20.70 ppm) and CH_2 (bonded to ammonium) (31.80 ppm).

Table S6: Calculated NMR parameters of ^{13}C and ^{31}P of α -ZrP, ZAMPAOX and ZAEPACI

Compound	^{31}P		^{13}C	
	σ_{iso}	δ_{iso}	σ_{iso}	δ_{iso}
α -ZrP	290.50	-21.06	-	-
	291.26	-21.82	-	-
ZAMPAOX			4.32	160.64 (C=O, oxalate)
	295.63	-25.60	10.65	154.45 (C-O-Zr, oxalate)
	285.66	-15.50	13.27	151.92 (C-O-Zr, oxalate)
			139.84	27.15 (CH_2 -P)
ZAEPACI	279.93	-10.53	135.80	31.80 ($\text{CH}_2\text{-NH}_3^+$)
	280.47	-11.05	146.35	20.70 (CH_2 -P)

**Figure S4:** Simulated prediction of ^{31}P NMR spectra of α -ZrP (A), ZAMPAOX (B) and ZAEPACI (C).

References

- [1] S. Baroni, P. Giannozzi, A. Testa. *Phys. Rev. Lett.* 1987, **58**, 1861 – 1864.
- [2] S. Baroni, S. Gironcoli, A. Dal Corso, P. Giannozzi. *Theory. Rev. Mod. Phys.* 2001, **73**, 515 – 562
- [3] R. C. Slade, J. A. Knowles, D. J. Jones and J. Rozière, *Solid State Ionics*, 1997, **96**, 9 – 19.
- [4] P. Colomban; A. Novak. *Journal of Molecular Structure*, 1989, **198**, 277-295.
- [5] S. Horsley, D. Nowell and D. Stewart, *Spectrochimica Acta Part A: Molecular Spectroscopy*, 1974, **30**, 535 – 541.
- [6] M. Taddei, P. Sassi, F. Costantino and R. Vivani, *Inorganic Chemistry*, 2016, **55**, 6278 – 6285.
- [7] C.J. Pickard, F. Mari, *Phys. Rev. B*, 2001, **63**, 245101.
- [8] J. R. Yates, C. J. Pickard, F. Mari, *Phys. Rev. B*, 2007, **76**, 024401.
- [9] G. L. Turner et al., *Journal of Magnetic Resonance (1969)*, 1986, **70**, 408 – 415.
- [10] N. J. Clayden, J. Chem. Soc., *Dalton Trans.*, 1987, 1877–1881.
- [11] T. F. Kemp, M. E. Smith, *Solid state nuclear magnetic resonance*, 2009, **35**, 243 – 252.
- [12] S. R. Tavares, F. Wypych and A. A. Leitão, *Applied Clay Science*, 2017, **143**, 107 – 114.