

## Electronic Supplementary Information

### Title

Kinetics and mechanism of hydrolysis of  $\text{PF}_6^-$  accelerated by  $\text{H}^+$  or  $\text{Al}^{3+}$  in aqueous solution

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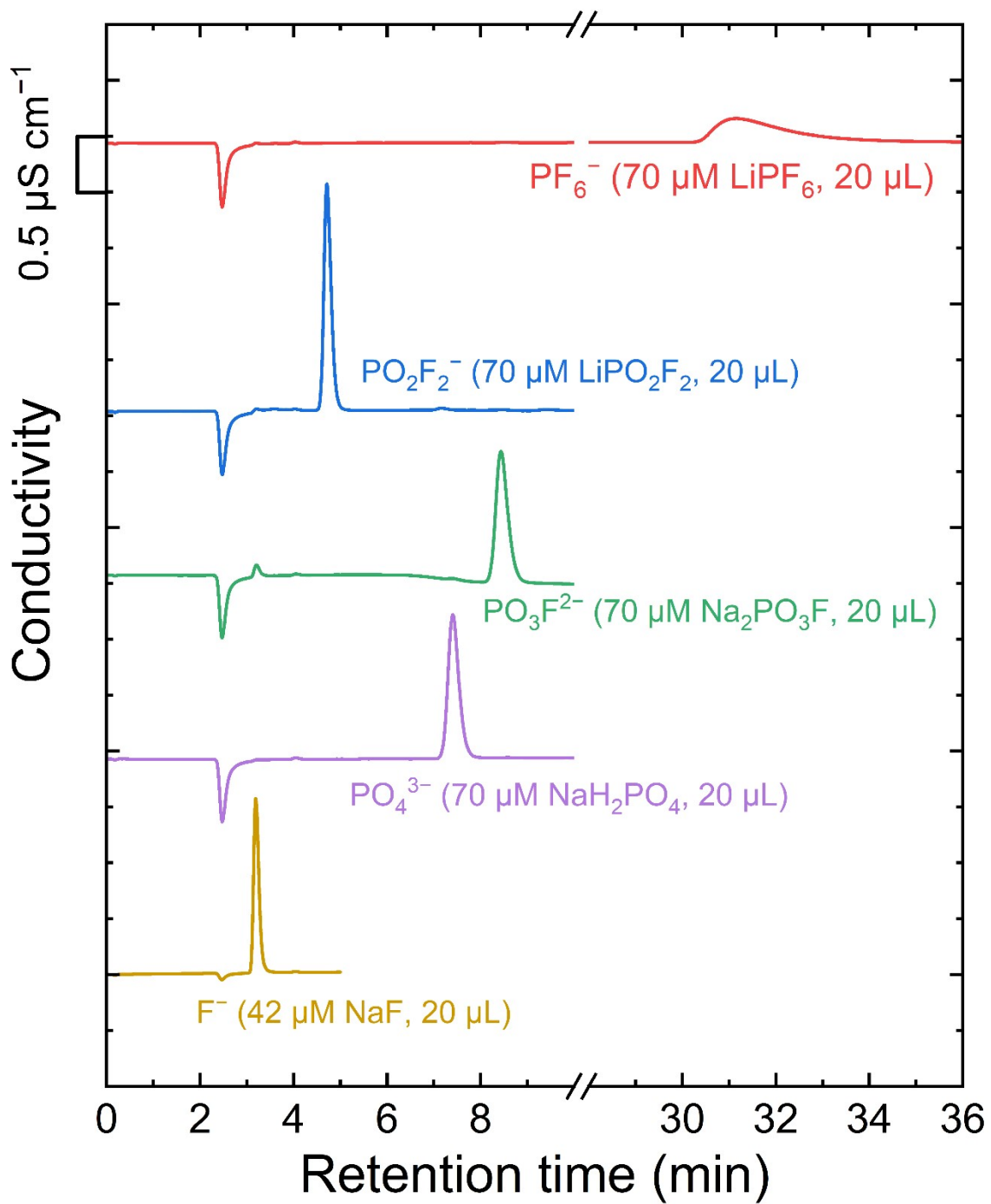


Fig. S1 Representative chromatograms of standard solutions in ion chromatography.

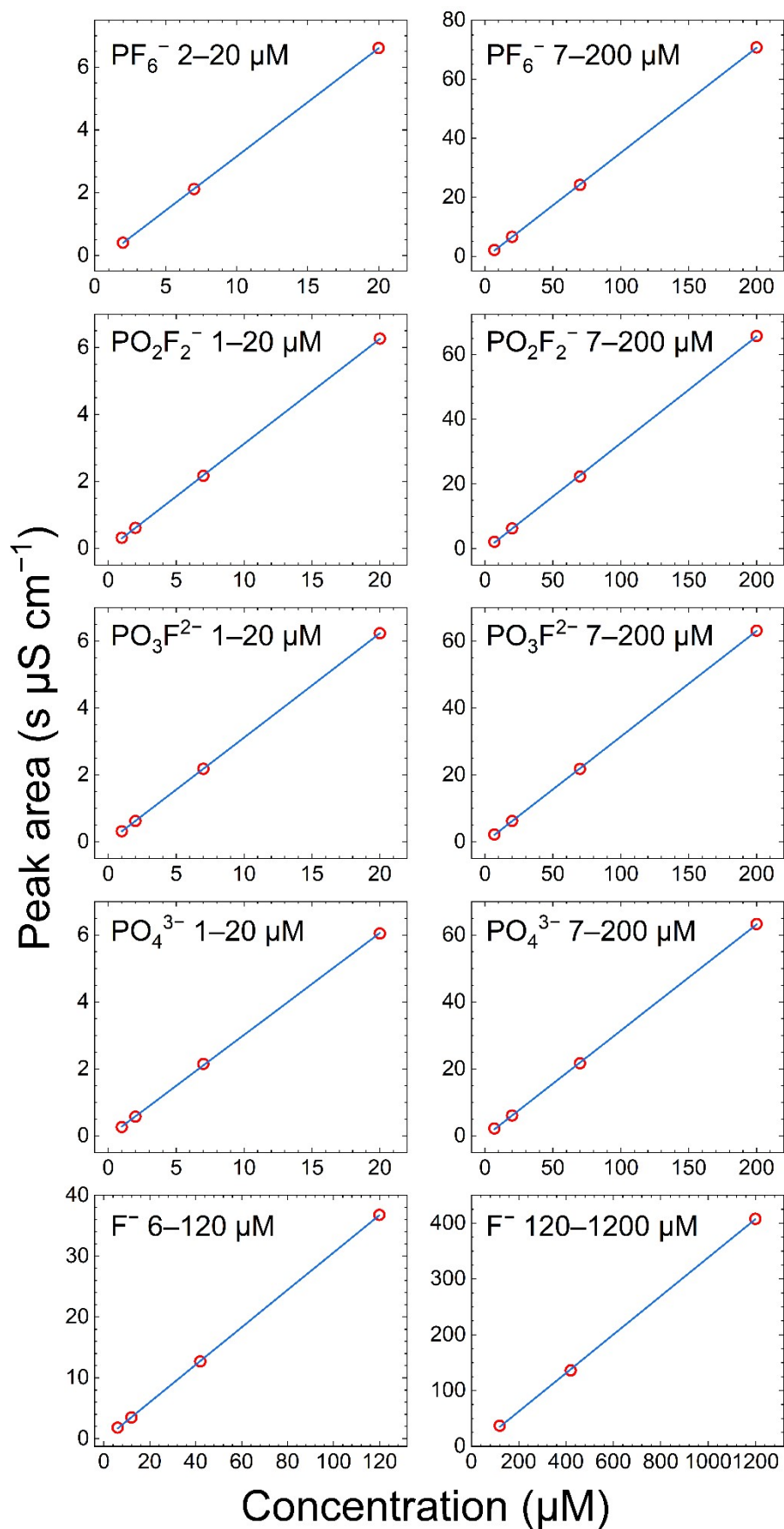


Fig. S2 Calibration curves for ion chromatography. Different calibration curves were used for different concentration ranges. The open red circles are the peak areas for the standard solution concentrations, and the solid blue lines are their regression lines.

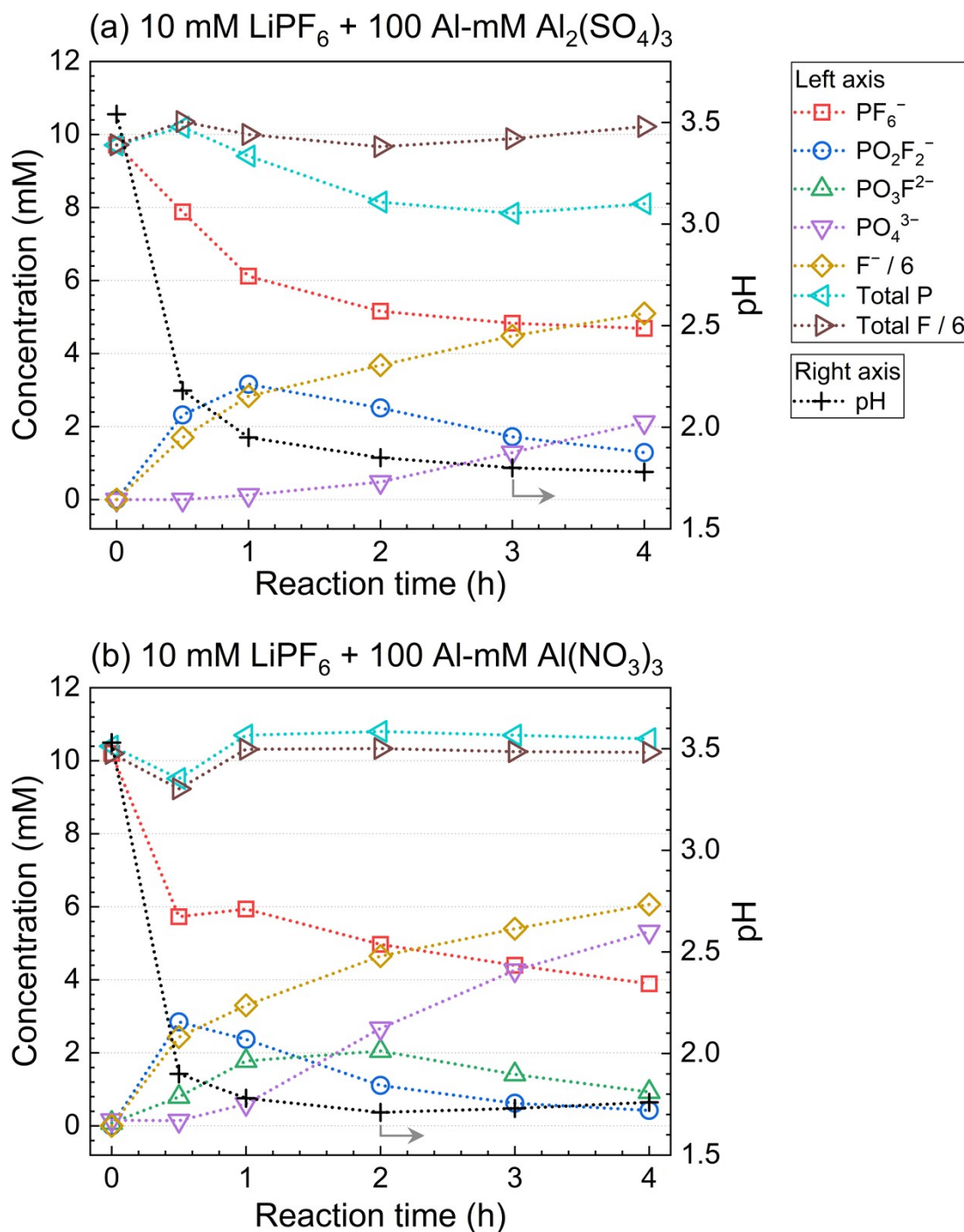


Fig. S3 Concentration over time of PF<sub>6</sub><sup>-</sup>, PO<sub>2</sub>F<sub>2</sub><sup>-</sup>, PO<sub>3</sub>F<sub>2</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, and F<sup>-</sup> measured by ion chromatography when 10 mM LiPF<sub>6</sub> solutions with (a) 100 Al-mM Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and (b) 100 mM Al(NO<sub>3</sub>)<sub>3</sub> were kept at 90 °C. Total P and total F were calculated from the sum of each anion concentrations. When Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> was added, PO<sub>3</sub>F<sub>2</sub><sup>-</sup> was not quantified because the chromatogram peaks of PO<sub>3</sub>F<sub>2</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> are overlapped. The gap between 10 mM and total P is expected to indicate the concentration of PO<sub>3</sub>F<sub>2</sub><sup>-</sup>. Regardless of the difference of anion, the hydrolysis rates show almost the same trend. When Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> is used, the hydrolysis rate is relatively slow, as indicated by the rate of PO<sub>4</sub><sup>3-</sup> formation. This may be since SO<sub>4</sub><sup>2-</sup> is relatively strongly coordinated to Al<sup>3+</sup> and the ligand exchange rate with F<sup>-</sup> for hydrolysis is reduced.

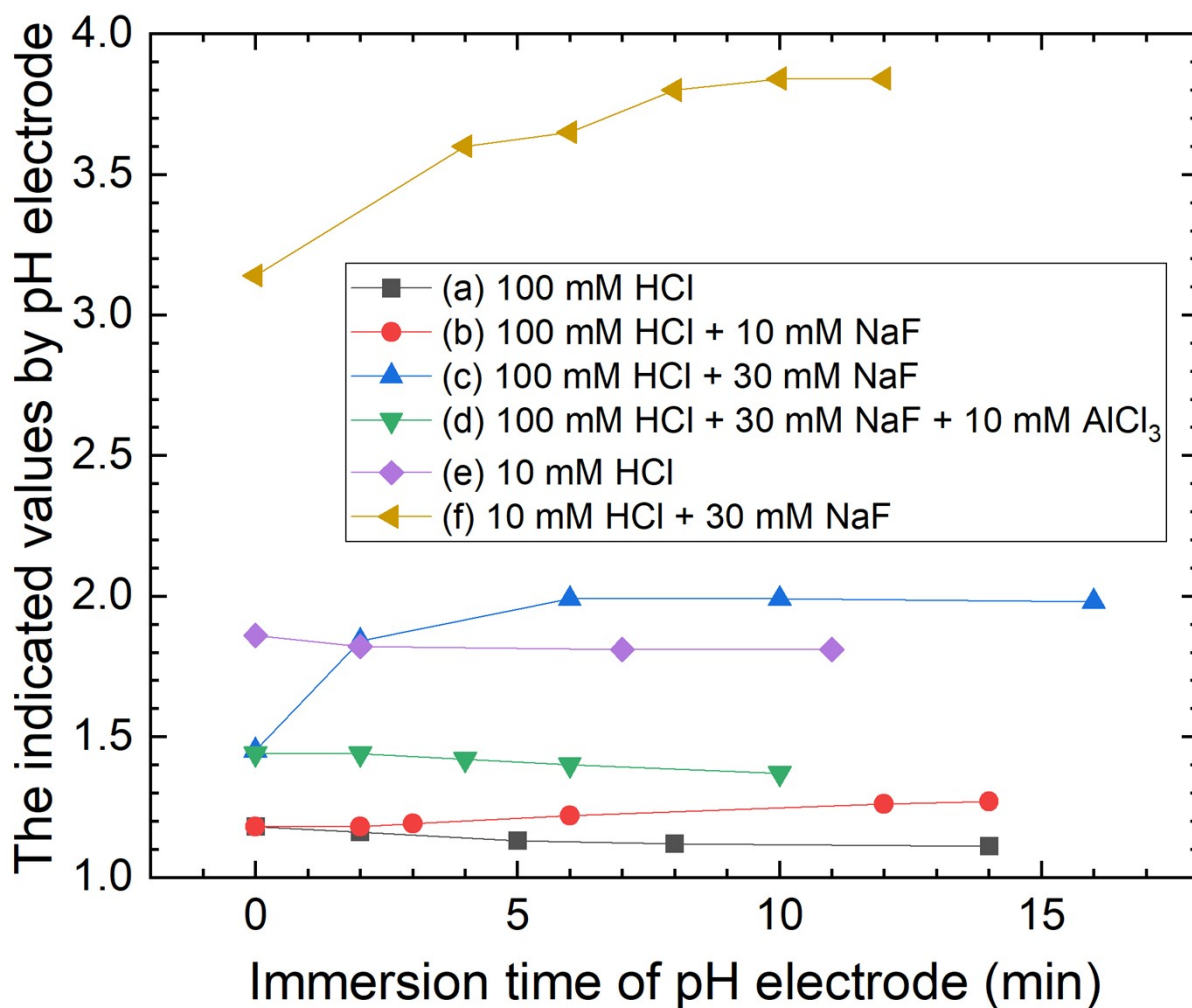


Fig. S4 The effect of  $F^-$  on pH measurement by pH electrode was investigated. The solutions with various HCl, NaF, and  $AlCl_3$  concentrations were prepared as shown in the legend. The pH electrode was immersed into these solutions, and the pH values were measured. The pH electrode was washed with 1 M HCl and calibrated before each measurement. This measurement shows that the indicated values by pH electrode increase over time with higher concentrations of HF. This is probably because of HF on the pH electrode. As an exception, when  $Al^{3+}$  is present, the indicated values by pH electrode are stable. The reason for this pH stability is expected to be the formation of complexes such as  $AlF^{2+}$ , which significantly reduces the activity of HF.

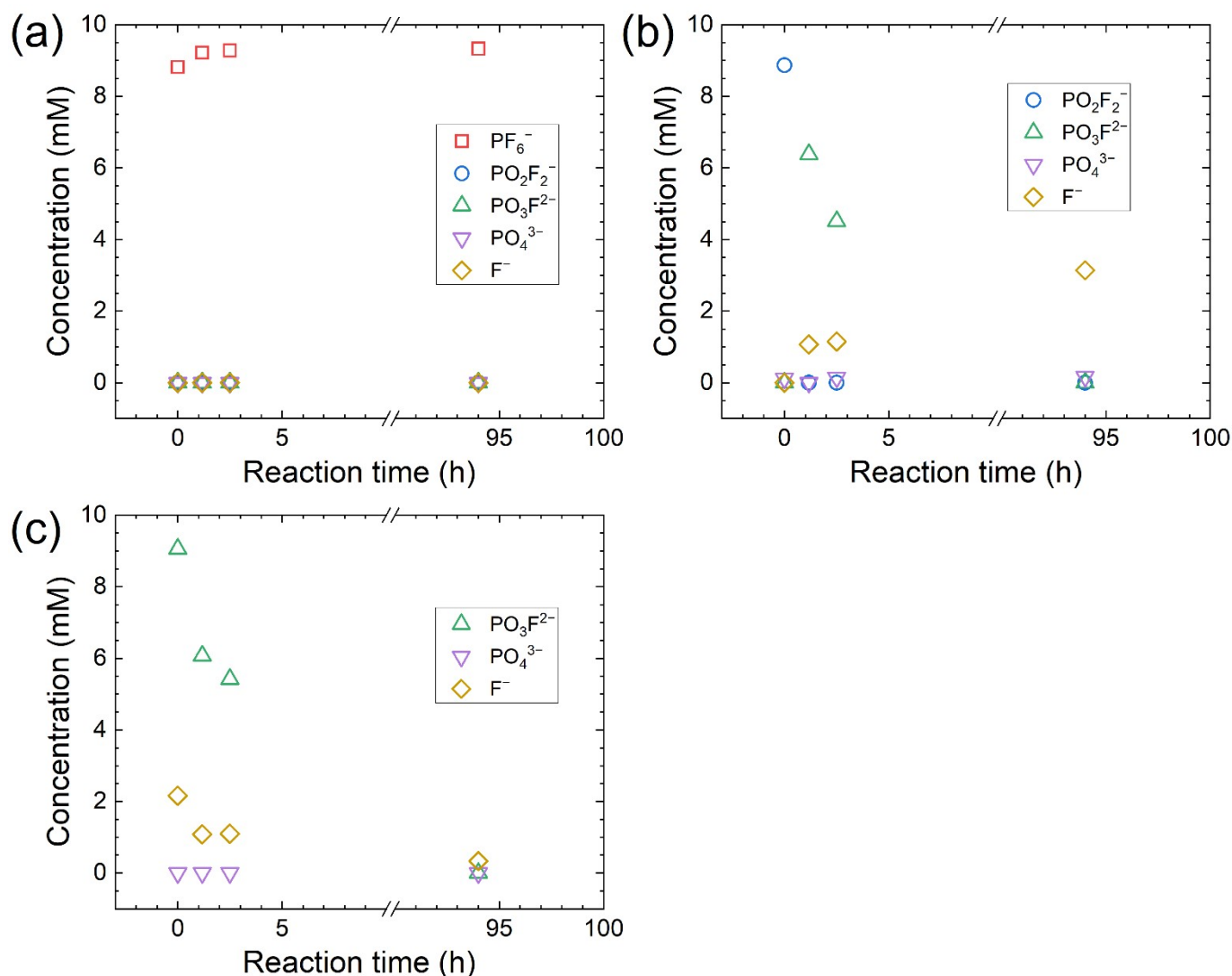


Fig. S5 Change of concentrations of  $\text{PF}_6^-$ ,  $\text{PO}_2\text{F}_2^-$ ,  $\text{PO}_3\text{F}_2^-$ ,  $\text{PO}_4^{3-}$ , and  $\text{F}^-$  when (a) 10 mM  $\text{LiPF}_6$ , (b) 10 mM  $\text{LiPO}_2\text{F}_2$ , and (c) 10 mM  $\text{Na}_2\text{PO}_3\text{F}$  were mixed with 108 mM  $\text{Ca}(\text{OH})_2$  (sat.) and kept at room temperature. The values of pH were around 12. The concentrations of anions were measured by ion chromatography. Fig. S5 (a) shows that  $\text{PF}_6^-$  is not decomposed in alkaline solution. Fig. S5 (b) and (c) shows that  $\text{PO}_2\text{F}_2^-$  is completely decomposed in 1 hour, but the decomposition of  $\text{PO}_3\text{F}_2^-$  is relatively slow; about 40 % decomposition in 1 hour in alkaline solution. The produced  $\text{PO}_4^{3-}$  and  $\text{F}^-$  are precipitated as shown in Fig. S6.

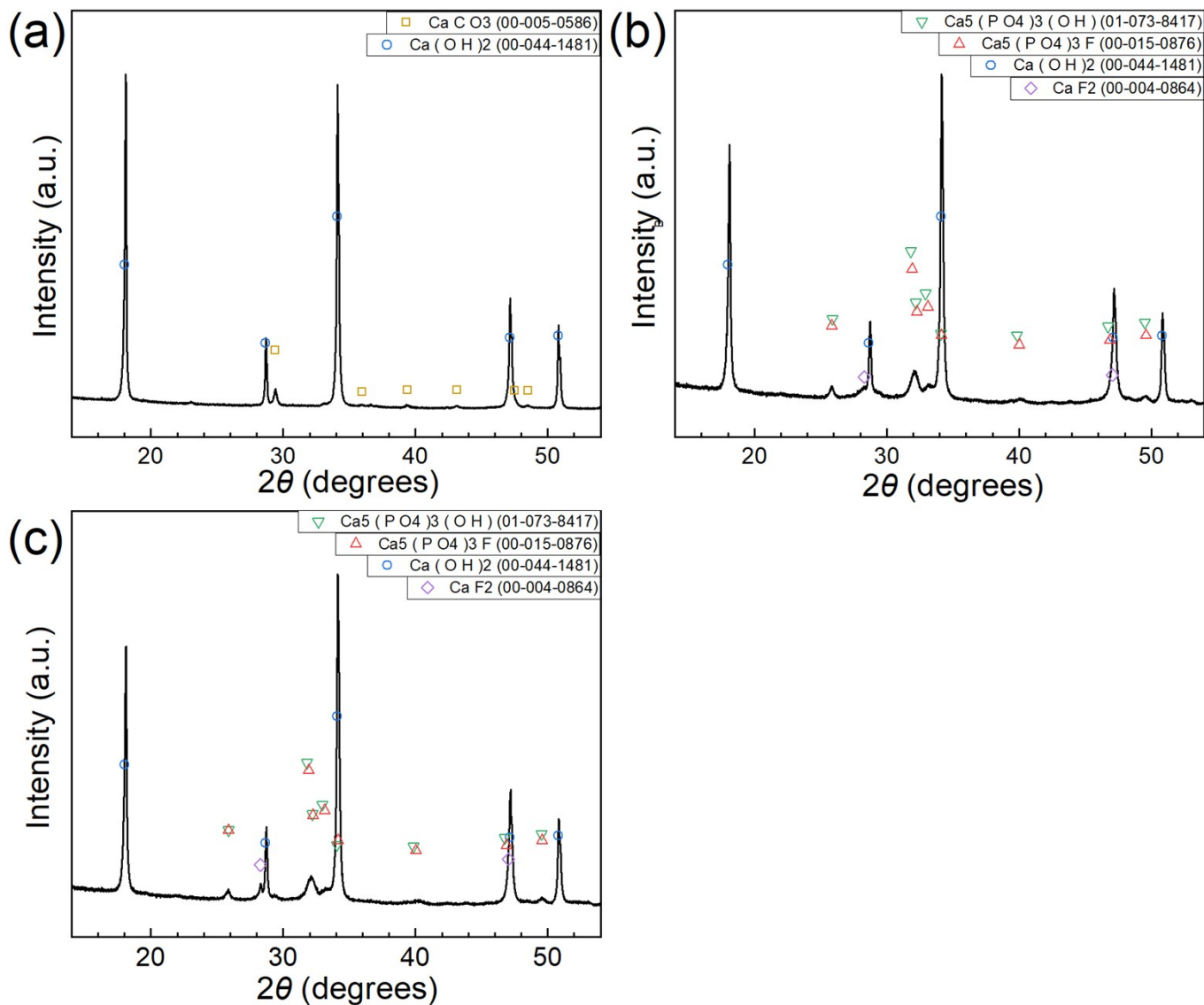


Fig. S6 The XRD patterns of the precipitates formed in the experiment as Fig. S5; (a) 10 mM  $\text{LiPF}_6$  solutions with 108 mM  $\text{Ca}(\text{OH})_2$  (sat.), (b) 10 mM  $\text{LiPO}_2\text{F}_2$  solutions with 108 mM  $\text{Ca}(\text{OH})_2$  (sat.), and (c) 10 mM  $\text{Na}_2\text{PO}_3\text{F}$  solutions with 108 mM  $\text{Ca}(\text{OH})_2$  (sat.). In the  $\text{Ca}(\text{OH})_2$  saturated solution,  $\text{PO}_2\text{F}_2^-$  and  $\text{PO}_3\text{F}_2^-$  are decomposed, and  $\text{PO}_4^{3-}$  and  $\text{F}^-$  are precipitated as hydroxyapatite ( $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ ), fluorapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ), or fluorite ( $\text{CaF}_2$ ).

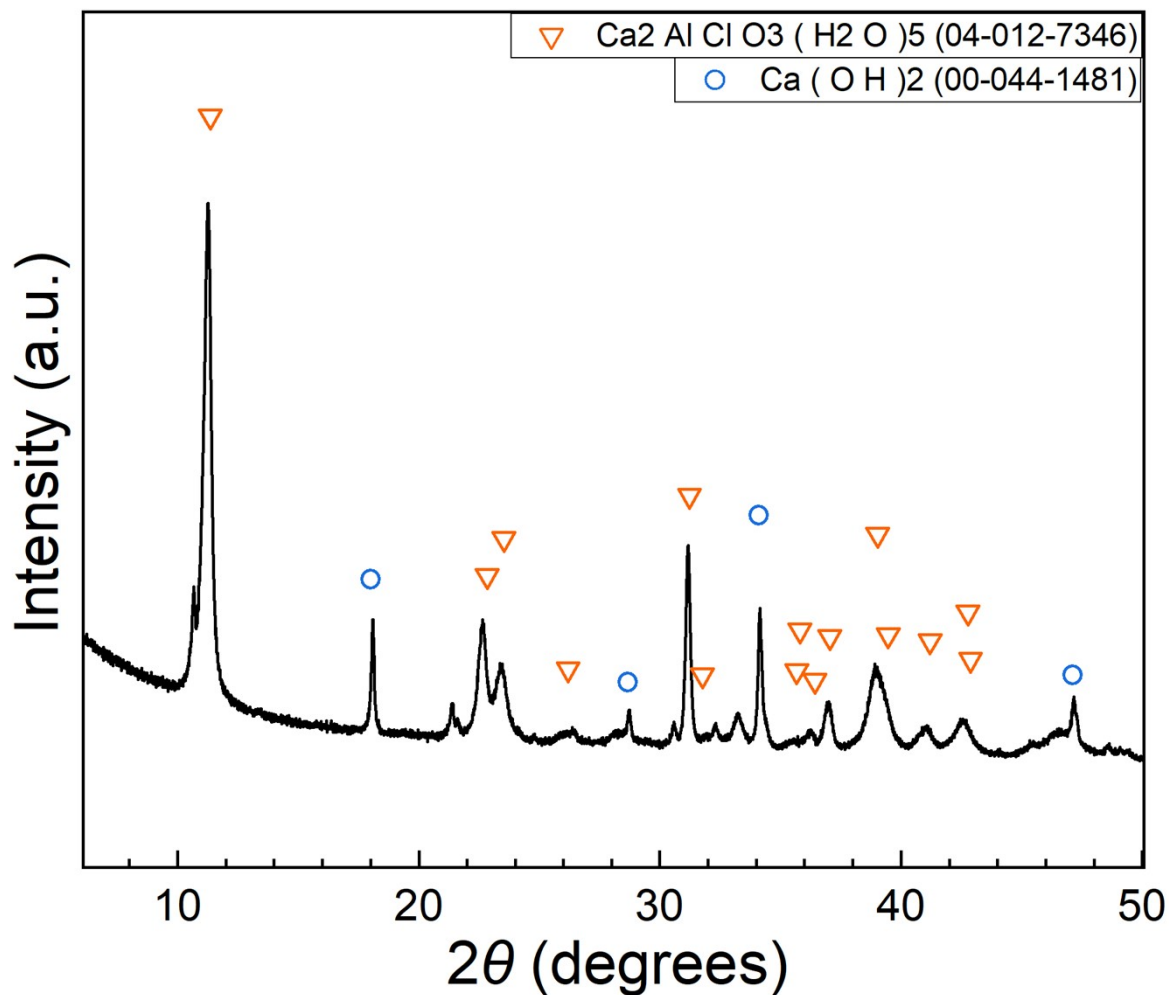


Fig. S7 The XRD pattern of the precipitate in the same experiment as Fig. 11. The solution of 10 mM  $\text{LiPF}_6$  and 100 mM  $\text{AlCl}_3$  was prepared and kept at 90 °C for 1 hour. Then 432 mM  $\text{Ca}(\text{OH})_2$  was mixed and kept at room temperature for 1 hour.