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Supporting Information

Direct Growth of Layered Intercalation Compounds via Single Step One-pot *in situ* Synthesis

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EXPERIMENTAL SECTION

Materials. A series of linear polyethylene glycols (PEG) with various molecular weights: ca. 400, 600, 1000, 1900, and 8000 (abbreviated as PEG-400, PEG-600, PEG-1000, PEG-1900, PEG-8000) were purchased from Alfa Aesar and used as received. $ZrOCl_2 \cdot 8H_2O$ (98%, Sigma-Aldrich), phosphoric acid (85%, Sigma-Aldrich), poly(sodium 4-styrene-sulfonate) (30 wt.% aqueous solution, MWs 70,000, Sigma-Aldrich), urea (>99.0%, J.T. Baker), polyethyleneimine (PEI) with an average molecular weight of 600 (Sigma-Aldrich), polyvinyl alcohol (PVA, weight average molecular weight of ~27,000, 98.0-98.8% hydrolysis, Kuraray), poly(sodium 4-styrene-sulfonate) (PSS, MWs 70,000, 35wt% water solution from Sigma-Aldrich), acrylamide (98.0%, TCU America), 1-butyl-3-methylimidazolium ($BMIM^+$) chloride (>98.0%, Sigma-Aldrich) were all used as received without further purification.

Characterization. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 diffractometer with Bragg-Brentano θ-2θ geometry (40 kV and 30 mA), using a graphite monochromator with Cu Kα radiation with λ= 1.542 Å. Samples were gently packed in a sample holder for characterization.

Scanning electron microscopy (SEM) images were acquired on a field emission-SEM (FE-SEM, JSM-6335F) from JEOL. The samples were sputter coated with a thin layer (ca. 3 nm) of Pt/Pd (80/20) prior to the SEM imaging.

Direct synthesis of α-ZrP based layered intercalation compounds. Polyethylene glycol (PEG)/α-ZrP layered intercalation compounds were synthesized *via* a hydrothermal reaction,[28] during which 4.0 g of 20.0 wt% $ZrOCl_2$ aqueous solution was

mixed with a pre-determined amount of PEG. After the PEG was dissolved, a pre-determined amount of concentrated H_3PO_4 was added so that the H_3PO_4 and $ZrOCl_2$ mole ratio reached 10:1. Additional deionized water was added to dilute the concentration of H_3PO_4 to reach 4.0 M. The mixture was treated at 100 °C for 24 hours in a 20 mL container that was well sealed.

In one series of reactions, PEG-600 was used. The mass ratio of PEG-600 to α-ZrP (assuming all the Zr^{4+} cations were converted to α-ZrP) was varied from 0.25:1 to 2.00:1. In another series of reactions, linear PEGs with various molecular weights (MWs), including PEG-400, PEG-600, PEG-1000, PEG-1900, PEG-8000, were used. The mass ratio of each of these PEGs to α-ZrP (assuming all the Zr^{4+} cations were converted to α-ZrP) was maintained at 1:00 to 1.

A neat α-ZrP sample was synthesized in the absence of PEG under the same reaction conditions as a control. In addition, this neat α-ZrP was mixed with PEG-600 (mass ratio of PEG-600 to α-ZrP is 2:00 to 1), and the mixture was hydrothermally treated at 100 °C for 24 hours in a same container. This reaction was to check whether the pre-synthesized neat α-ZrP can be intercalated by PEG-600 under the same reaction conditions.

The α-ZrP based intercalation compounds containing other guest species, including other polymers (PVA, PEI), small molecules (acrylamide), and ions (1-butyl-3-methylimidazolium $BMIM^+$), were also synthesized *via* the same reaction approach and under the same reaction conditions.

After reaction, the products were washed and collected by centrifugation three times. After that, they were dried at 70 °C for 24 hours. The dried samples were ground with an agate mortar and pestle into fine powders for characterizations.

Direct synthesis of MgAl-LDH based layered intercalation compounds. A 30.0 mL solution composed of $Mg(NO_3)_2$ (0.20 M) and $Al(NO_3)_3$ (0.05 M) was mixed with urea at a molar ratio of (urea):(total metal ion)= 4:1 and a pre-determined amount of poly(sodium 4-styrene-sulfonate) (PSS). The mixture was added into a Teflon lined hydrothermal reactor and heated at 100 °C for 24 hours. The mass ratio of PSS to LDH (assuming all the metal cations were converted to LDH) was varied from 0.25:1 to 2.00:1. A neat MgAl-LDH sample was synthesized in the absence of PSS under the same reaction conditions as a control. After reaction, the products were washed and collected by centrifugation three times. After that, they were dried at 100 °C for 24 hours. The dried samples were ground with an agate mortar and pestle into fine powders for characterizations.

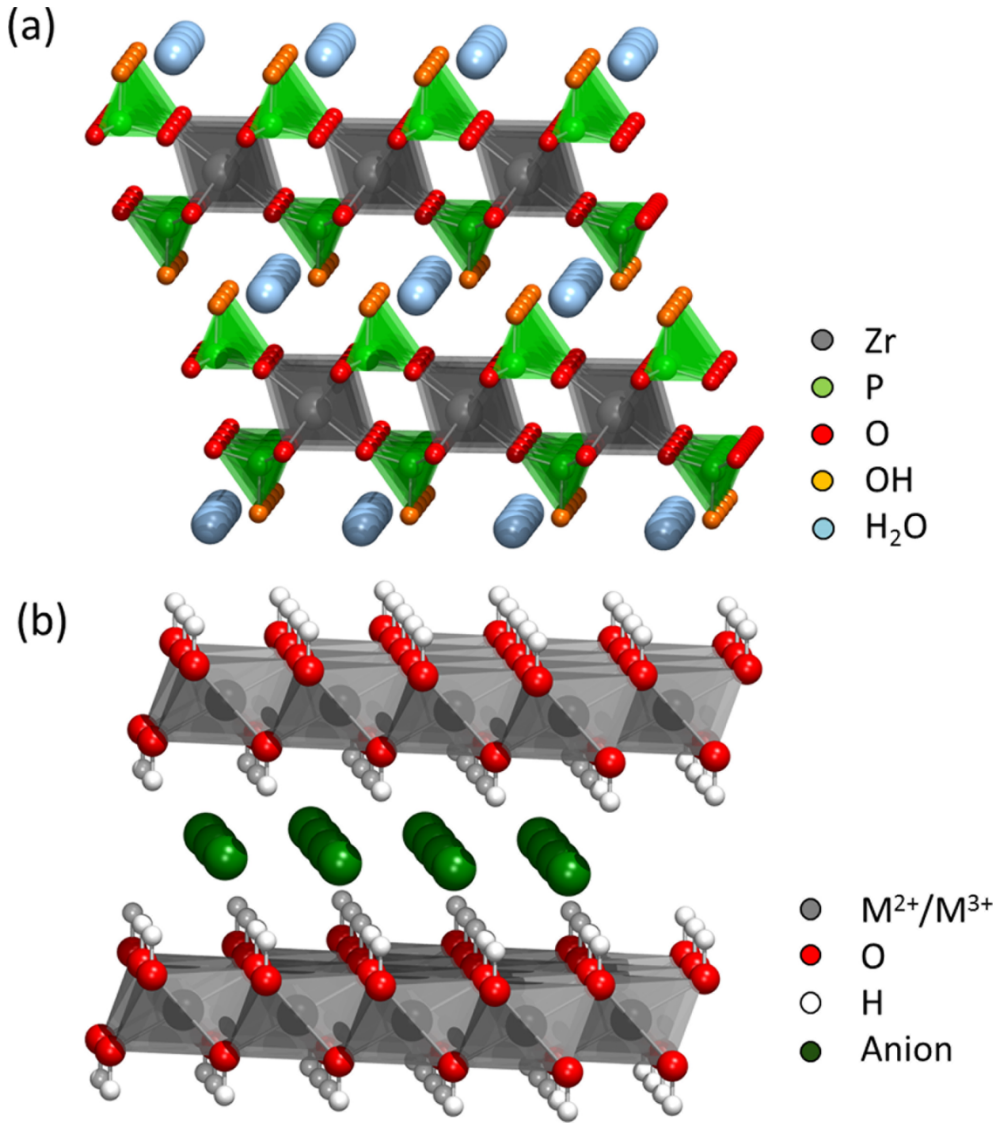

Figure S1. Structure of (a) α-zirconium phosphate and (b) layered double hydroxide.

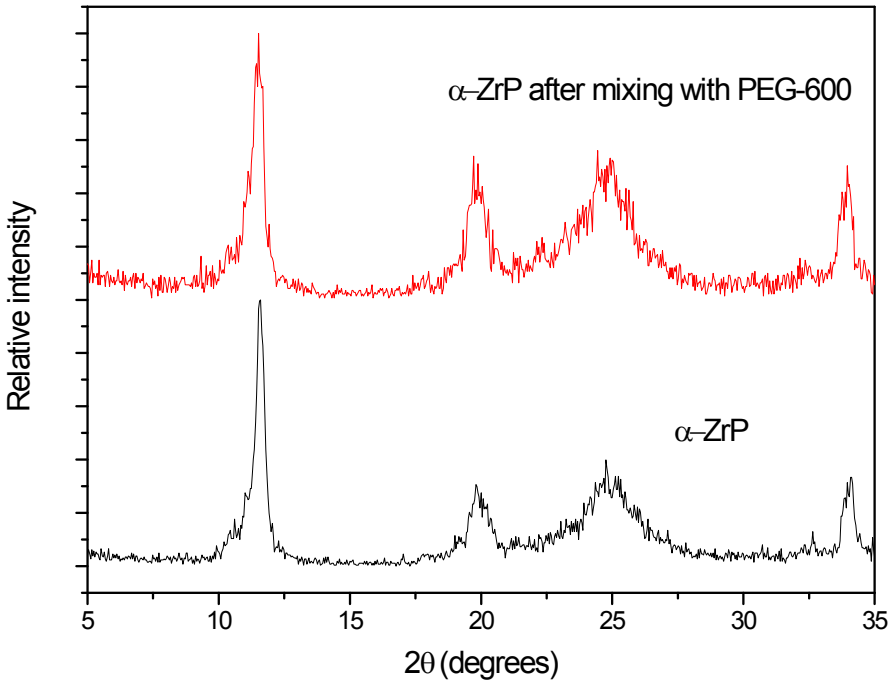

Figure S2. XRD patterns of pristine α-ZrP and the mixture of α-ZrP and PEG-600 (2.00:1 mass ratio) after mixing under the hydrothermal reaction conditions (100 °C for 24 hours).

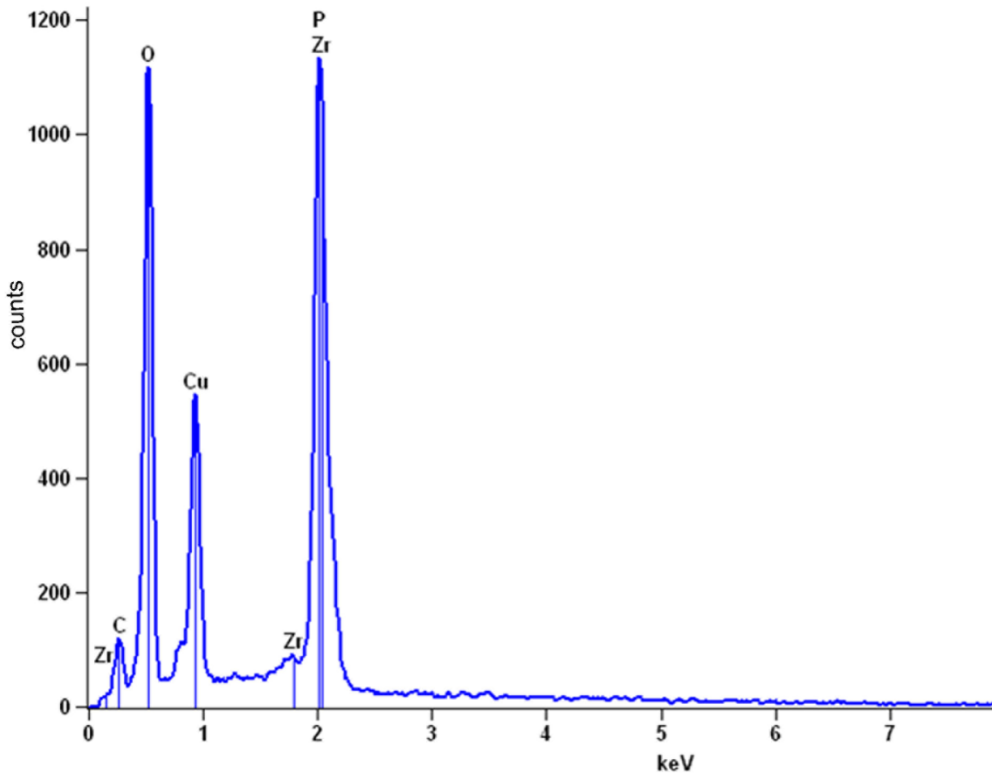

Figure S3. EDX analysis of PEG-600/α-ZrP=1.00/1.

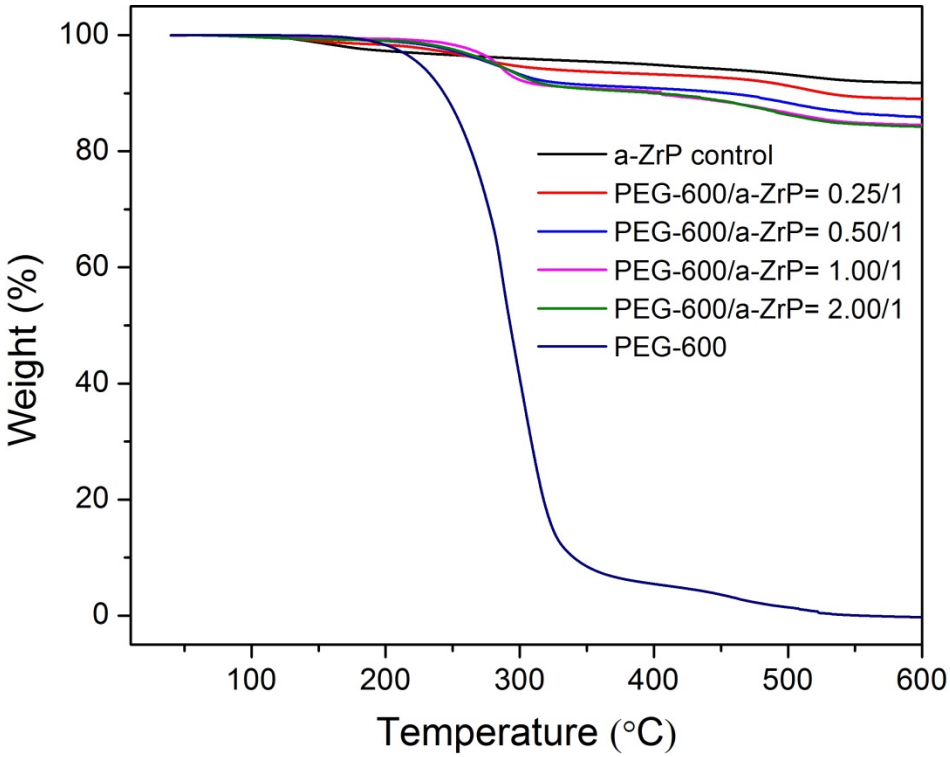

Figure S4. TGA analysis of PEG-600/α-ZrP intercalation compounds with different weight ratios.

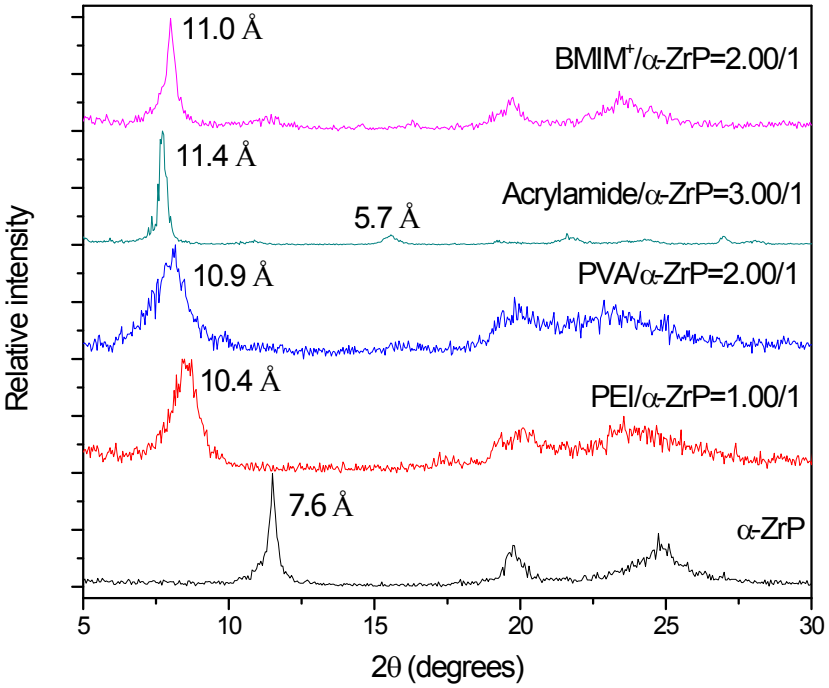

Figure S5. XRD patterns of α-ZrP based intercalation compounds. Those intercalation compounds were synthesized with various coordinators at 100 °C for 24 hours. The labeled ratio represents mass ratio.

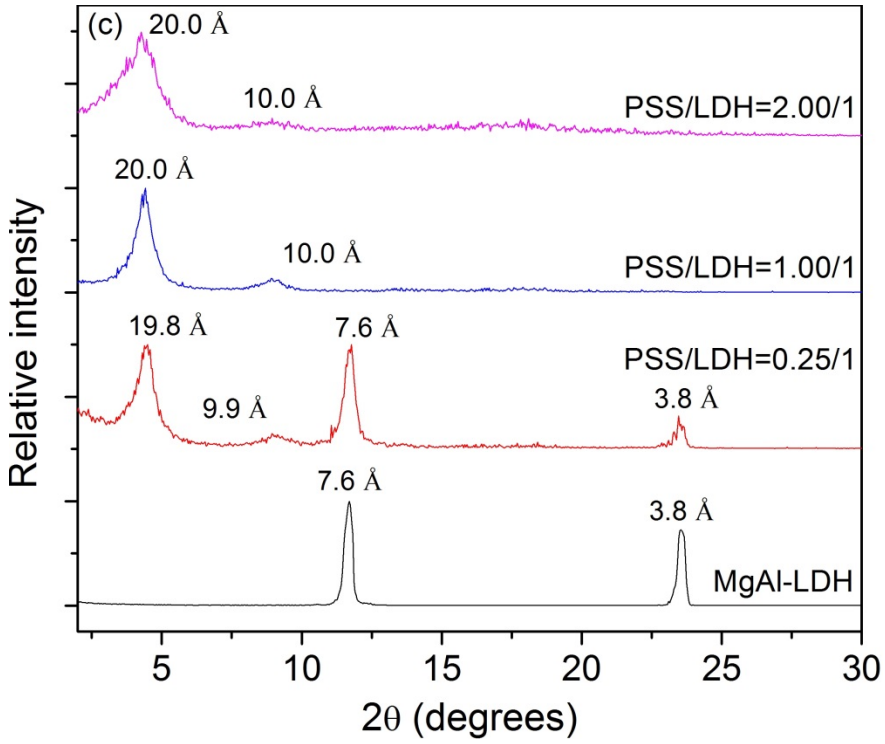

Figure S6. Intercalation compounds synthesized with various PSS/LDH mass ratios (100 °C for 24 hours).