Supplementary Material (ESI) for Chemical Communications

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Hierarchically Organized Architecture of Potassium Hydrogen Phthalate and Poly(Acrylic Acid): Toward A General Strategy for Biomimetic Crystal Design

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Detailed Experimental Method

Preparation of Precursor Solution. Stock solutions containing potassium hydrogen phthalate (KAP; 100 g dm^{-3}, 0.49 M, Kanto Chemical, 99.0%) were prepared using purified water at room temperature around 25 °C. Poly(acrylic acid) (PAA; C_{PAA} = 0–50 g dm^{-3}, M_w = 250 000, 35wt% aqueous solutions, Aldrich Chemical) was added into the stock solutions. After these materials were completely dissolved, 10 dm^{-3} of the precursor solution was poured into a polypropylene sample bottle (30 mm in diameter and 70 mm in height). Other procedure is described in the main text.

Sample Preparation for Electron Microscope Analysis. We took some part of the totally mineralized material and then observed the morphology of crystals by using FESEM without further wash. FESEM samples were coated by osmium ultra-thin film (plasma osmium coater, HPC-1S, Vacuum Device). In the case of STEM observation, the powdered samples were added in dehydrated ethanol and then the vessel was put in a sonic bath for 30 minutes to ensure good dispersion. The dispersion liquid was dropped on a cupper grid supported by collodion membrane.

Dye Inclusion. The resultant KAP/PAA composites were immersed in 0.2 mM RB ethanol solutions and then the vessels were put in a sonic bath for 30 minutes. The immersion was carried out over a day. The PL spectra were measured at room temperature (Shimadzu RF-5300PC spectrofluorophotometer using a xenon lamp (150 W) as a light source). A certain amount of the powdered sample was filled in specified sample holder.

Supplementary Figures

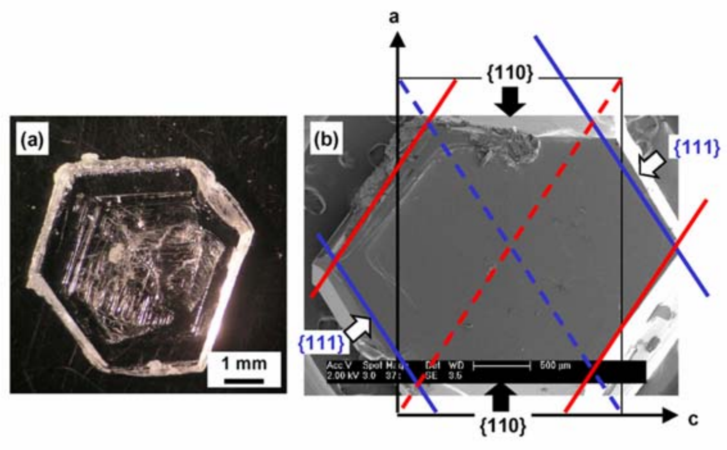

Figure S1. A clear KAP single crystal with hexagonal shape. (a) optical microscope image, (b) FESEM images with the crystallographic direction that is estimated from the unit cell structure and the dihedral angles. When PAA was not added in the precursor solution, the composite of KAP and PAA with hierarchical structure was never observed.

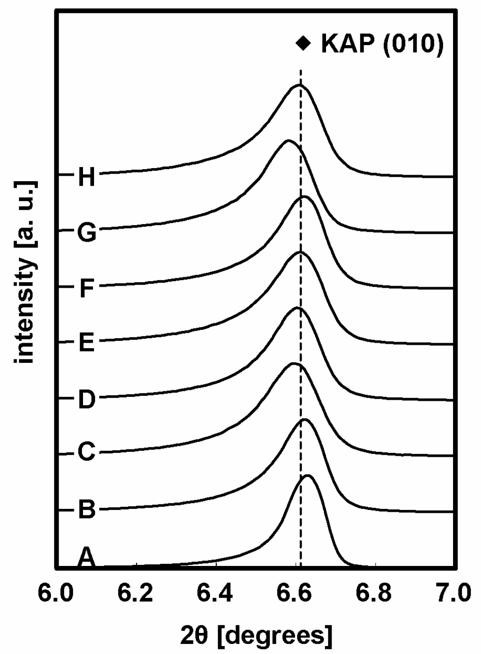

Figure S2. XRD profiles of the resultant KAP/PAA composites (C_{PAA}= 0 (A), 5 (B), 8 (C), 15 (D), 21 (E), 28 (F), 37 (G), 46 (H) g dm^{-3}). The peak broadening, resulting from the crystallite size effect, was not clearly observed in these spectra. Therefore, we concluded that the oriented assembly formed in the KAP/PAA composite. JCPDS #24-1870.

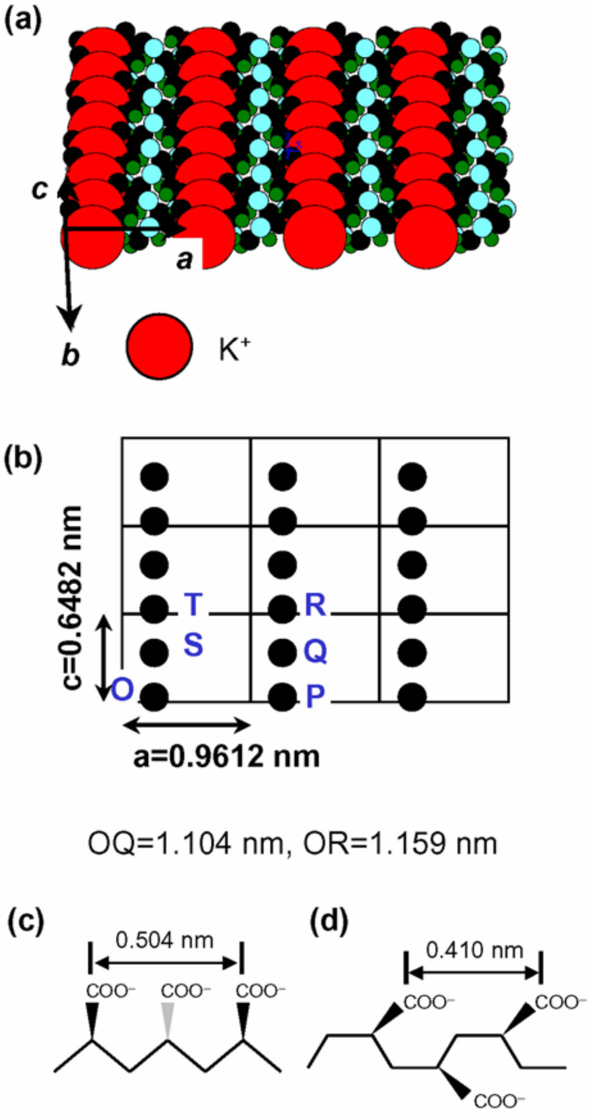

Figure S3. Schematic illustration for the (010) face of KAP crystal. (a) bird view, (b) surface cleavage, (c and d) estimation for the distance of carboxy groups in the PAA molecule. The potassium ions are regularly arranged on the (010) face and the flexible PAA chains could interact with potassium ions on the (010) face through electrostatic interaction. The atomic arrangement of KAP on (010) face was illustrated by CaRine crystallography and the atomic parameters were taken from the following ref. S1.

[ref. S1] Y. Okaya, *Acta Cryst.* 1965, **19**, 879.

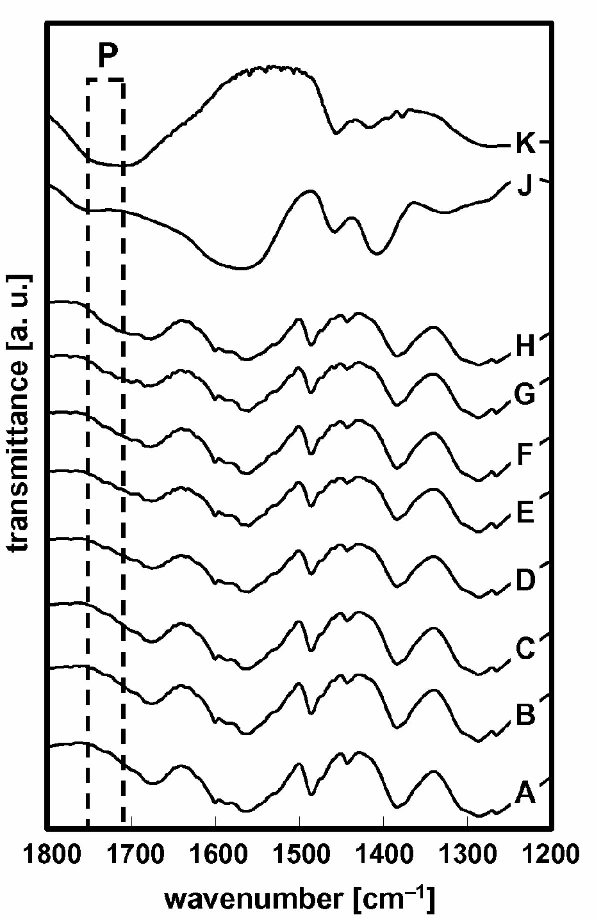

Figure S4. FT-IR spectra of KAP/PAA composite material. The absorption band P indicates the hydrogen bondings of the excess PAA molecules that are not interacted with KAP crystals. The peak Q is caused by the hydrophilic group of aromatic compound. (C_{PAA}= 0 (A), 5 (B), 8 (C), 15 (D), 21 (E), 28 (F), 37 (G), 46 (H) g dm^{-3}, sodium salt (J) and acid salt (K) of poly(acrylic acid) powder with average Mw 2000). FT-IR study of the intermolecular interaction of PAA was also referred to the following literature (ref. S2).

[ref. S2] J. Dong, Y. Ozaki, K. Nakashima, *Macromolecules*, 1997, **30**, 1111.