

Electronic Supplementary Information

Octacalcium phosphate with incorporated terephthalate ion derivatives: Novel guest molecules and unique fluorescence properties

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Experimental procedures

Synthesis

OCP with incorporated 4-(carboxymethyl)benzoate or 1,4-phenylenediacetate ions was synthesised as follows: 1–25 mmol of 4-(carboxymethyl)benzoic acid (4-CMBA; Tokyo Chemical Industry Co., Ltd., Tokyo, Japan) or 1,4-phenylenediacetic acid (1,4-PDAA; Sigma-Aldrich Co., St. Louis, MO, USA) was dissolved in 100 mL of ultrapure water. The pH of the solution was adjusted to 5.5 using aqueous ammonia (28 mass% NH₃; Wako Pure Chemical Industries, Ltd., Osaka, Japan) at 60 °C. Subsequently, 5.0 mmol of phosphoric acid (85% H₃PO₄; Wako Pure Chemical Industries, Ltd.) and 8.0 mmol of calcium carbonate (calcite, CaCO₃; Nacalai Tesque Inc., Kyoto, Japan) were added. The mixture was stirred at 60 °C for 3 h, and then the pH of the slurry was adjusted to 5.0 using hydrochloric acid (1 mol/L HCl; Wako Pure Chemical Industries, Ltd.) to dissolve residual calcium carbonate. Before HCl addition, the pH values of representative samples synthesised using 25 mmol of 4-CMBA and 1,4-PDAA were 5.9 and 5.7, respectively. After stirring for an additional 30 min, the particles in the slurry were collected by vacuum filtration, rinsed with ultrapure water and ethanol, and dried at 40 °C for at least 12 h. The samples synthesised using *X* mmol of 4-CMBA and 1,4-PDAA were denoted as CMBA-*X* and PDAA-*X*, respectively.

The general chemical formula of OCP with incorporated dicarboxylate ions is



When $x = 1$ (i.e. the maximum value), the molar ratio of calcium, phosphate, and dicarboxylic acid is 8:5:1. In this synthetic process, we used 8 mmol of calcium carbonate and 5 mmol of phosphoric acid. However, more than 1 mmol of the dicarboxylic acid was required to synthesise OCP with incorporated dicarboxylate ions exhibiting a stoichiometric composition. In particular, single-phase samples were only obtained with a large excess (25 mmol) of carboxylic acid (see Fig. 1 vs Figs. S2 and S3).

OCP without dicarboxylate ions was synthesised as follows: 6.0 mmol of phosphoric acid was added to 100 mL of ultrapure water. After adding 8.0 mmol of calcium carbonate, the mixture was stirred at 60 °C for 3 h. Subsequently, the pH of the slurry was decreased to 5.0 using hydrochloric acid and then stirred for an additional 30 min. The particles in the slurry were collected by vacuum filtration, rinsed with ultrapure water and ethanol, and dried at 40 °C for at least 12 h. The obtained sample was denoted as Pure-OCP.

Characterisation

The crystalline phases of the samples were characterised using powder X-ray diffraction (XRD; MiniFlex600, Rigaku Corp., Tokyo, Japan) with Cu *K* α radiation. To evaluate the (100) interplanar spacing (d_{100}) of representative samples, fluorophlogopite (Topy Industries Ltd., Tokyo, Japan) was added as an internal standard (OCP sample:fluorophlogopite mass ratio = 2:1) prior to the XRD measurements.

The chemical structures of the samples were characterised using Fourier transform infrared (FTIR) spectroscopy (FT/IR-6200, JASCO Corp., Tokyo, Japan). FTIR measurements were performed using the KBr pellet method, in which the sample was mixed with KBr powder at a mass ratio of 1:300.

The absorption properties of the samples in the ultraviolet–visible range were evaluated using ultraviolet–visible spectroscopy (V-770, JASCO Corp.) with the diffuse reflection method. The relative reflectance was measured using Spectralon[®] as a reference.

The fluorescence spectra of the samples at room temperature (approximately 25 °C) were collected using a fluorescence spectrometer (FP-8300, JASCO Corp.) with excitation in the ultraviolet-light region (254, 312, and 365 nm). In these measurements, stray light had a significant influence on the fluorescence spectra, especially because the samples exhibited relatively weak fluorescence. Therefore, fluorescence from the sample and stray light were distinguished based on the spectrum obtained for calcium carbonate (calcite), which is a non-fluorescent material. A photomultiplier tube voltage of 330 V was used for all fluorescence measurements, except those of PDAA-25. As PDAA-25 exhibited a high fluorescence intensity, the photomultiplier tube voltage was decreased to 250 V. In addition, the fluorescence of the samples was visualised using UV lamps at 254, 312, and 365 nm (VL-6.LC, Vilber Lourmat, Marne-la-Vallée, France; EB-160C/J, Spectronics Corp., Melville, NY, USA).

XRD patterns

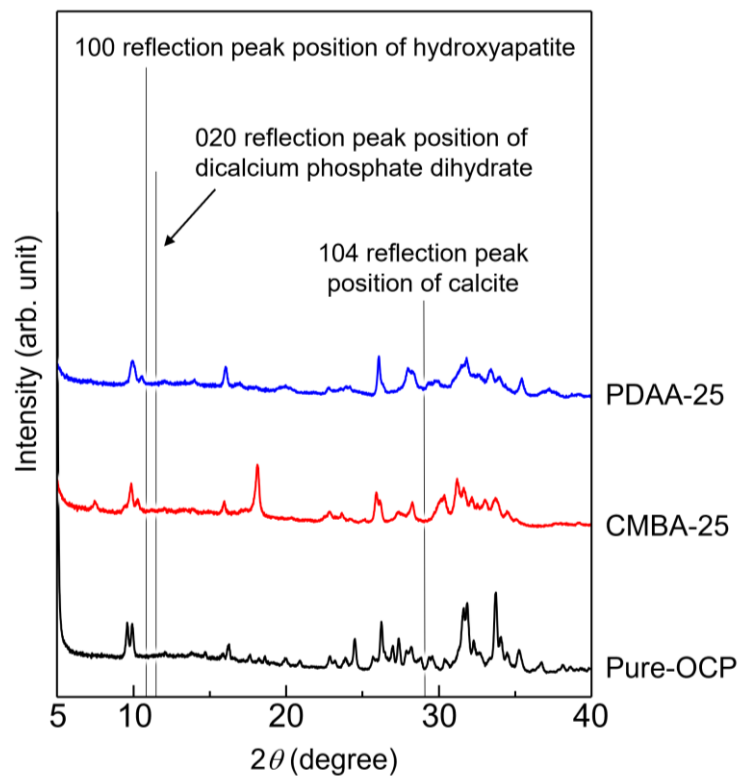


Fig. S1 Magnified XRD patterns of Pure-OCP, CMBA-25, and PDAA-25. The typical reflection peak positions of hydroxyapatite, dicalcium phosphate dihydrate, and calcite are also shown, as these are the possible impurity phases in the final product based on our synthetic process. The observed XRD patterns indicate that these phases were not present in Pure-OCP, CMBA-25, and PDAA-25.

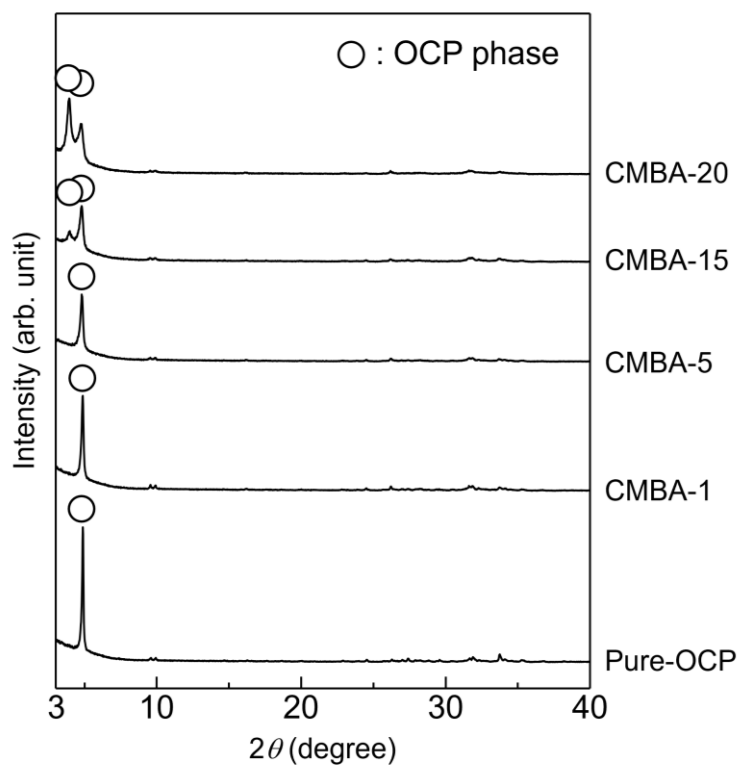


Fig. S2 XRD patterns of Pure-OCP and CMBA- X ($X = 1, 5, 15, \text{ or } 20$).

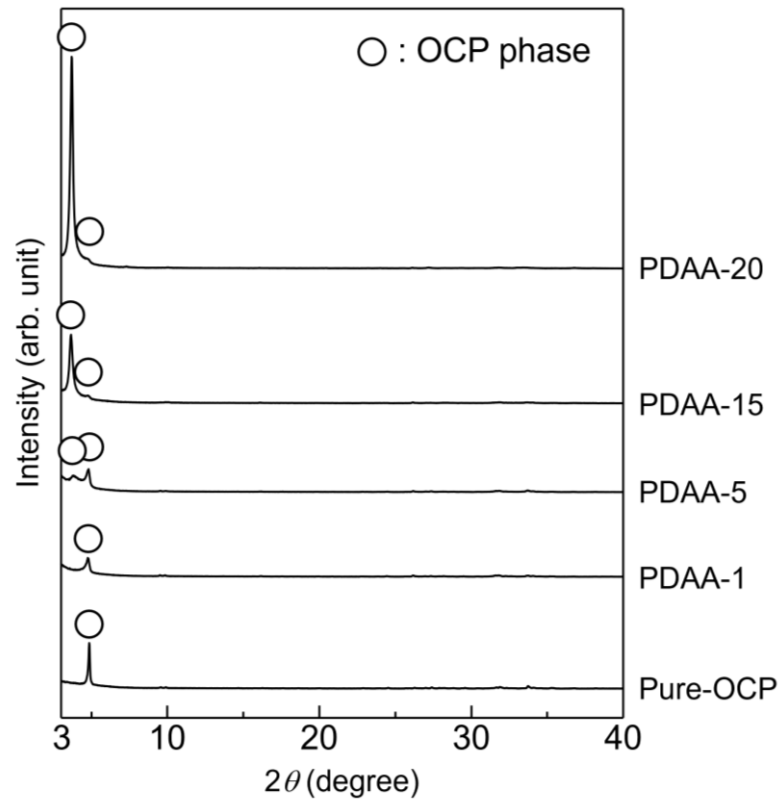


Fig. S3 XRD patterns of Pure-OCP and PDAA- X ($X = 1, 5, 15, \text{ or } 20$).

Bonding angle calculation

Here, the process used to calculate bonding angle θ' in Fig. S4 is explained. Using eq (1), the L value of 1,4-PDAA was calculated from $d_{100}(\text{exp.})$ for OCP with incorporated 1,4-phenylenediacetate ions ($=2.53$ nm). The back-calculated L value (denoted as L' in Fig. S4) of 1,4-PDAA is 0.816 nm. As the aromatic ring of 1,4-PDAA is rigid and difficult to deform, the increase in the L value from 0.77 nm to 0.816 nm ($=L'$) is predominately due to the θ' value (Fig. S4). To simplify the calculation of the θ' value, four carbon atoms (C2, C1, C4, and C5) are assumed to exist on a straight line.

In Fig. S4, the C2–C5 and C2–C3' distances are 0.587 and 0.151 nm, respectively. Therefore, the O–C3' and O–C2 distances, which correspond to half of L' ($=0.816$ nm) and half of the C2–C5 distance, respectively, are 0.408 and 0.294 nm, respectively. According to the cosine theorem, $\cos\theta'$ is -0.645 ; hence, θ' is 130° .

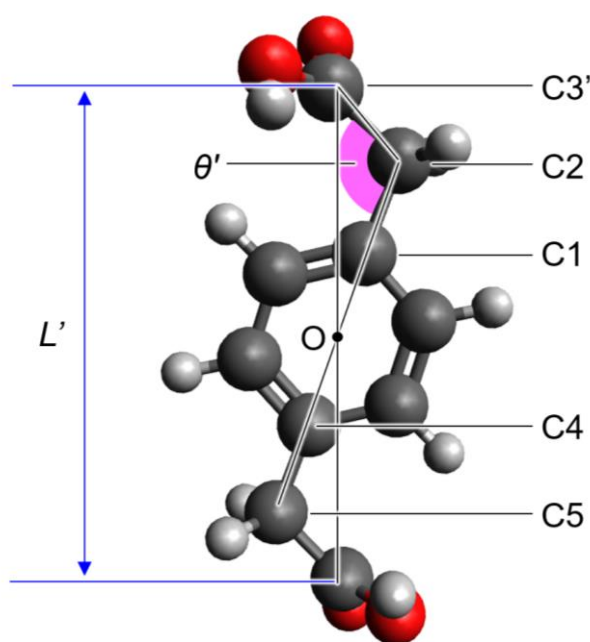


Fig. S4 Molecular structure of 1,4-PDAA.

Appearance of Pure-OCP, 4-CMBA, and 1,4-PDAA under visible and UV light

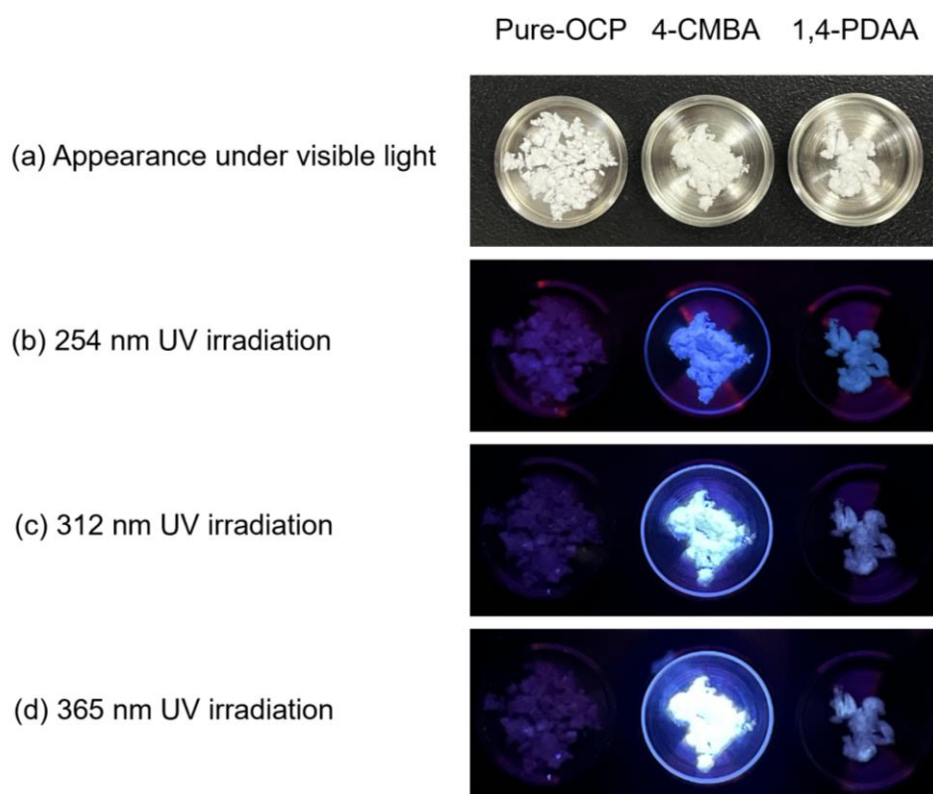


Fig. S5 Appearance of Pure-OCP, 4-CMBA, and 1,4-PDAA under (a) visible light and UV irradiation at (b) 254 nm, (c) 312 nm, and (d) 365 nm.