

Supplementary Information

Synthesis of octacalcium phosphate with incorporated 1,4,5,8-naphthalenetetracarboxylate ions

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Synthesis of OCP samples

1,4,5,8-naphthalenetetracarboxylic acid (NTCA, 95%, BLD Pharmatech Ltd., Shanghai, China) was dissolved in ultrapure water to prepare 2.5, 5.0, 7.5, 10, and 20 mM solutions. The pH of the NTCA solution was 5.5 at 60 °C. A 28 mass% aqueous ammonia solution (Wako Pure Chemical Industries, Ltd., Osaka, Japan) was used for pH adjustment. Subsequently, 5.0 mmol of phosphoric acid (85% aqueous solution, Wako Pure Chemical Industries, Ltd.) was added to the NTCA solution (100 mL), followed by the addition of calcium carbonate (8.0 mmol) (calcite phase, 99.5%, Nacalai Tesque Inc., Kyoto, Japan). The slurry was stirred at 500 rpm at 60 °C. After 3 h, the pH of the slurry was reduced to 5.0 using a hydrochloric acid solution (1 M aqueous solution, Wako Pure Chemical Industries, Ltd.) and was stirred for 30 min. Then, the precipitate was isolated by suction filtration, rinsed, and then dried.

To synthesize the control OCP sample (without carboxylate ions), phosphoric acid (6.0 mmol) was added to ultrapure water (100 mL) at 60 °C under stirring (500 rpm), followed by the addition of calcium carbonate (8.0 mmol). After 3 h, the pH of the slurry was decreased to 5.0 by adding an appropriate amount of HCl solution. Subsequently, after 30 min of stirring at 60 °C, precipitates were isolated by suction filtration, rinsed with ultrapure water and ethanol, and dried at 40 °C overnight. This sample was denoted as CONTROL.

Characterisation

The crystal phases of the samples were determined by X-ray diffraction (XRD; MiniFlex600, Rigaku Corp. Ltd. Tokyo, Japan) using Cu- $K\alpha$ radiation (0.154 Å). To evaluate the d_{100} values of the samples, fluorophlogopite (Topy Industries Ltd., Tokyo, Japan) was added as an internal standard at 20 mass% with respect to the sample mass before measurement.

The morphology and composition of the samples were observed using a scanning electron microscope equipped with an energy-dispersive X-ray spectrometer (SEM-EDS; SU9000, Hitachi High-Tech Corp., Tokyo, Japan).

The chemical structures of representative samples were characterised by Fourier-transform infrared spectroscopy (FTIR; FT/IR-6200, JASCO Corp., Tokyo, Japan) using the KBr tablet method with a sample to KBr mass ratio of 1:300. IR spectrophotometry-grade KBr supplied by Wako Pure Chemical Industries was used.

The stable structures of NTCA in a vacuum were estimated using the universal force field method with Avogadro software (Ver. 1.2.0). The molecular size was obtained from the stable structures.

The photoluminescence (PL) properties of representative samples were characterised at room temperature (approximately 25 °C) using a fluorescence spectrometer (FP-8300, JASCO Corp.).

Because the PL peaks of the samples were weak, the fluorescence spectrum of calcium carbonate (calcite), which does not exhibit fluorescence, was measured, and difference spectra were obtained.

Specifically, the PL spectrum of calcite was subtracted from the spectra of the samples to eliminate the effects of stray light on the PL spectra of the samples.

XRD patterns

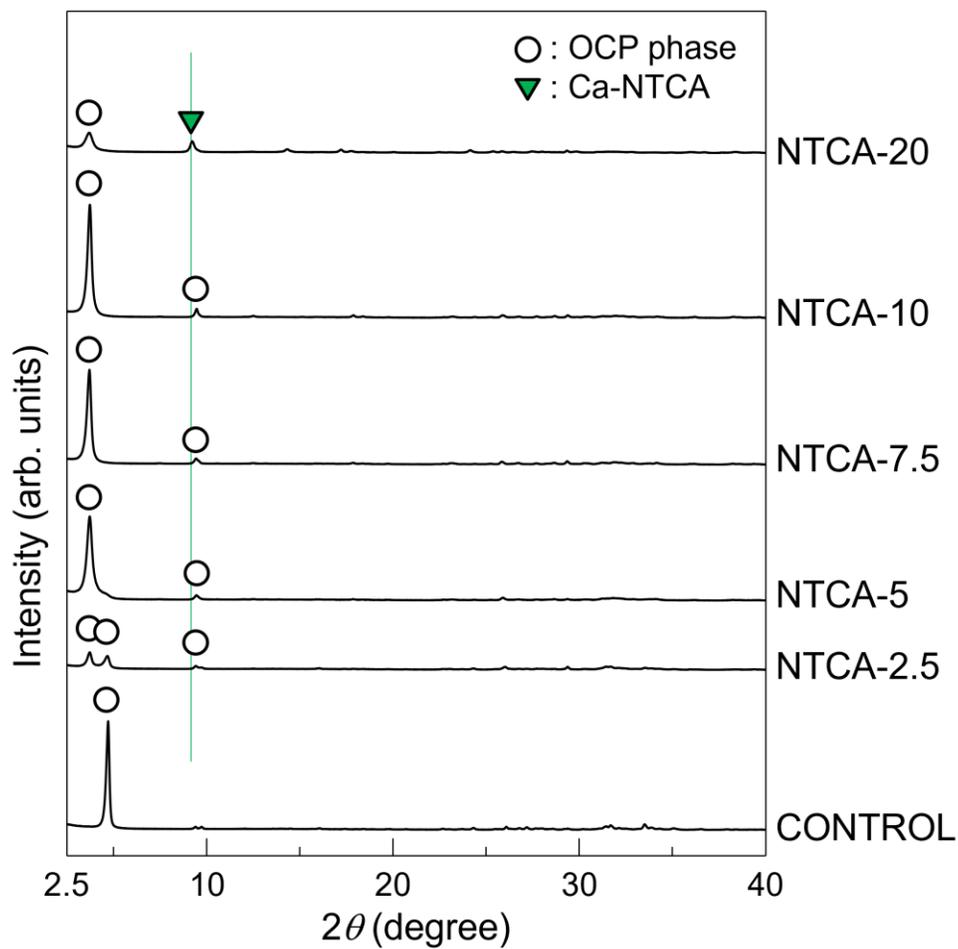


Figure S1. XRD patterns of synthesised samples. The green line indicates the position of the typical reflection peak of a salt composed of calcium and NTCA (Ca-NTCA). Note that the reflection peak positions for the OCP phase and Ca-NTCA are similar, but not identical.

XRD pattern

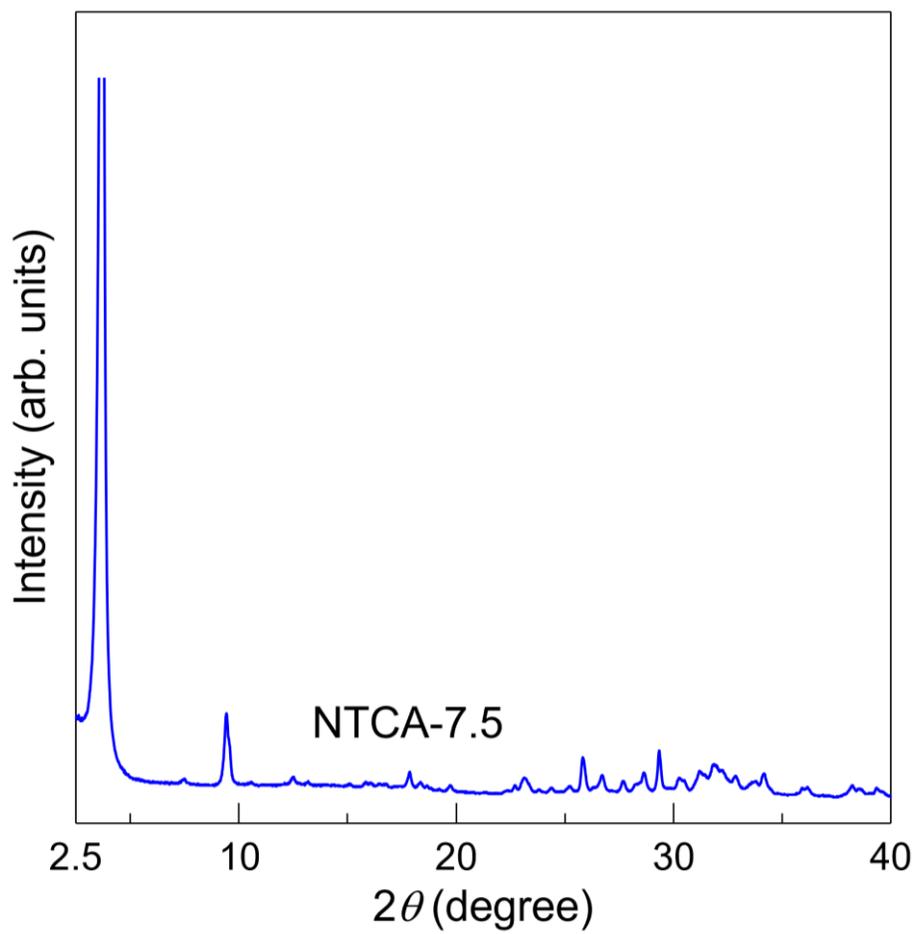


Figure S2. Enlarged XRD pattern of NTCA-7.5.

PL spectra

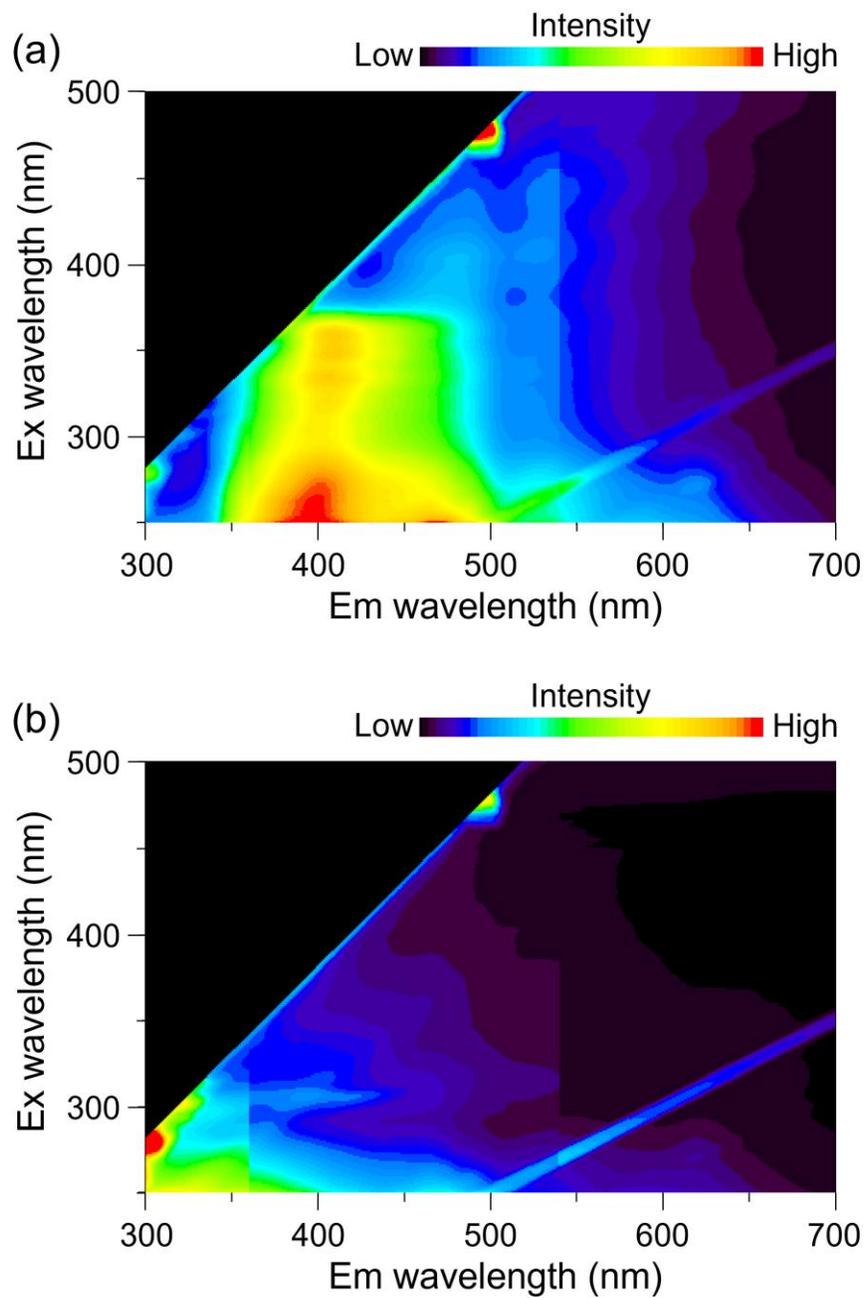


Figure S3. 3D PL spectra of (a) NTCA-7.5 and (b) calcium carbonate (calcite).