

# An investigation into photofunctional interfaces of 8-hydroxyquinoline/hydroxyapatite hybrids



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## ABSTRACT

Organic/inorganic hybrids of 8-hydroxyquinoline (8Hq) molecule and hydroxyapatite nanocrystal (HAP) were mechanochemically prepared. In the hybrids, a green photoluminescence peak at 500 nm newly appeared, suggesting the chemical bonding of the 8Hq molecule with the Ca<sup>2+</sup> ions of HAP. Then, the organic/inorganic interfacial photofunction was clarified by a molecular orbital calculation. The interfacial chemical bonding between the O and N atoms of 8Hq and the Ca<sup>2+</sup> ions of HAP was attributed to both covalent O–Ca and ionic N–Ca. The resultant wave functions revealed that the green luminescence was attributed to metal-to-ligand charge transfer (MLCT) from the O atoms of phosphate group (HAP) to the  $\pi$ -cloud (8Hq) in the HOMO of the hybrids. Therefore, the photofunctional interfaces of the hybrids were successfully demonstrated.

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## 1. Introduction

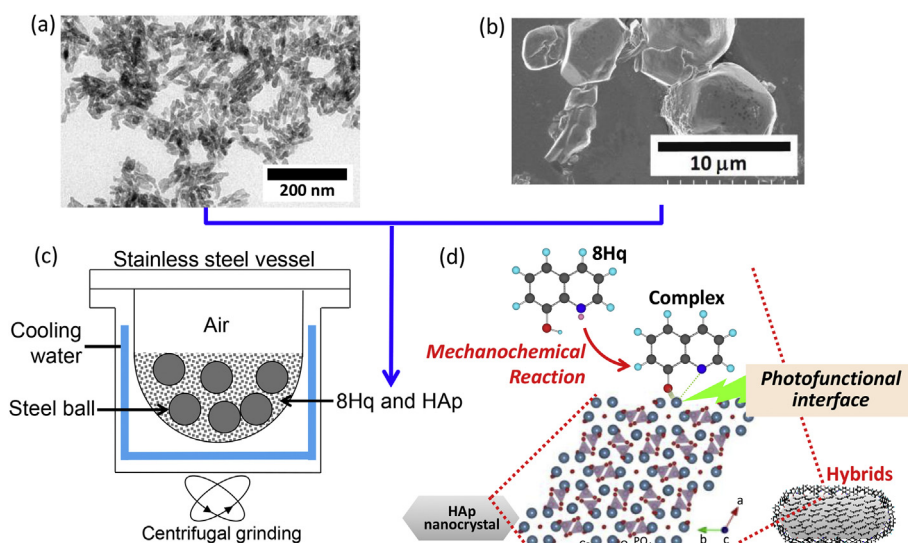
Metallo–organic complex formation provides unique photochemical properties due to the intramolecular interactions as well as the intermolecular interactions [1–3], which allows to be used for various optoelectronic devices [4,5]. One of the interesting ligand molecules is 8-hydroxyquinoline (8Hq; C<sub>9</sub>H<sub>7</sub>NO), which has been investigated due to the light-emitting properties by chelating with six central metal ions (Ca<sup>2+</sup>, Zn<sup>2+</sup>, Al<sup>3+</sup>, Mg<sup>2+</sup>, Zn<sup>2+</sup>, etc.) [6,7]. For example, tris(8Hq)aluminum(III) (Alq) has been applicable for an organic light-emitting materials [8] and have been of great importance for the chelate ligand interactions in the confined nanospaces [9,10]. It has been reported the interfaces between the Alq molecules and Ca ions, suggesting that the Ca ions were interacted with the oxygen (O) atom of 8Hq [11,12]. 8Hq as the ligand molecule is a compound capable of forming the chelate complexes in a liquid phase due to its proton (H)-donating and the complexes can exhibit the photoluminescence at visible-light regions.

The complexes have various electronic states not only from the central metals but also from the ligand molecules with diversity, tailorability and multifunctionality [13,14], suggesting the importance of the molecular arrangement on the solid surfaces. Accordingly, it has been desirable and meaningful to synthesize the functional complexes immobilized in the inorganic solid surfaces [15]. For example, the 8Hq ligand immobilized in the interlayer spaces of clays indicated the functional inorganic-organic complexes [16,17]. Thus, we have proposed that the *in situ* complex formation on the solid surfaces is one of the novel preparative routes to construct functional surfaces as well as organic-inorganic hybrids. In our previous communication, the effective interfacial interactions of 8Hq with the Ca ions of hydroxyapatites (HAP; Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>) nanocrystals were successfully prepared [18]. However, the luminescence mechanisms for the Ca–8Hq complexes on the H-accepting HAP nanocrystals have not yet been clarified. Therefore, the understanding of the physico-chemically driving force on the chelate complexes on HAP is essential to the designing of novel optoelectronic materials.

In this study, the preparation of organic-inorganic hybrids from the HAP nanocrystals (Fig. 1a) and neat 8Hq powder (Fig. 1b) by a mechanochemical solid-state reaction method (Fig. 1c), and the photofunctional interfaces were investigated using a discrete variational (DV)-X $\alpha$  molecular orbital calculation (Fig. 1d) to clarify

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**Fig. 1.** (a) TEM image of the HAp nanocrystals, and (b) FE-SEM image of the neat 8Hq powder. (c) experimental set-up for the mechanochemical reaction and (d) the possible interfacial reaction scheme of the mechanochemically-prepared hybrids.

the photofunctional organic/inorganic interfaces of 8Hq/HAp hybrids. Here, the HAp is a highly-biocompatible ceramic [19–24] and acts as both an acid catalyst of Ca ions and a basic catalyst of phosphate groups [25–27] that is widely used for various biomedical applications [28–34]. For the novel hybrid systems, the preparation technique of this study is thought to be a useful way to coordinate 8Hq on the HAp, which will not be accessible from solutions [35–37]. We have already proposed a mechanochemical treatment for modifying various metal oxides [38–40], which is a very powerful tool to modify the solid reactivity with heteroatoms and guest-molecules [41–43]. Accordingly, the activated HAp surfaces can be mechanochemically prepared and controlled to produce the densely reactive O-rich states at the near-surfaces. The goal of the mechanochemical reactions is to find the major factors that determine the favorable states of the complexed 8Hq ligands. Therefore, the 8Hq molecules and HAp will form novel hybrids, and the complexes of 8Hq on the Ca- and phosphate-abundant HAp surfaces can lead to design the rules for the photofunctional molecular interaction states.

## 2. Experimental procedure

### 2.1. Materials

The preparation of the HAp nanocrystals followed the procedure of our previous reports [44,45].  $K_2HPO_4$  (12 mmol) was dissolved into 100 mL of deionized water and the pH of the solution was adjusted to 12 using tetramethylammonium hydroxide (TMAOH). 60 mL of deionized water containing  $CaCl_2 \cdot 2H_2O$  (20 mmol) was added to the  $K_2HPO_4$  aqueous solution. The initial molar ratio of Ca/P was fixed at 1.67. Then, the precursor solution was refluxed at 40 °C overnight to be the final pH of 7.5. The solution was centrifuged and the sediment solid product was washed with ultrapure water and ethanol. The washed product was dried at 100 °C for 12 h. 8Hq as a special grade chemical was purchased from Wako Chemical Co., Ltd. All the reagents used in the present investigations were used without further purification.

### 2.2. Method of mechanochemical reaction

The experimental apparatus setup of the hybrid preparation is

shown in Fig. 1c. The vessel made from a stainless steel rod (SUS304) with an inner volume of 70 mL was surrounded by a water jacket to control the inner temperature. Twenty steel balls (SUJ-2) of the different diameters of 4.0, 6.4 and 9.8 mm were used as the milling media. The HAp and 8Hq powders were added into the vessel in the amounts of 200 mg and 50 mg, respectively, and vacuumed for 1 day. The vessel mounted on a centrifugal device (Nisshin Giken Co., Ltd., NEV-MA-8) was swung at the rate of 40.2 rad/s for 1 h. The medium balls rotate along the inside wall and press against it by the centripetal force in a circular pathway. When the balls compress the trapped powders, the kinetic energy transfer from the medium to the samples occurs and the compressed force can be determined by Eq. (1).

$$F = mr\omega^2 \quad (1)$$

Thus, the calculated force using the ball diameters of 4.0, 6.4 and 9.8 mm is 10, 45, 175 mN, and the resultant hybrids were abbreviated as 8Hq/HAp1, 8Hq/HAp2, 8Hq/HAp3, respectively. The mixture of the powders without the milling was abbreviated 8Hq/HAp0.

### 2.3. Characterization of hybrids

X-ray diffraction (XRD) patterns were recorded by a Smart Lab (Rigaku Co., Ltd.) using a monochromatized  $CuK\alpha$  radiation. According to Scherer's equation ( $K = 0.9$ ), the crystalline sizes were estimated from the half width of the 100 and 002 diffractions. The morphologies were observed using a transmission electron microscope (TEM: JEM-1400, JEOL Co., Ltd.) at an accelerating voltage of 120 kV and a field emission scanning electron microscope (FE-SEM: SU8230, Hitachi High-Technologies Co., Ltd.). Photoluminescence properties were evaluated by a luminescence spectroscopy and microscopy. The spectra were recorded on a FP-8500 spectrophotometer (JASCO Co., Ltd.) with the excitation wavelength at 372 nm from a Xe lamp under room temperature (atmosphere: air, excitation-slit/detection-slit: 2 nm/2 nm, measure time: 0.1 s, step width: 1.0 nm, sample weight: 150 mg, shape: pellet), and the detection was used by a photomultiplier tube. The luminescence intensities centered at the top of 420 and 500 nm, which are abbreviated as  $I_{420}$  and  $I_{500}$ , were respectively calculated by the

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