1 PB-055

Synthesis and Optical Properties of Metal Organic Structure (MOF) - Plasmonic Metal Nanoparticle Composite.

([1]*Coll. Sci. Tech. , Nihon Univ.* , [2]*Graduate School of Coll. Sci. Tech. , Nihon Univ.*) Kumagai Tomohiro,[1] ○Daiki Sugimoto,[2] Takumi Eguchi,[2] Kosuke Sugawa,[1] Joe Otsuki[1]

Keywords: Metal organic frameworks; Metal nanoparticles; Localized surface plasmon resonance; Porphyrin.

【Background】Metal organic flameworks (MOFs) are characteristic porous materials having a wide range of possibilities for application such as an efficient catalyst and a gas sensing platform. Porphyrin-based MOFs such as PCN-224 can be applied as a sensitizer of singlet oxygen generation because of their stable water-dispersibility. We have been studying the interaction between strong electromagnetic fields induced by a localized surface plasmon resonance (LSPR) of metal nanoparticles and porphyrin. Consequently, photoexcitation was found to be enhanced at Q-band region. In this study, we improve the optical properties of porphyrin-based MOFs by applying the local electromagnetic fields to them.

【Experiment】MOFs (PCN-224) were prepared by refluxing a solution of 5,10,15,20-tetra (4carboxyphenyl) porphyrin, benzoic acid, and zirconium chloride in dimethylformamide (DMF). Then, the MOFs were transferred into an aqueous phase by a centrifugation. Next, Au nanoparticles were synthesized by the citrate reduction method. The synthesized nanomaterials were mixed to obtain their hybrids.

【Results】TEM images of the synthesized MOFs and the Au nanoparticles are shown in Fig. 1. The respective sizes are estimated to be 30 - 40 nm, and 50 - 70 nm. The fluorescence excitation spectra (λ_{em} = 710 nm) of the hybrids are shown in Fig. 2. The fluorescence intensity around the Soret band was significantly quenched, the intensity around 650 nm was rather enhanced. These results suggest that for the fluorescence of porphyrin in the MOFs near the Au nanoparticles the quenching and the enhancement compete.

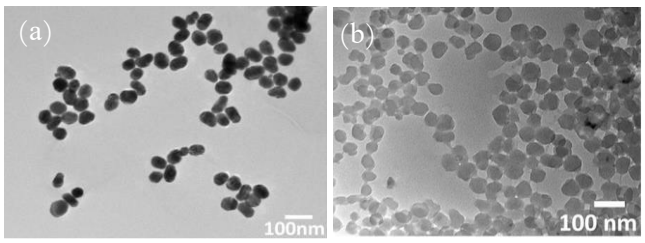

Fig.1 TEM images of (a) AuNPs, (b) MOFs in DMF.

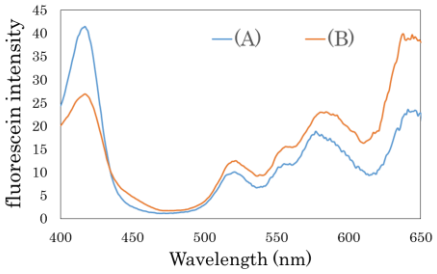

Fig.2 Fluorescence excitation spectra of aqueous solution containing (A) the MOFs and (B) the hybrids.

(1) J. Am. *Chem. Soc.* **2016**, 138, 3518−3525. (2) J. Am. *Chem. Soc*. **2017**, 139, 13804−13810.