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Triplet-Triplet Annihilation-based upconversion reaction driven in solid phase system using photofunctional MOFs.

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Recently, triplet-triplet annihilation upconversion (TTA-UC) systems, which can, in principle, be driven by low photon density light such as sunlight, have attracted much attention. They consist of photofunctional bimolecular (sensitizer and annihilator) systems and are driven based on multi-step energy transfers between them. In the practical solid-phase systems, the energy transfer efficiencies may be reduced due to decrease in the molecular diffusion rates. Increasing the molecular concentration in the solid-phase may increase the energy transfer efficiency, while photofunctions of the molecules themselves (fluorescence quantum yields, excitation lifetime, and so on) may be compromised. In this study, we develop TTA-UC solid nanoparticles consisting of precision annihilator assemblies doped with sensitizers using a metal-organic flameworks (MOFs) technique. And these nanoparticles were assembled on solid surfaces. The TTA-UC MOFs (UC-MOFs) were prepared using a Pd-porphyrin derivative (Pd(II) meso-tetra(4-carboxyphenyl)porphine) as a model sensitizer, an anthracene derivative (4,4'-(anthracene-9,10-diyl)dibenzoic acid) as an annihilator, and a zirconium cluster. The extinction spectra of the dispersion solution of synthesized UC-MOFs (Fig. 1(a)) showed peaks at 350-400 nm attributed to the anthracene derivative and around 410 and 530 nm attributed to the Pd-porphyrin derivative, suggesting that the UC-MOFs were formed. In addition, the extinction peak derived from the Pd-porphyrin derivative increased with increasing concentration of sensitizer in the precursor solution, indicating that the doping amount of the sensitizer can be controlled. The emission spectra of the dispersion solution (Fig. 1(b), excitation wavelength: 532 nm) showed an upconversion emission around 450 nm, which is attributed to the fluorescence of anthracene derivatives. The sensitizer concentration suitable for the effective upconversion emission was also determined. In this presentation, we also report on the emission characteristics after the development on a solid surface.

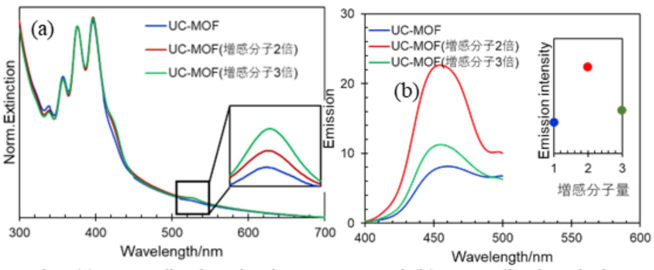

Fig.1(a) Normalized extinction spectra and (b) Normalized emission spectra (λ_{ex}=532nm) of UC-MOF.

1) J. Park et al., *J. Am. Chem. Soc.,* **2018**, *140*, 5493.