Effect of localized surface plasmon resonance on photophysical properties of thermally activated delayed fluorescence molecule (4CzIPN)

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Triplet-triplet annihilation-based upconversion (TTA-UC), which can work even at low optical densities, is being investigated for applications in solar devices. Recently, we reported the enhancement and quenching of upconverted emission in the combined systems of TTA-UC and plasmonic silver nanoparticles.[1)] Our laboratory recently focuses on the TTA-UC consisting of thermally activated delayed fluorescent (TADF) molecules as a sensitizer for the large anti-stokes shift. In this study, we discuss the effect of LSPR on the photophysics of 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN) as a TADF molecule.

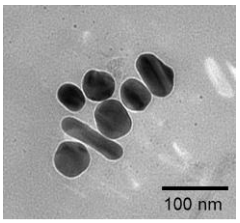

Fig.1 TEM image of AgNPs.

The Ag nanoparticles (AgNPs) with a diameter of 50 ± 8 nm (TEM image: Fig. 1) employed as a plasmonic nanoparticle showed an extinction peak at 450 nm, which was overlapped with fluorescence band (around 505 nm) of 4CzIPN. The fluorescence consists of TADF and prompt fluorescence. The hybrids of AgNPs and 4CzIPN were prepared by modifying polymer thin film containing 4CzIPN on the glass plate on which the AgNPs were immobilized with an arbitrary density (4CzIPN/AgNPs). And a polyvinylalcohol derivative (PVA) was coated on the hybridized film to prevent the attack by oxygen(4CzIPN/AgNPs/PVA). In the absence of PVA, the fluorescence of 4CzIPN was significantly quenched by the existence of AgNPs (Fig. 2(A)), indicating the efficient quenching of prompt fluorescence. On the other hand, in the presence of PVA, the total fluorescence (prompt and TADF) was slightly enhanced by the AgNPs (Fig. 2(B)). Considering Fig. 2(A) and (B), only the TADF was significantly enhanced. These results can be attributed to the change in the intersystem crossing efficiency of 4CzIPN.

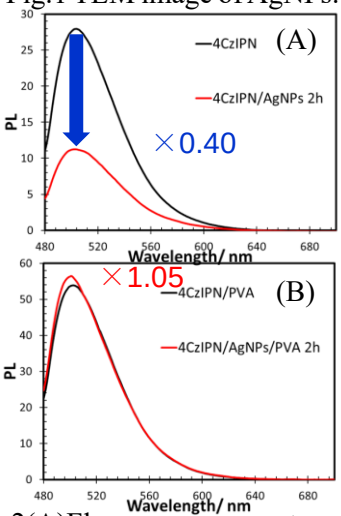

Fig.2(A)Fluorescence spectra in the absence of PVA and (B) the presence of PVA.

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Reference: 1) S. Jin et al., *ACS Photonics*, **2018**,5,5025.2)