



Research paper

Plasmon-enhanced phosphorescence of hybrid thin films of metal-free purely organic phosphor and silver nanoparticles



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ABSTRACT

We present phosphorescence enhancement of 2,5-dihexyloxy-4-bromobenzaldehyde (Br6A), a metal-free organic phosphor, by means of Ag nanoparticles (NPs) through surface plasmon excitation. The emission enhancement and lifetime reduction was observed in the fluorescence and phosphorescence suggesting that the phosphorescence enhancement can be achieved in the same manner as in fluorescence, through the increase of photoabsorption and the enhanced emission rate by the field enhancement around the metal nanostructures. Our results help to improve the understanding of the phosphorescence enhancement mechanism of a new class of purely organic phosphors.

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1. Introduction

Phosphorescence and fluorescence are radiative transitions of molecules that are electronically excited by photoabsorption. Fluorescence results from electronic transition between singlet states, whereas phosphorescence is emitted during the transition between triplet excited and singlet ground states. Because of the non-matching spin quantum numbers of triplet and singlet states, phosphorescence can only appear through intersystem crossing between the singlet and triplet states via spin-orbit coupling of the heavy atoms present in the molecules; therefore, the time scale of the phosphorescence transition is much longer than that of the fluorescence transition [1,2]. However, the absence of the spin-matching requirement in the phosphorescence transition has a practical advantage in that the theoretical efficiency of phosphorescence emission by charge injection can reach 75%, whereas that of fluorescence is only 25% [3].

This ideal phosphorescence emission efficiency has been demonstrated by organometallic compounds [4]; however, these organometallic phosphors contain rare and expensive metal ions

such as Ir or Pt [2,5,6]. Recently, metal-free purely organic phosphorescent materials molecules were devised by using halogen bonding between El-Sayed rule satisfying aromatic aldehyde and bromine, a heavy atom, instead of heavy metals atoms to achieve efficient spin-orbit coupling and consequent high-efficiency phosphorescent emission [1,7,8]. For example, Br6A can be made into bright phosphorescent films by being embedded into isotactic-poly methyl methacrylate (iPMMA) [9], incorporated into polyvinyl alcohol (PVA) by hydrogen bonding [10], or covalently bound in a polymer matrix [11], using simple spin-coating method, suggesting promising application of purely organic phosphors in various solid films.

The surface plasmon excitation and thus enhanced the light-matter interaction [12] has been used to increase the emission intensity of organic light-emitting materials for practical high-performance OLED [13–15]. For example, the addition of silver nanoparticles (Ag NPs) in the emission layer was observed to significantly increase the efficiency of OLEDs [16]. There have also been a few reports on the enhancement of phosphorescence emission by interfacing metallic nanostructures; however, the origin of the observed phosphorescence enhancement is unclear because these metallic structures not only excite surface plasmons but also promote spin-orbit coupling, resulting in an increased chance of conversion from the singlet to triplet state [17,18]. Moreover, the much longer lifetime of phosphorescence emission, in the range of milliseconds, suggests the possibility of much larger

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enhancement by surface plasmon excitation if the phosphorescence enhancement stems from the increased emission rates by metallic interfaces [19]. Therefore, systematic study of plasmonic enhancement of metal-free organic phosphors could result in a significant advancement in the understanding of the phosphorescence enhancement mechanism by surface plasmons.

Here, we prepared hybrid thin films of Br6A and Ag NPs embedded in iPMMMA. We studied the effect of the Ag NPs' surface plasmon on the fluorescence and phosphorescence of Br6A. In general the fluorescence and phosphorescence were enhanced by $\sim 30\%$ depending on the size of the Ag NPs, and their lifetimes also decreased by $\sim 30\%$. Our results provide a better understanding of the effect of surface plasmons on phosphorescence and fluorescence emission of purely organic phosphors.

2. Experimental details

Br6A prepared by organic synthesis [1] and iPMMMA (Sigma-Aldrich) were dissolved in chloroform with a 1:100:10,000 wt% ratio of Br6A:iPMMMA:chloroform. Ag NPs with 20 or 80 nm diameters (BBI Solution Corp.) were drop-cast onto glass substrates that were pre-treated with poly L-lysine solution (Sigma-Aldrich) to achieve firm attachment of the Ag NPs. The Br6A/iPMMMA solution was stirred for 1 h at ambient temperature, and 0.5 mL of the solution was spin-coated on the Ag NPs-tethered glass substrate and then the uniform incorporation of Br6A molecules within iPMMMA is expected, where Br6A molecules are attached through halogen bonding to ester groups of iPMMMA [9]. With the weight percentages of Br6A and iPMMMA used here, the number density of Br6A molecules and the average distance between Br6A molecules were estimated to be $\sim 1.7 \times 10^{19}/\text{cm}^3$ and 3.9 nm, respectively. To obtain a thin film, the spin speed was set at 3000 rpm for 30 s. Fig. 1(a) schematically illustrates the resulting iPMMMA thin film having the Ag NPs on the bottom and embedded Br6A. The thickness of the hybrid thin film was measured to be ~ 200 nm by a surface profiler.

Photoluminescence (PL) spectra of sample films were measured using a lab-made laser confocal microscope. The excitation source was a diode laser with 375-nm wavelength (BDL-375, B&H GmbH). The PL signal collected by a 0.9 numerical aperture objective lens was guided through an optical fiber with a 200- μm core diameter to a 30-cm-long monochromator equipped with a cooled charge-coupled device (CCD). The PL images in thin film were obtained by an electron-multiplying charge-coupled device (EMCCD) with 365-nm wavelength excitation from an ultraviolet lamp. Fluorescence decay profiles were measured by a manufactured time-correlated single-photon counting system (Simple-Tau 150, B&H

GmbH), and phosphorescence decays were obtained using by 355 nm pulse of ND-YAG laser (INDI-40-10, Spectra-Physics) and a fast photomultiplier tube (H107231-20, Hamamatsu) equipped with a spectrometer (SP2150, PI).

3. Results and discussion

We first discuss the variation of the spectral intensity between fluorescence and phosphorescence of the Br6A thin film with the number of laser exposures. Typical spectra of Br6A consist of two prominent peaks originating from the fluorescence and phosphorescence transitions in the spectral ranges of 400–450 nm and 500–550 nm, respectively, as observed in Fig. 2(a) [1]. The phosphorescence emission dominates over the fluorescence emission in a well-crystallized Br6A film due to the efficient halogen bonding and tight packing for enhanced spin-orbit coupling and suppressed collisional quenching, respectively [10,11,20]. The PL spectra from our sample also displayed this dominant phosphorescence, indicating good crystal formation. However, with increasing exposures to laser excitation at the same location, the intensity of the fluorescence peak gradually increased, whereas the phosphorescence emission gradually decreased, as observed in Fig. 2(a). After nine laser exposures, the intensity of the fluorescence peak was three times higher than that in the first exposure, whereas the phosphorescence peak intensity decreased by 65% compared with that of the first exposure. The total PL intensity and fluorescence and phosphorescence intensities are plotted as a function of the number of laser exposures in Fig. 2(b).

We attribute the observed variation of fluorescence and phosphorescence to 'beta-relaxation,' namely, a polymer backbone conformation reorganization of PMMA [21,22]. Originally, the iPMMMA structure surrounding the Br6A was expected to decrease the collisional non-radiative decay of Br6A since iPMMMA does not have beta-relaxation [9]. However, the laser exposure should be inevitably accompanied by local heating, which can weaken or even break the halogen bonding within Br6A crystals followed by halogen bonding formation between Br6A and matrix iPMMMA, which in turn weakens the intersystem crossing from S_1 to T_1 , reducing the triplet electron population and consequent decrease in phosphorescence but increase in fluorescence. To verify this hypothesis we conducted control experiments. Note that the total PL intensity was higher for larger phosphorescence, which indicates that activation of phosphorescence plays a key role in maximizing the overall PL efficiency of these Br6A films. In addition, the stability of Br6A phosphorescence with heat serves as a primary constraint for the practical use of Br6A as a phosphorescence-emitting mate-

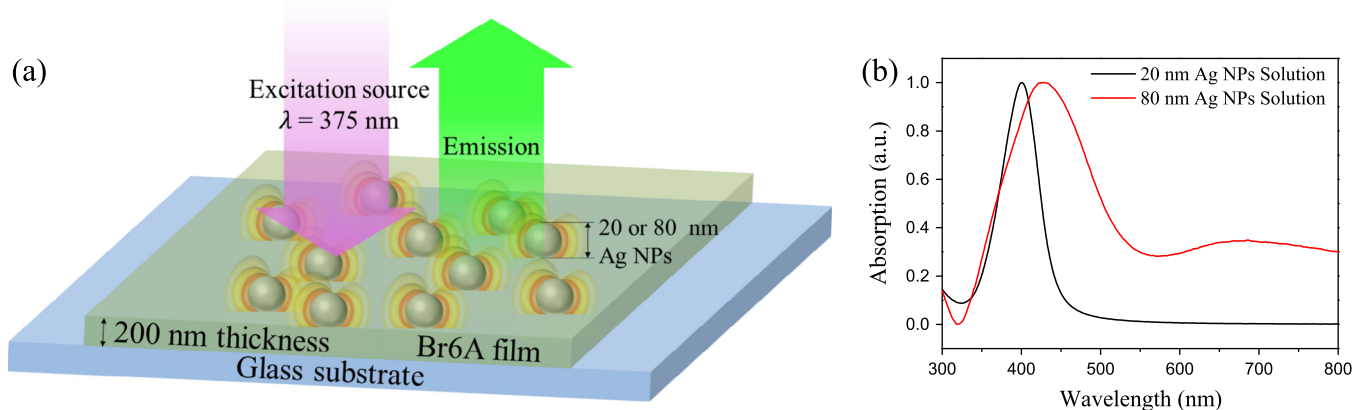


Fig. 1. (a) Schematic illustration of Br6A/Ag NP hybrid thin film. (b) Absorption spectra of aqueous Ag NP solutions.

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