Analysis of Photoluminescence Behaviors of Phosphorescent Polyimide and Imide Compound under Very High Pressure

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I. Introduction

Organic luminescent materials are applicable to many fields; such as displays, light emitting devices (LEDs), photovoltaic devices, and spectrum convertors for solar cells and crop cultivation. Recently, polyimides (PIs) are increasingly attracting many interests due to the potential applications as novel photoluminescence materials bearing excellent thermal, chemical, and environmental stability. Photoluminescence properties of PIs strongly depend on not only the chemical and electronic structures of the repeating unit but also the aggregation state. We have reported that the luminescence intensities of fluorescent PIs are reduced under very high pressure up to 8 GPa due to the enhancement of non-radiative deactivation caused by inter-molecular interactions [1]. This phenomenon called Aggregation-Caused Quenching (ACQ), which is not preferable to develop solid luminescent materials. On the other hand, we have developed phosphorescent PIs by introducing heavy bromine atoms in main chain (**Fig. 2(a)**) [2,3]. Interestingly, the luminescence intensity of phosphorescent PIs were significantly increased at lower temperatures, which is attributable to suppressing local molecular motion. Therefore, the phosphorescent PIs has a potential to breakthrough ACQ in the aggregation state.

In this study, the correlations between the aggregation state and the photoluminescent properties were examined for phosphorescent PI (DB-PI) and its model compound (DB-MC) based on photoluminescence spectroscopy under very high pressure (**Fig. 1**).

II. Experimental

To generate pressure up to 10 GPa, PIs films were loaded into a diamond anvil cell (DAC, Syntech Co. Ltd.) (**Fig. 2(b)**) equipped with culet of synthetic diamond anvils with 600 μm diameter. The ruby fluorescence technique was used to measure the pressure inside the sample chamber. The emission spectra of the PIs films were measured with multichannel CCD spectrometer (Hamamatsu Photonics Co., Ltd.), using a LED (λ_{ex} =365 nm, Hamamatsu Photonics Co., Ltd.) as a light source.

III. Result and Discussion

Photoluminescence properties of DB-PI and DB-MC were examined by photo-emission spectra of a DB-PI film and DB-MC dispersed in PMMA matrix (1 wt%) by varying pressure from 0.1 MPa (atmospheric) up to 10 GPa. Phosphorescence intensity of DB-PI was reduced by applying pressure, which is attributable to non-radiative deactivation enhanced by reduction in inter-molecular distance (**Fig. 3(a)**). In contrast, that of DB-MC was significantly increased with an increase in pressure, which is attributed to effective suppression of non-radiative deactivation process caused by aggregation and/or local molecular motion (**Fig. 3(b)**). This result clearly indicates that control of aggregation state and local molecular motion of PIs is effective and most important to develop highly luminescent materials based on phosphorescence.

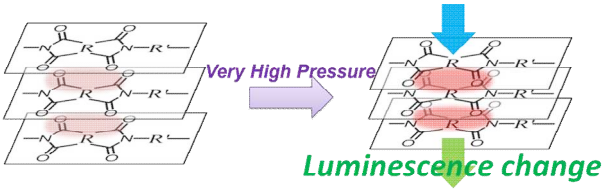

Figure 1. Schematic illustration of changes in structure and luminescence properties of PIs induced by high pressure

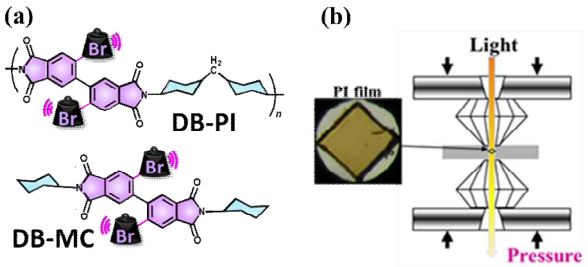

Figure2. (a) Chemical structure of DB-PI and DB-MC and (b) schematic illustration of DAC.

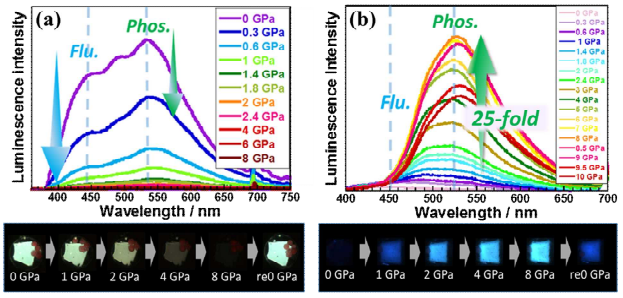

Figure 3. Variations in emission spectra of (a) DB-PI film and (b) DB-MC dispersed in PMMA matrix caused by applying pressure to 10 GPa.

References

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