Pressure-Induced Enhancement of Phosphoresce from Bromine-Containing Imide Compound and Polyimide

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I. Introduction

Piezochromic materials are a type of stimuli-responsive materials that change their luminescent color in response to pressure such as grinding or stretching. Most of the piezochromic materials developed in recent years are organic materials exhibiting fluorescence emission. This is because they seldom show phosphorescence at room temperature due to the weak spin-orbit coupling and the long triplet state lifetime. Our group has developed room-temperature phosphorescent imide compound (DBr-MC) and polyimide (DBr-PI) by introducing heavy halogens into the acid dianhydride moiety (**Fig. 1**) [1]. Recently, we found that hydrostatic pressure applied to DBr-PI induces a significant red-shift of the phosphorescence peak wavelength and an increase in phosphorescence intensity [2]. In this study, we aimed to evaluate the efficiency of pressure-induced enhancement of phosphorescence for DBr-MC and DBr-PI and elucidate the photophysical processes under high pressure.

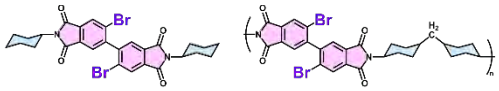

Fig. 1 Chemical structures of DBr-MC (left) and DBr-PI (right).

II. Experimental

Thin films of DBr-PI and DBr-MC dispersed in PMMA at 1.0 wt% were used for measurements. UV-vis absorption/ spectra and luminescence lifetimes were measured in the diamond anvil cell filled with a thin film, a hydraulic medium (Daphne 7575, Idemitsu Kosan Co., Ltd.), and ruby particles as indicator of pressure inside the cell.

III. Results and Discussion

The UV-vis absorption spectra of these films under high pressure are shown in **Fig. 2**. The absorption edges were red-shifted with increasing pressure due to the stabilization of the excited state and the decrease of the transition energy caused by an enhancement of van der Waals interaction accompanied by the shortening of interchain distance.

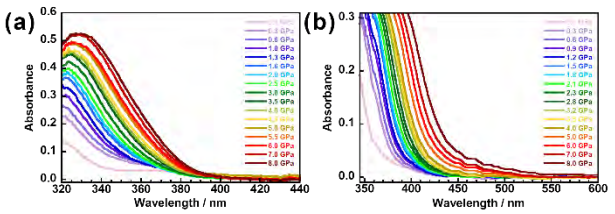

Fig. 2 UV-vis absorption spectra of **(a)** DBr-MC and **(b)** DBr-PI.

The pressure dependence of the phosphorescence area of the emission spectra normalized by the absorbance at the excitation wavelength (365 nm) of the thin films (I_P) and phosphorescence lifetimes (τ_P) are shown in **Figs. 3** and **4**. Since DBr-MC and DBr-PI show dual emission of fluorescence and phosphorescence, the I_P was calculated by decomposing the spectra into these peaks with two Gaussian functions. The I_P of DBr-MC increased to 2.8 GPa (28,000 atom) and remained constant at higher pressures. This suggests that intermolecular energy transfer is suppressed in isolated molecules, and that molecular motion is sufficiently suppressed up to 2.8 GPa. The τ_P of DBr-MC showed a maximum at 1.3 GPa, suggesting that local molecular motion is suppressed, and the triplet exciton is stabilized below 1.3 GPa. In contrast, the τ_P decreases while the I_P increases above 1.3 GPa, suggesting that the transition from the excited triplet state to the singlet ground state is promoted by the heavy atom effect of bromine atoms. Meanwhile, the I_P and τ_P of DBr-PI reached their maxima at 0.9 GPa, indicating that the suppression of local molecular motion by pressurization is dominant below 0.9 GPa. The I_P and τ_P are decreasing above 0.9 GPa because the excitation energy transfer is enhanced by the shortening of intermolecular chain distance. This is supported by the fact that the I_P of isolated DBr-MC is almost constant in the pressure range above 2.8 GPa.

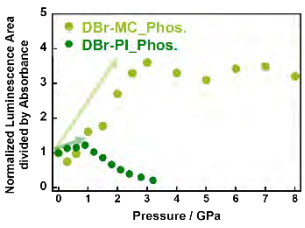

Fig. 3 The areas of the luminescence spectra of each thin film normalized by their absorbance at the excitation wavelength.

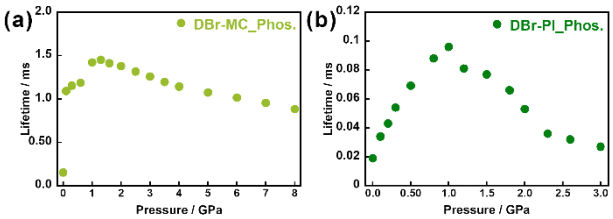

Fig. 4 Pressure dependence of phosphorescence lifetimes for **(a)** DBr-MC and **(b)** DBr-PI.

In conclusion, it was clarified that the application of very high pressure to DBr-PI has two contradictory effects: 1) an increase in the absorbance at the excitation wavelength caused by the red-shift in absorption, and a reduction in non-radiative deactivation by suppressing local molecular motions, and 2) an enhancement of energy transfer caused by the shortening of interchain distances, which leads to further non-radiative deactivation. Consequently, the phosphorescence enhancement of DBr-PI is less pronounced than that of DBr-MC and reaches its maximum at a lower pressure. This study revealed one aspect of the correlation between the aggregated state of PI and its luminescence properties. This knowledge is expected to promote the development of polymer materials exhibiting pressure-induced luminescence enhancement.

References

[1] K. Kanosue, S. Ando et al. *Mater. Chem. Front.*, **3**, 39–49 (2019).
[2] R. Isoda, S. Ando et al. 第 70 回高分子討論会予稿集 (2021).