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Observation and Analysis of High Pressure-Enhanced Luminescence of Phosphorescent Bromine-Containing Imide Compounds and Polyimides

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INTRODUCTION:

Polyimides (PIs) are one of the representative super engineering plastics exhibiting excellent thermal, chemical, and radiation stabilities due to their rigid repeating units and strong intermolecular interactions. Therefore, PIs have been applied in a wide range of industrial fields such as automotive, photonics, and aerospace industries. Recently, room temperature phosphorescence (RTP) of organic molecules has attracted much attention because of their extraordinarily large Stokes shifts (>10,000 cm^{-1}) and ultra-long luminescence lifetimes (10^{-3}–10 s). We have recently developed novel PIs exhibiting RTP by introducing heavy halogens such as bromine and iodine into the acid dianhydride moiety in semi-aromatic PIs [1-2]. The optical properties of the PIs depend not only on their chemical structures but also on their aggregation states. The application of hydrostatic pressure is an effective method to change the aggregation states of PIs dramatically without any decomposition. We have reported that the fluorescence intensity of fluorescent PIs decreases by applying pressure because the compressed intermolecular distance enhances the excited energy transfer that induces non-radiative deactivation [3-4]. In contrast, phosphorescence is known to compete with non-radiative deactivation process associated with local molecular motion and quenching by ambient oxygen. Hence, the intensity and the lifetime of phosphorescence increase at low temperatures and under vacuum where the local molecular motions and energy quenching are deactivated. Therefore, we expect that the phosphorescence intensity can be increased by suppressing the molecular motion under high pressure. In this study, the phosphorescent properties of a bromine-containing imide compound (DBr-MC, **Figure 1(a)**) and a PI (DBr-PI, **Figure 1(b)**) are discussed in terms of local molecular motion and energy transfer processes in the excited states based on the emission spectra and emission lifetimes measured under variable pressures from atmospheric pressure (0.1 MPa) to 8.5 GPa.

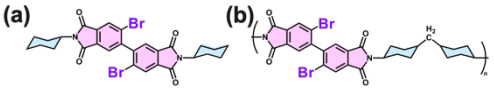

Figure 2. Chemical structures of **(a)** DBr-MC and **(b)** DBr-PI.

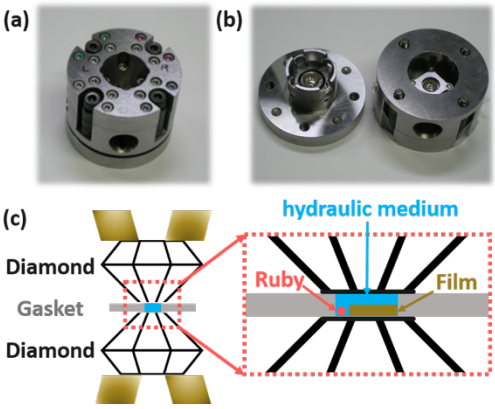

Figure 1. Photographs of a diamond anvil cell (DAC) in **(a)** closed and **(b)** open states. **(c)** Diagram of a DAC viewed from a cross section parallel to the transmitted optical axis.

EXPERIMENTAL:

DBr-MC dispersed in poly(methyl methacrylate) (PMMA) at a concentration of 1.0 wt% and a film of DBr-PI were cut into pieces with approximately 0.2×0.2 mm^2 squares. These films were loaded into a diamond anvil cell (DAC, Syntech Co. Ltd., **Figure 2**) together with a hydraulic medium (Daphne 7474, Idemitsu Kosan Co., Ltd.) and a ruby particle as the indicator of inside pressure. The emission spectra and emission decay curves were measured at elevated pressures from 0.1 MPa to 8.5 GPa.

RESULTS AND DISCUSSION:

The pressure dependence of the emission spectra of DBr-MC dispersed in PMMA and DBr-PI film are shown in **Figure 3** with their microphotographs under UV irradiation, and the pressure dependence of their phosphorescence lifetimes are shown in **Figure 4**. DBr-MC and DBr-PI showed prominent phosphorescence emission in the wavelength range of 500–570 nm with long luminescence lifetimes on the order of 10^{-6} to 10^{-3} s.

The phosphorescence intensity of DBr-MC gradually increased with pressure and reached ca. ten times higher at 8.0 GPa than that at 0.1 MPa. This indicates that non-radiative deactivation associated with intermolecular excitation energy transfers of DBr-MC was sufficiently suppressed

because DBr-MC was homogeneously dispersed and isolated in PMMA. In addition, the non-radiative deactivation induced by local molecular motion was also suppressed by applying high pressure. Accordingly, the phosphorescence intensity of DBr-MC film increased with increasing the pressure.

Meanwhile, the phosphorescence intensity of DBr-PI increased up to 0.9 GPa, which is about five times higher than that 0.1 MPa, whereas it decreased at the higher pressures. This indicates that local molecular motions are more dominant in the non-radiative deactivation below 0.9 GPa than energy transfer. However, a contribution of the energy transfer to the non-radiative deactivation was enhanced and exceeded that of molecular motion above 0.9 GPa because the emission species in DBr-PI films are much more concentrated and the energy transfer can be more enhanced by applying pressure than DBr-MC in PMMA.

The pressure dependence of the phosphorescence lifetime of both DBr-MC and DBr-PI rapidly increased with the pressure up to around 1 GPa, and then slowly decreased above 1 GPa. The increase in the phosphorescence lifetime below 1 GPa is attributable to the decrease in the rate constants of the non-radiative deactivation due to the effective suppression of molecular motion. The former is attributable to the increase in the rate constant of the non-radiative deactivation due to the increases in the energy transfer efficiency and the rate constants of inter system crossing promoted by the external heavy atom effect. The energy transfer efficiency in DBr-MC is limited because it is dispersed and isolated each other in PMMA, while that of DBr-PI can be gradually accelerated because the inter-chain distance of DBr-MC becomes shorter with applying pressure. Therefore, the phosphorescence lifetime of DBr-MC gradually decreased, whereas the that of DBr-PI more steeply decreased.

Accordingly, the application of high pressures to a phosphorescent PI has two competing effects; 1) reduction of non-radiative deactivation by suppressing local molecular motions and 2) enhancement of energy transfer caused by the reduction of interchain distances, which leads to additional non-radiative deactivations. Consequently, the phosphorescence intensity of the phosphorescent PI is maximized at a pressure of 0.9 GPa due to the balance between the degrees of aggregation and the local molecular motion.

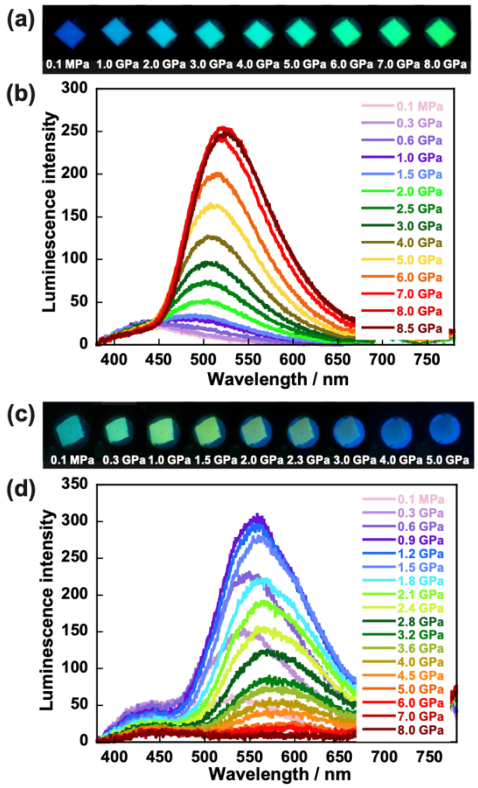

Figure 3. Photographs of the **(a)** DBr-MC and **(c)** DBr-PI film under UV irradiation and pressure dependence of the emission spectra observed for **(b)** DBr-MC and **(d)** DBr-PI film. (λ_{ex} = 365 nm)

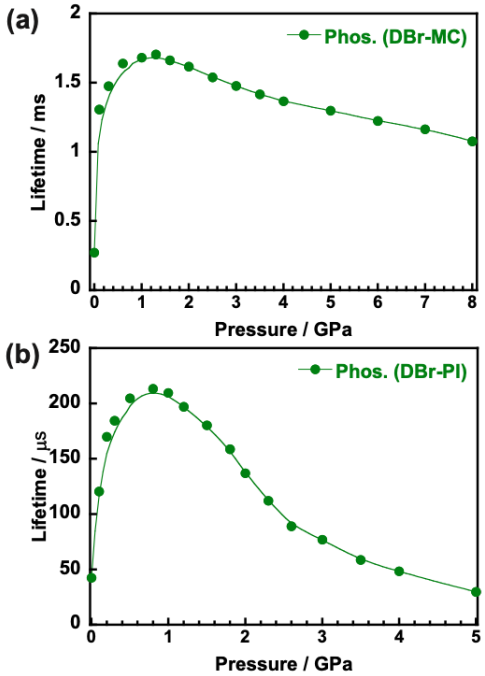

Figure 4. Pressure dependence of the phosphorescence lifetime observed for **(a)** DBr-MC film (λ_{ex} = 360 nm, λ_{em} = 510 nm) and **(b)** DBr-PI film (λ_{ex} = 360 nm, λ_{em} = 540 nm).

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