# Pressure induced variations in optical properties of brominated imide compound and polyimide

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## Introduction

Polyimides (PIs) are well known super-engineering plastics possessing outstanding thermal, chemical, and radiation stabilities originating from their rigid repeating unit structures and strong intermolecular interactions. Therefore, they have been applied in a wide range of industries, such as automotive, photonics, and aerospace industries. Recently, room-temperature phosphorescence (RTP) of organic molecules has attracted much attention owing to its potential applications based on extraordinarily large Stokes shifts (>10 000 $cm^{-1}$) as well as ultra-long luminescence lifetimes ($10^{-3}$ to 10 s). Therefore, RTP-PIs are expected to be used as spectrum convertors in solar cell or agricultural film. We have successfully synthesized RTP-PIs by introducing heavy halogen atoms, such as bromine and iodine, into the dianhydride moiety of semi-aromatic PIs [1−2]. The optical properties of PIs strongly depend on not only the chemical structures but also the aggregation state. The application of hydrostatic pressure is an effective method to change the aggregation state of PIs dramatically without any decomposition. We have reported that the fluorescence intensity of fluorescent PIs decreased with increasing efficiency of the energy transfer due to the compression in the intermolecular direction under high pressure [3−4]. On the other hand, since phosphorescence is strongly affected by non-radiative deactivation process associated with local molecular motion, suppression of the molecular motion by applying high pressure could enhance the intensity of phosphorescence. In this study, we discussed the phosphorescent properties of a brominated imide compound and a PI in terms of molecular mobility and energy transfer processes in the excited states on the basis of the emission spectra measured under atmospheric and high pressures up to 8.5 GPa.

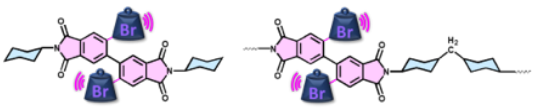


**Fig. 1** Chemical structures of DBr-MC (model, left) and DBr-PI (polyimide, right).

## Experimental

A thin film of a brominated imide compound (DBr-MC, **Fig. 1**) dispersed in PMMA at a concentration of 1.0 wt% and a brominated PI (DBr-PI, **Fig. 1**) 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., **Fig. 2**) together with a hydraulic

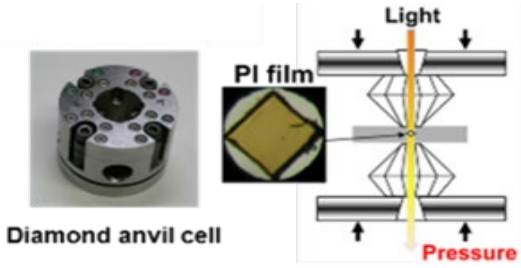


**Fig. 2** Photographs and cross-sectional drawing of diamond anvil cell (DAC).

medium (Daphne 7474, Idemitsu Kosan Co., Ltd.) and a ruby particle. The emission spectra were measured at elevated pressures from atmospheric to 8.5 GPa. The ruby fluorescence technique was used to measure the pressure inside the sample chamber.

## Results and Discussion

The pressure dependences of the emission spectra of DBr-MC and DBr-PI are shown in **Figs. 3, 4**. DBr-MC and DBr-PI showed prominent phosphorescence emission peaks at 500–570 nm. The phosphorescence intensity of DBr-MC gradually increased and reached to ca. ten times larger than the atmospheric pressure. This result indicates that non-radiative deactivation caused by intermolecular energy transfer was sufficiently suppressed for DBr-MC in PMMA, and thus the phosphorescence intensity was enhanced by suppression of molecular motion under high pressure. In a similar way, the phosphorescence intensity of DBr-PI increased up to 0.9 GPa, while it turned to decrease above the pressure. This indicates that the contribution of the non-radiative deactivation by suppression of molecular motion was more significant below 0.9 GPa than that of non-radiative activation via energy transfer, whereas the contribution of the energy transfer was enhanced and exceeded the effect of the suppression of molecular motion above 0.9 GPa because of the significant decrease in the interchain distance. Accordingly, the application of pressure to PIs has two conflicting effects which 1) reduce non-radiative deactivation due to the suppression of molecular motion and 2) increase non-radiative deactivation due to the enhancement of energy transfer with decreasing the interchain distance. As a consequence, the emission intensity of the phosphorescent PI was maximized with just the appropriate aggregated state under a pressure of 0.9 GPa.

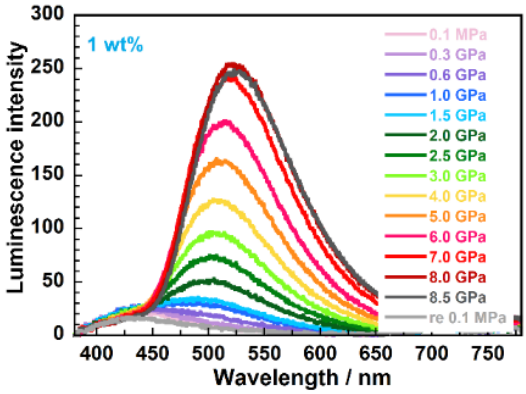


**Fig. 3** Pressure dependence of the emission spectra observed for DBr-MC film.

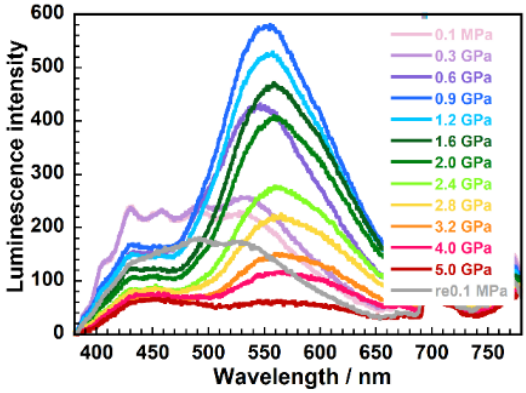


**Fig. 4** Pressure dependence of the emission spectra observed for DBr-PI film.

## References


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