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Analysis of Phosphorescence Enhancement of Bromine-Containing Phosphorescent Polyimides under High Pressure

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[Introduction] Our group has been successfully developing polyimides (PIs) exhibiting phosphorescence at room temperature by introducing heavy halogen atoms such as bromine and iodine into fluorescent semi-aromatic PIs composed of alicyclic diamines and aromatic acid dianhydrides[1,2]. It is known that the optical properties of solid polymer materials depend not only on their chemical structures but also on the aggregated states of their molecular chains. The application of hydrostatic pressure to polymer chains, is an effective way to perturb the aggregated state of PIs. We have reported that the interchain distance of PIs decreases, and excitation energy transfer is enhanced under elevated hydrostatic pressure, resulting in a reduction of fluorescence intensity[3,4]. In this study, we investigated the photophysical processes of bromine-containing phosphorescent PIs under high pressure.

[Experimental] A thin film of bromine-containing PI; DBr-PI (**Fig. 1(a)**) was prepared to measure emission spectra, luminescence decay curves, and quantum yields at room temperature and liquid nitrogen temperature (77 K) under atmospheric pressure. Moreover, these optical measurements as well as UV-vis absorption spectra were acquired under high hydrostatic pressure in a diamond anvil cell (DAC) filled with the daphne oil 7474 (Idemitsu Kosan Co., Ltd.) as a hydraulic medium and with ruby particles as an indicator of pressure inside the cell.

[Results & Discussion] Photographs under UV irradiation and the pressure dependence of the emission spectra of DBr-PI are shown in **Figs. 1(b)** and **(c)**, respectively. DBr-PI displays green color under UV irradiation (**Fig. 1(b)**) and exhibits fluorescence at 430 nm as well as phosphorescence at 530–570 nm (**Fig. 1(c)**). The phosphorescence intensity increased up to 0.9 GPa, which is 4.3 times higher than that at atmospheric pressure (0.1 MPa), and then decreased at higher pressures. The pressure dependence of the absorption spectra of DBr-PI is shown in **Fig. 1(d)**. The absorption of DBr-PI was 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 with a shortening of inter-chain distance. Since the absorption spectra also changes with pressure, the phosphorescence intensities are normalized by the absorbance at 365 nm, which correspond to the excitation wavelength (**Fig. 2(a)**). The normalized phosphorescence intensity shows the maximum value at 0.9 GPa, which is 1.2 times larger than that under atmospheric pressure. Based on these results, the pressure dependences of the phosphorescence rate constant k_P and the non-radiative deactivation rate constant from the triplet excited state k_{TS} are calculated based on the following hypotheses; 1) the quantum yields of internal conversion is negligible at 77 K, 2) the quantum yields of fluorescence and phosphorescence are proportional to the area ratios of the emission spectra, and 3) the intersystem crossing rate constant is independent of temperature and pressure. The ratio of k_P/k_{TS} shows the maximum at 0.9 GPa (**Fig. 2(b)**), which is consistent with the maximum of phosphorescence intensity (**Fig. 2(a)**). In conclusion, the application of pressure to DBr-PI has two contradictory effects, which are 1) an increase in the absorbance at the excitation wavelength accompanied with the red shift in absorption, and a reduction of non-radiative deactivation by suppressing the local molecular motions, and 2) an enhancement of energy transfer caused by the shortening of interchain distances, which leads to additional non-radiative deactivation. Due to these competing effects, the phosphorescence intensity is showed the maximum value at 0.9 GPa.

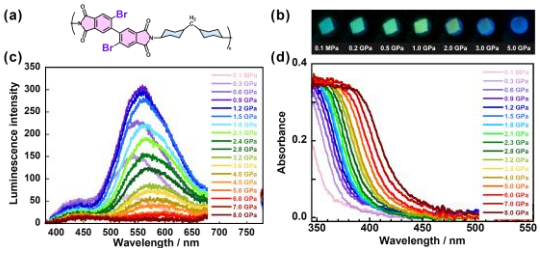

Fig. 1 (a) Chemical structure of DBr-PI. **(b)** Photographs of DBr-PI under UV irradiation. Pressure dependence of **(c)** luminescence spectra (λ_{ex} = 365 nm) and **(d)** absorption spectra for DBr-PI.

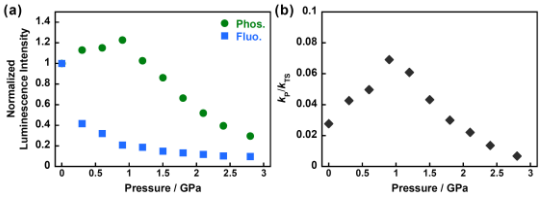

Fig. 2 Pressure dependence of **(a)** luminescence intensity divided by absorbance and **(b)** rate constant ratio (k_P/k_{TS}) for DBr-PI.

Reference: [1] K. Kanosue, et al., *Macromolecules*, **49**, 1848 (2016).[2] K. Kanosue, et al., *Mater. Chem. Front.*, **3**, 39 (2019). [3] K. Takizawa, et al., *Macromolecules*, **45**, 4764 (2012). [4] E. Fujiwara, et al., *J. Phys. Chem. B*. **122**, 8985 (2018).