Pressure-induced Variations in Fluorescence Properties of Polyimide Films Displaying Excited-state Intramolecular Proton Transfer

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Polyimides (PI) are widely used as high-performance engineering plastics exhibiting high thermal stability and mechanical strength. We have recently developed semi-aliphatic PIs exhibiting bright red fluorescence with a very large Stokes shift via excited-state intramolecular proton transfer (ESIPT) [1], and their fluorescence properties are strongly influenced by the aggregation structures of PI chains.[2] In this study, the ESIPT fluorescence of a semi-aliphatic PI (3H-DC, Fig.1) film was analyzed by streak camera under very high pressure up to 8 GPa.

To apply pressure up to 8 GPa, a 3H-DC film was loaded into a diamond anvil cell. The PI showed an enol emission (400 nm) as well as a keto emission (570 nm) arose by ESIPT (Fig. 2a). In addition, a fluorescence from aggregated-chains excited via the Förster resonance energy transfer (FRET) was observed around 500 nm, which is competitive with the ESIPT process.[1] Based on the analysis of streak images, the fluorescence intensity ratio of the emission from the aggregated form and the keto emission was estimated at each pressure. As shown in Fig. 2b, the former was gradually increased by applying pressure up to 4 GPa because of the enhanced FRET efficiency induced by reduction of inter-molecular chain distances. Consequently, the emission from the aggregated form of PI chain via FRET process became more dominant at elevated pressures compared with that of the ESIPT process which gives a large Stokes shift keto emission.

Fig. 1. Molecular structure of PIs.

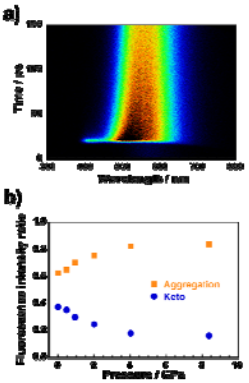

Fig. 2. (a) Streak image of 3H-DC at atmospheric pressure. (b) Pressure dependence of the fluorescence intensity ratio.

Keywords: *polyimide, excited state intramolecular proton transfer, ultrafast time-resolved spectroscopy, very high pressure*

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