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Analysis of Fluorescence Properties of Polyimide Films Displaying Excited-state Intramolecular Proton Transfer under Very High Pressure

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[Introduction] Polyimides (PI) are known as high-performance engineering plastics exhibiting high thermal and physical stabilities. Recently, fluorescent emission properties of PIs have been widely studied.[1,2] Semi-aliphatic PIs consisting of pyromellitic dianhydride having a −OH group at the benzene ring (3HPMDA) and alicyclic diamines exhibited a very large Stokes shift fluorescence via excited-state intramolecular proton transfer (ESIPT) mechanism where the proton at the −OH group is transferred from the enol to the keto form. It is known that the aggregation structures significantly affect the optical properties of PIs. Recently, we have reported the pressure-induced variations in fluorescence properties caused by reduction in inter-chain distances under high pressure.[3] In this study, the ESIPT fluorescence property of a PI film was investigated by using streak camera measurement under very high pressure up to 8 GPa.

[Experimental] The molecular structure of a semi-aliphatic PI prepared from 3HPMDA and alicyclic diamines (3H-DC) is shown in **Fig. 1**. To generate pressure up to 8 GPa, the PI film was loaded into a diamond anvil cell (DAC, Syntech Co. Ltd.) (**Fig. 2**). The standard ruby fluorescence technique was used to determine the pressure inside the sample space.[4] The streak images of the PI film were measured with a streak camera system (Hamamatsu, C5680).

[Results & Discussion] The streak image of 3H-DC excited by 343 nm laser at atmospheric pressure is shown in **Fig. 3**. The PI exhibited an enol emission around 400 nm and a keto emission around 570 nm generated via ESIPT. In addition, a fluorescence observed around 500 nm is attributable to that from the aggregated-chains excited via the Förster resonance energy transfer (FRET) process, which is competitive with the ESIPT process.[2] The fluorescence intensity decay curves observed in the ranges of 400-420 nm and 570-590 nm were analyzed by two exponential decay components in each wavelength region. In addition, the fluorescence intensity ratio of each component (A_n) was defined as $A_n = I_n/\Sigma I_n$ (I_n: relative intensity, ΣI_n: the summation of two components in one wavelength region) at each pressure. The decay components in the former wavelength region are assignable to the ESIPT and the FRET process (*comp.1*) and the enol emission (*comp.2*), respectively. On the other hand, the decay components in the latter wavelength region are attributable to the emission from aggregated forms (*comp.3*) and the keto emission (*comp.4*), respectively. As shown in **Fig. 4**, A_1 is almost constant in all the pressure range. On the other hand, A_3 is gradually increased and A_4 is decreased with increasing the pressure up to 4 GPa. These results are explainable by an increase in the efficiency of FRET due to the reduction of inter-molecular chain distances. In conclusion, the FRET process, which generates the fluorescence of aggregated form of PI chains, became dominant compared with the ESIPT process which gives the keto emission at elevated pressures.

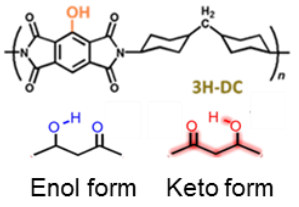

Fig. 1 Molecular structure of 3H-DC.

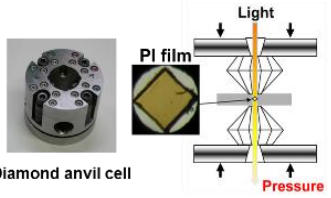

Fig. 2 Photo images and cross-sectional drawing of diamond anvil cell (DAC).

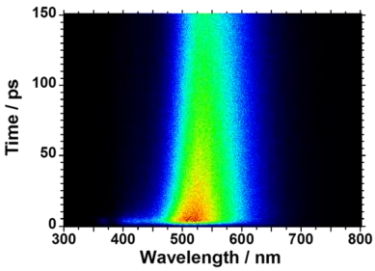

Fig. 3 Streak image of 3H-DC at atmospheric pressure.

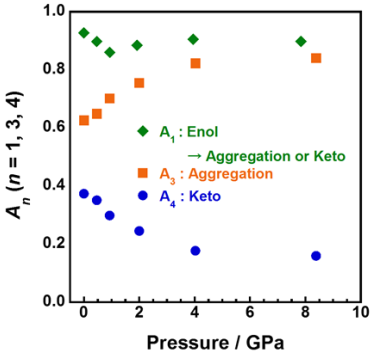

Fig. 4 Pressure dependence of A_n of components 1, 3 and 4.

Reference : [1] J. Wakita, et al., *J. Phys. Chem. B*, **19**, 15212 (2009). [2] K. Kanosue, et al., *Macromolecules*, **48**, 1777 (2015). ibid. 49, 1848 (2016). [3] K. Takizawa, et al., *Macromolecules*, **47**, 3951 (2014). [4] G. J. Piermarini, et al., *J. Appl. Phys.*, **44**, 5377 (1973).