The effect of intermolecular interactions on optical properties of highly Fluorescent Fluorinated Polyimides

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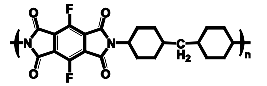
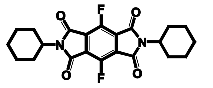
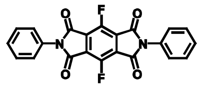
[Introduction] Polyimides (PIs) are recently applied to optical waveguides and components due to their high thermal stability, high transparency and the controllability in refractive indices and birefringence. We have been investigating the optical absorption and fluorescence properties of PIs. In general, two types of electron transitions are observed for PIs. The first one is the locally excited (abbreviated as LE) transition that occurs between the molecular orbitals (MOs) located at the dianhydride moieties. The second one is the charge transfer (abbreviated as CT) transitions occurring between the MOs located at the electron-donating diamine and the electron-accepting dianhydride moieties. Wholly aromatic PIs generally exhibit very low efficiency in fluorescence emission due to the strong intra- and inter-molecular CT interactions. Recently, we have developed 'highly fluorescent PIs' by using alicyclic diamines. They emit blue, green and red fluorescence[1]. The red fluorescence attributable to the LE and CT transitions are observed for a thin film of P2FDA/DCHM (scheme1-a) (Fig.1), but these transitions cannot be reproduced by quantum chemical (TD-DFT) calculations of P2FDA/CHA (scheme1-b). This suggests that these transitions might not originate from a single polymer chain. In this study, the absorption and fluorescence spectra of P2FDA/CHA under atmospheric pressure and the absorption spectra of P2FDA/DCHM under high hydrostatic pressure (up to 400 MPa) are examined to investigate the effect of intermolecular interactions on the photophysical processes in P2FDA/DCHM.



a : P2FDA/DCHM



b : P2FDA/CHA



c : P2FDA/2Ph

Scheme1 Structures of PI and model compound

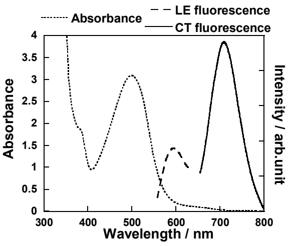


Fig.1 UV-vis and fluorescence spectra of P2FDA/DCHM thin film

[Experimental] P2FDA/CHA was prepared by the thermal imidization of the corresponding amic acid. The product was characterized by solid-state ^{19}F NMR and FT-IR. P2FDA/DCHM PI film was prepared by thermal imidization of poly(amic acid) silyl eter (PASE) obtained by *in situ* silyation method[2].

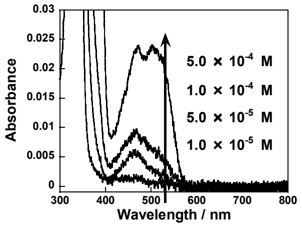


Fig.2 UV-vis and fluorescence spectra of P2FDA/CHA chloroform solution

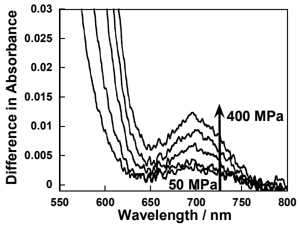


Fig.3 Pressure dependence of absorption difference spectra of P2FDA/DCHM thin film (7.7 μm thick)

[Results and Discussion] The characteristics of the concentration dependences of absorption spectra for P2FDA/CHA solution are as follows. (i) The absorption bands at 400~500 nm (band I) are observed only over 5×10^{-5} M. (ii) Significant concentration dependence is observed in the spectral shapes (Fig.2), which suggests that band I do not originate from a single molecule of P2FDA/CHA. In contrast, the band I is well reproduced by TD-DFT for face-to-face dimer of P2FDA/2Ph (scheme1-c), which demonstrates that the band I originates from the aggregates of P2FDA moieties. In addition, the fluorescence peaks are observed around 500~600 nm with the excitation at 400~500 nm. The accordance of these absorption and fluorescence peaks with those of P2FDA/DCHM suggests that the LE transition of P2FDA/DCHM originates from polymer aggregates. Besides, the CT absorption observed for P2FDA/DCHM thin film increases with increasing the pressure (Fig.3). We have reported that the intermolecular CT transition was enhanced due to the enhancement of the CT interaction with applying high pressure, which is due to the decrease in intermolecular distance[3]. Hence, the CT absorption for P2FDA/DCHM can be assigned to the intermolecular CT transition, which suggests that the CT absorption and the corresponding fluorescence originate from polymer aggregates of P2FDA/DCHM. These results indicate that the optical absorption and fluorescence originate, not from a single repeating unit of P2FDA/DCHM, but from the P2FDA aggregates. In conclusion, the intermolecular interactions represented by the formation of aggregate pose significant effects on the absorption and fluorescence wavelengths. [1] Y. Urano, Y. Oishi, S. Ando, *Polym. Prep. Jpn.*, **52**, 3480 (2003). [2] Y. Oishi, K. Ogasawara, H. Hirahara, K. Mori, *J. Photopolym. Sci. Technol.*, **14**, 37 (2001). [3] J.Wakita, Y.Urano, K.Uetake, S.Ando.,*Polym. Prep. Jpn.*, **54**(1), 1333 (2005).