Highly Fluorescent Polyimides Exhibiting Large Stokes Shifts Based on Excited-State Intramolecular Proton Transfer

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For the development of colorless and long-wavelength fluorescent polyimides (PIs) based on excited-state intramolecular proton transfer (ESIPT), three kinds of semi-aliphatic PIs (Fig. 1) were prepared by using a pyromellitic dianhydride having an −OH group at the benzene ring and alicyclic diamines with/without side chains, and their fluorescence properties were examined in the solid state. In the UV/vis absorption spectra (Fig. 2), all the films demonstrated intense absorption peaks at around 360 nm, which are attributable to local excitation (LE) absorptions occurring at the dianhydride moiety of PI chains. In addition, another absorption bands are observed at around 460 nm, which originate from aggregation forms of PI chains. The intensities of these bands were significantly reduced by introducing steric side chains (−CH_3 and –CF_3) to the diamine moieties. In the fluorescence spectra (Fig. 2) when the main absorption bands were excited, intense fluorescence peaks with extraordinary large Stokes shift (ν = 10829, 11083 cm^{-1}, respectively) were observed for 3H-DC and 3H-6F at around 590 nm. These peaks are readily attributable to the emissions from the proton transferred forms generated via ESIPT upon excitation [1]. In contrast, the emission peak from 3H-DM demonstrated a smaller Stokes shift, which is attributable to the emission from its aggregation form. This could be due to the difference in the intermolecular hydrogen bonding structure in the solid films. In conclusion, the introduction of ESIPT structures to the main chains of PIs and the control of aggregation states by use of steric hindrances at the diamine moieties are effective way to synthesize novel colorless and long-wavelength fluorescent PIs.

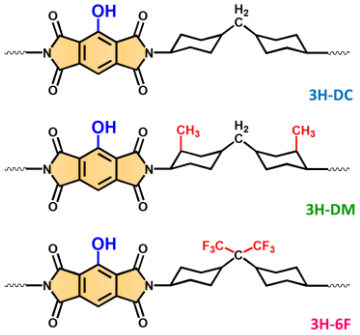

Fig. 1. Chemical structures of a series of fluorescent PIs.

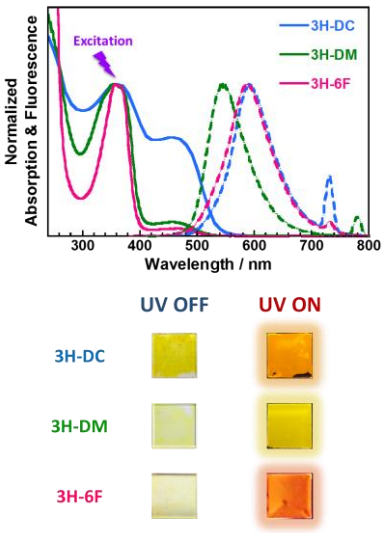

Fig. 2. Absorption (solid) and fluorescence (dashed) spectra of PI films (Fig. 1) and their photo images under white-light and UV (λ = 365 nm) irradiation.

References

[1] Wakita, J., Inoue, S., Kawanishi, N., Ando, S., *Macromolecules*, **2010**, *43*, 3594-3605.