An Imide Compound and Polyimides Forming Multiple Intramolecular Hydrogen Bonds and Exhibiting Large Stokes-shifted Yellow Fluorescence

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INTRODUCTION

Polyimides (PIs) have attracted broad attention as the representative super-engineering plastics because of their excellent comprehensive properties. Among them, highly fluorescent PIs have been reported [1], especially PIs showing large Stokes-shifted fluorescence via excited-state intramolecular proton transfer (ESIPT)[2] are promising materials for wavelength converting applications. However, the PIs exhibiting ESIPT frequently form aggregates in the solid state due to the rigid dianhydride moieties[3]. In this study, a flexible dianhydride with dual hydrogen bonds and ESIPT ability, 2,2'-dihydroxy-3,3',4,4'-benzophenonetetra-carboxylic dianhydride (DHBA) was synthesized, and the optical properties of the DHBA-based model compound (DH-MC, **Fig. 1**) and PIs (DH-PI, **Fig. 2**) were reported.

EXPERIMENTAL

All PI films were prepared by spin-coating of the poly(amic acid) solution (15 wt% in DMAc) followed by thermal imidization at 220°C under nitrogen flow. UV/vis absorption spectra, fluorescent excitation/emission spectra, and photoluminescent quantum yields of the PI films were measured with a Hitachi U-3500 spectrophotometer, Hitachi F-4500 fluorescence spectrometer, and a calibrated integrating sphere (HAMAMATSU C9920), respectively.

RESULTS AND DISCUSSION

DH-MC has multiple proton donors and proton acceptors. Therefore, it possibly forms three H-bonding structures, as shown in **Fig. 1**. DFT calculation predicted that MC-1 is the most stable structure, and this is consistent with the results from FT-IR and single-crystalline X-ray analysis. DH-MC (powder) and DH-PI film exhibited a large Stokes-shifted (~11000cm^{-1}) yellow fluorescence via the ESIPT process. Besides, they show intense yellowish coloration due to the formation of anionic species. In the wavelength converting spectrum, DH-PI absorbs UV and blue lights with enhancing yellow light (**Fig. 3**). By copolymerization of DHBA (3 mol%) with 4,4'-oxydiphthalic anhydride (ODPA), a colorless copolyimide (CoPI-0.03, **Fig. 2**) was successfully obtained, and it exhibited bright yellow fluorescence. As shown in **Fig. 4**, this CoPI film absorbs only UV light and enhances yellow light, which is suitable for solar spectral convertor applications.

Keywords: Polyimide, ESIPT, Stokes shift, Spectral conversion

References

[1] J. Wakita, S. Ando, et al., *J. Phys. Chem. B,* **113**, 15212-15224 (2009). [2] J. Wakita, S. Ando, et al., *Macromolecules*, **43**, 3594-3605 (2010). [3] K. Kanosue, S. Ando, et al., *Macromolecules*, **49**, 1848-1857 (2016).

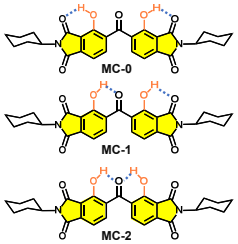

Fig. 1. Possible H-bonding structures of DH-MC.

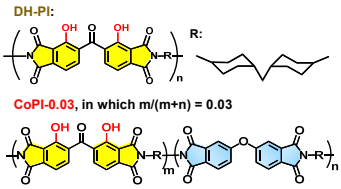

Fig. 2. Chemical structures of DH-PI and CoPI-0.03.

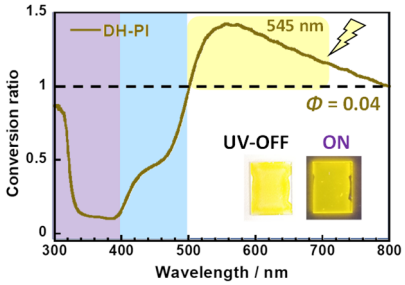

Fig. 3. Wavelength converting spectrum of DH-PI. (inserted: Photos of DH-PI under white light and UV irradiation at 365 nm).

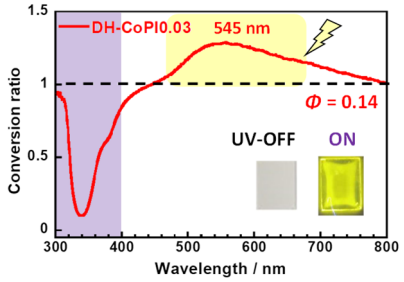

Fig. 4. Wavelength converting spectrum of CoPI-0.03. (Inserted: Photos of DH-PI under white light and UV irradiation 365 nm).