Development of Highly Transparent Polyimide Copolymers Displaying Very Large Stokes Shifted ESIPT Fluorescence for Solar Spectral Converter

°Naiqiang Liang, Mayuko Nara, Eisuke Fujiwara, Ryohei Ishige and Shinji Ando
Department of Chemical Science and Engineering, Tokyo Institute of Technology

Introduction

Polyimide (PI) is a kind of polymer with excellent comprehensive properties. In particular, a group of semi-aromatic PIs can exhibit strong fluorescence due to the suppression of charge transfer (CT) from the diamine to dianhydrid moieties.[1,2] Our group has reported PI film using 1-hydroxy pyromellitic dianhydride (PHDA, **Fig. 1**), which shows a very large Stokes shifted photoluminescence based on excited-state intramolecular proton transfer (ESIPT) in the PHDA unit. The PHDA-based PI is one of the promising materials for solar spectral converters used in extreme environments.[3] However, due to the CT absorption induced by the strong aggregation of the PHDA unit, this PI film shows yellowish color, as well as low fluorescent efficiency, which is not desirable for practical applications. To solve this problem, we designed a series of PI copolymers based on PHDA and 4,4'-oxydiphthalic anhydride (ODPA) as displayed in **Fig. 2**, and investigated their photophysical behaviors.

Experiment

PI films were prepared by spin coating of the poly(amic acid) solution (15 wt% in DMAc) on silica substrates and subsequent thermal imidization at 220 °C under nitrogen atmosphere.

Results and Discussion

The fluorescence spectra and photos of PI copolymer films are presented in **Fig. 3**. The relatively weak fluorescent peak at 405 nm is assignable to the ODPA unit, and the strongest fluorescent peak at 595 nm is assignable to the ESIPT emission from the keto form of PHDA unit. All copolymer films were colorlessness with transparency, which indicates the suppression of molecular aggregation. Although the molar ratio of PHDA units in these copolymer films is only several mol%, all copolymer films still retain reddish fluorescence with large Storks shifts, which proves that efficient energy transfer occurred from the large excess of ODPA unit to the small amount of PHDA unit. Among the series of PI copolymer films, a PI with 3 mol% of PHDA is most suitable for solar spectral converter because of the strong ESIPT fluorescence and high transparency due to comparably weak aggregation. The photoluminescent efficiency of this film reaches 0.2, which was ca. 3 times higher than the PHDA/DCHM PI homopolymer (0.068). We demonstrated that efficient energy transfer is beneficial to develop functional fluorescent materials.

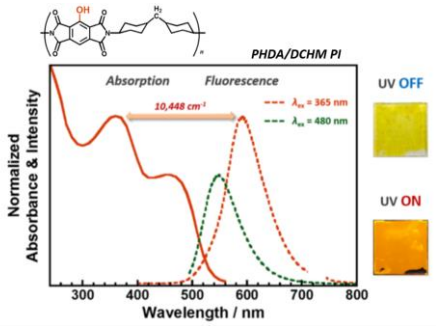

Fig. 1 Photograph and excitation/emission spectra of PHDA/DCHM PI homopolymer

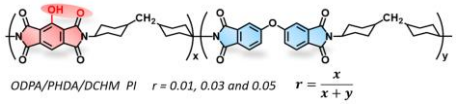

Fig. 2 ODPA/PHDA/DCHM PI copolymers

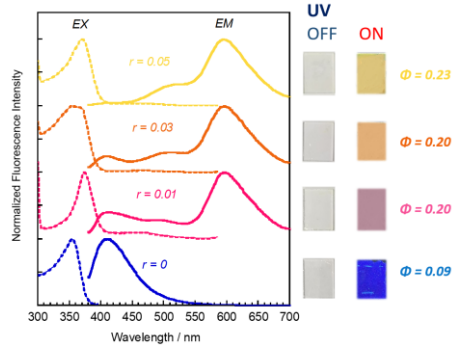

Fig. 3 Fluorescence spectra and photographs of ODPA/PHDA/DCHM PI copolymers.

References

1) J. Wakita, H. Sekino, K. Sakai, Y. Urano, S. Ando, *J. Phys. Chem. B*, **46**, 113, 2009
2) J. Wakita, S. Inoue, N. Kawanishi, S. Ando, *Macromolecules,* **8**, 43, 2010.
3) K. Kanosue, V. Gulbinas, S. Ando, *Macromolecules,* **5**, 49, 2016.