Highly Transparent Fluorescence Polyimide Copolymers with Large Stokes Shifted Photoluminescence Based on Excited State Intramolecular Proton Transfer

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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.[1,2] For example, 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 an extreme environment.[3] However, due to the charge-transfer (CT) absorption induced by the strong aggregation of the PHDA unit, this PI film shows yellowish color, as well as low fluorescent efficiency, which may becomes an obstacle to practical applications. To solve this problem, we have synthesized a series of PI copolymers based on PHDA and 4,4'-oxydiphthalic anhydride (ODPA, Fig. 2), as displayed in **Fig. 2**, and investigated the photophysical behavior of these copolymer films.

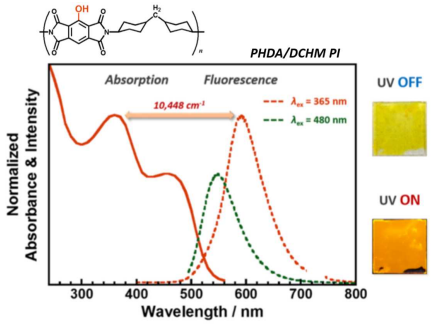

Fig. 1 Photograph and excitation/emission spectra of PHDA/DCHM PI homopolymer

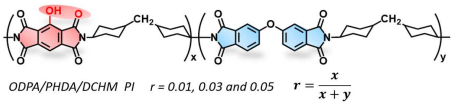

Fig. 2 ODPA/PHDA/DCHM PI copolymers

Results and Discussion:

The fluorescence spectra and photographs 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 PHDA unit. All copolymer films exhibit colorlessness and high transparency, which clearly indicates the molecular aggregation is suppressed. Although the molar ratio of PHDA unit 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 converter because of the strong ESIPT fluorescence and comparably weak aggregation. The photoluminescent efficiency of this film reaches to 0.2, which was ca. 3 times higher than the PHDA/DCHM PI homopolymer (0.068). These highly transparent and large Stokes shifted photoluminescent films have great potential for solar spectral conversion.

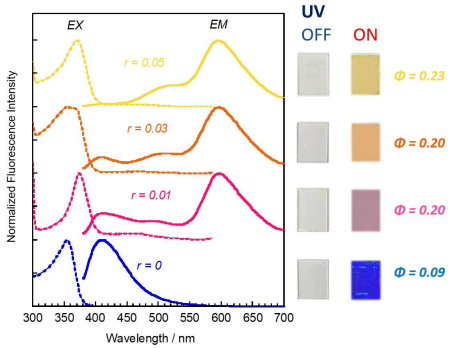

Fig. 3 Fluorescence spectra and photographs of ODPA/PHDA/DCHM PI copolymers.

References:

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