Highly Transparent Polyimide Copolymer Exhibiting Orange Photoluminescence Based on Excited State Intramolecular Proton Transfer

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Polyimides (PIs) is a kind of engineering plastic with excellent comprehensive performance. Among them, highly fluorescent PIs have been reported (Figure 1) [1]. Compared with other photoluminescent materials, fluorescent PIs have many advantages like excellent thermal stability, exceptional chemical stability, superb mechanical strength, and structural diversity.

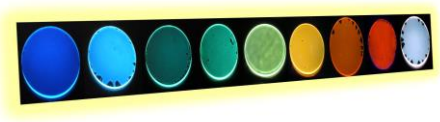

Figure 1. Highly fluorescence PI film.

Fluorescent PIs of the early stage can show different fluorescence colors. However, their Stokes shifts, which means the difference between the emission and excitation wavelengths, were not large enough. In order to get PI films with very large Stokes shift, PI based on excited state intramolecular proton transfer (ESIPT) strategy have been developed.[2] ESIPT is a photophysical process, as shown in Figure 2. ESIPT molecule includes an intramolecular hydrogen bond. Before photo-excitation, a molecule exists as 'enol form'. After excitation, due to the increasing acidity of proton donor and increasing basicity of proton acceptor, intramolecular proton transfer occurs, then the whole molecule transforms to 'keto form'. After emission, the reverse proton transfer occurs, and the molecule goes back to the original enol form. The biggest advantage of ESIPT photophysical process is its extremely large Stokes shift.

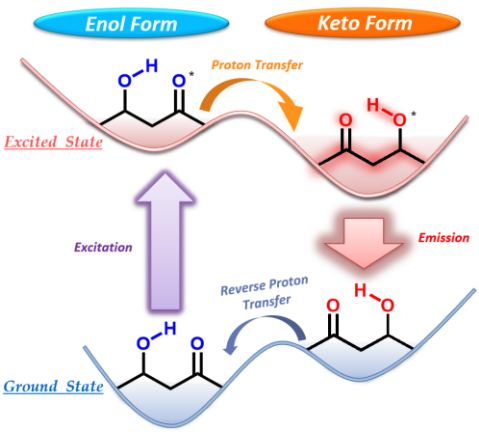

Figure 2. ESIPT photophysical process.

Our group has reported PIs based on 1-hydroxy pyromellitic dianhydride (PHDA) which can exhibit very large Stokes shifted orange emission by ESIPT.[3] (Figure 3) However, due to the highly planar structure, PHDA based homo-PIs form strong aggregation, which causes intense yellowish color with green emission, as well as reduced photoluminescence efficiency, which makes real application to solar converter difficult.

Copolymerization is a good way to reduce the aggregation of monomeric components, and a new type of PHDA based PI copolymer (co-PI) was synthesized by copolymerization with 4,4'-oxydiphthalic anhydride (ODPA). In this co-PI, PHDA content was only 3 mol%. Although the ODPA moiety itself emits blue fluorescence, the co-PI film still displays long wavelength bright orange fluorescence due to the Förster resonance energy transfer (FRET) from the ODPA unit to PHDA unit in the main chains. Moreover, owing to the homogeneous dispersion of PHDA moiety, aggregation formation was strongly suppressed, which resulted in a colorless, totally transparent, and highly fluorescent co-PI film with very large Stokes shift (>12000 cm^{-1}). These results indicate that PHDA based co-PIs has a great potential for solar spectral converter.

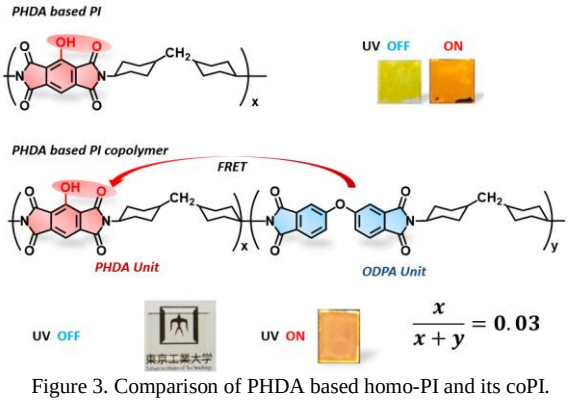

Figure 3. Comparison of PHDA based homo-PI and its coPI.

References:

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