Highly Transparent Polyimide Copolymers Exhibiting Orange Excited State Intramolecular Proton Transfer Photoluminescence

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I. Introduction

Fluorescence polyimide is a kind of photoluminescent materials which has excellent comprehensive properties. Compare with other photoluminescent materials, fluorescence PI has many advantages like excellent thermal stability, exceptional chemical stability, good mechanical strength, and structure diversity. Due to the above reason, fluorescence PI has great potential to be used as the solar converter.

Our group has developed a series of semi-aromatic fluorescence PI with relatively high quantum yield. [1] However, for these traditional PIs, their Stokes shift, which means the difference between exciting wavelength and emission wavelength, it's not large enough. For real application, large Stokes shift PI is preferable. So, PI based on excited state intramolecular proton transfer (ESIPT) photophysical process have been developed.[2] ESIPT is a photophysical process, as shown in Figure 1, ESIPT molecule contains an intramolecular hydrogen bond. Before excitation, molecular at 'enol form'. However, after excitation, due to the increasing acidity of proton donor and increasing basicity of proton acceptor, intramolecular proton transfer happens, molecular transfer to 'keto form'. After emission, molecular go back to 'enol form'. The biggest advantage of ESIPT is that it can show a large Stokes shift.

Our group has reported 1-hydroxy pyromellitic dianhydride (PHDA) based homo PI which can show very large Stokes shift orange emission.[3] However, due to the highly planar structure, PHDA is easy to be aggregated, which result in yellow color, less Stokes shift green emission, and low quantum yield. In this experiment, in order to get PHDA based PI with low aggregation, a new kind of PHDA based PI copolymer was synthesized, as shown in Figure 2.

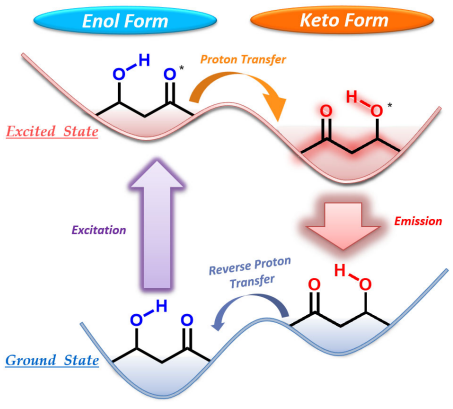

Figure 1 ESIPT Photophysical Process

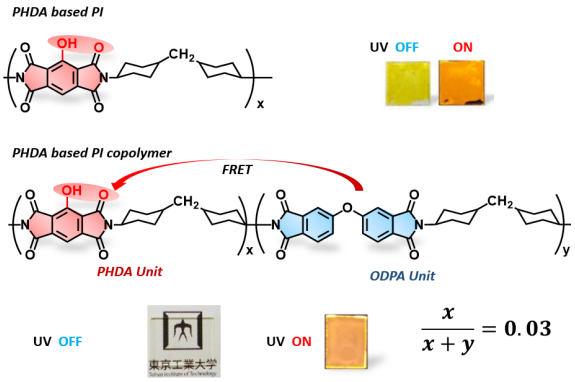

Figure 2 Comparison of PHDA based homo-PI and its coPI.

II. Results and Discussion

In this experiment, PHDA based PI copolymer was synthesized. In this copolymer, the PHDA unit only takes 3 mol%, while 4,4'-oxydiphthalic anhydride (ODPA) unit take 97 mol%. Furthermore, the ODPA unit has blue fluorescence. However, due to the energy transfer from the ODPA unit, the whole membrane still mainly shown large Stokes shift orange emission. (as indicated in Figure 2) In the same way, due to the homogeneous distribution of PHDA unit, this co-PI shown high transparency which comes from suppressed aggregation. These data demonstrated that PHDA based co-PIs can be a promising material for solar converter film.

References

[1] J. Wakita, H. Sekino, K. Sakai, Y. Urano, S. *The Journal of Physical Chemistry B*, 46, 113, 2009.
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[3] K. Kanosue, R. Augulis, D. Peckus, R. Karpicz, T. Tamulevicius, S. Tamulevicius, V. Gulbinas, S. Ando, *Macromolecules*, 5, 49, 2016.