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Highly Transparent and Orange Fluorescent Polyimide Copolymers based on Excited Intramolecular Proton Transfer in the Main Chain

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Introduction:

Polyimide (PI) is a super-engineering plastic with excellent thermal stability, chemical stability, and mechanical strength. Furthermore, PIs which emit different fluorescence colors have been reported, and fluorescent PI has a great potential to be used as solar spectral converter which converts UV light to useful visible light.[1]For conventional fluorescent PIs, the Stokes shifts (difference of wavelengths between emission and excitation) are not sufficiently large for the applications, such as solar converters, which requires a large Stoke shift and high transparency in the visible region. In order to develop PIs with large Stokes shifts, our group has reported a series of fluorescent PIs based on excited state intramolecular proton transfer (ESIPT). [2] ESIPT is a particular photophysical process, which involves proton transfer in the excited state, as shown in Fig. 1. ESIPT fluorescence displays a very large Stokes shift because an excited enol form is readily converted into a keto form which emit red-shifted fluorescence. We have reported PIs based on 1-hydroxy pyromellitic dianhydride (PHDA) which exhibited a very large Stokes-shift fluorescence of orange color. [3] However, due to the highly planar structure, PHDA unit is very easily aggregated in the solid state, resulting in a strong yellowish color (i.e. aggregation absorption) and green emission with a smaller Stokes shift (i.e. aggregation emission), which is a disadvantage for practical application for the solar converters.

In order to reduce the formation of aggregation, a series of novel PHDA based copolyimides (co-PIs) with 4,4'-oxydiphthalic anhydride (ODPA) were prepared. ODPA unit exhibits blue fluorescence, while the PHDA unit exhibits red ESIPT fluorescence. Although PHDA unit was incorporated into the co-PIs by only several mol%, the resultant co-PI films still maintain reddish color fluorescence. This fact clearly indicates that efficient energy transfer occurred from the ODPA to the PHDA unit. Furthermore, the fluorescence color can be controlled from pink to yellow by varying the copolymerization ratio. Finally, we have successfully developed highly transparent and large Stokes shifted co-PI material.

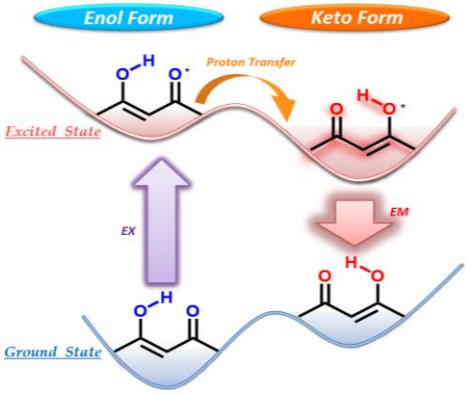

Fig. 1 ESIPT photophysical process

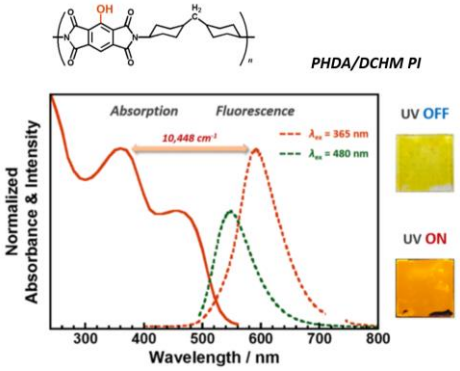

Fig. 2 Phogograph and excitation/emission spectra of PHDA/DCHM PI

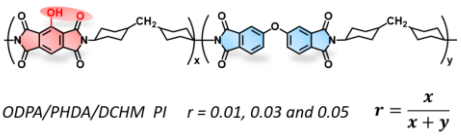

Fig. 3 Chemical structure of ODPA/PHDA/DCHM PI copolymer

Experiment:

All PI films with different PHDA ratios were prepared by spin coating of poly(amic acid) solutions (20 wt% in DMAc) followed by thermal imidization at 210 °C under nitrogen. UV/vis absorption spectra, fluorescent excitation/emission spectra, and relative photo-luminescent quantum yields of PI films were measured by U-3500 spectrophotometer (Hitachi Hi-Technologies), F-4500 fluorescence spectrometer (Hitachi Hi-Technologies), and calibrated integrating sphere (HAMAMATSU C9920), respectively.

Results & Discussion:

Fig. 4 shows the fluorescence spectra and photographs of ODPA/PHDA/DCHM co-PI films. Relatively weak blue fluorescence at 405 nm can be observed, which is attributable to the fluorescence from the ODPA unit in the main chain. A strong fluorescence peak observed at 595 nm is assignable to the ESIPT fluorescence from the PHDA unit. Moreover, a fluorescence from the aggregation at 530 nm can also be observed. From the photograph image, it can be identified that all the co-PI membranes are highly transparent. Furthermore, with increasing PHDA concentration, polymer fluorescence changed from pink to yellow.

In order to evaluate the degree of aggregation formation, relative fluorescence intensity of the aggregation fluorescence to the ESIPT fluorescence intensity was shown in Fig. 5. Obviously, at higher PHDA copolymerization ratio, aggregation fluorescence is increased. It is reasonable that at higher PHDA copolymerization ratio, the probability of aggregation form becomes higher than smaller ratios.

Owing to the different relative intensities of the fluorescence from ODPA unit (blue color), aggregation (green color) and ESIPT (red color), the total emission colors of these co-PIs change with the copolymerization ratio. As shown in Fig. 6, while the PHDA copolymerization ratio is low (0.01), the co-PI film displayed pink color fluorescence, which derives from the mixture of blue and red fluorescence. With increasing the PHDA copolymerization ratio to 0.03, both ESIPT and aggregation fluorescence are enhanced, and the color of co-PI gradually changed to orange. At a high PHDA copolymerization ratio (0.05), the color became more yellowish because the aggregation fluorescence becomes dominant against the ESIPT fluorescence. These results prove that the emission color can be finely controlled by changing the copolymerization ratio.

Among the series co-PIs based on PHDA/ODPA units, copolymerization ratio of 0.03 is preferable because of relatively strong ESIPT fluorescence intensity and comparably weak aggregation fluorescence. The photoluminescent quantum yield of this film reached to 0.2, which is three times higher than the PHDA/DCHM homopolymer (0.068) [3]. By the simple copolymerization method, we have obtained highly transparent co-PI films exhibiting strong ESIPT fluorescence. These findings indicate that the PHDA based ESIPT co-PIs are promising and good candidates for solar spectral converter in the near future.

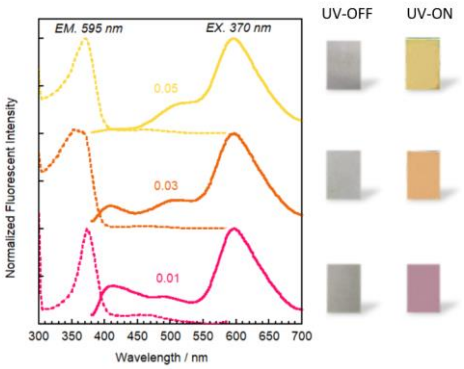

Fig. 4 Fluorescence spectra and phogographs of ODPA/PHDA/DCHM co-PIs.

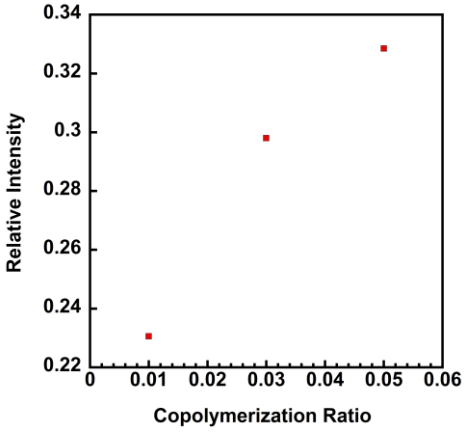

Fig. 5 Relationship between relative intensity of aggregation fluorescence and copolymerization ratio of the co-PIs.

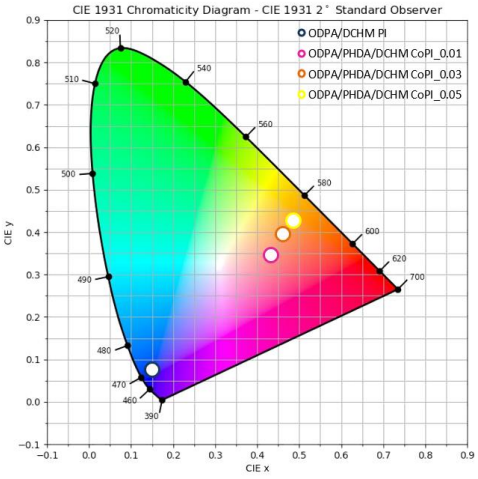

Fig. 6 CIE coordinates of homo- and co-PIs with different PHDA copolymerization ratio.

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, R. Augulis, D. Peckus, R. Karpicz, T. Tamulevicius, S. Tamulevicius, V. Gulbinas, S. Ando, *Macromolecules*, **5**, 49, 2016.