# Highly Transparent and Large Stokes Shift Orange Fluorescent Polyimide Copolymers based on Excited Intramolecular Proton Transfer

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Polyimide (PI) is a kind of polymer material which shows excellent comprehensive properties. Moreover, our group has reported several kinds of fluorescent PIs based on excited-state intramolecular proton transfer (ESIPT). In particular, semi-aliphatic PIs derived from 1-hydroxy pyromellitic dianhydride (PHDA) showed bright photoluminescence with a very large Stokes shift (the difference between the excitation and emission wavelengths) (**Fig. 1**).[1,2] These PI films have great potential to be used for solar converter, which can convert UV light to long-wavelength visible light.[3] However, PHDA-based PI film also face problems: 1) The films show coloration due to formation of aggregated forms. 2) the fluorescence efficiency is relatively low due to energy transfer from the enol form to the aggregated form, 3) the synthesis of ESIPT monomer PHDA needs several steps. To dissolve this problem, we have synthesized 4,4'-oxydiphthalic anhydride (ODPA)-based PI copolymers, as shown in **Fig. 2**. In this copolymer, the ODPA unit emits blue fluorescence, and the PHDA unit shows red ESIPT fluorescence, together with green fluorescence from the aggregated forms. By keeping PHDA unit at a low ratio, aggregation formation can be suppressed, as well as reducing the PHDA content. Furthermore, due to energy transfer from ODPA unit to PHDA unit, large Stokes shift emission can be expected.

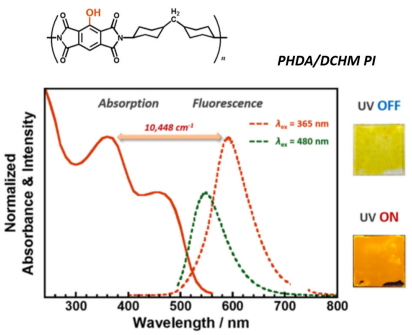
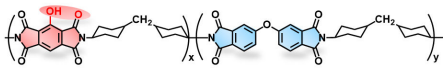



**Fig. 1** Phogograph and excitation / emission spectra of PHDA/DCHM PI.



ODPA/PHDA/DCHM PI r = 0.01, 0.03 and 0.05 $r = \frac{x}{x+y}$

**Fig. 2** Chemical structure of ODPA/PHDA/DCHM PI copolymer.

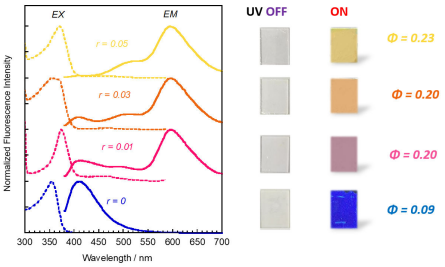



**Fig. 3** Fluorescence spectra and phogographs of ODPA/PHDA/DCHM co-PIs

In this study, we tried to prepare PI copolymers with different PHDA ratios (*r = 0.01, 0.03, and 0.05*). All the copolymer films were highly transparent and showed obvious fluorescent emission having three components: 1) blue fluorescence from ODPA unit. 2) green fluorescence from aggregated forms, and 3) red fluorescence from PHDA via ESIPT. Furthermore, Because of the energy transfer from ODPA to PHDA units, all the film showed obvious ESIPT fluorescence as we expected. Interestingly, due to the relative variations in fluorescence intensities among different emissive components, the fluorescence colors of the PI copolymer films were finely controlled from pink through orange to red, as shown in **Fig. 3**. These facts demonstrates that the PI copolymers are promising for solar spectral convertors.

[1] K. Kanosue, R. Augulis, D. Peckus, R. Karpicz, T. Tamulevicius, S. Tamulevicius, V. Gulbinas, S. Ando, *Macromolecules*, **5**, 49, 2016.

[2] J. Wakita, S. Inoue, N. Kawanishi, S. Ando, *Macromolecules*, **8**, 43, 2010.

[3] J. Wakita, H. Sekino, K. Sakai, Y. Urano, S. Ando, *J. Phys. Chem. B,* **46,** 113, 2009.

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