

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

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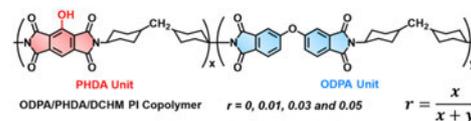
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【Abstract】

Our group has reported highly fluorescent (FL) polyimide (PI) based on 1-hydroxy pyromellitic dianhydride (PHDA), which exhibits a large Stokes shifted photoluminescence by excited-state intramolecular proton transfer (ESIPT). However, the ESIPT fluorescence is competing with the emission from aggregated form of PHDA unit. Thus, in this paper, we report a series of novel PI copolymers (co-PIs) based on 4,4'-oxydiphthalic anhydride (ODPA) and PHDA. Compared to the homopolymer, the co-PIs have higher transparency due to the suppression of PHDA unit aggregation. Moreover, with an increase of the PHDA unit concentration, the fluorescent color of these copolymers changed from pink to yellow through orange with increasing aggregation forms of PHDA unit, which can increase energy transfer efficiency. Finally, we demonstrated that a copolymer with the molar ratio of PHDA unit at 0.03 (3.0 mol%) exhibited high transparency, bright orange color fluorescence with a large Stokes shift (10220 cm^{-1}), as well as high quantum efficiency ($\Phi = 0.20$) when irradiated by UV light ($\lambda = 370\text{ nm}$). This is due to the ESIPT process after efficient energy transfer from ODPA unit to PHDA unit ($E_{\text{FRET}} = 0.52$). The molecular design based on copolymerization of FL-PIs with ESIPT moiety should be one of the promising strategies to fabricate solar converting films.

【Introduction】

Polyimide (PI) is a kind of polymer with excellent comprehensive properties [1]. Our group has reported a highly fluorescent PI based on 1-hydroxy pyromellitic dianhydride (PHDA) and 4,4'-diamino-dicyclohexylmethane (DCHM), which exhibits a large Stokes shifted photoluminescence from excited-state intramolecular proton transfer (ESIPT) [2]. Thus, this PI film can be a promising material for the solar converter application. However, due to the aggregated forms of the PHDA unit, this PI film shows a yellowish color, less Stokes-shifted fluorescence with green color, and low quantum efficiency, which are unfavorable for the solar converting applications. To suppress the formation of aggregates of the PHDA unit, we report a series of novel PI copolymers (co-PIs) based on 4,4'-oxydiphthalic anhydride (ODPA) and PHDA in this study. In these co-PIs, the mole ratio of PHDA unit against ODPA was kept at relatively small values (varying from 0.01 to 0.03), for efficient suppression of aggregation formation.



Scheme 1 ODPA/PHDA/DCHM PI Copolymer

Finally, all the photophysical properties of these co-PIs were discussed on the basis of static and time-resolved luminescent spectra measurements.

【Experimental】

The synthesis of PHDA dianhydride has been reported elsewhere [2]. All the PI films were prepared by the conventional two steps thermal imidization method from poly(amic acid) silyl ester (PASE) solution: the prepared PASE solution was spin-coated on a fused silica substrate, followed by drying at 70 °C for 1 h and subsequent thermal curing at 220 °C for 1.5 h. All the heating procedures were conducted under nitrogen flow, and the heating rate was set at 3.0 °C/min.

【Results and Discussion】

As stated above, the aggregation formation of PHDA unit is unfavorable, because it makes films yellowish color and reduces PL efficiency of the resultant PI films. In this study, to suppress the aggregated forms, a series of co-PIs, ODPA/PHDA/DCHM, was designed, in which the molar ratio of PHDA unit (r) was set from 0.01 to 0.05. **Fig. 1a** shows the UV/visible light absorption spectra and the photographic images of all co-PI films. As seen in the photographic images, all the co-PI films were colorless and highly transparent, which was also supported by the small absorbance in the visible region (400–800 nm). In these spectra, the absorption peaks can be separated into the band at 340 nm, which is assignable to the ODPA unit [3, 4] and that at 370 nm to the PHDA unit [1]. Thus, the absorption intensity at 370 nm gradually increased at higher PHDA concentrations.

Fig. 1b presents a magnified view of the absorption spectra normalized by film thickness to compare the absorption at 400–500 nm. Around 470 nm, a weak absorption was observed, which was assigned to the aggregated form of PHDA unit according to our previous report [2]. Thereby, it is reasonable that this intensity exhibited a positive

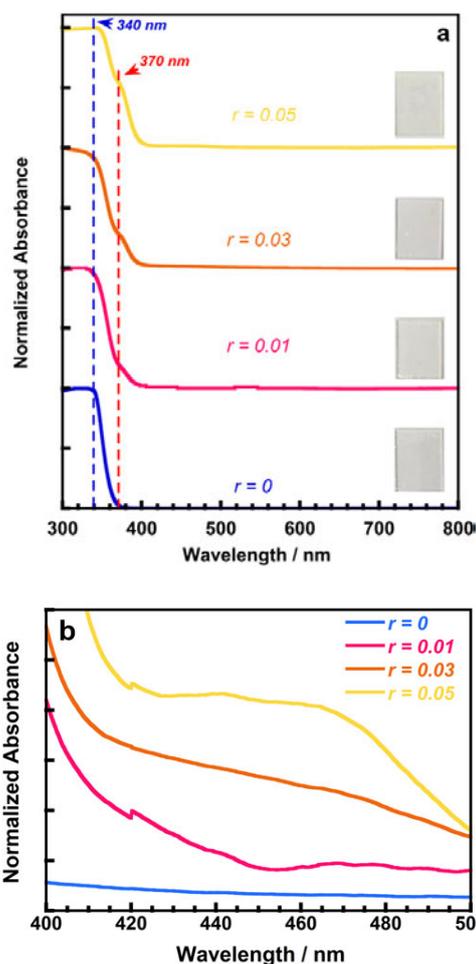


Fig. 1 (a) UV/Vis absorption spectra and photographic images of PI homopolymer and copolymers. (b) Magnified UV/Vis absorption spectra.

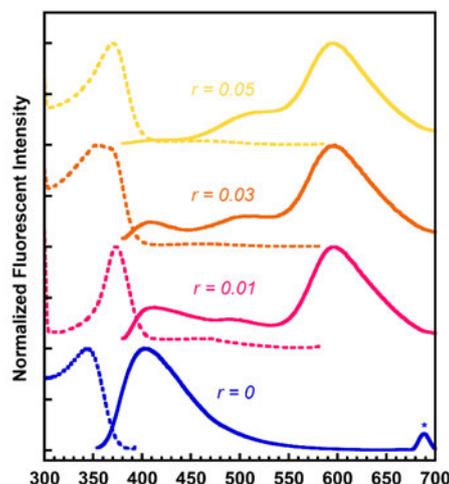


Fig. 2 EX/EM spectra of homopolymer and copolymers

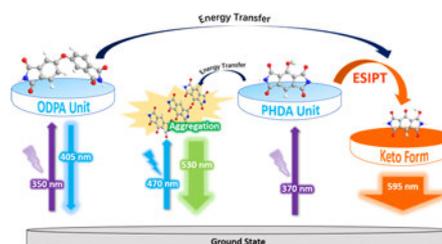
correlation with the concentration of PHDA unit.

Fig. 2 shows the excitation (Ex.)/emission (Em.) spectra ($\lambda_{ex} = 370 \text{ nm}$, $\lambda_{em} = 595 \text{ nm}$) of the co-PIs. In the co-PIs, three photoluminescent peaks were observed: the emission observed at 405 nm was assigned to the fluorescence peak of the LE transition of the ODPA moiety, that at 530 nm was to the fluorescence peak from the aggregate forms of PHDA moiety, and that at 595 nm was to the fluorescent peak of the keto form of PHDA moiety generated via the ESIPT process. (as presented in **Scheme 2**). Of interest is that through the molar ratios of PHDA moiety was less than 0.05, the fluorescence intensity from the keto form of PHDA generated via ESIPT is much stronger than that of the LE transition at the ODPA moiety. This result clearly indicates that efficient energy transfer occurs from the blue fluorescent ODPA to the red fluorescent PHDA moieties.

The fluorescence spectra shown in **Fig. 2** were fitted with Gaussian broadening functions, and then the integrated areas of fluorescent (FL) intensity of each component are listed in **Table 1**. The FL intensity of the ODPA component (\int_{405nm}) decreased with increasing the molar ratio of PHDA moiety (the order: $0 > 0.01 > 0.03 > 0.05$). This is the opposite trend to the FL intensity of the aggregation emission (\int_{530nm}) and the total photoluminescent quantum yield (Φ_{all}). Among these co-PI films, that of 0.03 of the PHDA ratio exhibited the strongest ESIPT fluorescence with the highest \int_{530nm} , at which the energy transfer from ODPA to PHDA moieties became the most efficient, and the aggregation formation of the PHDA moiety was suppressed.

These co-PIs exhibited three fluorescent peaks with different wavelengths, which resulted in the gradual but obvious fluorescence color changes from blue, pink, orange and yellow for the PHDA molar ratios of 0, 0.01, 0.03 and 0.05, respectively (**Fig. 3**).

Average photoluminescent lifetime $\langle \tau \rangle$ is a very important parameter to analyze the photophysical processes, especially for the Förster resonance energy transfer (FRET) [5]. **Fig. 4** presents the



Scheme 2 Schematic representation of photophysical process of copolymer films.

Table 1 Integrated area ratio (\int) and total quantum yield (Φ) of the PI copolymer films.

r	\int_{405nm}	\int_{530nm}	\int_{595nm}	Φ_{all}
0	1	0.0	0.0	0.09
0.01	0.28	0.14	0.58	0.20
0.03	0.10	0.29	0.61	0.20
0.05	0.02	0.38	0.60	0.23

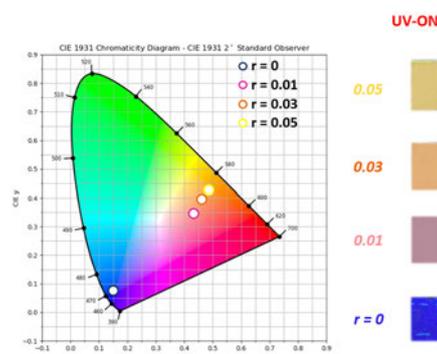


Fig. 3 CIE coordinates (left) and photographic images (right) of ODPA/DCHM PI homopolymer and ODPA/PHDA/DCHM PI copolymers under UV light (370 nm)

Table 2 Average photoluminescent lifetime $\langle \tau \rangle$ at different wavelength and energy transfer efficiency E_{FRET}

r	$\langle \tau \rangle_{405nm}$	$\langle \tau \rangle_{530nm}$	$\langle \tau \rangle_{595nm}$	E_{FRET}
0	7.66	ND	ND	0
0.01	5.27	6.33	3.35	0.31
0.03	3.69	6.40	3.43	0.52
0.05	3.09	6.38	3.84	0.60

ND: Not detectable

photoluminescent decay curves of all co-PI films, and **Table 2** summarizes the estimated average lifetimes $\langle\tau\rangle$. The value of $\langle\tau\rangle_{405\text{nm}}$ (average fluorescent lifetime of the ODPa moiety) decreased with increasing the PHDA ratio, which is an opposite trend to the energy transfer efficiency (E_{FRET}). This result is explainable by the increase in the PHDA moiety as the energy acceptor (in turn, ODPa moiety is the energy donor). At the same time, the value of $\langle\tau\rangle_{530\text{nm}}$, which is mainly related to the aggregation fluorescence, and $\langle\tau\rangle_{595\text{nm}}$, mainly related to the ESIPT keto emission, did not show significant changes. Furthermore, the value of $\langle\tau\rangle_{595\text{nm}}$ was slightly increased at the highest PHDA ratio ($r = 0.05$), which was attributable to the contribution of the aggregation fluorescence at 595 nm observed in the static emission spectra. Among these co-PIs, the film with $r = 0.03$ exhibited the highest transparency with colorlessness, the strongest ESIPT keto emission owing to the satisfactorily high energy transfer efficiency. Thus, copolymer $r = 0.03$ was the most suitable for the solar spectral converting application.

【Conclusion】

The photoluminescent behaviors of a series of novel polyimide copolymers (co-PIs) based on PHDA and ODPa are investigated. To suppress the aggregation formation of the PHDA moiety, the molar ratio of PHDA unit (r) in the co-PIs was reduced as low as 0.01 ~ 0.05, which resulted in colorlessness and high transparency. Despite such a low concentration of PHDA, these films exhibited obvious ESIPT-based keto emission at the PHDA moiety, which clearly indicated the efficient intra- and intermolecular FRET processes from the ODPa to the PHDA moieties. Furthermore, by increasing the r value from 0.01 to 0.05, the fluorescence color changed from pink to yellow via orange. Although the aggregation emission was also enhanced, energy transfer efficiency was improved with increasing the r value. Finally, among all the co-PI films, that with $r = 0.03$ exhibited the highest transparency with colorlessness, the strongest ESIPT-based keto emission as well as the satisfactorily high energy transfer efficiency. This film is highly suitable and promising for solar spectral converter applications.

【References】

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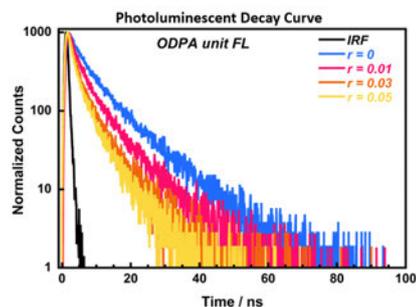


Fig. 4 Copolymers' photoluminescent decay curves of ODPa unit fluorescence