

論文 / 著書情報
Article / Book Information

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Title(English)	Development of Colorless Polyimide Films Exhibiting Large Stokes Shifted Photoluminescence Based on ESIPT for Solar Spectral Conversion Applications
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(博士課程)
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論文要約

THESIS OUTLINE

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Department of, Graduate major in	応用化学	コース
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申請学位 (専攻分野) :	博士	(工学)
Academic Degree Requested	Doctor of	
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要旨 (英文 800 語程度)

Thesis Summary (approx.800 English Words)

This thesis focuses on the development of colorless and transparent polyimide (PI) films exhibiting large Stokes-shifted photoluminescence via excited-state intramolecular proton transfer (ESIPT) phenomenon applicable to solar spectra conversion.

In Chapter 1, the basics of photoluminescence and the photophysical processes of ESIPT are summarized. Besides, the recent research progress of highly fluorescent PIs is presented.

In Chapter 2, a series of copolyimides (CoPIs) synthesized from 4,4'-oxydiphthalic anhydride (ODPA), 4,4'-diaminocyclohexylmethane (DCHM), and 3-hydroxyphthalic anhydride (3HPA) as an end-group (OD-DC-3H) exhibited large Stokes-shifted fluorescence ($10,544\text{ cm}^{-1}$) via the ESIPT at 3HPA moieties. However, the fluorescence quantum yields of these PIs were relatively low due to the ODPA moiety which has the same absorption band as 3HPA. Thus, another series of CoPIs using non-fluorescent 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) instead of ODPA (6F-DC-3H) were synthesized and characterized. All the 6FDA-based PI films are optically transparent in the visible region, and those having 3HPA end-groups exhibit green fluorescence at 530 nm when excited at 340 nm. As compared with the corresponding ODPA-based PIs, the 6FDA-based PIs demonstrated significantly higher quantum yields in the solid-state ($\Phi = 0.14\text{--}0.25$). One reason is that the bulky and less polar $-\text{CF}_3$ groups leads to loose molecular packing of PI chains, which effectively inhibits aggregation-induced quenching (AIQ). Another reason is the absence of energy transfer to/from the non-fluorescent 6FDA moiety due the reduced intermolecular dipolar-dipolar interactions. Accordingly, the experimental results demonstrate that the introduction of bulky $-\text{CF}_3$ groups is a promising approach to afford highly fluorescent end-capped PIs exhibiting large Stokes-shifted fluorescence.

In Chapter 3, a series of novel CoPI films were prepared through the copolymerization of 3-hydroxy-pyromellitic dianhydride (PHDA) and ODPA with DCHM diamine. In these CoPIs, the molar ratio of PHDA moiety was controlled below 5% to avoid AIQ between PHDAs, and they exhibited large Stokes-shifted ($10,220\text{ cm}^{-1}$) orange fluorescence via ESIPT. All these CoPI films on fused silica substrates are colorless and transparent. Besides, they show a prominent ESIPT fluorescence due to the efficient energy transfer from the ODPA to PHDA moieties. In particular, a CoPI film with 3% PHDA content (CoPI-0.03) was colorless and showed the strongest orange fluorescence, which is the most suitable for wavelength conversion applications. As the molar ratio of PHDA increases, the fluorescence color of the CoPIs gradually changes from pink, orange, to yellow partly due to the enhancement of emission from the anion form of

PHDA moiety. The absorption and emission spectra of an imide compound derived from PHDA (PH-MC) also suggested the existence of anion form in solution. However, the CoPI films formed on soda-lime-silica (soda) glass substrates showed a pale-yellow color as well as yellowish fluorescence. This phenomenon is explainable by the enhancement of anion form of PHDA generated on the highly basic surface of soda glass. To suppress the formation of anions, a small amount of sulfuric acid was doped into precursor solutions of the CoPIs prior to thermal imidization, and thus colorless and transparent films exhibiting large Stokes-shifted orange fluorescence were successfully obtained on soda glass substrates. The wavelength-converting spectra of the CoPI films demonstrated that the UV radiation in the solar light is effectively absorbed, and its energy is converted to visible light at 500–700 nm with a high quantum efficiency of ca.20 %.

In Chapter 4, 2,2'-dihydroxy-3,3',4,4'-benzophenonetetracarboxylic dianhydride (DHBA) was synthesized, and novel PI (DH-PI) and an imide compound (DH-MC) were developed. The DHBA moiety includes two phenolic groups as proton donors and three carbonyl groups as proton acceptors. Thus, DH-MC can possess three different structures of hydrogen bonding (H-bonding) : MC-0, MC-1, and MC-2. The quantum chemical calculation showed that the most stable H-bond structure is MC-1, which is consistent with the single-crystalline XRD analysis and the FT-IR absorption spectra. In the solid-state, DH-MC and DH-PI showed large Stokes-shifted ($\sim 11000\text{ cm}^{-1}$) yellow fluorescence via ESIPT. Additionally, they exhibit small Stokes-shifted fluorescence emitted from the anion form of DHBA moiety which causes yellowish coloration. According to Chapter 3, a CoPI film prepared from DHBA and ODPA with a 3% DHBA content (CoPI-0.03) showed good transparency and prominent yellow fluorescence due to the dilution effect and the efficient energy transfer from the ODPA to DHBA moieties in the excited state, and it absorbs UV radiation in the sun light and enhances the yellow light as evidenced in the wavelength converting spectrum.

In Chapters 5 and 6, the results obtained through this study are summarized, and the future prospect of application of PIs exhibiting large Stokes-shifted photoluminescence via ESIPT for wavelength conversion are featured.