Highly Fluorescent Polyimides for Wavelength Converting Applications

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Abstract

Semi-aliphatic polyimides (PIs), which emit large Stokes shift fluorescence via excited-state intramolecular proton transfer (ESIPT) process, were newly prepared by using a pyromellitic dianhydride having an −OH group (3HPMDA) and alicyclic diamines with/without bulky side groups (3H-DC and 3H-6F). Both PI films exhibit reddish-color ESIPT emissions at around 590 nm with very large Stokes shifts of more than 10,000 cm^{-1}. As for 3H-6F, the PI film exhibits high colorlessness due to the suppression of the inter-chain aggregation formation by introducing the bulky side groups in the diamine moiety. The introduction of –OH group into the pyromellitic structure and bulky side chains into the diamine moiety effectively provide an efficient fluorescent emission at longer wavelengths as well as a transparency in the visible region.

Introduction

Fluorescent polymers have attracted much interest due to their inherent advantages, i.e. light-weight, facile processing and flexibility of films by spin coating. They are expected to be applied for wavelength converting materials, which convert short wavelength light to longer wavelength, for a wide range of applications, such as flat panel displays, photovoltaic devices and crop cultivations. Polyimides (PIs) are representative high-performance polymers exhibiting outstanding thermal and physical stabilities, and they have been used in a wide range of high-tech industries. Recently, studies newly providing fluorescence properties to PIs have been carried out in order to develop novel thermally-stable fluorescent materials [1,2]. However, as for reported fluorescent PIs, the energy gaps between the absorption and fluorescence (Stokes shifts) are very small (Figure 1). Since wavelength converting materials strongly desire the large Stokes shift fluorescence properties, in order to apply fluorescent PIs to such applications, the further innovative molecular design is necessary. More recently, our group reported that a phthalimide compound having a hydroxy (−OH) group in its anhydride moiety (3HNHPI) exhibited a very large Stokes shift fluorescence (ν = 11394 cm^{-1}) via excited-state intramolecular proton transfer (ESIPT : Figure 2) [3]. In this study, 3-hydroxy-pyromellitic dianhydride (3HPMDA), having an −OH group in the benzene ring of pyromellitic dianhydride, was synthesized, and two kinds of corresponding PIs with/without bulky side groups in the diamine moieties (3H-DC and 3H-6F : Figure 4) were subsequently synthesized and their fluorescence properties in film were examined. In order to investigate the fluorescence properties of the PIs, a corresponding imide model compound (3H-Ch : Figure 3) was also synthesized and its fluorescence properties in solution were examined. This study aims to design new types of "highly fluorescent PI" by incorporating ESIPT units in the main chain, in which the absorption and fluorescence wavelengths can be controlled in a wide range.

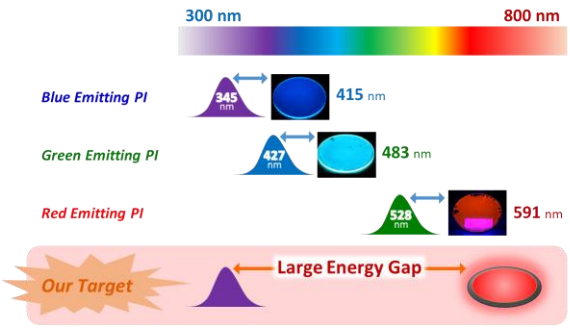

Figure 1. Conventional Fluorescent PIs and Their Stokes Shift of Fluorescence.

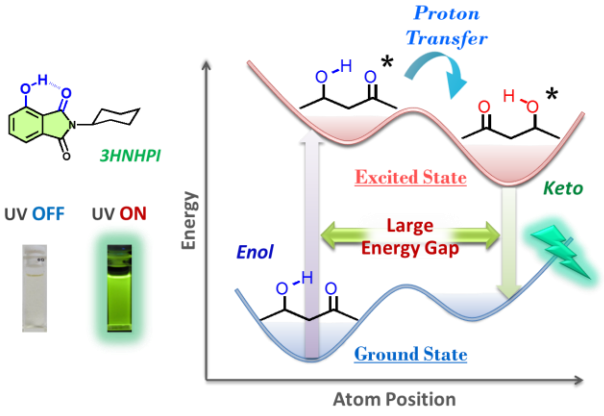

Figure 2. Photophysical Process of 3HNHPI via ESIPT.

Experimental

The precursor of PI, poly(amic acid) silylester (PASE), was prepared by the *in situ* silylation method. The corresponding diamine and a silylation agent were stirred in DMAc under cooling. 3HPMDA was added to the solution and then stirred for overnight. The viscous solution thus obtained was spin-coated onto a fused silica substrate, followed by soft-baking at 70 °C for 1 h and subsequent thermal imidization at 220 °C for 1.5 h under nitrogen flow.

Results and Discussion

The UV/vis absorption and fluorescence spectra of the imide model compound, 3H-Ch, dissolved in $CHCl_3$ (1.0×10^{-5} M) are shown in Figure 3. 3H-Ch shows an intense absorption peak at 369 nm, which is attributable to a local excitation (LE) absorption occurring at the dianhydride moiety. In addition, another weak absorption are observed at around 440 nm, which originate from the aggregation form. A strong fluorescence peak was observed at 592 nm with the excitation at 367 nm. This peak demonstrate a very large Stokes shift of 10412 cm^{-1} arising from excited-state intramolecular proton transfer (ESIPT).

The UV/vis absorption and fluorescence spectra of 3H-DC and 3H-6F PI films are shown in Figure 4. These PI films show absorption peaks at around 360 nm and 460 nm, which are readily attributable to the LE bands and the aggregation absorption bands, respectively. The intensity of the aggregation band was significantly reduced by introducing steric side chains ($-CF_3$) to the diamine moiety, which provides the PI film a high transparency and colorlessness in the visible region. In the fluorescence spectra when the main absorption bands were excited, intense fluorescence peaks with a very large Stokes shift (ν = 10829 cm^{-1} for 3H-DC, 11083 cm^{-1} for 3H-6F, respectively) were observed at around 590 nm. These peaks are readily attributable to the emissions from the proton transferred forms generated via ESIPT upon excitation. As shown in Figure 4, these PI films exhibit reddish-color fluorescent emission under UV light irradiation. In conclusion, the introduction of ESIPT structures to the main chains of PIs and the control of aggregation states by use of steric hindrances at the diamine moieties are effective way to synthesize novel colorless and long-wavelength (large energy gap) fluorescent PIs.

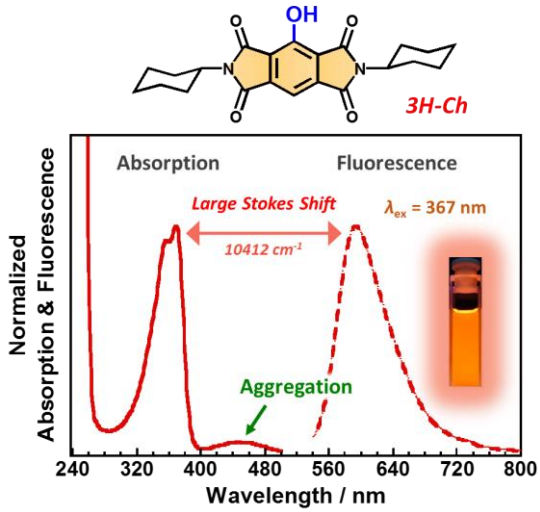

Figure 3. Absorption and Fluorescence Spectra of 3H-Ch in $CHCl_3$ Solution.

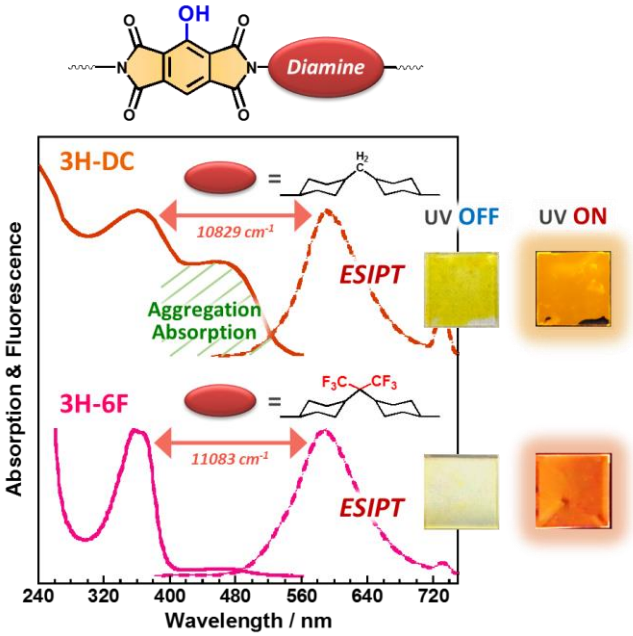

Figure 4. Absorption and Fluorescence Spectra of 3H-DC and 3H-6F PI Films.

References

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