

Molecular Design, Synthesis and Properties of Multi-Color Fluorescent Polyimides Based on the Excited State Intramolecular Proton Transfer (ESIPT) Mechanism

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Introduction

Thermally stable fluorescent polymers have been attracting attentions for use in spectrum converter for Si-type solar cells. Polyimides (PIs) are known to show weak fluorescent emission in UV/visible region.^{1,2} Wavelength and intensity of fluorescence of PI films are significantly affected by the electronic states of source materials (dianhydride and diamine) and the aggregation structures in solids because their optical properties (absorption, excitation, and emission) are inherently dependent on their electronic structures possessing charge transfer (CT) nature.^{3,4} In addition, the efficiency of fluorescent emission (*i.e.* quantum yield, ϕ) of conventional PIs is very low (< 0.05) due to their strong intra- and intermolecular CT. In this study, excited-state proton transfer (ESIPT) mechanism occurring at intramolecular hydrogen bonding structure was introduced into phthalimide and pyromellitic diimide moieties in model compounds and at the termini of a highly fluorescent PI to enhance the fluorescence intensity and Stoke's shift of PI films.

Results and Discussion

The lowest energy electronic transition (LET) of sBPDA-PDA PI is assignable to a CT(π - π^*) as shown in Fig.1, which leads to nonradiative deactivation after excitation. In contrast, the LET in sBPDA-DCHM PI is assignable to a locally excited LE(π - π^*) which leads to direct radiative emission. Due to its LE nature, the emission wavelength can be predicted by the electron affinity of dianhydride. We have demonstrated that highly fluorescent semi-aromatic PIs (HFPIs) can be systematically designed based on the time-dependent (TD)-density functional theory (DFT) and successfully synthesized a series of HFPIs which emit enhanced fluorescence of the three primary colors (blue, green, and red).^{5,6} Fig.2 shows a typical blue fluorescence of 10FEDA/DCHM PI with $\phi = 0.11$. The HFPI films are tough, flexible, and exhibit T_g s over 200°C with thermal degradation temperatures (T_d s) over 400°C. Furthermore, we have reported that white-light emitting PIs can be obtained by judicious combinations of perfluorinated and non-fluorinated dianhydrides having ether-linkages with fluorinated/unfluorinated alicyclic diamines. However, for use in spectrum converter for solar cells, highly transparent and colorless PI films with strong emission at longer wavelengths (green, yellow to red) are to be developed.

We have recently proposed a novel molecular design concept for colorless and multicolor light-emitting polyimides (PIs) based on the excited-state proton transfer (ESIPT) mechanism.⁷ Firstly, the UV/Vis absorption and fluorescence spectra of imide compounds with and without intramolecular hydrogen bonding between hydroxyl (-OH) group and imide carbonyl group were extensively investigated. As shown in Fig.3, *N*-cyclohexyl-phthalimide (NHPI) exhibits very weak blue fluorescence because the LET of NHPI is assignable to CT(π - π^*). In contrast, an enol form of *N*-cyclohexyl-3-hydroxy-phthalimide (3H-NHPI) is immediately converted to a keto form through LE(π - π^*) transition followed by intramolecular proton transfer. The excited keto form exhibits a strong green-color ESIPT emission at 534 nm with excitation at

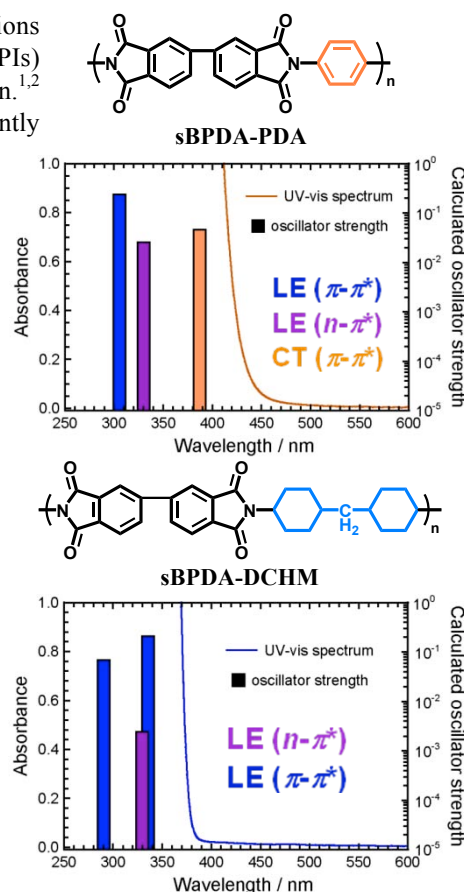


Figure 1. Molecular structures, experimental UV/vis absorption spectra, and calculated oscillator strengths of weakly (BPDA-PDA) and highly fluorescent (BPDA/DCHM) PI films.



Figure 2. Photos of a highly fluorescent polyimide films on silica substrates without/with UV irradiation.

332 nm. The Stokes' shift and the quantum efficiency of the emission are as large as 11394 cm^{-1} and $\phi=0.40$, respectively. To our best knowledge, this is the first example of imide compound which possesses well-defined ESIPT mechanism. The energetically relaxed keto form is spontaneously converted to enol form. On the other hand, *N*-cyclohexyl-4-hydroxy-phthalimide (4H-NHPI) exhibits a strong blue fluorescence with a relatively small Stokes' shift (7720 cm^{-1}) due to the absence of ESIPT mechanism. As a result of introducing $-\text{OH}$ group into phthalimide moiety, the LET of NHPI ($\text{CT}(\pi-\pi^*)$) was effectively converted to $\text{LE}(\pi-\pi^*)$ in 3H-NHPI and 4H-NHPI. Moreover, 4H-NHPI shows significant solvatochromism and high sensitivity to pH due to deprotonation at the $-\text{OH}$ group.

Subsequently, an HFPI prepared from 4,4'-oxidiphthalic dianhydride and 4,4'-diaminocyclohexylmethane (ODPA-DCHM) was end-capped with 3-hydroxyphthalic anhydride. The PI films are colorless and exhibit two characteristic emission peaks at 400 and 530 nm. The photophysical processes are shown in Fig. 4. The former emission is attributable to the inherent $\text{LE}(\pi-\pi^*)$ emission from the main chain, and the latter is attributable to an ESPIT emission from the termini due to efficient energy transfer from the main chain. Due to mixing of these two emissions, the PI films show gradated multicolor (blue, light-blue, white, light-green) emission depending on the amount of termini, whilst maintaining good transparency and colorlessness. The Stokes' shift is as large as $9800\text{--}10700\text{ cm}^{-1}$.

Furthermore, as shown in Fig.5, *N,N'*-dicyclohexyl-3,6-dihydroxypyromellitimide (36DHPMDI) exhibits red-color emission consisting of two fluorescent peaks at 457 nm (weak) and 637 nm (strong) with excitation at 432 nm. The former is attributable to the emission from the excited enol form, and the latter is attributable to the excited mono-keto form generated through ESIPT in which the Stokes' shift is 8000 cm^{-1} . In this system, di-keto form with dual proton transfer was not formed. Although 36DHPMDI show a weak absorption at shorter wavelengths in the visible region, the strong red emission with near-UV excitation is suitable to spectrum converter for Si-type solar cells. In addition, 36DHPMDI dissolved in methanol exhibits strong red emission at 634 nm with excitation at 526 nm, which is attributed to direct excitation of keto form existing in the ground state. This compound also shows significant solvatochromism and high sensitivity to pH due to deprotonation.

Conclusions

Several imide compounds and HFPIs having $-\text{OH}$ groups were synthesized, and their photophysical processes were analyzed using UV/Vis absorption, excitation/emission spectra and TD-DFT calculations. It was demonstrated that ESIPT mechanism can be an effective and versatile tool to control and enhance the fluorescence emission of imides and HFPIs.

References

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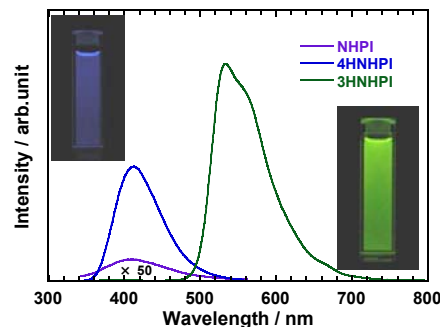
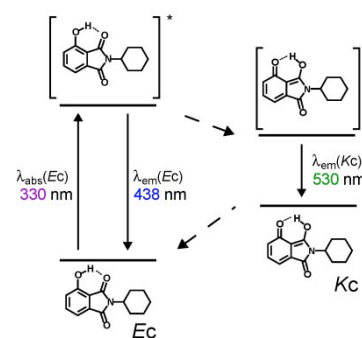


Figure 3. Photos under UV irradiation and fluorescent spectra of imide model compounds without/with intramolecular hydrogen bonding (ESIPT mechanism).

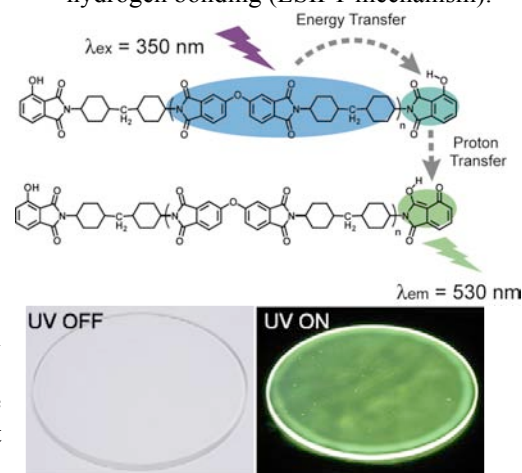


Figure 4. Photos of a highly fluorescent polyimide films having ESIPT moiety at the termini without/with UV irradiation.

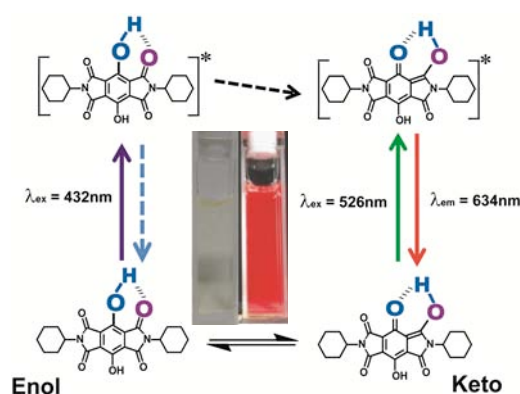


Figure 5. Photophysical processes through ESIPT of an imide compound having two intramolecular hydrogen bondings. Bright red fluorescence is observed.