Synthesis and Properties of Highly Fluorescent Fluorinated Polyimides that Emit Lights of the Three Primary Colors

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Abstract
Semi-aromatic polyimides (PIs) that emit enhanced fluorescence of the three primary colors (red, green, and blue) were newly designed in aid of TD-DFT calculations and successfully synthesized using combinations of perfluorinated or non-fluorinated dianhydride having ether-linkages and fluorinated / unfluorinated alicyclic diamines. The PI films thus obtained are tough, flexible, and have $T_g$’s over 200°C. The wavelengths of fluorescence can be predicted by calculated electron affinities of dianhydries, and the maximum intensities of fluorescence are >100 times as strong as that of a conventional PI.

Introduction
Thermally stable fluorescent polymers have been attracting attentions for use in OLED devices and spatial optical phase modulators. Polyimides (PIs) are known to show fluorescence in the visible region [1,2]. However, the wavelengths and intensities are significantly affected by the electronic properties of raw materials and the states of aggregation because the fluorescence in PIs originates from the charge transfer (CT) excitation and emission mechanisms [3]. In addition, the quantum yields of the fluorescence observed for conventional PIs are very low due to their strong CT nature. Hence, the keys to provide highly fluorescent PIs are, firstly the suppression of CT, secondly the enhancement of LE occurring at the anhydride moiety, and thirdly the suppression of quenching caused by aggregation. Consequently, 4FPh/Ch is expected to be more fluorescent than Ph/An. In addition, the introduction of less polarizable and bulky –CF₃ groups could be effective to enhance the fluorescence. Hence, we chose perfluorinated dianhydrides (P2FDA &10FEDA) and alicyclic diamines, in which some –CF₃ groups are attached.

According to the design concept described above, the corresponding PIs depicted in Scheme 1 were synthesized. The PI films obtained by thermal curing at 300°C for 1.5h under N₂ (ca.10 µm-thick) are transparent, tough, and flexible.

Calculation and Experimental
For estimating the one-electron transitions of models, the time-dependent (TD)-DFT theory with B3LYP functional was adopted [4]. 6-311G(d) basis set was used for geometry optimizations under no constraints, and 6-311++G(d,p) basis set was used for calculations of excitation energies and oscillator strengths.

The methods of preparing NMP solutions of poly(amic acid silyl ester) (PASE) and thermal imidization of the spin-coated PASE films have been reported elsewhere [5]. The dianhydrides developed for the synthesis of perfluorinated polyimides were used for the present synthesis [6].

Results and Discussion
Fig. 1 shows the calculated absorption spectra of model compounds derived from fluorinated/non-fluorinated phthalic anhydride and aniline/cyclohexylamine. Comparing with Ph/An, 4FPh/Ch exhibits a hypsochromic shift and hypochromic effect for the CT absorption but a slight bathochromic shift and a significant hyperchromic effect for the LE absorption. It is well-known that the intra- and intermolecular CT interactions of PIs markedly reduce their fluorescence emission. Hence, the keys to provide highly fluorescent PIs are, firstly the suppression of CT, secondly the enhancement of LE occurring at the anhydride moiety, and thirdly the suppression of quenching caused by aggregation. Consequently, 4FPh/Ch is expected to be more fluorescent than Ph/An. In addition, the introduction of less polarizable and bulky –CF₃ groups could be effective to enhance the fluorescence. Hence, we chose perfluorinated dianhydrides (P2FDA &10FEDA) and alicyclic diamines, in which some –CF₃ groups are attached.

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Fig. 1 Calculated absorption spectra of model compounds for PIs using TD-DFT theory.
As shown in Fig. 2, the reddish and pale yellowish color of the P2FDA and 10FEDA-derived PIs originate from the characteristic absorption peaks at 500 and 400 nm, respectively. These peaks were assigned to the LE transitions at the dianhydride moieties [7]. In contrast, the PIs from nonfluorinated dianhydrides exhibit no characteristic peaks. The $T_g$'s measured by DSC are at 205−265˚C, and the thermal degradation temperatures (10%wt-loss) are over 400˚C.

10FEDA also gives enhanced fluorescence at ca.420 nm. These are novel blue-light emitting PIs.

In addition, the excitation and emission peaks of PIs are located in the same range regardless of the diamine structure when dianhydride structure is fixed. This fact clearly indicates that the CT interactions are effectively suppressed, and the LE excitation/emission mechanisms occurring at dianhydride moieties are predominant in these PIs.

### Conclusion

We successfully developed novel materials of ‘highly fluorescent polyimides’ that emit lights of the three primary colors. These PIs are promising as novel thermally stable materials for organic light-emitting devices and flat panel displays.

### References