

Molecular Design, Synthesis, and Properties of Highly Fluorescent Fluorinated Polyimides

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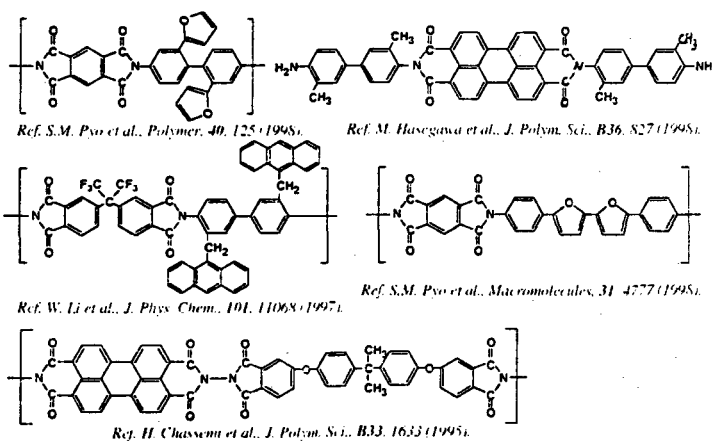
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Abstract

Semi-aromatic fluorinated polyimides (PIs) exhibiting enhanced fluorescent emission in the visible region are newly designed in aid of TD-DFT calculations, and they were successfully synthesized from the combinations of two kinds of perfluorinated dianhydrides or four kinds of unfluorinated dianhydrides, and fluorinated /unfluorinated alicyclic diamines. The PI films obtained are tough, flexible, and transparent, exhibit T_g 's over 200°C, and the thermal degradation temperatures are over 410°C. The intensities of the strongest fluorescence appearing in the bluish green region for the 10FEDA-derived PIs and those in the violet blue region for the PIs derived from aromatic dianhydride having low electron affinities are more than 100 times as strong as that of a conventional PI. Although the fluorescence of P2FDA-derived PIs are 5-8 times stronger than those of the 10FEDA-derived PIs, we developed novel semi-aromatic polyimides (PIs) that emit enhanced fluorescence of the three primary colors (red, green, and blue).

Introduction

Thermally stable fluorescent polymers have been attracting attention for use in OLED devices and spatial optical phase modulators. Polyimides, the most popular thermally stable polymers, 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 formed during thermal curing because the fluorescence in PIs is generally associated with the charge transfer (CT) excitation and emission mechanism [3]. In addition, the quantum yields of the fluorescence observed for conventional PIs are low due to their strong CT nature. In the present study, we propose a novel thermally stable material of "highly fluorescent fluorinated polyimides" and report their thermal, optical, and fluorescence properties.



Scheme 1 Conventional fluorescent polyimides containing fluorescent-dyemoties in the main or side chains.

Calculation and Experimental

For evaluating one-electron transitions in PIs, the time-dependent (TD)-DFT theory with B3LYP functional was adopted [4], in which 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 calculations were performed using Gaussian-98 (Rev.A11) software. 1,4-Bis(3,4-dicarboxytrifluorophenoxy)tetra fluorobenzene dianhydride (10FEDA) and 1,4-difluoropyromellitic dianhydride, which have been developed for perfluorinated polyimides [5], were kindly supplied by NTT Corp, and 4,4'-diaminocyclohexyl-hexafluoropropane (6FDC) and 2,2'-bis(tri fluoromethyl)-4,4'-diaminobicyclohexyl (TFDC) were generously supplied by Central Glass Co.Ltd. 4,4'-Diamino cyclohexyl methane (DCHM) was purchased from Tokyo Kasei. The methods for preparing NMP solutions of poly(amic acid silyl ester) (PASE) and thermal imidization of spin-coated PASE films have been reported elsewhere [6].

Results and Discussion

Fig.1 shows the molecular orbitals that play important roles for the CT (HOMO→LUMO) and the localized excitation (LE: HOMO-*n*→LUMO) absorptions for imide model compounds. Comparing with a standard model-Ph/An, the combination of polyfluorinated anhydride and alicyclic amine (model-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 inter-molecular CT interactions of PI chains markedly reduce their fluorescence emission. Hence, the key-points to provide

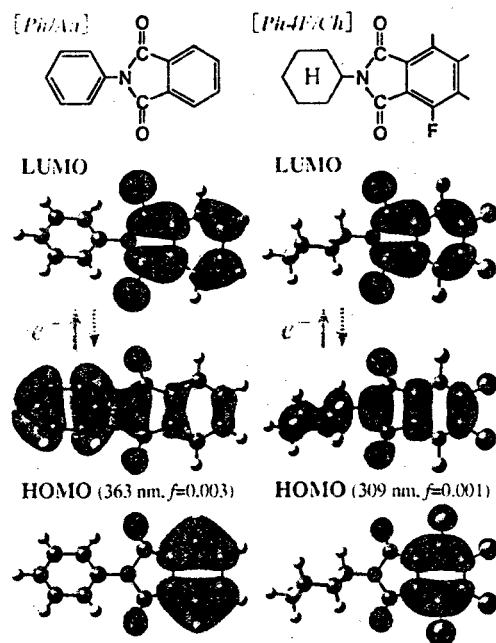


Fig. 1 Molecular orbitals essential for the CT (HOMO→LUMO) and LE (HOMO-*n*→LUMO) absorptions for models. The calculated wavelengths and oscillator strengths for the one-electron transitions to LUMO are shown in parenthesis.

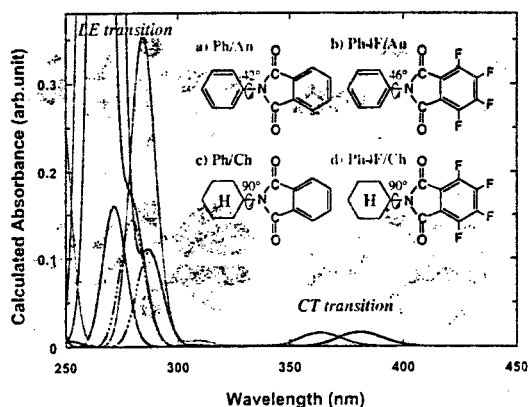


Fig. 2 Calculated absorption spectra of four models using the TD-DFT theory.

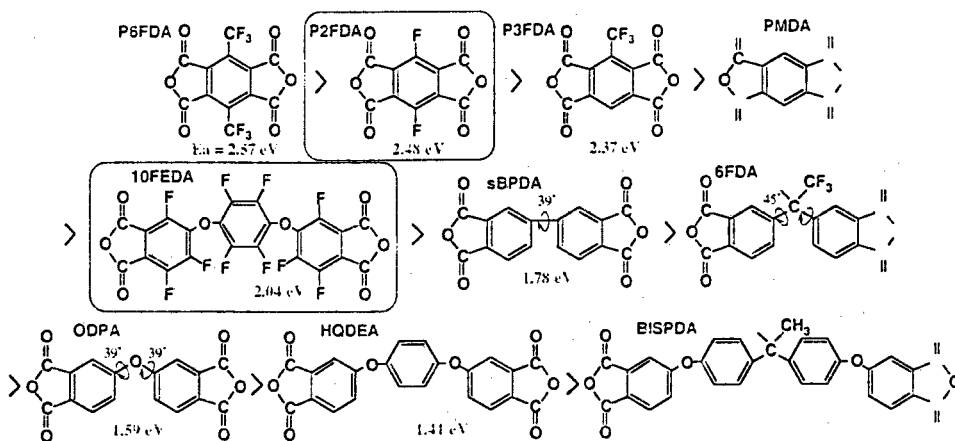
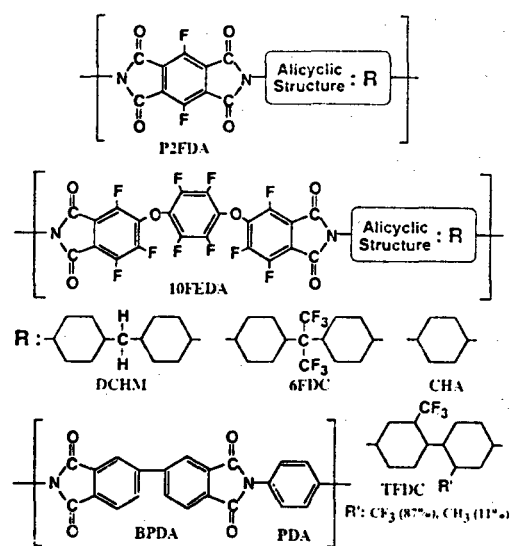


Fig. 3 Calculated electron affinities of dianhydrides (B3LYP/6-311G(d)).

highly fluorescent PIs are, firstly, the suppression of CT interactions, secondly, the promotion of LE emission occurring at the anhydride moiety, and thirdly, the suppression of the emission-quenching caused by molecular aggregation. Consequently, 4FPh/Ch is expected to be more fluorescent than Ph/An. In addition, the introduction of less polarizable and bulky $-CF_3$ groups should be effective to strengthen the fluorescence. Hence, we decided to use a perfluorinated dianhydride, P2FDA, 10FEDA, and alicyclic diamines, some of which include $-CF_3$.

According to the design concept described above, the PIs depicted in Scheme 2 were synthesized. In order to avoid gelation and to improve solubility of precursors, the in-situ silylesterification method was adopted [6]. The PI films obtained by thermal curing at 300°C for 1.5h under N_2 (ca. 10 μ m-thick) are transparent, tough, and flexible. The pale yellowish color of 10FEDA-derived PIs and the deep red color of P2FDA-derived PIs originate from the characteristic absorption peaks at 400 and 500 nm, respectively. These peaks were assigned to the local excitation at the dianhydride moieties [7]. The T_g 's were observed at 205–300°C, and the thermal degradation temperatures (10% wt-loss) are 410–440°C. As shown in Fig. 4, the fluorescent emission observed at 470–480 nm for 10FEDA-derived PI films are >100 times as strong as that of a conventional fluorescent PI (BPDA/PDA). Note that the peak at 400 nm in the excitation spectra (not shown) coincides well with



Scheme 2. Newly designed highly fluorescent PIs that can be synthesized from P2FDA, 10FEDA and alicyclic diamines, and a conventional aromatic PI (BPDA/PDA). Aromatic dianhydrides with low E_a can be used.

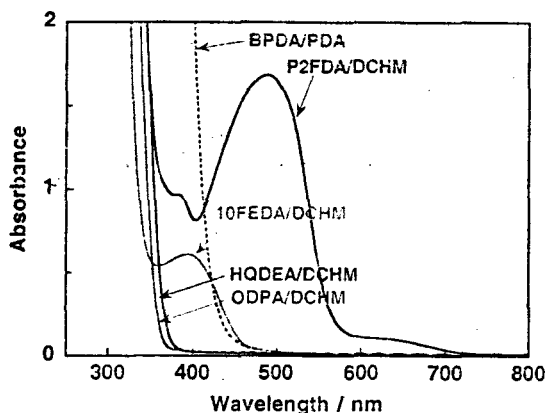


Fig. 3 Experimental UV/Vis absorption spectra of the PIs formed on silica. The PIs derived from P2FDA and 10FEDA exhibit characteristic peaks in at 500 and 400nm regardless of the diamine structures.

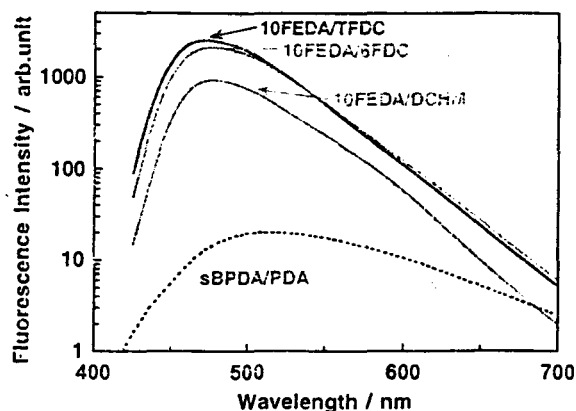


Fig. 4 Experimental emission (fluorescence) spectra of PIs derived from 10FEDA and BPDA/PDA. The excitation peak (not shown) coincides with the characteristic absorption peak in Fig. 3.

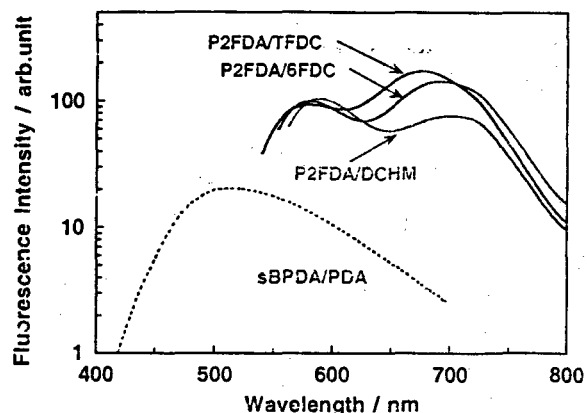


Fig. 5 Experimental emission (fluorescence) spectra of PIs derived from P2FDA and BPDA/PDA. The excitation peak (not shown) coincides with the characteristic absorption peak in Fig. 3.

the characteristic absorption peak as seen in Fig. 3. In addition, the excitation and emission peaks are located in the same ranges regardless of the diamine structures. These facts indicate that the CT interactions are effectively suppressed, and the LE excitation/ emission mechanism is predominant in these PIs. Situation is similar for the P2FDA-derived PIs, but the fluorescent emission at 580 and 680–700 nm are much weaker than those of the 10FEDA-derived PIs. This suggests that the CT emission mechanism still remains due to the significant intermolecular interactions between the P2FDA moieties.

Finally, we tried to use non-fluorinated aromatic dianhydrides having low electron affinities, ODDPA, HQDEA, and BISPDA (Scheme 1). The lowered electron-withdrawing properties of these dianhydrides should reduce the intra- and intermolecular CT interactions, which can enhance the LE excitation and emission mechanisms. As shown in Fig.6, the PIs synthesized from such dianhydrides and alicyclic diamines exhibit strong emission at 380–420 nm (violet to blue). The intensities of the fluorescence is as strong as those of the 10FEDA-derived PIs.

Conclusion

Novel semi-aromatic polyimides (PIs) that emit enhanced fluorescence of the three primary colors (red, green, and blue) were designed in aid of TD-DFT calculations and successfully synthesized using combinations of perfluorinated dianhydrides or

non-fluorinated dianhydrides having ether-linkages and fluorinated / unfluorinated alicyclic diamines. The PI films are tough, flexible, and have T_g 's over 200°C. The wavelengths of the fluorescence can be predicted from the electron affinities of dianhydrides and controlled by changing their structures. The maximum fluorescence intensities in the blue and bluish green regions are more than 100 times as strong as that of a conventional PI. These PIs are promising as thermally stable materials for organic light-emitting devices and flat panel displays in near future.

References

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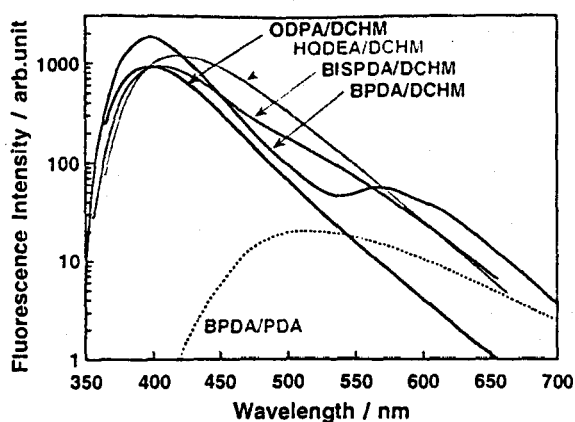
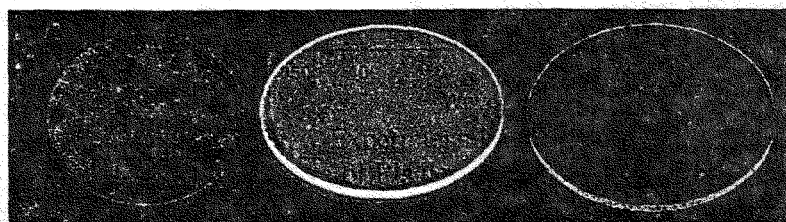


Fig. 6 Experimental emission (fluorescence) spectra of PIs derived from non-fluorinated dianhydrides having low electron affinities.



P2FDA/DCHM 10FEDA/DCHM BPDA/DCHM
Fig. 7 Photos of the PIs newly synthesized, and thermally imidized on silica. The films are illuminated by UV light (350 nm).