

Synthesis and Optical Properties of Rod-like Fluorinated Polyimides Having High Charge-Transfer Interactions

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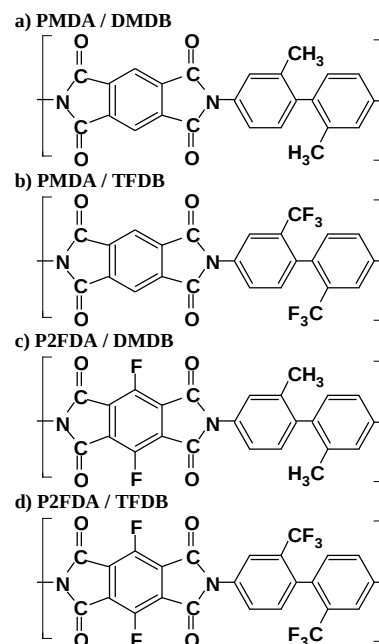
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Abstract : The optical properties, such as UV/Vis absorption spectra, fluorescence spectra, refractive indices, and birefringence of rod-like polyimides (PIs) derived from difluoropyromellitic dianhydride (P2FDA) are compared with those derived from pyromellitic dianhydride (PMDA). Since all the PIs have a common skeletal structure, the effect of fluorinated substituents can be systematically investigated. The PI films derived from P2FDA exhibit interesting optical properties, *i.e.* bright-red to reddish-brown colors, a characteristic absorption peak at 500 nm, and weak emission peaks appearing at longer wavelengths. These phenomena can be interpreted in terms of the strong electron-withdrawing ability of P2FDA and the increased intra- and intermolecular charge transfer (CT) interactions. In addition, the PIs derived from 2,2'-bis(trifluoromethyl)-4,4'-diaminobenzene (TFDB) show two excitation peaks that originate from a CT band and a band localized at the dianhydride.

Keywords : Polyimides, Optical absorption, Charge transfer interactions, Fluorescence, Refractive index, Birefringence, TMA analysis, TGA curves

1. Introduction

Fluorinated polyimides (PIs) have been expected as optical transmitting materials because of their amorphous nature, good transparency at the visible and near-infrared wavelengths, and high thermal stability [1]. We have developed a series of partially fluorinated [2] and perfluorinated PIs [3] that exhibit high optical transparency at the wavelengths for optical communications and the techniques for controlling their optical, thermal, and mechanical properties [4]. They have been applied for optical waveguides, dielectric filters, thin and flexible optical waveplates, and polarizers [5]. On the way of developing perfluorinated PIs, we have synthesized difluoropyromellitic dianhydride (P2FDA). The calculated electron affinity of P2FDA is significantly higher than that of pyromellitic dianhydride (PMDA), indicating that P2FDA has strong electron-accepting ability. It is well known that aromatic PIs form intra- and intermolecular charge transfer (CT) complexes, and the degree of CT interactions strongly depend on the electron-withdrawing ability of dianhydride and the electron-donating ability of diamine [6]. This indicates that P2FDA should give significant influences on the CT interactions and optical properties of PIs, and P2FDA can be used to synthesize polyimides having high CT interactions. We have reported that a PI derived from P2FDA exhibits much deeper color than those derived from conventional dianhydrides [7]. In this study, we focus our interests on the investigation of the thermal, mechanical, and optical properties of rod-like PIs derived from P2FDA



Scheme 1

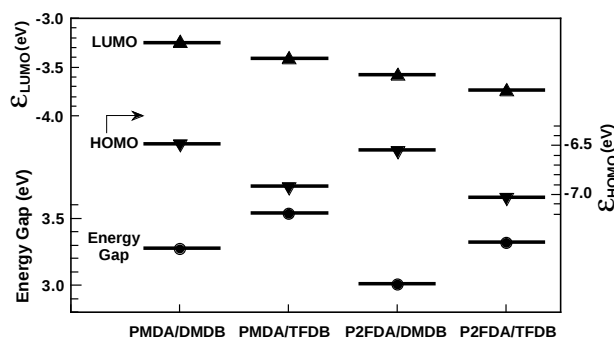


Fig. 1 Calculated energy gaps and MO energies of HOMO and LUMO for model compounds of PIs. (Scheme 2)

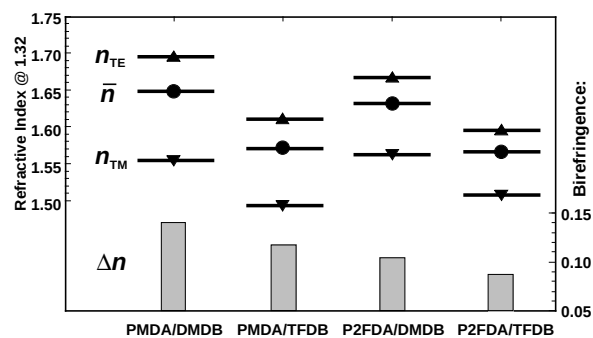


Fig. 2 Refractive indices in the TE & TM polarizations, average refractive indices and in-plane/out-of-plane birefringence of polyimides.

by comparing those of the PIs derived from a conventional PMDA. In particular, the optical properties, such as refractive indices, birefringence, UV/Vis optical absorption, and fluorescence emission/excitation behaviors are of our interests.

2. Experimental & Calculations

In order to assess the effects of fluorination to dianhydride and diamine moieties, four kinds of PIs having a common skeletal structure were synthesized (Scheme 1). P2FDA was synthesized by the oxidation of 1,4-difluorotetracyanobenzene followed by dehydration using sulfuric acid. 2,2'-Dimethyl-4,4'-diaminobenzene (DMDB) and 2,2'-bis(trifluoromethyl)-4,4'-diaminobenzene (TFDB) were supplied by Wakayama Seika Kogyo Co.Ltd. and Central Glass Co.Ltd, respectively. They were sublimated under reduced pressure. The preparation of poly(amic acid) (PAA), precursor of the PI, and the thermal, mechanical, and optical properties of PIs derived from PMDA has been partly described elsewhere [2,8]. The DMAc solutions of PAA (10-15 wt%) were spin-coated onto fused silica substrates (2.5 mm-thick) and thus heated to 350°C at a heating rate of 10°C/min, kept for 1h, and then cooled to room temperature. The average thickness of the PI films prepared for optical absorption spectra was 4 μm, and that for fluorescence spectra was 10 μm. Thermogravimetric analysis (TGA) was conducted for a small amount (ca.10 mg) of PI films peeled from substrates using a Shimadzu TGA-50 analyzer. PI films were heated to 900°C at 10°C/min under nitrogen. Thermal mechanical analysis (TMA) was conducted for a 5 x 15 mm specimen of PI films using a Shinku-Riko TM-7000 analyzer. In order to release the residual stress, PI films peeled from substrates were annealed at 350°C for 1h before the measurements. Optical absorption spectra ($\lambda = 200$ to 2000 nm) of PIs spin-coated and cured on fused-silica substrates (2.5 mm-thick) were measured using a Hitachi U-3500 spectrophotometer, and fluorescence spectra were measured using a Hitachi F-4500 fluorescence photometer with the reflection-configuration. The refractive indices of films formed on silica substrates were measured with a prism coupler (Metricon PC-2000) at a wavelength of 1320 nm. The incident light is linearly polarized in the transverse electric (TE) or transverse magnetic (TM) polarization. The in-plane/out-of-plane birefringence (Δn) was calculated as $(n_{TE} - n_{TM})$.

For molecular orbital (MO) calculations, the 6-31G(d) basis set was used for geometry optimizations under no constraints, and the 6-31G(d,p) basis set was used for calculations of molecular orbital energies, ionization potentials, and electron affinities at the density functional level of theory (DFT) using the three-parameter Becke-style hybrid functional (B3LYP). All the calculations were performed using the program of Gaussian-98 [9] (Rev.A9 & A11) installed on a Compaq Alpha server GS320 at the computer center of Tokyo Institute of Technology.

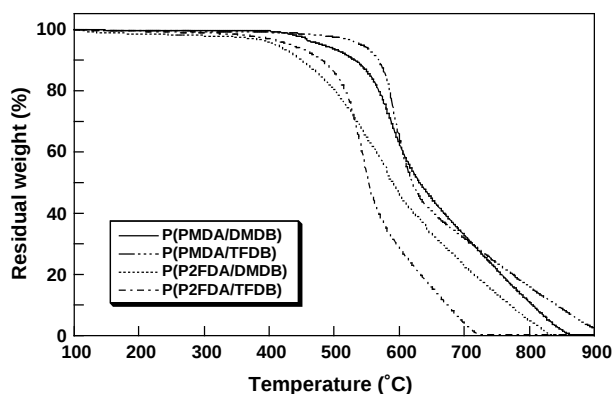


Fig. 3 TGA curves of polyimide films.

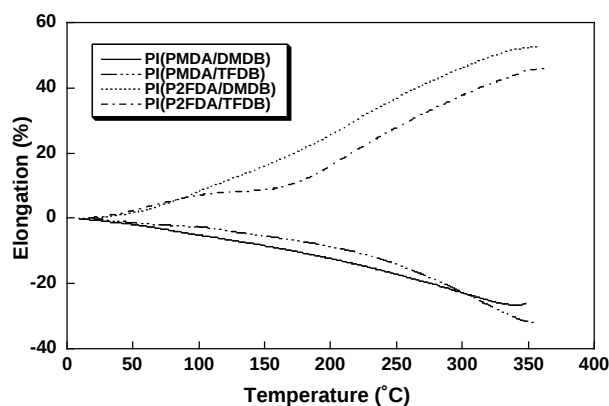
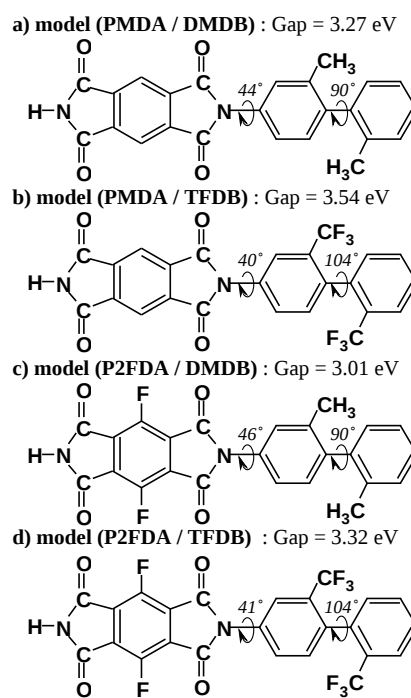


Fig. 4 TMA curves of polyimide films annealed at 350°C.

3. Results and Discussion

3.1 Calculation of Molecular Orbital Energies

The electron affinity of P2FDA calculated using the DFT theory (B3LYP/6-31G**) (2.48 eV) is significantly higher than that of pyromellitic dianhydride (PMDA) (2.13 eV), indicating that P2FDA has stronger electron-accepting ability. On the other hand, the calculated ionization potential of DMDB (6.76 eV) is lower than that of TFDB (7.14 eV), indicating that DMDB has stronger electron-donating ability. Figure 1 shows the MO energies and energy gaps between HOMO and LUMO calculated for model compounds of PIs (Scheme 2). The LUMO levels are displaced to lower energies by the fluorination of dianhydride, whereas the HOMO levels are dominated by the diamine structure. These trends coincide well with the fact that the major part of LUMO is located on the dianhydride moiety, while that of HOMO is located on the diamine moiety and the imide nitrogen. These results indicate that the combination of P2FDA and DMDB, which generates a model compound having a small HOMO–LUMO energy gap (3.01 eV), should provide higher charge-transfer (CT) interactions. On the other hand, the combination of PMDA and TFDB, which generates a model compound having a large energy gap (3.54 eV), should provide lower CT interactions. The models of PMDA/DMDB (3.27 eV) and P2FDA/TFDB (3.32 eV) exhibit intermediate values of energy gap. These electronic structures should be reflected on the optical properties of the corresponding PIs.



Scheme 2

3.2 Refractive Indices and Birefringence

Figure 2 shows the refractive indices and the in-plane/out-of-plane birefringence (Δn) of PIs. Since the fluorine content and molecular volume of PIs are significantly increased by incorporation of $-\text{CF}_3$ groups, the average refractive indices (n) of the PIs derived from TFDB are 4.2–4.8 % lower than those derived from DMDB. On the other hand, the effect of fluorine substitution in dianhydride (PMDA $\rightarrow$ P2FDA) is limited (0.4–1.0 %) because of the small increase in fluorine content. In addition, P2FDA/TFDB, in which both moieties are fluorinated, exhibits the smallest Δn , which originates from a decrease in anisotropy of molecular polarizability and that in molecular volume by fluorination. The decrease in refractive indices and dielectric constants caused by fluorine substitutions has

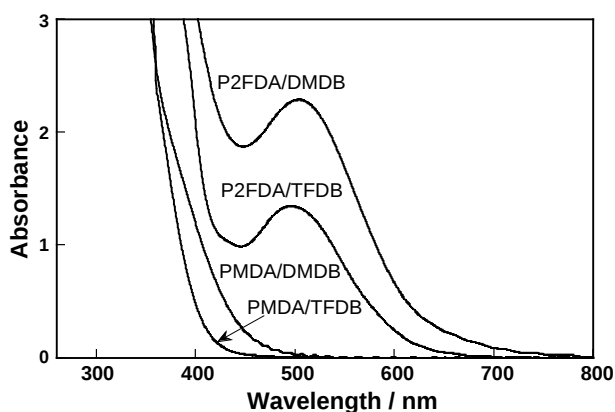


Fig. 5 Absorption spectra of the polyimide films (4 μ m).

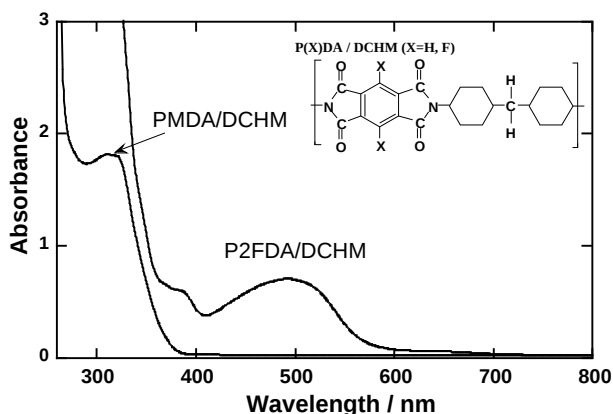


Fig. 6 Absorption spectra of the polyimide films derived from alicyclic diamine (DCHM).

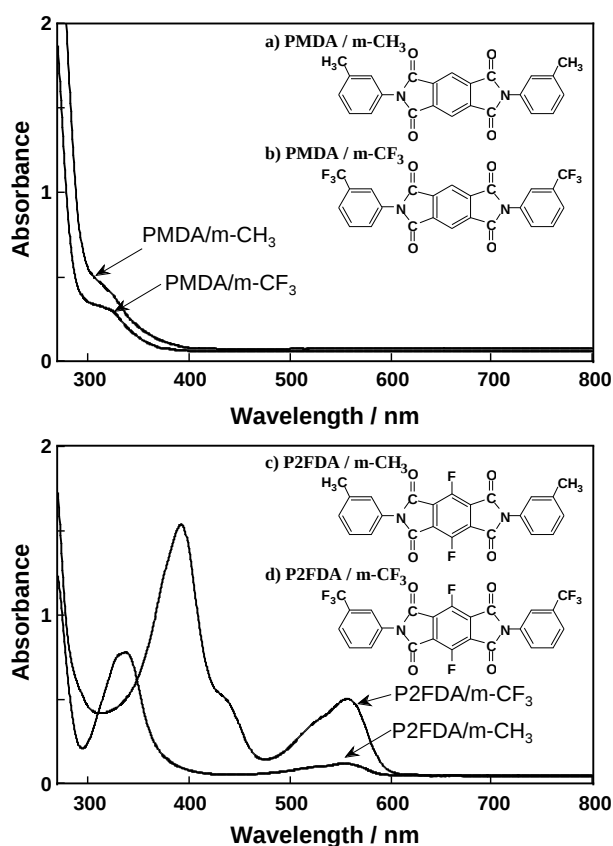


Fig. 7 Absorption spectra of model compounds dissolved in DMSO (1.25×10^{-4} M).

been assigned to local electronic polarization and fractional free volume effects [10]. Fluorinated compounds have larger molecular volumes than those expected from their van der Waals volumes. On the other hand, unfluorinated PMDA/DMDB exhibits the largest Δn , which reflects the large anisotropy in molecular polarizability and the high degree of molecular packing in the unfluorinated polyimide.

3.3 TGA and TMA measurements

The TGA curves in Figure 3 indicate that the 5 % weight-loss temperatures of (a) PMDA/DMDB, (b) PMDA/TFDB, (c) P2FDA/DMDB, and (d) P2FDA/TFDB are 481°C, 540°C, 410°C, and 431°C, respectively. Note that the PIs derived from TFDB exhibit higher degradation temperatures than those from DMDB. This can be attributed to the high thermal stability of $-\text{CF}_3$ group. In contrast, the PIs derived from P2FDA exhibit significantly lower degradation temperatures than those from PMDA. The fluorines directly bonded to benzene ring of dianhydride may be easily eliminated by heat, and polymer degradation is promoted. The TMA curves in Figure 4 indicates the coefficients of thermal expansion (CTE) are -3.6 , -3.7 , 7.7 , and 6.1 (ppm/°C) for PIs (a)–(d), respectively. A negative CTE value has been reported for PMDA/TFDB (b) [8]. Note that the CTE become positive by the incorporation of fluorines into dianhydride, not by the incorporation into diamine. This systematic result indicates that the CTE values are mainly influenced by the dianhydride structure, not by the diamine structures despite the higher fluorine contents in the PIs derived from TFDB. The positive CTE values observed for the PIs derived from P2FDA indicate that the intermolecular packing state and its variations by heating are significantly modified by the fluorination of dianhydride. This should be related to the relatively low Δn of these PIs.

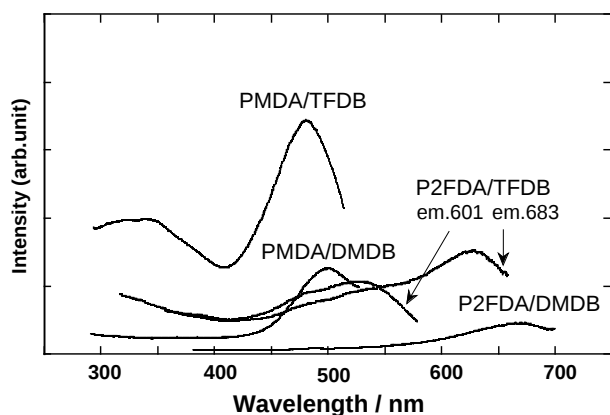


Fig. 8 Excitation spectra of the polyimide films. Two excitation peaks are observed for PMDA/TFDB and P2FDA/TFDB.

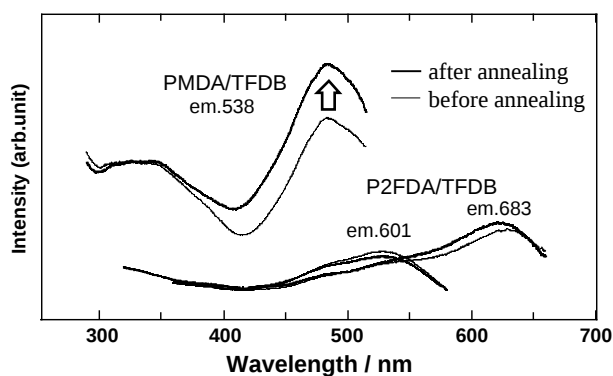


Fig. 10 Changes in the excitation spectra caused by annealing at 350°C for 4h for the TFDB polyimides.

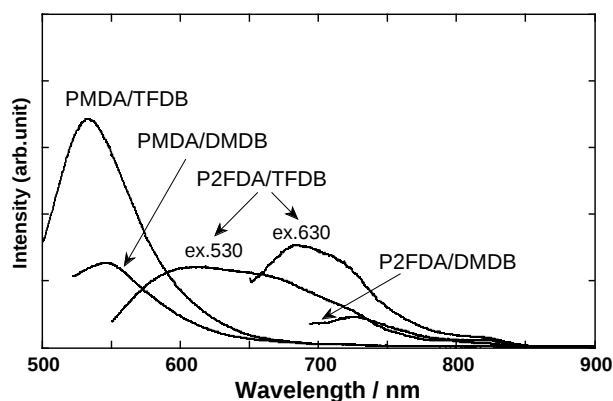


Fig. 9 Emission spectra of the polyimides. Two independent emission are observed for P2FDA/TFDB.

3.4 Optical Absorption Spectra

It should be noted first the unusual coloration of PIs derived from P2FDA. P2FDA/TFDB shows bright-red, and P2FDA/DMDB shows red-dish-brown color, though both PIs are transparent. To our knowledge, such colorations have never been reported for PIs whose source materials have no color. (All the source materials in this study are white solids.) On the other hand, PMDA/DMDB shows yellowish color, which is typical for unfluorinated PIs, and PMDA/TFDB shows very pale yellow, which is also typical for partially fluorinated PIs [8].

Figure 5 shows the UV/Vis absorption spectra of the PI films (4 μm -thick). The PIs derived from P2FDA exhibit a distinct peak at 500 nm, and the absorption edges (λ_0) are significantly displaced to longer wavelengths by 200-300 nm than those from PMDA. These peaks should be the main cause of the unusual coloration. Dine-Hart *et al.* [11] discussed first the color of PI films in terms of CT interactions, and they showed that imide compounds derived from PMDA significantly changed in color with the electron-donating abilities of amine-moieties. In addition, we have demonstrated that the coloration of PIs is well explained in terms of the degree of electron-accepting abilities of dianhydride when the diamine moiety is fixed [7]. If the absorption peak at 500 nm is closely related to the CT interactions, this peak should be displaced depending on the degree of CT. However, as shown in Figure 6, the PI synthesized from P2FDA and an alicyclic diamine (DCHM), in which little CT interactions are expected, also exhibits an absorption peak at 500 nm despite its lower peak intensity. Hence, this peak is assigned to the π - π^* transition within the P2FDA moiety. Another distinct peak observed at 320 nm in PMDA/DCHM has been assigned to the local π - π^* transition at the PMDA moiety [12]. Furthermore, the absorption edges (λ_0) are shifted as DCHM < TFDB < DMDB in an increasing order for both of PMDA and P2FDA-based PIs. This agrees well with the order of the calculated band gaps and thus the degree of CT interactions. The PIs having high CT interactions show longer λ_0 s, which clearly indicates that the absorptions related to CT interactions are located close to the absorption edges. Figure 7 shows the absorption spectra of model compounds of the PIs. The models (a) and (b) show only weak absorption at 310 nm originating from the π - π^* transition at the PMDA moiety. In contrast, the absorption peaks observed for models (c) and (d) are much more intense than those of (a) and (b). In addition, the absorption peaks are displaced to longer wavelengths than those of the corresponding

PIs. The peak at 560 nm is assigned to a π - π^* transition within the P2FDA moiety, and strong peaks at 340 nm for (c) and at 390 nm for (d) are assigned to localized π - π^* transitions at the P2FDA moiety.

3.5 Fluorescence Excitation/Emission Spectra

Figures 8 and 9 show the excitation and emission spectra of the PI films (10 μ m-thick). The peak wavelengths in the excitation spectra agree well with those of absorption edges for all the PIs except for the emission peak at a shorter wavelength for P2FDA/TFDB. This indicates that the fluorescence of PIs in this study is closely related to the CT interactions. In addition, the order of emission peaks (PMDA/TFDB < PMDA/DMDB < P2FDA/TFDB < P2FDA/DMDB) agrees well with that of the absorption edges. P2FDA/DMDB shows an emission peak at 728 nm and an excitation peak at 670 nm, which are much longer than those of the other PIs and conventional polyimides [13,14]. This clearly demonstrates that the stronger CT interactions can be introduced by the combination of highly electron-accepting P2FDA and highly electron-donating DMDB. In addition, the PIs having larger energy gaps show stronger emission signals. For instance, the substitution of TFDB for DMDB causes significant increases in emission intensity. PMDA/TFDB that has the largest band gap shows the strongest emission at 534 nm, and two peaks are observed in the excitation spectrum at 320 nm and 480 nm. In order to clarify the origin of these excitation peaks, this PI film was annealed at 350°C for 4h (Figure 10). The excitation peak at 480 nm was significantly intensified by annealing, though that at 320 nm was not affected. Hence, the former was assigned to the intermolecular CT band, and the latter was assigned to a band localized at PMDA moiety. A similar phenomenon was also observed for P2FDA/TFDB, though annealing caused much smaller changes in the excitation spectra. Note that P2FDA/TFDB, in which both moieties are fluorinated, exhibits two pairs of emission and excitation peaks. One of the excitation peaks coincides well the major absorption peak at 530 nm, and the other coincides with the absorption edge at 630 nm. This fact indicates that two independent chromophores can be separately excited by a band localized at P2FDA moiety and an intermolecular CT band. These two bands generate different light-emitting species in the excited states. These interesting fluorescence behaviors observed for the TFDB-based PIs should be related to the reduced intermolecular CT interactions caused by two $-\text{CF}_3$ groups. In contrast, P2FDA/DMDB shows a very weak fluorescence, which coincides well with that fact that the increase in CT interactions in PIs reduces emission intensity [15].

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