

Synthesis and characterization of star-shaped imide compounds

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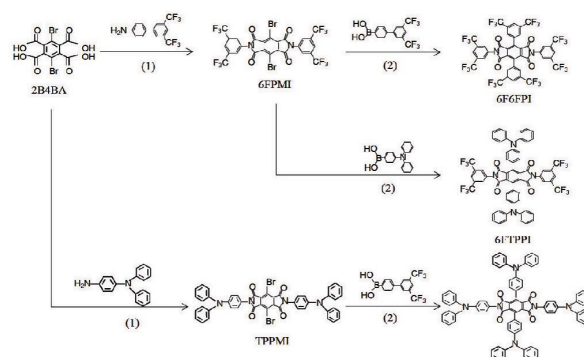
ABSTRACT: Novel star-shaped imide compounds containing electron-donating triphenylamine and/or electron-withdrawing bis(trifluoromethyl)phenyl side groups were synthesized via a two-step process. First, 3,6-dibromo-benzene-1,2,4,5-tetracarboxylic acid (2B4BA) was reacted with 4-aminophenyl (diphenylamine) (ATPA) or 3,5-bis(trifluoromethyl)aniline (6FA) by imide reaction. Then, Suzuki coupling reaction was carried out on these compounds with 4-(N,N-diphenylamino)-1-phenyl boronic acid (BTPA) or 3,5-bis(trifluoromethyl)phenyl boronic acid (6FBB), resulting in 3,6-bis[4-(diphenylamino)phenyl]-N,N'-bis[4-(diphenylamino)phenyl]pyromellitimide (TTPPMI), 3,6-bis[3,5-bis(trifluoromethyl)phenyl]-N,N'-bis[3,5-bis(trifluoromethyl)phenyl]pyromellitimide (6F6FPI) or 3,6-bis[4-(diphenylamino)phenyl]-N,N'-bis[3,5-bis(trifluoromethyl)phenyl]pyromellitimide (6FTPPPI). The imide compounds obtained were characterized by NMR, FT-IR, DSC, TGA, melting point analyzer, EA, and solubility measurements. In addition, their optical and electrical properties were evaluated by fluorescence spectroscopy, UV-vis spectroscopy, and cyclic voltammetry (CV). 6F6FPI exhibited deep blue emission (443 nm), along with high T_m (382 °C) and relatively high T_g (148 °C).

During the past decades, considerable research have been conducted on organic light emitting materials, especially on blue emitters [1] since they can be easily converted to green or red emitters via doping, but they require larger band gaps and defined optical properties, making more difficult to prepare than other color emitters. Currently, two-types of blue emitters are being investigated; small molecules and polymers. The former has received great attention because of their good optical and electrical properties, as well as their structural uniformity and ease of purification [2]. However, these molecules, in general, show poor solubility, thereby requiring thermal deposition rather than inexpensive solution processing.

Conjugated polymers, on the other hand, have received great attention since they can form robust films via inexpensive solution processing. Ever since polyphenylenevinylene was utilized for the first PLED in 1990 [3], a number of polymers have been prepared [4], such as polyfluorenes and polycarbazoles, providing deep blue emission and high quantum efficiency. However, these conjugated polymers have critical drawbacks such as difficulties in preparing high molecular weight polymers and poor long term color stability, being attributed to their rigid backbone structure and complicated chemistry, and to excimer formation [5] due to their low T_g (< 100 °C) [6], respectively.

Given this, polyimides can be a promising candidate for PLEDs due to their high T_g , in addition to their excellent optoelectronic properties [7], but their drawback is poor solubility. In fact, a number of polyimides with conjugation groups have been prepared for PLEDs, but preparation of soluble polyimides with blue emission and high T_g (~ 300 °C) proved to be difficult. Recently, imide-based small molecules exhibiting deep blue emission and good solubility but low T_g (< 120 °C) have also been reported [8]. In this study, therefore, an attempt was made to prepare imide-based star-shape compounds having a rigid backbone structure of pyromellitic dianhydride (PMDA) for high T_g and conjugated electron-withdrawing (trifluoromethyl) and/or electron-donating (triphenylamine) side groups for good optical and electrical properties. In addition, they were designed to have a molecular weight high enough to form robust films, but low enough to give good solubility, as well as mono-dispersed molecular weight distribution.

Scheme 1. Synthesis of imide compounds; (1) AcOH, N₂, reflux for 24 h, (2) toluene/MeOH, N₂, Pd(PPh₃)₄, aq. Na₂CO₃, reflux for 6 days



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As shown in Scheme 1, imide compounds are successfully prepared (see Supporting Information) and their UV-vis absorption and PL were measured. One of these compounds, TPTPPI exhibited absorption peaks at 290 and 410 nm (Fig. 1) which are being attributed to π - π^* transition resulting from the triphenyl moieties [9] and the intermolecular charge transfer of anhydride moiety [10], respectively. This is a typical examples of D- π -A molecules [11]. However, only a single absorption peak was observed at 305 nm and 260 nm from 6FTPPI and 6F6FPI, respectively, due to the electron-withdrawing nature of CF₃ groups [12].

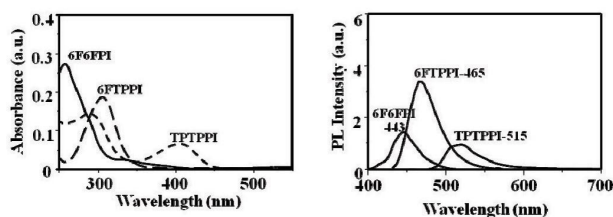


Fig. 1. UV absorption (left) and PL (right) of the imide compounds.

From the UV absorption edge wavelengths, their band gaps were calculated with the equation of $E_g = 1240/\lambda_0$, providing 2.77, 3.52, and 3.97 eV, respectively (Table 1), which demonstrated the effect of electron-withdrawing CF₃ group [12]. In the PL emission study, 6F6FPI exhibited deep blue emission (443 nm), followed by emission at 465 (6FTPPI) and 515 nm (TPTPPI), reflecting the decreased number of electron-withdrawing CF₃ groups. Despite its deep blue emission, 6F6FPI exhibited much lower PL peak intensity than 6FTPPI, but slightly higher than that of TPTPPI, as shown in Table 1. This can be attributed to non-coplanar conformation of 6FTPPI due to its two different types of side group compared with 6F6FPI and TPTPPI.

Table 1. Optical and electrical properties of imide compounds.

Imide compound	λ_{abs} (nm) ^a	λ_{em} (nm) ^b	$\lambda_{abs, onset}$ (nm)	Band gap ^c (eV)	$E_{ox, onset}$ (V) ^d	HOMO (eV)	LUMO (eV)
TPTPPI	290, 410	515	447	2.77	0.47	-4.87	-2.10
6FTPPI	305	465	352	3.52	0.58	-4.98	-1.46
6F6FPI	260	443	312	3.97	-	-	-

a. by UV-vis, 0.1 mg/ml in CHCl₃. b. by PL, 0.1 mg/ml in CHCl₃. c. from UV-vis absorption edge ($E_g = 1240/\lambda_0$), d. by CV

Cyclic voltammetry of the star-shaped imide compounds was evaluated. 6FTPPI sample exhibited onset of oxidation potential of 0.58 V and two oxidation peaks at 0.73 and 0.96 V, which may be attributed to the polymerization [13] and oxidation [14] of triphenylamine moiety, respectively. Similar CV spectra were observed from the TPTPPI providing onset of oxidation potential of 0.47 V, while no oxidation was shown with 6F6FPI, being explained by the absence of electron-donating groups such as triphenylamine moiety. From the oxidation potentials, HOMO energy levels of the compounds were calculated from the equation of $IP = -([E_{onset}]^{ox} + 4.4)$ eV, where IP is the ionization potential and $[E_{onset}]^{ox}$ is the onset oxidation potential [15], which resulted in -4.87 and -4.98 eV for TPTPPI and 6FTPPI, respectively (Table 1). As expected, the HOMO level

increased as the electron-withdrawing CF₃ groups are attached [12]. For TPTPPI and 6FTPPI, the LUMO energy levels were -2.10 and -1.46 eV, respectively, as calculated from the HOMO levels and optical band gaps measured from the UV absorption edge, decreasing as the CF₃ moieties are attached.

KEYWORDS: star-shaped imide compound, trifluoromethyl, triphenylamine, organic light emitting diode, blue emission

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SUPPORTING INFORMATION

Experimental procedures; synthetic and characterization of the imide compounds are available free of charge via the Internet at <http://photos.or.kr>

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