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Synthesis and characterization of difunctional blue light-emitting molecules containing hole-transporting triphenylamino units

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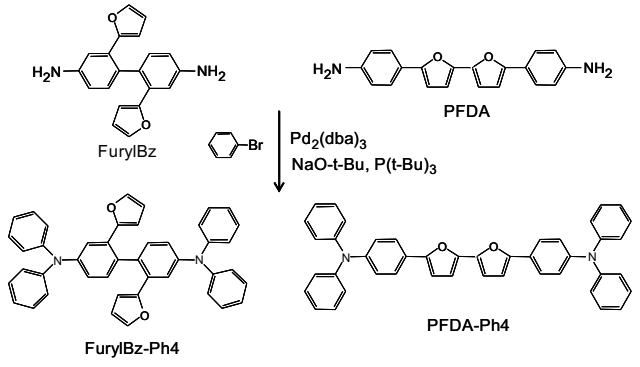
Abstract—The synthesis of new difunctional (i.e., light-emitting and hole-transporting) fluorophore molecules, 2,2′-difuryl-4,4′-(*N*,*N*,*N*′,*N*′-tetraphenyl)diaminobiphenyl and 5,5′-bis(4-*N*,*N*′-diphenylaminophenyl)-2,2′-bifuryl, which contain hole-transporting triphenylamino units, are reported. These difunctional molecules emit intense blue photoluminescence and further reveal high HOMO energy values as well as high glass transition temperatures.

The synthesis of luminescent organic materials has received a great deal of attention because of their potential use in light-emitting devices (LEDs). Several attempts have been made to combine the essential functions of fluorescence and charge transport in a single molecule.[1–3] For example, the derivatives of 1,3,5-tris(diaryl-amino)benzenes with various aryl substituents exhibit difunctionality as both hole-transporting materials and emitters.[3] Our research group is interested in the synthesis of difunctional (i.e., emitting and hole-transporting) materials that have both a low ionization potential, which minimizes the hole injection barrier from the transparent anode, and a high glass transition temperature, which ensures the thermal stability of the material.

In this article, we report the synthesis and properties of difunctional blue light-emitting molecules containing hole-transporting triphenylamino units, 2,2′-difuryl-4,4′-(*N*,*N*,*N*′,*N*′-tetraphenyl)diaminobiphenyl (FurylBz-Ph4) and 5,5′-bis(4-*N*,*N*′-diphenylaminophenyl)-2,2′-bifuryl (PFDA-Ph4). As can be seen in Scheme 1, the compounds are composed of light-emitting π-conjugation and hole-transporting triphenylamino units. In particular, the π-conjugation units consist of furyl rings containing oxygen atom, which has a relatively large electronegativity, compared to that of carbon and nitrogen atoms in other common π-conjugation compounds based on phenyl rings and/or vinyl moieties as well as that of nitrogen atom in hole-transporting triarylamines. Furthermore, such oxygen atom has two lone pair electrons, whereas the nitrogen atom possesses one lone pair electrons. Taking into account these characteristics of the oxygen atom, the furyl rings of the emitting units may cooperatively work with the triphenylamino units, positively contributing to the hole-transportation. The syntheses of 2,2′-bis(furyl)benzidine (FurylBz) and 5,5′-bis(4-aminophenyl)-2,2′-bifuryl (PFDA) were carried out according to a previously reported



Scheme 1. Syntheses of 2,2′-difuryl-4,4′-(*N*,*N*,*N*′,*N*′-tetra-phenyl)-diaminobiphenyl (FurylBz-Ph4) and 5,5′-bis(4-*N*,*N*′-diphenylamino-phenyl)-2,2′-bifuryl (PFDA-Ph4).

Keywords: Light-emitting units; Hole-transporting units; Difunctionalty; Blue light emit; Photoluminescence; Quantum yield.
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procedure.[4–7] FurylBz-Ph4 and PFDA-Ph4 were then synthesized using the Buchwald coupling reactions of 4-bromobenzene with FurylBz and PFDA, respectively, carried out in toluene at 100 °C for 24 h in the presence of tris(dibenzylidene-acetone) dipalladium [$Pd_2(dba)_3$], tri-*t*-butylphosphine [P(*t*-Bu)$_3$], and sodium *tert*-butoxide (NaO-*t*-Bu). The products were purified using silica-gel column chromatography and identified using proton and carbon nuclear magnetic resonance (^{1}H and ^{13}C NMR), Fourier-transform infrared (FT-IR) spectroscopy, and mass spectroscopy.

The photoluminescence (PL) properties of the fluorophores and of the fluorescent FurylBz-Ph4 and PFDA-Ph4 were investigated. The photoluminescence spectra were measured at room temperature using a fluorescence spectrophotometer (PTI Fluorescence System) with a Xenon lamp. For both excitation and emission monochromators, the band-passes were 2 nm. The PL spectra of the samples were obtained for solutions with a concentration of 1.5×10^{-5} g/mL in 1,4-dioxane. Their ultraviolet-visible (UV–vis) spectra are shown in Figure 1. The spectrum of FurylBz in 1,4-dioxane has an absorption maximum at 328 nm, which is considered to be due to the π–π^* transition leading to the formation of a singlet exciton.

The solution of FurylBz was then excited at this wavelength of 328 nm, which resulted in a PL emission peak at 434 nm. PFDA exhibits a broad, featureless absorption spectrum whose low energy edge lies at approximately 376 nm. The PL spectrum of PFDA contains two emission peaks at 415 and 440 nm when excited at a wavelength of 380 nm. Both fluorophores emit a very intense blue fluorescence.

The UV–vis spectra of FurylBz-Ph4 and PFDA-Ph4 have absorption peaks at 298 and 400 nm, respectively. When FurylBz-Ph4 in solution was excited at 300 nm, it displayed the most intense fluorescence spectrum. The PL emission spectrum of FurylBz-Ph4 has a peak maximum at 436 nm.

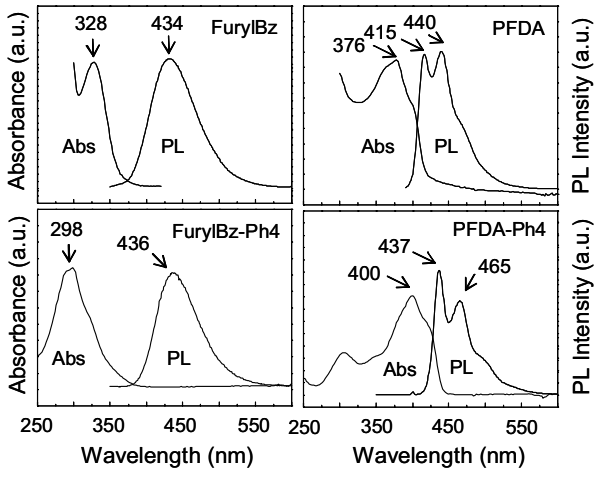

Figure 1. UV–visible absorption and photoluminescence spectra of FurylBz, PFDA, FurylBz-Ph4, and PFDA-Ph4 in 1,4-dioxane.

The spectra of PFDA-Ph4 in solution have an absorption peak at 400 nm, and two PL peaks at 437 and 465 nm when excited at 400 nm. This bathochromic shift with respect to the spectra of PFDA indicates that PFDA-Ph4 has a longer π-conjugation length than its fluorophore. According to molecular simulation results for PFDA, its phenyl and furyl rings are nearly coplanar in both its *trans* and *cis*-isomers.[7] This planar geometry might enhance the π-conjugation between the substituted phenyl rings and the PFDA unit. In contrast, FurylBz has a kinked structure composed of a benzidine unit and two furyl side groups. The blue-shifted absorption maximum of FurylBz-Ph4 thus implies that the efficiency of π-electron delocalization in FurylBz-Ph4 is lower than in FurylBz because of the need to minimize the steric hindrance created by the substitutions of the amino end groups. The appearance of vibronic peak maxima in the PFDA and PFDA-Ph4 emission spectra indicate that these molecules take on two different conformations in which their energy difference is very small. We also measured the PL quantum yields of the two compounds. Relative PL quantum yield was determined by comparing the ratio of the fluorescence emission intensity maximum to the UV–vis absorbance at the excitation wavelength used for the sample with that of a standard. The absorbances of all sample solutions were kept between 0.05 and 0.08 by varying the sample concentration in order to avoid any inner filter effects.

In this study, quinine sulfate was employed as the standard: the quantum yield of quinine sulfate in 1.0 N H_2SO_4 at 23 ± 1 °C has been reported to be $\Phi_f = 0.55$ when excited at 365 nm.[8–11] The refractive indices of pure 1.0 N H_2SO_4 and 1,4-dioxane, that is, of the standard and the solvent, were used in the estimation of the quantum yields. The quantum yields reported here were averaged over at least three measurements, with a standard deviation below 0.03 (Table 1). The PL quantum yields of FurylBz and PFDA were measured to be 0.52 and 0.92, respectively. The fluorophores FurylBz-Ph4 and PFDA-Ph4 exhibit slightly lower quantum yields (0.41 and 0.73, respectively). These reductions in the quantum yield may be due to unfavorable changes in molecular conformation due to the incorporation of the aryl groups on the amino end groups (Fig. 2).

FurylBz-Ph4 and PFDA-Ph4 were further examined in solution using cyclic voltammetry measurements in order to measure their ionization potentials. The measurements were carried out in a three electrode cell and potentiostat assembly at a platinum electrode using millimolar solutions in methylene chloride containing 0.1 M of the supporting electrolyte and tetrabutylammonium hexafluorophosphate ($TBAPF_6$). The potentials were measured with respect to that of Ag/AgCl as the reference electrode, and each measurement was calibrated with an internal standard, the ferrocene/ferrocenium (*Fc*) redox system. The HOMO energy values for PFDA-Ph4 and FurylBz-Ph4 were calculated based on a value of −4.8 eV for *Fc* with respect to the zero vacuum level. This value was obtained from the calculated value of −4.6 eV for the standard electrode potential

Table 1. Optical, electrochemical, and thermal properties of the compounds

Compound	Absorption λ_{max} (nm)	Emission λ_{max} (nm)	Φ_f (%)	$T_g/T_c/T_m$[a] (°C)	T_d[b] (°C)	E_{ox} versus Ag/AgCl (V)	E_{ox} versus *Fc* (V)	HOMO (eV)
FurylBz-PPh4	298	436	0.41	81/143/270	420	0.90	0.46	−5.26
PFDA-PPh4	400	436, 464	0.73	77/139/223	401	0.57	0.13	−4.93
FurylBz	328	434	0.52					
PFDA	376	415,440	0.92					

[a] Determined by differential scanning calorimetry (DSC) at a heating rate of 2.0 °C/min under a nitrogen atmosphere.
[b] Determined by TGA at a heating rate of 10.0 °C/min under a nitrogen atmosphere.

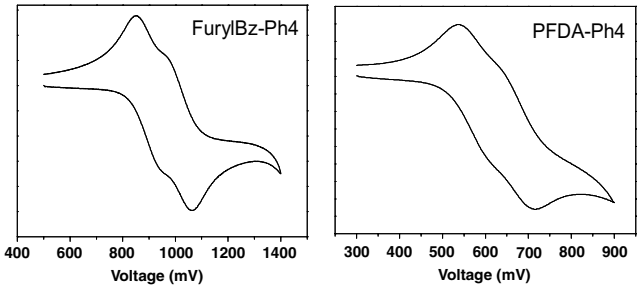

Figure 2. Cyclic voltammograms of FurylBz-Ph4 and PFDA-Ph4 in methylene chloride and 0.1 M $TBAPF_6$ at a scan rate of 50 m/V.

using a normal hydrogen electrode (NHE) on the zero vacuum level and the value of 0.2 V for *Fc* versus NHE. The measured oxidation potentials (E_{ox}) and the HOMO energy values for FurylBz-Ph4 and PFDA-Ph4 are given in Table 1.

FurylBz-Ph4 exhibits two distinct oxidation stages corresponding to the two oxidizable nitrogen centers. Two oxidation stages are also observed for PFDA-Ph4, but the distinction between them is not as clear as for FurylBz-Ph4. The peak separation values of the two compounds at a scan rate of 50 mV/s are approximately 100 mV, as is expected for reversible single-electron transfers. The HOMO values were determined from the first oxidation potential values with respect to *Fc*, as shown in Table 1. PFDA-Ph4 has a higher HOMO value (−4.93 eV) than FurylBz-Ph4 (−5.26 eV). This means that PFDA-Ph4 is expected to have a lower energy barrier to hole injection from an indium tin oxide (ITO) electrode when it is used as a hole transport blue emitter in an organic LED.

The thermal properties of the materials were examined using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). FurylBz-Ph4 and PFDA-Ph4 exhibit unambiguous glass transitions at 81 and 77 °C, respectively, which indicate the amorphous nature of these partially crystalline compounds. Since crystallization caused by Joule heating tends to create grain boundaries that limit charge transport and prevent good contact, the relatively high glass transition temperatures of these compounds indicate that they can be used in the fabrication of LEDs with glassy films. These two compounds are thermally stable up to 400 °C under a nitrogen atmosphere. Their glass transition temperatures (T_g), melting temperatures (T_m), and recrystallization temperatures (T_c) are summarized in Table 1.

In conclusion, we have demonstrated the synthesis and photoluminescence properties of new fluorophores containing hole-transporting triphenylamino units (i.e., FurylBz-Ph4 and PFDA-Ph4). Efficient blue light emission is observed from solutions of both compounds. In addition, both the compounds exhibit relatively high glass transition temperatures and high HOMO energy values. Hence they have potential as bifunctional materials with hole-transporting and emitting capabilities, and also can be used as photoconductors and photorefractive materials.

Acknowledgements

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