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Solution-Processable Polyphenylphenyl Dendron Bearing Molecules for Highly Efficient Blue Light-Emitting Diodes

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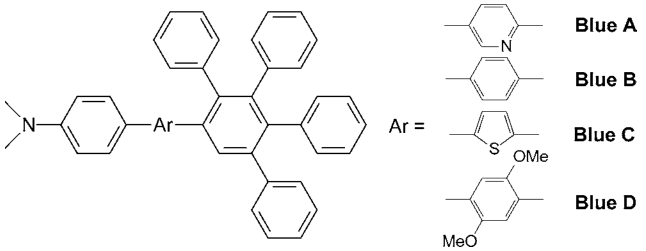
ABSTRACT



Novel solution-processable blue light-emitting materials Blue A–D, bearing a polyphenylphenyl dendron, have been synthesized and characterized. The energy levels and band gaps can be facilely tuned by changing the central aromatic ring of the molecules. A highly efficient deep blue light-emitting OLED device based on Blue C with a maximum current efficiency of 2.2 cd/A has been achieved using PVK as the host material through a solution process.

Electroluminescent materials have attracted significant attention ever since the first contribution of small molecular organic light-emitting diodes (SMOLED) by Tang[1] et al. and polymeric light-emitting diodes (PLED) by Friend[2] et al. due to their great potential application in flat panel displays. In the past decade, great efforts have been paid to develop novel electroluminescent materials with intense luminescent efficiency, good thermal/electrical/optical stability, and desirable film morphology.[3−7] Most of the organic light-emitting materials developed so far have high quantum efficiency in solution but few exhibit high quantum yield in films due to the existence of more nonradiative decay channels, which are associated with aggregates, excimers, exciplexes, and impurities in the solid state. Complete amorphous morphology of films can effectively prevent the formation of aggregates, excimers, and exciplexes, which can result in higher quantum efficiency and a stable emission spectrum. From the structural aspect, molecules with asymmetric and nonplanar structure can be readily processed into amorphous films through either spin coating or vacuum deposition. Starburst and dendrimer-type conjugated molecules or conjugated molecules bearing such types of hyperbranched side groups have been developed for this purpose.[8−10] However, the application of these hyperbranched structural materials as an emissive layer for OLED application is very limited due to the tedious synthesis and purification procedure. Recently, a new type of fully conjugated polyphenylphenyl

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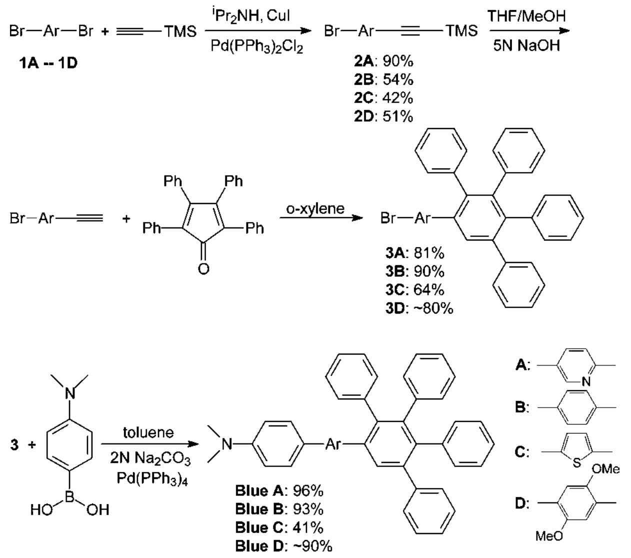
(tetraphenylphenyl and pentaphenylphenyl) dendron has been successfully incorporated into both small molecular weight light-emitting materials[11] and polymeric light-emitting materials[12,13] through simple synthetic procedure.[14] Such dendrons have been proven to be effective molecular construction blocks to inhibit the formation of molecular aggregation or $\pi-\pi$ stacking in the solid state.[12,13] In this letter, we report our new research effort in developing highly efficient light emitting materials, which are composed of three segments with well-defined conjugated length to achieve blue light emission. The molecules are designed with different central aromatic rings, which are coupled with tetraphenylphenyl group at one side and an *N*,*N*-dimethylaminophenyl attached at the other. Obviously, incorporation of nonplanar polyphenylphenyl dendron into the molecules is to suppress the chance of formation of molecular aggregates in films. This dendron structure also renders the molecules good thermal stability and solubility for spin coating. Solution process could simplify the device fabrication procedure and can reduce the cost. Attachment of a strong electron-donating group of *N*,*N*-dimethylaminophenyl ring at another end of the molecule can further enhance the device efficiency by elevating the HOMO energy levels of the molecules for ease of hole injection/transporting in the film. The central group is varied from an electron-donating thienyl ring, 2,5-dimethoxyphenyl ring, and phenyl ring to an electron-withdrawing pyridyl ring for the aim of tuning the energy levels and charge-transporting properties of the resulting materials. Deep blue light-emitting OLED devices with good device performance have readily been fabricated from the newly developed materials through solution process.

These four blue light-emitting polyphenylphenyl compounds, **Blue A**−**D**, were synthesized following the synthetic routes outlined in Scheme 1. Palladium-catalyzed Sonogashira coupling reactions between the dibromo compounds and (trimethylsilyl)acetylene were employed to introduce the ethynyl group into the central aromatic ring. When equal molar numbers of the starting materials were used, good to excellent yields of monosubstituted products can be obtained (yields ranged from 42% to 90%). The extremely high yield of compound **2A** is due to the good selectivity of oxidative addition of 2-bromo of 2,5-dibromopyridine to the palladium catalyst over the 5-bromo position. Thereafter, tetraphenylphenyl groups were introduced into the molecular backbones through the simple Diels−Alder cycloaddition reaction between the arylethynyl and tetraphenylcyclopentadienone. Pure products of **3A**, **3B**, and **3C** can be easily obtained through recrystallization or flash column purification. However, purification of **3D** is rather difficult because of the similar solubility and polarity between the product and the starting materials. Therefore, the crude product **3D** was directly used for the next reaction to prepare compound **Blue D**. *p*-Dimethylaminophenyl groups were introduced to the molecular backbones through the Suzuki coupling reaction to improve the hole charge transport property of the molecules. The Suzuki coupling reactions achieved very high yields (>90%) except for **Blue C**. Pure **Blue D** was also obtained after silica gel column purification. The impurity in crude compound **3D** did not affect this coupling reaction.

Scheme 1



Thermal properties of the materials **Blue A**−**D** were investigated with thermal gravimetric analyses (TGA) and differential scanning calorimetry (DSC). All the materials show very good thermal stabilities. The onset decomposition temperatures are 332, 296, 306, and 326 °C for **Blue A**−**D**, respectively. Obvious glass transmission temperatures (T_g) were observed for **Blue B**−**D** at 124, 100, and 118 °C, respectively, in the second heating run. High T_g is believed to be good for long lifespan device operation. No T_g for **Blue A** was observed probably because of the existence of strong dipole−dipole interaction between **Blue A** molecules, which makes the molecules too rigid in solid state.

Ultraviolet absorption (UV), photoluminescence (PL) spectra, and the relative fluorescence quantum efficiencies (η_{PL}) of the four compounds in chloroform solution with the concentration of about 1×10^{-5} M were measured at room temperature. The quantum efficiencies were determined to be 33%, 14%, 35%, and 7.0% for **Blue A**−**D**, respectively, using quinine sulfate (1×10^{-5} M dissolved in 0.1 M H_2SO_4) as a reference. As shown in Table 1, the $\pi-\pi^*$ energy band gaps of these materials were estimated from the UV spectra absorption edges to be 3.10, 3.25, 2.84, and 3.25 eV for **Blue A**−**D**, respectively. It can be seen that the energy band gaps of these compounds can be easily tuned by changing the central aromatic ring in the compounds, and the lower band gap of **Blue C** is ascribed to the electron-rich nature as well as the better conjugation of the thienyl ring with the two adjacent phenyl rings linked at 2 and 5 positions. Theoretical calculation indicated the dihedral angle of the most stable

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Table 1. Physical Properties of the Materials

material	T_d (°C)	T_g (°C)	UV λ_{max} in $CHCl_3$ (nm)	band gap (eV)	PL λ_{max} in $CHCl_3$ (nm)	η_{pl} in $CHCl_3$	p-doping (V)			energy levels (eV)	
							E_{onset}	E_a	E_c	HOMO	LUMO
Blue A	332	/	332	3.10	382 (429)	33%	0.70	0.95	0.77	−5.10	−2.00
Blue B	296	124	323	3.25	373	14%	0.66	0.91	0.62	−5.06	−1.81
Blue C	306	100	362	2.84	419	35%	0.50	0.72	0.52	−4.90	−2.06
Blue D	326	118	329	3.25	396	7.0%	0.56	0.82	0.60	−4.96	−1.71

conformation between thienyl ring and phenyl ring is about 40°, while that in biphenyl is 45−46°.[15,16] The energy band gap of **Blue D** will not be affected by the alkoxy substituents on the central phenylene ring compared to **Blue B**. However, the maximum absorption of **Blue D** is red shifted by 6 nm compared to **Blue B** in solution. It is noteworthy that the PL spectrum of **Blue A** is much broader than the others and also shows a large Stockes shift. The full width at half-maximum (fwhm) of PL spectra of **Blue B−D** are 59, 73, and 55 nm and the Stockes shifts are 50, 57, and 67 nm, respectively; the fwhm and Stockes shift of **Blue A** are 108 and 97 nm, respectively. Similar broader emission was also observed in solutions using different solvent, e.g., hexane, toluene, and THF. The much broader PL spectrum and large Stockes shift are characteristic of intermolecular excimer emission, which have been observed in a few conjugated polymers.[17−19] The formation of excimers of **Blue A** in solution may be attributed to the strong dipole−dipole interaction between two molecules due to existence of strong electron-donating phenylamino group and electron-withdrawing pyridine ring in the same molecule.

Cyclic voltammetry (CV) was employed to investigate the electrochemical behaviors of these materials. The CV graphs were obtained with positively scan from 0 to 1.2 V with the materials in 0.10 M of tetrabutylammonium perfluorate phosphate (Bu_4NPF_6) in anhydrous CH_2Cl_2 solution. The onset potentials for oxidation of the materials were observed to be 0.70, 0.66, 0.50, and 0.56 V (vs SCE) for **Blue A−D**, respectively. The HOMO energy levels were estimated to be −5.10, −5.06, −4.90, and −4.96 eV for the four materials according to the equation HOMO $= -([E_{onset}]^{ox} + 4.4)$ eV.[20] The HOMO energy level for **Blue C** is the highest and higher than that of **Blue A** by 0.20 eV. It is obvious that the electron-donating nature of the central aromatic ring can help to raise the HOMO energy levels and electron-withdrawing groups will lower the HOMO levels of the materials. Therefore, the HOMO energy levels of the compounds can be easily controlled by changing the central aryl group or introducing substituents with different electronic properties. The respective LUMO energy levels of the compounds were estimated to be −2.00, −1.81, −2.06, and −1.71 eV, by combining the HOMO energy levels together with the energy band gaps obtained from the edge absorption of the solution samples. All data are summarized in Table 1, from which we can find that **Blue C** possesses the highest HOMO energy level, lowest LUMO energy level, and lowest energy band gap among the four materials.

Multilayer devices were fabricated to investigate the performance of the four blue light-emitting materials with the device configuration of ITO/PEDOT:PSS (50 nm)/blue material:PVK (2%, w:w) (50 nm)/BCP (10 nm)/Alq_3 (20 nm)/LiF (0.5 nm)/Al (200 nm). The first layer of poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonic acid) (PEDOT:PSS) was spin-coated on a glass substrate with patterned ITO to form a hole injection layer. After this, dried in an oven at 120 °C for 5 min. A solution containing 4 mL of toluene, 40 mg of PVK, and 0.8 mg of blue light-emitting material (2% dispersed in PVK) was spin-coated onto the first layer to form an emitting layer with a thickness of about 50 nm. On the emissive layer, 10 nm of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), 20 nm of aluminum tris-8-hydroxyquinoline (Alq_3), 0.5 nm of LiF, and 200 nm of Al were thermally deposited sequentially under vacuum of 3×10^{-4} Pa. The organic electroluminescent devices obtained were examined in a drybox with a Keithley 2420 source meter and with a calibrated photodiode. EL spectra were recorded with an Ocean Optics USB2000 miniature fiber optic spectrometer. The current density-voltage and luminance-voltage characteristics for device of **Blue C** are

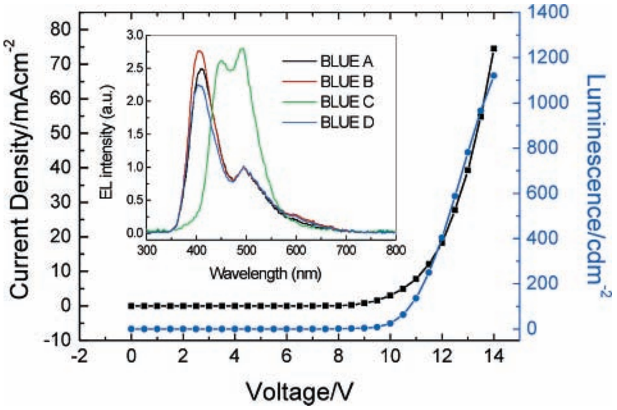

Figure 1. Current density−voltage and luminance−voltage characteristics of OLED device of **Blue C** with a configuration of ITO/PEDOT: PSS (50 nm)/**Blue C**:PVK (2%, w:w) (50 nm)/BCP (10 nm)/Alq_3 (20 nm)/LiF (0.5 nm)/Al (200 nm). Insert is the EL spectra of the four materials **Blue A−D**.

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plotted in Figure 1, and the EL spectra of the four materials are shown as an insert. The turn on voltage (at a brightness of 1.0 cd/m^2) of **Blue C** is 8 V and the device reaches the maximum luminance of 1120 cd/m^2 at 14 V. The EL spectrum of **Blue C** shows two peak emission at 451 and 493 nm, with the CIE coordinates of (0.158, 0.201), corresponding to deep blue emission. **Blue A**, **B**, and **D** emit sky blue light with the maximum emission at about 406 nm and a clear side peak at 496 nm. The peak wavelength of emission, the CIE coordinates and the current efficiency/quantum efficiency of the devices are summarized in Table 2. It is interesting to note that device based on **Blue C** demonstrated much higher EL efficiency with a maximum current efficiency of 2.2 cd/A (400 cd/m^2 at 18 mA/cm^2) and external quantum efficiency of 1.6%, whereas the device efficiencies of other three materials are of only about 0.15 cd/A and 0.15% with the same device configuration. To the best of our knowledge, 2.2 cd/A is the highest efficiency reported so far for small molecules blue light-emitting devices fabricated through solution process. Solution process is cost-effective compared to vacuum deposition and thus is more desirable. This efficiency is also comparable to most of the reported small molecules blue OLEDs fabricated through vacuum deposition.[21,22]

Table 2. Device Performances of the Four Materials

material	EL $\lambda_{\max}$ (nm)	CIE (x, y)	η_{Curr} (cd/A)	η_{ex} (%)
Blue A	409 (496)	0.188, 0.179	0.16	0.16
Blue B	406 (496)	0.200, 0.186	0.15	0.15
Blue C	451 (493)	0.158, 0.201	2.2	1.6
Blue D	406 (496)	0.197, 0.201	0.15	0.14

Much lower electroluminescent efficiencies of the other three materials compared to **Blue C** could be ascribed to two factors: (i) PL efficiency lower than that of **Blue C**, especially for **Blue B** and **D**, and (ii) the mismatching energy levels of the three light-emitting materials with that of the host material of PVK, as shown in Figure 2. By comparing the energy levels of **Blue C** with PVK, it can be seen that both the HOMO and LUMO of **Blue C** are lying between the energy levels of PVK. Thus both the hole and electron charge carriers injected into PVK from the hole injection layer and electron transport layer, respectively, could be easily transferred to the guest material of **Blue C**. Therefore, the charge recombination and light emission will occur at the guest materials rather than PVK. On the contrary, in devices of **Blue A**, **B**, and **D**, the holes are able to be transferred from PVK to the guest materials but the electrons will mostly be trapped in the host matrix. Thus, most excitons will be generated from the host materials in the three cases. The EL spectra of **Blue A**, **B** and **D** indicated that the emission is mainly from the host materials as expected, which demonstrated characteristic PVK emission peaked at 406 to 409 nm.[23] The side peak emission at 496 nm with low intensity is from the guest materials. As we know that PVK is a good host and hole transport material but not a good light emitter for OLEDs, the much lower efficiency for devices of **Blue A**, **B**, and **D** is thus rational.

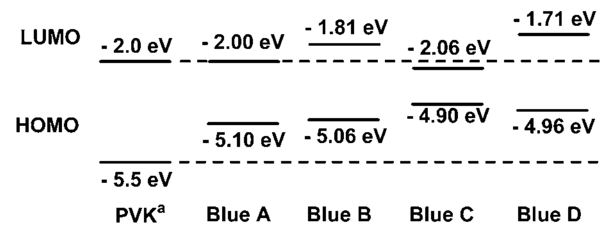

Figure 2. Energy levels of PVK and the four blue light-emitting materials. The energy levels of PVK were cited from ref 24. The values are in good agreement with the data obtained from electrochemical measurement performed in our lab.

In summary, a series of novel blue light-emitting materials comprising a polyphenylphenyl dendron, phenylamino group, and central aromatic ring that varied from pyridylene, phenylene, thienylene, and 2,5-dimethoxyphenylene has been synthesized through a simple synthetic route. All the materials show good thermal stability and high glass transition temperature (>100 °C). The four materials demonstrate very good solubility in common organic solvents, which makes them promising candidates for OLED device fabrication through solution process. The electronic properties of the resulting materials can be easily tuned through changing the central aromatic ring. A highly efficient and deep blue light-emitting OLED device has been demonstrated by using compound **Blue C** as the emitter and PVK as the host material through spin coating. The current efficiency and external quantum efficiency of **Blue C** are 2.2 cd/A and 1.6%, respectively, which is the highest efficiency reported so far for solution-processed small molecules blue OLEDs. The higher EL efficiency of **Blue C** compared to the others is ascribed to the higher PL efficiency and matched energy levels between **Blue C** and the host material (PVK), in which the charge carriers injected into the PVK matrix can be fully transferred to the guest materials to achieve highly efficient light emission.

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Supporting Information Available: Synthetic procedures, UV−vis and PL spectra, and cyclic voltammetric graphs for the compounds of **Blue A−D**. This material is available free of charge via the Internet at http://pubs.acs.org.

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