Date: 02-08-12 11:49:24

Eurjocan Journal of Organic Chemistry

DOI: 10.1002/ejoc.201200641

Synthesis, Properties and Applications of Biphenyl Functionalized 9,9-Bis(4diphenylaminophenyl)fluorenes as Bifunctional Materials for Organic Electroluminescent Devices

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Keywords: Hyperconjugation / UV/Vis spectroscopy / Biaryls / Semiconductors / Photochromism / Light-emitting diodes

Four new bifunctional materials, namely **BPTF**, **CBPTF**, **CMBPTF** and **BPVTF**, having 9,9-bis(4-diphenylaminophenyl)fluorene as a molecular platform and biphenyl derivatives as end-capping substituents were synthesized and characterized. Their optimized structures revealed that both triphenylamine moieties at the C-9 position of the fluorene ring generated a bulky molecular structure. These molecules showed strong blue emission in both solution and in the solid state, and were thermally stable amorphous materials with glass transition temperatures up to 207 °C. The abilities of these materials to act as blue-light-emitting materials for blue OLEDs and hole-transporting materials for green OLEDs in terms of device performance and thermal proper-

Introduction

Organic light-emitting diodes (OLEDs) have attracted a great deal of attention due to their potential applications in full-color or large-area flat panel displays, backlight, and general illumination.^[1] In the past decades, we have seen great progress in the development of electroluminescent materials with high luminescent efficiency, good thermal/optical stability, excellent charge-carrier injection and transport, and designed film morphology, as well as in the fabrication of high-performance devices.^[2] For full-color display applications, blue, green, and red materials and devices with high emission efficiency and high color purity are required. The performance of deep-blue OELDs are usually inferior to those of green and red OLEDs due to poor carrier injection into the emitters,^[3] and hence the electroluminescent

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- Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201200641.

ties were superior to commonly used N,N'-diphenyl-N,N'bis(1-naphthyl)-(1,1'-biphenyl)-4,4'-diamine (NPB). Efficient, and bright nondoped deep-blue and Alq3-based green OLEDs with maximum luminance efficiencies and CIE coordinates of 2.48 cd A⁻¹ and x = 0.15 and y = 0.07, and 4.40 cd A⁻¹ and x = 0.28 and y = 0.52 were achieved, respectively, with **BPTF** having two biphenyl substituents as active layers. Both devices showed low turn-on voltages of 3.1 and 2.8 V, respectively. Notably, the color purities of these deepblue and green devices were close to the National Television Standards Committee blue (CIE coordinates of x = 0.14 and y = 0.08) and green (CIE coordinates of x = 0.26 and y = 0.65) standards.

(EL) properties of the blue materials need to be improved, particularly in terms of EL efficiencies and color purity. The materials that emit a deep-blue color with excellent Commission International De L'Eclairage (CIE) coordinates of x = 0.14 and y = 0.08 for the National Television Standards Committee (NTSC) standard blue need to have excited energies near 3.1 eV.^[4] Such deep-blue emitters have high ionization potentials and low electron affinities. Although many blue light-emitting materials based on pyrene,^[5] anthracene,^[6] fluorenes,^[7] aromatic hydrocarbon,^[8] and triarylamine^[9] derivatives have been reported, the EL efficiencies of these deep-blue OLEDs (CIE coordinates of x = 0.15 and y = 0.10) are rather poor compared to those of sky-blue OLEDs (CIE coordinates of x = 0.15 and y > 0.15). Therefore, the search for new efficient deep-blue fluorescent materials with high performance remains a major challenge.

Among the blue emitters, inclusion of moieties such as fluorenes, spirofluorenes, oligomeric fluorenes, polyfluorenes (PFs), and their derivatives have been intensively investigated and these are regarded as the most promising candidates for blue OLEDs.^[10] However, the application of these materials as potential candidates for deep-blue OLEDs is still problematic because of deficiencies including low color purity due to unwanted emission at longer wavelengths from the aggregates, excimers, and fluorenone defects,^[11]



Scheme 1. Synthesis of the target molecules. Reagents and conditions: (a) CrO₃, acetic anhydride, room temp., 92%; (b) triphenylamine, CH₃SO₃H, 190 °C, 61 %; (c) [Pd(PPh₃)₄], 2 M Na₂CO₃, THF, heat; (d) carbazole, Cu, K₂CO₃, 18-crown-6, o-dichlorobenzene, heat; (e) 1. nBuLi, THF, -78 °C; 2. 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, -78 °C to room temp. and 3. acidic work up; (f) 5bromo-2-iodotoluene, [Pd(PPh₃)₄], K₂CO₃, THF/H₂O, heat.

and inefficient hole-injection that requires the use of holetransporting layers to obtain a balance in charge carriers, leading to a complex device structure.^[12,3] The hole-injection ability of these fluorene derivatives has been successfully improved by many approaches such as blending with hole-transporting triarylamines,^[13] end-capping the polymer chain with triarylamines,^[14] copolymerization with triarylamine-containing monomers,^[15] and substitutions at the C-9 position of the fluorene block with triarylamines.^[16] The latter approach was proven to be more effective, and involved a less complex synthesis. For example, 9,9-bis(4diphenylaminophenyl)fluorene [9,9-bis(triphenylmine)fluorene] has been successfully used as a building block for the synthesis of many blue emitting PFs and derivatives with improved hole-injection and suppressed aggregation.^[17] Hence, using this fluorene building block to construct new molecular materials might be a simple approach to the development of efficient deep-blue emitters.^[18] Therefore, we herein implemented all required aspects in the designed molecules (Scheme 1). The use of 9,9-bis(4-diphenylaminophenyl)fluorene as a molecular framework offers an ideal bulky molecule with high thermal stability and an improved hole injection and transport ability from the pendent triphenylamine (TPA) units.^[19] The presence of such bulky groups at the C-9 position of the framework would also suppress the aggregation phenomena and reduce excimer formation, resulting in a stable blue emission.^[20,16] Incorporation of a biphenyl moiety into this platform should assure intense deep-blue emission.^[21] The use of fluorene and biphenyl groups has a number of advantages, including the capability of the material to emit in the blue part of the visible spectrum, and to increase chemical and photochemical stability.^[22] The high steric hindrance in the molecule also leads to good solubility and, thus, thermally stable amorphous thin films could be deposited by inexpensive solution processes. This would result in the generation of new bifunctional materials with combined blue emitting and hole-transporting properties. In this work, we present the synthesis and characterization of such materials, namely BPTF, CBPTF, CMBPTF, and BPVTF. An investigation of their physical and photophysical properties, and their applications as active layers in OLEDs is also reported.

Results and Discussion

Synthesis and Quantum Calculations

The designed molecules were synthesized as outlined in Scheme 1. We began with air oxidation of 2,7-dibromofluorene (1) with KOH/air in dimethyl sulfoxide (DMSO) to give 2,7-dibromofluorenone (2) as a yellow solid in low yield (31%). An improved yield of fluorenone 2 was accomplished by oxidation of 1 with CrO_3 as an oxidizing reagent in acetic anhydride, which produced 2 in good yield

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(92%). The 9,9-bis(4-diphenylaminophenyl)fluorene (3) intermediate was then synthesized by a tandem protocol that involved treatment of 2 with an excess of triphenylamine, catalyzed by CH₃SO₃H at 190 °C, and the product 3 was obtained as a white solid in 61% yield. Coupling of 3 with commercially available 4-biphenylboronic acid and 4-biphenylvinyleneboronic acid under Suzuki cross-coupling conditions catalyzed by $[Pd(PPh_3)_4]$ in the presence of Na₂CO₃ as base in tetrahydrofuran (THF) afforded BPTF and **BPVTF** in good yields as white and yellow solids, respectively; coupling of 3 with 4-carbazol-9-ylbiphenyldioxaborolanes 4 and 5 (see below) under the same conditions gave CBPTF and CMBPTF as white solids in good yields of 75 and 82%, respectively. The borolanes 4 and 5 were prepared in two steps. Ullmann coupling of commercially available 4,4'-dibromobiphenyl (6) with carbazole catalyzed by Cu/18-crown-6 in the presence of K_2CO_3 as base in o-dichlorobenzene followed by lithiation of the resultant compound 7 with nBuLi in THF, trapping the anion formed with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and acidic workup, gave 4 as a white solid in 85% yield. Suzuki cross-coupling of 2-[4-(carbazol-9-yl)benzene]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9) with 5-bromo-2-iodotoluene followed by treatment of the resultant compound 10 with nBuLi/2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane afforded borolane 5 as a white solid in 71% yield. The chemical structures and purities of these materials were established unambiguously through the use of NMR spectroscopy, mass spectrometry, and elemental analysis. Importantly, all the compounds showed good solubility in organic solvents, which opened the door to solution processing techniques.

To understand the electronic properties and the geometries of the synthesized molecules, quantum chemical calculations were performed by using the TDDFT/B3LYP/6-31G (d,p) method;^[23] the results are shown in Figure 1 and in the Supporting Information. The optimized structures of these compounds revealed that both TPA moieties at the C-9 position of the fluorene ring generated high steric hindrance, resulting in a bulky molecular structure and thereby preventing a close π - π stacking interaction of the molecule. In the highest occupied molecular orbitals (HOMO) of **BPTF, CBPTF, CMBPTF**, and **BPVTF**, π -electrons are localized on the TPA pendant groups, whereas in their lowest unoccupied molecular orbitals (LUMO), the excited electrons are delocalized over the quinoid-like fluorene-biphenyl plane. The HOMO–LUMO energy gaps (E_g cal.) obtained from quantum chemical calculations were found to be in the range of 3.06–3.49 eV. These values were slightly higher than those estimated from the optical absorption edge (E_g) (Table 1). There are factors that could be responsible for the discrepancy because the orbital energy difference between HOMO and LUMO is still an approximation of the transition energy because the transition energy also contains significant contributions from some two-electron integrals. The real situation is that an accurate description of the lowest singlet excited state requires a linear combination of a number of excited configurations.



Figure 1. The HOMO and LUMO orbitals of BPTF.

Photophysical and Physical Properties

The optical properties of **BPTF**, **CBPTF**, **CMBPTF** and **BPVTF** were investigated in dilute CH_2Cl_2 solution and as a thin film obtained by thermal evaporation on a quartz substrate (Figure 2, Table 1). Their absorption spectra in solution showed two absorption bands: one at approximately 300 nm assigned to the π - π^* local electron transition of the pendant TPA moieties, and a second, strong absorption band at longer wavelengths (327–395 nm) corresponding to the π - π^* electron transition of the fluorene–biphenyl conjugated backbone. The latter absorption band of **CBPTF** was red-shifted compared to that of **BPTF** due to the π -electrons in the ground sate being able to delocalize over the fluorene–biphenyl backbone and carbazole through the lone electron pair of the nitrogen atom of the

Table 1. Physical and photophysical properties of the synthesized molecules.

	Thin file λ_{abs}	m [nm] ^[a] λ _{em}	${\varPhi_{\mathrm{F}}}^{\mathrm{[b]}}$	$T_{\rm g}/T_{\rm c}/T_{\rm m}/T_{\rm 5d} \ [^{\circ}{\rm C}]^{[c]}$	$E_{1/2}$ vs. SCE [V] ^[d] E^{10}, E^{20}, E^{30}	E _{pc}	$E_{\rm g} [{\rm eV}]^{[{\rm e}]}$	$E_{\rm g}$ cal. [eV] ^[f]	HOMO/LUMO [eV] ^[g]
BPTF	327	426	0.35	166/ - / - /456	0.98, 1.51	0.73	3.31	3.47	-5.32/-2.01
CBPTF	346	438	0.24	207/324/359/487	0.98, 1.23	0.74, 0.83	3.19	3.39	-5.32/-2.13
CMBPTF	327	408, 426	0.20	192/270/320/343	0.98, 1.30	0.74, 0.81	3.26	3.49	-5.33/-2.07
BPVTF	395	446, 467	0.49	164/246/320/330	0.96, 1.22, 1.37	_	2.88	3.06	-5.29/-2.91

[a] Measured as a thin film obtained by thermal evaporation. [b] Measured in CH_2Cl_2 solution. [c] Obtained from DSC and TGA measurements. [d] Obtained from CV at a scan rate of 50 mV/s. [e] Estimated from the optical absorption edge, $E_g = 1240/\lambda_{onset}$. [f] Obtained from quantum calculations using TDDFT/B3LYP/6-31G (d,p). [g] Calculated by HOMO = $-(4.44 + E_{onset})$, and LUMO = HOMO $- E_g$, where E_{onset} is the onset potential of the oxidation.

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carbazole. The absorption band of **CMBPTF** was nearly identical to that of **BPTF** and blue shifted with respect to CBPTF. This is due to the methyl substituent on the biphenyl moiety of CMBPTF restricting free rotation of the biphenyl moiety, limiting the interaction between the fluorene-biphenyl and carbazole moieties. However, BPVTF possesses a more extended π -conjugation backbone due to the presence of the vinylene bond between the fluorene and biphenyl units, as observed in the DFT calculation, and its absorption spectrum was further red-shifted. In the solid state, similar absorption features with a slight redshift compared to their corresponding solution spectra were observed. These materials exhibited strong emission intensity and deep-blue emission in both solution and the solid state. Their fluorescence quantum yields ($\Phi_{\rm F}$) measured in CH₂Cl₂ solution using quinine sulfate solution in 0.01 M H_2SO_4 ($\Phi_F = 0.54$) ranged from 0.20 to 0.49. The solution photoluminescence (PL) spectra of BPTF, CBPTF and CMBPTF showed a featureless emission peak in the blue region (448-454 nm), whereas the spectrum of BPVTF exhibited two emission peaks at 459 and 482 nm. The thinfilm PL emission spectra of these materials appeared at the same region as their solution PL spectra, indicating that less ordered solid state packing occurred in this case due to their bulky molecular structures.



Figure 2. UV/Vis absorption (-) and PL spectra (---) measured (a) in CH₂Cl₂ solution and (b) as a thin film obtained by thermal deposition on quartz substrate.

For OLED applications, thermal stability of organic materials is crucial for device stability and lifetime. Thermal instability or low glass transition temperature (T_g) of the amorphous organic layer may result in degradation of organic devices due to morphological changes. The thermal properties of **BPTF**, **CBPTF**, **CMBPTF** and **BPVTF** were therefore investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Table 1, and the Supporting Information). These results suggested that all compounds were thermally stable materials with 5% weight loss temperatures (T_{5d}) well over 330 °C. DSC thermograms of all compounds displayed baseline shift due to glass transition temperatures (T_g) ranging from 166 to 207 °C. These results indicated that the materials were stable amorphous materials with high $T_{\rm g}$ values that were higher than those of commonly used HTMs such as N,N'diphenyl-N,N'-bis(1-naphthyl)-(1,1'-biphenyl)-4,4'-diamine (NPB) ($T_g = 100$ °C) and N,N'-bis(3-methylphenyl)-N,N'bis(phenyl) benzidine (TPD) ($T_g = 63 \text{ °C}$), and other triphenylamine derivatives.^[24] The results proved that the use of 9,9-bis(4-diphenylaminophenyl)fluorene as a molecular platform could improve the amorphous stability of the materials, which, in turn, could increase the service time in device operation and enhance the morphological stability of the thin film.^[25] Moreover, the abilities of these materials to form molecular glass and dissolve in organic solvents offers the possibility of preparing good thin films by both thermal evaporation and solution casting techniques, which are highly desirable for fabrication of OLED devices.

Electrochemical behaviors of all compounds were investigated by cyclic voltammetry (CV) (Figure 3, Table 1). In all cases, the first quasi-reversible oxidation wave appeared at nearly the same position (0.96-0.98 V) and was assigned to the removal of electrons from the TPAs and carbazoles, resulting in the formation of the corresponding radical cations, whereas the rest oxidation waves indicated the removal of electrons from the fluorene-biphenyl backbone. CV curves of BPTF, CBPTF and CMBPTF showed additional peaks at lower potential on the cathodic scan $(E_{\rm pc})$ at 0.73 and 0.83 V, which corresponded to electrochemical coupling reactions of the TPA radical cation (TPA⁺) and carbazole radical cation (CAZ⁺⁺), respectively. Repeated CV scans of these compounds also revealed an increasing change in their CV curves, demonstrating a series of electrochemical reactions leading to electro-polymerization of those radical cation species on the glassy carbon electrode surface. The multiple CV scans of BPVTF revealed a small change in CV curves, indicating a weak oxidative coupling of the pendent TPAs; thus, among the synthesized materials, **BPVTF** is a more electrochemically stable molecule. Usually, this type of electrochemical coupling reaction is detected in most TPA and carbazole derivatives with unsubstituted *p*-position of the phenyl ring and unsubstituted 3,6positions, such as in case of 2,7-bis[2-(4-diphenylaminophenyl)-1,3,4-oxadiazol-5-yl]-9,9-bis-*n*-hexylfluorene.^[26] A proposed oxidation and electrochemical coupling reaction of these materials is outlined in Figure 4. During the first oxidation, electrons are removed from nitrogen atom of both TPA and carbazole moieties to give radical cation (TPA^{$\cdot+$} and CAZ^{$\cdot+$}) form A, which undergoes electron delocalization to generate resonance forms B, C and D. These radical cations are highly reactive species and readily undergo dimerization coupling to form a stable neutral molecule. Resonance forms A, B and D, having the radical sited

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Figure 3. (a) CV curves of the synthesized materials, and multiple CV scans of (b) **BPTF**, (c) **CBPTF**, and (d) **BPVTF** measured in CH_2Cl_2/nBu_4NPF_6 at a scan rate of 50 mV/s.



Figure 4. A proposed oxidation and electrochemical reaction of triphenylamine and carbazole moieties.

either on the nitrogen atom (A) or on *ortho*-C atoms (B and D), are less likely to undergo dimerization coupling reactions due to high steric hindrance, thus this electrochemical reaction is more likely to take place through resonance form C.

However, the TPA units of **BPVTF** are unlikely to undergo such electrochemical reactions due to steric hindrance from the adjacent 4-biphenylvinylene moiety, which keep them away from each other and prevents coupling. Furthermore, this type of electrochemical reaction will become inactive in nondiffusion systems or in the solid state. Moreover, under these CV experiment conditions, no distinct reduction process was observed in any of the cases. The HOMO and LUMO energy levels of **BPTF**, **CBPTF**, **CMBPTF**, and **BPVTF** were calculated from the oxidation onset potentials (E_{onset}) and energy gaps (E_{g}) and the results are summarized in Table 1. The HOMO levels of these materials ranged from 5.29 to 5.33 eV, matching well with the work functions of the gold (Au) or indium tin oxide (ITO) electrodes and, hence, favoring the injection and transport of holes.

Electroluminescence Properties

Owing to their intense blue fluorescence and their HOMO levels (5.3 eV) lying between those of PEDOT:PSS (5.00 eV) and Alq3 (5.80 eV), the new synthesized materials

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BPTF, CBPTF, CMBPTF, and BPVTF could be used as bifunctional materials, namely blue light-emitting and holetransporting materials. This encouraged us to investigate the use of these compounds as emissive layers (EML) for blue OLED and hole-transporting layer (HTL) for Alq3based green OLED. The blue light-emitting diodes with the device structure of indium tin oxide (ITO)/PEDOT:PSS/ EML(50 nm)/BCP(40 nm)/LiF(0.5 nm):Al(150 nm) and green light-emitting diodes with the device structure of ITO/PEDOT:PSS/HTL(40 nm)/Alq3(50 nm)/LiF(0.5 nm): Al(150 nm) were fabricated. Tris(8-hydroxyquinoline) aluminum [Alq3; acting as the green light-emitting (EML) and electron-transporting layers (ETL)], the conductive polymer, poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) [PEDOT:PSS; acting as the hole injection layer], and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline [BCP; acting as the hole blocking layer (HBL)], were integrated together to enable the creation of high-performance devices. From our study and other reports,^[27] it was found that the incorporation of PEDOT:PSS in the device as a hole injection layer not only increased the maximum luminance from 6127 cd m^{-2} (η of 1.29 cd A⁻¹) in device XI to 26067 cd m⁻² $(\eta \text{ of } 4.40 \text{ cd } \text{A}^{-1})$ in device VI, but also significantly decreased the turn-on voltage from 5.8 V to 2.8 V (Table 2). Moreover, their EL spectra were almost identical. It has been pointed out that the lower operating voltage of PE-DOT:PSS-based devices can be attributed to the rough and porous surface of the spin-coated PEDOT:PSS polymer layer, which increases the contact area to enhance hole injection and lowers the barrier at the organic-organic interface by relocating the barrier to the more conductive PE-DOT:PSS layer.^[28] To enable high-performance devices, therefore, PEDOT:PSS was integrated into all devices as a hole injection layer. To compare blue light-emitting and hole-transporting abilities of the synthesized materials, NPB, a commonly used commercial HTM, was employed as reference EML and HTL materials and the reference devices (V and X) of the same structure were fabricated.

As nondoped blue emitters, under applied voltage, devices I–III emitted bright deep-blue light with maximum peaks centered at 420, 419, and 428 nm, respectively, whereas device IV emitted a sky-blue light with peak centered at 467 nm (Figure 5a). The electroluminescence (EL) spectra of all diodes matched with their corresponding PL spectra. No emission shoulder at longer wavelength owing to excimer and exciplex species formed at the interface of EML and HBL materials, which often occurs in the devices fabricated from EML with planar molecular structure, was detected in the EL spectra of devices I-III. The EL spectrum of device IV, having BPVTF as EML, displayed an emission shoulder corresponding to excimer and exciplex emissions.^[29] The former might arise from the ladder-type aggregate of the planar 2,7-bis[4-(biphenyl-4-yl)vinylene]fluorene moiety, whereas the latter is often observed at the interface of organic/organic layers in an OLED and can be tuned by adjusting the thickness of those layers.^[30] In devices I-III, the formation of these species could be prevented by the nonplanar nature of the biphenyl-fluorene backbones as well as the bulky nature of the 9,9-bis(4-diphenylaminophenyl)fluorene implemented as the molecular platform. Additionally, stable emission was obtained from all devices; the EL spectra did not change significantly over the entire driven voltages (see the Supporting Information). The current density-voltage-luminance (I-V-L) characteristics of the devices are shown in parts b-d of Figure 5, and their electrical parameters are summarized in Table 2. The light turn-on voltage at 1 cd m⁻² for all devices was in the range of 3.1-3.5 V and the operating voltage at 100 cd m⁻² was in the range of 4.9-5.7 V, indicating good performance was achieved for all the devices. The device characteristics in terms of maximum brightness, turn-on voltage, and maximum luminous efficiency clearly verified that the blueemitting abilities of these newly synthesized materials were greater than NPB-based blue device (device V). The results also revealed that **BPTF**, bearing two biphenyl moieties attached to the 2,7-positions of the 9,9-bis(4-diphenylaminophenyl)fluorene framework, had the best EML properties among these four materials in terms of both device performance and purity of emission color. Device I showed a high maximum brightness of 7277 cd m⁻² at 10.2 V, a maximum luminous efficiency of 2.48 cd A⁻¹, a maximum external quantum efficiency of 0.35%, and a low turn-on voltage

Device	Structure	$V_{\rm on}^{[a]}$	V ₁₀₀ ^[b]	$\lambda_{\max}^{[c]}$	$L_{\max}^{[d]}$	<i>I</i> ^[e]	$\eta^{[f]}$	EQE ^[g]	CIE ^[h]
Ι	ITO/PEDOT:PSS/BPTF/BCP/LiF:A1	3.1	4.9	420	7277	564	2.48	0.35	0.15, 0.07
II	ITO/PEDOT:PSS/CBPTF/BCP/LiF:A1	3.3	4.9	419	2603	476	1.06	0.35	0.16, 0.10
III	ITO/PEDOT:PSS/CMBPTF/BCP/LiF:Al	3.5	5.3	428	2230	467	0.91	0.30	0.16, 0.04
IV	ITO/PEDOT:PSS/BPVTF/BCP//LiF:A1	3.4	5.7	467	2248	411	0.72	0.12	0.17, 0.23
V	ITO/PEDOT:PSS/NPB/BCP/LiF:A1	3.4	5.5	436	343	241	0.73	0.24	0.15, 0.07
VI	ITO/PEDOT:PSS/BPTF/Alq3/LiF:Al	2.8	4.9	516	26067	1075	4.40	0.22	0.28, 0.52
VII	ITO/PEDOT:PSS/CBPTF/Alg3/LiF:Al	2.8	4.5	516	24000	1197	4.31	0.21	0.28, 0.52
VIII	ITO/PEDOT:PSS/CMBPTF/Ålq3/LiF:Al	3.1	5.3	517	23802	917	4.13	0.20	0.29, 0.53
IX	ITO/PEDOT:PSS/ BPVTF /Alq3/LiF:Al	3.3	5.5	516	21675	919	3.85	0.19	0.28, 0.52
Х	ITO/PEDOT:PSS/NPB/Alq3/LiF:Al	3.1	4.1	516	30044	1362	4.45	0.22	0.30, 0.54
XI	ITO/ BPTF /Alq3/LiF:Al	5.8	6.5	516	6127	1114	1.29	0.10	0.28, 0.52
XII	ITO/PEDOT:PSS/Alq3/LiF:Al	4.2	5.4	518	4961	693	0.91	0.05	0.30, 0.54

Table 2. Device characteristics of OLEDs.

[a] Turn-on voltage [V] at 1 cd m^{-2} . [b] Voltage [V] at luminance of 100 cd m^{-2} . [c] Emission maximum [nm]. [d] Maximum luminance $[\text{cd m}^{-2}]$. [e] Current density at maximum luminance $[\text{mA cm}^{-2}]$. [f] Luminance efficiency $[\text{cd A}^{-1}]$. [g] External quantum efficiency [%]. [h] CIE coordinates (x, y).

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Figure 5. (a) PL (-) and EL (---) spectra; (b) V-L characteristics; (c) I-V characteristics; (d) variation of luminance efficiency with current density of the fabricated blue OLED devices using the synthesized materials as EML.

of 3.1 V, which is considered to be one of the lowest turnon voltages for deep-blue OLED. This device also emitted intense deep-blue color (420 nm) with CIE coordinates of x= 0.15 and y = 0.07, which is close to the National Television System Committee (NTSC) deep-blue (CIE coordinates of x = 0.14 and y = 0.08) standard.^[4] A lower device performance was observed from devices II (CBPTF as EML) and III (CMBPTF as EML), displaying a maximum luminous efficiency of 1.06 and 0.93 cd A^{-1} , respectively. The trend in device luminous efficiencies of devices I-III matched very well with the observed decrease in PL quantum efficiencies of the EML on going from BPTF to CBPTF to CMBPTF (Table 1). It has been demonstrated that the efficiency of an OLED depends both on the balance of electrons and holes, and on the $\Phi_{\rm F}$ of the emitter.^[31] Analysis of the band energy diagrams of these diodes also revealed that the HOMO levels of BPTF, CBPTF, **CMBPTF**, and **BPVTF** (5.29–5.33 eV) sat perfectly between those of the hole injection layer (PEDOT:PSS, 5.00 eV) and HBL (BCP, 6.50 eV), resulting the an efficient charge recombination in the emitting layer and better device performance (see the Supporting Information). Fluorescence quantum yield ($\Phi_{\rm F}$) of **BPVTF**, however, was higher than BPTF, and was also significantly higher than those of **CBPTF** and **CMBPTF**. In contrast, the emission efficiency of device V, having BPVTF as EML, was relatively low among these four EMLs. The reason for the poor performance of device IV might come from the presence of excimer and exciplex emission at the longer wavelength side in the EL spectrum.^[32] Excimer formation has also been found on polyfluorenes (PFs).^[33]

As HTLs, devices VI-IX exhibited light turn-on voltages at 1 cd m^{-2} in the range of 2.8–3.3 V and the operating voltages at 100 cd m⁻² in the range of 4.9–5.5 V, indicating good performance is achieved for all the devices (Figure 6, Table 2). By comparison with the reference device XII, it was found that the incorporation of BPTF, CBPTF, CMBPTF, and BPVTF in the devices as HTL not only increased the maximum luminance from 4961 cd m⁻² (η of 0.91 cd A⁻¹) to 21675–26067 cd m⁻² (η of 3.85–4.40 cd A⁻¹) in devices VI-IX, but also significantly decreased the turnon voltage from 4.2 V to 2.8-3.3 V. Furthermore, their EL spectra were nearly identical. Moreover, the device characteristics in terms of luminous efficiency clearly demonstrated that the hole-transporting abilities of these materials were comparable to those of the NPB-based device (device X). Device VI, having compound BPTF as HTL, exhibited the best performance with a high maximum brightness of 26067 cd m^{-2} for green OLED at 10.4 V, a low turn-on voltage of 2.8 V, a maximum luminous efficiency of 4.40 cd A^{-1} , and a maximum external quantum efficiency of 0.22%. A comparable device performance was observed from devices VII (CBPTF as HTL) and VIII (CMBPTF as HTL) (Table 2). Under the applied voltage, all devices (VI–VIII) exhibited a bright-green emission with peaks centered at 516 nm, and CIE coordinates of x = 0.28 and y = 0.52(Figure 6, a). The electroluminescence (EL) spectra of these diodes were identical, and matched with the PL spectrum of Alq3, the EL of the reference devices (X-XII), and also of other reported EL spectra of Alq3-based devices.^[34] No emission at the longer wavelength owing to exciplex species formed at the interface of HTL and ETL materials, which



Figure 6. (a) EL spectra; (b) V-L characteristics; (c) I-V characteristics; (d) variation of luminance efficiency with current density of the fabricated green OLED devices using the synthesized materials as HTL.

often occurs in the devices fabricated from HTL with planar molecular structure, was detected.^[35] In our case, the formation of exciplex species could be prevented by the bulky nature of the 9,9-bis(4-diphenylaminophenyl)fluorene. From these results, and in view of the fact that a barrier for electron-migration at the Alq3/HTL interface (ca. 0.9 eV) is higher than those for hole-migration at the HTL/ Alq3 interface (ca. 0.5 eV), under the present device configuration of ITO/PEDOT:PSS/HTL(50 nm)/Alq3(50 nm)/ LiF(0.5 nm):Al(200 nm), BPTF, CBPTF, CMBPTF and BPVTF would act only as HTL, and Alq3 would act preferably as an electron blocker more than as a hole blocker and charge recombination thus confined to Alg3 layer. More importantly, a stable emission was obtained from all diodes (VI-VIII), with the EL spectra and CIE coordinates remaining unchanged over the entire applied voltages (see the Supporting Information). Although many blue-emitting and hole-transporting materials have been reported, in terms of the amorphous morphology, high $T_{\rm g}$, and device efficiency, BPTF is among the best bifunctional materials available.

Conclusions

We have successfully designed and synthesized four new bifunctional materials, namely **BPTF**, **CBPTF**, **CMBPTF**, and **BPVTF**, as nondoped deep-blue light-emitting and hole-transporting materials for OLEDs. By the use of 9,9bis(4-diphenylaminophenyl)fluorene as a molecular platform, we were able to maintain high blue emissive ability of the fluorene in the solid state, and improve the amorphous stability of these materials. Strong deep-blue emission in solution was also obtained. All of the compounds were thermally stable amorphous materials, with the lowest glass transition temperature being 166 °C. Their abilities to act as both blue light-emitting materials for blue OLEDs and as hole-transporting materials for green OLEDs in terms of device performance and thermal properties were greater than commonly used NPB. Importantly, BPTF, bearing two biphenyl moieties attached to the 2,7-positions of the 9,9bis(4-diphenylaminophenyl)fluorene, showed promising potential as both a deep-blue light-emitting and hole-transporting material for use in OELD devices. Nondoped deepblue OLEDs with a maximum luminance efficiency of 2.48 cd A^{-1} , and green OLEDs with maximum luminance efficiency of 4.40 cd A⁻¹, were achieved with low turn-on voltages of 3.1 and 2.8 V, respectively. Notably, the color purities of these deep-blue (CIE coordinate of x = 0.15 and y = 0.07) and green (CIE coordinate of x = 0.28 and y =0.52) devices were close to the NTSC blue and green standards. High EL efficiencies and good color qualities make these materials very promising for display applications. The use of this type of molecular platform might be an effective way to prepare high $T_{\rm g}$ amorphous materials for long-lifetime device applications, especially for high-temperature applications in OLEDs or other organic optoelectronic devices.

Experimental Section

General: All reagents were purchased from Aldrich, Acros, or Fluka and used without further purification. All solvents were sup-

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plied by Thai companies and used without further distillation. THF was heated to reflux with sodium and benzophenone, and freshly distilled prior to use. Dichloromethane for cyclic voltammetry (CV) measurements was washed with conc. H₂SO₄ and distilled twice from calcium hydride. ¹H and ¹³C NMR spectra were recorded with a Bruker AVANCE 300 MHz spectrometer. Infrared (IR) spectra were measured with a Perkin-Elmer FTIR spectroscopy Spectrum RXI spectrometer. Ultraviolet-visible (UV/Vis) spectra were recorded with a Perkin-Elmer UV Lambda 25 spectrometer and photoluminescence spectra, and the fluorescence quantum yields ($\Phi_{\rm F}$) were recorded with a Perkin–Elmer LS 50B Luminescence Spectrometer as dilute CH₂Cl₂ solution and thin film obtained by thermal evaporation. Quinine sulfate solution in 0.01 M H₂SO₄ ($\Phi_{\rm F}$ = 0.54) was used as a reference standard.^[36] Differential scanning calorimetric (DSC) analysis and thermogravimetric analysis (TGA) were performed with a METTLER DSC823e thermal analyzer and a Rigaku TG-DTA 8120 thermal analyzer, respectively, with a heating rate of 10 °C/min under a nitrogen atmosphere. Cyclic voltammetry (CV) measurements were carried out with an Autolab potentiostat PGSTAT 12 with a threeelectrode system (platinum counter electrode, glassy carbon working electrode, and Ag/Ag+ reference electrode) at scan rate of 50 mV/s in the presence of tetrabutyl ammonium hexafluorophosphate (*n*Bu₄NPF₆) as a supporting electrolyte in CH₂Cl₂ under an argon atmosphere. Melting points were measured with an Electrothermal IA 9100 series digital melting point instrument and are uncorrected. High-resolution mass spectrometry (HRMS) analysis was performed with a Bruker micrOTOF (Q-ToF II) mass spectrometer. Elemental analysis was performed with a PerkinElmer 2400 Series II CHNS/O Elemental Analyzer at Chulalongkorn University.

Quantum Chemical Calculations: The ground state geometries of all molecules were fully optimized by using density functional theory (DFT) at the B3LYP/6-31G (d,p) level, as implemented in Gaussian 03.^[23] TDDFT/B3LYP calculations of the lowest excitation energies were performed at the optimized geometries of the ground states.

Fabrication and Characterization of OLEDs: OLED devices using the synthesized materials as EML with configuration of ITO/PE-DOT:PSS/EML(50 nm)/BCP(40 nm)/LiF(0.5 nm):Al(150 nm), and double-layer green OLED devices using the synthesized materials as HTL with configuration of ITO/PEDOT:PSS/HTL(40 nm)/ Alg3(50 nm)/LiF(0.5 nm):Al(150 nm) were fabricated and characterized as follows. The patterned indium tin oxide (ITO) glass substrate with a sheet resistance 14Ω /square (purchased from Kintec company) was thoroughly cleaned by successive ultrasonic treatment in detergent, deionized water, 2-propanol, and acetone, and then dried at 60 °C in a vacuum oven. A 50 nm thick PEDOT:PSS hole injection layer was spin-coated on top of the ITO from a 0.75 wt.-% dispersion in water at a spin speed of 3000 rpm for 20 s and dried at 200 °C for 15 min under vacuum. Thin films of each organic EML or HTL were deposited on top of the PEDOT:PSS layer by evaporation from resistively heated alumina crucibles at an evaporation rate of 0.5-1.0 nm s⁻¹ in vacuo evaporator deposition (ES280, ANS Technology) under a base pressure of ca. 10^{-5} mbar. The film thickness was monitored and recorded with a quartz oscillator thickness meter (TM-350, MAXTEK). A 40 nm thick holeblocking layer of BCP or a 50 nm thick green-emitting layer of Alq3 was then deposited on the organic EML or HTL, respectively, without breaking the vacuum chamber. The chamber was vented with dry air to load the cathode materials and pumped back; a 0.5 nm thick layer of LiF and a 150 nm thick layer of aluminum

were subsequently deposited through a shadow mask on the top of the EML/HTL film without braking vacuum to form active diode areas of 4 mm². Measurement of the device efficiency was performed according to M. E. Thomson's protocol and external quantum efficiencies of the device were calculated by using the previously reported procedure.^[37] Current density–voltage–luminescence (I-V-L) characteristics were measured simultaneously by the use of a Keithley 2400 source meter and a Newport 1835C power meter equipped with a Newport 818-UV/CM calibrated silicon photodiode. The EL spectra were acquired with an Ocean Optics USB4000 multichannel spectrometer. All the measurements were performed under ambient atmosphere at room temperature.

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9.9-Bis(4-diphenylaminophenyl)-2,7-dibromofluorene (3): A mixture of **2** (2.57 g, 6.79 mmol), triphenylamine (16.67 g, 67.99 mmol), and CH₃SO₃H (0.45 mL) was heated at 190 °C for 6 h. The cooled mixture was poured into water and the greenish precipitate was filtered, washed with water, and dried to afford the crude product. Purification by column chromatography (silica gel; CH₂Cl₂/hexane) followed by recrystallized (methanol/CH₂Cl₂) afforded a light white solid (3.72 g, 61%). ¹H NMR (300 MHz, CDCl₃): δ = 6.99 (d, *J* = 9.0 Hz, 4 H), 7.00 (t, *J* = 9.0 Hz, 8 H), 7.09 (d, *J* = 9.0 Hz, 8 H), 7.26 (t, *J* = 9.0 Hz, 8 H), 7.55 (t, *J* = 9.0 Hz, 4 H), 7.58 (d, *J* = 9.0 Hz, 2 H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ = 64.65, 121.55, 121.76, 122.77, 123.06, 124.5, 124.68, 128.69, 129.27, 129.38, 130.82, 137.66, 137.98, 146.74, 147.52, 153.47 ppm; HRMS: calcd. for C₄₉H₃₄Br₂N₂ 808.1089; found 809.1169 [M + H]⁺.

2,7-Bis[4-(biphenyl-4-yl)]-9,9-bis(4-diphenylaminophenyl)fluorene (BPTF): A mixture of 3 (0.70 g, 0.86 mmol), 4-biphenylboronic acid (0.43 g, 2.16 mmol), [Pd(PPh₃)₄] (99 mg, 0.086 mmol), and an aqueous Na₂CO₃ solution (2 M, 10 mL) in THF (15 mL) was degassed with N₂ for 5 min. The mixture was heated at reflux under an N₂ atmosphere for 20 h. After the mixture was cooled to room temperature, water (50 mL) was added and the mixture was extracted with CH_2Cl_2 (2 × 50 mL). The combined organic phase was washed with water, brine solution, dried with anhydrous Na₂SO₄, filtered, and the solvents were removed to dryness. Purification by column chromatography (silica gel; CH₂Cl₂/hexane) followed by recrystallization (methanol/CH2Cl2) afforded a white solid (0.74 g, 90%); m.p. >250 °C. FTIR (KBr): $\tilde{v} = 3415, 3030, 1600, 1480,$ 1300, 813, 751 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): $\delta = 6.94-7.01$ (m, 8 H), 7.08 (d, J = 7.80 Hz, 8 H), 7.19–7.25 (m, 12 H), 7.35– 7.40 (m, 2 H), 7.48 (t, J = 7.80 Hz, 4 H), 7.64–7.73 (m, 16 H), 7.80 (d, J = 7.80 Hz, 2 H) ppm. ¹³C NMR (75 MHz, CDCl₃): $\delta = 64.76$, 120.58, 122.83, 123.07, 124.51, 124.88, 126.64, 127.08, 127.40, 127.55, 127.59, 128.87, 128.98, 139.08, 139.44, 140.19, 140.30, 140.70, 146.35, 147.67, 152.65 ppm. HRMS: calcd. for C₇₃H₅₂N₂ 956.4130; found 955.1625 [M⁺]; C₇₃H₅₂N₂ (957.23): calcd. C 91.60, H 5.48, N 2.93; found C 91.69, H 5.47, N 2.80.

2,7-Bis[4-(biphenyl-4-yl)vinylene]-9,9-bis(4-diphenylaminophenyl)fluorene (BPVTF): Synthesized from **3** (0.5 g, 0.62 mmol) and *trans*-2-(4-biphenyl)vinyleneboronic acid (0.29 g, 1.30 mmol) in a similar manner to **BPTF**, and obtained as a yellow solid (0.40 g, 71%); m.p. > 250 °C. FTIR (KBr): $\tilde{v} = 3410, 3026, 1590, 1470, 1325, 1275, 827, 760 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): <math>\delta = 6.96-$ 7.03 (m, 9 H), 7.10 (d, J = 8.10 Hz, 9 H), 7.15–7.26 (m, 15 H), 7.34–7.39 (m, 2 H), 7.47 (t, J = 7.80 Hz, 4 H), 7.58–7.67 (m, 15 H), 7.76 (d, J = 7.80 Hz, 2 H) ppm. ¹³C NMR (75 MHz, CDCl₃): $\delta = 64.10, 120.40, 122.84, 123.00, 124.52, 125.94, 126.90, 127.34, 127.86, 128.80, 128.97, 129.11, 129.19, 136.43, 136.93, 139.27, 139.49, 140.26, 140.65, 146.33, 147.67, 152.58 ppm. HRMS: calcd. for C₇₇H₅₆N₂ 1008.4443; found 1009.6281 [M⁺]; C₇₇H₅₆N₂$



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(1009.30): calcd. C 91.63, H 5.59, N 2.78; found C 91.33, H 5.47, N 2.90.

4-Bromo-4'-(carbazol-9-yl)biphenyl (7): A mixture of carbazole (3.35 g, 20.03 mmol), 6 (25.00 g, 80.13 mmol), K₂CO₃ (5.53 g, 40.06 mmol), Cu powder (1.27 g, 20.03 mmol), and 18-crown-6 (0.79 g, 3.04 mmol) in o-dichlorobenzene (90 mL) was stirred and heated at reflux under an N₂ atmosphere for 44 h. The solvent was completely removed under vacuum to give a brown residue that was then dissolved in CH₂Cl₂ (100 mL) and water (100 mL). The organic phase was separated and washed with water, brine solution, dried with anhydrous Na₂SO₄, filtered, and the solvents were removed to dryness. Purification by column chromatography (silica get; CH₂Cl₂/hexane) gave a white solid (5.10 g, 64%). FTIR (KBr): $\tilde{v} = 3413, 1604, 1526, 1450, 1335, 1231, 1077, 1002 \text{ cm}^{-1}$. ¹H NMR $(300 \text{ MHz}, \text{CDCl}_3)$: $\delta = 7.31$ (t, J = 7.50 Hz, 2 H), 7.41-7.49 (m, 4 H), 7.56 (d, J = 8.70 Hz, 2 H), 7.62–7.67 (m, 4 H), 7.79 (d, J =8.40 Hz, 2 H), 8.17 (d, J = 7.50 Hz, 2 H) ppm. ¹³C NMR (75 MHz, $CDCl_3$): $\delta = 109.79, 120.08, 120.37, 121.98, 123.49, 126.01, 127.46,$ 127.51, 128.08, 128.34, 128.53, 128.72, 132.03, 132.10, 137.29, 139.04, 139.20, 139.31, 140.80 ppm. HRMS: calcd. for C₂₄H₁₆BrN 397.0466; found 397.5682 [M⁺].

4-Bromo-4'-(carbazol-9-yl)-2-methylbiphenyl (10): A mixture of 9 (3.65 g, 9.88 mmol), 5-bromo-2-iodotoluene (3.50 g, 11.86 mmol), and K₂CO₃ (8.19 g, 59.30 mmol) in a mixture of THF (60 mL) and water (20 mL) was stirred and degassed with N2 for 5 min and then [Pd(PPh₃)₄] (0.57 g, 0.49 mmol) was added. The reaction mixture was heated to reflux under an N2 atmosphere for 18 h. After the mixture was cooled to room temperature, water (100 mL) was added and the mixture was extracted with CH_2Cl_2 (2 × 70 mL). The combined organic phase was washed with water, brine solution, dried with anhydrous Na₂SO₄, filtered, and the solvents were removed to dryness. The crude residue was purified by column chromatography (silica gel; CH₂Cl₂/hexane) to give a white solid (3.15 g, 77%). FTIR (KBr): $\tilde{v} = 3412$, 1605, 1528, 1490, 1453, 1336, 1232, 1077, 1003 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 2.40 (s, 3 H), 7.23–7.36 (m, 1 H), 7.44–7.56 (m, 10 H), 7.66 (d, J = 9.00 Hz, 2 H), 8.20 (d, J = 9.00 Hz, 2 H) ppm. ¹³C NMR (75 MHz, CDCl₃): $\delta = 20.35, 109.79, 120.08, 120.37, 121.98, 123.49, 126.01, 127.46,$ 127.51, 128.08, 128.34, 128.53, 128.72, 132.03, 132.10, 137.29, 139.04, 139.20, 139.31, 142.81 ppm. HRMS: calcd. for C₂₅H₁₈BrN 411.0623; found 411.3369 [M⁺].

2-[4-(Carbazol-9-yl)-biphenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4): A solution of 7 (3.00 g, 7.53 mmol) in THF (150 mL) was degassed with N_2 and cooled to -78 °C in a dry-ice/acetone bath. nBuLi (1.6 M in hexane, 9.41 mL, 15.06 mmol) was added by using a syringe and the mixture was stirred at room temperature for 20 min. The mixture was cooled to -78 °C in an dry-ice/acetone bath and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.68 g, 9.03 mmol) was added. The reaction mixture was warmed to room temperature and stirred overnight. Water (50 mL) was added and the mixture was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phased was washed with water, brine solution, dried with anhydrous Na2SO4, filtered, and the solvents were removed to dryness. Recrystallization (CH₂Cl₂/hexane) gave a white solid (2.85 g, 85%). FTIR (KBr): $\tilde{v} = 3415$, 1610, 1529, 1452, 1360, 1255, 1142, 1091, 1007 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 2.42 (s, 12 H), 7.31 (t, J = 7.5 Hz, 2 H), 7.41–7.50 (m, 4 H), 7.66 (d, J = 7.8 Hz, 2 H), 7.72 (d, J = 7.5 Hz, 2 H), 7.86 (d, J = 7.8 Hz, 2 H), 7.97 (d, J = 7.5 Hz, 2 H), 8.17 (d, J = 7.5 Hz, 2 H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 24.92, 83.93, 109.85, 120.00, 120.33, 123.46, 125.98, 126.43, 127.34, 128.61, 135.44, 137.17, 140.09, 140.85, 142.88 ppm. HRMS: calcd. for $C_{30}H_{28}BNO_2$ 445.2213; found 446.0125 [M + H⁺].

4-[4'-(Carbazol-9-yl)-2-methylbiphenyl]-4,4,5,5-tetramethyl-1,3,2-di-oxaborolane (5): Synthesized from **10** (2.80 g, 6.79 mmol) in a similar manner to **4**, and obtained as a white solid (2.21 g, 71 %). FTIR (KBr): $\tilde{v} = 3414$, 1611, 1521, 1425, 1359, 1316, 1099, 852 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): $\delta = 1.43$ (s, 12 H), 2.42 (s, 3 H), 7.29–7.47 (m, 4 H), 7.50–7.64 (m, 7 H), 7.77 (d, J = 7.5 Hz, 1 H), 7.81 (s, 1 H), 8.17 (d, J = 7.5 Hz, 2 H) ppm. ¹³C NMR (75 MHz, CDCl₃): $\delta = 20.35$, 24.90, 83.88, 109.87, 119.97, 120.32, 123.43, 125.95, 126.65, 129.33, 130.53, 132.39, 134.71, 136.52, 136.98, 140.88, 140.97, 143.00 ppm. HRMS: calcd. for C₃₁H₃₀BNO₂ 459.2370; found 459.5677 [M⁺].

2,7-Bis[4-(carbazol-9-yl)-4-biphenyl-4-yl]-9,9-bis(4-diphenylaminophenyl)fluorene (CBPTF): Synthesized from **3** (0.50 g, 0.62 mmol) and **4** (0.64 g, 1.35 mmol) in a similar manner to **BPTF**, and obtained as a white solid (0.60 g, 75%); m.p. > 250 °C. FTIR (KBr): $\tilde{v} = 3412$, 3027, 1617, 1491, 1275, 812, 748 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): $\delta = 6.98-7.03$ (m, 8 H), 7.11 (d, J = 7.80 Hz, 8 H), 7.22–7.28 (m, 10 H), 7.34 (t, J = 7.20 Hz, 4 H), 7.48–7.54 (m, 8 H), 7.72–7.82 (m, 16 H), 7.87–7.93 (m, 8 H), 8.19 (d, J = 7.80 Hz, 4 H) ppm. ¹³C NMR (75 MHz, CDCl₃): $\delta = 62.80$, 109.87, 120.02, 120.35, 120.64, 122.88, 123.05, 123.46, 124.54, 124.88, 125.99, 126.68, 127.41, 127.52, 127.75, 128.38, 128.98, 129.21, 137.00, 139.19, 139.39, 139.72, 140.09, 140.64, 140.86, 147.66, 152.74 ppm. HRMS: calcd. for C₉₇H₆₆N₄ 1287.5321; found 1287.2800 [M⁺]; C₉₇H₆₆N₄ (1287.62): calcd. C 90.48, H 5.17, N 4.35; found C 90.62, H 5.00, N 4.35.

2,7-Bis[4-(carbazol-9-yl)-2-methylbiphenyl-4-yl]-9,9-bis(4-diphenylaminophenyl)fluorene (CMBPTF): Synthesized from 3 (0.5 g, 0.62 mmol) and 5 (0.62 g, 1.35 mmol) in a similar manner to BPTF, and obtained as a white solid (0.67 g, 82%); m.p. 216 °C. FTIR (KBr): $\tilde{v} = 3410, 3032, 1590, 1500, 1464, 1275, 814, 748 \text{ cm}^{-1}$. ¹H NMR (300 MHz, CDCl₃): δ = 2.51 (s, 4 H), 6.98–7.03 (m, 8 H), 7.11 (d, J = 7.80 Hz, 8 H), 7.23 (d, J = 8.10 Hz, 10 H), 7.34 (t, J = 7.20 Hz, 4 H), 7.47 (t, J = 7.80 Hz, 8 H), 7.53–7.68 (m, 16 H), 7.71–7.76 (m, 4 H), 7.91 (d, J = 7.80 Hz, 2 H), 8.19 (d, J = 7.80 Hz, 4 H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 20.87, 60.05, 109.87, 120.02, 120.35, 120.64, 122.88, 123.05, 123.46, 124.54, 124.88, 125.99, 126.68, 127.41, 127.52, 127.75, 128.38, 128.98, 129.21, 137.00, 139.19, 139.39, 139.72, 140.09, 140.64, 140.86, 147.66, 152.74 ppm. HRMS: calcd. for C₉₉H₇₀N₄ 1315.5634; found 1315.8442 [M⁺]; C₉₉H₇₀N₄ (1315.67): calcd. C 90.38, H 5.36, N 4.26; found C 89.95, H 5.09, N 4.67.

Supporting Information (see footnote on the first page of this article): Synthesis of **2**, quantum calculation results, DSC-TGA and CV curves, energy diagrams, and EL spectra of the fabricated OLEDs, and ¹H NMR and ¹³C NMR spectra.

Acknowledgments

This work was financially supported by the Thailand Research Fund (RMU5080052). We acknowledge the scholarship support from the Center of Excellence for Innovation in Chemistry (PERCH-CIC), Ubon Ratchathani University, and the Strategic Scholarships for Frontier Research Network for Research Groups (CHE-RES-RG50) from the Office of the Higher Education Commission, Thailand.

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Received: May 14, 2012 Published Online: ■

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Bifunctional Materials for Organic Electroluminescent Devices



Bifunctional Materials

Newly designed biphenyl functionalized 9,9-bis(4-diphenylaminophenyl)fluorenes show promising potential as deep-blue emitters and hole-transporters for OLEDs. Efficient nondoped deep-blue and Alq3-based green OLEDs with maximum luminance efficiencies of 2.48 and 4.40 cd/A are achieved, respectively



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Synthesis, Properties and Applications of Biphenyl Functionalized 9,9-Bis(4-diphenylaminophenyl)fluorenes as Bifunctional Materials for Organic Electroluminescent Devices

Keywords: Hyperconjugation / UV/Vis spectroscopy / Biaryls / Semiconductors / Photochromism / Light-emitting diodes