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Dyes and Pigments 77 (2008) 238−244
DYES and PIGMENTS
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Blue organic light-emitting devices using novel styrylarylene host and dopant materials

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Received 2 March 2007; received in revised form 16 May 2007; accepted 17 May 2007
Available online 8 June 2007

Abstract

Four styrylamine-based blue dopant materials were synthesized using either the Wittig−Hornor or the Heck reaction. Blue organic light-emitting diodes were successfully prepared and characterized. The organic light-emitting diodes comprised ITO/DNTPD/NPB/TPM-BiP:NBD(5%)/Alq_3/Al−LiF in which NPB was used as the hole transport layer, DNTPD as the hole injection layer, 4,4′-bis[1-phenyl-2-(4,4′-biphenyl)vinyl]-*p*-terphenyl (TPM-BiP) as the blue-emitting host, Alq_3 as the electron transport layer and Al as the cathode.

Keywords: Blue OLED; Styrylamine dopant; Styrylarylene host

1. Introduction

Organic light-emitting diodes (OLEDs) have attracted considerable attention due to their many advantages for commercial applications, such as high brightness, low power consumption, ability to emit a wide range of colors and application in full color organic displays [1−5]. The multilayer organic light-emitting diode was first demonstrated by Tang and VanSlyke [2]. Three components, namely red, green and blue are needed to obtain a full color display; while red and green emitters for OLEDs are readily available, efficient and stable organic blue emitters are rare. As a result, the development of high-performance blue light-emitting organic devices is of interest [6−18]. Recently, research into blue light-emitting materials has centered on fluorene conjugated derivatives. However, a major problem still exists in terms of their lifetime and color purity which limit their application in displays. One effective way to solve this problem is to synthesize new organic materials with superior properties.

OLEDs have a short lifetime because of the deterioration of the luminescent layers. Accordingly, improved lifetime can be achieved by the use of thermally stable host and dopant materials. Generally, both host and supporting layer materials having a high glass transition temperature (T_g) are needed to obtain a long lifetime. In particular, the host material is closely related to the lifetime of the luminescent layers. In this work, 4,4′-bis[1-phenyl-2-(4,4′-biphenyl)vinyl]-*p*-terphenyl (TPM-BiP), which has a high T_g was used as the host material. As the color purity of a blue light emitter is determined by the dopant and is improved by shifting the emission region to shorter wavelengths, styrylamine-based dopant materials, whose maximum emission range lies close to the blue region (450−470 nm) and which should yield reasonably high color purity at wavelengths lower than 450 nm, were selected for study.

This paper concerns the synthesis of the novel, styrylamine dopant materials 4-(1,2-diphenylvinyl)-4′-(2-triphenylvinyl)biphenyl (**1**), 4-(1,2-diphenylvinyl)-4′-(2-triphenylvinyl)terphenyl (**2**),

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doi:10.1016/j.dyepig.2007.05.012

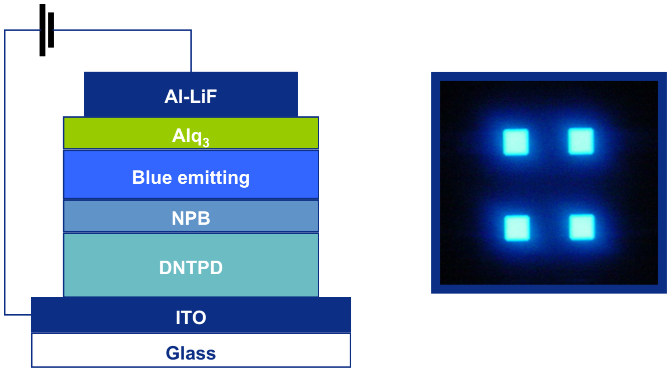


Fig. 1. The structure of the blue OLED device.

4-(1,2-diphenylvinyl)-4′-[2-[*p*-(*N*-carbazolyl)phenyl]vinyl]biphenyl (**3**) and 4-(1,2-diphenylvinyl)-4′-[2-[*p*-(*N*-carbazolyl)phenyl]vinyl]terphenyl (**4**) as well as the styrylarylene host material 4,4′-bis[1-phenyl-2-(4,4′-biphenyl)vinyl]-*p*-terphenyl (TPM-BiP) and studied the blue OLEDs derived therefrom.

2. Experimental

2.1. Materials and measurements

4-Bromo-4′-(1,2-diphenylvinyl)biphenyl and 4-vinyl triphenylamine were synthesized according to the method previously reported [19–21]. 4′-(1,2-Diphenylvinyl)biphenyl-4-carbaldehyde and diethyl (4-carbazol-9-yl-benzyl)phosphonate were prepared as previously described [22,23]. 4,4′-Bis[1-phenyl-2-(4,4′-biphenyl)vinyl]-*p*-terphenyl (TPM-BiP) was prepared by reacting 4,4′-bisbenzoyl-*p*-terphenyl with diethyl (biphenylmethyl)phosphonate via the Wittig–Hornor reaction [23]. Palladium acetate, triethylamine, tributylphosphine, potassium carbonate and potassium *t*-butoxide (95%) were used without further purification. THF and DMF (Aldrich Chem. Co.) were distilled over sodium and calcium hydride. FT-IR spectra were obtained using a Biorad Excaliber FTS-3000MX spectrophotometer and ^{1}H NMR spectra were recorded on a Varian Unity Inova (200 MHz) spectrometer. Photoluminescence (PL) spectra were recorded on a Jasco FP-6500 fluorescence spectrophotometer and UV–vis spectra were obtained using a Shimadzu UV/VIS spectrophotometer UV-1601PC.

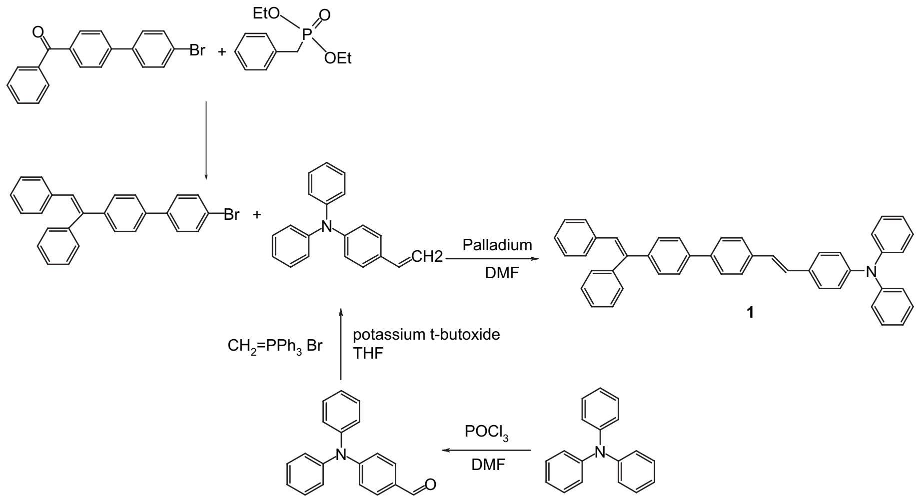
2.2. Synthesis of [4-[2′-[4-(1,2-diphenylvinyl)biphenyl-4-yl]vinyl]phenylphenyl]diphenylamine (**1**)

4-Bromo-4′-(1,2-diphenylvinyl)biphenyl (5.93 g, 21.8 mmol), 4-vinyl triphenylamine (3.00 g, 7.2 mmol), palladium acetate (0.08 g, 0.36 mmol) and DMF were stirred in a two necked round bottomed flask under a nitrogen atmosphere for 1 h. To the resulting solution, triethylamine (7.29 g, 72 mmol) and then tributylphosphine (0.15 g, 1 mol%,) were added dropwise over a period of 30 min. The mixture was refluxed for 12 h at 90 °C under a nitrogen atmosphere. After cooling to ambient temperature, the reaction mixture was extracted with ethyl ether and washed with water. The organic layer was evaporated and the resulting powdery product was purified by column chromatography from ethyl acetate to give a yellow crystalline solid.

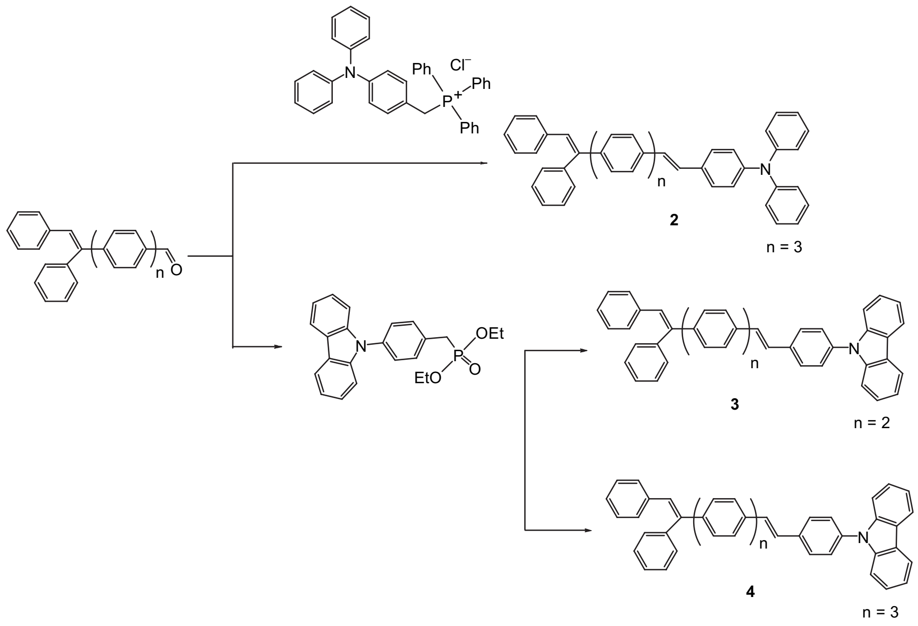
Dopant **1**: yield 85%. ^{1}H NMR (CDCl$_3$): δ 7.2–7.4 (m, 10H, ArH–diphenylvinyl), 7.4–7.5 (m, 8H, ArH–biphenyl), 6.4–6.6 (m, 8H, ArH–N), 7.0–7.1 (m, 4H, ArH–N). 6.9–7.0 (m, 3H, vinyl). FT-IR (KBr, cm^{-1}): 3120 (aromatic C–H), 2915 (aliphatic C–H), 1496 (aromatic C=C), 1288 (amine C–N).

2.3. Synthesis of [4-[2-[4″-(1,2-diphenyl-vinyl)-[1,1′,4′,1″]terphenyl-4-yl]vinyl]phenyl]diphenylamine (**2**)

4″-(1,2-Diphenyl-vinyl) [1,1′,4′,1″]terphenyl-4-carbaldehyde (10 g, 24.3 mmol), (4-diphenylaminobenzyl)triphenylphosphonium bromide (6.64 g, 29.1 mmol) and THF were stirred in a two-necked flask for 2 h. To the resulting solution, potassium *t*-butoxide (3.26 g, 29.1 mmol) was added dropwise over a period of 20 min. The resulting solution was refluxed overnight at 80 °C and the ensuing reaction mixture was



Scheme 1.



Scheme 2.

extracted with dichloromethane and water. The organic layer was evaporated and the resulting powdery product was purified by column chromatography from dichloromethane/hexane to give a yellow crystalline solid.

4-(1,2-Diphenylvinyl)-4′-[2-[*p*-(*N*-carbazolyl)phenyl]vinyl] biphenyl (**3**) and 4-(1,2-diphenylvinyl)-4′-[2-[*p*-(*N*-carbazolyl)phenyl]vinyl]terphenyl (**4**) were synthesized by a similar method to that described above but diethyl (4-carbazol-9-ylbenzyl)phosphonate was employed instead of (4-diphenylaminobenzyl)triphenylphosphonium bromide .

Dopant **2**: yield 90%. ^{1}H NMR ($CDCl_3$): δ 7.1–7.3 (m, 10H, ArH–diphenylvinyl), 7.4–7.5 (m, 12H, ArH–terphenyl), 6.4–6.6 (m, 8H, ArH–N), 7.0–7.1 (m, 4H, ArH–N), 6.9–7.0 (m, 3H, vinyl). FT-IR (KBr, cm^{-1}): 3120 (aromatic C–H), 2915 (aliphatic C–H), 1496 (aromatic C=C), 1288 (amine C–N).

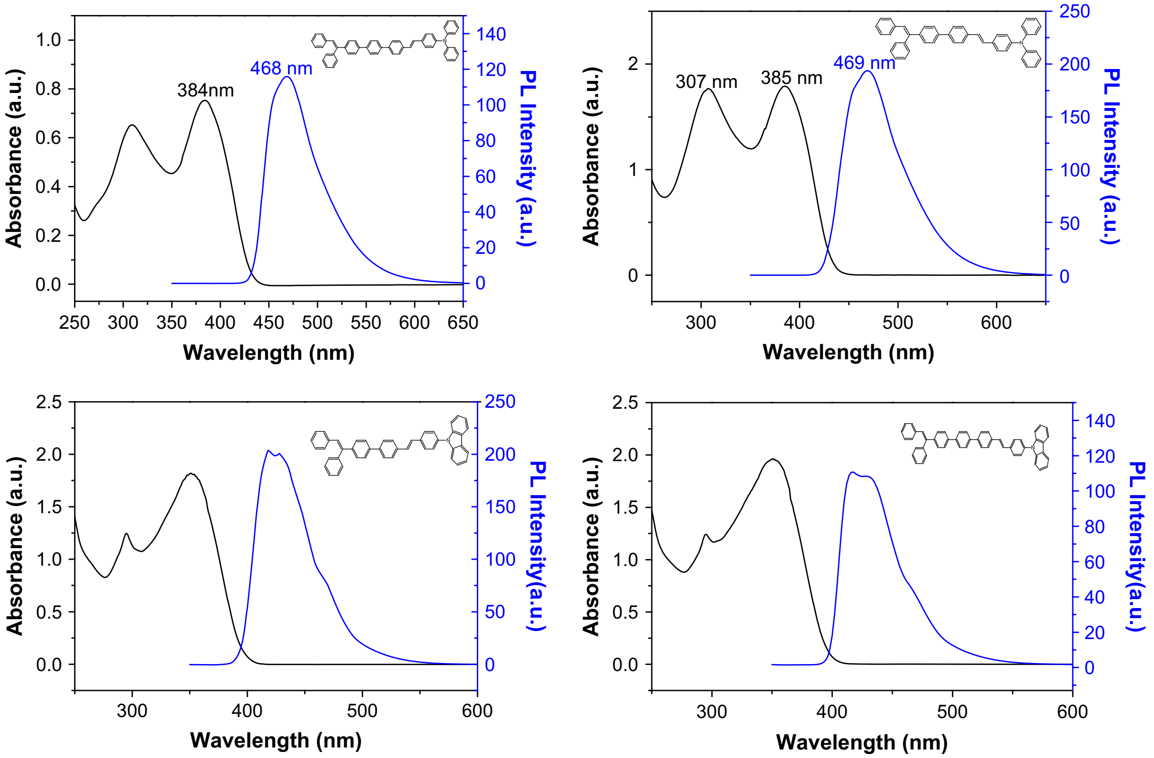


Fig. 2. UV–vis and PL spectra of styrylamine blue dopant materials **1**–**4**.

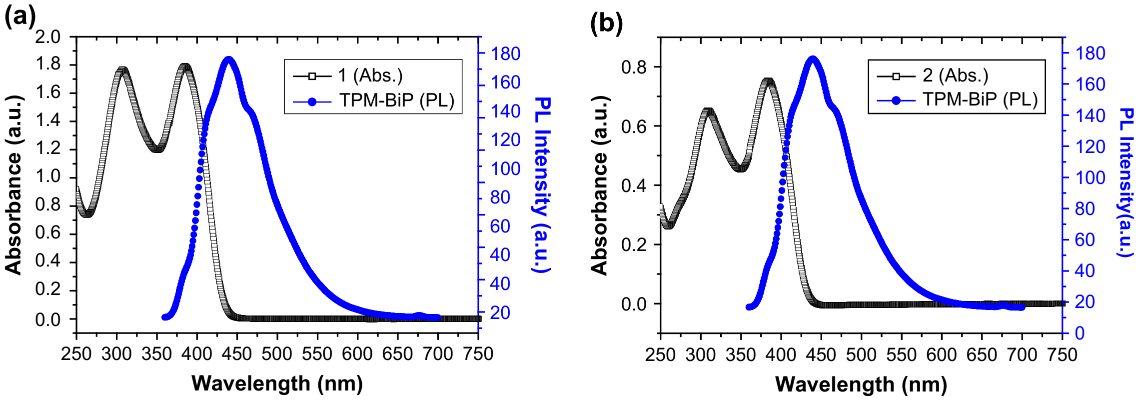


Fig. 3. Absorption spectra of (a) **1** and (b) **2**, and PL spectrum of TPM-BiP.

Dopant **3**: yield 68%. ^{1}H NMR (CDCl$_3$): δ 7.1–7.4 (m, 10H, ArH–diphenylvinyl), 7.4–7.5 (m, 8H, ArH–biphenyl), 7.3–7.4 (m, 4H, ArH–N), 7.0–7.5 (m, 8 H, ArH–N), 6.9–7.0 (m, 3 H, vinyl). FT-IR (KBr, cm^{-1}) 3120 (aromatic C–H), 2915 (aliphatic C–H), 1496 (aromatic C=C), 1288 (amine C–N).

Dopant **4**: yield 59%. ^{1}H NMR (CDCl$_3$): δ 7.1–7.4 (m, 10H, ArH–diphenylvinyl), 7.4–7.6 (m, 12H, ArH–terphenyl), 7.3–7.4 (m, 4H, ArH–N), 7.0–7.5 (m, 8H, ArH–N), 6.9–7.0 (m, 3H, vinyl). FT-IR (KBr, cm^{-1}): 3120 (aromatic C–H), 2915 (aliphatic C–H), 1496 (aromatic C=C), 1288 (amine C–N).

2.4. OLED fabrication and measurement

Prior to device fabrication, a 2 mm × 2 mm square of ITO with a resistance of 12 Ω/□ on glass was cleaned by sonication in deionized water, boiled in IPA for 20 min, and dried with nitrogen. Finally, the substrates were dry cleaned using plasma treatment in an O$_2$ and Ar environments. Organic layers were deposited sequentially by thermal evaporation from resistively heated alumina crucibles onto the substrate at a rate of 1.0 Å/s. The thickness of *N*,*N*′-bis-[4-(di-*m*-tolylamino)phenyl]-*N*,*N*′-diphenylbiphenyl-4,4′-diamine (DNTPD), *N*,*N*′-dinaphthalene-1-yl-*N*,*N*′-diphenyl-4,4′-diamine (NPB), TPM-BiP:NBD(5%) (EML) and aluminum tris(8-hydroxyquinoline) (Alq$_3$, ETL) layers were 400, 200, 300 and 200 Å, respectively. Before deposition of the metal cathode, LiF was deposited onto the organic layers with a thickness of 10 Å. A high-purity aluminum cathode was deposited at a rate of 1–5 Å/s of thickness 2000 Å as the top layer as shown in Fig. 1.

After the evaporation chamber had been vented with nitrogen gas, the device was immediately transferred into a glove box. A thin bead of epoxy adhesive was applied from a syringe around the edge of a clean cover glass. To complete the package, a clean cover glass was placed on the top of the device and the epoxy resin was cured under intense UV radiation for 3 min. The current–voltage characteristics of the encapsulated devices were measured on a programmable electrometer having current and voltage sources, Source Measure Unit, model Keithley 237. Luminance and EL spectra were measured using a PR650 system (Photo Research Co. Ltd.).

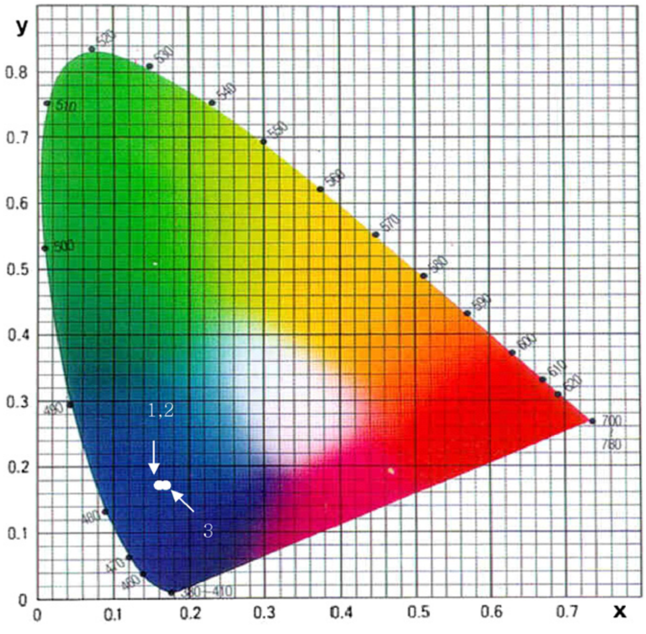


Fig. 4. CIE 1931 coordinates diagram of device (1) TPM-BiP:**1** (0.16,0.17), (2)TPM-BiP:**2** (0.16,0.17), (3) TPM-BiP undoped (0.17,0.17).

3. Results and discussion

3.1. Synthesis and characterization

Dopant **1** was prepared by the Heck reaction of 4-bromo-4′-(1,2-diphenylvinyl)biphenyl with 4-vinyl triphenylamine using palladium acetate as a catalyst whilst **2** was prepared by the Wittig reaction of 4′-(1,2-diphenyl-vinyl)terphenyl-4-carbaldehyde with (4-diphenylaminobenzyl)triphenylphosphonium bromide in the presence of potassium carbonate. Both **3** and **4** were synthesized by a method similar to the procedure used for the preparation of **2** but using diethyl(4-carbazol-9-yl-benzyl)phosphonate instead of (4-diphenylaminobenzyl)triphenylphosphonium bromide. The four dopant materials, **1–4**,

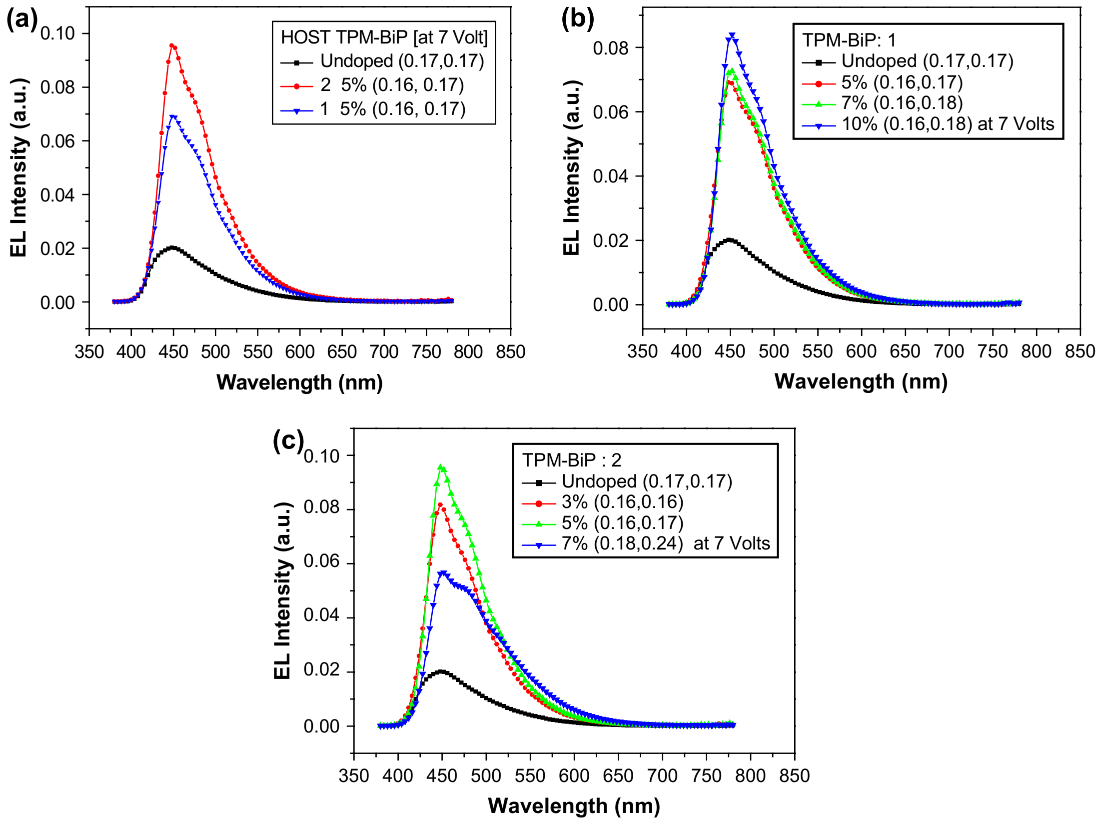


Fig. 5. The normalized EL spectra of devices obtained from (a) TPM-BiP, doped with (b) **1** and (c) **2**.

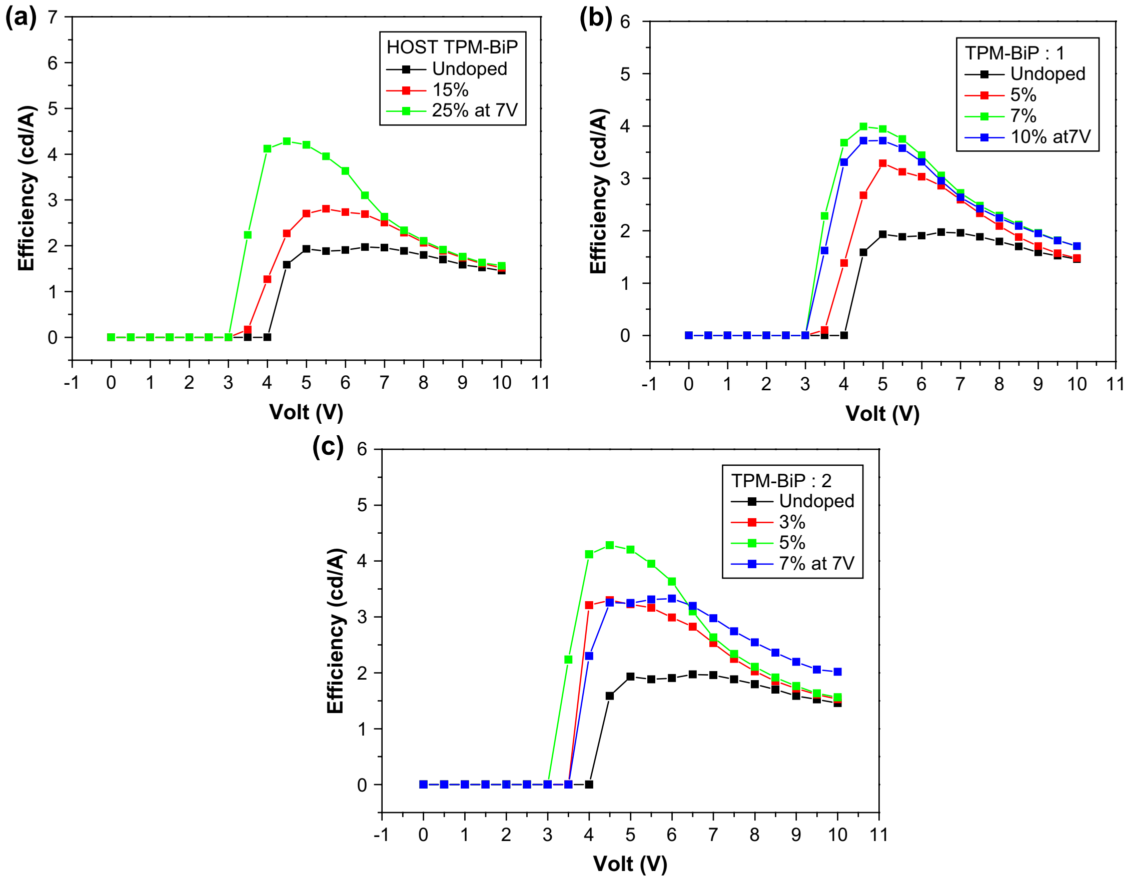


Fig. 6. EL efficiency versus current density of the EL device obtained from TPM-BiP doped with (a) 5% dopant materials, (b) **1** and (c) **2**.

Table 1
Various properties of dopant and host materials

Properties			Dopant and Host		
			1	**2**	TPM-BiP
Thermal		T_m (°C)	113	310	343
		T_d (°C)	150	402	>500
		T_g (°C)	76	82	115
Optical		Abs_{max} (nm)	385	384	337
		Em_{max} (nm)	469	468	440
EL	Blue; host: TPM-BiP at 7 V	mA/cm^2	37.46	47.67	–
		cd/A	2.43	2.63	–
		lm/W	1.09	1.18	–
		cd/m^2	977	1255	–
		CIE-x	0.16	0.16	–
		CIE-y	0.17	0.17	–

were identified and characterized by ^{1}H NMR, FT-IR, UV–visible and PL spectroscopies. In the case of dopants **1** and **2**, as the C–C coupling reaction proceeded through the Heck reaction as shown in Schemes 1 and 2. The strong aldehyde peak in the IR spectrum disappeared. In the case of dopants **3** and **4**, a new vinylic proton peak appeared at around 6.9–7.0 ppm in the NMR spectrum.

3.2. Optical properties

In the UV–visible spectra, the maximum absorption wavelengths of **1**–**4** appeared at $\lambda_{max} = 385$, 384, 351 and 350.5 nm in chloroform, respectively. Their solid-state PL spectra showed strong bands in the blue region at 469, 468, 418 and 416 nm, respectively, as shown in Fig. 2. The UV–visible absorption and PL spectra of **3** and **4** were shifted to shorter wavelengths than those of **1** and **2**. It is believed that efficient energy transfer from the dopant to the host material occurs between the absorption of the dopant and emission of the host as shown in Fig. 3. Blue light emission was observed for the photoluminescence when it was excited at around 465–475 nm.

3.3. Structure of OLED device

The holes are transported through the DNTPD layer [Hole Injection Layer (HIL)] and the NPB layer [Hole Transport Layer (HTL)] into the emitting layer and are blocked at the interface of the styrylamine emitting layer. The electrons originating from the cathode are injected into the emitting layer through LiF (buffer layer) and Alq_3 (Electron Transport Layer, ETL). When the two charges were combined, excitons were formed and light was emitted between the emitting and Alq_3 layers.

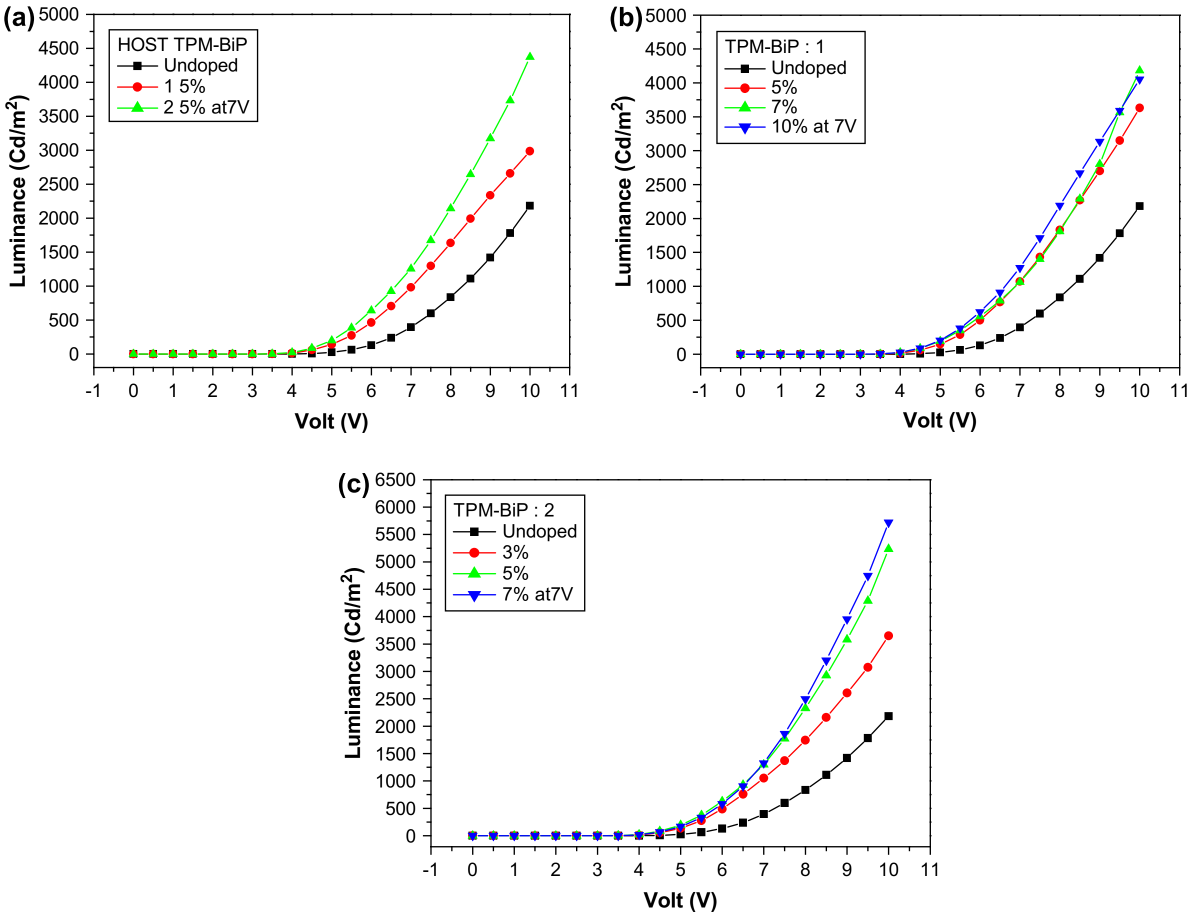


Fig. 7. Luminance versus voltage characteristics of EL device obtained from TPM-BiP doped with (a) 5% dopant materials, (b) NBD-1 and (c) NBD-2.

3.4. EL properties

The CIE x, y coordinates of devices comprising **1** and **2** were (0.16,0.17) and (0.16,0.17), respectively, for blue emission as shown in Fig. 4. The EL emission spectra of the OLEDs obtained from TPM-BiP and 5% **1** and **2** as the emitting layer at 7 V can be seen in Fig. 5. Fig. 5(a) shows the EL spectra for the devices with the emitting layer consisting of styrylamine and the new host material, TPM-BiP. Dopants **3** and **4** containing the carbazole moiety did not match with TPM-BiP because short wavelength light was emitted. The EL emission spectra of the OLEDs comprising TPM-BiP as the emitting layer with 0, 5, 7 and 10% of **1** and **1** only can be seen in Fig. 5(b) and (c). When **1** (10%) and **2** (5%) were used, the highest luminance efficiency was observed although highest color purity was observed in the case of the devices made of TPM-BiP doped with 5% **1** and **2**.

The current efficiencies of the devices obtained using the various dopants are shown in Fig. 6. Dopants **1** and **2** showed EL efficiencies of 2.43 cd/A (1.09 lm/W) and 2.63 cd/A (1.18 lm/W) at 7 V, respectively. Dopant **1** had maximum brightness of 977 cd/m^2 at 37.46 mA/cm^2. In the case of **2**, a brightness of 1255 cd/m^2 was observed at 47.67 mA/cm^2 as shown in Table 1. As current density increased gradually, the luminescent efficiency increased abruptly to 6.3 cd/A. This phenomenon is caused by the formation of the excitons required to emit light. The device obtained using **1** as the emitting material showed a deep blue EL spectrum at 450 nm and an efficiency of 2.43 cd/A. Dopant **2** exhibited relatively higher efficiency of 2.63 cd/A. These results show that the new dopants containing the styrylamine moiety are very effective in improving the EL efficiency in the TPM-BiP host system.

3.5. Luminance–voltage characteristic

The luminance–voltage characteristics of the OLED devices are shown in Fig. 7. Light emission occurs at ∼5 V and maximum luminance is 2896 cd/m^2 at 10 V in the case of **1**. The device made using **2** showed a maximum luminance of 4372 cd/m^2 at 10 V. The forward current was obtained when the ITO electrode was biased positively and the Al–LiF electrode biased negatively. The forward current increased with increasing forward bias voltage for the EL devices. Blue light emission was observed for the EL devices under forward bias. With increasing forward bias, both of the currents increased rapidly after turn-on voltage was applied. The threshold voltage for luminescence is ∼5 V in the device with an emitting layer made of TPM-BiP and the new blue dopant of thickness 300 Å.

4. Conclusions

New blue dopant materials based on a styrylamine derivative were used to construct blue OLEDs. The EL devices comprising TPM-BiP doped with **1** and **2** at a concentration of 5% exhibited efficient blue light emission at 450 nm. Dopants **1** and **2** showed EL efficiencies of 2.43 cd/A (1.09 lm/W) and 2.63 cd/A (1.18 lm/W) at 7 V, respectively, in the case of the ITO/DNTPD/NPB/TPM-BiP:Dopant/Alq$_3$/Al–LiF device. When used as dopant materials for the TPM-BiP host material, they displayed higher emitting efficiency and color purity.

Acknowledgement

This work was supported by grant No. RT104-01-02 from the regional Technology Innovation program of the Ministry of Commerce Industry and Energy (MOCIE).

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