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Novel hole-transporting materials based on 1,4bis(carbazolyl)benzene for organic light-emitting devices

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Novel hole-transporting molecules containing 1,4-bis(carbazolyl)benzene as a central unit and different numbers of diphenylamine moieties as the peripheral groups have been synthesized and characterized. These compounds are thermally stable with high glass transition temperatures of 141–157 °C and exhibit chemically reversible redox processes. Their amorphous state stability and hole transport properties can be significantly improved by increasing the number of diphenylamine moieties in the outer part and by controlling the symmetry of the carbazole-based molecules. These compounds can be used as good hole-transporting materials for organic electroluminescent (EL) devices. The device performance based on tri- and tetra-substituted carbazole derivatives is comparable to that of a typical 4,4'-bis[N-(1-naphthyl)-N-phenylamino] biphenyl (NPB)-based device.

Introduction

The development of organic light-emitting diodes (OLEDs) has been the subject of intense academic and industrial research directed to the fabrication of large-area multicolor and full color flat-panel displays.¹ Since the discovery of double-layer organic light-emitting diodes (LEDs) based on Alq₃ [tris-(8quinolinolato)aluminium] as the emitting material and triphenylamine as hole-transporting material by Tang and VanSlyke,² intensive research has been focused on the development of new hole-transporting molecules and tremendous progress has been made in this area.3 Among them, triphenylamine-like compounds, such as N,N'-di-m-tolyl-N,N'diphenyl-1,1'-biphenyl-4,4'-diamine (TPD) and 4,4'-bis[N-(1naphthyl)-N-phenylamino] biphenyl (NPB) have been proved to be excellent hole-transporting materials and have shown a wide range of practical applications. These classes of materials offer many attractive properties such as high charge carrier mobility and ease of sublimation. However, they possess some disadvantages for use in long-lifetime LED devices such as their relatively low glass transition temperature ($T_g = 65$ °C for TPD and $T_g = 100$ °C for NPB), ease of crystallization and unsatisfactory morphological stability.⁴ To solve these problems, many efforts have been devoted to the synthesis of new hole-transporting materials with high thermal stability and good morphological stability. For example, Shirota proposed the starburst-shape concept to develop a series of dendrimerlike amines with high charge carrier mobility, for suppressing crystallization formation and improving the morphological stability of deposited films during the device operation.⁵ Some spiro-linked amines⁶ and oligomeric amines^{3c,i} were reported to exhibit good thermal and morphological stability. Recently, Tao and co-workers⁷ synthesized a series of carbazole compounds with peripheral arylamines possessing high glass transition temperatures ($T_g = 120-194$ °C) and found the OLED devices based on the resulting carbazole compounds to be promising in terms of lifetime. Nevertheless, for effective molecular design aspects, well-defined conjugated molecules need to be developed which present excellent thermal stability, morphological stability and good hole-transporting properties.

The carbazole derivatives generally possess good thermal stability and hole transport properties. The triphenylamine derivatives such as TPD and NPB have shown promising hole transport characteristics. The combination of carbazole derivatives and triphenylamine derivatives is expected to offer the improved thermal and morphological stabilities as well as their good hole transport properties. In the present work, we design and synthesize a series of novel holetransporting molecules with 1,4-bis(carbazolyl)benzene (1) (Chart 1) as the central blocks and diphenylamine as the outer blocks for organic light-emitting devices. Using 1,4bis(carbazolyl)benzene as a center building block is expected to increase the glass transition temperature (T_g) and thermal stability. The incorporation of diphenylamine moieties in the periphery can provide the improved hole injection and transport properties.

Experimental

General

The resulting compounds were characterized by ¹H NMR spectra using a Varian 400 MHz spectrometer with chloroform-d as solvent and tetramethylsilane as internal standard. UV-vis and fluorescence spectra were recorded on a Varian Cray 50 spectrophotometer and on a Perkin-Elmer LS 50 B luminescence spectrometer, respectively; the elemental analyses were performed using a Bio-Rad elemental analysis system. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were carried out under a nitrogen atmosphere at a heating rate of 20 $^{\circ}$ C min⁻¹, with a TGA 2950 thermogravimetric analyzer and a Perkin-Elmer TGA 7 Thermal analysis system, respectively. Cyclic voltammetry (CV) was performed on an EG&G model 283 potentiostat/galvanostat system with a three-electrode cell in a solution of Bu₄NClO₄ (0.1 M)/dichloromethane at a scan rate of 100 mV s⁻¹ with a platinum counter electrode and Ag/AgCl silver reference electrode.



Chart 1 The structure of compounds 1-6.

Materials

Synthesis of 1. A mixture of CuI (0.57 g, 3 mmol), 18-Crown-6 (0.264 g, 1 mmol), K₂CO₃ (16.6 g, 120 mmol), 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU) (2 mL), dibromobenzene (7.1 g, 30 mmol) and carbazole (10 g, 60 mmol) was heated at 170 °C for 11 h under nitrogen. After cooling to room temperature, the mixture was quenched with 1 N HCl, the precipitate was filtered and was washed with NH₃H₂O and water. The grey solid was recrystallized twice from chloroform to afford 1 as colorless crystals (19.3 g, 79%). UV-vis absorption spectra (CH₂Cl₂): $\lambda_{max} = 295$ ($\varepsilon = 10\,900$), 325, 340 nm. ¹H NMR (400 MHz, CDCl₃): δ /ppm 7.35 (td, 4 H, J = 7.3, 1.2 Hz), 7.48 (td, 4 H, J = 7.3, 1.2 Hz), 7.57 (d, 4 H, J = 8.4 Hz), 7.83 (s, 4 H), 8.19 (d, 4 H, J = 7.9 Hz).

Synthesis of 2. Compound 1 (4.1 g, 10 mmol) was dissolved in boiling glacial acetic acid (100 mL), and potassium iodide

(1.1 g, 6.6 mmol) and finely-powdered potassium iodate (1.6 g, 7.5 mmol) were added. The solution was refluxed at 80 °C for 4 h. Then the mixture was poured into water, the precipitate was filtered and washed with water. Without further purification, this iodinated mixture in which 2I was the main product was reacted directly with diphenylamine (6.8 g, 40 mmol), CuI (0.2 g, 1 mmol), 18-Crown-6 (0.08 g, 0.3 mmol), K₂CO₃ (11.1 g, 80 mol), and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU) (1.5 mL) at 170 °C for 18 h under nitrogen. After cooling to room temperature, the mixture was subsequently poured into 1 N HCl and then extracted with dichloromethane. The organic layer was washed with NH₃H₂O and water, dried with anhydrous Na₂SO₄, followed by evaporation; the resulting residue was purified with column chromatography using hexane/methylene chloride as eluant. Yield 62%. UV-vis absorption spectra (CH₂Cl₂): $\lambda_{max} = 294 (\varepsilon = 12400), 307 (\varepsilon =$ 10100) nm. ¹H NMR (400 MHz, CDCl₃): δ/ppm 6.98 (t, 2 H, J = 7.6 Hz), 7.12 (d, 4 H, J = 7.6 Hz), 7.25 (t, 4 H, J = 7.6 Hz), 7.29-7.52 (m, 8 H), 7.56 (d, 3 H, J = 8.0 Hz), 7.83 (s, 4 H), 7.97 (s, 1 H), 8.04 (d, 1 H, J = 8.0 Hz), 8.19 (d, 2 H, J = 8.0 Hz). MS (FAB):*m*/*z*576 (M⁺, 100%). Elemental analysis: calc.: C, 87.62; H, 5.08; N, 7.30. Found: C, 87.41; H, 5.13; N, 7.26%.

Synthesis of 4. Compound 1 (4.1 g, 10 mmol) was dissolved in boiling glacial acetic acid (100 mL), and potassium iodide (2.2 g, 13.2 mmol) and finely-powdered potassium iodate (3.2 g, 15 mmol) were added. The solution was refluxed at 80 °C for 4 h. Then the mixture was poured into water, the precipitate was filtered and washed with water. Without further purification, this iodinated mixture in which 4I was the main product was reacted directly with diphenylamine (13.6 g, 80 mmol), CuI (0.4 g, 2 mmol), 18-Crown-6 (0.16 g, 0.6 mmol), K₂CO₃ (22.2 g, 160 mol), and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU) (2 mL) at 170 °C for 18 h under nitrogen. After cooling to room temperature, the mixture was subsequently poured into 1 N HCl and then extracted with dichloromethane. The organic layer was washed with NH₃H₂O and water, dried with anhydrous Na₂SO₄, followed by evaporation; the resulting residue was purified with column chromatography using hexane/methylene chloride as eluant. Yield 60%. UV-vis absorption spectra (CH₂Cl₂): $\lambda_{max} = 304$ $(\varepsilon = 10200)$ nm. ¹H NMR (400 MHz, CDCl₃): δ /ppm 7.03 (t, 4 H, J = 7.6 Hz), 7.19 (d, 8 H, J = 7.6 Hz), 7.30 (t, 8 H, J = 7.6 Hz), 7.36-7.62 (m, 8 H), 7.89 (s, 4 H), 8.02 (s, 2 H), 8.08 (d, 4 H, J = 8.0 Hz). MS (FAB): m/z 743 (M⁺, 100%). Elemental analysis: calc.: C, 87.30; H, 5.16; N, 7.54. Found: C, 87.11; H, 5.36; N, 7.44%.

Synthesis of 5. Compound 1 (4.1 g, 10 mmol) was dissolved in boiling glacial acetic acid (150 mL), and potassium iodide (4.4 g, 26.4 mmol) and finely-powdered potassium iodate (6.4 g, 30 mmol) were added. The solution was refluxed at 80 °C for 4 h. Then the mixture was poured into water, the precipitate was filtered and washed with water. Without further purification, this iodinated mixture in which 5I was the main product was reacted directly with diphenylamine (27.2 g, 160 mmol), CuI (0.8 g, 4 mmol), 18-Crown-6 (0.32 g, 1.2 mmol), K₂CO₃ (44.4 g, 320 mol), and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)pyrimidinone (DMPU) (2.5 mL) at 170 °C for 18 h under nitrogen. After cooling to room temperature, the mixture was subsequently poured into 1 N HCl and then extracted with dichloromethane. The organic layer was washed with NH₃H₂O and water, dried with anhydrous Na₂SO₄, followed by evaporation; the resulting residue was purified with column chromatography using hexane/methylene chloride as eluant. Yield 85%. UV-vis absorption spectra (CH₂Cl₂): $\lambda_{max} = 309$ $(\varepsilon = 10200)$ nm.¹H NMR (400 MHz, CDCl₃): δ /ppm 7.00 (t, 6 H, J = 7.6 Hz), 7.16 (d, 12 H, J = 7.6 Hz), 7.25 (t, 12 H, J = 7.6 Hz), 7.29–7.58 (m, 9 H), 7.86 (s, 6 H), 7.99 (s, 1 H), 8.04 (d, 1 H, J = 8.0 Hz). MS (FAB): m/z 910 (M⁺, 100%). Elemental analysis: calc.: C, 87.10; H, 5.21; N, 7.70. Found: C, 86.99; H, 5.46; N, 7.34%.

Synthesis of 6. Compound 1 (4.1 g, 10 mmol) was dissolved in boiling glacial acetic acid (200 mL), and potassium iodide (8.8 g, 52.8 mmol) and finely-powdered potassium iodate (12,8 g, 60 mmol) were added. The solution was refluxed at 80 °C for 4 hours. Then the mixture was poured into water, the precipitate was filtered and washed with water. Without further purification, this iodinated mixture in which **6**I was the main product was reacted directly with diphenylamine (54.4 g, 320 mmol), CuI (1.6 g, 8 mmol), 18-Crown-6 (0.64 g, 2.4 mmol), K₂CO₃ (88.8 g, 640 mol), and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU) (3 mL) at 170 °C for 18 h under nitrogen. After cooling to room temperature, the mixture was subsequently poured into 1 N HCl and then extracted with dichloromethane. The organic layer was washed with NH₃H₂O and water, dried with anhydrous Na₂SO₄, followed by evaporation; the resulting residue was purified with column chromatography using hexane/methylene chloride as eluant.Yield 32%. UV-vis absorption spectra (CH₂Cl₂): $\lambda_{max} = 309$ ($\varepsilon =$ 10 600) nm. ¹H NMR (400 MHz, CDCl₃): δ /ppm 6.97 (t, 8 H, J = 7.6 Hz), 7.12 (d, 16 H, J = 7.6 Hz), 7.24 (t, 16 H, J =7.6 Hz), 7.27–7.39 (m, 8 H), 7.49 (d, 4 H, J = 8.0 Hz), 7.86 (s, 4 H). MS (FAB): m/z 1077 (M⁺, 100%). Elemental analysis: calc.: C, 86.96; H, 5.24; N, 7.80. Found: C, 86.67; H, 5.36; N, 7.64%.

Synthesis of 3. Synthesis of 9-(4-bromophenyl)carbazole (7). A mixture of CuI (1.14 g, 6 mmol), 18-Crown-6 (0.53 g, 2 mmol), K₂CO₃ (16.6 g, 120 mmol), 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU) (2 mL), dibromobenzene (14.2 g, 60 mmol) and carbazole (10 g, 60 mmol) was heated at 170 °C for 11 h under nitrogen. After cooling to room temperature, the mixture was quenched with 1 N HCl, the precipitate was filtered and washed with NH₃H₂O and water. The grey solid was purified with column chromatography using hexane as eluant. Yield 62%. ¹H NMR (400 MHz, CDCl₃): δ /ppm 7.28–7.41 (m, 6 H), 7.45 (d, 2 H, J = 8.2 Hz), 7.72 (d, 2 H, J = 8.2 Hz), 8.13 (d, 2 H, J = 7.6 Hz).

Synthesis of 3,6-diiodo-9-(4-bromophenyl) carbazole (8).7 (0.65 g, 2 mmol) was dissolved in boiling glacial acetic acid (40 mL) and potassium iodide (0.66 g, 3.96 mmol) and finely-powdered potassium iodate (0.96 g, 4.5 mmol) were added. The solution was refluxed at 80 °C for 4 h. Then the mixture was poured into water, the precipitate was filtered and washed with water. A purified 8 (1.14 g, 98%) was obtained as a white solid by recrystalization from chloroform/ethanol.

Synthesis of 3,6-diphenylamine-9-(4-bromophenyl)carbazole (9). To a 250 mL round-bottomed flask containing 70 mL of toluene, using argon as the purge gas and a Dean-Stark trap under a reflux condenser, were added in the following order while maintaining good stirring: 8 (1.15 g, 2 mmol), diphenylamine (1.35 g, 8 mmol), 1,10-phenanthroline (29.7 mg, 0.15 mmol), cuprous chloride (14.9 mg, 0.15 mmol), potassium hydroxide (1.35 mg, 24 mmol) and toluene (50 mL). The reaction mixture was refluxed at 125 °C for 20 h. The mixture was quenched with 1 N HCl, extracted with toluene, washed with NH₃H₂O and water, and dried with Na₂SO₄. After evaporation of the solvent under vacuum, the residue was purified with column chromatography using hexane/methylene chloride as eluant. Yield 76%. ¹H NMR (400 MHz, CDCl₃): δ /ppm 6.93 (t, 4 H, J = 7.6 Hz), 7.06 (d, 8 H, J = 7.6 Hz), 7.20 (t, 8 H, J = 7.6 Hz), 7.27–7.30 (m, 4 H), 7.47 (d, 2 H, J =8.4 Hz), 7.72 (d, 2 H, J = 8.4 Hz), 7.80 (s, 2 H). MS (FAB): m/z 657 (M⁺, 100%).

Synthesis of 3. Compound 9 was reacted with carbazole by the same Ullmann reaction procedure as for the synthesis of 1, and the product was purified with column chromatography using hexane/methylene chloride as eluant. Yield 81%. UV-vis absorption spectra (CH₂Cl₂): $\lambda_{max} = 294$ ($\varepsilon = 10\,900$), 313 ($\varepsilon =$ 10300) nm. ¹H NMR (400 MHz, CDCl₃): δ /ppm 6.95 (t, 4 H, J = 7.6 Hz), 7.09 (d, 8 H, J = 7.6 Hz), 7.22 (t, 8 H, J = 7.6 Hz), 7.27–7.50 (m, 8 H), 7.55 (d, 2 H, J = 8.0 Hz), 7.80 (s, 2 H), 7.83 (s, 4 H), 8.18 (d, 2 H, J = 7.6 Hz). MS (FAB): m/z 743 (M⁺, 100%). Elemental analysis: calc.: C, 87.30; H, 5.16; N, 7.54. Found: C, 87.21; H, 5.36; N, 7.34%.

LED fabrication and measurements

Double-layer OLED devices using 1-6 as the hole-transporting layer and Alq₃ [tris-(8-quinolinolato)aluminium] as the emitting as well as the electron transport layer were fabricated. For comparison, a typical device using NPB as the hole transport layer was also constructed. All devices were prepared by vacuum deposition of 400 Å of the hole-transporting layer,



Scheme 1 Synthetic routes to compounds 1, 2, 4, 5 and 6

followed by 600 Å of Alq₃. Lithium fluoride (10 Å) was deposited as the cathode, which was capped with 1000 Å of aluminium. Hole-only devices were fabricated by sequential vacuum deposition of **1–6** onto an indium-tin-oxide (ITO)-coated glass substrate, followed by vacuum deposition of aluminium onto the organic layer. Vacuum deposition was carried out at a pressure of 10^{-5} Torr. The electroluminescence (EL) spectra were recorded using a Perkin-Elmer LS 50B luminescence spectrometer while applying a direct current from a current/voltage source. The current–voltage (I–V) and light intensity–voltage (L–V) curves were measured using a Keithley 2400/2000 current/voltage source unit with a calibrated silicon photodiode.

Results and discussion

Syntheses

The synthetic routes of the six carbazole-based compounds are shown in Scheme 1 and Scheme 2. The 1,4-bis(carbazolyl)benzene (1)^{3b} is synthesized from carbazole as the starting material by a modified Ullmann reaction. After iodination of 1, the intermediates with different numbers of iodine substituents (by controlling the quantity of potassium iodide and potassium iodate) are directly reacted with diphenylamine. Purification by column chromatography afforded pure 1,4-bis(carbazolyl)benzene derivatives with different numbers of diphenylamine units

in good yields, such as 3-diphenylamino-1,4-bis(carbazolyl)benzene (2), 3,6'-di(diphenylamino)-1,4-bis(carbazolyl)benzene (4), 3,3',6-tri(diphenylamino)-1,4-bis(carbazolyl)benzene (5) and 3,3',6,6'-tetra(diphenylamino)-1,4-bis(carbazolyl)benzene (6). In order to further identify the structure of 4, 3,6di(diphenylamino)-1,4-bis(carbazolyl)benzene (3), in which two diphenylamino substituents are located at the same side of the 1,4-bis(carbazolyl)benzene core, is synthesized by a different method from the syntheses of 2, 4, 5 and 6, as shown in Scheme 2. The structure of 4 is confirmed by comparing the ¹H NMR spectra of 3 and 4. All carbazole-based compounds are obtained as yellow-green powders and are characterized by ¹H-NMR, MS spectroscopy and elemental analysis.

Thermal properties

The thermal properties of the new compounds were determined by DSC and TGA measurements (Table 1). As expected, the resulting compounds possess excellent thermal stability.

Their thermal decomposition temperatures (T_d) are in the range of 377–487 °C and are increased with increasing the number of diphenylamine moieties in the periphery. The glass transition temperatures (T_g) are higher than those of commercially used NPB $(T_g = 100 \text{ °C})$, depending upon the number of diphenylamine moieties and their structural symmetry. For 4 $(T_g = 141 \text{ °C})$ and 6 $(T_g = 157 \text{ °C})$, their symmetric structures may be responsible to their corresponding



Scheme 2 Synthetic route to compound 3

 Table 1
 Physical data for compounds 1–6 and NPB

Compound	$T_{\rm g}/T_{\rm m}{}^a/^{\circ}{\rm C}$	$T_{\rm d}^{\ b}/^{\circ}{\rm C}$	λ_{\max}^{c}/nm	$\lambda_{\rm em}^{c}/{\rm nm}$	$E_{\rm ox}/{\rm mV}$	HOMO/LUMO ^d /eV	Hole drift mobility $[cm^2 (Vs)^{-1}]$
NPB	100/265	479	271, 342		762, 936	5.12/2.12	1.89×10^{-6}
1	$-e^{e}/327$	321	295, 325, 340	345	993, 1320	5.40/1.94	
2	110/216	377	294, 307	421	776, 1194	5.13/1.58	6.71×10^{-8}
3	$-e^{\prime}/316$	426	294, 313	432	783, 1031	5.14/1.68	3.29×10^{-8}
4	141/248	424	304	421	796, 1245	5.15/1.64	1.74×10^{-6}
5	147/ ^f	436	309	429	763, 906, 1199	5.12/1.72	1.93×10^{-6}
6	157/ ^f	487	309	432	744, 939, 1088	5.10/1.74	2.47×10^{-6}

^{*a*} Obtained from DSC measurements. ^{*b*} Obtained from TGA measurements. ^{*c*} Measured in CH₂Cl₂ solution. ^{*d*} HOMO energy was calculated with reference to ferrocence (4.8 eV).⁸ LUMO energy was derived from the relation, band gap = HOMO – LUMO (where the band gap was derived from the observed optical edge). ^{*e*} Cannot form stable amorphous glass. ^{*f*} Obtained as stable amorphous glass.

higher T_g values. Although 3 and 4 have the same numbers of diphenylamine units, they exhibit quite different thermal behavior due to the different symmetry in their structures. DSC shows no evidence of the glass transition for 3. It should be noticed that there is no indication of crystallization and melting in DSC curves for 5 and 6, implying that they have excellent amorphous glass state stability.^{36,9} These results indicate that the 1,4-bis(carbazolyl)benzene unit increases the rigidity of the molecular backbone, resulting in high T_g , where the symmetry plays the important role in the enhancement of T_g and the mophological stability can be improved by increasing the number of the diphenylamine moieties in the periphery.

Optical properties

The absorption and photoluminescence spectra of all carbazolebased compounds in CHCl₃ solution were measured and values are listed in Table 1. It can be seen that compounds 2 and 3 show two absorption bands centered at about 294 and 310 nm, which can be attributed to the cabazole moiety and π - π * transition of the molecular backbone. With increasing the number of diphenylamine moieties, the feature bands at 294 nm, characteristic of the carbazole moiety, disappear. In the case of 4, 5 and 6, only one-absorption band centered at around 306 nm is observed, implying that there is no unsubstituted carbazole unit within the structure. In contrast, all these new compounds exhibit quite different potoluminesent spectra with 1. Their photoluminescence spectra are located in the range of 420-430 nm, about 80-90 nm red-shifted with respect to 1, which is caused by the electron-donating nature of the diphenylamine moiety. Compared to the 3-substituted 1 derivatives 2 and 4, the maximum emissions of the 3,6-disubstituted 1 derivatives 3,5 and 6 are red-shifted by about 10 nm, indicating that 3,6-disubstituted 1 derivatives have much better conjugation than the 3-substituted ones.

Electrochemical properties

The electrochemical properties of all carbazole-based compounds were investigated by cyclic voltammetry, as shown in Fig. 1. The resulting data are also summarized in Table 1. In the mono- and di-substituted derivatives (2 and 4), there are two chemically reversible oxidation processes, which can be attributed to the oxidation of the diphenylamino moiety at the 3-position of 1 and of the 1,4-bis(carbazolyl)benzene core itself, respectively.^{7a} In the tri- and tetra-substituted derivatives (5 and 6), three chemically reversible oxidation processes are observed, in which the first and third oxidation waves are corresponding to two oxidation potentials of 2 and 4, and the second oxidation potential is consistent with that of the 3,6-disubstituted derivative 3, which can be attributed to the oxidation of the diphenylamino moiety at the 6-position of 1. These results suggest that the carbazole derivatives containing the 3,6-disubstituted diphenylamino moieties undergo the stepwise oxidation process. $^{3\overline{b},10}$ The HOMO values of these compouds are estimated by cyclic



Fig. 1 Cyclic voltammograms of compounds in CH_2Cl_2 containing 0.1 M tetrabutylammonium perchlorate at 25 °C.

voltammetry and are listed in Table 1. We can see from Table 1 that their HOMOs fall in the range of 5.10-5.15 eV, which is independent of both the number of diphenylamine moieties in the periphery and their structural symmetry, and which are very closed to the HOMO value of NPB. These are lower than that of 1, without the diphenylamino moieties, which shows a HOMO level of 5.40 eV. From these results, we can conclude that the HOMO levels of the resulting compounds are determined by the diphenylamino moieties. Thus, the role of the diphenylamino moieties for significant improvement in the holeinjection properties can be expected, as observed in the following double-layer device results. To investigate their hole-transporting properties, the hole drift mobility of the resulting compounds is calculated by using the hole-only devices with the structure of ITO/2–6/Al,^{11,12} as summarized in Table 1. It can be seen that the hole drift mobility is greatly dependent upon the number and the position of the diphenylamine moiety. For instance, the hole drift mobility is ordered in 6 > 5 > 4 > 2, in accordance with the increasing number of diphenylamine moieties. Compound 6 exhibits a high hole drift mobility of 2.47 $\times 10^{-6}$ cm² (Vs)⁻¹ which is in same order of magnitude with typical NPB under the same measurement conditions. Although 4 and 3 have the same number of diphenylamine moieties, their hole drift mobilities are quite different, depending upon the position of diphenylamine. The hole drift mobility in the former one is found to be two orders of magnitude larger than that in the latter, implying that the hole drift mobility is strongly influenced by the symmetry of the molecules. Based on these results, it is deduced that the symmetric structure may be the practical way for achieving high charge mobility.

Electroluminescent properties

In order to further study their charge-transporting properties, double-layer LED devices with the structure of ITO/ $HTL(40 \text{ nm})/Alq_3(60 \text{ nm})/LiF/Al$ were fabricated using 1–6 as



Fig. 2 Current and luminance versus voltage characteristics of the double-layer devices based on 6 (left) and NPB (right).

 Table 2
 Performance characteristics of 1–6 and the NPB-based devices

Compound	Turn-on	Max.	Max. current	Max. power
	voltage/	brightness/	efficiency/	efficiency/
	V	cd m ⁻²	cd A ⁻¹	lm W ⁻¹
NPB	4.5	14 628	4.62	1.90
1	8.2	254	0.10	0.03
2	4.2	4867	1.76	0.57
3	3.4	10 109	3.83	1.48
4	3.5	14 090	4.47	1.95
5	3.3	13 740	4.47	2.14
6	3.2	15 739	4.79	2.56

the hole-transporting layer and Alq₃ as the emitting layer and electron-transporting layer. For comparison, the typical doublelayer device with the configuration of ITO/NPB/Alq3/LiF/Al was also fabricated. Their device performance results are summarized in Table 2 and Fig. 2. Except for 1, all of the devices exhibit a low turn-on voltage of 3.2-4.5 V, which is consistent with their HOMO levels. These suggest that the peripheral diphenylamine moiety plays a critical role in determining the hole-injection ability of the resulting molecules. The devices based on 4, 5 and 6 have much better performance in terms of brightness, current and power efficiency than those of 2 and 3, due to the relatively low hole-drift mobility in these later two compounds. For example, in the case of **6**, its maximum brightness is about 15739 cd m⁻² at a driving voltage of 16 V. The current efficiency and power efficiency are determined to be 4.79 cd A^{-1} and 2.56 lm W^{-1} , respectively. These are higher than for NPB-based device with a brightness of 14628 cd m⁻² and a current efficiency of 4.62 cd ¹ as well as a power efficiency of 1.90 lm W^{-1} . In contrast, the A^{-} maximum brightness in the 1-based device is 254 cd m^{-2} at the driving voltage of 22 V, and the current and power efficiencies are 0.10 cd A^{-1} and 0.03 $\mbox{lm}\ W^{-1},$ respectively. The effect of the number of diphenylamine moieties and the symmetry of the molecules on the device performance is obvious. Their brightness, current and power efficiency are gradually improved with increasing the number of diphenylamine moieties in the order of 2 < 4 < 5 < 6, with increasing the symmetry of the molecules in the order of 3 < 4 < 6.

Conclusions

In summary, we have designed and synthesized a series of novel hole-transporting molecules with 1,4-bis(carbazolyl)benzene as the central unit and the diphenylamine moieties as substituents at the 3- and/or 6-positions of the carbazole group. The resulting carbazole-based molecules are thermally stable with high glass transition temperatures of 141–157 °C, due to the rigid carbazole central unit. Their amorphous stability, hole injection and transport properties can be significantly improved by increasing the number of peripheral diphenylamine moieties and by controlling the symmetry of the structure. The device performance based on tri- and tetra-substituted carbazole derivatives is comparable to that of a typical NPB-based device and these

materials may be promising in long-lifetime LED device applications.^{3*i*,13} This synthetic strategy seems to be general for developing new hole-transporting materials with large molecular size having excellent thermal and morphological stability. Further investigation on this aspect is currently in progress in our laboratory.

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