

SYNTHESIS AND CHARACTERIZATION OF NOVEL BLUE LIGHT-EMITTING HOLE-TRANSPORTING MATERIALS

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Abstract

A series of novel blue light-emitting hole-transporting molecules bearing the core structures of phenylene and oligofluorenes ($n = 1$ to 3) end-capped with hole-transporting carbazole was synthesized by Ullmann coupling reaction and Suzuki coupling reaction. Their electronic absorption and emission properties vary depending on the molecular structure of the cores. All compounds fluoresce a strong blue colour in both solutions and solid states. On excitation the energy is transferred from the outer carbazole units into the fluorescent core.

Keywords: Blue light-emitting materials, hole transporting materials, organic light-emitting diode, carbazole, fluorene

Introduction

Since the discovery of the use of poly (p-phenylene vinylene) (PPV) as an active layer in organic light-emitting diode (OLED) (Burroughes *et al.*, 1990), the development of light-emitting materials for OLED has attracted a large amount of attention. This is due to their promising applications in full-colour, flat-panel displays as well as being a perspective of academic research (Tang *et al.*, 1989; Forrest, 2003). To develop a full-colour display, a blue electroluminescent emitter is required. Over the last few years, polyfluorene (PF) and its derivatives have emerged as a promising new class of blue light-emitters for use in OLED (Kim *et al.*, 2000). However, electroluminescent (EL) devices based

on small molecule fluorescent organic materials are regarded as the most well-established in the field of OLED (Markham *et al.*, 2002). In comparison to light-emitting polymers, they are pure materials with well-defined conjugated lengths and molecular structures, and definite molecular weights, which make them superior to polymers for a systematic investigation of structure-property relationships. Recently, many oligofluorenes have been used as high performance blue light-emitters for application in OLED (Wong *et al.*, 2002). The performance of EL devices is notably influenced by the charge balance between the hole and electron from the opposite electrodes. One simple and useful

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method of balancing the rate of injection of electrons and holes is to construct a multi-layer device comprising a hole-transport layer and an electron-transport layer, with one or both being luminescent (Greenham *et al.*, 1993; Pei and Yang, 1995). Many carbazole derivatives have been extensively studied for different applications due to their good hole-transport and luminescent properties (Grazulevicius *et al.*, 2003). It was also found that thermal stability of organic compounds was greatly improved upon incorporation of a carbazole moiety in the core structure (Koene *et al.*, 1998). Carbazole can be covalently linked to other molecular moieties through its 3-, 6- or 9-positions (Pielichowski and Kyziot, 1974; McClenaghan *et al.*, 2003). Recently, in our laboratory, several carbazole end capping materials have been synthesized and their properties have been studied (Vajeekamol and Kwasakaew, 2003). In this communication, we report on the synthesis and investigation of structure-photophysical property relationships of fluorene-carbazole based organic materials processing dual functions, blue light-emission, and hole-transport with additional high thermal stability.

Materials and Methods

Reagents

1,4-Dialkoxybenzene (Weder and Wrighton, 1996), 2,7-dibromofluorene (Kelley *et al.*, 1997), and 2,7-dibromofluorene (Kelley *et al.*, 1997) were synthesized using standard literature methods. The other chemicals were obtained from commercial sources and used without purification. Tetrahydrofuran (THF) was refluxed with sodium and benzophenone under nitrogen atmosphere, and freshly distilled before used. Nitrobenzene was distilled from calcium hydride under high vacuum. Analytical thin layer chromatography (TLC) was performed with Merck TLC aluminum plate coated with silica gel 60 F254. Column chromatography was carried out using flash chromatography technique with silica gel 60 (0.063 - 0.2 mm).

General Method for Ullmann Coupling Reaction

A mixture of carbazole, dibromo compound, copper-bronze, anhydrous potassium carbonate and dry nitrobenzene in two-neck round bottom flask was heated at reflux under nitrogen atmosphere for 18 h. Solvent was completely removed under high vacuum and ammonia solution was added. The aqueous solution was extracted with dichloromethane, and the organic phase was washed with water, brine solution, and dried over sodium sulphate anhydrous. The solvent was removed to dryness and the residue was purified by flash column chromatography.

Characterisation

All new compounds were characterized by standard spectroscopic methods. ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 300 MHz spectrometer using CDCl_3 as solvent in all cases. Chemical shifts (δ) are reported relative to the residual solvent peak in part per million (ppm). Infrared spectra were measured on a Perkin-Elmer FT-IR spectroscopy spectrum RXI spectrometer as KBr pellets. UV-Visible spectra were recorded as a dilute solution in spectroscopic grade chloroform on a Perkin-Elmer UV Lambda 25 spectrometer. Fluorescence spectra were recorded with a Perkin-Elmer LS 50B Luminescence Spectrometer in a dilute solution of spectroscopic grade chloroform. Mass spectra were obtained with a Thermo Finnigan GC-MS spectrometer using EI mode. Melting points were measured on an Electrothermal IA 9000 Series of Digital Melting Point Instruments and are uncorrected.

Physical data for 3; M.p. 126°C; UV-vis λ_{max} (CHCl_3)/nm 237 ($\log \epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 5.02), 293 (4.60), 314 (4.30), and 338 (4.10); IR ν_{max} (KBr pellet/ cm^{-1}) 3,052, 2,929, 1,596, 1,518, 1,335, 1,232, 1,013 and 749; m/z (EI) 664 (M^+ , 50%), 552 ($\text{M}^+-(2\text{-ethylhexyl})$, 24%), 440 ($\text{M}^+-(2\text{-ethylhexyl})$, 100%); $^1\text{H-NMR}$ δ_{H} (ppm) (300 MHz, CDCl_3) 0.55 (6 H, t, $J = 7.3$ Hz), 0.68 (6 H, t, $J = 6.9$ Hz), 0.88 - 0.98 (16 H, m), 1.26 - 1.29 (2 H, m), 3.66 (4 H, d, $J = 5.4$ Hz), 7.31 - 7.36 (8 H, m, 3 H -, 1 H -, 6 H -, and 8 H -carba-

zole), 7.39 (2 H, s, benzene-*H*), 7.48 (4 H, m, 2 *H*-, and 7 *H*-carbazole) and 8.18 (4 H, d, $J = 7.3$ Hz, 4 *H*-, and 5 *H*-carbazole); ^{13}C -NMR δ_{C} (75 MHz, CDCl_3) 10.8, 13.9, 22.7, 23.4, 28.8, 30.1, 39.1, 72.2, 110.4, 115.9, 119.7, 120.1, 123.4, 125.7, 126.7, 141.3, and 149.9

Physical data for 6; M.p. 114°C; UV-vis λ_{max} (CHCl_3)/nm 235 ($\log \epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 4.93), 294 (4.59), and 340 (4.60); IR ν_{max} (KBr pallet/ cm^{-1}) 3,045, 2,926, 1,597, 1,450, 1,230 and 748; m/z (EI) 664 (M^+ , 70%), 508 ($\text{M}^+ - \text{C}_{11}\text{H}_{24}$, 32%), 495 ($\text{M}^+ - \text{C}_{12}\text{H}_{26}$, 20%), 332 ($\text{M}^+ - 2(\text{carbazole})$, 62%); ^1H -NMR δ_{H} (ppm) (300 MHz, CDCl_3) 0.83 (6 H, t, $J = 6.9$ Hz), 0.90 - 0.94 (4 H, m, C (5) H), 1.18 - 1.28 (12 H, m), 2.04 - 2.10 (4 H, m), 7.30 - 7.37 (4 H, m, 3*H*-, and 6 *H*-carbazole), 7.44 - 7.52 (8 H, m, 1 *H*-, 2 *H*-, 7 *H*-, and 8 *H*-carbazole), 7.61 - 7.65 (4 H, m, 1 *H*-, 3 *H*-, 6 *H*-, and 8 *H*-fluorene), 8.00 (2 H, d, $J = 8.7$ Hz, 4 *H*-, and 5 *H*-fluorene) and 8.20 (4 H, d, $J = 7.7$ Hz, 4 *H*-, and 5 *H*-carbazole); ^{13}C -NMR δ_{C} (75 MHz, CDCl_3) 14.0, 22.5, 24.1, 29.6, 31.6, 40.2, 55.7, 109.8, 119.9, 120.4, 121.0, 121.9, 123.4, 125.9, 126.0, 136.8, 139.6, 141.0, and 152.9.

Physical data for 7; M.p. 62 - 64°C; UV-vis λ_{max} (CHCl_3)/nm 241 ($\log \epsilon/\text{dm}^3\text{mole}^{-1}\text{cm}^{-1}$ 4.50), 266 (4.40), 294 (4.31) and 326 (4.33); IR ν_{max} (NaCl pallet/ cm^{-1}) 3,022, 2,931, 1,598, 1,454, 1,221 and 744; m/z (EI) 414 ($\text{M}^+ - \text{C}_6\text{H}_{13}\text{Br}$, 30%), 330 ($\text{M}^+ - \text{C}_{12}\text{H}_{26}\text{Br}$, 40%), 245 (100%), 178 (72%); ^1H -NMR δ_{H} (ppm) (300 MHz, CDCl_3) 0.74 - 0.84 (10 H, m), 1.14 - 1.22 (12 H, m), 1.98 - 2.03 (4 H, m), 7.31 - 7.36 (2 H, m, 3 *H*-, and 6 *H*-carbazole), 7.45 (4 H, d, $J = 3.0$ Hz, 1 *H*-, 2 *H*-, 7 *H*-, and 8 *H*-carbazole), 7.53 - 7.58 (4 H, m, fluorene-*H*), 7.65 (1 H, d, $J = 8.4$ Hz, 5 *H*-fluorene), 7.89 (1 H, d, $J = 7.8$ Hz, 4 *H*-fluorene) and 8.19 (2 H, d, $J = 7.8$ Hz, 4 *H*-, and 5 *H*-carbazole); ^{13}C -NMR δ_{C} (ppm) (75 MHz, CDCl_3) 14.0, 22.5, 23.8, 29.6, 31.5, 40.2, 55.7, 109.7, 119.8, 120.4, 120.9, 121.2, 121.4, 121.8, 123.4, 125.9, 126.3, 130.2, 136.8, 139.3, 141.0, 152.2, and 153.2.

Physical data for 9; M.p. 98°C; UV-vis λ_{max} (CHCl_3)/nm 240 ($\log \epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 4.87); 265 (4.69), 294 (4.61) and 360 (4.95); IR ν_{max}

(KBr pallet/ cm^{-1}) 3,056, 2,928, 1,597, 1,461, 1,233, 817 and 746; ^1H -NMR δ_{H} (ppm) (300 MHz, CDCl_3) 0.81 - 0.89 (30 H, m), 1.17 (36 H, b), 2.11 - 2.20 (12 H, m), 7.32 - 7.37 (4 H, m, 3 *H*-, and 6 *H*-carbazole), 7.45 - 7.52 (8 H, m, 1 *H*-, 2 *H*-, 7 *H*-, and 8 *H*-carbazole), 7.59 - 7.60 (4 H, m, fluorene-*H*), 7.72 - 7.78 (8 H, m, fluorene-*H*), 7.87 - 1.92 (4 H, m, fluorene-*H*), 7.97 (2 H, d, $J = 8.7$ Hz, fluorene-*H*) and 8.21 (4 H, d, $J = 7.6$ Hz, 4 *H*-, and 5 *H*-carbazole); ^{13}C -NMR δ_{C} (ppm) (75 MHz, CDCl_3) 14.0, 23.8, 31.5, 40.2, 55.6, 109.8, 119.8, 120.0, 120.1, 120.4, 120.9, 121.5, 121.9, 123.4, 125.8, 125.9, 126.2, 126.3, 136.3, 139.5, 140.1, 140.4, 140.9, 141.1, 151.8, 151.9, and 152.9.

Physical data for 14; M.p. 200°C; UV-vis λ_{max} (CHCl_3)/nm 235 ($\log \epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 4.99), 294 (4.62) and 349 (4.90); IR ν_{max} (KBr pallet/ cm^{-1}) 3,057, 2,926, 1,597, 1,463, 1,230, 818 and 749; ^1H -NMR δ_{H} (ppm) (300 MHz, CDCl_3) 0.83 (12 H, t, $J = 7.2$ Hz), 0.87 - 0.92 (8 H, m), 1.17 - 1.22 (24 H, m), 2.07 - 2.18 (8 H, m), 7.32 - 7.37 (4 H, m, 3 *H*-, and 6 *H*-carbazole), 7.44 - 7.51 (8 H, m, 1 *H*-, 2 *H*-, 7 *H*-, and 8 *H*-carbazole), 7.59 - 7.61 (4 H, m, fluorene-*H*), 7.72 (2 H, s, fluorene-*H*), 7.75 (2 H, d, $J = 8.1$ Hz, fluorene-*H*), 7.90 (2 H, d, $J = 7.8$ Hz, 5*H*-fluorene), 7.97 (2 H, d, $J = 7.4$ Hz, 4 *H*-fluorene) and 8.20 (4 H, d, $J = 8.4$ Hz, 4 *H*-, and 5 *H*-carbazole); ^{13}C -NMR δ_{C} (75 MHz, CDCl_3) 14.0, 22.6, 23.9, 29.6, 31.5, 40.3, 55.6, 109.8, 119.9, 120.2, 120.4, 120.9, 121.5, 121.9, 123.4, 125.9, 125.9, 126.4, 136.4, 139.6, 140.1, 140.7, 151.9, and 152.9.

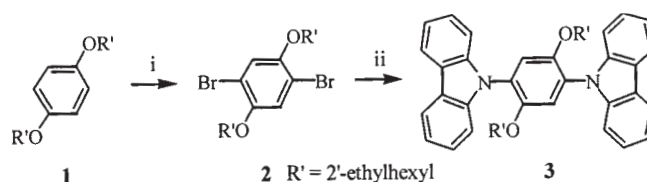
Results and Discussion

The synthesis of the target blue light-emitting molecules is shown in Schemes 1, 2 and 3. Radical bromination of 1,4-dialkoxybenzene 1 (Weder and Wrighton, 1996) with Br_2 in acetic acid, followed by Ullmann coupling of the resultant with carbazole in the presence of K_2CO_3 as base and Cu-bronze as catalyst in nitrobenzene at refluxing temperature gave 1,4-dicarbazole-2,5-dialkoxybenzene 3 as a white solid in 81% yield (Scheme 1). The ^1H -NMR spectrum of 3 in CDCl_3 exhibited a singlet signal at 7.39 ppm corresponding to two symmetrical protons of

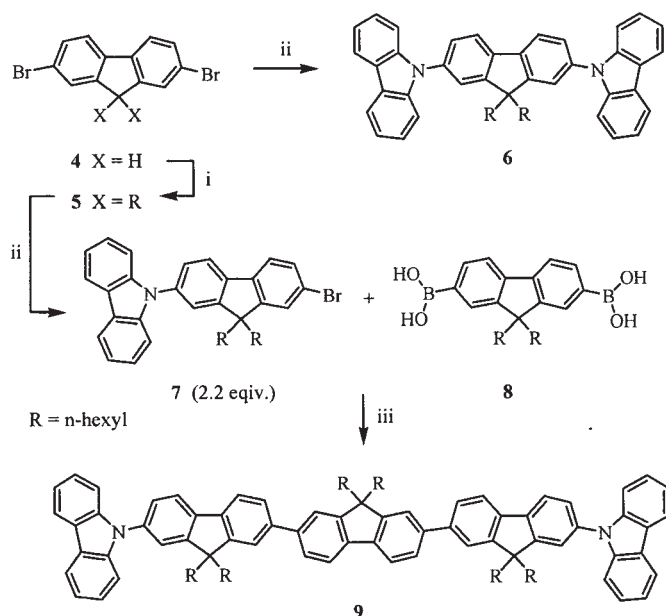
phenyl ring and a doublet signal at 8.18 ppm ($J = 7.3$ Hz, 4 *H*- and 5 *H*-carbazole).

2,7-Dibromofluorene **4** (Kelley *et al.*, 1997) was alkylated on 9-position with *n*-hexylbromide through a phase transfer reaction in the presence of 50% NaOH as base and benzyl triethylammonium chloride as phase transfer catalyst (PTC) in DMSO to produce 2,7-dibromo-9,9-bis-*n*-hexylfluorene **5** in 65% yield. Coupling of **5** with 2.2 equivalents of carbazole under Ullmann amination conditions gave the desired compound, 2,7-dicarbazole-9,9-bis-*n*-hexylfluorene **6**, as a white solid in a quantitative yield. The $^1\text{H-NMR}$ spectrum of **6** in CDCl_3

showed two doublet signals at 8.00 ppm ($J = 8.7$ Hz, 4 *H*-, and 5 *H*-fluorene) and 8.20 ppm ($J = 7.7$ Hz, 4 *H*-, and 5 *H*-carbazole) in a ratio of 1:2. This is an indication that both ends of the molecule are attached with two carbazole units. Under similar conditions with only 1 equivalent of carbazole used, 7-bromo-2-carbazole-9,9-bis-*n*-hexylfluorene **7** was isolated in 45% yield as a colourless solid. The $^1\text{H-NMR}$ spectrum showed a characteristic mono-adduct compound. A doublet signal corresponding to 4 *H*- and 5 *H*-capped carbazole located at 8.19 ppm ($J = 7.8$ Hz). Unequivalent 4 *H*- and 5 *H*-fluorene protons were observed as two doublet peaks at 7.89



Scheme 1. Reagents and conditions: i) Br_2 , acetic acid, rt; ii) carbazole, K_2CO_3 , Cu-bronze, Ph-NO_2 , reflux



Scheme 2. Reagents and conditions: i) 50% NaOH, *n*-hexylbromide, benzyl triethylammonium chloride, DMSO, rt; ii) carbazole, K_2CO_3 , Cu-bronze, Ph-NO_2 , reflux; iii) $\text{Pd(PPh}_3)_4$, Na_2CO_3 (2 M), THF, reflux

ppm ($J = 7.8$ Hz) and 7.65 ppm ($J = 8.4$ Hz), respectively. Suzuki coupling reaction of 7 with 9,9-bis-n-hexylfluorene-2,7-diboronic acid 8 by using $\text{Pd}(\text{PPh}_3)_4$ as catalyst, Na_2CO_3 aqueous solution as base in THF yielded the target 2'',7''-dicarbazole-tri(9,9-bis-n-hexylfluorene-2,7-diyl) 9 as a light yellow solid in 60% (scheme 2.)

The ^1H -NMR spectrum corresponded to the structure of 9 in which 4 H - and 5 H -capped carbazole protons were observed as a doublet signal at 8.21 ppm ($J = 7.6$ Hz) as shown in Figure 1.

Alkylation of 2-bromofluorene 10 (Kelley *et al.*, 1997) on 9-position with n-hexylbromide

in the presence of base and PTC afforded 2-bromo-9,9-bis-n-hexylfluorene 11 as a colourless liquid in 69% yield. The product was then converted to a dimer using $\text{Ni}(0)$ -catalysed homocoupling reaction with $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, Zn powder and PPh_3 as catalysts in DMF to give the fluorene dimer 12 in 23% yield. Subsequent selective bromination of the resultant on 2- and 7-positions using Br_2 in the presence of I_2 gave 2,7-dibromo-di(9,9-bis-n-hexylfluorene-2,7-diyl) 13 in 81% yield. The final incorporation of a carbazole moiety on both terminal ends was achieved with Ullmann coupling to yield 2,7-dicarbazole-di(9,9-bis-n-hexylfluorene-2,7-diyl)

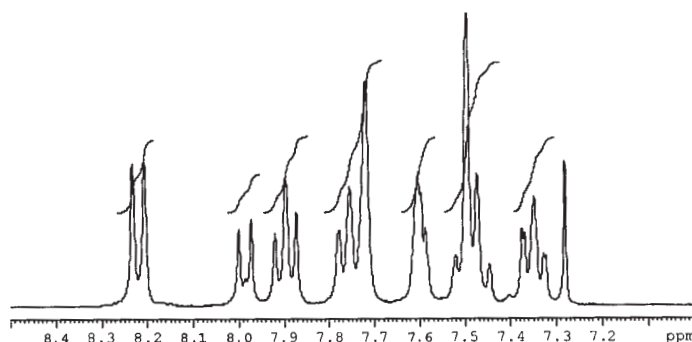
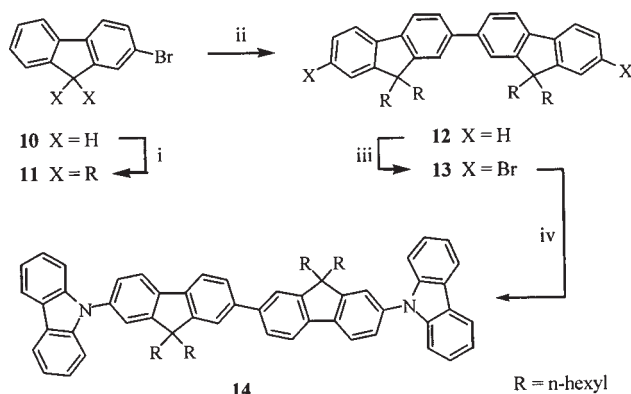


Figure 1. Expansion of the aromatic region of the ^1H -NMR spectra of 9



Scheme 3. **Reagents and conditions:** i) 50% NaOH, n-hexylbromide, benzyl triethylammonium chloride, DMSO, rt; ii) $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, Zn, PPh_3 , DMF, rt; iii) Br_2 , I_2 , DCM, rt; iv) carbazole, K_2CO_3 , Cu-bronze, Ph-NO_2 , reflux

14 as a white solid in 67% (Scheme 3). The ^1H -NMR spectrum exhibited three well-separated doublet signals at 7.90 ppm ($J = 7.8$ Hz, 5 *H*-fluorene), 7.97 ppm ($J = 8.4$ Hz, 4 *H*-fluorene) and 8.20 ppm ($J = 7.8$ Hz, 4 *H*- and 5 *H*-carbazole) in a ratio of 1:1:2. All compounds 3, 6, 14, and 9 were fully characterized by standard spectroscopic methods.

The absorption spectra of 3, 6, 14, and 9 in CHCl_3 solution are shown in Figure 2. The electronic absorption behavior of the carbazole-capped oligofluorenes 3, 6, 14, and 9 exhibited two major absorption bands in the visible region, the strong absorption band at longer wavelength corresponding to the π - π^* electron transfer of the entire chromophore and the less intense band around 294 nm being assigned to the π - π^* local excitation of a carbazole moiety at the terminal ends. The former electronic absorption band exhibited a perfect correlation to the molecular structures. The absorption intensities are progressively increased as the number of the fluorophore moieties per molecule increased. The absorption maxima are continuously red-shifted as the conjugation length of the respective oligomeric core increased. This result can be explained in terms of decreasing HOMO-LUMO energy gap as a delocalization

of π -electron system along the backbone is extended. Compounds 3, 6, 14, and 9 exhibited a maximum absorption at 314, 340, 349, and 360 nm, respectively, which was substantially red-shifted relative to those of phenylene, fluorene, bifluorene (330 nm), and trifluorene (350 nm) (Lee and Tsutsui, 2000), respectively. This indicates that there is a π -conjugation through the lone electron pair at the nitrogen atom of the carbazole units and that π -electrons are delocalised over the entire conjugated backbone.

Figure 3 shows a plot of the lowest transition energy (E_g) versus the inversed numbers of fluorene ring for oligomers in CHCl_3 solution. The curve showed a linear relation between E_g and the inversed numbers of fluorene rings.

$$E_g (\text{eV}) = 0.57/n + 2.78$$

The photoluminescence (PL) emission spectra for 3, 6, 14, and 9 in CHCl_3 solution are shown in Figure 4. All compounds 3, 6, 14, and 9 in this study are blue fluorescence with their maximum emission wavelengths being gradually red-shifted with respect to an increase of the conjugation length of the fluorescent core. The dicarbazole phenylene 3 exhibited a maximum

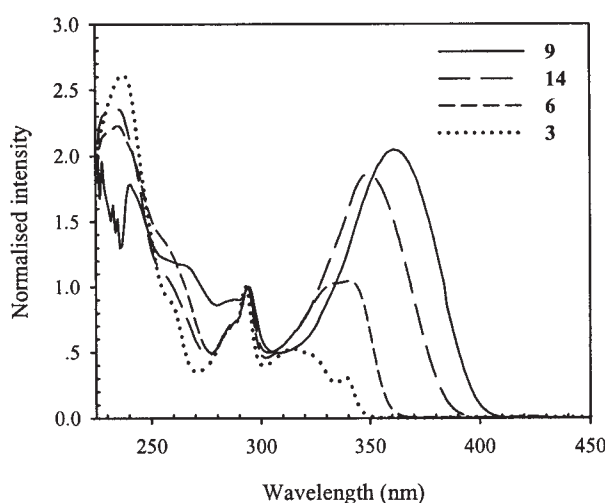


Figure 2. The UV-Vis absorption spectra of 3, 6, 14, and 9 in CHCl_3 solution ($\sim 10^{-5}$ M)

peak at 345 nm, while the dicarbazole fluorene 6, bifluorene 14, and trifluorene 9 showed strong peaks at 361, 391, and 414 nm, respectively, which were nearly identical to those of phenylene, fluorene, bifluorene (392 nm), and trifluorene (422 nm) (Lee and Tsutsui, 2000), respectively. This suggests that incorporation of a hole-transporting carbazole moiety at both ends of molecules has little, if any, effect on their emission mechanisms. Interestingly, the PL spectra of all compounds excited at carbazole unit (294 nm) had an identical shape and

intensity to the PL spectra when excited at the fluorescent core. These results confirm that the carbazole transferred the whole excited energy to the luminescent core causing the emission of the core structure. The colour coordinates in *CIE* chromaticity for 3, 6, 14, and 9 are (0.154, 0.048), (0.156, 0.043), (0.159, 0.029), and (0.161, 0.035), respectively, which are in the pure blue region.

For OLED applications, thermal stability of the organic materials is important for the device stability and life time. The degradation

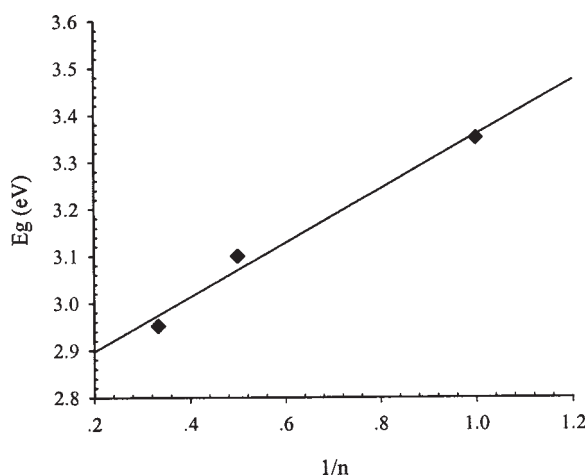


Figure 3. Energy (E_g) of the lowest electronic transition for 6, 14, and 9 in CHCl_3 solution versus the inversed numbers ($1/n$) of fluorene ring in the conjugated cores

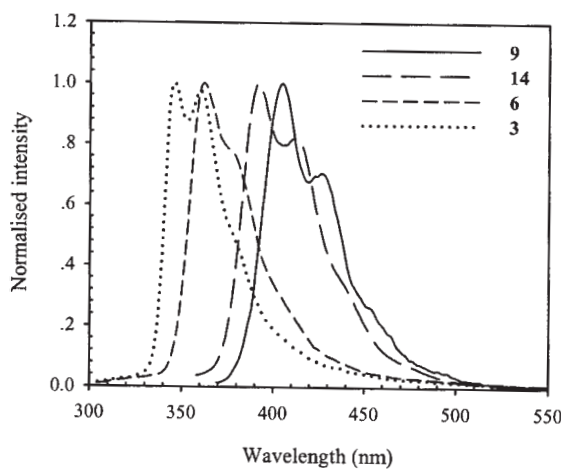


Figure 4. The fluorescence emission spectra of 3, 6, 14, and 9 in CHCl_3 solution ($\sim 10^{-5}$ M)

of organic electroluminescent devices depends on morphological change resulting from the thermal instability of the amorphous organic layer. All compounds 3, 6, 14, and 9 were in amorphous phase at room temperature. Their melting temperatures were significantly greater than those of phenylene, fluorene, bifluorene and trifluorene, respectively. As expected, attachment of the carbazole moieties on both ends of the molecules enhances their thermal stabilities.

Conclusion

In conclusion, a series of carbazole end-capped molecules were successfully synthesized using an Ullmann amination reaction of the dibromo precursors and carbazole. The electronic absorption and emission spectra in CHCl_3 solution of these materials are readily changed by the conjugation length and number of the aromatic units. The attached hole-transporting carbazole moieties have a slight effect on the emission properties of the core structures. These compounds were emissive of blue light with high thermal stability which is potentially useful for applications in electroluminescent devices.

Acknowledgments

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