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## Communications

### Syntheses and Photophysical Properties of New Carbazole-Based Conjugated Multi-Branched Molecules

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#### Introduction

Recently, semiconducting organic materials have attracted considerable interest as suitable candidate materials in the fields of electronics and optoelectronics.<sup>1-3</sup> Among the many applications of these organic materials, electroluminescent (EL) devices using organic materials with a low molar mass are the most popular and have already been employed in practical applications such as flat-panel or flexible display devices.<sup>4-9</sup>

Efficient hole carrier transport is a prerequisite for achieving high performance EL devices accompanied by well-balanced hole injection and electron injection. In a multilayer device, the individual layers should be optimized to have suitable highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels. By fine tuning these energy levels, many promising HTL materials in a multilayer device were suggested to

enhance hole injection and block electrons; thus, confined excitons were formed in the EML.<sup>10,11</sup>

The use of functional multi-branched molecules has been proposed for the fabrication of the functional layer in EL devices since their molecular architecture is unique and they possess characteristics to optimize the proper HOMO and LUMO energy levels. They can be easily synthesized such that they are free from impurities that can behave as carrier traps. They can also be employed for carrier transporting materials and as luminescent host materials in EL devices.<sup>12</sup> Carbazole derivatives were well adopted to design a hole transport molecules or host molecules in a light harvesting material systems. Recently, Li *et al.* reported the interesting properties of carbazole-based multi-branched molecule.<sup>13,14</sup> 1,3,5-Tris(2-(9-ethylcarbazyl-3)ethylene)benzene (TECEB) was prepared as a hole-transporting material for organic light-emitting devices (OLEDs). They claimed that it is comparable to 1,4-bis(1-naphthyl phenylamino)biphenyl (NPB) in terms of highest-occupied molecular orbital/lowest unoccupied molecular orbital energy levels and carrier drift mobility. They also exhibit better device performance to enhance the luminance properties of the standard multilayer EL device using TECEB layer. Although it was suggested to be superior to NPB in terms of its higher glass-transition temperature ( $T_g = 130^\circ\text{C}$ ) and ease of synthesis, it is not suitable to the wet processing of the multilayered EL device. It should be evaporated to form a hole transporting layer under a high vacuum. The objective of this work is to prepare the soluble multi-branched molecules bearing carbazole peripheral groups and investigate their photophysical properties.

We herein report the synthesis, electrochemical characterization, and photophysical properties of a novel class of conjugated multi-branched molecules bearing carbazoles as peripheral groups and various conjugative aromatic cores. In addition, we selected the promising candidate to show the best film forming property and fabricate the composite film after doping [2,6-bis[2-[5-(dibutylamino)phenyl]vinyl]-4H-pyran-4-ylidene] propanedinitrile (DADB) with the concentration. We investigated the possibility to show red or white emission through complete or partial Förster resonance energy transfer process, respectively.

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## Experimental

**Synthesis.** We synthesized the intermediate compounds, **1**, **4**, **5**, **11**, and **12** by following the literature method.<sup>15-18</sup>

**Synthesis of Compound 2:** An oven dried, mag-stirred, 250 mL RBF was charged with a solution of methyltriphenylphosphonium iodide (2.90 g, 7.20 mmol) and potassium-*tert*-butoxide (0.81 g, 7.20 mmol) in 100 mL THF. 50 mL THF solution of 9-hexyl-9*H*-carbazole-3-carbaldehyde (2.00 g, 7.20 mmol) was slowly added into the mother mixture. After completion of the reaction, the mixture was filtered to remove the residual salt. The filtrate was concentrated and hexane was added to make precipitation of triphenylphosphate. The organics were then dried over MgSO<sub>4</sub>, filtered, and solvent was removed *in vacuo*. The resulting crude product was then purified by silica-gel column chromatography (EtOAc/hexane = 1 : 3) to yield 1.72 g (87%) of a white liquid.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 0.87 (t, 3H), 1.24-1.31 (m, 4H), 1.36-1.40 (m, 2H), 1.82-1.90 (m, 2H), 4.27 (t, 2H), 5.21 (d, *J* = 11.0 Hz, 1H), 5.70 (d, *J* = 16.0 Hz, 1H), 6.89-6.96 (m, *J* = 9.0 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 0.82 (s, 1H). Anal. Calcd. for C<sub>20</sub>H<sub>23</sub>N: C, 86.59; H, 8.36; N, 5.05. Found: C, 86.49; H, 8.01; N, 4.92.

**Synthesis of Compound 6:** 3.00 g (10.8 mmol) of 9-hexyl-3-vinyl-9*H*-carbazole, 1.05 g (3.00 mmol) of **3**, 1.50 g (10.8 mmol) of K<sub>2</sub>CO<sub>3</sub> and 3.48 g (10.8 mmol) of tetrabutylammonium bromide (TBAB) were mixed in 100 mL DMF and the mixture was allowed to stir for 10 min under argon atmosphere. Then, 0.10 g (0.45 mmol) of Pd(OAc)<sub>2</sub> were added at once into mother solution. The reaction mixture was allowed to stir at 110 °C for 36 h. The mixture was filtered and extracted with dichloromethane/water. The organic layers were collected and dried under MgSO<sub>4</sub>. Chromatography on silica gel (hexane/chloroform = 1 : 5) gave 1.84 g (68%) of product **6**. *T*<sub>g</sub> 50 °C; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 8.29 (s, 3H), 8.15 (d, *J* = 8.0 Hz, 3H), 7.73 (d, *J* = 8.0 Hz, 3H), 7.64 (s, 3H), 7.48 (t, *J* = 8.0 Hz, 3H), 7.45 (d, *J* = 16.0 Hz, 3H, -CH=CH-), 7.39-7.42 (m, 6H), 7.26 (t, *J* = 8.0 Hz, 3H), 7.23 (d, *J* = 16.0 Hz, 3H, -CH=CH-), 4.28 (t, 6H), 1.84-1.91 (m, 6H), 1.25-1.42 (m, 18H), 0.87 (t, 9H); Anal. Calcd. for C<sub>66</sub>H<sub>69</sub>N<sub>3</sub>: C, 87.66; H, 7.69; N, 4.65. Found: C, 87.24; H, 7.60; N, 4.45; MALDI-TOF MS *m/z* calcd C<sub>66</sub>H<sub>69</sub>N<sub>3</sub> (M+H)<sup>+</sup> 904.5564, Found 904.0753.

**Synthesis of Compound 7:** The same procedure was employed to prepare the compound **7**: Instead of **3**, we used **4** for this reaction. Yield 55%. *T*<sub>g</sub> 87 °C; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 8.27 (s, 3H), 8.14 (d, *J* = 8.0 Hz, 3H), 7.86 (s, 3H), 7.68-7.76 (m, 15H), 7.48 (t, *J* = 8.0 Hz, 3H), 7.44 (d, *J* = 16.0 Hz, 3H, -CH=CH-), 7.37-7.42 (m, 6H), 7.25 (t, *J* = 8.0 Hz, 3H), 7.22 (d, *J* = 16.0 Hz, 3H, -CH=CH-), 4.29 (t, 6H), 1.84-1.91 (m, 6H), 1.26-1.41 (m, 18H), 0.88 (t, 9H);

Anal. Calcd. for C<sub>84</sub>H<sub>81</sub>N<sub>3</sub>: C, 89.08; H, 7.21; N, 3.71. Found: C, 88.75; H, 7.16; N, 3.38; MALDI-TOF MS *m/z* calcd C<sub>84</sub>H<sub>81</sub>N<sub>3</sub> (M+H)<sup>+</sup> 1132.6503, Found 1132.5851.

**Synthesis of Compound 8:** The same procedure was employed to prepare the compound **8**: Instead of **3**, we used 3,5,3',5'-tetrabromo-biphenyl, **5** for this reaction. Yield 63%. *T*<sub>g</sub> 78 °C; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ 8.35 (s, 4H), 8.18 (d, *J* = 8.4 Hz, 4H), 7.80 (s, 6H), 7.55 (d, *J* = 15.0 Hz, 4H, -CH=CH-), 7.47 (t, *J* = 8.4 Hz, 4H), 7.41-7.45 (m, 8H), 7.33 (d, *J* = 15.0 Hz, 4H, -CH=CH-), 7.28 (t, *J* = 8.4 Hz, 4H), 4.32 (t, 8H), 1.86-1.95 (m, 8H), 1.27-1.45 (m, 24H), 0.89 (t, 12H); Anal. Calcd. for C<sub>92</sub>H<sub>94</sub>N<sub>4</sub>: C, 87.99; H, 7.54; N, 4.46. Found: C, 87.30; H, 7.44; N, 4.07; MALDI-TOF MS *m/z* calcd C<sub>92</sub>H<sub>94</sub>N<sub>4</sub> (M+H)<sup>+</sup> 1255.7551, Found 1255.7677.

**Synthesis of Compound 10:** A round-bottomed flask (250 mL) was oven dried and cooled under argon atmosphere. 3,5-Dibromobenzaldehyde (7 g, 26.5 mmol), 9-hexyl-3-vinyl-9*H*-carbazole (17.7 g, 63.7 mmol), Pd(OAc)<sub>2</sub> (0.3 g, 1.33 mmol), TBAB (8.55 g, 26.5 mmol), and K<sub>2</sub>CO<sub>3</sub> (8.8 g, 63.7 mmol) were dissolved in DMF (50 mL). The reaction mixture was heated to 110 °C in an oil bath and stirred for 40 h. The DMF was then removed under reduced pressure and the residue was dissolved in MC and extracted with water and brine. The organic layer was then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered. The filtrate was concentrated *in vacuo*. The resulting crude product was then purified by silica-gel column chromatography (hexane/CHCl<sub>3</sub> 1 : 2) to yield 11.3 g (65 %) of a white yellow solid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 10.10 (s, 1H), 8.29 (s, 2H), 8.18 (d, *J* = 8.0 Hz, 2H), 7.93 (s, 3H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.51 (t, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 16.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 16.0 Hz, 2H), 4.31 (t, 4H), 1.86-1.94 (m, 4H), 1.39-1.46 (m, 4H), 1.29-1.37 (m, 8H), 0.90 (t, 6H). Anal. Calcd for C<sub>47</sub>H<sub>48</sub>N<sub>2</sub>O C, 85.93; H, 7.37; N, 4.26. Found: C, 85.90; H, 7.53; N, 4.07.

**Synthesis of Compound 13:** **10** (614 mg, 0.94 mmol) and **11** (204 mg, 0.45 mmol) were dissolved in 30 mL of dry THF. The resulting solution was added dropwise slowly to THF solution (20 mL) of KOBu<sup>t</sup> (168 mg, 1.50 mmol) at 0 °C. Then the reaction mixture was warmed to room temperature and stirred under N<sub>2</sub> for 12 h. The reaction was quenched by adding a small amount of HCl solution and extracted with dichloromethane. The organic phase was dried over MgSO<sub>4</sub>. Chromatography on silica gel (hexane/chloroform 1 : 5) gave 545 mg (83%) of product **15**. *T*<sub>g</sub> 85 °C. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 8.29 (s, 4H), 8.17 (d, *J* = 8.0 Hz, 4H), 7.74 (d, *J* = 8.0 Hz, 4H), 7.70 (d, *J* = 8.0 Hz, 4H), 7.67 (d, *J* = 8.0 Hz, 4H), 7.62 (s, 6H), 7.50 (t, *J* = 8.0 Hz, 4H), 7.45 (d, *J* = 16.0 Hz, 4H, -CH=CH-), 7.40-7.43 (m, 8H), 7.21-7.32 (m, 12H), 4.29 (t, 8H), 1.85-1.93 (m, 8H), 1.28-1.43 (m, 24H), 0.89 (t, 12H); Anal. Calcd. for C<sub>108</sub>H<sub>106</sub>N<sub>4</sub>: C, 88.84; H, 7.32; N, 3.84. Found: C, 88.88; H, 7.47; N, 3.57; MALDI-TOF MS *m/z* calcd C<sub>108</sub>H<sub>106</sub>N<sub>4</sub>

(M+H)<sup>+</sup> 1459.8490, Found 1459.7548.

**Synthesis of Compound 14:** The same procedure was employed to prepare the compound **13**: Instead of **3**, we used **12** for this reaction. Yield 64%. *T<sub>g</sub>* 83 °C; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 8.19 (s, 6H), 8.10 (d, *J* = 8.0 Hz, 6H), 7.64 (d, *J* = 8.0 Hz, 6H), 7.63 (s, 3H), 7.56 (s, 9H), 7.44 (t, *J* = 8.0 Hz, 6H), 7.32-7.37 (m, 12H), 7.19-7.27 (m, 18H), 7.12 (d, *J* = 16.0 Hz, 6H, -CH=CH-), 4.11 (t, 12H), 1.74-1.81 (m, 12H), 1.24-1.33 (m, 36H), 0.58 (t, 18H); Anal. Calcd. for C<sub>150</sub>H<sub>150</sub>N<sub>6</sub>: C, 88.45; H, 7.42; N, 4.13. Found: C, 88.34; H, 7.57; N, 3.90; MALDI-TOF MS *m/z* calcd C<sub>150</sub>H<sub>150</sub>N<sub>6</sub> (M+H)<sup>+</sup> 2036.1995, Found 2035.9026.

**Instrumental Analysis.** <sup>1</sup>H-NMR spectra were recorded on a Varian Mercury NMR 400 Hz spectrometer using deuterated chloroform (CDCl<sub>3</sub>-*d*) purchased from Cambridge Isotope Laboratories, Inc. Elemental analysis was performed by using an EA1112 (Thermo Electron Corp.) elemental analyzer. Time-of flight mass spectrometry (MALDI-TOF) was performed using a Voyager-DE STR MADI-TOF (matrix; DHB) mass spectrometer.

Thermal properties were studied under a nitrogen atmosphere on a Mettler DSC 821<sup>e</sup> instrument. Thermal gravimetric analysis (TGA) was conducted on a Mettler TGA50 thermal analysis system under a heating rate of 10 °C/min. The redox properties of the synthesized compounds were examined by cyclic voltammetry (Model: EA161 eDAQ). The thin films were coated on a platinum plate using chloroform as a solvent. The electrolyte solution employed was 0.10 M tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) in a freshly dried acetonitrile. The Ag/AgCl and Pt wire (0.5 mm in diameter) electrodes were utilized as reference and counter electrodes, respectively. The scan rate was at 50 mV/s.

**Absorption and Photoluminescence Spectroscopy.** Studying absorption and PL spectral behaviour, thin films of multi-branched molecules were fabricated on quartz sub-

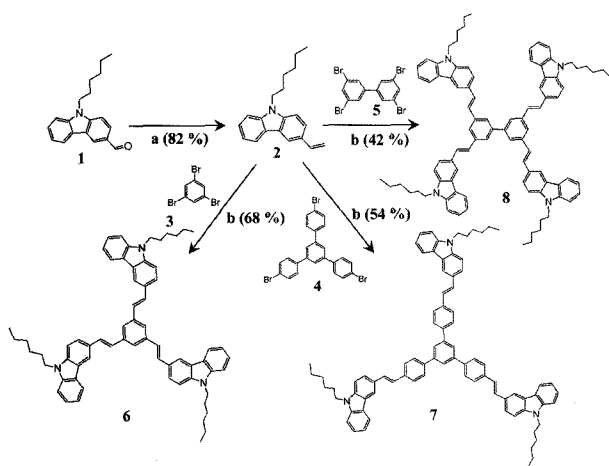
strates as follows. The solution (2.5 wt%) of each molecule in monochlorobenzene was filtered through an acrodisc syringe filter (Millipore 0.2 μm) and subsequently spin-cast on the quartz glass. The films were dried overnight at 60 °C for 48 h under vacuum. Absorption spectra of film samples and chloroform solution (conc. 1.0 × 10<sup>-6</sup> mole/L) were obtained using a UV-vis spectrometer (HP 8453, PDA type) in the wavelength range of 190-1,100 nm. PL spectra were recorded with an AMINCO-Bowman series-2 luminescence spectrometer.

## Results and Discussion

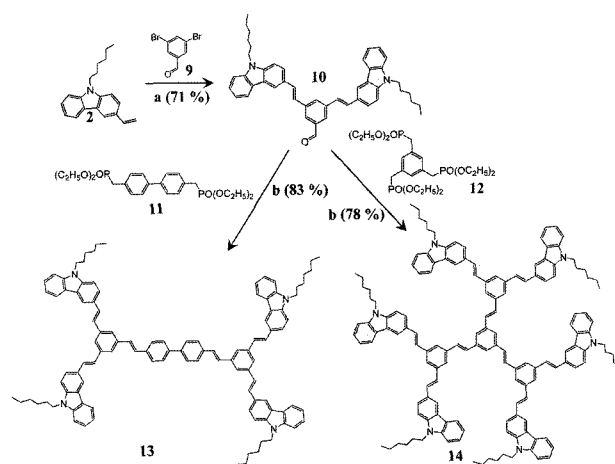
We herein report the synthesis, electrochemical characterization and photophysical characterization of a novel class of conjugated multi-branched molecules bearing carbazoles as peripheral groups and various conjugative aromatic cores. For synthesizing **6**, **7**, and **8**, we firstly prepared three aromatic cores such as **3**, **4**, and **5**. Trimerization of bromo acetophenone derivative by treatment with SiCl<sub>4</sub> in ethanol was attempted and furnished the compound, **4** in 60% yield without a complex mixture of product.<sup>16</sup> 3,5,3',5'-Tetrabromo-biphenyl (**5**) was synthesized by oxidative coupling with CuCl<sub>2</sub> and lithiation of 1,3,5-tribromobenzene.<sup>17</sup>

The convergent syntheses of the multi-branched molecules were conducted based on the typical Heck coupling reaction of **2** and the aromatic cores (Scheme I). The molecules **6**, **7**, and **8** were prepared by a palladium-catalyzed reaction of **2** and tribromo- or tetrabromo-substituted aromatic cores. The reaction yield of this coupling reaction is fairly high-around 42%-68%.

The synthesis of **10** was also conducted by using **2** and 3,5-dibromo-benzaldehyde, **9** through the Heck coupling reaction. **11** and **12** were synthesized using triethylphosphite in the presence of 4,4'-bis-bromomethyl-biphenyl and 1,3,5-tris-bromomethyl-benzene in a quantitative yield.<sup>18</sup> Using



**Scheme I.** Reagents and conditions: (a) Ph<sub>3</sub>PCH<sub>3</sub>I, K<sub>t</sub>-OBu, THF, rt, 2 h; (b) Pd(OAc)<sub>2</sub>, K<sub>2</sub>CO<sub>3</sub>, TBAB, DMF, 110 °C, 36 h.

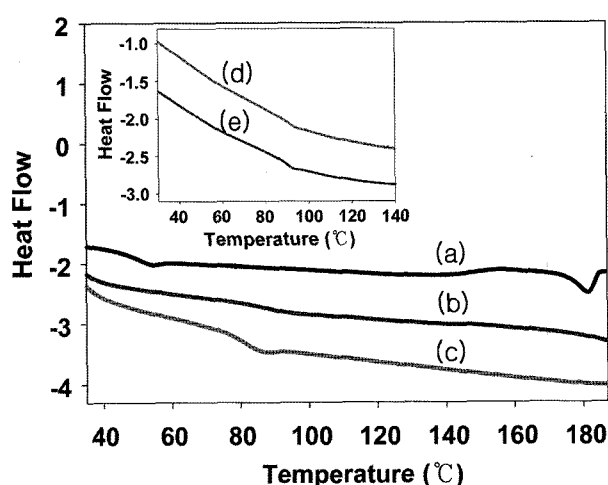


**Scheme II.** Reagents and conditions: (a) Pd(OAc)<sub>2</sub>, K<sub>2</sub>CO<sub>3</sub>, TBAB, DMF, 110 °C, 36 h; (b) K<sub>t</sub>-OBu, THF, rt, 12 h.

**Table I. Measured and Calculated Parameters for Five Carbazole-Based Multi-Branched Molecules**

Compound	$T_m$ (°C)	$T_g$ (°C)	$T_d$ (°C)	HOMO <sup>a</sup> (eV)	LUMO <sup>b</sup> (eV)	$E_g^c$ (eV)	$\lambda_{max}/nm^d$ solution (film)	$\lambda_{ex}/nm$	$\lambda_{em}/nm^d$ solution (film)	$\Phi_f^e$ solution (film)
6	181	50	430	-5.49	-2.50	2.99	346 (350)	353	417 (441,539)	0.083 (0.029)
7	-	87	440	-5.32	-2.39	2.93	356 (360)	358	435 (448,539)	0.394 (0.132)
8	-	78	450	-5.34	-2.30	3.04	345 (349)	354	425 (437,538)	0.129 (0.013)
13	-	85	445	-5.29	-2.39	2.90	353 (356)	364	430 (453)	0.359 (0.075)
14	-	83	432	-5.39	-2.39	3.00	342 (343)	351	427 (444,532)	0.195 (0.043)

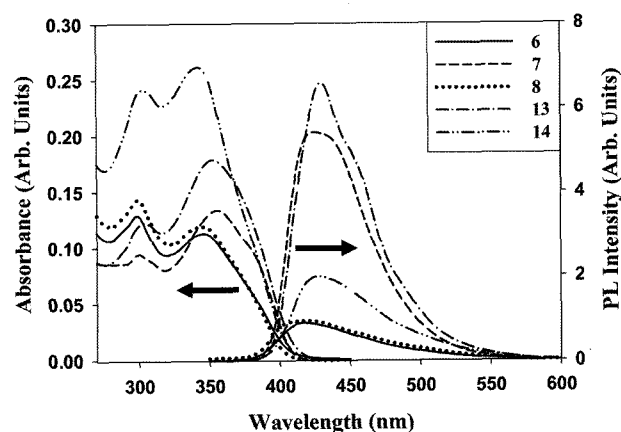
<sup>a</sup>The electrolyte solution employed was 0.10 M tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) in a freshly dried acetonitrile. The Ag/AgCl and Pt wire (0.5 mm in diameter) electrodes were utilized as reference and counter electrodes, respectively. Calculated from HOMO = (4.40 +  $E_{ox}^{onset}$ ). <sup>b</sup>Calculated from LUMO = HOMO -  $E_g^{opt}$ . <sup>c</sup>Estimated from the onset of absorption edge ( $E_g = 1240/\lambda_{onset}$ ). <sup>d</sup>Absorption and PL spectra of solutions (chloroform:  $1 \times 10^{-6}$  M) and films (spin-coating: 50 nm). <sup>e</sup>Solution fluorescence quantum efficiency measured in chloroform relative to 9,10-diphenylanthracene (DPA) in cyclohexane ( $\Phi_{PL} = 0.90$ ); film quantum efficiency estimated relative to DPA in poly(methyl methacrylate) as a standard ( $\Phi_{PL} = 0.83$ ).



**Figure 1.** DSC thermograms of new multi-branched molecules bearing carbazole peripheral units. (a) 6, (b) 7, (c) 8, (d) 13, (e) 14.

two kinds of phosphonate, **11** and **12**, we carried out the Horner-Emmons reaction in the presence of potassium *t*-butoxide to obtain a moderately high yield of **13** and **14**, that is, 78%–83% (Scheme II). The identity and purity of the synthetic materials were confirmed by <sup>1</sup>H-NMR, MALDI-TOF mass spectrometry, and elemental analysis. These synthetic materials were found to have a good self-film-forming property and showed good solubility in various organic solvents such as chloroform, xylene, chlorobenzene, and tetrahydrofuran (THF).

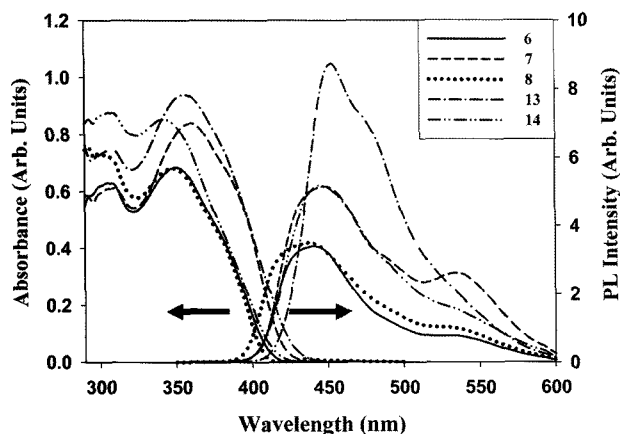
The thermal properties of the multi-branched molecules were characterized by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). In contrast to **6**, the molecules such as **7**, **8**, **13**, and **14** exhibit no discernible crystalline-isotropic transition up to 250 °C, observed in DSC thermograms (see Table I). The glass transition temperatures ( $T_g$ s) of the five molecules are 50, 87, 78, 85, and 83 °C for **6**, **7**, **8**, **13**, and **14** respectively. This indicates that three molecules can exhibit an amorphous morphology in



**Figure 2.** Absorption and PL spectra of the multi-branched molecules in chloroform ( $1 \times 10^{-6}$  M).

solid films except **6** and **13**, which are useful for application to HTL or host materials in an OLED. The glass transition temperatures were found to depend on the size and molecular weight of the molecule. **6** has the lowest glass transition temperature due to the molecular size effect. TGA measurements at a heating rate of 10 °C/min under nitrogen revealed good thermal stability. All multi-branched molecules are thermally stable up to 430–450 °C.

Figure 2 displays the absorption and PL spectra of the synthesized compounds in dilute chloroform solutions. Five branched molecules all have *meta*-substituted carbazole moieties and the conjugation length is almost identical in the molecules. That results in the fact that the absorption and emission maxima of all molecules appeared at around almost identical wavelength. The absorption spectra in solutions reveal characteristic absorption peaks of carbazole between 300 and 360 nm. Generally, the red-shift of  $\lambda_{max}$  in a film relative to that in a solution is observed due to intermolecular interaction between the molecules existing in the ground state. However, no synthesized molecule in the film state exhibited significant red-shift in the spectrum, which



**Figure 3.** Absorption and PL spectra of the film of multi-branched molecules with a thickness of 50 nm.

indicates that there is no undesirable intermolecular interaction resulting in the isolation of the photophysical properties (see Figure 2).

The PL spectra of five molecules in solutions and films are featureless and are almost a mirror-image of the low-energy absorption band. The spectral shapes indicate that the low glass transition temperature below 100°C induces the various molecular conformations diversifying the energy states. The PL spectra of the synthesized molecules in films exhibit a red-shift by 12–24 nm and become broader in comparison to the spectra in chloroform.

These features are usually observed for organic and polymer conjugated materials mainly due to the different polarity of the environments. In particular, the PL spectra of **6** exhibited the largest red-shift ( $\Delta\lambda = 24$  nm), which indicates relatively stronger intermolecular interactions.

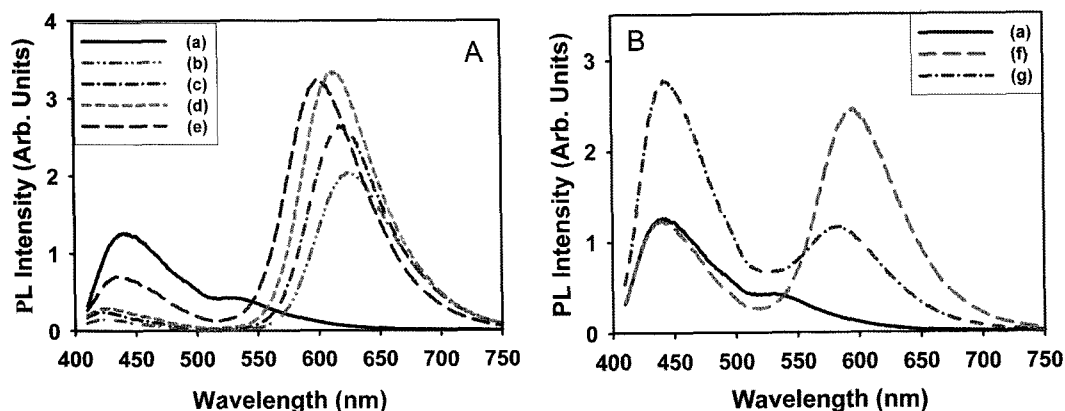
Compared to the PL spectra in solution states, the emission intensity at around 530–550 nm increased in the spectra of thin films. It is presumably attributed to a larger extent of excimer or to intermolecular interaction (see Figure 3).

The PL quantum yield ( $\Phi$ ) of the samples in chloroform were measured using 9,10-diphenyl anthracene as the reference standard.<sup>19</sup> The quantum yields of the films were also found to be 2.9, 13.2, 1.3, 7.5, and 4.3% for **6**, **7**, **8**, **13**, and **14**, respectively.<sup>20</sup>

The electrochemical properties of the synthesized compounds were examined by cyclic voltammetry (Model: EA161 eDAQ) in order to study the molecular energy levels. The molecular thin films were coated on a platinum plate using chloroform as a solvent. The potentials were obtained relative to an internal ferrocene reference (Fc/Fc<sup>+</sup>). The HOMO and LUMO levels were determined to be in the range of -5.29 ~ -5.49 eV and -2.30 ~ -2.50 eV, respectively (see Table I). On considering suitable energy levels [HOMO level at -6.0 ~ -5.0 eV; LUMO level at -2.0 ~ -3.0 eV] for the HTL in the multilayer structural EL device, these values indicate that the compounds can potentially be used as an HTL for efficient cascading carrier transport and as an electron blocking layer.

In order to examine the functions of these compounds as host materials in LEDs, DADB<sup>21</sup> was mixed into **14** at six different concentrations in monochlorobenzene. Subsequently, thin films were fabricated on a quartz substrate for obtaining the PL spectra with excitation at 351 nm. Figure 4A shows the variation of the PL spectra with the DADB concentration (conc. = 1–10 wt%). **14** exhibited mainly blue emission; the maximum intensity of emission appeared at around 444 nm with a weak shoulder at 532 nm. With an increase in the concentration of DADB, the intensity at 444 nm decreases drastically. Further, red emission at around 600–620 nm increases significantly.

DADB is capable of electronic excitation *via* Förster energy transfer from the host material. Photoluminescence (PL) studies of the doped matrix demonstrated that a significantly high energy transfer from **14** to DADB is achieved. We speculated that efficient energy transfer from a singlet and triplet state of the carbazole moiety to the DCM deriva-



**Figure 4.** PL spectra of the films of **14** and its mixtures with DADB. A: (a) **14**, (b) 10 wt%, (c) 5 wt%, (d) 3 wt%, (e) 1 wt%; B: (f) 0.5 wt%, (g) 0.1 wt%. The thickness of films were 30 nm.

tives can enhance red emission in the DADB doped matrix. When doped with 3 wt% DADB, we were able to obtain the highest PL intensity at 602 nm. The concentration of DADB could be optimized to 3 wt% in this experiment.

In Figure 4B, we took PL spectra with the relatively smaller concentration of DADB (conc. = 0.1-0.5 wt%). Resulting from the incomplete energy transfer, blue and red emission appeared together. This is quite promising method to exhibit white emission from the light harvesting system.

## Conclusions

We have synthesized novel multi-branched molecules for hole transport materials and as host materials for red or white emitting EL devices. The HOMO and LUMO energies of the synthesized molecules are suitable for hole transporting materials in a multilayer EL device. The absorption and PL spectra indicate that the molecules bearing carbazoles as peripheral groups can exhibit highly isolated photo-physical properties. It also can be considered that these carbazole-labeled multi-branched molecules can potentially be used for red or white organic light-emitting devices optimizing the concentration of DADB.

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