

# Synthesis of electrochemically and thermally stable amorphous hole-transporting carbazole dendronized fluorene

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## Abstract

A novel amorphous hole-transporting carbazole dendrimer, 2,7-bis[3,6-di(carbazol-9-yl)carbazol-9-yl]-9,9-bis-*n*-hexylfluorene (**G2CF**), was synthesized by a divergent approach involving bromination and Ullmann coupling reactions. **G2CF** showed UV–vis absorption bands at 304 and 332 nm in chloroform solution and the photoluminescence spectra showed a maximum peak at 373 nm in a bluish-purple region. Differential scanning calorimetry (DSC) and cyclic voltammetry (CV) analysis revealed **G2CF** was an electrochemically and thermally stable amorphous material with a high glass transition temperature ( $T_g$ ) of 237 °C. The organic light-emitting device having the structure of ITO/**G2CF**/Alq<sub>3</sub>/LiF:Al exhibited a bright green emission with a maximum luminescence of 11,000 cd/m<sup>2</sup> at 16 V and a turn-on voltage of 5.4 V.

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## 1. Introduction

Organic light-emitting devices (OLEDs) have shown potential to be low-cost, full color flat panel displays due to their merits of high brightness, easy fabrication, and the availability of a wide range of emission colors [1,2]. The past decade has seen great progress in both device fabrication techniques and material developments [3]. One of the key developments has been made by Tang and VanSlyke who demonstrated that the used of hole-transporting layers (HTLs) for hole injection from the anodes into the light-emitting layer provides the significant improvement of the OLED device performance [4]. Since, much attention has been paid for developing the new hole-transporting materials [5]. In particular, low molecular weight amorphous materials have received interest as candidates for HTL materials due to their easy purification by vapor deposition or column chromatographic techniques and uniform thin film can be simply processed by coating techniques.

To our best knowledge, the most commonly used amorphous hole-transporting materials (AHTMs) was triarylamine compounds such as 4,4'-bis(1-naphthylphenylamino)biphenyl (NPB) and 4,4'-bis(*m*-tolylphenylamino)biphenyl (TPD), which have excellent hole-transporting properties. However, their low thermal and morphological stability usually lead to the degradation of the devices. For highly efficient and long lifetime OLED devices, AHTM having high mobility of hole, high glass transition temperature ( $T_g$ ), stable amorphous state, easy form good thin film by spin-coating techniques, and preferable a simple preparation is desirable. Optimizing all of these requirements is still a difficult challenge for scientists. So far, many AHTMs with high  $T_g$  values such as carbazole derivatives containing peripheral diarylamine units [6], carbazole units [7], carbazole and phenylazomethine dendron units [8] and bis(4-*tert*-butylphenyl)carbazole units [9], and dicarbazoyl derivatives featuring peripheral diphenylamine units [10], triphenylamines-substituted fluorine [11] and triaryldiamines containing spiro(adamantane-2,9-fluorene) core [12], and starburst tris(*N*-3-methylphenyl-*N*-(9-ethylcarbazyl-3)amino) triphenylamine [13] have been reported. In this paper, we report the synthesis and characterization of the new carbazole

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dendronized fluorene compound, which conveniently prepared by divergent approach in three steps. The hole-transporting property was investigated by preparing a double-layer device with the light-emitting material, Alq<sub>3</sub>.

## 2. Experimental

### 2.1. Materials

All reagents were purchased from Aldrich, Acros or Fluka and used without further purification. All solvents were supplied by Thai companies and used without further distillation. Nitrobenzene was distilled under reduced pressure from calcium hydride prior to use. Dichloromethane for cyclic voltammetry experiment was washed with conc. H<sub>2</sub>SO<sub>4</sub> and distilled twice from calcium hydride.

### 2.2. Synthesis of 2,7-bis(carbazol-9-yl)-9,9-bis-*n*-hexylfluorene (GICF)

A mixture of 2,7-dibromo-9,9-bis-*n*-hexylfluorene (1.00 g, 2.03 mmol), carbazole (0.78 g, 4.70 mmol), Cu-bronze (50 mg, 0.89 mmol), potassium carbonate (1.13 g, 8.20 mmol) in freshly distilled nitrobenzene (13 ml) was stirred at reflux under N<sub>2</sub> atmosphere for 24 h. After evaporation of the solvent in *vacuo*, ammonia solution (30 ml) was added and the mixture was stand for 2 h. Dichloromethane (100 ml) and water (100 ml) were added. The organic phase was separated, washed with water (100 ml × 2), brine solution (100 ml), dried over anhydrous sodium sulfate, filtered and the solvent was removed to dryness. Purification by column chromatography over silica gel eluting with a mixture of dichloromethane and hexane (1:4) followed by recrystallization from a mixture of dichloromethane and methanol gave white solids. Yield was 1.34 g (98%); IR (KBr) 3045, 2926, 1597, 1450, 1334 and 1230 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 0.83 (6H, t, *J* = 6.9 Hz), 0.90–0.94 (4H, m), 1.18–1.28 (12H, m), 2.04–2.10 (4H, m), 7.30–7.37 (4H, m), 7.44–7.52 (8H, m), 7.61–7.65 (4H, m), 8.00 (2H, d, *J* = 8.7 Hz) and 8.20 (4H, d, *J* = 7.7 Hz); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 14.03, 22.54, 24.05, 29.60, 31.55, 40.23, 55.74, 109.78, 119.96, 120.42, 121.04, 121.88, 123.44, 125.97, 126.01, 136.75, 139.59, 141.03 and 152.90; HRMS-ESI (*m/z*): [MH<sup>+</sup>] calcd. for C<sub>49</sub>H<sub>49</sub>N<sub>2</sub>, 665.3890; found, 665.3888.

### 2.3. Synthesis of 2,7-bis(3,6-dibromocarbazol-9-yl)-9,9-bis-*n*-hexylfluorene

*N*-Bromosuccinimide (1.44 g, 8.09 mmol) was added in small portions to a solution of GICF (1.31 g, 1.97 mmol) in tetrahydrofuran (50 ml). The reaction mixture was stirred at room temperature under N<sub>2</sub> atmosphere for 20 h. The mixture was extracted with dichloromethane (100 ml). The organic phase was separated, washed with water (100 ml × 2), brine solution (100 ml), dried over anhydrous sodium sulfate, filtered and the solvents were removed to dryness. Purification by recrystallization from a mixture of dichloromethane and methanol gave light brown solids. Yield was 1.67 g (87%); IR (KBr): 3056, 2924,

1609, 1467, 1282 and 1057 (Ar–Br) cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 0.82–0.89 (10H, m), 1.15–1.31 (12H, m), 2.02–2.08 (4H, m), 7.30 (4H, d, *J* = 9.0 Hz), 7.53–7.58 (8H, m), 8.00 (2H, d, *J* = 7.8 Hz) and 8.28 (4H, d, *J* = 1.8 Hz); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 14.00, 22.49, 24.05, 29.53, 31.51, 40.11, 50.90, 55.86, 111.45, 113.16, 121.40, 121.71, 123.35, 124.03, 125.98, 129.48, 136.01, 139.91, 140.00 and 153.15; HRMS-ESI (*m/z*): [MH<sup>+</sup>] calcd. for C<sub>49</sub>H<sub>45</sub>Br<sub>4</sub>N<sub>2</sub>, 977.0311; found, 977.0308.

### 2.4. Synthesis of 2,7-bis[3,6-di(carbazol-9-yl)carbazol-9-yl]-9,9-bis-*n*-hexylfluorene (G2CF)

A mixture of 2,7-bis(3,6-dibromocarbazol-9-yl)-9,9-bis-*n*-hexylfluorene (1.20 g, 1.22 mmol) carbazole (1.02 g, 6.10 mmol), Cu-bronze (80 mg, 1.22 mmol), potassium carbonate (1.43 g, 10.31 mmol) in freshly distilled nitrobenzene (20 ml) was stirred at reflux under N<sub>2</sub> atmosphere for 24 h. After evaporation of the solvent in *vacuo*, ammonia solution (30 ml) was added and the mixture was stand for 2 h. Dichloromethane (100 ml) and water (100 ml) were added. The organic phase was separated, washed with water (100 ml × 2), brine solution (100 ml), dried over anhydrous sodium sulfate, filtered and the solvent was removed to dryness. Purification by column chromatography over silica gel eluting with a mixture of dichloromethane and hexane (1:4) followed by recrystallization from a mixture of dichloromethane and methanol gave light yellow solids. Yield was 1.76 g (55%); IR (KBr); 3044, 2923, 1596, 1457, 1229, 1156 and 812 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 0.80 (6H, t), 1.03 (4H, m), 1.23–1.28 (12H, m), 2.20–2.27 (4H, m), 7.30–7.36 (8H, m), 7.45 (16H, d, *J* = 3.6 Hz), 7.67 (4H, dd, *J* = 8.7 Hz, *J* = 1.8 Hz), 7.75 (4H, d, *J* = 8.7 Hz), 7.83–7.85 (4H, m), 8.16–8.22 (10H, m) and 8.35 (4H, d, *J* = 1.8 Hz); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 14.00, 22.53, 24.55, 29.06, 32.03, 40.59, 56.07, 109.41, 111.02, 119.73, 120.54, 120.80, 122.04, 122.56, 123.08, 124.22, 126.03, 126.34, 126.55, 130.46, 136.38, 140.14, 140.80, 141.98 and 153.57; HRMS-EI (*m/z*): [MH<sup>+</sup>] calcd. for C<sub>97</sub>H<sub>77</sub>N<sub>6</sub>, 1325.6204; found, 1325.6192; Anal. calcd. for C<sub>97</sub>H<sub>76</sub>N<sub>6</sub>: C, 87.88; H, 5.78; N, 6.34; found, C, 87.80; H, 5.78; N, 6.31.

### 2.5. Measurements

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AVANCE 300 MHz spectrometer using CDCl<sub>3</sub> as solvent in all cases. IR spectra were measured on a Perkin-Elmer FT-IR spectroscopy spectrum RXI spectrometer as KBr pellets. UV–vis spectra were recorded as a dilute solution in spectroscopic grade chloroform on a Perkin-Elmer UV Lambda 25 spectrometer. Photoluminescence (PL) spectra were recorded with a Perkin-Elmer LS 50B Luminescence Spectrometer as a dilute solution in spectroscopic grade chloroform. Differential scanning calorimetry (DSC) measurement was carried out under nitrogen atmosphere using a METTLER DSC823e thermal analyzer at a heating rate of 10 °C/min. Thermogravimetric analysis (TGA) measurement was performed on a Seiko EXSTAR 6000 TG/DTA 6300 thermal analyzer at a heating rate of 10 °C/min.

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