

## Synthesis and Characterization of Novel Fluorene-Carbazole Core Derivative for Emitting Materials

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### Abstract

Fluorene and electron rich carbazole materials are commonly used in opto-electronic devices. Novel, substituted carbazole and fluorene core derivatives (TM1, TM2 and TM3) were designed, synthesized and characterized. The three novel  $\pi$ -conjugated emitting materials consist of naphthalene and thiophene substituted carbazole-fluorene dual core. The aromatic parts of these target molecules have high luminescence and excellent thermal stability. The steric side group of naphthalene and thiophene can prevent intermolecular packing, moreover, the long alkyl chain can improve solubility and thermal stability. The target molecules, 9-(9, 9-didodecyl-7-(thiophen-2-yl)-9H-fluoren-2-yl)-3, 6-di(thiophen-2-yl)-9H-carbazole (TM1), 9-(7-(3, 6-di(thiophen-2-yl)-9H-carbazol-9-yl)-9, 9-didodecyl-9H-fluoren-2-yl)-3, 6-di(thiophen-2-yl)-9H-carbazole (TM2), and 9-(7-(3, 6-bis(3, 6-di-tert-butyl-9H-carbazol-9-yl)-9H-carbazol-9-yl)-9, 9-didodecyl-9H-fluoren-2-yl)-3, 6-bis(5-(naphthalen-1-yl)thiophen-2-yl)-9H-carbazole (TM3), were successfully synthesized using well known reaction including of Ullmann coupling and Suzuki coupling reaction. All of the products have been confirmed by Nuclear magnetic resonance spectroscopy, Mass spectrometry and FT-IR spectroscopy techniques. These molecules will be used as emitting materials in organic light emitting diodes.

**Keywords:** Carbazole; Fluorene; Naphthalene; Organic light emitting diodes

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### Introduction

In the past two decades, attention in organic optoelectronic field has increased dramatically, especially organic light emitting diodes (OLEDs) and dye sensitized solar cell [1]. In particular, OLED has been focused much attention because its shows potential to applications in color display screen, and it will be used as the next generation lighting sources such as flexible displays [2]. OLEDs are developed into two ways divided by fabrication process [3]. The first efficient organic light emitting diode device was constructed as single layer structure consisted of ITO (indium tin oxide) as anode, hole-transporting layer, electron transporting layer and metal cathode

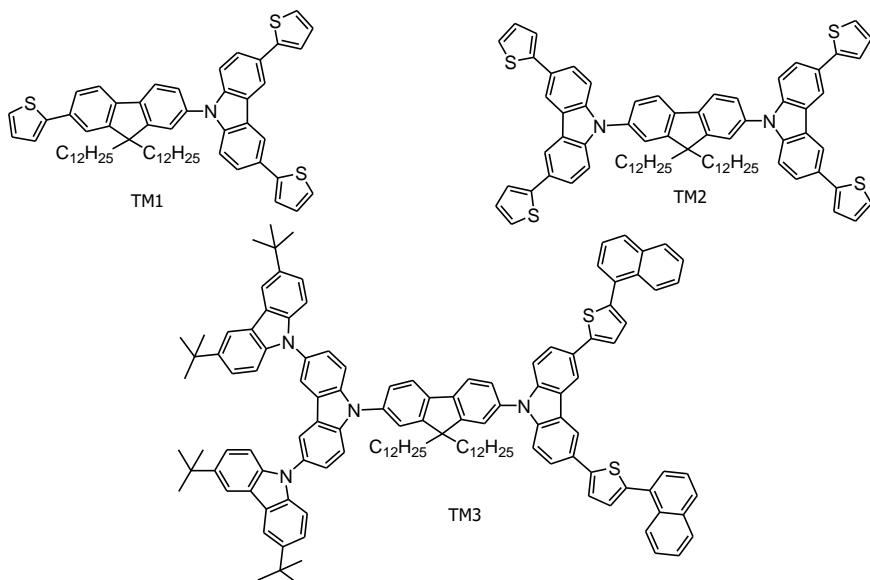
[4]. The complicated multilayer OLEDs with excellent device performance are fabricated from vapor deposition method. However, the space of vapor deposition chamber limited the development of large-size panel displays. To overcome of this limitation, solution process is used as an alternative way to fabricate the large scale OLEDs. Since the break new ground work of Tang and Friend in 1987, these day OLEDs technology is used in mobile and television screen and they have been used as commercialized products [5]. While, there are a lot of challenges for improving the properties of these devices such as materials and device fabrication which limits OLEDs applications and life time. Blue, green, and red emitting materials are very important and required to achieve the full-color display. Recently, many research groups have devoted to develop these emitters with high color purity and stability [6]. In OLEDs applications, the materials with amorphous morphology are required for high charge transporting and light emitting transparent reason. Therefore, the high thermal stability materials with amorphous morphology can be fabricated for thermally stable OLEDs and increased lifetime of the devices [7]. For that reason, the materials with low glass transition temperature are not suitable for OLEDs because they will gradually form crystalline to get restrictions which boundary the charge transport and decreased the lifetime of OLEDs [8].

Small organic molecules with conjugated core and steric side groups have been intensively studied for using as materials in OLED, over the past decades. A lot of these derivatives containing a conjugated core group, for example, pyrene, fluorene and anthracene have been synthesized and characterized to increase the device efficiency by tuning of their structures consisting of conjugation length, morphology and charge transport property in the light-emitting materials [9].

Despite this progress, the quenching effect can occur and unequal charge mobility of these compounds in solid form usually immerged in OLEDs operation. These effects decrease the quantum efficiency of the OLEDs devices [10]. Consequently, novel nonplanar and high steric structure molecules are developed. These novel structures can prevent molecular aggregation with thermal and morphological stability. Recently, many stable amorphous molecules with good thermal and morphological stability have been reported such as diarylfluorene-substituted triarylamine [11], carbazole derivatives [12]. Carbazole and fluorene derivatives have been wildly applied as emitting and charge transport materials in OLEDs since the derivatives have the high photoluminescence and electroluminescence properties, moreover, they also have the excellent electrochemical and thermal properties. Introducing of different steric alkyl or aryl groups at the C-3 and -6 positions of carbazole or C-2 and -7 positions of fluorene can improve not only the thermal property, but also increase the solubility in organic solvent. Consequently, many stable and tunable emitting materials are conveniently synthesized. In addition, the bulky alkyl groups connected to carbazole and fluorene moieties can enhance a good film forming in solid state [13, 14].

Recently, star-shaped derivative of carbazole has been reported by Zassoski and co-workers for application as blue emitting material from which an external quantum efficiency of 6.84% with a CIE(x,y) of (0.24, 0.35) using a non-doped condition [15]. Braveenth and co-workers reported the properties of thermally stable hole transporting molecule using carbazole and triphenylamine moiety as cores without any crystalline formation occurred in higher decomposition temperature [16]. These results increase speed the development of high performance materials used in OLEDs and its continuing used in commercial markets.

In this work, we have designed, synthesized and characterized of new fluorescent organic compounds (TM1, TM2 and TM3) containing carbazole and fluorene moiety as core. Thiophene, naphthalene and 3, 6-di-tert-butyl-9H-carbazol were used as the side groups. Introducing of these bulky aromatic parts has been affected to be improve in desired molecular morphology, increase the glass-transition temperature ( $T_g$ ) and enhance the charge transporting ability. The heterocyclic thiophene unit is generally used to organic materials because to its outstanding optic, electronic and redox properties [17]. A combination of this functional core with the steric aromatic side groups is infrequently reported in the literature and neovel carbazole and fluorene core with high charge mobility and excellent emission property could be constructed. The synthetic methods are not only easy but also the purification by common silica gel column chromatography. This work shows the simple synthetic pathway of these target molecules and the materials could be used as amorphous emitting layer or charge transport materials in optoelectronic applications. The molecular structure of the target molecules is shown in Fig. 1.



**Fig. 1** Molecular structure of the target molecules.

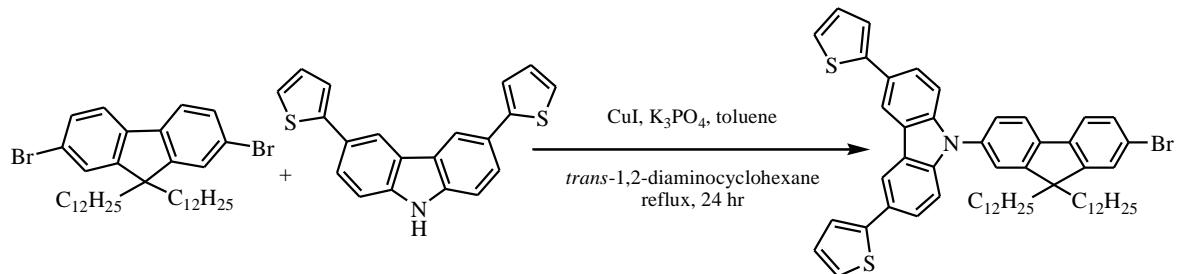
## Materials and Methods

Brüker AVANCE 300 MHz spectrometer with fully decoupled were used to get the  $^1\text{H-NMR}$  and  $^{13}\text{C}$  NMR spectra. High-resolution matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectra were recorded with a Bruker Autoflex MALDI-TOF mass spectrometer. The IR spectra were carried out on a Perkin-Elmer FT-IR spectroscopy as KBr disks or neat liquid between two sodium chloride cells. The absorption peaks of the IR spectra are reported in wavenumber ( $\text{cm}^{-1}$ ). The melting points of the compounds were determinate using an Electrothermal MEL-TEMP apparatus.

The reagents and solvents used in this work were purchased from Aldrich, Acros, Fluka or Thai Supplie Company and used without purification. Analytical thin-layer chromatography (TLC) was performed to detect of the target products with Merck aluminium plates coated with silica gel 60 F<sub>254</sub>. Gravity feed chromatography was used to purified both of intermediates and target molecules. All of column chromatography was successfully done using Merck silica gel mesh

60 Å. The solvent mixtures are used and the portions are given by volume. 9-(9-(7-(3, 6-bis (5-bromothiophen-2-yl)-9H-carbazol-9-yl)-9, 9-didodecyl-9H-fluoren-2-yl)-6-(3, 6-di-tert-butyl-9H-carbazol-9-yl)-9H-carbazol-3-yl)-3, 6-di-tert-butyl-9H-carbazole, 3, 6-di (thiophen-2-yl)-9H-carbazole, and 2, 7-dibromo-9, 9-didodecyl-9H-fluorene were prepared according to the literature methods by P. Moonsin et al. [18].

### Synthesis and Characterization



**Fig. 2** The synthesis condition of 9-(7-bromo-9, 9-didodecyl-9H-fluoren-2-yl)-3, 6-di (thiophen-2-yl)-9H-carbazole.

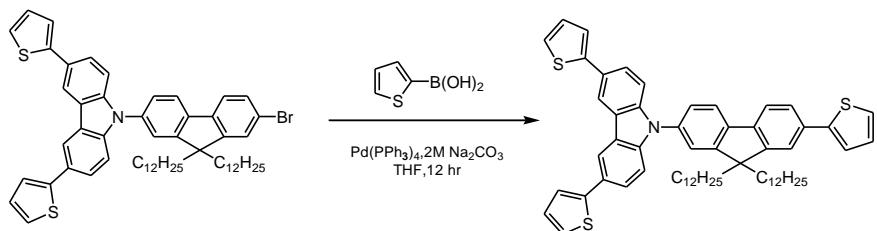
The key intermediate 9-(7-bromo-9, 9-didodecyl-9H-fluoren-2-yl)-3, 6-di(thiophen-2-yl)-9H-carbazole, for the synthesis of TM1, was obtained from Ullmann coupling between 2, 7-dibromo-9, 9-didodecyl-9H-fluorene (1.83 g, 2.77 mmol), 3, 6-di(thiophen-2-yl)-9H-carbazole (0.45 g, 1.39 mmol), copper iodide (0.26 g, 0.69 mmol), potassium phosphate (0.74 g, 3.47 mmol) and toluene (50 ml) showed in Fig. 2. The mixture was degassed for 3 minutes and protected under nitrogen gas, and then *trans*-1, 2-diaminocyclohexane (0.08 g, 0.69 mmol) was injected, respectively. Next, the reaction mixture was heated to reflux temperature for 24 h by covering under nitrogen gas. The reaction mixture was cooled to room temperature, filtered through silica gel and washed with dichloromethane (3 × 360 ml). The combine dichloromethane solution was washed with water (2 × 50 ml), brine solution (30 ml). The organic solution was dried using sodium sulfate anhydrous, filtered and the solvent was removed off under vacuum. The product of this reaction was purified by column chromatography using 10% dichloromethane: hexane as eluting solvent to give 9-(7-bromo-9, 9-didodecyl-9H-fluoren-2-yl)-3, 6-di(thiophen-2-yl)-9H-carbazole as light green solid (0.62 g, 50%).

Melting point: 144 – 145 °C

FT-IR (KBr):  $\nu_{\text{max}}$  = 3018.08, 2926.49, 2854.95, 1611.36, 1484.09, 1468.26, 1430.01, 1367.05, 1287.94, 1214.96, 909.01, 878.66, 810.09, 746.05, 695.49, 667.08, 628.23, 604.03 and 489.41  $\text{cm}^{-1}$

$^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.45 (2H, *s*), 7.90 (2H, *d*,  $J$  = 7.8 Hz), 7.73 (2H, *d*,  $J$  = 8.10 Hz), 7.64 (2H, *d*,  $J$  = 8.10 Hz), 7.55 (4H, *d*,  $J$  = 6.0 Hz), 7.43 (2H, *d*,  $J$  = 8.4 Hz), 7.31 (2H, *d*,  $J$  = 4.80 Hz), 7.16 (2H, *d*,  $J$  = 3.60 Hz) 2.02 (4H, *s*), 1.23 – 1.15 (40H, *m*) and 0.87 (6H, *t*,  $J$  = 6.30 Hz) ppm

HRMS-ESI calcd for  $\text{C}_{57}\text{H}_{68}\text{BrNS}_2$ :  $m/z$  909.3977 found 909.7146 [ $\text{M}^+$ ]



**Fig. 3** The synthesis condition of 9-(9,9-didodecyl-7-(thiophen-2-yl)-9H-fluoren-2-yl)-3, 6-di(thiophen-2-yl)-9H-carbazole (TM1).

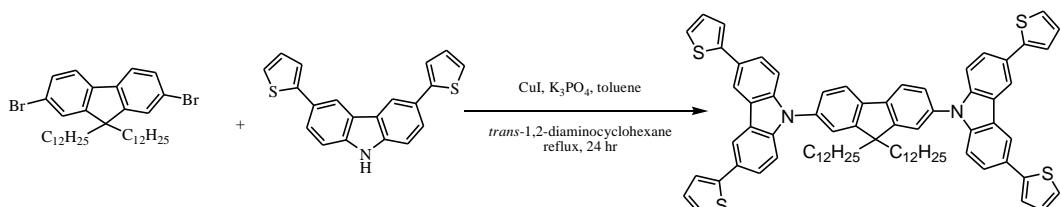
The TM1 was successfully achieved from Suzuki cross coupling reaction presented in Fig. 3, between 9-(7-bromo-9, 9-didodecyl-9H-fluoren-2-yl)-3, 6- di(thiophen-2-yl)-9H-carbazole (0.36 g, 0.40 mmol) and 2-thiophene boronic acid (0.07 g, 0.60 mmol) using  $\text{Pd}(\text{PPh}_3)_4$  (0.02 g, 0.02 mmol) as catalyst and 2M  $\text{Na}_2\text{CO}_3$  (0.83 g, 7.96 mmol) as base in THF (15 ml) as solvent. The mixture was degassed for 3 minutes to remove oxygen gas and then covered with nitrogen atmosphere. Next the reaction was heated to reflux temperature for 12 h. After the mixture was being cooled to room temperature, water (50 ml) was added. The resulting product solution was extracted with dichloromethane ( $3 \times 30$  ml). The combine organic layer was washed with water (100 ml), and brine solution (50 ml). The organic phase was dried over sodium sulfate anhydrous. The solid phase was filtered and the vacuum pump was used to remove the solvent to dryness. Column chromatography was used to purify the residue over silica gel eluting with 10% dichloromethane: hexane to give TM1 as green wish oil (0.18 g, 50%).

FT-IR (KBr):  $\nu_{\text{max}} = 3068.17, 3008.07, 2921.07, 2850.65, 1610.03, 1584.17, 1484.09, 1463.97, 1429.61, 1366.65, 1320.86, 1286.51, 1255.03, 1231.00, 1215.06, 1119.08, 1062.04, 959.00, 874.37, 849.01, 805.68, 754.16, 689.76, 668.30, 6.22.05, 566.69, 494.01$  and  $422.15 \text{ cm}^{-1}$

$^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ) :  $\delta$  8.42 (2H, *s*), 7.89 (2H, *d*,  $J = 7.8$  Hz), 7.70 (2H, *d*,  $J = 7.8$  Hz), 7.64 (2H, *d*,  $J = 8.70$  Hz) 7.54 (4H, *d*,  $J = 8.40$  Hz), 7.41 (4H, *d*,  $J = 8.40$  Hz), 7.29 (3H, *d*,  $J = 4.80$  Hz), 7.14 (2H, *t*,  $J = 3.90$  Hz), 2.00 (4H, *t*,  $J = 6.30$  Hz), 1.26 – 1.12 (40H, *m*) and 0.87 (6H, *t*,  $J = 6.00$  Hz) ppm.

$^3\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  153.27, 152.41, 145.37, 140.94, 139.59, 139.25, 136.40, 130.34, 128.07, 127.19, 126.37, 125.75, 124.95, 123.99, 123.87, 122.41, 121.64, 121.59, 121.33, 121.09, 118.01, 110.29, 77.50, 77.08, 76.65, 55.79, 40.19, 31.96, 30.92, 29.97, 29.69, 29.38, 23.97, 22.72 and 14.16 ppm.

HRMS-ESI-TOF calcd for  $\text{C}_{61}\text{H}_{71}\text{NS}_3$ :  $m/z = 913.4749$  found 913.7167 [ $\text{M}^+$ ]



**Fig. 4** The synthesis condition of 9-(7-(3, 6-di(thiophen-2-yl)-9H-carbazol-9-yl)-9, 9-didodecyl-9H-fluoren-2-yl)-3, 6-di(thiophen-2-yl)-9H-carbazole (TM2).

To successfully get the TM2, the Ullmann coupling reaction was carried out as following in Fig. 4. 2, 7-dibromo-9, 9-didodecyl-9H-fluorene (2.49 g, 1.64 mmol), 3, 6-di(thiophen-2-yl)-9H-carbazole (0.55 g, 1.65 mmol), copper iodide (0.15 g, 0.82 mmol) as catalyst, potassium phosphate (0.87 g, 4.10 mmol) as base and toluene (50 ml) as solvent were mixed in 100 ml round bottom flask. The mixture was degassed for 3 minutes and protected under nitrogen gas, then a co catalyst, *trans*-1, 2-diaminocyclohexane (0.09 g, 0.82 mmol) was injected to the mixture. The reaction mixture was heated to reflux temperature for 24 h under nitrogen atmosphere. The resulting reaction was poured to silica gel after cooled to room temperature for removing the solid phase and washed by dichloromethane ( $3 \times 50$  ml). The combine organic solution was washed with water (50 ml), brine solution (50 ml). Sodium sulfate anhydrous was used to remove the water in the mixture, filtered of the solid phase and the solvent was stripped off under vacuum. Column chromatography was used to purify the crude product by using 10% dichloromethane: hexane as eluting solvent to afford TM2 as light yellow solid (1.10 g, 56%).

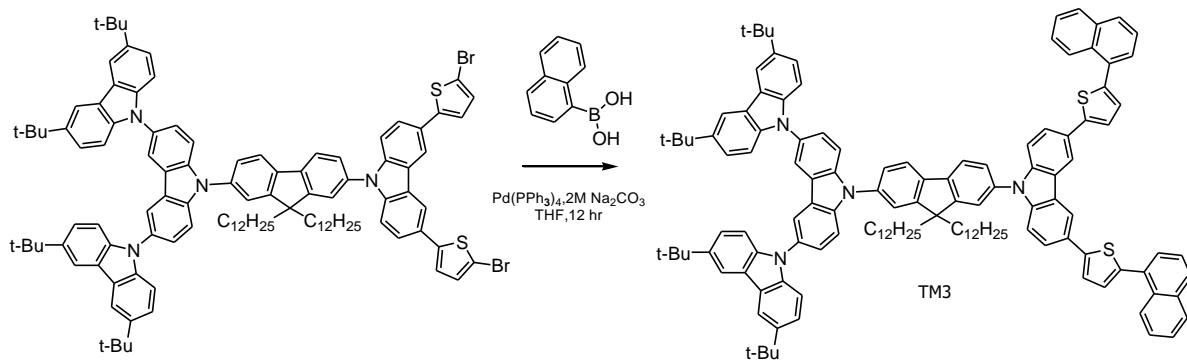
Melting point: 149 – 150 °C

FT-IR (KBr):  $\nu_{\text{max}} = 3077.03, 2924.06, 2852.08, 1609.93, 1480.07, 1427.05, 1361.02, 1320.86, 1286.51, 1231.07, 904.42, 849.01, 807.11, 726.97, 692.62, 649.69, 602.47, 569.55, 488.08$  and  $421.01 \text{ cm}^{-1}$ .

$^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.46 (4H, *s*), 8.03 (2H, *d*,  $J = 8.40$  Hz), 7.77 – 7.74 (4H, *dd*,  $J = 1.50, 8.40$  Hz), 7.63 (4H, *d*,  $J = 6.00$  Hz), 7.49 (4H, *d*,  $J = 8.40$  Hz), 7.43 (4H, *d*,  $J = 3.00$  Hz), 7.33 (4H, *d*,  $J = 5.10$  Hz), 7.18 – 7.16 (4H, *dd*,  $J = 3.60, 4.80$  Hz), 2.09 (4H, *t*,  $J = 3.90$  Hz), 1.28 – 1.22 (40H, *m*) and 0.86 (6H, *t*,  $J = 6.90$  Hz) ppm.

$^3\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  153.06, 145.35, 140.95, 139.71, 136.44, 128.08, 127.20, 125.86, 124.98, 124.02, 123.88, 122.42, 121.68, 121.24, 118.03, 110.33, 77.46, 77.04, 76.62, 55.85, 40.20, 31.92, 30.93, 30.01, 29.71, 29.69, 29.47, 29.35, 24.21, 22, 67 and 14.12 ppm.

HRMS-ESI-TOF calcd for  $\text{C}_{77}\text{H}_{80}\text{N}_2\text{S}_4$ :  $m/z = 1160.5204$  found 1160.9516 [ $\text{M}^+$ ].



**Fig. 5** The synthesis condition of 9-(7-(3, 6-bis (3, 6-di-tert-butyl-9H-carbazol-9-yl)-9H-carbazol-9-yl)-9, 9-didodecyl-9H-fluoren-2-yl)-3, 6-bis(5-(naphthalen-1-yl) thiophen-2-yl)-9H-carbazole (TM3).

The naphthalene derivative (TM3) was obtained from Suzuki cross coupling between 9-(7-(3, 6-bis(5-bromothiophen-2-yl)-9H-carbazol-9-yl)-9, 9-didodecyl-9H-fluoren-2-yl)-6-(3, 6-di-tert-butyl-9H-carbazol-9-yl)-9H-carbazol-3-yl)-3, 6-di-tert-butyl-9H-carbazole (0.30 g, 0.17 mmol) derived from the previous work of our group and 2-naphthalene boronic acid (0.12 g, 0.70

mmol) in Fig. 5.  $\text{Pd}(\text{PPh}_3)_4$  (0.004 g, 0.003 mmol) was used as catalyst and 2M  $\text{Na}_2\text{CO}_3$  (0.37 g, 3.50 mmol) as base in THF (15 ml) as solvent as shown in Fig. 6. The reaction mixture was degassed for 3 minutes and protected under nitrogen gas, and then heated to reflux temperature for 12 h. After being cooled to room temperature, water (30 ml) was added to the resulting mixture. Then the reaction mixture was extracted with dichloromethane ( $3 \times 20$  ml). The organic phase was washed with water (30 ml), and brine solution (20 ml). The combined organic solution was dried by sodium sulfate anhydrous, filtered and the solvent was evaporated to dryness. The crude product was purified by column chromatography over silica gel eluting with 50% dichloromethane: hexane to give TM2 as green wish solid (0.22 g, 37 %).

Melting point: 207.50 – 209.40 °C

FT-IR (KBr):  $\nu_{\text{max}} = 3051, 2954, 2924, 2852, 2304, 1872, 1731, 1609, 1585, 1479, 1392, 1363, 1340, 1324, 1294, 1283, 1263, 1234, 1201, 1168, 1134, 1104, 1077, 1034, 963, 922, 895, 879, 840, 809, 769, 774, 735, 704, 655, 612, 563, 507, 470$  and  $422 \text{ cm}^{-1}$ .

$^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.55$  (2H, s), 8.49 – 8.42 (2H, m), 8.30 (2H, s), 8.19 (4H, s), 8.12 (2H, t,  $J = 6.00$  Hz), 7.98 – 7.79 (8H, m), 7.71 (8H, q,  $J = 6.00$  Hz), 7.58 – 7.48 (14H, m), 7.40 (2H, s), 7.37 (2H, s), 7.33 (2H, d,  $J = 6.00$  Hz), 2.14 (4H, t,  $J = 1.20$  Hz) 1.50 (36H, s), 1.20 (40H, s) and 0.80 (6H, t,  $J = 6.00$  Hz) ppm.

$^{13}\text{C-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 153.32, 153.14, 145.54, 142.62, 141.05, 140.52, 140.50, 140.20, 134.02, 132.58, 131.80, 128.47, 128.42, 128.38, 128.02, 126.51, 126.07, 125.87, 125.36, 124.08, 124.02, 123.59, 123.19, 122.70, 116.26, 109.11, 55.99, 53.42, 34.76, 32.07, 31.85, 30.07, 29.72, 29.66, 29.65, 29.61, 29.49, 29.30, 22.63, 14.13$  and 14.07 ppm.

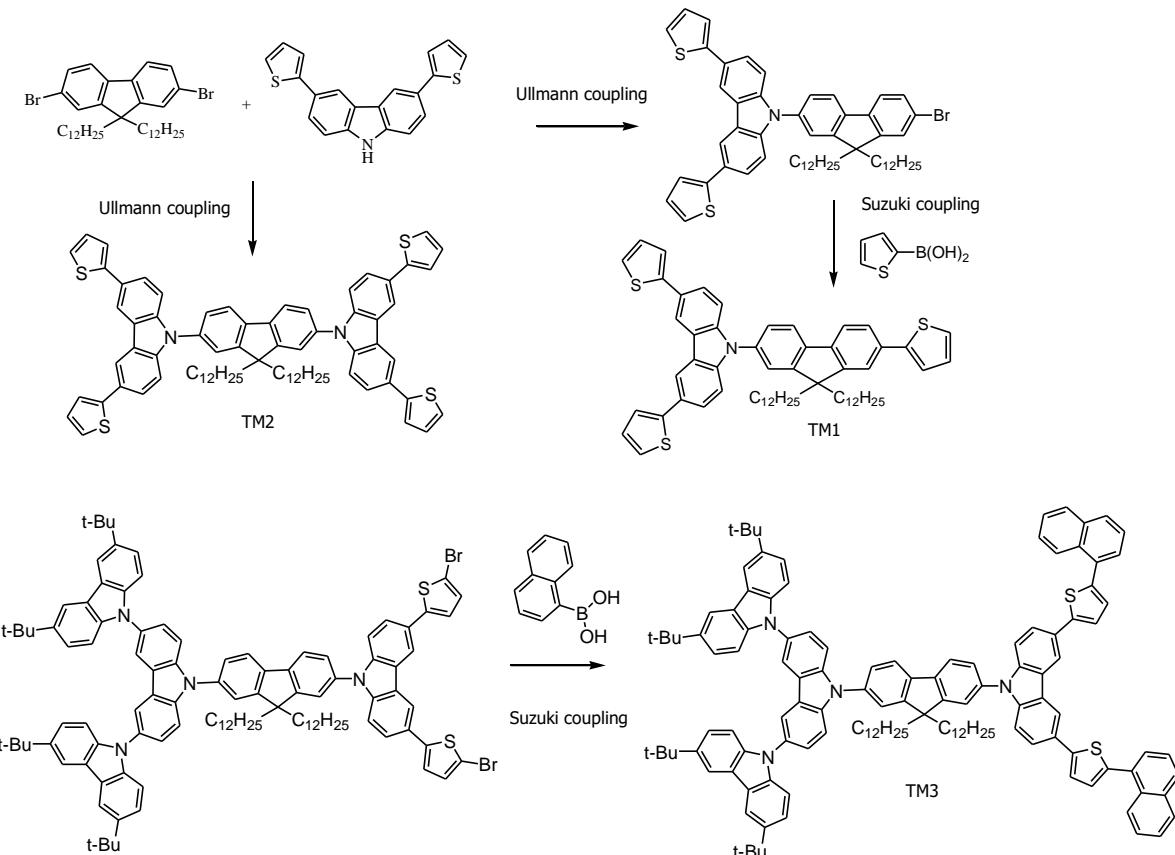
HRMS-ESI calcd for  $\text{C}_{129}\text{H}_{134}\text{N}_4\text{S}_2$ :  $m/z = 1803.005$  found 1804.3208 [ $\text{M}^+$ ].

## Results and Discussion

The new emitting materials (TM1, TM2 and TM3) are developed, with carbazole and fluorene core, thiophen (T) or thiophene napthyl (TN) linkers. The selection of carbazole and fluorene core was supported by their high absorption and thermal ability. Thiophene and thiophene napthyl were connected with the core not only to extend absorption property but also and to enhance thermal stability.

The TM1, TM2 and TM3 were successfully synthesized via the synthetic route presented in Fig. 6, where the didodecyl groups are substituted at the C-9 position of fluorene ring. The introduction of long chain hydrocarbon moieties and bulky of *tert*-butyl group is expected to not only protecting of interaction between the backbones of these molecules, but also increasing the thermal stability and solubility.

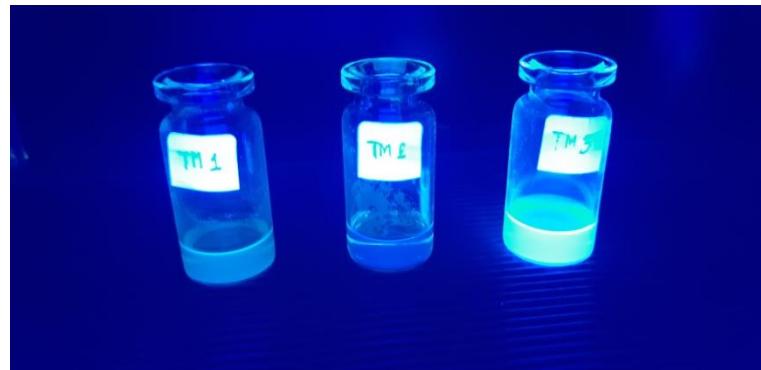
The smallest target molecule (TM1) with three thiophen moieties was synthesized via Suzuki cross coupling between 9-(7-bromo-9, 9-didodecyl-9H-fluoren-2-yl)-3, 6- di(thiophen-2-yl)-9H-carbazole and 2-thiophene boronic acid to give the target product in moderate yield. Ullmann coupling reaction of 2, 7-dibromo-9, 9-didodecyl-9H-fluorene and 3, 6-di(thiophen-2-yl)-9H-carbazole successfully gave the more steric molecule (TM2). Finally, Suzuki coupling reaction of the 9-(9-(7-(3,6-bis(5-bromothiophen-2-yl)-9H-carbazol-9-yl)-9, 9-didodecyl-9H-fluoren-2-yl)-6-(3, 6-di-*tert*-butyl-9H-carbazol-9-yl)-9H-carbazol-3-yl)-3, 6-di-*tert*-butyl-9H-carbazole with 2-naphthalene boronic acid can obtain the highest molecule (TM3) in acceptable yield.



**Fig. 6** The synthetic route of TM1, TM2, and TM3.

Identification of target molecular structures was accomplished using a combination technique of the proton and carbon-NMR, Mass spectrometry and FT-IR spectroscopy. The proton-NMR spectra in  $\text{CDCl}_3$  of TM1, TM2 and TM3 showed a characteristic singlet signal at chemical shift around 8.55 – 8.42 ppm of two protons of 4H and 5H in carbazole moiety, doublet of doublet signal at 7.18 – 7.16 (4H,  $J = 3.60, 4.80$  Hz) are assigned to H of thiophene ring, respectively. The rest of aromatic protons are overlap with each other which is difficult to identify. Moreover four of methylene protons (- $\text{CH}_2$ -) of dodecyl side chains were observed at chemical shift 2.14 – 2.00 indicate that this alkyl group connected to 9-position of fluorene moiety. The IR spectrum of these compound reveals C-S stretching of thiophene ring around  $695 - 692 \text{ cm}^{-1}$ , C=C stretching of aromatic ring at  $1611 - 1480 \text{ cm}^{-1}$ , C-H stretching of aromatic compound at  $3068 - 3008 \text{ cm}^{-1}$  and C-H stretching of aliphatic side chain at  $2926 - 2850 \text{ cm}^{-1}$ . The  $^{13}\text{C}$ -NMR in  $\text{CDCl}_3$  of the dyes showed a characteristic singlet at chemical shift around 153 – 152 ppm of carbon of 4C and 5C in carbazole moiety.

The chemical structures of these dyes were strongly supported by HRMS-ESI-TOF mass spectroscopy. The high molecular weight and steric structure of TM3 increases the melting point higher than that of TM1 and TM2. All of the target dyes are good soluble in common organic solvents because of the presence of *tert*-butyl and dodecyl groups in the molecules. Moreover, the TM3 emitted green wish color in Fig. 7 with more brightness than that of TM1 and TM2 excited by UV-light because of the naphthalene moiety connected to the thiophene part in the TM3. Finally, all of the target molecules can emit the light when expose to exciting source which concludes that they can be used as emitting material.



**Fig. 7** The fluorescence emitting light of TM1, TM2 and TM3 excited with UV-light source.

## Conclusion

This work demonstrated the design, synthesis and characterization of organic emitting materials, TM1, TM2 and TM3, with the structure of donor- $\pi$ -conjugated fluorene-carbazole core. The simple synthetic method and well known reactions were performed to complete the synthesis of all intermediates and the target molecules. Common flash column chromatography was used to purify the products of each reaction. The three target molecules were identified by Nuclear magnetic resonance spectroscopy, Mass spectrometry and FT-IR spectroscopy techniques. This work provided a simple method for synthesis of carbazole-fluorene core material. The physical and optical properties including performance of the OLEDs of these materials will be tested and reported in the near future.

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## References

- [1] H.W. Bae, G.W. Kim, R. Lampande, J.H. Park, I.J. Ko H.J, Yu, C.Y. Lee, J.H. Kwon, Efficiency enhancement in fluorescent deep-blue OLEDs by boosting singlet exiton generation through triplet fusion and charge recombination rate, *Org. Electron.* 70 (2019) 1 – 6.
- [2] M. Jung, J. Lee, H. Jung, S. Kang, A. Wakamiya, J. Park, Highly Efficient pyrene blue emitters for OLEDs based on substitution position effect, *Dyes Pigm.* 158 (2018) 42 – 49.
- [3] P. Wang, S. Fan, J. Liang, L. Ying, J. You, S. Wang, X. Li, Carbazole-diphenylimidazole based bipolar material and its application in blue, green and red single layer OLEDs by solution processing, *Dyes Pigm.* 142 (2017) 175 – 182.
- [4] B.E. Koene, D.E. Loy, M.E Thompson, Asymmetric Triaryldiamines as Thermally Stable Hole Transporting Layer for Organic Light-Emitting Devices, *Chem. Mater.* 10(8) (1998) 2235 – 2250.

- [5] C.Y. Chuang, P.I. Shih, C.H. Chien, F.I. Wu, C.F. Shu, Bright-White Light-Emitting Devices Based on a Single Polymer Exhibiting Simultaneous Blue, Green, and Red Emissions, *Macromolecules*. 40(2) (2006) 247 – 252.
- [6] Y. Jia, Y. Zhang, S. Fan, X. Zhaq, H. Liu, X. Dong, S. Wang, X. Li, Achieving non-doped deep-blue OLEDs by applying bipolar imidazole derivatives, *Org. Electron.* 69 (2019) 289 – 296.
- [7] C.M. Hart, C.J. Drucy, C.M.J. Mutsaers, M. Matter, D.M. de Leeuw, Low-cost all polymer integrated circuits, *Appl. Phys. Lett.* 73(1) (1998) 108 – 116.
- [8] R.D. Hreha, C.P. George, A. Haldi, B. Domercq, M. Malagoli, S. Barlow, J.L. Bredas, S.R. Marder, 2, 7-bis(diaryl amino)-9, 9-dimethylfluorenes as hole transport materials for organic light-emitting diodes, *Adv. Funct. Mater.* 13(12) (2003) 967 – 973.
- [9] N. Cocherel, C. Poriel, L. Vignau, J.F. Bergamini, J.R. Berthelot, DiSpiroXanthene-IndenoFluorene: A New Blue Emitter for Nondoped Organic Light Emitting Diode Applications, *Org. Lett.* 12(3) (2009) 452 – 455.
- [10] V. Promarak, M. Ichikawa, T. Sudyoadsuk, S. Saengsuwun, S. Jungsuttiwong, T. Keawin, Thermally and electrochemically stable amorphous hole-transporting materials based on carbazole dendrimers for electroluminescent devices, *Thin Solid Films.* 516(10) (2008) 2881 – 2888.
- [11] S.M. Bonesi, M.A. Ponce, S.E. Balsells, A study of substituent effect on <sup>1</sup>H and <sup>13</sup>C NMR spectra of mono, di and poly substituted carbazoles, *J. Heterocycl. Chem.* 41(2) (2005). 858 – 867.
- [12] K.T. Wong, Y.Y. Chien, R.T. Chen, C.F. Wang, Y.T. Lin, C.C. Wu, Synthesis and properties of 9, 9 diarylfluorene based triaryldiamines. *Org. Lett.* 3(15) (2001) 2285 – 2288.
- [13] F. Liu, C. Tang, Q.Q. Chen, S.Z. Li, H-B. Wuc, L.H. Xie, B. Peng, W. Wei, Y. Cao, W. Huang, Pyrene functioned diarylfluorenes as efficient solution processable light emitting molecular glass, *Org. Electron.* 10(2) (2009) 256 – 265.
- [14] V. Promarak, A. Punkvuong, T. Sudyoadsuk, S. Jungsuttiwong, S. Saengsuwun, T. Keawin, K. Sirithip, Synthesis and Characterization of *N*-carbazole end-capped oligofluorene-thiophenes, *Tetrahedron.* 63(36) (2007) 8881 – 8890.
- [15] P. Zassowskia, P. Ledwon, A. Kurowska, A.P. Hermana, M. Lapkowskia, V. Cherpak, Z. Hotra, P. Turyk, K. Ivaniuk, P. Stakhira, G. Sych, D. Volyniuk, J.V. Grazuleviciuse, 1, 3, 5-Triazine and carbazole derivatives for OLED applications, *Dyes Pigm.* 149 (2018) 804 – 811.
- [16] B. Braveenth, H.W. Bae, I.J. Ko, W. Qiong, Q.P.B. Nguyen, P.G.S. Jayashantha, J.H. Kwon, K.Y. Chai, Thermally stable efficient hole transporting materials based on carbazole and triphenylamine core for red phosphorescent OLEDs, *Org. Electron.* 51 (2017) 463 – 470.
- [17] H. Tik, K.L. Lee, K.L. Tong, S.K. So, M. Louis, Synthesis and electroluminescence of thiophene-based bipolar small molecules with different arylamine moieties, *Synth. Met.* 155(1) (2005) 116 – 124.
- [18] P. Moonsin, Synthesis and Characterization of Novel di-Acceptors Carbazole Derivatives for Application in Dye Sensitized Solar Cells, *J. Mater. Sci. Appl. Energy.* 7(2) (2018) 271 – 281.