JMSAE
Journal of Materials Science and Applied Energy
Journal home page: jmsae.snru.ac.th

Synthesis and Characterization of Novel Fluorene Emitting Materials for Application to Organic Light Emitting Diodes

Minta Kotmit[a], Preecha Moonsin[b], Kanokkorn Sirithip[c], Tanud Tanachatchairatana[b, *]

[a]*Program of Science Education, Faculty of Science, Ubon Ratchathani Rajabhat University,*
Ubon Ratchathani, 34000 Thailand
[b]*Program of Chemistry, Faculty of Science, Ubon Ratchathani Rajabhat University,*
Ubon Ratchathani, 34000 Thailand
[c]*Department of Science and Technology, Faculty of Liberial Arts and Science, Roi Et Rajabhat University,*
Roi Et, 45120 Thailand

*Corresponding Author: tanud2000@hotmail.com

Received 2 April 2020; **Revised** 12 May 2020; **Accepted** 28 December 2020; **Available online:** 1 January 2021

Abstract

In order to study the synthesis and characterization of two novel fluorene emitting materials for application to organic light emitting diodes, the 3, 3", 6, 6"-tetra-tert-butyl-9'-(7-(3, 6-di-tert-butyl-9H-carbazol-9-yl)-9, 9-didodecyl-9H-fluoren-2-yl)-9'H-9, 3', 6', 9"-tercarbazole (TM1) and 9', 9""-(9, 9-didodecyl-9H-fluorene-2,7-diyl)bis(3, 3", 6, 6"-tetra-tert-butyl-9'H-9, 3', 6', 9"-tercarbazole) (TM2) have been constructed using well-known Ullmann coupling reaction. Nuclear Magnetic resonance spectroscopy, Mass spectrometry and FT-IR spectroscopy were used to confirm the structures of the target molecules. The carbazole-fluorene dual core of the resulting material is beneficial for their morphology, conjugation length and solubility. The physical and optical properties of them will be compared. These molecules will be used as emitting materials in organic light emitting diodes.

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

© 2021 Center of Excellence on Alternative Energy reserved

Introduction

The organic light emitting diodes technology was introduced into a commercial since 1987 [1]. This technology has got a great interest in the use of monitors, light sources and mobile devices [2, 3]. Opportunities for the technological development of fluorescent materials are still present. Essentially, A red, green and blue color OLED was needed for the development of a complete color screen. Adopting OLEDs are used in fluorescent materials. The materials to withstand high thermal and morphological stability can be used to produce OLED that is resistant to high heat and increases device service lifetime [4]. Materials that change the state of Tg and tend to crystallize well are inappropriate for OLEDs because they will form grain boundaries which transporting limited electrical capacity and shorten the OLEDs lifetime [5].

Over the past decades, has been interested in developing π-organic conjugated molecules for use as a phosphor. Many of the fluorescent organic compounds that have been studied are fluorescent materials in OLED, to increase the efficiency of the device through the adjustment of conjugation, morphology and charge motion [6]. Despite this progress, the fluorescent organic compounds used in OLED are affected by the concentration quenching effect in solid state and the movement of unbalanced carriers which leads to the low quantum state of the device [7]. Therefore, a new material with a large nonplanar structure is loaded to prevent molecular filling and high hole-transporting capabilities to obtain highly efficient OLEDs. A large number of stable amorphous molecules have been reported such as diarylfluorene-substituted triarylamine [8], carbazole derivatives [9], and many chromophores. They must have thermal stability and morphology for film-forming under vacuum conditions. For processing equipment in the form of polymers must be a smooth film with no small holes. However, light-emitting polymer materials cannot be purified by conventional methods such as chromatography columns and repeated crystallization [10] . Recently, a new category of low molecular weight electroluminescent materials tends to be light-emitting material. They have substances that have a given chemical structure, high purity, and efficiency. In addition, this is also cheap. However, the process of synthesis and purification is still quite difficult. Another alternative to the development is the combination of small molecules and efficient polymers for easy synthesis, purification, and good film-forming capabilities by coatings. Fluorine derivatives are another molecule of interest to solve problems [11]. In addition, structural changes are needed to achieve a higher Tg value in order to increase heat and morphological stability for actual use [12]. In this article, we report a new methodology to solve the light-emitting problems of amorphous material molecules. To achieve the fluorene-carbazole building block was employed [13]. Fluorene moiety is very rigid and its derivatives usually show low solubility and high tendency to crystallize. In order to solve these problems, two long chain hydrocarbons of dodecyl groups were connected to the fluorine moiety core at the position of C9 [14]. Carbazole groups were linked to the C2 and C7 position of the fluorene unit to enhance not only the conjugation length but also give rise to the emission color and thermal stability [15]. Among the various heterocyclic compounds, carbazole has been widely accepted as an effective electron donor system. The presence of a pyrrole ring in the system increases the carbazole electron enrichment system. It possesses good thermal properties and excellent optical properties. Moreover, a stable and non-destructive substance by acids or bases, showing very good transport of a wide energy gap as well as photoconductivity. Further, the carbazole core can be easily functionalized at different positions with a variety of functional groups, permitting an improved solubility and fine-tuning of the electronic as well as optical properties [16]. Carbazole derivatives are well known for their intense blue fluorescence and are used in OLEDs [17]. For the effective operation of the equipment, the HOMO and LUMO of the supply must be suitable for the HOMO of the anode transport layer and the LUMO of the cathode transport layer, respectively. Carbazole derivatives must respond under the conditions of the energy level to get blue light in the OLED. Carbazole's blue photoluminescence is not affected by alkyl substitution at positions 3 and 6 [18]. The addition of alkyl groups in the carbazole will increase the solubility in organic solvents, which is very useful in forming thin films by rotating coatings. 3,6-Dialkylcarbazole is therefore chosen as the frame structure to create new materials [19]. Fluorene moiety was used as the building block of small organic molecules for various optoelectronic devices applications [20]. Results obtained from fluorene derivatives are formed from the combination of π -conjugation meaning better absorption band. It is also possible to predict the solubility and production capacity caused by the combination of two alkyl chains that have fluorine better. The formation of fluorene-carbazole has many desired characteristics. These light-emitting molecules are of great interest in their application in the electroluminescent (EL) device. The synthesis of fluorene and carbazole derivatives and the photoluminescent properties of this substance are quite limited. From the reporting of some optical and electrical properties of π-conjugated molecules especially the photoluminescent properties, therefore very promising. It is a great interest in the preparation of these derivatives. It was reported that Suzuki and Ullmann's C-C and C-N bonding reactions are an effective method for the synthesis of new groups of fluorene-producing substances. We also present the optical and thermal properties of these substances which indicate they have the potential for OLED devices.

In this study, we designed and synthesized two new fluorescent organic compounds (TM1 and TM2) containing carbazole and fluorene building blocks. The introduction of the bulky and nonplanar 3, 6-dialkylcarbazole moiety has been shown the efficiency of preventing molecular filling, improving the glass-transition temperature (Tg) and increasing the transportation hole properties. The combination of the functional property multiplication of these three moieties is rarely found in the literature reviews and is effective in the synthesis of a new type of fluorescent emitter with good properties and has a highly stable state emission efficiency. The process of synthesis and purification of the target molecules is easy. Including able to be used to solve problems in optoelectronic applications.

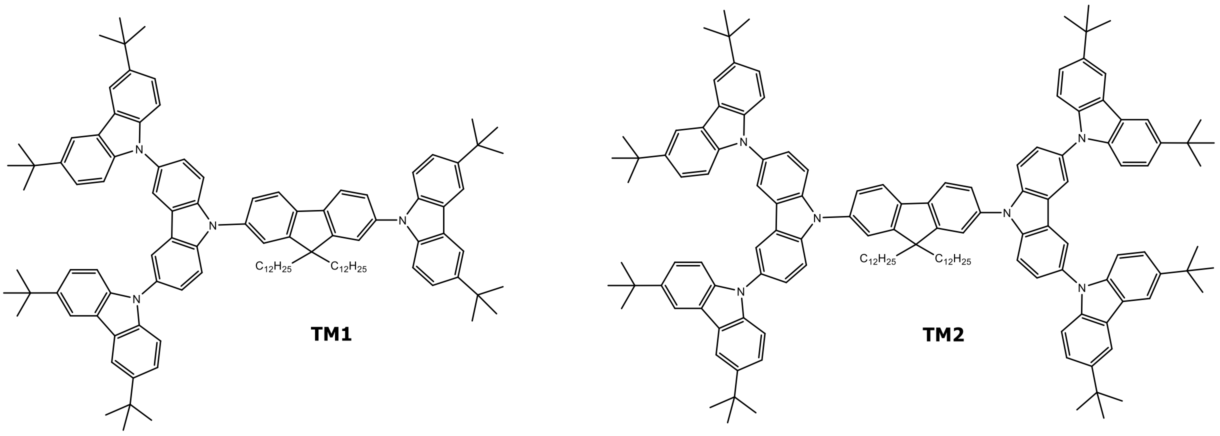

Fig. 1 Molecular structure of the target molecules.

Materials and Methods

Proton and carbon nuclear magnetic resonance spectra were performed on Brüker AVANCE (300 MHz) spectrometer and were fully decoupled. A Bruker Autoflex MALDI-TOF mass spectrometer was used to record of High-resolution matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectra. The IR spectra were performed on a Perkin-Elmer FT-IR spectroscopy. The absorption peaks are quoted in wavenumber (cm^{-1}). The melting points of the compounds were determinate using an Electrothermal MEL-TEMP apparatus. All reagents and solvents are purchased from Aldrich, Acros, Fluka, or Thai parcels and received unless otherwise stated. Thin layer chromatography (TLC) was performed with aluminum plates coated with silica gel 60 F_{254} and silica gel mesh 60 Å for column chromatography was carried from Merck. The solvent mixtures are used and the portions are given by volume. The key intermediated of 3, 6-di-tert-butyl-9H-carbazole, 9-(9-(7-bromo-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-tert-butyl-9-(6-(3, 6-di-tert-butyl-9H-carbazol-9-yl)-9H-carbazol-3-yl)-9H-carbazole and 2, 7-

dibromo-9, 9-didodecyl-9H-fluorene were synthesized following to the report of P. Moonsin et al [21].

Synthesis and Characterization

TM1

To a solution mixture of 9-(9-(7-bromo-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 (0.53 g, 0.38 mmol) in 3, 6-di-tert-butyl-9H-carbazole (0.11 g, 0.38 mmol), copper iodide (0.15 g, 0.38 mmol), potassium phosphate (0.24 g, 1.15 mmol) and toluene (50 ml) was stirred under nitrogen gas, and then added *trans*-1, 2-diaminocyclohexane (0.23 g, 2.02 mmol). The reaction mixture was refluxed under N_2 atmosphere for 24 hrs. After cooling to room temperature, the reaction mixture was filtered with silica gel and wash by dichloromethane (3 × 50 ml). The combined organic layer was washed with water (50 ml), brine solution (50 ml), dried over sodium sulfate anhydrous, filtered and the solvent was stripped off under vacuum. The crude product was purified by column chromatography eluting with 10% dichloromethane: hexane to afford (TM1) as white solid (0.31 g, 53 %).

Melting point: 229 – 232 ºC.

FT-IR (KBr): ν_{max} = 3016.65, 2959.41, 2926.49, 2854.94, 2252.47, 17713.06, 1609.93, 1582.74, 1479.70, 1363.79, 1324.02, 1295.10, 1262.18, 1219.25, 1034.65, 904.42, 812.83, 770.00, 726.97, 649.69, 613.92, 567.09, 505.16, 470.81, and 424.01 cm^{-1}.

^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.30 (2H, *s*), 8.22 (2H, *s*), 8.20 (4H, *s*), 8.10, 8.04 (2H, *dd*, *J* = 8.10, 18 Hz), 7.79 (2H, *d*, *J* = 9.30 Hz), 7.73 (2H, *d*, *J* = 8.40 Hz), 7.67 (4H, *d*, *J* = 8.10 Hz), 7.56 – 7.48 (6H, *m*), 7.40 (4H, *d*, *J* = 8.40 Hz), 7.28 (2H, *s*), 2.0 (4H, *d*, *J* = 1.20 Hz), 1.53 – 1.49 (54H, *m*), 1.32 – 1.18 (40H, *m*), and 0.84 (6H, *t*, *J* = 3.90 Hz) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ 153.25, 152.82, 142.98, 142.59, 140.55, 140.38, 140.19,139.30, 138.87, 137.53, 136.06, 130.94, 127.81, 126.03, 125.66,124.03, 123.66, 123.59, 123.49, 123.17, 121.84, 121.53, 121.25, 121.14, 119.42, 116.40, 116.25, 113.97, 111.13, 109.22, 109.12, 77.46, 77.07, 76.61, 55.86, 40.33, 34.79, 34.75, 32.07, 31.86, 30.92, 30.08, 29.65, 29.60, 29.48, 29.29, 24.25, 22.64, and 14.09 ppm.

HRMS-ESl-TOF calcd for $C_{109}H_{134}N_4$: $m\ z^{-1}$ 1499.0609 found 1499.1145.

TM2

Ullmann coupling reaction was used to obtained the TM2. To a 100 ml of round bottom flash 2, 7-dibromo-9, 9-didodecyl-9H-fluorene (1.21 g, 1.82 mmol), and 3, 6-di-tert-butyl-9-(6-(3, 6-di-tert-butyl-9H-carbazol-9-yl)-9H-carbazol-3-yl)-9H-carbazole (1.45 g, 2.02 mmol), copper iodide (0.38 g, 2.02 mmol), potassium phosphate (1.28 g, 6.06 mmol) in toluene (50 ml) as solvent were mixed togather. And then *trans*-1, 2-diaminocyclohexane (0.23 g, 2.02 mmol) was added. The reaction mixture was refluxed under N_2 atmosphere for 24 hrs. After cooling to room temperature, the reaction mixture was filtered with silica gel and wash by dichloromethane (50 ml × 3). The combined organic layer was washed with water (50 ml), alkaline solution (50 ml), dried over sodium sulfate anhydrous, filtered and the solvent was stripped off under vacuum. The crude product was purified by column chromatography eluting with 20% dichloromethane:hexane to afford (TM2) as white solid (2.01 g, 46 %).

Melting point: 280 – 282 ºC.

FT-IR (KBr): ν_{max} = 3019.51, 2961.04, 2927.92, 2856.37, 1489.72, 1479.70, 1364.09, 1324.02, 1295.10, 1262.18, 1215.06, 1034.65, 909.01, 881.52, 812.83, 752.73, 668.30, 613.92, 568.12, 505.16, 471.01, and 426.45 cm^{-1}.

^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.31 (4H, *s*), 8.19 (8H, *s*), 7.82 (4H, *s*), 7.74 (4H, *d*, *J* = 8.70 Hz), 7.67 (4H, *d*, *J* = 8.70 Hz), 7.49 (8H, *d*, *J* = 8.70 Hz), 7.39 (8H, *d*, *J* = 8.40 Hz), 7.28 (4H, *s*), 2.19 (4H, *m*), 1.49 (54H, *m*), 1.28 – 1.12 (40H, *m*), and 0.80 (6H, *d*, *J* = 6.30 Hz) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ 153.31, 142.61, 140.49, 140.17, 140.01, 136.47, 131.02, 126.05, 124.08, 123.58, 123.17, 121.92, 121.53, 119.44, 116.25, 111.10, 109.09, 77.44, 77.01, 76.59, 40.34, 34.74, 32.05, 31.79, 30.91, 30.08, 29.58, 29.50, 29.22, 24.34, 22.58, and 14.04 ppm.

HRMS-ESl-TOF calcd for $C_{141}H_{164}N_6$: *m z*$^{-1}$ 1941.3071 found 1941.4657.

Results and Discussion

The two emitting materials (TM1 and TM2) with carbazole and fluorene building block were developed. High absorption and good thermal properties of carbazole were excellent for the building block moiety part. Fluorene core was introduced to extend the π-conjugated system and to enhance thermal stability.

The TM1 and TM2 were successfully synthesized via the facile synthetic route presented in Fig. 2. The steric long chain hydrocarbon moieties at the C-9 position of fluorene ring and the bulky *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 in organic solvent. The TM1 with less carbazole moiety was synthesized via Ullmann coupling reaction of 9-(9-(7-bromo-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 and 3, 6-di-tert-butyl-9H-carbazole. Ullmann coupling reaction of 2, 7-dibromo-9, 9-didodecyl-9H-fluorene and 3, 6-di-tert-butyl-9-(6-(3,6-di-tert-butyl-9H-carbazol-9-yl)-9H-carbazol-3-yl)-9H-carbazole to give TM2 with more carbazole part in acceptable yield.

A combination analysis of the ^{1}H-NMR, ^{13}C-NMR, Mass spectrometry and FT-IR spectroscopy spectra pattern were used to identify their molecular structures. The ^{1}H-NMR in $CDCl_3$ of TM1 (Fig. 3) and TM2 (Fig. 4) showed a characteristic singlet signal at chemical shift around 8.30 in TM1 and 8.31 ppm in TM2 of two protons of 4H and 5H in carbazole moiety, singlet signal at chemical shift around 8.22 in TM1 and 8.19 ppm in TM2 of two protons of $4H^b$ and $5H^b$ of the other carbazole unit (Fig. 2). The rest of aromatic protons are overlap with each other which is difficult to identify. Moreover four of methylene protons ($-CH_2-$) of dodecyl side chains were observed at chemical shift 2.19 and 2.00 indicate that this alkyl group connected to 9-position of fluorene moiety. The IR spectrum of these compound reveals C-H stretching of aromatic ring around 3019-3016 cm^{-1}, C=C stretching of aromatic ring at 1609 – 1479 cm^{-1}, and C-H stretching of aliphatic side chain at 2961 – 2854 cm^{-1}. The ^{13}C-NMR in $CDCl_3$ of the dyes showed a characteristic singlet at chemical shift around 153 and 152 ppm of C4 and C5 of carbazole group. The HRMS-ESI-TOF spectrum of TM1 and TM2 showed the molecular ion peak at m z^{-1}

1499.0609, and 1941.3071, respectively. Both of them are good soluble in a wide variety of organic solvents including most chlorinated solvents because of the presence of *tert*-butyl and dodecyl groups in the donor moieties. Thermal properties of the derivatives were investigated by Electrothermal MEL-TEMP apparatus. Melting point for TM1 was observed at 229 – 232 °C while TM2 exhibited the melting points of 280 – 282 °C. Both dyes showed blue fluorescence under shot wavelength light (Fig. 5) and high melting point which can be used for organic materials. Moreover, the more carbazole moieties of a structurally symmetrical TM2 exhibited higher melting point temperature than asymmetrical structure TM1.

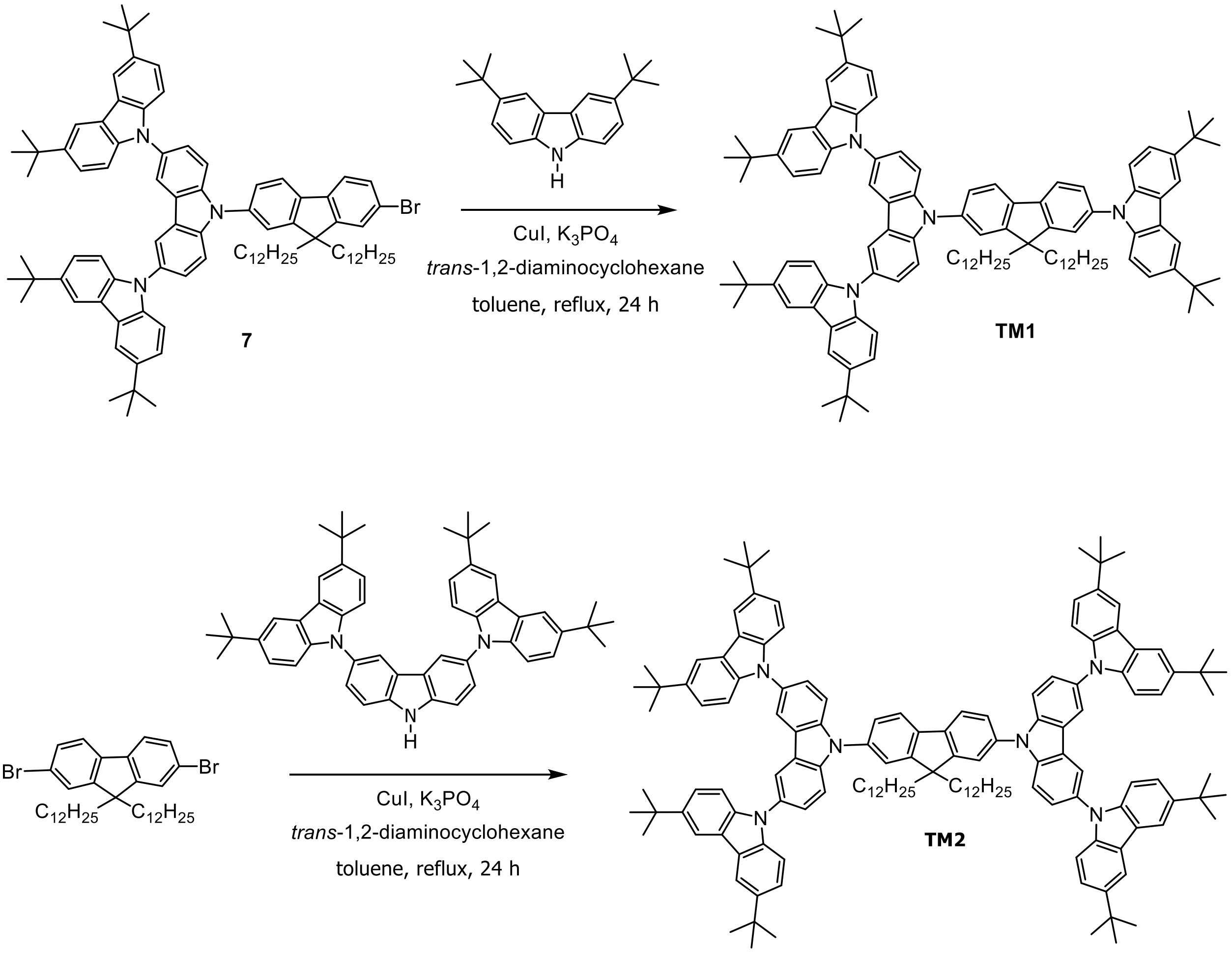

Fig. 2 The synthetic route of TM1 and TM2.

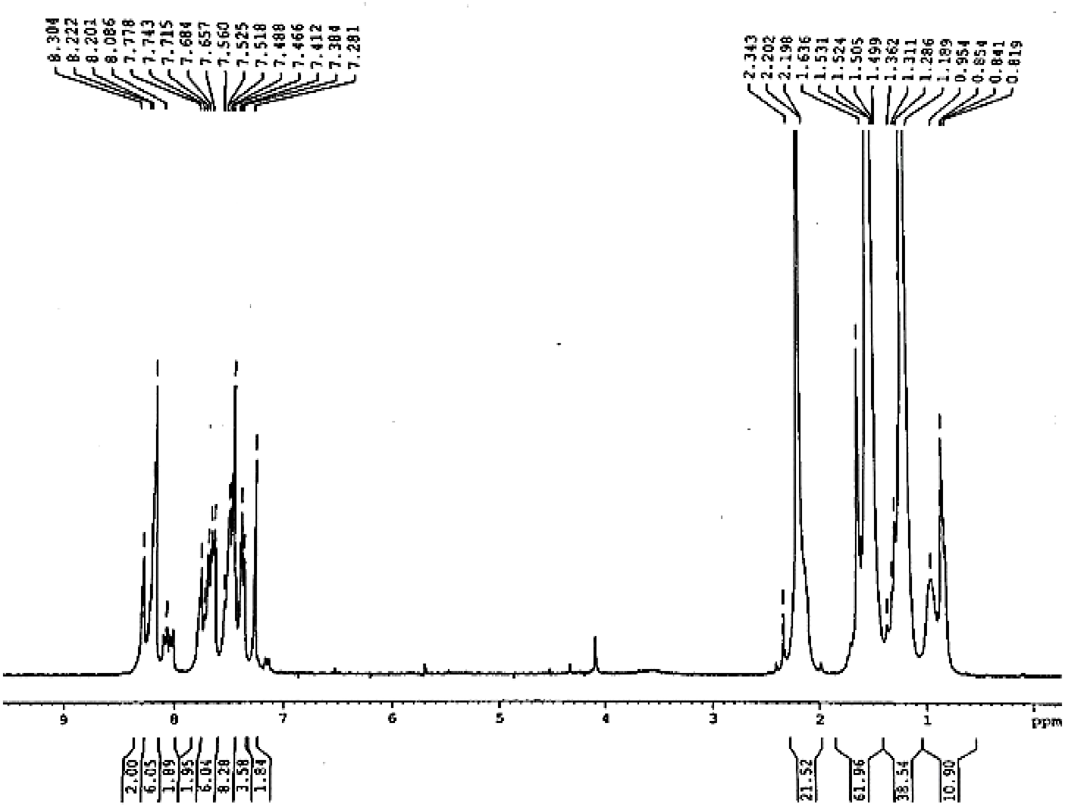

Fig. 3 ^{1}H-NMR spectrum of TM1.

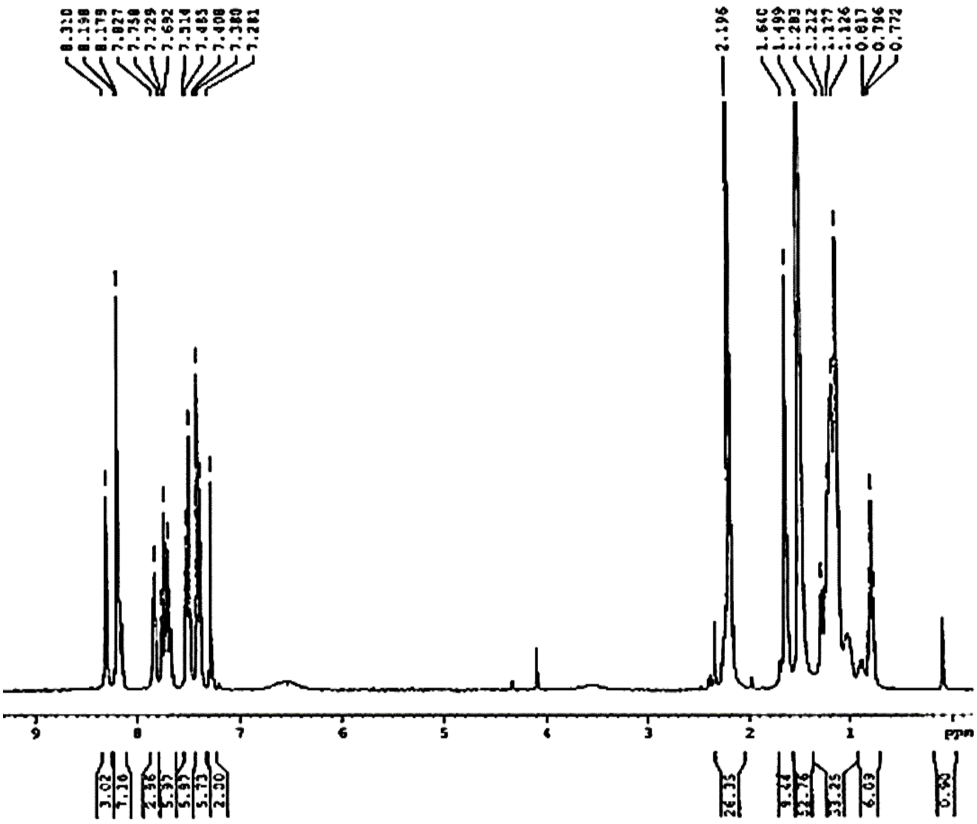

Fig. 4 ^{1}H-NMR spectrum of TM2.

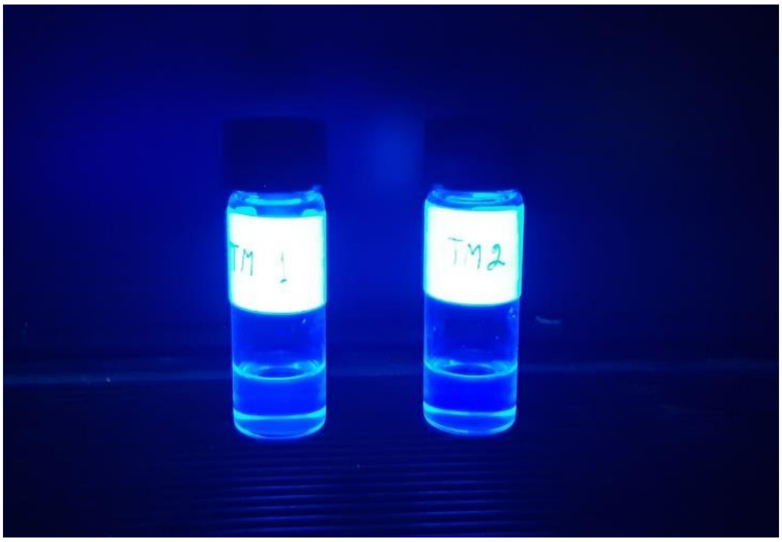

Fig. 5 Blue Fluorescence under Shot Wavelength Light of TM1 and TM2.

Conclusion

This work demonstrated the synthesis and characterization of two symmetrical and asymmetrical emitting materials for application to organic light emitting diodes. The symmetrical TM1 and asymmetrical TM2 have been synthesized by Ullmann coupling reaction and characterized by ^{1}H-NMR, ^{13}C-NMR, Mass spectrometry and FT-IR spectroscopy. We thing that the carbazole-fluorene dual core of the resulting materials are beneficial for their morphology, conjugation length and solubility. The optical and physical properties of them will be determined including the efficiency of the fabricated devices will be compared in the next step. Finally, these molecules will be used as emitting blue ray materials in organic light emitting diodes in the near future.

Acknowledgement

We would like to thank Program of Chemistry Faculty of Science Ubon Ratchathani Rajabhat University for financial support.

References

[1] C.W. Tang, S.A. Vanslyke, Organic electroluminescent diodes, Appl. Phys. Lett. 51(12) (1987) 913 – 915.

[2] 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.

[3] Y. Choi, R. Ha, H. Cha, Fully Automated OLED Display Power Modeling for Mobile Devices, Pervasive Mob. Comput. (2018) 41 – 55.

[4] 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 (1998) 108 – 116.

[5] R.D. Hreha, C.P. George, A. Haldi, B. Domercq, M. Malagoli, S. Barlow, J.L. Bredas, S.R. Marder, 2,7-bis(diarylamino)-9,9-dimethylfluorenes as hole transport materials for organic light-emitting diodes, Adv. Funct. Mater 13(12) (2003) 967 – 973.

[6] 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.

[7] 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.

[8] S.M. Bonesi, M.A. Ponce, S.E. Balsells, A study of substituent effect on ^{1}H and ^{13}C NMR spectra of mono, di and poly substituted carbazoles, Heterocyclic Chem. 41(2) (2005) 858 – 867.

[9] 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.

[10] J. Caia, L. Maa, H. Niua, P. Zhaob, Y. Liana, W. Wangc, Near infrared electrochromic naphthalene-based polyimidescontaining triarylamine: Synthesis and electrochemical properties, Electrochim. Acta. 112 (2013) 59 – 67.

[11] W.-Y. Lai, R. Xia, Q.-Y. He, PA. Levermore, W. Huang, DDC. Bradley DDC, Enhanced Solid-state luminescence and low-threshold lasing from starburst macromolecular materials, Adv. Mater. 21(3) (2009) 355 – 360.

[12] Y. Zou, J. Zou, T. Ye, H. Li, C. Yang, H. Wu, Unexpected propeller-like hexakis (fluoren-2-yl) benzene cores for six-arm star-shaped oligofluorenes: highly efficient deep-blue fluorescent emitters and good hole-transporting materials, Adv. Funct. Mater. 23(14) (2013) 1781 – 1788.

[13] X. Liang, K. Wang, R. Zhang, K. Li, X. Lu, K. Guo, H. Wang, Y. Miao, H. Xu, Z. Wang, Tetra-carbazole substituted spiro[fluorene-9, 90-xanthene]-based hole-transporting materials with high thermal stability and mobility for efficient OLEDs, Dyes Pigm. 139 (2017) 764 – 771.

[14] 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.

[15] V. Promarak, A. Punkvuang, 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.

[16] Q. Dong, H. Lian, Z. Gao, Z. Guo, N. Xiang, Z. Zhong, H. Guo, J. Huang, W.-Y. Wongce, Novel spirofluorene/indole/carbazole-based hole-transport materials with high triplet energy for efficient green phosphorescent organic light-emitting diodes, Dyes Pigm. 137 (2017) 84 – 90.

[17] Q. Dong, F. Tai, H. Lian, Z. Chen, M. Hu, J. Huang, Thermally stable bipolar host materials for high efficiency phosphorescent green and blue organic light-emitting diodes, Dyes Pigm. 143 (2017) 470 – 478.

[18] A. Venkateswararao, K.-R.-J. Thomas, C.-P. Lee, C.-T. Li, K.-C. Ho, Organic dyes containing carbazole as donor and π-linker: optical, electrochemical, and photovoltaic properties, ACS Appl. Mater. Interfaces. 6(4) (2014) 2528 – 2539.

[19] S.S. Soni, K.B. Fadadu, J.V. Vaghasiya, B.G. Solanki, K.K. Sonigara, A. Singh, Improved molecular architecture of D–π–A carbazole dyes: 9% PCE with a cobalt redox shuttle in dye sensitized solar cells, J. Mater. Chem. A. 3(43) (2015) 21664 – 21671.

[20] H. Tik, K.L. Lee, K.L. Tong, S.K. So, M. Louis, Synthesis and electroluminescence of thiophene-based bipolar small molecules with different aryl amine moieties, Synth. Met. 155(1) (2005) 116 – 124.

[21] 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.