SETSCI Conference Indexing System,
Volume 3 (2018), 760-763

ISAS 2018-Winter
2nd International Symposium on Innovative Approaches in Scientific Studies
November 30 – December 2, 2018, Samsun, Turkey

Synthesis, Characterization of The Novel Carbazole Core Structures and Investigations of Photodiode Properties

Müjdat Çağlar[1]*, Kamuran Görgün[2] and Merve Yandımoğlu[2]

[1]Department Physics, University of Eskisehir Technical, Eskisehir, Turkey
[2]Department of Chemistry, Faculty of Arts and Science, Eskişehir Osmangazi University, Eskisehir 26480, Turkey
*Corresponding author: mujdatcaglar@gmail.com
+Speaker: mujdatcaglar@gmail.com
Presentation/Paper Type: Oral

Abstract –Palladium-catalyzed Suzuki Miyaura cross coupling reactions (SM Coupling) are made using organoboronic acid and halides. 9-(4-anthracene-9-yl-phenyl)-9H-carbazole (III) was synthesized by using Ullman and Suzuki coupling reactions. Structural analysis of the 9-(4-anthracene-9-yl-phenyl)-9H-carbazole (III) compounds obtained by this method has been elucidated by ^{1}H-NMR. This compound was dissolved by chloroform and the borosilicate glass was coated with drop casting method. Transmittance measurement of this film was taken and optical band value was determined. The heterojunction structure (n-Si/III) was fabricated by using the obtained compounds. The electrical properties of the fabricated photodiode were investigated.

Keywords – *Carbazole, Suzuki-Miyaura Coupling, Ullman Coupling, photodiodes*

I. INTRODUCTION

Studies in recent years show that carbazole-based molecules have been grown rapidly and acquired increasing attention for optoelectronics. Carbazole derivatives are well-known electron rich systems using as hole-transporter and charge transporter materials in OLED devices because of their well thermal stability, high triplet energy, capability of glass formation properties [1-4]. These molecules demonstrated good performance as host materials of blue phosphorescent OLEDs [5,6]. Also carbazole unit can be handily modified by substitution at 9-position, thereby providing to increase the solubility and tune the photophysical properties of the molecule [7].

Since the invention of organic light-emitting diodes (OLEDs) devices by Tang and VanSlyke in 1987 [8], many new film-forming electroactive low molecular mass compounds have been synthesized due to the large potential applications of OLED devices such as flat-panel displays and flexible display technologies. These compounds are used as hole transport, electron transport, or emitting layers in OLEDs. In conjugated molecules, generally higher hole mobility is observed compared to the conjugated double bonded systems in which unconjugated groups are separated [9].

Anthracene derivatives have been extensively used as the blue host material in OLEDs due to their great optical properties, such as fluorescence emitters [10]. In addition, the fluorescent color of anthracene can be easily adjusted from blue to green as a result of binding symmetric or asymmetric molecule groups at the C-9 and C-10 positions [11].

In this study, 9-(4-anthracene-9-yl-phenyl)-9H-carbazole (III) was synthesized by using Ullman and Suzuki coupling reactions of novel carbazole derivative. The film was coated on n-Si and glass substrates using this material. The optical band band gap value found from optical transmittance measurements. The photodiode based on these small molecule semiconductor was fabricated and electrical properties of this device were investigated.

II. MATERIALS AND METHOD

All reagents were commercial quality or purified before using. The organic solvents used were HPLC grade or purified by a standard procedure. The chemical structure and synthetic route of the targeted material is shown in Figure 1.

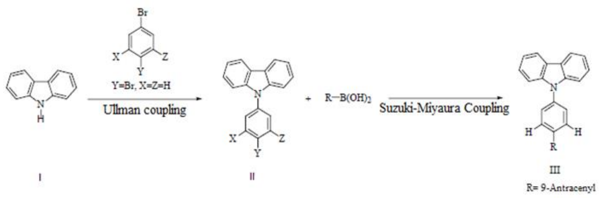

Fig 1. Synthetic rote of 9-(4-Antracen-9-yl-phenyl)-9H- carbazole III

2.1. Synthesis 9-(4-bromophenyl)-9H-carbazole (II)

1,4-dibromobenzene (5.3 g, 22.4 mmol), copper(I) iodide (285 mg, 1.5 mmol), 1,10-phenanthroline (135 mg, 0.75 mmol), K_2CO_3 (4.1 g, 29.9 mmol) were added into carbazole (2.5 g, 15.0 mmol) dissolved in 50 mL dry DMF inside a dual necked flask and then the reaction was refluxed for 24 h under nitrogen atmosphere. Then, this reaction mix reached to room temperature and solvent was removed under vacuum. Remaining residue was extracted by dichloromethane. The product was then obtained by column chromatography on silica gel with hexane as the eluent, to get white solid. Isolated yield (II) (3.4 g, 71%). ^{1}H NMR ($CDCl_3$, 500 MHz): 7.20–7.37 (m, 6H), 7.44 (d, 2H, *J*= 8.3 Hz), 7.69 (d, 2H, *J*= 8.3 Hz), 8.07 (d, 2H, *J*=7.6 Hz) (Fig. 2)

2.2. Synthesis 9-(4-anthracene-9-yl-phenyl)-9H-carbazole (III)

9-(4-bromophenyl)-9H-carbazole (0.2g, 1 eq) THF (15mL) was dissolved in the flask 9-anthracene boronic acid (0.2g, 1.2 eq), K_2CO_3 (2 M, 0.6 mL), tetrakis(triphenylphosphine) palladium 3 mol% was added into it. The mixture was placed magnetic stirrer operated at 70°C for 12h refluxed. After being cooled, the mixture was extracted with CH_2Cl_2, and the organic phase was washed with water, dried over Na_2SO_4 and filtered. Solvent was evaporated under a vacuum, followed by column chromatography over silica gel with a mixture of n-hegzan as eluent, resulted in the product 9-(4-anthracene-9-yl-phenyl)-9H-carbazole (III) as a white solid in 50% yield (0.130 g). ^{1}H NMR ($CDCl_3$, 500 MHz): 8,60 (1H, s), 8.05 (3H, d, *J*=9.01 Hz), 7.73 (3H, d, *J*=8.82 Hz), 7.71 (2H, d, *J*=8.53 Hz), 7.62 (1H, dd, *J*=8.89 Hz), 7.62 (1H, d, *J*=9.09 Hz), 7.46 (2H, t, *J*= 8.86 Hz), 7.45 (2H, dd, *J*=8.37), 7.44 (2H, d, *J*=8.86 Hz), 7.37 (2H, dd, *J*=6.34 Hz), 7.35 (2H, dd, *J*=6.525 Hz) (Fig. 3)

The 9-(4-anthracene-9-yl-phenyl)-9H-carbazole (III) was ultrasonically dispersed in chloroform for 2 h. The solutions were coated onto the surface of n-Si and borosilicate substrates using drop-casting method and n-Si/p-III heterojunction diode was made. In this structure, gold top contact and silver bottom contact were used. Gold was evaporated in VAKSIS PVD system and for silver bottom contact silver paint was used. ^{1}H NMR of the II and III were obtained on a BRUKER DPX FT NMR (500 MHz) and (125 MHz) spectrometers at 298 K (Germany). The transmittance measurement of the III was performed with SHIMADZU UV2450 UV-vis scanning spectrometer. The current–voltage (*I*–*V*) characteristics of the photodiodes were recorded by a semiconductor characterization system (KITHLEY 4200SCS) and a solar cell measurement system (FYTRONIX SOLAR CELL SYSTEM).

III. RESULTS

9-(4-bromophenyl)-9H-carbazole, 9-anthracene boronic acid, tetrakis(triphenylphosphine) palladium and K_2CO_3 were used and the targeted III was synthesized by using Suzuki-Miyaura coupling reaction method. Chemical structure was confirmed by ^{1}H NMR analysis method. In ^{1}H NMR (Figure 3) analysis of the targeted compound, totally 21 proton signals were marked as 8.60 singlet, 8.05 duplet, 7.73 duplet, 7.71 duplet, 7.62 duplet, 7.46 triplet, 7.45 duplets to duplets, 7.44 duplet, 7.37 duplets to duplets and 7.35 duplet signals.

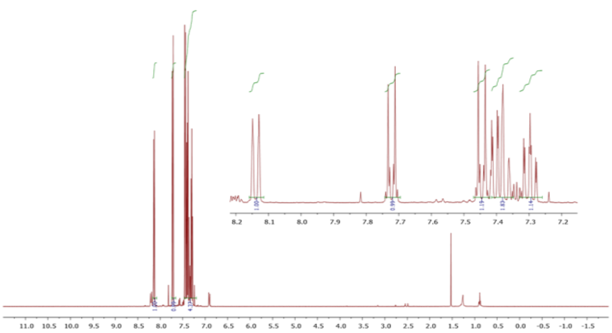

Fig. 2 ^{1}H NMR spectra of 9-(4-bromophenyl)-9H-carbazole (II)

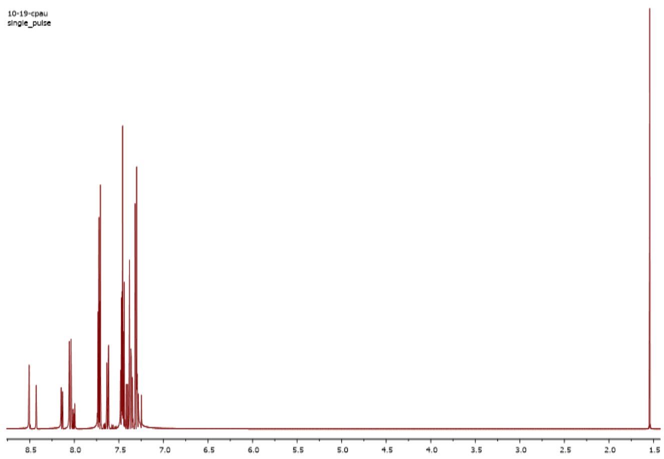

Fig. 3 ^{1}H NMR spectra of 9-(4-anthracene-9-yl-phenyl)-9H-carbazole (III)

The transmittance spectrum of the 9-(4-anthracene-9-yl-phenyl)-9H-carbazole (III) film was measured in the range of 300–600 nm, as shown in Fig. 4. The transmittance is over >74% in the visible region.

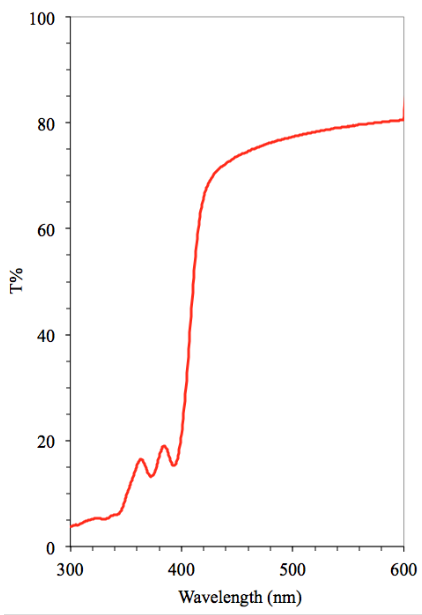

Fig. 4 Transmittance spectra of 9-(4-anthracene-9-yl-phenyl)-9H-carbazole (III)

The optical band gap value (E_g) is determined by the Tauc equation [12] using the of 9-(4-anthracene-9-yl-phenyl)-9H-carbazole (III) film's transmittance graph. A plot of $(\alpha h\nu)^2$ vs. photon energy graph is drawn for this and given in Fig. 5. The E_g value of the film was obtained from the intercept of $(\alpha h\nu)^2$ versus hν curve plotted and given in Fig. 5.

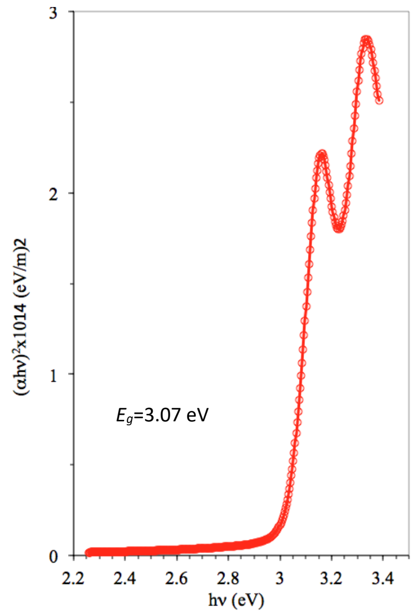

Fig. 5 $(\alpha h\nu)^2$ vs. hν graph of 9-(4-anthracene-9-yl-phenyl)-9H-carbazole (III)

The current-voltage characteristics of n-Si/p-III photodiode carried out under dark and various illumination intensities are shown in Fig. 6. As seen in Fig.6, the current of the diodes in reverse bias region increased with light illumination intensity, whereas the forward current did not change with the illumination. This indicates that the separation of electron-hole pairs in reverse bias region is longer than that of forward bias region. Therefore, the diodes exhibited the conventional photoconducting mechanism. Under dark condition, the diodes exhibited the rectifying behaviour.

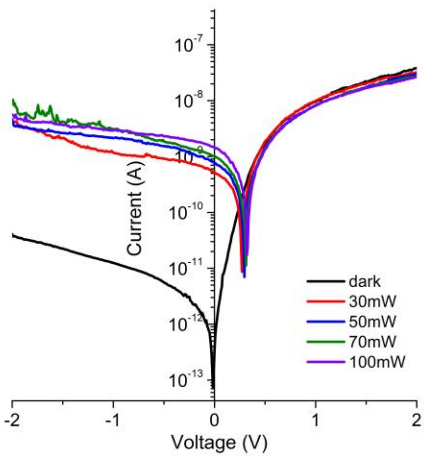

Fig. 6 Current-Voltage graph of n-Si/III photodiode

In order to analyse the photoconducting mechanism, we used the relation, $I_{PH}=\alpha P^m$, where, α is a constant, I_{PH} is the photocurrent, *m* is an exponent and *P* is the illumination intensity. The log($\square_{PH}$)–log*P* graph is drawn to find the m value. The plots of log ($\square_{PH}$) versus log(□) curves are shown in Figure 7. The obtained □ value of the photodiode was found to be 0.53.

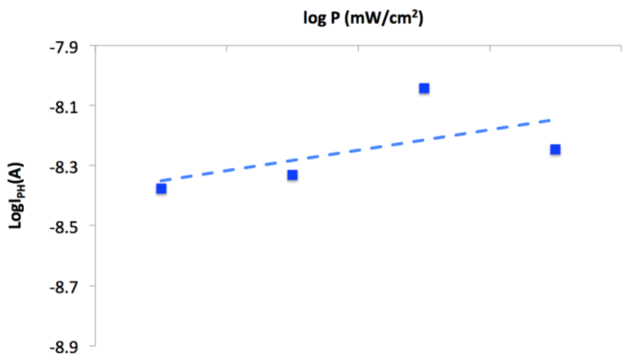

Fig. 7. Photocurrent versus illumination intensity plot of n-Si/III photodiode

IV. CONCLUSION

9-(4-anthracene-9-yl-phenyl)-9H-carbazole (III) was synthesized by using Ullman and Suzuki coupling reactions. The structural analysis of this compound has been elucidated by ^{1}H-NMR and it confirms this structure. This compound was dissolved by chloroform and the borosilicate glass was coated with drop casting method. By using transmittance measurement of the film, optical band value was determined as 3.07 eV. The synthesized 9-(4-anthracene-9-yl-phenyl)-9H-carbazole (III) was used to fabricate heterojunction structure (n-Si/p-III). The obtained device exhibited photodiode characteristic. Further investigations are continuing to improve the photodiode performance of obtained device.

ACKNOWLEDGMENT

This work was supported by Eskişehir Osmangazi University Commission of Research Project under Grant no. 2016-1321.

REFERENCES

[1] S. Kotowicz, M. Siwy, M. Filapek, J. G. Malecki, K. Smolarek, J. Grzelak, S. Mackowski, A. Slodek, and E. Schab-Balcerzak, "New donor-acceptor-donor molecules based on quinoline acceptor unit with Schiff base bridge: synthesis and characterization," J. Lumin., vol. 183, pp. 458-469, Mar. 2017.

[2] I. Bhattacharjee, N. Acharya, H. Bhatia, and D. Ray, "Dual Emission through Thermally Activated Delayed Fluorescence and Room-Temperature Phosphorescence, and Their Thermal Enhancement via Solid-State Structural Change in a Carbazole-Quinoline Conjugate," J. Phys. Chem. Lett., vol. 9, pp. 2733–2738, May. 2018.

[3] J. Li, and A. C. Grimsdale, "Carbazole-based polymers for organic photovoltaic devices," Chem. Soc. Rev., vol. 39, pp. 2399-2410, Feb. 2010.

[4] J. Huang, J.-H. Su, X. Li, M.-K. Lam, K.-M. Fung, H.-H. Fan, K.-W. Cheah, C. H. Chen, and H. Tian, "Bipolar anthracene derivatives containing hole- and electron-transporting moieties for highly efficient blue electroluminescence devices," J. Mater. Chem., vol. 21, pp. 2957-2964, Jan. 2011.

[5] E. Stanislovaityte, J. Simokaitiene, S. Raisys, H. Al-Attar, J. V. Grazulevicius, A. P. Monkman, and V. Jankus, "Carbazole based polymers as hosts for blue iridium emitters: synthesis, photophysics and high efficiency PLEDs" J. Mater. Chem. C, vol. 1, pp. 8209-8221, Oct. 2013.

[6] F. Dumur, L. Beouch, S. Peralta, G. Wantz, F. Goubard, and D. Gigmes, "Solution-processed blue phosphorescent OLEDs with carbazole-based polymeric host materials," Org. Electron., vol. 25, pp. 21-30, Oct. 2015.

[7] Y. Huo, J. Lu, S. Hu, L. Zhang, F. Zhao, H. Huang, B. Huang, and L. Zhang, "Photoluminescence properties of new Zn(II) complexes with 8-hydroxyquinoline ligands: Dependence on volume and electronic effect of substituents," J. Mol. Struct., vol. 1083, pp. 144–151, Mar. 2015.

[8] C. W. Tang, and S. A. VanSlyke, "Organic electroluminescent diodes," Appl. Phys. Lett., vol. 51, pp. 913-915, Jul. 1987.

[9] S. Grigalevicius, G. Buika, J. V. Grazulevicius, V. Gaidelis, V. Jankauskas, and E. Montrimas, "3,6-Di(diphenylamino)-9-alkylcarbazoles: novel hole-transporting molecular glasses," Synthetic Met., vol. 122, pp. 311-314, Jun. 2001.

[10] K. Nasu, T. Nakagawa, H. Nomura, C.-J. Lin, C.-H. Cheng, M.-R. Tseng, T. Yasuda, and C. Adachi, "A highly luminescent spiro-anthracenone-based organic light-emitting diode exhibiting thermally activated delayed fluorescence," Chem. Commun., vol. 49, pp. 10385-10387, Sep. 2013.

[11] M.-X. Yu, J.-P. Duan, C.-H. Lin, C.-H. Cheng, and Y.-T. Tao, "Diaminoanthracene Derivatives as High-Performance Green Host Electroluminescent Materials," Chem. Mater., vol. 14, pp. 3958-3963, Sept. 2002.

[12] J. I. Pankove, Optical Processes in Semiconductors, Prentice-Hall Inc., Englewoord Cliffs, NJ, 1971.