The Eurasia Proceedings of Science, Technology, Engineering & Mathematics (EPSTEM)
ISSN: 2602-3199

The Eurasia Proceedings of Science, Technology, Engineering & Mathematics (EPSTEM), 2023

Volume 25, Pages 59-66

ICBAST 2023: International Conference on Basic Sciences and Technology

Synthesis and Some Electrochemical Properties of Carbazole Derivative Monomers for Optoelectronic Device Design

Merve Yandimoglu
Eskisehir Osmangazi University

Kamuran Gorgun
Eskisehir Osmangazi University

Evrim Hur
Eskisehir Osmangazi University

Abstract: Low-cost instruments are used to achieve high sensitivity, accuracy and precision with electrochemical techniques, making them the most suitable analytical methods used to investigate the electrochemical properties of a new molecule. Among these techniques, cyclic voltammetry, which is widely employed, allows for the determination of electronic characteristics such as molecular energy levels and orbital structure, redox properties, sensor capabilities, surface activity, and more. The carbazole molecule can undergo derivatization from various positions, allowing for alterations in its electrical and optical properties. These compounds serve as heterocyclic building blocks that can be utilized as materials for organic sensitizers and semiconductors in optoelectronic devices. Due to the presence of a hydrogen atom in the nitrogen-hydrogen (N-H) bond within the carbazole structure, which can be replaced with different functional groups, carbazole is highly suitable for nitrogen-based derivatization studies. In this study, two different carbazole monomers (IIa and IIIa), which could be potential optoelectronic, were synthesized using the Ullman and Suzuki-Miyaura reaction and characterized using ^{1}H NMR, ^{13}C NMR, UV-Vis, and Flouresence spectroscopy techniques. The cyclic voltammetry experiments were performed using three different working electrodes (Au, Gc, Pt disk electrodes) for each compound. Since the optimum oxidation of the compounds was obtained from the voltammograms on the gold disk electrode, this electrode was used in the calculation of energy levels. HOMO and E_g values of the compounds were deduced from cyclic voltammetry experiments and the optical absorption bands, respectively.

Keywords: Organic optoelectronics, Suzuki-Miyaura reaction, Cyclic voltammetry, Band gap energy levels.

Introduction

Carbazole and its derivatives offer numerous advantages, such as excellent thermal and photochemical stability, solubility, easy modification, high quantum efficiency, electropolymerization capability, and strong intramolecular charge transfer (Zhu et al. 2015; Kandemir et al., 2018). Additionally, the carbazole structure can be readily functionalized at its 3-, 6-, or *N*-positions and covalently linked to other molecules (Justin Thomas et al., 2001).

These properties make these compounds valuable in various electroactive applications, including serving as light-emitting materials or hole-transporting materials in organic light-emitting diodes (OLEDs), organic sensitizers and semiconductors in optoelectronic devices, and sensors (Li et al., 2018; Liu et al., 2018; Battal et al., 2024; Karon & Lapkowski 2015).

- Selection and peer-review under responsibility of the Organizing Committee of the Conference

Cyclic voltammetry (CV) is considered one of the most precise methods for predicting energy band diagrams and characterizing the structures of compounds (Al-Ibrahim et al., 2005). The cyclic voltammetry technique, which has been successfully used to monitor the electrochemical behavior of a wide range of different compounds, stands out with advantages such as simplicity, sensitivity, speed, and low cost (Chooto, 2019). This technique allows for the measurement of oxidation potentials, which in turn enables the calculation of the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) values (Hwang & Chen, 2002). The first and most significant study on the electrochemical oxidation of carbazole was published by Ambrose and Nelson. According to their research, carbazole undergoes oxidation at approximately 1.2 V potential versus the Saturated Calomel Electrode (SCE) (Ambrose & Nelson, 1968).

In a previous study, the current-voltage characteristics of compound IIa photodiode at different illumination intensities were investigated. From the results obtained, it was determined that this diode absorbs light in the metal-semiconductor contact region (Gorgun et al. 2019a). In an another study, dye-sensitized solar cells were fabricated using IIIa compound as dye and ZnO and TiO_2 as photoelectrodes. The performances of the prepared cells were determined by current-voltage measurements. Remarkable results were obtained in the efficiency of compound IIIa cells prepared using Ruthenium sensitizer dye in TiO_2 photoelectrode (Gorgun et al., 2019b). In this study, electrochemical investigations of two different carbazole compounds, derived at the *N*-position, were carried out using cyclic voltammetry. HOMO energy levels were calculated from the obtained oxidation potentials, and E_g values were calculated from the absorption onset value. These data were used to determine the LUMO energy levels.

Method

Materials

All chemicals and solvents were obtained from Sigma-Aldrich. The organic solvents were purified by a standard procedure before using for reactions. The FT-IR spectra of the compounds were obtained with Bruker FT-IR Spectrometer (4000–400 cm^{-1}). ^1H NMR and ^{13}C NMR spectra were obtained on a JEOL ECZ500R UltrashieldTM 500 MHz and 125 MHz spectrometers. UV–Vis absorptions were obtained with SHIMADZU UV2450 UV-vis scanning spectrometer. Perkin-Elmer LS-55spectrophotometer was used to obtain the fluorescence spectra of the compounds. Cyclic voltammograms was performed with Gamry Reference 3000™ Potentiostat/Galvanostat/ZRA.

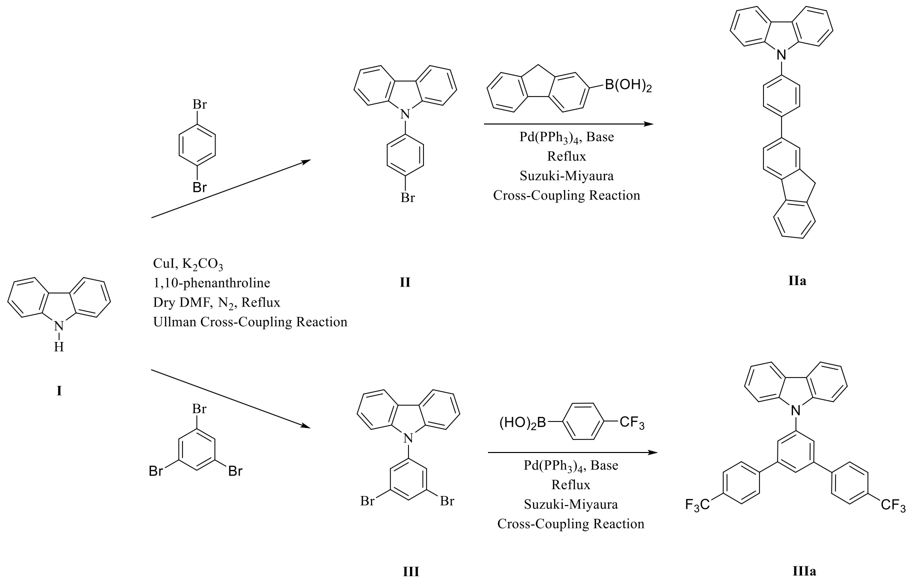

Figure 1. Synthetic route for the compounds IIa and IIIa.

Synthesis and Characterization of the Compounds

Synthesis of 9-(4-Bromophenyl)-9H-carbazole (II) (Görgün et al. 2019a).

To the solution of carbazole (I) (15.0 mmol) in 50 mL of dry *N,N*-dimethylformamide (DMF), 1,4-dibromobenzene (22.4 mmol), copper(I) iodide (1.5 mmol), 1,10-phenanthroline (0.75 mmol) and K_2CO_3 (30 mmol) were added and refluxed in N_2 atmosphere for 24 hours. Then the reaction mixture was cooled to room temperature and the solvent was removed in the evaporator. The residue was extracted in dichloromethane (DCM) and purified by column chromatography using n-hexane to obtain a white solid (compound II) (isolated yield 3.4 g, %71).

^{1}H NMR: (500 MHz, CDCl$_3$-d_1, δ): 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).

Synthesis of 9-(3,5-Dibromophenyl)-9H-carbazole(III) (Görgün et al. 2019b).

Carbazole mixture (I) (30 mmol), 1,3,5-tribromobenzene (45 mmol), copper(I) iodide (3.0 mmol), 1,10-phenanthroline (3 mmol), K_2CO_3 (60 mmol), and 60 mL of dry DMF was refluxed under N_2 atmosphere for 24 h. Then the reaction mixture was cooled to room temperature before the solvent was removed under vacuum and the residue was extracted with DCM. The product were then obtained by column chromatography on silica gel with hexane as the eluent, to get white solid (compound III) (isolated yield 6.0 g, 50%).
^{1}H NMR: (500 MHz, CDCl$_3$-d_1, δ): 7.35 (t, 2H), 7.42-7.50 (m, 4H), 7.73 (s, 2H, *J*=8.3 Hz), 7.80 (s, 1H), 8.1 (d, 2H, *J*=7.5 Hz).

Synthesis of 9-(4-(9H-Fluoren-2-yl)phenyl)-9H-carbazole (IIa) (Görgün et al. 2019a).

9-(4-Bromophenyl)-9H-carbazole (II) (1 eg), fluorene-2-boronic acid (1.2 eg), K_2CO_3 (2M, 0.683 mL), 3 mol% Pd(PPh$_3$)$_4$ and tetrahydrofuran (THF) (25 ml) were mixed in a flask and this mixture was boiled under reflux at 70 °C for 24 hours. After the solvent was evaporated under vacuum, it was extracted with DCM (3x30 mL) and sodium sulfate. Then, after the solvent was evaporated under vacuum, the desired crude product was obtained by using column chromatography on silica gel and dichloromethane/n-hexane (1:5 v:v) technique, as a white solid (compound IIa) (isolated yield 0.182 g, 65%).

FT-IR (υ, cm^{-1}): 3040, 1603, 1522, 1482, 1450, 1404, 1231, 821, 737.
^{1}H NMR (500 MHz, CDCl$_3$-d_1, δ): 8.18 (2H, d, *J*=8.0 Hz), 7.94-7.80 (5H, m), 7.66 (3H, d, *J*=8.5 Hz), 7.60 (1H, d, *J*=7.0 Hz), 7.5 (2H, d, *J*=8.0 Hz), 7.45 (2H, d, *J*=9.0 Hz), 7.43 (1H, t, *J*=7.0 Hz), 7.31 (3H, t, *J*=7.5 Hz), 4.00 (2H, s, methylene).

Synthesis of 9-(4,4''-Bis(trifluoromethyl)-[1,1':3',1''-terphenyl]-5'-yl)-9H-carbazole (IIIa) (Görgün et al. 2019b).

9-(3,5-Dibromophenyl)-9H-carbazole (III) (1 eg), 4-trifluoromethylbenzene boronic acid (22 eg), K_2CO_3 (2M, 1,364 mL) was mixed with 3 mol% Pd(PPh$_3$)$_4$ and THF (25 ml) in a flask, and this mixture was refluxed at 70 °C for 24 hours. After the solvent was evaporated under vacuum, it was extracted with DCM (3x30 mL) and dried over sodium sulfate. Then, after the solvent was evaporated under vacuum, the desired crude product was obtained from petroleum ether by column chromatography on silica gel, as a white solid (compound IIIa) (isolated yield 0.23 g, 85%).

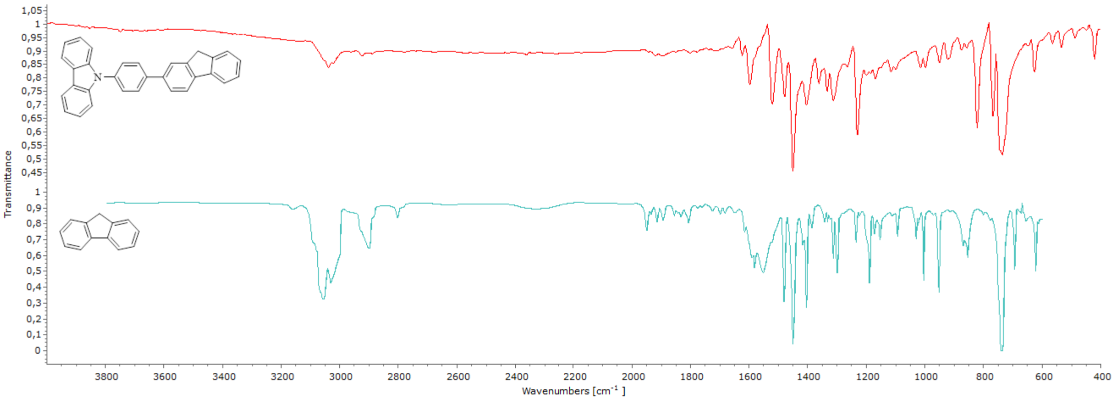

Figure 2. FT-IR spectrum of compound IIa.

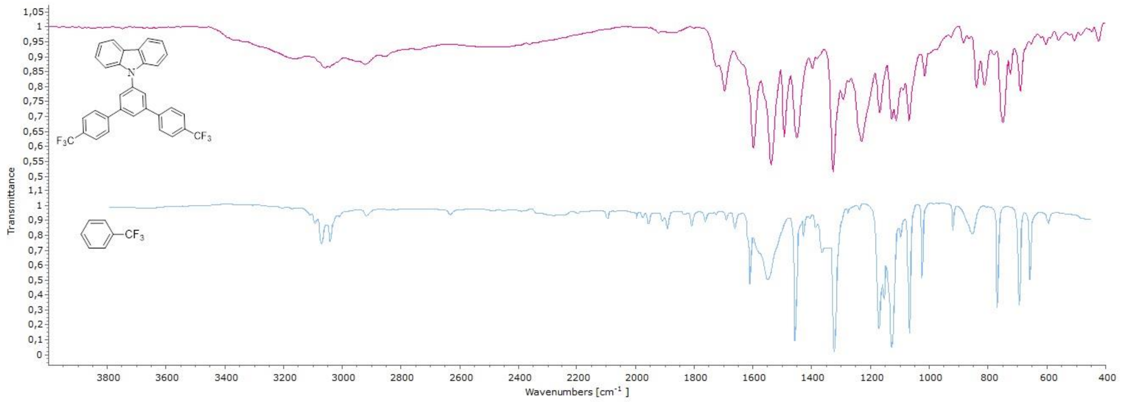

Figure 3. FT-IR spectrum of compound IIIa.

FT-IR (υ, cm^{-1}): 3064, 1698, 1600, 1539, 1453, 1329, 1231, 1170, 1130, 1112, 1069, 750, 691.
^{1}H NMR (500 MHz, $CDCl_3$-d_1, δ): 8.19 (2H, d, *J*=7.5 Hz), 7.9 (1H, s), 7.86 (2H, s), 7.82 (4H, d, *J*=9.0 Hz), 7.76 (4H, d, *J*=8.5 Hz), 7.52 (2H, d, *J*=7.5 Hz), 7.45 (2H, t, *J*=7.0 Hz, *J*=8.5 Hz), 7.33 (2H, t, *J*=6.5 Hz, *J*=8.5 Hz).
^{13}C NMR (125 MHz, $CDCl_3$-d_1, δ): 143.251, 142.454, 140.592, 139.181, 127.567, 126.146, 126.012, 125.983, 125.359, 125.081, 120.483, 120.310, 109.550, 29.497.

The IR spectra of compounds IIa and IIIa, as well as the spectra of the fluorene and (trifluoromethyl)benzene groups contained within these compounds, have been compared in Figures 2 and 3. The observed common signals support the accuracy of the structures of the synthesized compounds (NIST, 2023a; NIST, 2023b). The ^{1}H NMR spectra of compounds IIa and IIIa are presented in Figures 4 and 5, respectively.

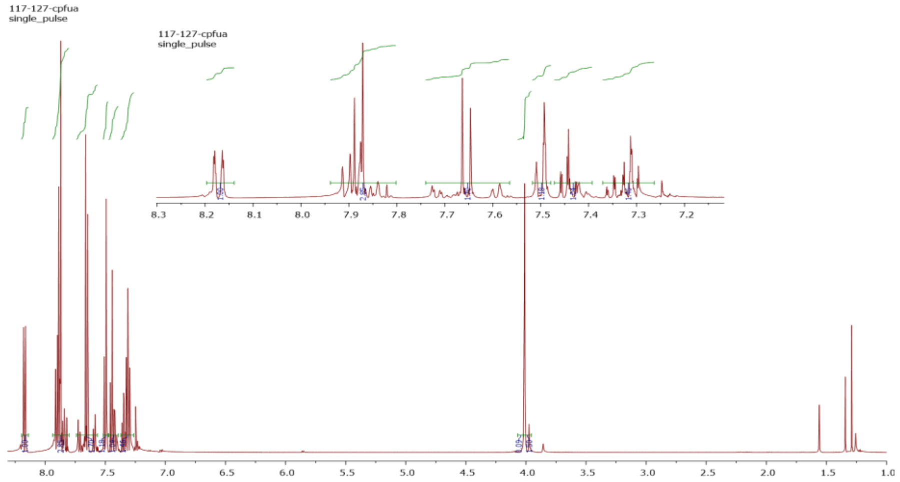

Figure 4. ^{1}H NMR spectrum of compound IIa.

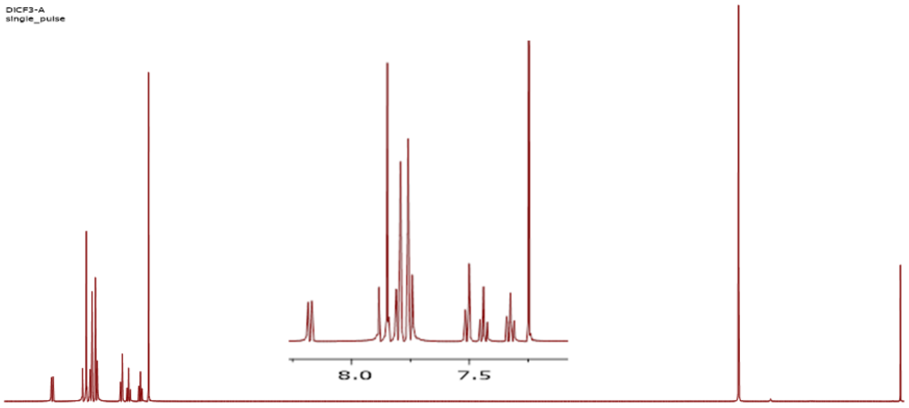

Figure 5. ^{1}H NMR spectrum of compound IIIa.

Optical Properties

The UV-GB absorption and fluorescence spectra of dilute solutions of compounds IIa and IIIa in various solvents (DCM, DMF, DMSO, n-hexane, THF and toluene) are shown in Figure 6. As shown in Figure 6a in dilute different solutions of compound IIa, π-π* transitions are observed in the 320 nm region. With an increase in solvent polarity, a general red shift (bathochromic effect) is typically observed. In addition, the fluorescence spectrum of compound IIa, a red shift is observed (Figure 6b). In the absorption spectrum of compound IIIa, the absorption maximum wavelengths of π-π* transitions show the red shift was observed with increasing polarity of solvents (Figure 6c). On the other hand, the fluorescence spectrum of compound IIIa has emission peaks in the range of 360-435 nm in all solutions. Two-shoulder emission peaks were observed at 415-435 nm in DCM. The effect of solvent polarity shows that red shift was observed with increasing polarity of solvents (Figure 6d).

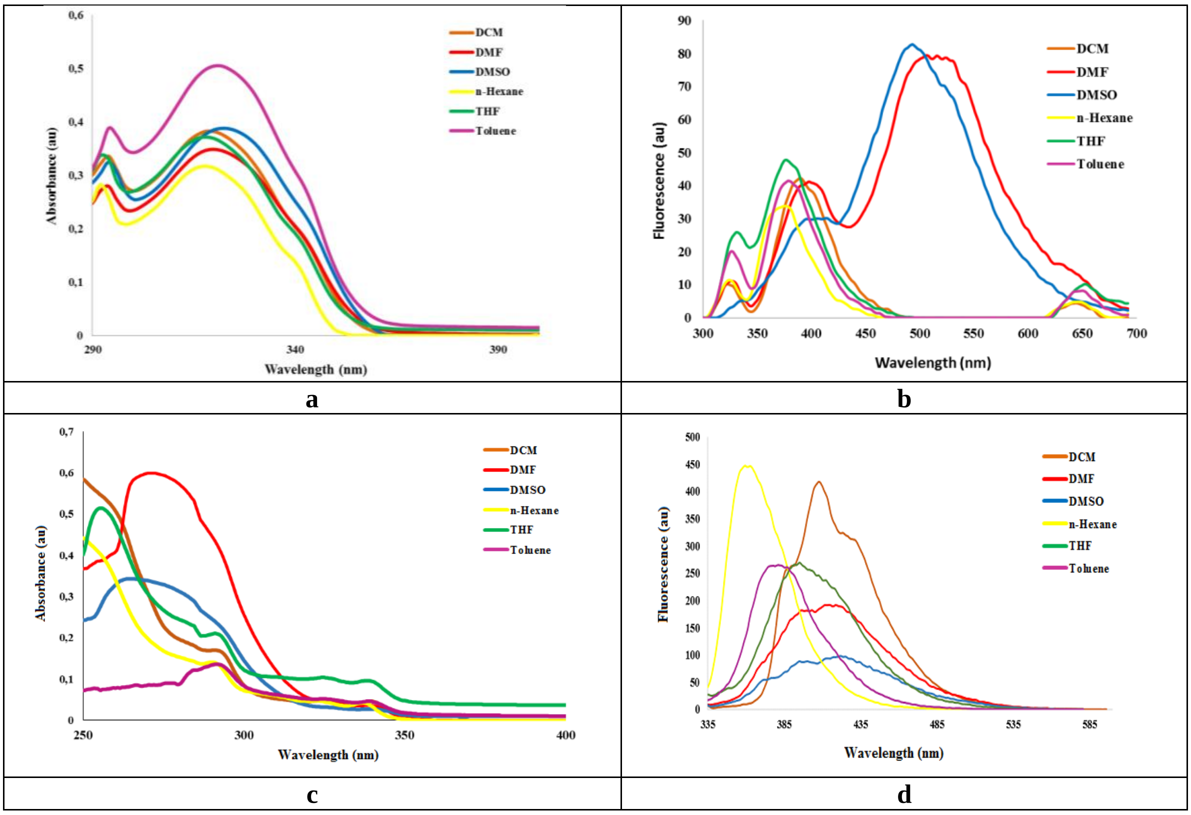

Figure 6. Absorption and emission spectra of compounds IIa and IIIa in different solvents. a) absorption spectrum of compound IIa (10^{-5} M), b) fluorescence spectrum of compound IIa (10^{-7} M), c) absorption spectrum of compound IIIa (10^{-5} M), d) fluorescence spectrum of compound IIIa (10^{-7} M).

Electrochemical Properties

In this study, a three-electrode type electrochemical cell with separate compartments for the reference electrode, counter electrode, and working electrode was employed. A silver wire (pseudo Ag/Ag^+) was used as the reference electrode, and a platinum wire was used as the counter electrode. Three different electrodes with a 3.0 mm diameter (Au, Gc, and Pt disk electrodes) were used as the working electrode. A solution containing 0.1 M tetrabutylammonium hexafluorophosphate (NBu_4PF_6) in DCM was used as the supporting electrolyte. The ferrocene-ferrocenium redox couple (Fc/Fc^+) was used as the internal reference.

Table 1. Electrochemical and optical data for the compounds.

	E^{ox}_{onset}[a] (V)	HOMO[b] (eV)	LUMO[c] (eV)	λ_{onset}[d] (nm)	Eg_{opt}[e] (V)
I	0.998	-5.58	-2.46	397	3.12
II	1.191	-5.71	-2.52	389	3.19
IIa	1.327	-5.65	-2.18	357	3.47
III	1.310	-5.81	-2.22	345	3.59
IIIa	1.333	-5.75	-2.19	348	3.56

[a]Determined from cyclic voltammetry experiments vs. Fc/Fc$^+$ in dichloromethane on gold working electrode (Au).
[b]Calculated based on HOMO= - [E_{onset}^{ox} - $E_{1/2,\ Fc,Fc+}$ + 4.8] eV (Sathiyan et al., 2016).
[c]Obtained from LUMO = HOMO + E_{gopt} (Yang et al., 2018).
[d]Calculated from the cross point of absorption onset line and corrected base line.
[e]Estimated from the onset wavelength of the optical absorption bands.

The electrochemical investigation of the compounds was conducted separately for each working electrode in a cyclic potential sweeping mode within the potential range of -0.2 to 1.6 V (vs. pseudo Ag/Ag$^+$ reference electrode) at a scan rate of 50 mV/s. The voltammograms were recorded using a 2x10^{-3} M solution of the molecules in DCM. The obtained cyclic voltammetry (CV) voltamograms are presented in Figure 7. Calculations were made based on the voltamogram values obtained for each electrode, and the best results were achieved using the Au disk electrode. The data obtained with the Au disk electrode are summarized in Table 1.

The onset oxidation potential was observed in the range of 0.998, 1.191, 1.327, 1.310, and 1.333 V and the HOMO energy levels were calculated based on these onset oxidation values, resulting in values of -5.58, -5.71, -5.65, -5.81, and -5.75 eV, additionally, the calculated LUMO energy levels were -2.46, -2.52, -2.18, -2.22, and -2.19 eV for compounds I, II, IIa, III, and IIIa, respectively. LUMO energy levels of the molecules were calculated based on the onset oxidation wavelengths of the optical absorption bands (Figure 8).

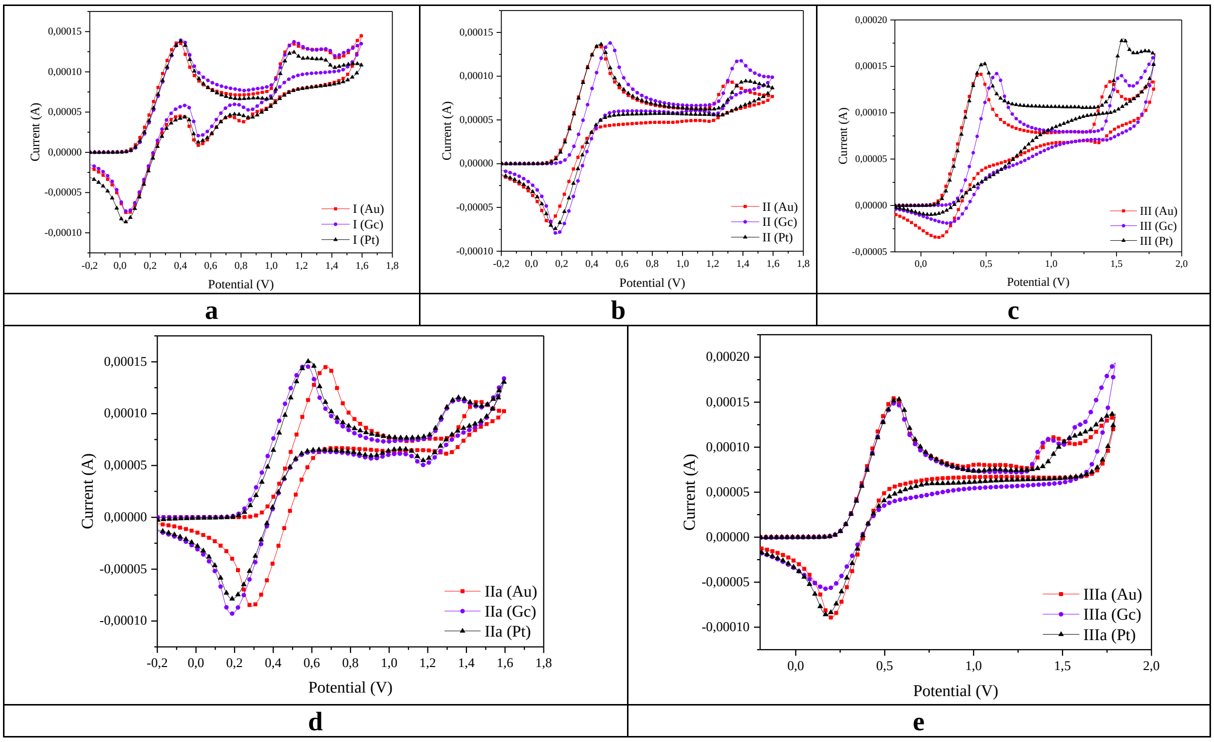

Figure 7. Cyclic voltammograms of all the synthesized compounds in dichloromethane at room temperature; Au/Gc/Pt disk as working electrode; scan rate ν = 50 mV/s, 0.1 M Bu_4NPF_6 in DCM.

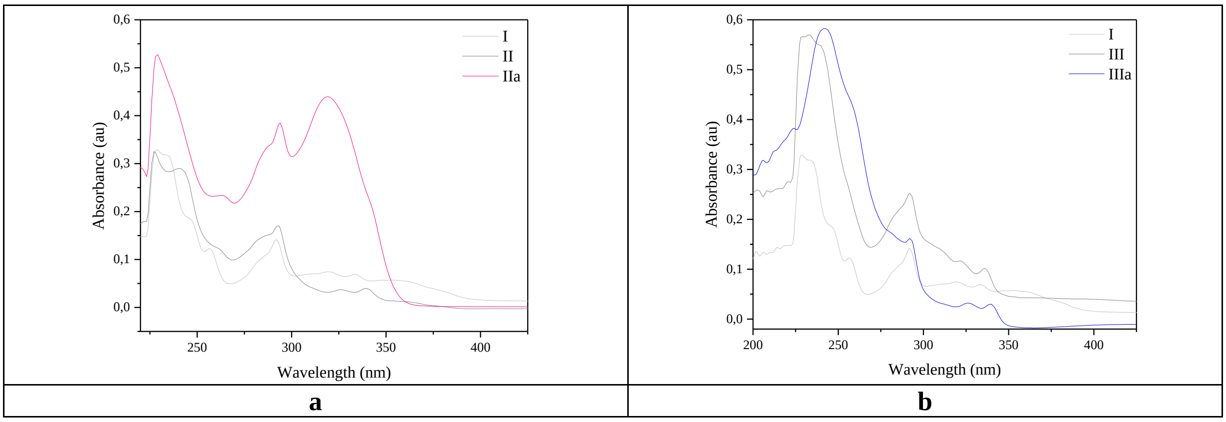

Figure 8. Absorbance spectra of all the compounds in dichloromethane at room temperature.

The increase in the LUMO energy levels of the molecules is thought to be associated with an increase in delocalization within the π-conjugation system of the molecules (Shen et al., 2011). In a study conducted by Agarwal and colleagues, it was reported that the HOMO energy levels of the carbazole-derived molecules they synthesized varied between -5.67 and -6.02 eV depending on the electron-withdrawing or electron-donating groups attached to the aryl group and also these molecules could be used as materials for solar cells (Agarwal et al. 2011). Based on this, it can be suggested that the carbazole-derived molecules synthesized in our study may be suitable for use in solar cells.

Conclusion

In this study, two different carbazole monomers (IIa and IIIa), previously synthesized in our group in our earlier studies (Gorgun et al., 2019a; Gorgun et al., 2019b), were synthesized and characterized using the Ullman and Suzuki-Miyaura reactions. After the characterization studies were completed, cyclic voltammetry experiments were conducted using three different working electrodes (Au, Gc, Pt disk electrodes) for the synthesized compounds (IIa and IIIa). Since the best oxidation of the compounds was achieved on the gold disk electrode, this electrode was utilized in the calculation of energy levels. The HOMO and E_g values of the compounds were determined using cyclic voltammetry experiments and optical absorption bands, respectively. As a result of the electrochemical and optical studies, the found energy values matched the values given in the literature (Agarwal et al., 2011), suggesting that these synthesized materials could be used in solar cell.

Scientific Ethics Declaration

The authors declare that the scientific ethical and legal responsibility of this article published in EPSTEM journal belongs to the authors.

Acknowledgements or Notes

* This article was presented as an oral presentation at the International Conference on Basic Sciences and Technology (www.icbast.net) held in Antalya/Turkey on November 16-19, 2023.
* This work was supported by Eskisehir Osmangazi University Commission of Research Project under Grant no. 2016-1321.
* We would like to thank Betul Derince for all her contributions.

References

Agarwal, N., Nayak, P. K., Ali, F., Patankar, M. P., Narasimhan, K. L., & Periasamy, N. (2011). Tuning of HOMO levels of carbazole derivatives: New molecules for blue OLED. *Synthetic Metals, 161*(5-6), 466-473.

Al-Ibrahim, M., Roth, H. K., Schroedner, M., Konkin, A., Zhokhavets, U., Gobsch, G., & Sensfuss, S. (2005). The influence of the optoelectronic properties of poly (3-alkylthiophenes) on the device parameters in flexible polymer solar cells. *Organic Electronics, 6*(2), 65-77.

Ambrose, J. F., & Nelson, R. F. (1968). Anodic oxidation pathways of carbazoles: I. carbazole and N-substituted derivatives. *Journal of the Electrochemical Society, 115*(11), 1159.

Battal, A., Kassa, S. B., Gultekin, N. A., Tavasli, M., & Onganer, Y. (2024). A reaction-based carbazole-dicyanovinyl conjugated colorimetric and ratiometric fluorescent probe for selective detection of cyanide ions. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 304*, 123350.

Chooto, P. (2019). *Cyclic voltammetry and its applications. Voltammetry*. IntechOpen, 1.

Gorgun, K., Caglar, M., Yandımoglu, M., & Sakarya, H. C. (2019). Eco-friendly carbazole-based molecules synthesis and their photodiode properties. Proceedings from: *6th International Materials Science and Nanotechology for Next Generation Conference*. Nigde, Turkey. Retrieved from http://msng2019.fytronix.com

Gorgun, K., Caglar, M., Yandımoglu, M., & Sakarya, H. C. (2019b). Synthesis of carbazole derived molecules with D-π-A structure and dye-sensitive solar cell applications. Proceedings from: *6th International Materials Science and Nanotechology for Next Generation Conference*. Nigde, Turkey Retrieved from http://msng2019.fytronix.com

Hwang, S. W., & Chen, Y. (2002). Photoluminescent and electrochemical properties of novel poly (aryl ether) s with isolated hole-transporting carbazole and electron-transporting 1, 3, 4-oxadiazole fluorophores. *Macromolecules, 35*(14), 5438-5443.

Justin Thomas, K. R., Lin, J. T., Tao, Y. T., & Ko, C. W. (2001). Light-emitting carbazole derivatives: potential electroluminescent materials. *Journal of the American Chemical Society, 123*(38), 9404-9411.

Kandemir, H., Kocak, A., Tumay, S. O., Çoşut, B., Zorlu, Y., & Sengul, I. F. (2018). Experimental and theoretical studies of carbazole-based Schiff base as a fluorescent Fe^{3+} probe. *Turkish Journal of Chemistry, 42*(2), 221-236.

Karon, K., & Lapkowski, M. (2015). Carbazole electrochemistry: A short review. *Journal of Solid State Electrochemistry, 19*, 2601-2610.

Li, M., Wang, Z., Liang, M., Liu, L., Wang, X., Sun, Z., & Xue, S. (2018). Low-cost carbazole-based hole-transporting materials for perovskite solar cells: influence of S, N-heterocycle. *The Journal of Physical Chemistry C, 122*(42), 24014-24024.

Liu, Y., Li, C., Ren, Z., Yan, S., & Bryce, M. R. (2018). All-organic thermally activated delayed fluorescence materials for organic light-emitting diodes. *Nature Reviews Materials,3*(4), 1-20.

NIST. (2023a). *Fluorene*. National Institute of Standards and Technology. Retrieved from https://webbook.nist.gov/cgi/cbook.cgi

NIST. (2023b). *Benzene, (trifluoromethyl)-*. National Institute of Standards and Technology. Retrieved from https://webbook.nist.gov/cgi/cbook.cgi?

Sathiyan, G., Thangamuthu, R., & Sakthivel, P. (2016). Synthesis of carbazole-based copolymers containing carbazole-thiazolo [5, 4-d] thiazole groups with different dopants and their fluorescence and electrical conductivity applications. *RSC Advances*, *6*(73), 69196-69205.

Shen, P., Tang, Y., Jiang, S., Chen, H., Zheng, X., Wang, X., & Tan, S. (2011). Efficient triphenylamine-based dyes featuring dual-role carbazole, fluorene and spirobifluorene moieties. *Organic Electronics, 12*(1), 125-135.

Yang, T., Xu, H., Wang, K., Tao, P., Wang, F., Zhao, B., & Xu, B. (2018). Bipolar host materials based on diphenylphosphine oxide and carbazole derivatives with high triplet energy: Synthesis, characterization and photoelectronic performance in PhOLEDs. *Dyes and Pigments, 153,* 67-73.

Zhu, W., Yang, L., Fang, M., Wu, Z., Zhang, Q., Yin, F., & Li, C. (2015). New carbazole-based Schiff base: Colorimetric chemosensor for Fe^{3+} and fluorescent turn-on chemosensor for Fe^{3+} and Cr^{3+}. *Journal of Luminescence, 158,* 38-43.

Author Information

Merve Yandimoglu
Eskisehir Osmangazi University
Eskisehir, Turkey
Contact e-mail: *mervesag26@gmail.com*

Kamuran Gorgun
Eskisehir Osmangazi University
Eskisehir, Turkey

Evrim Hur
Eskisehir Osmangazi University
Eskisehir, Turkey

To cite this article:

Yandimoglu, M., Gorgun, K., & Hur, E. (2023). Synthesis and some electrochemical properties of carbazole derivative monomers for optoelectronic device design. *The Eurasia Proceedings of Science, Technology, Engineering & Mathematics (EPSTEM), 25,* 59-66.