



# Carbazole Based (D- $\pi$ -A) Sensitizer: Synthesis, Characterization and its DSSC Application

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## Abstract

In this work, a new organic carbazole-based donor- $\pi$ -acceptor (D- $\pi$ -A) sensitizer, C3, comprising carbazole core as an electron donor, phenyl units as a  $\pi$ -conjugated bridge, and fluoro groups as an electron acceptor, has been synthesized and used for dye at ZnO based dye-sensitized solar cells (DSSCs). 3,6-di(2,4-difluorophenyl)-N-octyl carbazole (C3) was synthesized with halogenation and alkylation reaction and Suzuki-Miyaura cross-coupling reaction with good yields. Synthesized C3 sensitizer was characterized by FT-IR, <sup>1</sup>H NMR, and <sup>13</sup>C NMR. In addition, the optical (UV-Vis and fluorescence) and thermogravimetric properties of this compound were investigated. The hydrothermally synthesized ZnO nanopowder crystal structure was scrutinized by X-ray diffraction spectroscopy (XRD) and determined to belong to a hexagonal wurtzite structure. Scanning electron microscopy (SEM) images have shown that ZnO nanopowder has a highly dense and uniform leafy-like morphology. ZnO-based DSSC devices were fabricated using C3 and N719. The power conversion efficiencies (PCE) and open circuit photovoltage ( $V_{oc}$ ) of metal-free organic dye (C3), ruthenium dye (N719) and mixture dye (C3-N719) was measured 0.006% - 0.28 V, 0.461% - 0.44 V and 0.893% - 0.53 V respectively. Because of the increasing efficiency of N719-based DSSCs with C3, it was determined that C3 reduced dye aggregation so it could be used as a co-sensitizer.

**Keywords:** Carbazole, Suzuki-Miyaura Cross-Coupling Reaction, Organic Semiconductor, DSSC.

# Karbazol Temelli (D- $\pi$ -A) Duyarlaştırıcı: Sentezi, Karakterizasyonu ve DSSC Uygulaması

## Öz

Bu çalışmada, elektron donörü olarak karbazol çekirdeği,  $\pi$ -konjuge köprü olarak fenil birimleri ve elektron alıcısı olarak flor gruplarını içeren yeni bir organik karbazol bazlı donör- $\pi$ -alıcı (D- $\pi$ -A) duyarlaştırıcı bileşik C3 sentezlenmiş olup, ZnO bazlı boya duyarlı güneş pillerinde (DSSC'ler) boya olarak kullanılmıştır. 3,6-di(2,4-diflorofenil)-N-oktil karbazol (C3), ilk olarak halojenasyon ve alkilasyon reaksiyonu ve ikinci olarak Suzuki-Miyaura çapraz kenetlenme reaksiyonu ile iyi verimlerle sentezlenmiştir. Sentezlenen C3 duyarlaştırıcı, FT-IR, <sup>1</sup>H NMR ve <sup>13</sup>C NMR ile karakterize edilmiştir. Ayrıca bu bileşiğin optik (UV-Vis ve floresans) ve termogravimetrik özellikleri incelenmiştir. Hidrotermal yöntemlerle sentezlenen ZnO nanotozlarının kristal yapısı X-ışını kırınım spektrokopi (XRD) yöntemiyle incelenmiştir ve hegzagonal wurtzite yapıya sahip oldukları belirlenmiştir. Taramalı electron mikrokobu (SEM) görüntüleri ZnO nanotozlarının oldukça yoğun ve düngün yapraklı bir yapıya sahip olduklarını göstermiştir. C3 ve N719 kullanılarak ZnO tabanlı DSSC cihazlarının fabrikasyonu yapılmıştır. Metal içermeyen organik (C3), rutenyum (N719) ve karışım duyarlaştırıcılarının (C3-N719) güç dönüşüm verimleri (PCE) ve açık devre fotovoltajları ( $V_{oc}$ ) sırasıyla %0,006-0,28, %0.461-0.44 ve %0.893-0.53 olarak ölçülmüştür. N719 bazlı DSSC'lerin C3 ile artan verimi nedeniyle, C3'ün boya kümeleşmesini azalttığı ve böylece yardımcı duyarlaştırıcı olarak kullanılabileceği belirlenmiştir.

**Anahtar Kelimeler:** Karbazol, Suzuki-Miyaura Çapraz Kenetlenme Reaksiyonu, Organik Yarıiletken, DSSC.

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## 1. Introduction

The design and synthesis of organic electronic molecules have played an important role in the effectiveness of many optoelectronic materials (Mullekom et al., 2011) such as organic photovoltaics (OPV) (Hirade et al., 2013; Mishra & Bauerle, 2012), dye-sensitized solar cells (DSSC) (Barea et al., 2010; Kumar et al., 2014; Srinivas et al., 2009), organic thin-film transistors (OTFT) (Han et al., 2015), organic light-emitting diodes (OLEDs) (Cias & Slugovc, 2011). Increasing demand for environmentally friendly energy sources has increased the interest in solar energy conversion devices. Since the realization of dye-sensitized solar cells (DSSCs) by Regan and Grätzel (O'regan & Grätzel, 1991), DSSCs have come to the fore as competitor alternatives compared to conventional silicon-based photovoltaic devices (Golçalves et al., 2008) due to their relatively high performance, low production costs (Grätzel, 2009; Günes & Sariciftci, 2008) and simple manufacturing procedures (Grätzel, 2001).

The metal-free organic dyes having push-pull skeletons have gained importance due to their low cost (Yang et al., 2011), easy synthesis (Cui et al., 2011; Pushkara & Jen, 1994), and ease of structural modifications (Giribabu, et al., 2012) as well as their semiconductor properties and excellent thermal properties (Zhang, et al., 2009). These push-pull compounds have a donor- $\pi$ -acceptor (D- $\pi$ -A) structure and all parts of the compound have an important role in the determination of photovoltaic performance in DSSC (Patil, et al., 2018; Shen et al., 2011; Yang, et al., 2015). Many studies have modified the donor group to improve the power conversion efficiency (PCE) of DSSCs (Fischer et al., 2010; Kadam, Patil & Sekar, 2018). Carbazole (Lin et al., 2008; Marotta et al., 2013), coumarin (Hara et al., 2001), anthracene (Huang et al., 2011), cyanine (Ehret, Stuhl & Spitler, 2001), indole (Liu et al., 2014), triphenylamine (Wang et al., 2014), a phenothiazine (Hua et al., 2013) and phenoxazine (Tan et al., 2013) are among the donor groups in DSSCs. In addition, when long-chain alkyl groups are attached to donor groups, both dye aggregation can be reduced (Liu et al., 2012) and the electron-donating ability of donors can be increased (Namuangruk et al., 2012). The modification of carbazoles through the 2,7-positions provides an extension of  $\pi$ -conjugation, while the modification through the 3,6- positions boosts the electron donor ability (Zassowski et al., 2017). Carbazole, which is used as a donor group in molecules with a D- $\pi$ -A structure, attracts attention as an important component of organic materials for multiple optoelectronic applications (Karon & Lapkowski, 2015; Sathiyam et al., 2016). Electron-rich carbazole groups are widely used in the design of electroactive compounds (OTFTs [7], OLEDs (Su, Cai & Kido, 2011), and organic solar cells (Heredia et al., 2010; Lu et al., 2012; Tu et al., 2010) due to their excellent photoconductivity, luminescence (Thomas et al., 2001) strong intramolecular electron transfer and hole-carrying properties (Gupta et al., 2011), effective charge transfer, good thermal stability, high triple energy, glass formation capability, emission efficiencies (Dierschke, Grimsdale & Muellen, 2013). Carbazole derivatives can be easily modified at 3-, 6- and 9-positions (Kadam, Patil & Sekar, 2018). Carbazole's blue photoluminescence is not affected by the alkyl groups at the -N position (Zhang, Fujiki & Tang, 2002; Zheng et al., 2002). Transition metal-mediated crosslinking, ie. Suzuki-Miyaura, is a powerful method for the formation of C-C bonds such as Hiyama, Stille, Heck, Negishi, Kumada, and Sonogashira reactions. These

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commonly used methods have practical synthetic ways for direct formation of the C-C bond in coordination chemistry, catalysis, polymer synthesis, material science, and biological, medical, and supramolecular chemistry.

Metal oxides such as ZnO, SnO<sub>2</sub>, and Nb<sub>2</sub>O<sub>5</sub> are also used as porous semiconductors instead of the TiO<sub>2</sub> semiconductor, which is mostly used in DSSCs (Fukai et al., 2007; Memarian et al., 2011; Sayama, Sugihara & Arakawa, 1998; Wang et al., 2004; Zhang et al., 2010). Although its electronic structure is very similar to TiO<sub>2</sub>, the ZnO semiconductor, which has higher electron mobility and potentially faster kinetics (Quintana et al., 2007), has become prominent due to its lighter weight, lower cost, and ease of synthesis in various sizes and morphologies (Anta, Guillen & Tena-Zaera, 2012; Li et al., 2012; Vayssieres, 2003; Zhang & Cao, 2011). However, the use of ZnO in DSSCs results in a relatively low open-circuit voltage (V<sub>oc</sub>) and fill factor (FF) (Keis et al., 2000; Westermark et al., 2002). The main reason for this disadvantage is that many commercially available Ru-based dyes form aggregates rather than single layers on the ZnO surface (Chou, Zhang & Cao, 2007). A lot of work has been done to solve many of these problems and advance to ZnO-based DSSC device performance, such as designing core-shell structures to suppress electron-hole recombination, increasing the surface area, and improving oxide-dye binding (Kang et al., 2007; Law et al., 2006).

DSSC is a device that absorbs light from the sun with a layer of organic molecules and converts it directly into electrical energy. For the first time in 1991, DSSCs were developed by O'regan and Grätzel, a new technology emerged that left the fashion of silicon technology behind (O'regan & Grätzel, 1991). Dye sensitizer, one of the main components of DSSCs, absorbs sunlight and plays a significant role in solar energy conversion efficiency. In addition, the energy range of the dye used must be compatible with metal oxide films. Ruthenium polypyridine-type sensitizers have an effective efficiency of greater than 11%. However, ruthenium dye-based DSSCs suffer from the limitation of ruthenium sources and some environmental issues. In recent studies, many works have been conducted on the synthesis of new organic dyes as sensitizers in DSSCs. Molecules with donor- $\pi$ -acceptor (D- $\pi$ -A) structure were synthesized and these molecules were provided to have inter-molecular load transfer structures after absorbing light. Organic dyes/sensitizers have recently gained popularity and have replaced metal-based dyes due to their high absorbance values, easy structural design, and low cost compared to the expensive Ru metal. (Li et al., 2008).

The fluorine atom can improve electron mobility and the ability to adjust molecular energy levels (lower the LUMO level) (Chen et al., 2010; Cho et al., 2014; Paek et al., 2012; Roy et al., 2017). The small atomic radius of the fluorine atom and its high electronegativity makes it possible to use fluorine group-containing molecules as efficient light-collecting materials in DSSCs (Ashraf et al., 2020; Yu et al., 2013). The presence of fluorine groups on the aromatic ring in a molecule plays an effective role in the formation of more efficient photosensitizers for DSSCs (Ashraf et al., 2020). It is known that with the increase of fluorine groups in a molecule, the efficiency of conversion from the sun to electricity is also increased (Huang et al., 2013). T. Siodla et al., in their study in 2014 (Siodla et al., 2014), showed that the resonance effect of -F and -CF<sub>3</sub> groups in the phenyl ring can shorten the lengths of C-F bonds. According to this study, as a result of the calculations, it was found that the C-F bond length of these substituents in the para position tended to decrease and

the resonance increased twice. In addition, it is seen in the literature that compounds with at least one carbazole derivative attached to the benzene ring and at least one electron-withdrawing group in the ortho position are more easily conjugated with the substituents on the benzene ring (Chang 2010) (Kremser et al., 2008). Therefore, within this scope mentioned above, the presence of fluorine groups in the ortho and para positions is thought to play an important role in the observed efficiency value in the present compared to the previous study (Siodla et al., 2014; Kremser et al., 2008; Derince, Gorgun, Caglar & Caglar, 2022).

Herein, we report the carbazole derivatives characterized by FT-IR,  $^1\text{H}$  NMR, and  $^{13}\text{C}$  NMR. Optical and thermogravimetric properties of the newly synthesized carbazole-based sensitizer (C3) were determined using UV-Vis, fluorescence spectroscopic and TGA-DTA analysis methods. The target compound (C3) was used as a dye in the ZnO-based DSSC. Photovoltaic parameters of ZnO-DSSCs were determined from current-voltage measurements. As far as authors are concerned, a similar structure has not been done so far in the literature. Therefore, the present study introduces how this newly synthesized carbazole-based sensitizer (C3) affects the cell performance of ZnO-based DSSCs in the literature for the first time.

## 2. Material and Method

### 2.1. Chemicals

All chemicals and solvents were used HPLC grade purity purchase from Sigma Aldrich (Turkey) or used purified by standard procedures. In addition, Milli-Q grade water (18.2 M $\Omega$  cm) was used for all experiments.

### 2.2. Synthesis

#### 2.2.1. Synthesis of 3,6-dibromo-9H-carbazole (C1)

Carbazole (1 eq.) and *N*-bromosuccinimide (2 eq.) were dissolved in DMF at room temperature. The reaction mixture was cooled to 0 °C, then stirred for 2h and poured into pure water. After the filtration of the crude product, the solid recrystallized from ethanol to afford 3,6-dibromo-9H-carbazole as pale yellow crystals (Derince, Gorgun, Caglar & Caglar, 2022).

#### 2.2.2. Synthesis of 3,6-dibromo-9-octyl-9H-carbazole (C2)

The reaction of 3,6-dibromo-9H-carbazole with 1-bromooctane in DMSO under basic conditions (50% NaOH solution) gave the 3,6-dibromo-*N*-octylcarbazole. The reaction mixture was washed with diethyl ether and water. The white product was purified with column chromatography using *n*-hexane (Derince, Gorgun, Caglar & Caglar, 2022).

The data of the C1 and C2 molecules that we synthesized and characterized, is given in our previous article (Derince, Gorgun, Caglar & Caglar, 2022).

#### 2.2.3. Synthesis of 3,6-bis(2,4-difluorophenyl)-9-octyl-9H-carbazole (C3)

Reaction of Suzuki–Miyaura cross coupling (Miyaura, 2004) of 3,6-dibromo-*N*-octylcarbazole (1 eq.) with 2,4-difluorophenyl boronic acid (2.2 eq.) catalyzed with Pd(PPh<sub>3</sub>)<sub>4</sub> (2%) and K<sub>2</sub>CO<sub>3</sub> (5.5 eq.) was carried out in a 2:1, DME/H<sub>2</sub>O, v/v solvent mixture. The mixture was stirred at 80 °C for 5 h. After the crude product was washed with dichloromethane and water, the target product

(C3) was obtained by purification with column chromatography using *n*-hexadichloromethane (10:1) mixture. Molecular Formula: C<sub>32</sub>H<sub>29</sub>F<sub>4</sub>N, MW: 503.57 g/mol, Yield: 65%, mp. 61–63 °C. FT-IR  $\nu_{\text{max}}$  (cm<sup>-1</sup>): 2926, 2856, 1606, 1594, 1480, 844, 799.  $^1\text{H}$  NMR (500 MHz, CDCl<sub>3</sub>) ( $\delta$  ppm): 8.29 (s, 2H, H4, H5), 7.66 (dt, 2H, *J*=8.48 Hz,  $^4J$ =1.69 Hz, H5'), 7.55 (m, 2H, H2, H7), 7.50 (d, 2H, *J*=8.51 Hz, H6'), 6.96–7.06 (m, 4H, H1, H8, H3'), 4.34 (t, 2H, *J*=7.25 Hz), 1.94 (m, 2H), 1.24–1.53 (m, 10H), 0.93 (t, 3H, *J*=6.97 Hz).  $^{13}\text{C}$  NMR (125 MHz, CDCl<sub>3</sub>) ( $\delta$  ppm): 140.58, 131.66, 127.13, 126.02, 123.20, 121.24, 111.48, 108.85, 104.48, 43.17, 31.87, 29.50, 29.03, 27.27, 22.75, 14.23.

### 2.3. Fabrication of ZnO-DSSC

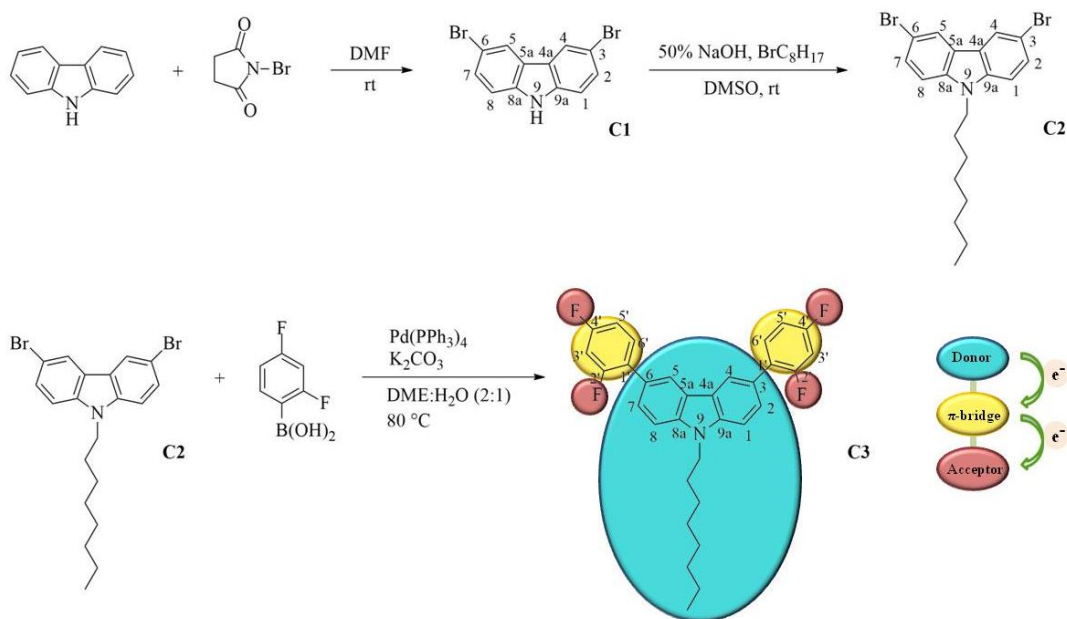
Firstly, fluorine-doped tin oxide (FTO) substrates were kept in an ultrasonic acetone solution bath for 15 minutes to clean and then rinsed with distilled water. They were dried at nitrogen ambient. Hydrothermally sensitized ZnO nanopowder was used as a photoanode. In the first step in the preparation of ZnO photoanode, ZnO paste was formed by mixing ZnO nanopowders with Triton-X 100 and acetylacetone. The obtained pastes were then coated with FTO glass using the doctor-blade method. The ZnO films were annealed for 1 h at 400 °C in air and then cooled at room temperature. The electrodes were immersed in three different dye solutions which are 0.5 mM N719 (ruthenizer 535 bis-TBA, Solaronix), 1.2 mM C3 dye, in a mixture of N719 and C3 dye (V<sub>N719</sub>:V<sub>C3</sub>=1:10) for 24 hours. Subsequently, it was fixed with a Pt counter electrode using dye-loaded electrodes on the FTO substrate to form a sandwich-type DSSCs. Finally, iodine solution [iodide/triiodide (I<sup>-</sup>/I<sup>3-</sup>) (Iodolyte, Solaronix) was injected into the sandwich-type DSSC.

### 2.4. Characterization

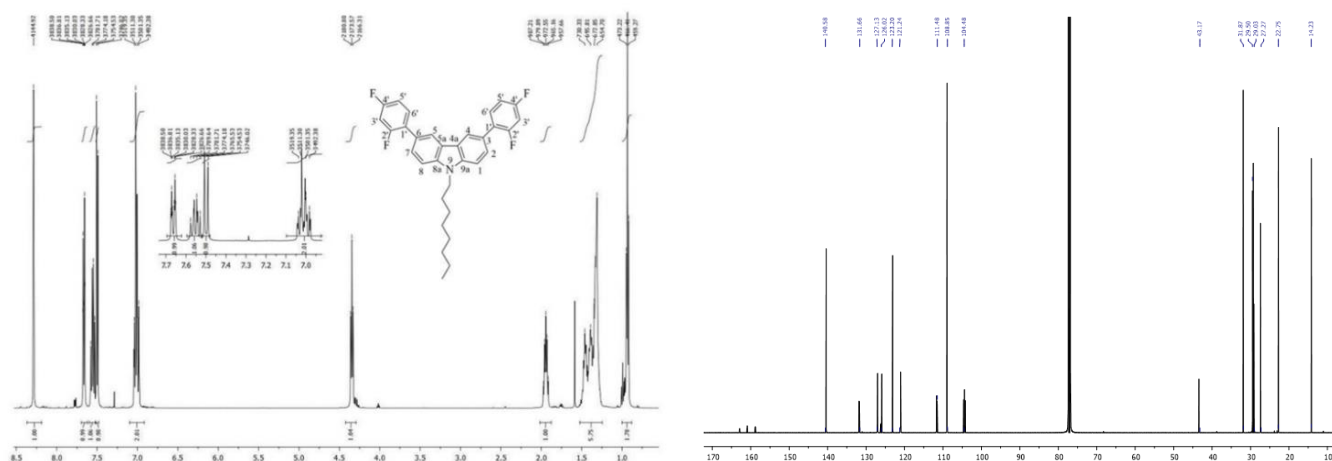
All compounds were characterized by  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra. These spectra were recorded with a JEOL ECZ500R UltrashieldTM 500 MHz and 125 MHz spectrometers, respectively, at 298 K (Japan) in ppm units with TMS as the internal standard. Thermal analyzes were carried out at the Central Research Laboratory Application and Research Center (ARUM) using the Perkin Elmer STA 8000 (25 °C–1600 °C) device. The FT-IR spectra of all compounds dispersed in KBr pellets were obtained with Bruker FT-IR Spectrophotometer (4000–400 cm<sup>-1</sup>). UV–Vis absorption and photoluminescence spectra of the C3 were obtained with SHIMADZU UV2450 UV-Vis scanning and Perkin–Elmer LS-55 spectrophotometers, respectively. The current-voltage characteristics of the DSSCs were made with the FYTRONIX OPTOSENSE solar cell measurement system using a voltage sweep rate of 0.01V/s under AM1.5G conditions.

## 3. Results and Discussion

According to the  $^1\text{H}$  NMR spectrum taken in CDCl<sub>3</sub>, there are 29 protons in the structure and these protons are individually marked by calculating match constants in the  $^1\text{H}$  NMR spectrum. The  $^1\text{H}$  NMR spectrum of the synthesized 3,6-bis(2,4-difluorophenyl)-9-octyl-9H-carbazole (C3) compound is given in Figure 1. In the  $^1\text{H}$  NMR spectra of compound C3, the peaks at 8.14 ppm (s, 2H), 7.66 ppm (d, 2H), 7.55–7.60 ppm (m, 2H), 7.02 ppm (d, 1H), 7.50 ppm (d, 2H), 6.98–7.04 ppm (m, 4H) are assigned to be H4, H5, H5', H2, H7, H6', H1, H8, H3', respectively, as aromatic protons. In addition, the presence of alkyl groups of this compound, the peaks at 4.24 ppm (t, 2H), 1.82 ppm (m, 2H), 1.20–1.30 ppm (m, 10H), 0.85 ppm (t, 3H) are assigned to be octyl-protons, as aliphatic protons.



Scheme 1. Synthesis of carbazole derivatives C1-C3

Figure 1. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectrum of the CDCl<sub>3</sub> solutions of the C3 compounds

Synthesis and characterization of molecules C1 and C2 have been reported previously (Derince, Gorgun, Caglar & Caglar, 2022). The <sup>13</sup>C NMR spectrum of the synthesized 3,6-bis(2,4-difluorophenyl)-9-octyl-9H-carbazole (C3) compound given in Figure 1. In the <sup>13</sup>C NMR spectra of compound C3, the peaks at 140.58, 131.66, 127.13, 126.02, 123.20, 121.24, 111.48, 108.85, 104.48 are assigned to be as aromatic carbons. In addition, the peaks at 43.17, 31.87, 29.50, 29.03, 27.27, 22.75, and 14.23 are assigned to be aliphatic carbons.

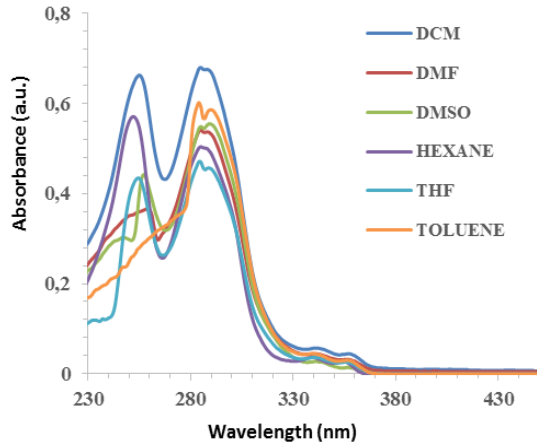
The UV-Vis absorption and emission spectra of C3 were measured in different solvents (n-hexane, toluene, THF, DCM, DMSO, and DMF) at 1x10<sup>-5</sup> M, 25 °C (Fig. 2a-b). Maximum wavelengths which belong to the carbazole-based peak of n-π\* transitions were observed between 252 nm and 259 nm, in n-hexane, THF, DCM, DMSO, DMF, and also carbazole-centered π-π\* transitions indicating difluorophenyl fragments which dominate the lowest excited states were observed between 283 nm

and 289 nm in these six different solvents. Furthermore, it was observed that the bathochromic effect increased with solvent polarity while the hypochromic effect was detected in toluene solution. The effect of solvent polarity on the fluorescence properties of the carbazole-centered molecule was studied. As shown in Fig. 2(b), the emission peaks of C3 were observed in the blue region between 379 nm and 390 nm in all solutions. The longest wavelength emission maxima was observed at 390 nm in DMSO and the shortest wavelength emission maxima was observed at 379 nm in n-hexane. So, C3 observed an increasing π-conjugation in DMSO.

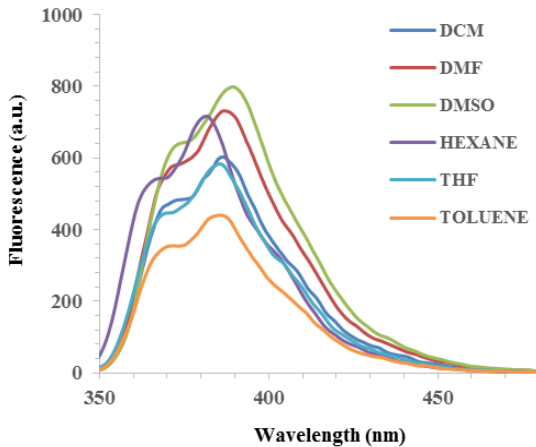
As seen from the thermogravimetric analysis (TGA-DTA) in Figure 3, the synthesized C3 exhibited great thermal stability at 351 °C with a 5% weight loss.

XRD pattern of ZnO nanopowder is shown in Figure 4. This figure confirmed that ZnO nanopowder is polycrystalline in

nature. The diffraction planes (100), (002), (101) (102), (110) (103), and (112) are in good consent with JCPDS card no. 36-1451 and belong to the hexagonal wurtzite structure. The morphology of the ZnO film has been studied using field emission microscopy (FESEM). The highly dense and smooth-leaf-like morphology of the ZnO powder is seen in this Figure 4. The length of the rods formed a leafy-like structure is about 2 nm and its diameter is 200 nm.



(a)



(b)

Figure 2. a) Absorbance spectra and b) Emission spectra of C3 in 10<sup>-5</sup> M different solvents

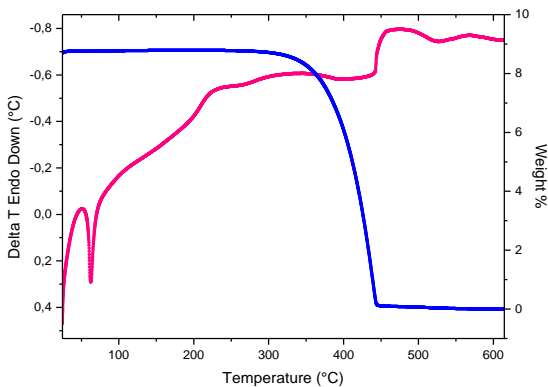


Figure 3. TGA Weight Loss and DTA graphic

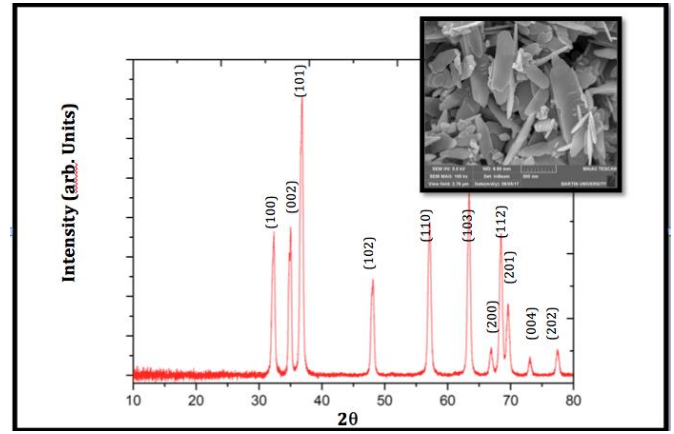


Figure 4. XRD spectra and SEM image of the ZnO nanopowder

Figure 5 shows the current density-voltage (J-V) graphs for DSSCs under AM1.5G simulated solar light (100mW/cm<sup>2</sup>). The Fill factor (FF) and conversion efficiency (n%) values are estimated using Equations (1) and (2) (Fonash, 2012),

$$n(\%) = \frac{FF \times V_{oc} \times I_{sc}}{P_{in}} \times 100 \quad (1)$$

$$FF(\%) = \frac{V_{max} \times I_{max}}{V_{oc} \times I_{sc}} \times 100 \quad (2)$$

where V<sub>oc</sub> is the open-circuit voltage at zero current density, I<sub>sc</sub> is the short circuit current at zero voltage, V<sub>max</sub> is the maximum voltage, I<sub>max</sub> is the maximum current density, and P<sub>in</sub> is the intensity of the incident light. The resulting values are summarized in Table 1.

Table 1. Photoelectrochemical parameters of the DSSCs with different dyes

DSSC	J <sub>sc</sub> (mA/cm <sup>2</sup> )	V <sub>oc</sub> (V)	FF	n (%)
N719	3.40x10 <sup>-3</sup>	0.44	0.077	0.461
C3	7.64x10 <sup>-5</sup>	0.28	0.073	0.006
N719+C3	4.42x10 <sup>-3</sup>	0.53	0.095	0.893

As seen in Table 1, C3 has improved the cell performance of DSSCs. C3 used as a co-sensitizers showed an enhancement in the efficiency of N719-based DSSCs up to ~94%. The reason for this enhancement can be attributed to a decrease in dye aggregation.

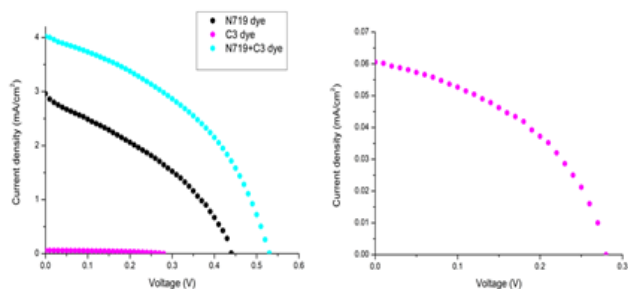


Figure 5. The current density-voltage graphs for DSSCs

## 4. Conclusions and Recommendations

In this present work, a new organic dye carbazole-based donor- $\pi$ -acceptor (D- $\pi$ -A) sensitizer was synthesized (C3) via Suzuki-Miyaura cross-coupling reaction with good yields and used in ZnO dye-sensitized solar cells (DSSCs). The molecule structure of synthesized C3 was confirmed by FT-IR,  $^1\text{H}$  NMR, and  $^{13}\text{C}$  NMR. Furthermore, optical (UV-Vis and fluorescence) and thermogravimetric properties of this compound were studied. The UV-Vis and carbazole derivative fluorescence spectra properties were measured for  $1 \times 10^{-5}$  M in n-hexane, THF, DCM, DMSO, DMF, and toluene solutions. In the UV-Vis spectra, it was observed that the bathochromic effect increased with solvent polarity while the hypochromic effect was detected in the solution of toluene. In addition, C3 emitted the longest wavelength emission maxima in DMSO at 390 nm and the shortest wavelength emission maxima in n-hexane at 379 nm. It was indicating that the maximum absorption was strongly influenced by the solvent polarity and  $\pi$ -conjugation in DMSO. On the other hand, C3 exhibited good thermal stability and also a decomposition temperature at 351 °C with a 5% weight loss from the thermogravimetric analysis (TGA-DTA). After ZnO-DSSCs were fabricated, power conversion efficiencies (PCE) of metal-free organic dye (C3), ruthenium dye (N719), and mixture dye (C3-N719) were measured as 0.006%, 0.461%, and 0.893% respectively. C3 was used as a co-sensitizer and exhibited an enhancement in the efficiency of N719-based DSSCs up to ~94%, mainly due to a decrease in dye aggregation.

## 5. Acknowledge

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