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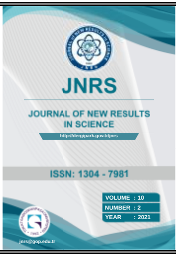

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Synthesis, structural and electrochemical characterization of quinoxaline-bridged benzodithiophene-carbazole based donor-acceptor-donor type organic semiconductor for OFET application

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Keywords:
Photovoltaic materials,
Donor-acceptor,
Organic semiconductor Materials,
Cyclic voltammetry

Abstract — In this study, the synthesis, structural, and electrochemical properties of quinoxaline-bridged functional benzodithiophene-carbazole (BDT-QCzb) based organic semiconductor materials that can be used in OFET devices were investigated. Donor-acceptor (D–A) type small molecules (SMs) are highly interested in several organic semiconductor materials. Considering the advantages of D-A type molecules, BDT-QCzb based materials were synthesized, and their structural characterization was performed by ^{1}H-NMR and ^{1}C-NMR. The energies of HOMO and LUMO levels in small-molecule organic semiconductors were determined experimentally by cyclic voltammetry (CV) and theoretically by the Spartan 18 software program. Surface characterization is made by Scanning Electron Microscopy (SEM). The electric properties of the materials are investigated by analyzing in OFET application in terms of charge mobility.

Subject Classification (2020):

1. Introduction

Organic electronic devices have significant potential due to their advantages that tunable optoelectronic properties, ease of structural modification; besides enables the device fabrication on flexible substrates compared with inorganic alternatives [1-3]. Lately, the device architecture that a p-type polymer donor and an n-type active layer junction as a phase-separated network became popular. Donor-acceptor (D-A) type materials have a very important interest among many organic semiconductor materials due to their advantages such as monodispersity, easier purification, possibility of bringing versatile functions [4-7]. To design the donor and acceptor materials that have high performance, maximizing the charge transfer in the material is a critical point for efficient charge separation. That is because designing and synthesis of molecular systems consisting of strong donor-acceptor units get attention lately [8, 9]. Although many articles focused on the improvement of π-conjugated D/A small molecules such as thiophene [10-12], furan [13, 14], thiazole [15, 16], porphyrin [17, 18] and diketopyrrolopyrrole (DPP) [19-21] are still under investigation, which makes materials innovation pushing this field forward. Various strategies are used to design and synthesize new π-conjugated systems with specific electronic

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properties. One strategy is to obtain a single molecule with a D-π-A structure to promote molecular charge transfer (ICT) interactions, provide better charge injection and at the same time achieve high efficiency [22]. While the electron-donating moieties are required to have the strong electron-donating ability and high molar extinction coefficients, the *π*-conjugated bridge must have a broad UV-vis absorption spectrum possess to sufficient light harvesting. In 2008, Hou and co-workers reported the first benzo[1,2-b:4,5-b′]dithiophene (BDT) based polymer for photovoltaic applications [23]. The most efficient donor materials reported to date contain 4,8-Dialkoxybenzo [1,2-b: 4,5-b '] dithiophene (BDT) group, and it has been widely used as an electron donor unit for the past few years [6, 23, 24]. Recently, as donor materials, BDT and its derivatives have drawn attention for low-bandgap π-conjugated polymers. Those organic compounds with a narrow HOMO-LUMO energy band gap are getting attention due to their potential polymer electronics applications. Having a structure consisting of a benzene ring with fused thiophene, BDT provides π-π stacking, high hole mobility and suitable matched energy level due to its symmetrical and planar structure [25, 26]. The molecules with these properties, which has an electron donor unit, have been synthesized over the last years, such as 4,8-Dialkoxybenzo[1,2-b:4,5-b']dithiophene (BDT). Besides, many organic small molecules consisting of BDTs and several charge-accepting moieties like benzotriazole (BTZ), 4,7-dithiophene-2-yl-2,1,3-benzothiadiazole (DTBT), thienopyrrole-4,6-dione (TPD) was studied. In this work, BDT-QCzb small molecule has been synthesized. Structural characterization of this material was carried out using 1H and 13C NMR, electrochemical characterization CV, photochemical characterization using UV and fluorescence techniques. Optical forbidden band gaps of the materials were calculated with UV and HOMO and LUMO energy level values with the CV technique. In addition, the electrical characterization of the organic field-effect transistor (OFET) device was made to examine these molecules' charge mobility.

2. Materials and Method

2.1. Materials

Carbazole, KOH, 1-bromobutane, 18-crown-6, AlCl3, oxalyl chloride, 4-bromodiaminobenzene, 2-ethylhexylbromide, zinc, Benzo [1,2-b: 4,5-b′] dithiophene-4,8-dione, trimethyltinchloride, n-buthyllithium, $Pd(PPh_3)_2Cl_2$, thin layer chromatography (TLC), MgSO4, HCl, NaHCO3, silica gel, toluene, THF, ethanol chloroform, methylene chloride hexane vb. all chemicals and solvents were purchased from Aldrich, ACROS, Fluka and TCI.

2.2. Method

All chemicals and solvents were reagent grades and purchased from Aldrich, ACROS, Fluka, TCI. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Brukery 400 MHz spectrometer using CDCl3 solvent. Optical and electrochemical measurements UV-Vis-NIR Pelkin Elmer Lamda 950 absorption and Edinburg İnstrument FS5 fluorescence spectroscopy. Cyclic voltammetry (CV), 0.1-M solution of tetrabutylammonium hexafluorophosphate ($(TBA)PF_6$) in acetonitrile at room temperature with a scanning rate of 100 mV/s. During the CV measurements, a platinum wire as the counter, a silver wire as the reference, and a glassy-carbon working electrode were used. The redox couple of ferrocene/ferrocenium ion (Fc/Fc^+) was used as an external standard. The Spartan 18 program was utilized to perform the DFT calculations.

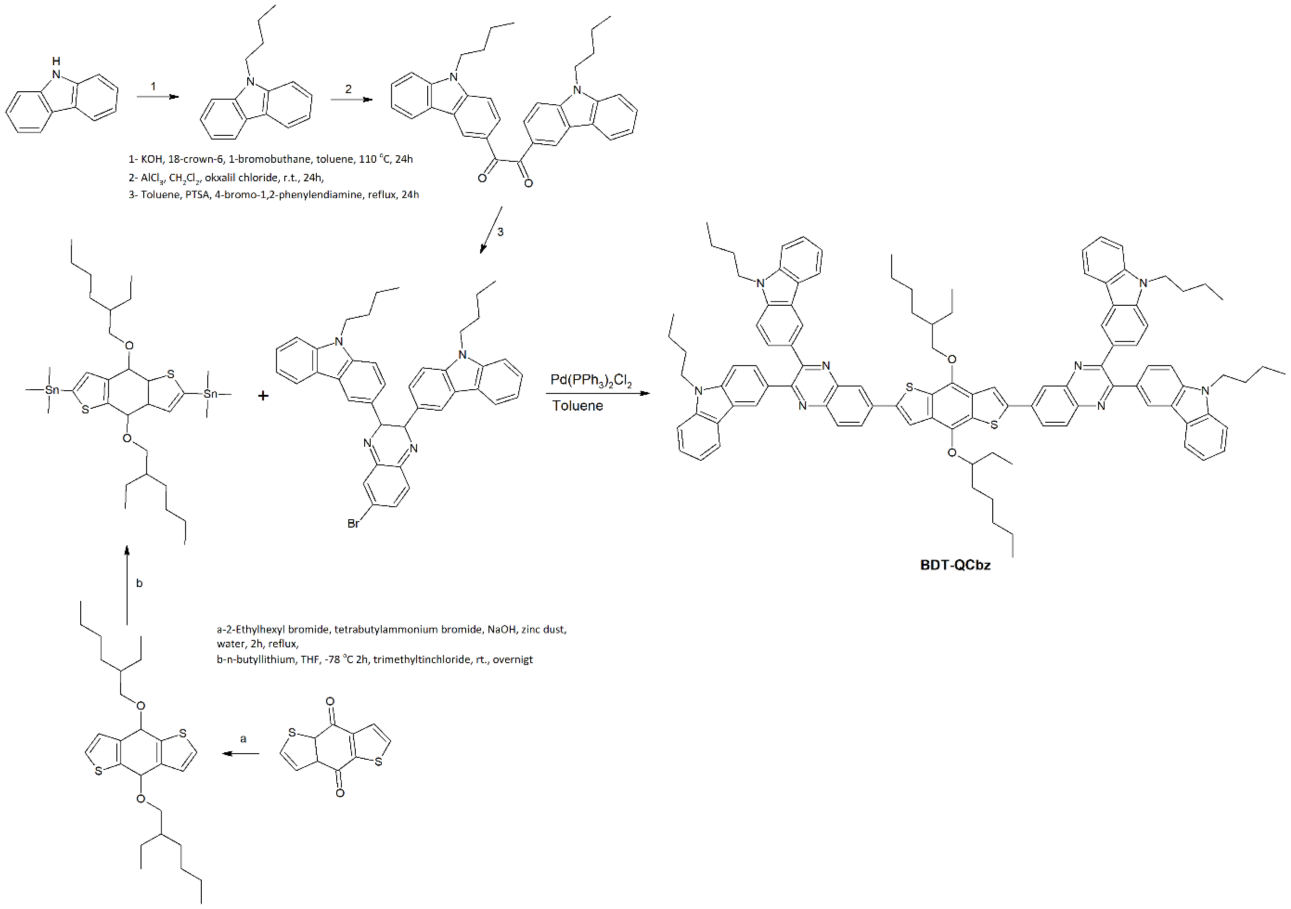
The standard procedure for cleaning film surface is that the ITO substrates ($1*1\ cm^2$) were ultrasonically cleaned in detergent, deionized water, acetone, and isopropyl alcohol. After routine solvent cleaning, the substrates were treated with UV ozone for 15 min. Then a modified ITO surface was obtained by spin-coating a layer BDT. The OFET device was tested with a probe station and a Keithley 2400 source/measuring unit.

It is focused on synthesizing a similar structure material consisting of a benzene ring with fused thiophene, provides π-π stacking as shown in scheme 1. After that, an organic field-effect transistor (OFET) device is fabricated on top of the polymeric gate-insulator with top drain-source is illustrated in Scheme 2.

2.3. Synthesis

The acceptor-donor type molecule were synthesized according to literature procedures [6, 27]. The main structures of synthesized 2,6-Bis(trimethylstannyl)-4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b′]dithiophene (BDT) starting from Benzo[1,2-b: 4,5-b ′] dithiophene-4,8-dione was carried out according to the procedure applied by Huo et all (HUO, 2008). 3,3'-(6-bromokinoksalin-2,3-diil)bis(9-butyl-9H-carbazole) (QCbz) was prepared using 1,2-bis(9-butyl-9H-carbazole-3-il)etan-1,2-dion and 4-bromodiaminobenzene according to literature. (Koyuncu, 2014)

2,6-bis[3,3'-(kinoksalin-2,3-diil)bis(9-butyl-9H-carbazole]-4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b′]dithiophene **(BDT-QCzb)** was synthesized by Still Coupling method. di(triphenylphosphine)dichlorid palladium (2) [Pd(2)(PPh_3)$_2$$Cl_2$] was used as a catalyst in the reaction with Still method. The structure of BDT-QCzb synthesized by Still Coupling is shown scheme 1.



Scheme 1. The route followed for the synthesis of BDT-QCzb.

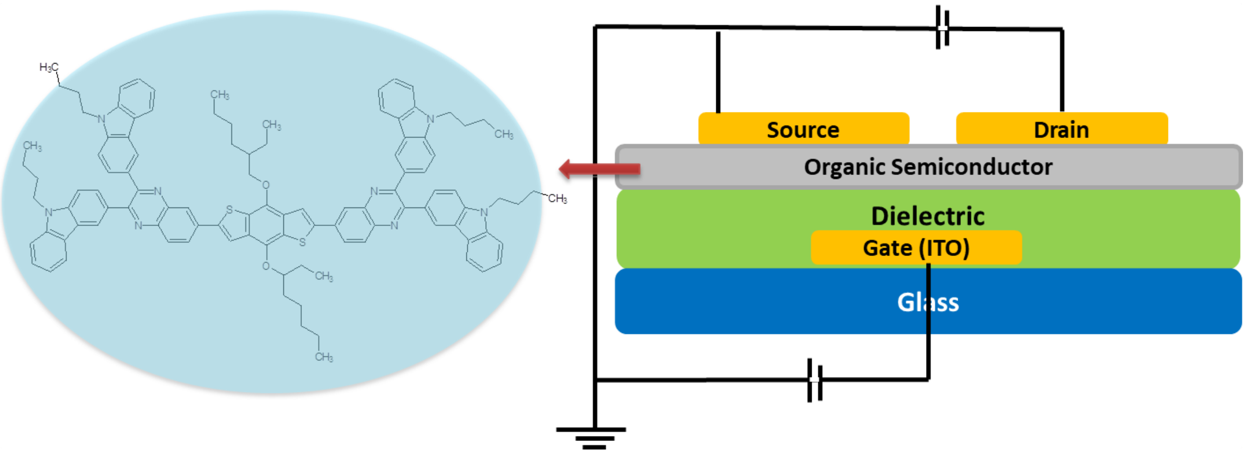


Figure 1. Chemical structure of BDT-QCzb based donor-acceptor (D–A) type small-molecule organic semiconductor.

Compared to conventional thiophene-based molecules, the small molecule exhibited great physical features such as proper HOMO energy levels, high charge carrier mobility, and fine thermal stability. The studies of BDT-QCbz show that at the 4 and 8 positions of BDT for the linear alkoxy chains finalize processable low molecular-weight (Mw) materials.

3. Result and Discussion

3.1. Structural and Electrochemical Characterization

Particularly, low symmetry led to show the different material properties such as photo-electro-magnetic, single-molecular magnet, near-infrared absorption and so on [35]. Besides, flatness is more important than irregular stacking in the π-conjugated system to achieve an efficient charge injection. Some critical methods increase the electronic coupling between adjacent molecules and reduce reorganization energy, such as coordination, molecular conformational locks, and intramolecular hydrogen bonds [10]. The problems regarding how terminal groups affect the D-A-D-π electronic structure of π-conjugated molecules should be revealed at the molecular level.

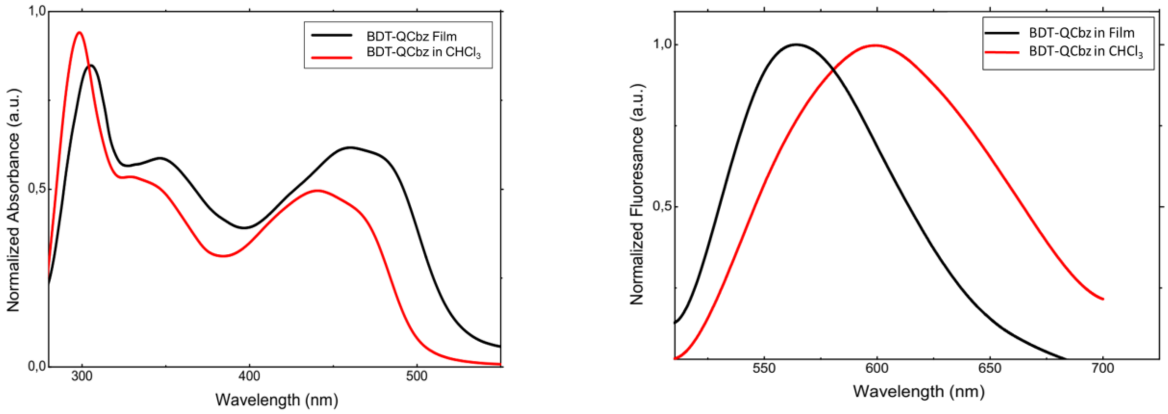


Figure 2. Absorption and emission spectra of BDT-QCbz molecule.

Optical characterization of the molecule was done by Perkin Elmer Lamda 950 UV-Vis-NIR spectrophotometer. Liquid phase measurement of BDT-QCbz molecule was prepared in chloroform ($2x10^{-5}$ M), and a 5mg/ml solvent system was prepared in chloroform for solid-phase study and covered on glass substrate using rotation technique. As seen in Fig. 1, the peaks visible in the solvent phase of the molecule are 298, 340, 441 nm, respectively. Two peaks at 298 and 340 nm are n-π * transitions from heteroatoms (S, N, O) found on molecules belonging to acceptors and donor groups and π-π * transitions resulting from π bonds. The 441 nm wide peak is thought to be the intramolecular charge transfer band of the donor-acceptor structure, which is formed as a result of the combination of electron donor carbazol and electron acceptor quinoxaline groups on a single molecular structure. The peaks of the film phase are 305,348 and 462 nm, respectively. When the absorption spectrum of the molecule in the film phase is examined, it is understood that the maximum absorption peak values of the charge transfer band in the solution phase have shifted to red due to the increase in the intermolecular π-π interaction due to the planar structure of benzodithiophene and quinoxaline molecules. The redshift in the peak values observed in the solid phase compared to the solvent phase is approximately 21 nm. When we look at the absorption graph of the molecule, the lowest energy absorption the onset wavelength value of the band is approximately between 495 and 505 nm, and this value energetically is equivalent ($E = h.c / \lambda$) from "Plack's Theorem" optical band gap value has been calculated. Molecular emission measurements were made by Edinburgh Instrument FS5 fluorescence spectroscopy. Chloroform was used as a solvent in the liquid phase, and emission measurements were taken for both phases. As seen in Fig. 2, the max and the peak value are 598 and 564 nm, respectively. In the liquid phase, there was a shift of approximately 130 nm compared to the absorption value. For the solid phase, this shift value is around 120 nm. In the CV voltammogram, the reversible oxidation potential of the molecule was 1.26 volts, while the reversible reduction potential was found as -1.42 volts. $E_{HOMO}=-(E_{ox}-E_{Ferrocene}+4.8)$ eV; $E_{LUMO}=-(E_{red}-E_{Ferrocene}+4.8)$ eV. HOMO and LUMO values obtained from the equations were found as -5.66 eV and -2.98 eV, respectively. While the carbazole groups cause oxidation on the molecule, the reduction is due to the quinoxaline groups.

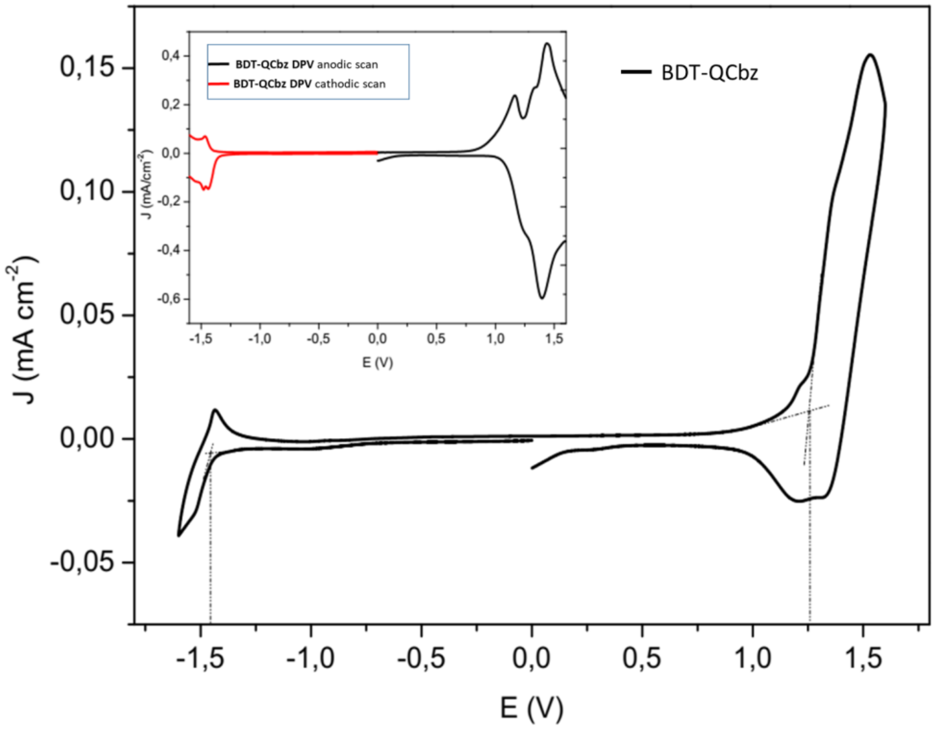
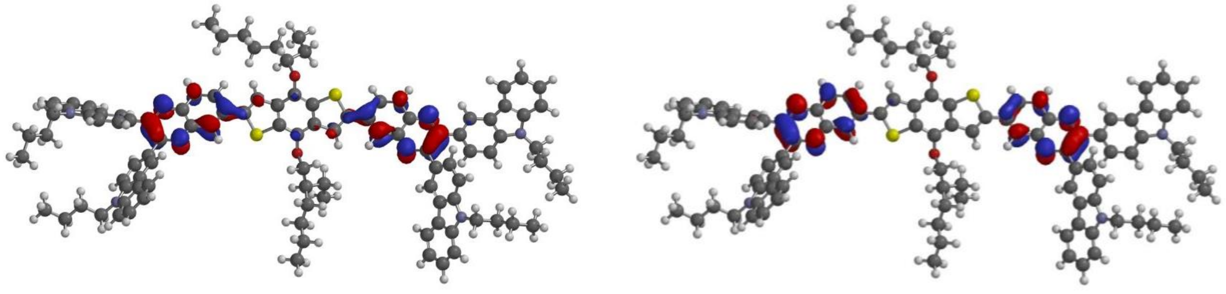
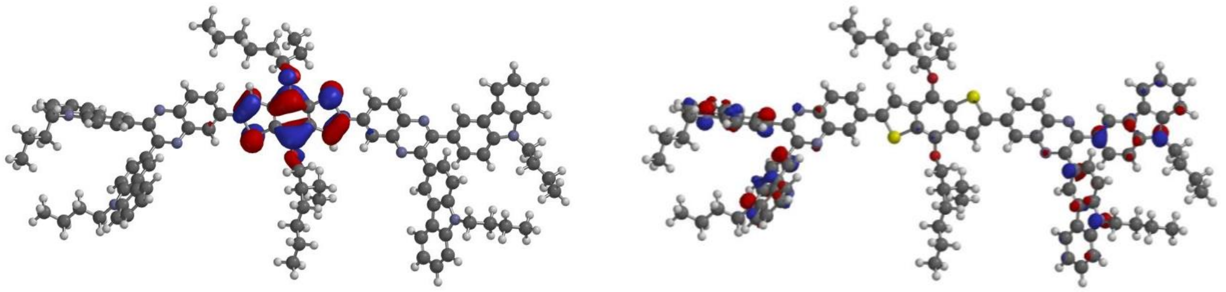


Figure 3. Cyclic voltammograms of BDT-QCbz molecule



Lumo **Lumo+1**



Homo **Homo-1**

Figure 4. Theoretical calculation of HOMO-LUMO energy levels of the electronic charge distributions on synthesized molecules by Spartan 18

Table 1. Optical Properties, Electrochemical and Electronic Energy Levels of the BDT-QCzb

E_g^{opt} (eV)	E_{ox} (V)	M_{HOMO}/T_{HOMO}(eV)	E_{red} (V)	M_{LUMO}/T_{LUMO} (eV)	E_g^{ec} (eV)
2.47	*1.26*	-5.66 / -4.87	*-1.42*	-2.98 / -1.81	*2,68*

M: Measurement, T: Theoretically

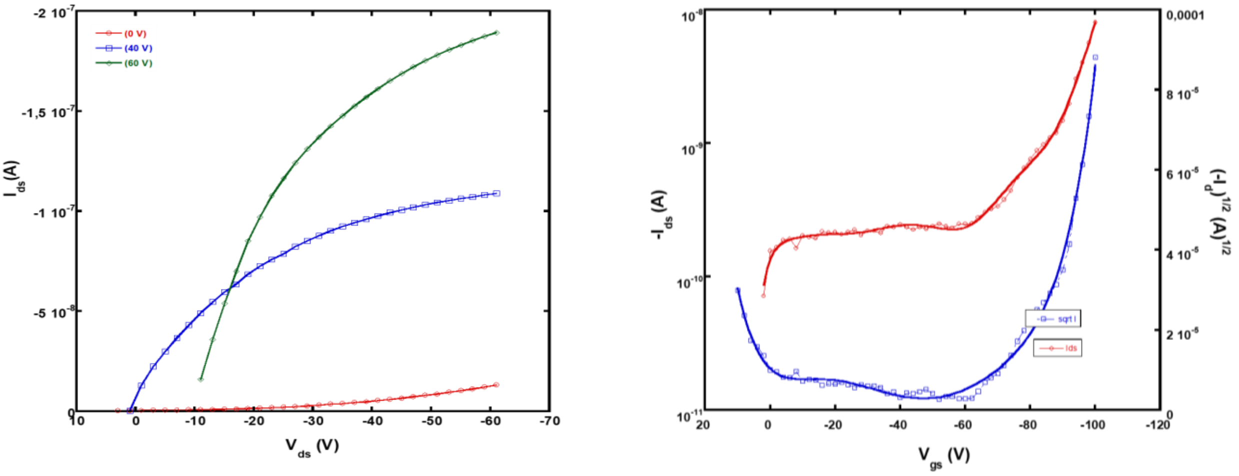


Figure 5. Output characteristics ($I_{ds} - V_{ds}$) of BDT-QCzb transistors on dielectrics for various V_{gs} in a device.

All measurements were taken under the same conditions—transfer characteristics for the device consisting of an organic semiconductor material that electron-rich thiophene groups. The curves were obtained under $V_{ds} = 50$ V (right). The left axis represents ($\log I_{ds} - V_{gs}$) curve, and the right axis $I_{ds}^{1/2} - V_{gs}$ curve.

The OFET was fabricated, and it presents typical n-channel transistor output characteristics as a function of Vgs. The drain current I_{ds} increases linearly with V_{ds} at low voltages as ohmic contacts (between drain-source and organic semiconductor). The saturation regime in an ideal thin-film-transistor (TFT) is to be high (Vds > Vgs). The presence of charges at the dielectric-semiconductor interface contributed to the high conductivity in the saturation regime. Fig. 5 (right) depicts the transfer characteristics (log Ids - Vgs) and (Ids1/2 - Vgs) of OFET at Vth = 50 V to illustrate turn-off and turn-on state behaviour by a sweeping gate voltage. The transfer characteristics of semiconductors show that BDT-QCzb has a good performance in OFET.

3.2. Surface Characterization

The morphology of the film was tested by scanning electron microscopy (SEM). Scanning electron microscope (SEM) is one of the common methods for imaging the morphology of the materials. Electrons interact with the material with the help of a probe that scans the surface. Secondary electrons are separated from the surface of the sample and recorded. Create contrast in the image due to the height differences in the sample. Zeiss VP 300 model SEM was used to determine the surface properties of the synthesized compounds. The film's images coated using the ITO surface rotation technique were taken at accelerating voltage of 5 kV and 10000kx magnification. One of the images shown in Fig. 6 is the bare ITO (a) and (b) BDT-QCzb film phase.

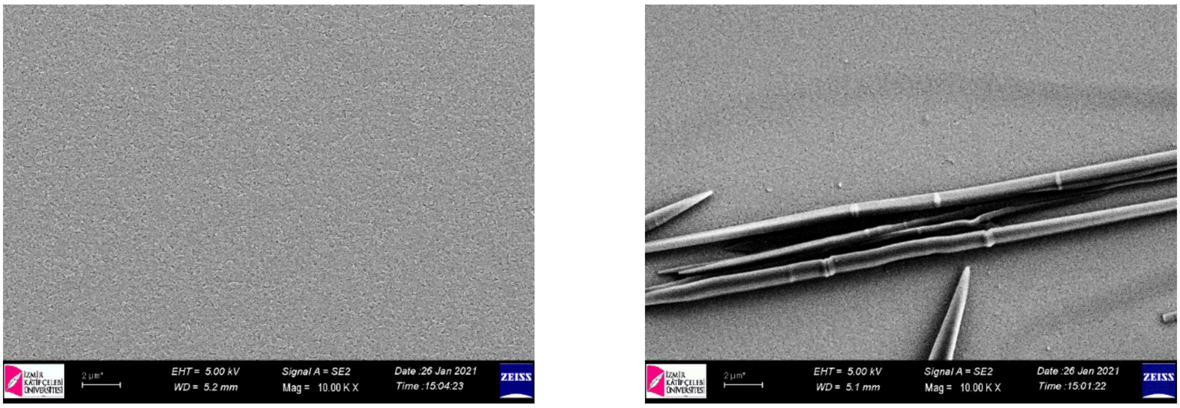


Figure 6. SEM imagine bare ITO (a) and (b) BDT-QCzb film on ITO.

4. Conclusion

An OFETs based on the quinoxaline-bridged benzodithiophene-carbazole is studied by incorporating polymeric dielectrics. It is found that the architect geometry of the functional groups modifies the surface potential and effect mobile charge carriers in OFET. The electrical performance of OFET can be enhanced by changing the morphology and structure of the active layer and the interfacial charge trapping states at insulator-semiconductor is affected by the hydroxyl in the dielectric of OFET. The results showed that quinoxaline-bridged benzodithiophene-carbazole has a good performance in OFET. The electron-rich thiophene groups enhance the surface morphology and charge carrier mobility due to improving the surface energy of the organic thin film. The presence of electron-rich thiophene groups fused to the benzene ring adds flatness to the molecular structure. This allows for an effective π - π interaction between molecules. The quinoxaline groups attached to the core structure give the structure an electron acceptor feature thanks to the nitrogen atoms (sp^2 hybrid) it contains. Electron-rich carbazole groups with high thermal stability in the side chains increase the electron density of the structure and contribute to the reduction of the forbidden band gap of the electron donor and electron acceptor structure on the same molecule.

Author Contributions

The author read and approved the last version of the manuscript.

Conflicts of Interest

The author declares no conflict of interest.

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