



Synthesis and Theoretical Investigation Using DFT of 2,3-Diphenylquinoxaline Derivatives for Electronic and Photovoltaic Effects

Dorota Zajac¹ · Dariusz Przybylski² · Jadwiga Sołoducho¹

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Abstract

Developing effective and low-cost organic semiconductors is an opportunity for the development of organic solar cells (OPV). Herein, we report the molecular design, synthesis and characterization of two molecules with D–A–D–A configuration: 2-cyano-3-(5-(8-(3,4-ethylenedioxythiophen-5-yl)-2,3-diphenylquinoxalin-5-yl)thiophen-2-yl)acrylic acid (**6**) and 2-cyano-3-(5-(2,3-diphenyl-8-(thiophen-2-yl)quinoxalin-5-yl)thiophen-2-yl)acrylic acid (**7**). Moreover, we investigated the structural, theoretical and optical properties. The distribution of HOMO/LUMO orbitals and the values of the ionization potential indicate good semiconducting properties of the compounds and that they can be a bipolar material. Also, the optical study show good absorption in visible light (λ_{abs} 380–550 nm). We investigate the theoretical optoelectronic properties of obtained compounds as potential materials for solar cells.

Keywords 2,3-Diphenylquinoxaline · organic optoelectronic · Stille, Suzuki reaction · conjugated polymers · organic semiconductors

Introduction

Organic photovoltaics (OPV) is a technology that uses organic compounds to create a thin layer of semiconductor materials, due to their unique advantages, such as simple preparation and modification, low weight, flexibility, and cost-effectiveness.^{1–3} In addition, the use of organic semiconductors provides a wide selection of materials and great opportunities to improve their physicochemical properties thanks to chemical synthesis. Moreover, the processing of such semiconductors is simpler than in the case of silicon cells, as large amounts of material are not required and the process can be performed on various substrates.^{4, 5} Currently, research aims at increasing the power conversion efficiency (PCE) of OPV. By developing or modifying new

organic semiconductors, the properties and morphology of the device are improved. Previous research reported 17.05% PCE for polymer solar cells.⁶ However, despite the progress achieved in the field of OPV, attempts are still being made to solve the limitations resulting from poor mobility of charge carriers and unsatisfactory light absorption.^{7–9} More bipolar (donor–acceptor, D–A) material development reports are available. Recent studies report that in order to obtain bipolar characteristics in the molecule, the energy levels must be adjusted so that the HOMO orbital has energy ≥ 5.6 eV, and the LUMO orbital has energy around 3.15 eV.^{10, 11} These are the basic conditions for the injection/charge transport of both electrons and holes under ambient conditions. Typically, thiophene, triphenylamine and carbazole derivatives are used as D components, while benzothiadiazole, diketopyrrolopyrrole and quinoxaline derivatives are used as A components for the construction of conjugated polymers of the D–A type and in different arrangements of donor and acceptor molecules throughout the molecule, e.g. D–A–D–A–D, A–D–A–D–A.^{12–20} 2,3-Diphenylquinoxaline (DPQ) is an efficient electron withdrawing unit due to its suitable electronegativity, stable quinoid structure and easy synthesis. It reduces charge recombination by inhibiting intermolecular aggregation due to two separate phenyl rings

✉ Dorota Zajac
dorota.zajac@pwr.edu.pl

¹ Faculty of Chemistry, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

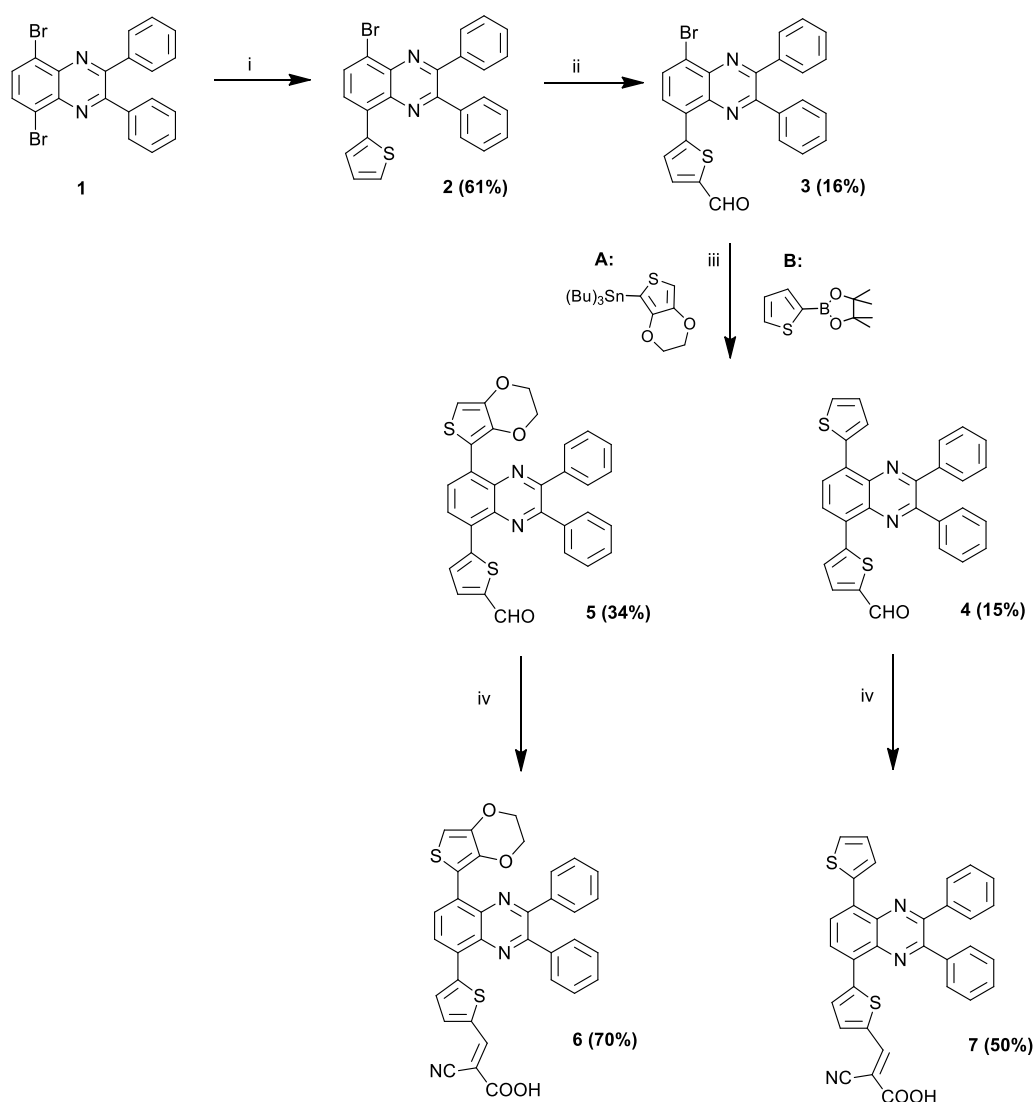
² Faculty of Microsystem Electronics and Photonics, Wrocław University of Science and Technology, Długa 61-65, 53-633 Wrocław, Poland

attached to a quinoxaline unit. Introducing DPQ as a helper acceptor can improve donor electron distribution, redshift the absorption spectra, fine-tune energy levels and improve photostability.^{21–24}

Molecular modeling has become a useful tool to investigate molecular and photoelectrochemical properties using quantum chemical computations. Density functional theory (DFT) with Becke3–Lee–Yang–Parr (B3LYP) method is one of the most accurate tools used to analyze an organic system's structural features and its properties.^{16, 25, 26} The observation of theoretical study, however, should be treated with caution, since the orbital energies are basis set dependent. Our previous experience shows that the physicochemical properties of heterocyclic compounds synthesized by our

research group are predicted with great accuracy by the cc-pVDZ base.^{27–29}

In this work, considering the important aspects of molecules with the D–A–D–A configuration in electron transport and their solid state application in optoelectronic devices, we designed and synthesized two DPQ-based compounds in which electron-donating ethylenedioxythiophene or thiophene was combined with electron accepting DPQ. Additionally, through thiophene as a linker, we connected cyanoacrylic acid to DPQ as an additional electron acceptor and an anchor group (Scheme 1). The design of the compounds was based on the following considerations: (i) thiophene and ethylenedioxythiophene are used as an electron donor to obtain more positive HOMO energy levels; (ii)



Scheme 1 Synthesis of DPQ derivatives (**6**, **7**): *i*: 2-(tributylstannyl)thiophene, PdCl₂(PPh₃)₂, THF, N₂, reflux, 24 h; *ii*: DMF, POCl₃, dichloroethane, N₂, 24 h; *iii*: Stille: (A) 2-(tributylstannyl)ethylenedioxythiophene, PdCl₂(PPh₃)₂, THF, N₂, reflux, 72 h; Suzuki: (B)

5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-thiophene, K₂CO₃, PdCl₂(PPh₃)₂, toluene, H₂O, MeOH, N₂, reflux, 48 h; *iv*: toluene, cyanoacetic acid, piperidine, N₂, 24 h.

2,3-diphenylquinoxaline is used as an electron withdrawing separator; (iii) thiophene is introduced as a donor and subsequent separator to extend conjugation of the entire system; (iv) a cyanoacrylic acid unit is used as an electron acceptor that acts as an anchor group to the substrate. Thanks to this structure, it is possible to extend the length of the molecule's conjugation and to extend the absorption. An additional acceptor in the form of DPQ may facilitate efficient charge transfer from the ground state to the excited state. Photovoltaic properties of solar cells based on 2-cyano-3-(5-(8-(3,4-ethylenedioxythiophen-5-yl)-2,3-diphenylquinoxalin-5-yl)thiophen-2-yl)acrylic acid (**6**) and 2-cyano-3-(5-(2,3-diphenyl-8-(thiophen-2-yl)quinoxalin-5-yl)thiophen-2-yl)acrylic acid (**7**) have been studied in this work. B3LYP/cc-pVDZ methods are used to obtain geometries and optimize the electronic properties, optical and photovoltaic parameters for 2,3-diphenylquinoxaline derivatives. We wanted to investigate a system that already has both electron donors and acceptors in its structure as a potential bipolar material, and find whether such a structural motif has the appropriate optoelectronic properties to use these compounds as active layers in cells.

Results and Discussion

Synthesis

The synthetic methods of two products, 2-cyano-3-(5-(8-(3,4-ethylenedioxythiophen-5-yl)-2,3-diphenylquinoxalin-5-yl)thiophen-2-yl)acrylic acid (**6**) and 2-cyano-3-(5-(2,3-diphenyl-8-(thiophen-2-yl)quinoxalin-5-yl)thiophen-2-yl)acrylic acid (**7**) are present in Scheme 1. The 3,4-ethylenedioxythiophene was monostannylated to 2-(tributylstannyl)-3,4-ethylenedioxythiophene with 99% yield with SnMe_3Cl in THF at -80°C . The first step of the reaction was a synthesis of the compound **2** (Stille coupling), which was based on the modification of the structure by adding a thiophene moiety, so that the presence of a sulfur atom in the ring had an activating effect by S-coordinating to lithium, followed by proton detachment by a butyl group during the *n*-BuLi metallation reaction. This was converted to the key precursor 5-(8-bromo-2,3-diphenylquinoxalin-5-yl)thiophene-2-carbaldehyde (**3**) through Vilsmeier–Heck reaction with 16% yield. Next step were palladium-catalyzed carbon-carbon bond formation reactions, i.e. Suzuki or Stille (5-(2,3-diphenyl-8-(thiophen-2-yl)quinoxalin-5-yl)thiophene-2-carbaldehyde (**4**) and 5-(8-(3,4-ethylenedioxythiophen-5-yl)-2,3-diphenylquinoxalin-5-yl)thiophene-2-carbaldehyde (**5**)). Finally, compounds **4** or **5** in reaction with cyanoacetic acid and piperidine, following the Knoevenagel condensation protocol, yielded **6** and **7** respectively. All the synthesized compounds were purified further by

using a column chromatography technique. The molecular structures of these target compounds and their intermediates were established by using different spectroscopic tools.

Theoretical Study

Density functional theory (DFT) calculations based on the B3LYP/cc-pVDZ level were performed to obtain the optimized molecular geometries as well as the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels of 2-cyano-3-(5-(8-(3,4-ethylenedioxythiophen-5-yl)-2,3-diphenylquinoxalin-5-yl)thiophen-2-yl)acrylic acid (**6**) and 2-cyano-3-(5-(2,3-diphenyl-8-(thiophen-2-yl)quinoxalin-5-yl)thiophen-2-yl)acrylic acid (**7**). The xyz coordinates of the optimized structures of **6** and **7** are included in supplementary material. The calculated HOMO and LUMO levels are delocalized over the molecular backbones (Fig. 1). In ambipolar materials, both hole and electron charge carriers are injected and transported to HOMO–LUMO energy levels. Consistent with the assumptions for ambipolar materials, compounds **6** (HOMO = -5.60 eV, LUMO = -3.04 eV) and **7** (HOMO = -5.83 eV, LUMO = -3.16 eV) have a HOMO orbital ≥ -5.60 eV,

and a LUMO orbital around -3.15 eV (Table I). This suggests that they are compounds with good conductive properties.

Furthermore, the lower ionization potential (IP) of **6** proves stronger electron-donating abilities than **7**. The higher LUMO energy level of the **6** (-3.04 eV for **6** and -3.16 eV for **7**) makes the barrier of electron injection smaller, and thus the charge injection capacity is greater. Comparing derivatives **6** and **7** suggests that **6** is a system with a better charge transfer (CT). The theoretically calculated absorption maxima (λ_{max}) of the investigated molecules **6** and **7** are summarized in Table I.

Compound **6** has the greater ΔG^{inject} (-0.73 eV) while **7** has the smaller value (-0.60 eV) (Table II.). Both ΔG^{inject} obtained is negative for every dye, so the e^- injection from the composed to TiO_2 is impulsive.

This result according to LHE of the **6**, shows that the structure of compound **6** extends the photocurrent reply, in comparison to compound **7**. Compared with **7**, the larger f of **6**, leading to the higher LHE (0.82 for **6** and 0.81 for **7**), compensates well for its green-shift adsorption spectrum. Results show that **6** have the higher V_{oc} (0.96 eV) than compound **7** (0.84 eV), thus the e^- injection is more effective due to the higher excited state linked to the semiconductor conduction band edge. Consequently, compound **6** presents favorable properties to potential application to organic solar cells because of the relatively similar LHE, larger ΔG^{inject} , and V_{oc} .

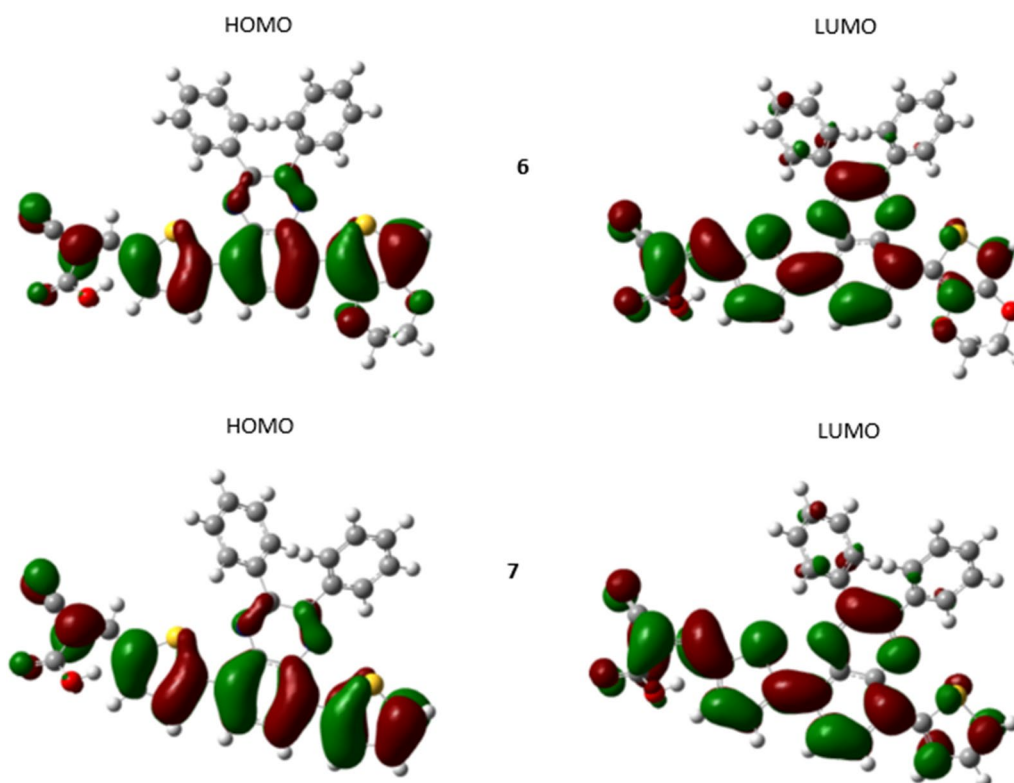


Fig. 1 Frontier molecular orbitals of **6** and **7**.

Table I Theoretical properties of investigated compounds: Eg—bandgap; IP—ionization potential; EA—electron affinity; λ_{\max} —absorption maxima; f —oscillator strength

Compound	HOMO (eV)	LUMO (eV)	Eg (eV)	IP (eV)	EA (eV)	λ_{\max} (nm)	f	Transition
6	− 5.60	− 3.04	2.56	− 6.20	− 2.09	532	0.74	H–L
7	− 5.83	− 3.16	2.67	− 6.45	− 2.20	510	0.73	H–L

Table II Calculated electrochemical parameters for investigated compounds: E^{dye} and $E^{\text{dye*}}$ —oxidation potential energy of the composed in the ground and excited state; LHE—light-harvesting efficiency; ΔG^{inject} —injection driving force; V_{oc} —open-circuit photovoltage

Compound	E^{dye} (eV)	$E^{\text{dye*}}$ (eV)	ΔG^{inject} (eV)	LHE	V_{oc} (eV)
6	5.60	3.27	− 0.73	0.82	0.96
7	5.83	3.40	− 0.60	0.81	0.84

The V_{oc} can be calculated by the analytical equation: $V_{\text{oc}} = E_{\text{LUMO}} - E_{\text{CB}}$.²⁵ E_{CB} : reduction potential of the conduction band of TiO_2 . So, in this study, we use $E_{\text{CB}} = -4.0$ eV for TiO_2 .³⁰

As shown in Fig. 2, the investigated molecules **6** and **7** show wide peaks (300–700 nm), corresponding to π – π^* transition and charge-transfer process within the molecules in the visible light region. The combination of good

absorption and ambipolar electronic properties suggests that they can be used as well in OLED as OPV.

Optical Properties

Figure 3 represents the corresponding absorption spectra of solutions **6** and **7** in THF. As can be noticed, both **6** (blue curve) and **7** (green curve) present an absorption peak situated between 285 nm and 550 nm. Compound **6** has an enlarged absorption spectrum in comparison to compound **7**, which may be due to the higher electron-donating properties of ethylenedioxythiophene than of thiophene ring.

The optical properties of the organic films of **6** and **7** deposited on the PEDOT:PSS/ITO/Glass substrates were evaluated in terms of plotting their transmission spectra in a spectral range between 285 nm and 1200 nm (Fig. 4). It can be seen that for the range from 285 nm to 380 nm, the characteristics are similar for both samples. For the range from

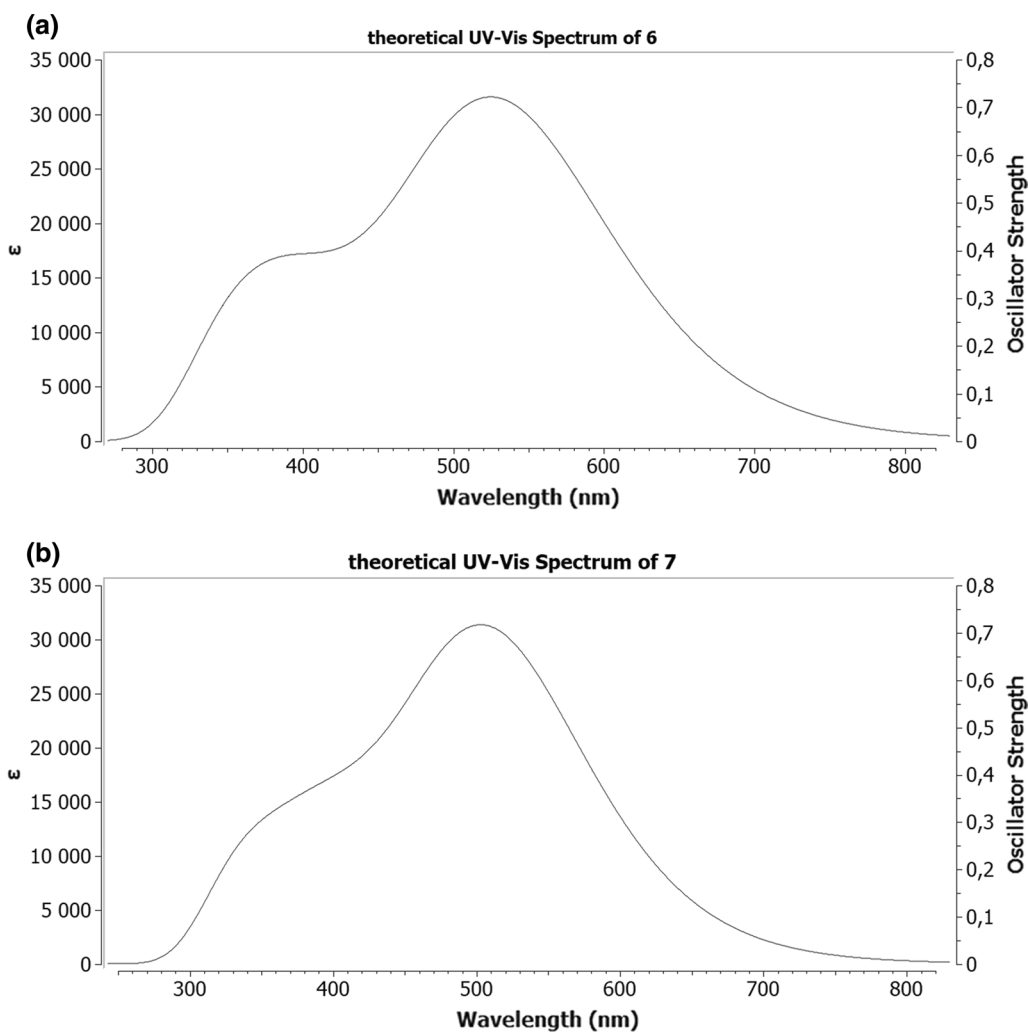


Fig. 2 Theoretical UV-Vis spectrum: (a) of compound **6**; (b) of compound **7**.

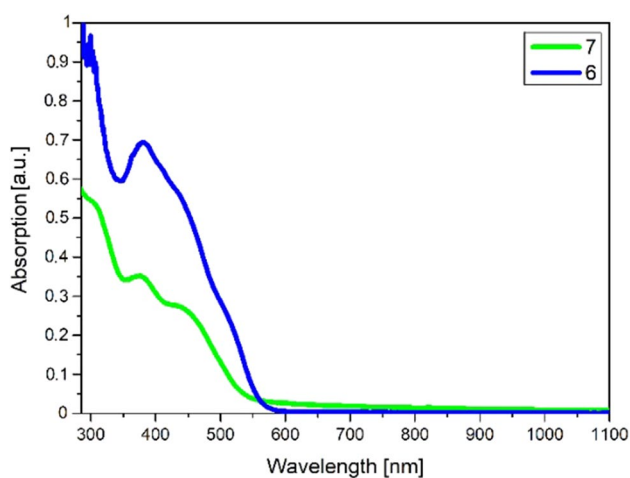


Fig. 3 Absorption spectra for solutions **6** and **7** in THF.

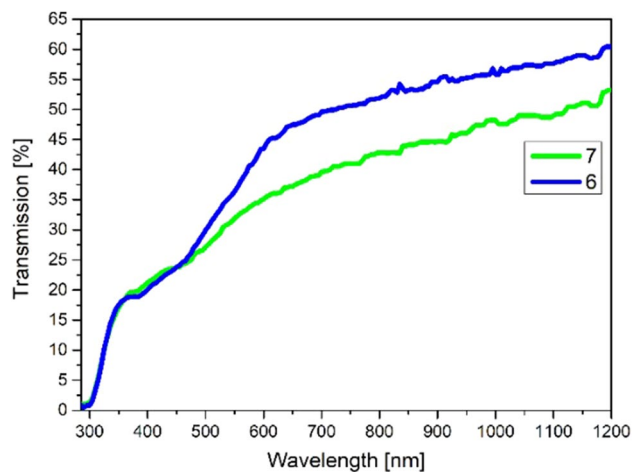


Fig. 4 Transmission spectra for active layers: **6**/PEDOT:PSS/ITO/Glass (blue) and **7**/PEDOT:PSS/ITO/Glass (green) (Color figure online).

285 to 300 nm, the transmission is 0%, because the glass is not transparent under 300 nm wavelength. Above 480 nm, the transmission of sample **6** increases in comparison to data for sample **7**. Sample **6** is more transparent to light than sample **7**. The highest transmission values are reached at 1200 nm.

Materials and Methods

Details of Theoretical Studies

The theoretical studies were performed by applying the density functional theory (DFT).³¹ The calculations were performed utilizing the B3LYP functional^{32–34} and standard cc-pVDZ atomic basis set.³⁵ The absorption spectra we studied applying time dependent DFT (TDDFT).³⁶ All the calculations were carried out using the Gaussian16 suite of codes.³⁷ The molecular graphics were produced applying GausView program.³⁸

Sample Characterization

The spin-coating process was performed using a Speciality Coating Systems Spin Coater G3P-8. The thickness of layers was measured using a Precision Measurement System Form Talysurf 120 made by Taylor Hobson Precision. The measuring probe with a sphere with 2 μm diameter was used. The analysis of the profiles of the samples surface profiles was performed using Talysurf software. Absorption spectra measurements for solutions **6** and **7** in THF were performed using a Optizen Alpha Hybrid Mecasys spectrophotometer. Absorption spectra were recorded at room temperature in the wavelength range of 280–1100 nm. Quartz cuvettes were used. The transmission of radiation for samples were measured using WVASE Ellipsometer in function of spectrophotometer (the light source was a xenon arc lamp). The range of wavelength was from 285 nm to 1200 nm. The measurement was recorded at room temperature.

Chemistry

Indium tin oxide coated glass slide, square (ITO) (surface resistivity 8–12 Ω/sq), poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (1.3 wt.% dispersion in H₂O, conductive grade) (PEDOT:PSS), aluminum (powder, 91%), n-Butyllithium (2.5 M in hexane), 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-thiophene (98%), 3,4-ethylenedioxythiophene (97%), 2-(tributylstannyl)thiophene (98%), bis(triphenylphosphine)palladium (II) dichloride (98%), cyanoacetic acid (99%), piperidine (99%), anhydrous N,N-dimethylformamide (99.8%), phosphorus(V) oxychloride (99%) were purchased from Aldrich.

5,8-Dibromo-2,3-diphenylquinoxaline (98%) was purchased from TCI Europe. Anhydrous potassium carbonate (99%) was received from Chempur. Anhydrous tetrahydrofuran was purchased from POCH. Tetrahydrofuran was dried over Na/benzophenone ketal before use. Other commercially available substances and reagents were used without any prior purification. Preparative column chromatography was performed on the glass column with Acros Organics silica gel for chromatography, 0.035–0.075 mm 60 Å. ¹H NMR and ¹³C NMR spectra were recorded in deuterated chloroform (CDCl₃) on Bruker Avance III 400 MHz Instruments or on Bruker Avance II 600 Instruments, respectively. Chemical shifts were locked to chloroform δH 7.26 (s) and δC 77.16 (t) signals. The molecular weights of the products were determined using a Bruker micrOTOF-Q spectrometer, FWHM-17500, 20 Hz. The percentage composition of the elements was measured on a vario EL cube analyzer from Elementar Americas.

Preparation of 5-bromo-2,3-diphenyl-8-(thiophen-2-yl)quinoxaline (**2**)

Bis(triphenylphosphine)palladium (II) dichloride (PdCl₂(PPh₃)₂) (0.32 g, 0.450 mmol) was added at room temperature under nitrogen atmosphere to a mixture of **1** (1.00 g, 2.27 mmol) and 2-(tributylstannyl)thiophene (0.89 g, 2.39 mmol) in anhydrous THF (50 mL). The resulting mixture was refluxed with stirring for 48 h. Then the reaction mixture was concentrated under reduced pressure, diluted with water, and extracted with EtOAc. The extract was washed with brine, dried over MgSO₄, and concentrated. The residue was purified by silica gel column chromatography (hexane-EtOAc in the gradient of polarity) to give **2** (0.61 g, 61.4%) as a yellow oil. According to³⁹

•¹H NMR (400 MHz, CDCl₃) δ (ppm): δ 8.01 (dd, *J*_r=8.4 Hz, *J*₂=34.4 Hz, 1H), 7.84 (d, *J*=3.6 Hz, 1H), 7.75–7.64 (m, 4H), 7.52 (t, *J*=5.4 Hz, 1H), 7.45–7.33 (m, 7H), 7.169 (t, *J*=4.4 Hz, 1H).

•¹³C NMR (151 MHz, CDCl₃) δ (ppm): δ 154.2, 153.2, 152.7, 151.8, 139.4, 138.8, 138.4, 138.3, 138.2, 138.0, 133.2, 132.8, 130.6, 130.3, 129.7, 129.4, 129.3, 128.5, 128.3, 127.4, 126.8, 126.5, 123.8, 122.5.

•MS (m/z): [M⁺] 442.0135

Elemental analysis: calc. (%) C: 65.02; H: 3.41; N: 6.32; S: 7.23; found: C:65.07; H:3.36; N:6.27; S:7.20.

Preparation of 5-(8-bromo-2,3-diphenylquinoxalin-5-yl)thiophene-2-carbaldehyde (**3**)

DMF (1.12 mL, 14.52 mmol) was added to a three-necked flask, under a nitrogen atmosphere. It was cooled in an ice bath, then POCl₃ (0.25 mL, 2.70 mmol) was added dropwise

and stirred for 40 min at room temperature. Compound **2** (0.92 g, 2.08 mmol) was dissolved in 30 mL of dichloroethane and added to the mixture. The resulting mixture was refluxed with stirring for 24 h. The reaction was terminated by adding 10 mL of cold water and 5 mL of 2 M NaOH. The reaction mixture was then filtered under reduced pressure, and the filtrate was extracted with chloroform. The crude product was purified by column chromatography (hexane-EtOAc in the gradient of polarity) to give **3** (0.152 g, 16.0%) as an orange solid. According to³⁹

- **¹H NMR** (400 MHz, CDCl₃) δ (ppm): δ 9.97 (s, 1H), 8.057 (dd, $J_1=8.00$ Hz, $J_2=33.6$ Hz, 2H), 7.85 (dd, $J_1=4.4$ Hz, $J_2=34.8$ Hz, 2H), 7.69–7.67 (m, 4H), 7.43–7.34 (m, 6H).
- **¹³C NMR** (151 MHz, CDCl₃) δ (ppm): δ 182.1, 155.7, 154.2, 153.4, 152.1, 140.0, 139.3, 138.6, 138.4, 138.2, 137.8, 133.5, 132.6, 130.2, 130.0, 129.9, 129.5, 128.9, 128.7, 128.4, 127.0, 126.5, 126.2, 124.0, 123.5.
- **MS** (m/z): [M⁺] 472.0218
- **Elemental analysis**: calc. (%) C: 63.70; H: 3.21; N: 5.94; S: 6.80; found: C:63.66; H:3.26; N:5.90; S:6.78.

Preparation of 5-(2,3-diphenyl-8-(thiophen-2-yl)quinoxalin-5-yl)thiophene-2-carbaldehyde (**4**)

Bis(triphenylphosphine)palladium (II) dichloride (PdCl₂(PPh₃)₂) (0.117 g, 0.100 mmol) was added at room temperature to a mixture of **3** (0.238 g, 0.505 mmol), potassium carbonate (0.209 g, 1.51 mmol), and 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-thiophene (0.192 g, 0.656 mmol) in toluene (30 mL), MeOH (6 mL), and water (6 mL). The resulting mixture was refluxed with stirring for 48 h under nitrogen atmosphere. Then the reaction mixture was concentrated under reduced pressure, diluted with water, and extracted with EtOAc. The extract was washed with brine, dried over MgSO₄, and concentrated. The residue was purified by silica gel column chromatography (hexane-EtOAc in the gradient of polarity) to give **4** (0.035 g, 14.6%) as a yellow solid.

- **¹H NMR** (400 MHz, CDCl₃) δ (ppm): δ 9.97 (s, 1H), 8.20 (dd, $J_1=8.00$ Hz, $J_2=12.8$ Hz, 2H), 7.94–7.91 (m, 2H), 7.82 (d, $J=4.00$ Hz, 2H), 7.74–7.71 (m, 3H), 7.56 (dd, $J_1=1.20$ Hz, $J_2=1.2$ Hz, 1H), 7.42–7.38 (m, 6H), 7.20 (dd, $J_1=4.00$ Hz, $J_2=5.20$ Hz, 1H).
- **¹³C NMR** (151 MHz, CDCl₃) δ (ppm): δ 182.5, 155.3, 153.7, 151.6, 141.2, 140.8, 138.9, 138.7, 138.3, 137.9, 132.8, 132.3, 130.4, 130.3, 129.7, 129.5, 129.2, 128.7, 128.6, 127.6, 127.2, 126.9, 126.6, 124.5, 124.0.
- **MS** (m/z): [M⁺] 475.0936
- **Elemental analysis**: calc. (%) C: 73.39; H: 3.82; N: 5.90; S: 13.51; found: C:73.34; H:3.80; N:5.87; S:13.47.

Preparation of 5-(8-(3,4-ethylenedioxythiophen-5-yl)-2,3-diphenylquinoxalin-5-yl)thiophene-2-carbaldehyde (**5**)

Bis(triphenylphosphine)palladium (II) dichloride (PdCl₂(PPh₃)₂) (0.021 g, 0.0297 mmol) was added at room temperature under nitrogen atmosphere to a mixture of **3** (0.07 g, 0.148 mmol) and 2-(tributylstannyl)ethylenedioxythiophene (0.096 g, 0.22 mmol) in anhydrous THF (20 mL). The resulting mixture was refluxed with stirring for 72 h. Then the reaction mixture was concentrated under reduced pressure, diluted with water, and extracted with EtOAc. The extract was washed with brine, dried over MgSO₄, and concentrated. The residue was purified by silica gel column chromatography (hexane-EtOAc in the gradient of polarity) to give **5** (0.027 g, 34.2%) as an orange solid.

- **¹H NMR** (400 MHz, CDCl₃) δ (ppm): δ 9.96 (s, 1H), 8.68 (d, $J=8.40$ Hz, 1H), 8.20 (d, $J=8.40$ Hz, 1H), 7.92 (d, $J=4.00$ Hz, 1H), 7.80 (d, $J=4.00$ Hz, 1H), 7.75–7.70 (m, 4H), 7.53–7.48 (m, 2H), 7.41–7.37 (m, 4H), 6.62 (s, 1H), 4.44–4.42 (m, 2H), 4.32–4.30 (m, 2H).
- **¹³C NMR** (151 MHz, CDCl₃) δ (ppm): δ 181.6, 158.3, 155.5, 152.0, 149.7, 145.6, 139.2, 138.6, 137.9, 137.4, 132.9, 131.7, 131.5, 129.4, 128.7, 128.3, 127.8, 127.5, 114.3, 94.0, 93.8, 65.4.
- **MS** (m/z): [M⁺] 533.0768
- **Elemental analysis**: calc. (%) C: 69.90; H: 3.78; N: 5.26; S: 12.04; found: C:69.94; H:3.82; N:5.31; S:12.09.

Preparation of 2-cyano-3-(5-(8-(3,4-ethylenedioxythiophen-5-yl)-2,3-diphenylquinoxalin-5-yl)thiophen-2-yl)acrylic acid (**6**)

In a three-necked round bottom flask, **5** (0.027 g, 0.051 mmol) was dissolved in toluene (20 mL). Cyanoacetic acid (0.013 g, 0.152 mmol) was added in an inert atmosphere of nitrogen. After 15 min piperidine (0.0043 g, 0.051 mmol) was added. The resulting mixture was refluxed with stirring overnight. Then the reaction mixture was concentrated under reduced pressure, diluted with water, and extracted with EtOAc. The extract was washed with brine, dried over MgSO₄, and concentrated. The residue was purified by silica gel column chromatography using dichloromethane-methanol (95:5) as the eluent to give **6** (0.021 g, 70%) as a brown solid.

- **¹H NMR** (400 MHz, CDCl₃) δ (ppm): δ 8.08 (s, 1H), 7.73–7.634 (m, 4H), 7.54–7.51 (m, 4H), 7.48–7.39 (m, 6H), 6.98 (s, 1H), 4.27–4.24 (m, 4H).
- **¹³C NMR** (151 MHz, CDCl₃) δ (ppm): δ 158.7, 154.2, 151.3, 150.1, 145.3, 138.7, 137.5, 130.3, 129.7, 128.5, 127.4, 127.3, 117.5, 114.1, 93.1, 92.8, 65.0.

•MS (m/z): [M⁺] 600.1036

•Elemental analysis: calc. (%) C: 68.10; H: 3.53; N: 7.01; S: 10.69; found: C:68.07; H:3.50; N:7.00; S:10.67.

Preparation of 2-cyano-3-(5-(2,3-diphenyl-8-(thiophen-2-yl)quinoxalin-5-yl)thiophen-2-yl)acrylic acid (7)

In a three-necked round bottom flask, **5** (0.035 g, 0.074 mmol) was dissolved in toluene (20 mL). Cyanoacetic acid (0.019g, 0.222 mmol) was added in an inert atmosphere of nitrogen. After 15 min piperidine (0.0063 g, 0.074 mmol) was added. The resulting mixture was refluxed with stirring overnight. Then the reaction mixture was concentrated under reduced pressure, diluted with water, and extracted with EtOAc. The extract was washed with brine, dried over MgSO₄, and concentrated. The residue was purified by silica gel column chromatography using dichloromethane-methanol (95:5) as the eluent to give **7** (0.032g, 50%) as a yellow solid.

•¹H NMR (400 MHz, CDCl₃) δ (ppm): δ 8.25 (s, 1H), 8.21–8.14 (m, 2H), 7.91–7.87 (m, 2H), 7.83–7.80 (m, 2H), 7.78–7.73 (m, 2H), 7.44–7.37 (m, 9H).

•¹³C NMR (151 MHz, CDCl₃) δ (ppm): δ 159.8, 154.8, 149.6, 144.4, 139.8, 138.2, 137.5, 130.1, 129.2, 128.7, 127.5, 126.2, 117.7, 93.0.

•MS (m/z): [M⁺] 542.0994

•Elemental analysis: calc. (%) C: 70.96; H: 3.54; N: 7.76; S: 11.84; found: C:70.94; H:3.51; N:7.72; S:11.81.

Conclusions

In summary, we designed, synthesized and characterized two 2,3-diphenylquinoxaline derivatives: 2-cyano-3-(5-(8-(3,4-ethylenedioxythiophen-5-yl)-2,3-diphenylquinoxalin-5-yl)thiophen-2-yl)acrylic acid (**6**) and 2-cyano-3-(5-(2,3-diphenyl-8-(thiophen-2-yl)quinoxalin-5-yl)thiophen-2-yl)acrylic acid (**7**). This multi-step synthesis proceeded with good yield. The quantum-chemical results show the bipolar properties of the obtained systems, e.g. narrow energy gap (2.09 and 2.20 eV), low ionization potential (−6.20 and −6.45 eV) and distribution of HOMO / LUMO orbitals. Moreover, experimental results on optical properties correlate well with the ab-initio study. They indicate good absorption in the visible light region (380–550 nm). Theoretical calculations show that **6** have the higher V_{oc} (0.96 eV), ΔG^{inject} (−0.73 eV) than compound **7** (0.84 eV, (−0.60 eV), thus the e[−] injection is more effective due to the higher excited state linked to the semiconductor conduction band edge. Consequently, compound **6** presents favorable properties to

potential application to organic solar cells because of the relatively similar LHE, larger ΔG^{inject}, and V_{oc}.

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Conflict of interest The authors declare that they have no conflict of interest.

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