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Push-Pull Heterocyclic Dyes Based on Pyrrole and Thiophene: Synthesis and Evaluation of Their Optical, Redox and Photovoltaic Properties

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Abstract: Three heterocyclic dyes were synthesized having in mind the changes in the photovoltaic, optical and redox properties by functionalization of 5-aryl-thieno[3,2-*b*]thiophene, 5-arylthiophene and *bis*-methylpyrrolylthiophene π-bridges with different donor, acceptor/anchoring groups. Knoevenagel condensation of the aldehyde precursors with 2-cyanoacetic acid was used to prepare the donor-acceptor functionalized heterocyclic molecules. These organic metal-free dyes are constituted by thieno[3,2-*b*]thiophene, arylthiophene, *bis*-methylpyrrolylthiophene, spacers and one or two cyanoacetic acid acceptor groups and different electron donor groups (alkoxyl, and pyrrole electron-rich heterocycle). The evaluation of the redox, optical and photovoltaic properties of these compounds indicate that 5-aryl-thieno[3,2-*b*]thiophene-based dye functionalized with an ethoxyl electron donor and a cyanoacetic acid electron acceptor group/anchoring moiety displays as sensitizer for DSSCs the best conversion efficiency (2.21%). It is mainly assigned to the higher molar extinction coefficient, long π-conjugation of the heterocyclic system, higher oxidation potential and strong electron donating capacity of the ethoxyl group compared to the pirrolyl moiety.

Keywords: heterocyclic push-pull dyes; thiophene; pyrrole; dye-sensitized solar cells; auxiliary donor/acceptor heterocycles; synthesis

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1. Introduction

Solar energy is a stimulating option for a renewable energy source, among others available, owing to its abundance, simplicity and ability for direct conversion into electricity [1,2].

Dye-sensitized solar cells (DSSCs) belong to the third-generation photovoltaic (PV) devices [3], recently achieving a certified photocurrent conversion efficiency (PCE) of 13% [4]. Although the 1-Sun PCE of DSSCs is lower when compared to other emerging PVs and conventional Si [5], DSSCs are attracting much research interest due to good performance under dim and diffused light, possibility to produce semi-transparent and flexible modules, simple architecture, sustainable components and low manufacturing cost [6–22]; it makes DSSCs very feasible for building-integrated PV glazing [3,6].

Nowadays, with the rapidly increasing number of low-power wireless communication devices, the Internet of Things (IoTs), the development of cordless powering for them has become imperative [23,24]. DSSCs are perfectly fitted for indoor use to address this challenge [25,26]: they display one of the highest among other PV technologies PCE under artificial light—a record of 34.5% of PCE under 1000 lx light was attained recently [4]. DSSCs are safe for residential use as they are free from toxic soluble lead or tin compounds; they can be produced with several true colors and have an attractive appearance for nice and harmonic interior integration. DSSCs devices have started entering the market of indoor PVs [26,27].

The development of new metal-free organic dyes for DSSCs takes much research effort, as properly designed and produced organic dye can display several advantages compared to traditional Ru-complexes [28–33], which are high molar extinction coefficients, easy and cheap synthesis and purification processes and variety and facility of structure alterations, which originate vast options for straightforward tuning of the optoelectronic properties.

Usually, the organic dyes applied have a push-pull structure (donor–π-bridge–acceptor/anchoring group), which promotes charge separation and transfer from the ground to the excited state, wide-ranging spectral sensitivity, photostability, controlled aggregation and charge recombination, appropriate Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) electronic energies and an anchoring group for binding to the surface of a semiconductor [7–22,34–36].

Several studies reveal that heterocyclic molecules of the donor-acceptor type are generally easy to synthesize. Additionally, the introduction of heterocycles with variable electronic structure (electron-deficient or rich) and low aromaticity, into the π-conjugated molecules are used to tune their optoelectronic and photovoltaic properties and improve their thermal and photochemical stability. It is also well known that the position of the heterocyclic nuclei on the π-spacers is an important factor. Both types of heterocycles, electron-rich, such as thiophene and pyrrole, and electron-deficient, such as azole and azine derivatives, i.e., (benzo)thiazole benzothiadiazole, pyridine, etc., can act simultaneously as π-bridges and electron donors or acceptors, respectively [37–53].

Consequently, in the previous two decades, a large amount of investigation regarding the structure/properties relationship of push-pull molecules have been reported due their applications in photovoltaic devices [1–27], nonlinear optics [37,54], Organic Light Emitting Diodes (OLEDs) [55], organic field-effect transistors (OFETs) [56], near infrared absorbing (NIR) dyes [57], etc.

Metal-free heterocyclic dyes bearing functionalized thiophene spacers (oligothiophenes, fused thiophenes, etc.) are usually the most efficient reported sensitizers for DSSC due to their excellent conjugation, charge-transfer properties and smaller geometry relaxation energy [1–27,58–61]. On the other hand, the pyrrole heterocycle has more rarely been used as a conjugated spacer in organic dyes [22,46,62–70], possibly due to its instability, even though it possesses a smaller resonance energy, and could be easily functionalized, not only on the 2-position, but also through the substitution reactions on the N–H bond. In fact, our recent research [39–44,46] as well as reported results of other investigators revealed that the stability of these push-pull systems could be enhanced and their optical and electrochemical properties could be finely adjusted by inserting a pyrrole heterocycle into a π-conjugated system and by alkylation or arylation of the nitrogen of the pyrrole heterocycle [63,64,66–69].

Several acceptor/anchoring moieties, such as phosphoric and sulfonic acid, rhodanine-3-acetic acid, aldehyde, pyridine, etc., can be used in DSSCs. Nevertheless, the most used is carboxylic acid in the form of cyanoacetic acid, due to its stability, easy synthesis and higher photovoltaic efficiencies. These results can be explained due to the coplanarity of this anchoring group with the π-bridge as well as the good coupling with titanium dioxide. It was also demonstrated that correctly designed organic dyes functionalized with two anchors are advantageous to light harvesting, electron (or hole) injection and dark current suppression and they are expected to have better temporal stability on the surface of the electrode compared with the corresponding dyes bearing a single anchoring group [19,22,34–36,48,71].

Earlier, we have communicated the synthesis and application of heterocyclic push-pull sensitizers for DSSCs with several combinations of π-spacers, electron donor and acceptor/anchoring moieties (Figure 1) [46–50].

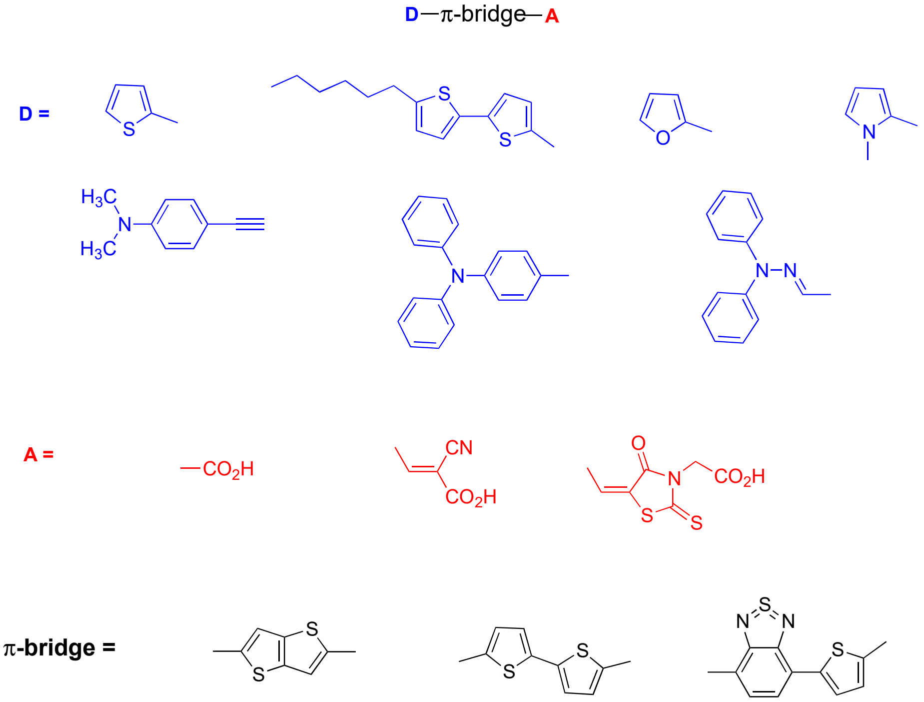


Figure 1. Push-pull heterocyclic sensitizers for DSSCs [46–50].

Taking into account our knowledge on the modification of electrochemical, optical and photovoltaic characteristics of push-pull molecules through the auxiliary electron acceptor or donor effect of heterocycles [39–50], as well as previous studies reported by other groups [7–22,33–36,63–70], we are expanding the research to the preparation of three thiophene and pyrrole-based donor-acceptor heterocyclic molecules. The novel push-pull dyes are constituted by 5-aryl-thieno[3,2-*b*]thiophene, 5-arythiophene and *bis*-methylpyrrolylthiophene π-bridges, with one or two cyanoacetic acid anchoring groups, and different electron-donor moieties (ethoxyl and pyrrole electron-rich heterocycle). Optical and electrochemical properties, as well as the efficacy in DSSCs, are assessed.

2. Materials and Methods

2.1. General

N-Methyl-2-pyrroleboronic acid pinacol ester, 2,5-dibromothiophene and 2-cyanoacetic acid were from Aldrich. All commercially reagents, solvents were used without purification. Precursors 5-(4′-(diethoxy)phenyl]thieno[3,2-*b*]thiophene-2-carbaldehyde **3** [72] and 5-(4′-(1*H*-pyrrol-1″-yl)phenyl)thiophene-2-carbaldehyde **4** [41] were synthesized by us using the experimental procedures described before. Thin-layer chromatography visualization under Ultraviolet-Visible UV light was used to monitor the reaction progress. The purification using silica gel chromatography and the characterization of the dyes, through melting point data, Nuclear Magnetic Resonance (NMR) and UV-visible spectra as well as the study of the redox properties, were obtained as described elsewhere [46,47,50,73].

2.2. Synthesis

2.2.1. General Procedure for the Synthesis of Precursor **1** through Suzuki-Miyaura Cross-Coupling

2,5-Dibromothiophene (0.241 g, 1.0×10^{-3} mol) was coupled with 1-methyl-1*H*-pyrrol-2-yl)boronic acid pinacol ester (0.580 g, 2.4×10^{-3} mol), in a mixture of 1,2-dimethoxyethane (DME) (8 mL), ethanol (2 mL), aqueous 2 M Na_2CO_3 (1.7 mL) and $Pd(PPh_3)_4$ (0.029 g, 3 mol%) at 85 °C under nitrogen. The reaction time (24 h) was determinate by thin layer chromatography (TLC). The reaction mixture was extracted, after cooling, with dichloromethane (3 × 20 mL), followed by extraction with a saturated solution of NaCl

(20 mL). After the separation of the phases the organic layer was washed with water (3 × 10 mL) and with a solution of NaOH (10%) (10 mL). The organic phase obtained was dried ($MgSO_4$) and filtered, and the solvent was removed, giving a crude mixture which was purified using a silica gel chromatography column and mixtures of dichloromethane and light petroleum of increasing polarity affording the pure coupled product **1** [74] **.**

2,5-*bis*(*N*-Methyl-1*H*-pyrrol-2-yl)thiophene **1**. Light green oil (90%). ^{1}H NMR (DMSO-*d*$_6$, 400 MHz) δ 3.74 (s, 6H, 2x NC*H*$_3$), 6.04–6.05 (m, 2H, 2x H-4′), 6.24–6.25 (m, 2H, 2x H-3′), 6.85–6.86 (m, 2H, 2x H-5′), 7.09 (d, 2H, 3- and 4-H, *J* = 4.0 Hz) ppm.

2.2.2. General Procedure for the Synthesis of Aldehyde **2** by Vilsmeier-Haack Formylation

$POCl_3$ (0.460 g, 3.0×10^{-3} mol.) was added to DMF (0.219 g, 3.0×10^{-3} mol) at 0 °C and the mixture was stirred for 5 min at 0 °C. Subsequently, precursor **1** (0.242 g, 1.0×10^{-3} mol.), dissolved in DMF (2 mL), was added dropwise with stirring. The reaction mixture was heated at 60 °C during 4 h, after which the solution was cooled down to room temperature and then transferred gradually into 10 mL of saturated sodium acetate aqueous solution and stirred during 30 min. The organic layer obtained was diluted with dichloromethane (25 mL), washed with saturated $NaHCO_3$ aqueous solution (2 × 25 mL) and dried with anhydrous $MgSO_4$. The crude aldehyde **2** was obtained after evaporation of the organic solvent under reduced pressure and its purification was made using a silica gel chromatography column with mixtures of dichloromethane and light petroleum ether with increasing polarity.

5,5′-(Thiophene-2,5-diyl)*bis*(1-methyl-1*H*-pyrrole-2-carbaldehyde **2**. Yellow solid (50%). ^{1}H NMR (DMSO-*d*$_6$, 400 MHz) δ 4.05 (s, 6H, 2x NCH$_3$), 6.58 (d, 2H, 2x H-4, *J* = 4.4 Hz), 7.10 (d, 2H, 2x H-3, *J* = 4.0 Hz), 7.52 (s, 2H, H-3′, H-4′), 10.9 (s, 2H, 2x CHO). MS (ESI) *m/z* (%) = 299 ([M + H]$^+$, 100). HMRS: *m/z* (ESI) found [M + H]$^+$ 299.0860; $C_{16}H_{15}N_2O_4S$ requires 299.0854.

2.2.3. General Procedure for the Synthesis of Dyes **5–7** by Knoevenagel Condensation of Aldehydes **2–4** with 2-Cyanoacetic Acid

Four drops of piperidine were added to ethanol solution of the aldehydes **2–4** (0.2×10^{-3} mol) and 2-cyanoacetic acid (0.022 g, 0.26×10^{-3} mol). The solution was stirred at reflux during 6 h. After this time the cooled mixture was evaporated to dryness. Recrystallization from diethyl ether gave the pure products. A similar experimental procedure was used for the synthesis of dye **7**, but in this case, 0.65×10^{-3} mol of 2-cyanoacetic acid was used.

2-Cyano-3-(5′-(4″-ethoxyphenyl)thieno[3,2-*b*]thiophen-2′-yl)acetic acid **5**. Orange solid (26%). Mp: 199–200 °C λ_{max} (Ethanol)/nm 399 (ε, M^{-1}cm^{-1} 31,370). ^{1}H NMR (DMSO-*d*$_6$, 400 MHz) δ 1.32 (t, 3H, C*H*$_3$, *J* = 6.9 Hz), 4.04 (q, 2H, CH$_2$, *J* = 6.9 Hz), 7.00 (d, 2H, H-3″, H-5″, *J* = 8.8 Hz), 7.63 (d, 2H, H-2″, H-6″, *J* = 8.8 Hz), 7.82 (s, 1H, H-3′), 7.98 (s, 1H, H-6′), 8.11 (s, 1H, H-3) ppm. Infrared (IR) (Nujol): υ 2206 (C≡N), 1615 (C=O) cm^{-1}. Mass Spectrometry (MS) (ESI) *m/z* (%) = 358 ([M + H]$^+$, 100). High Resolution Mass Spectra (HMRS): *m/z* (ESI) found [M + H]$^+$ 358.0580; $C_{18}H_{16}NO_3S_2$ requires 358.0571.

2-Cyano-3-(5′-(4″-(1*H*-pyrrol-1‴-yl)phenyl)thiophen-2′-yl)acetic acid **6**. Light brown solid (32%). Mp: 223–225 °C. λ_{max} (ethanol)/nm 379 (ε/dm^3 mol^{-1} cm^{-1} 26,858). ^{1}H NMR (DMSO-*d*$_6$, 400 MHz) δ 6.28 (2H, t$_{ap}$, H-3‴, H-4‴, *J* = 4.4 Hz), 7.43 (2H, t$_{ap}$, H-2‴, H-5‴, *J* = 4.4 Hz), 7.63–7.78 (6H, m, H-3′, H-4′, H-2″, H-3″, H-5″, H-6″), 8.07 (1H, s, H-3) ppm. ^{13}C NMR (DMSO-*d*$_6$, 400 MHz) δ 98.2, 111,1, (2 C), 116,5, 118,9 (2 C), 119,7 (2C), 125.0, 127.6, 129.0, 134.4, 140.5, 141.5, 146.6, 152.0, 163.6 ppm. MS (ESI) *m/z* (%) = 321 ([M + H]$^+$, 13), 259 (16), 127 (14), 86 (100). HMRS: *m/z* (ESI) found [M + H]$^+$ 321.0687; $C_{18}H_{13}N_2O_2S$ requires [M + H]$^+$ 321.0692.

3,3-(Thiophene-2″,5″-diyl*bis*(1′-methyl-1*H*-pyrrole-5′,2′-diyl))*bis*(2-cyanoacetic acid) **7**. Black solid (48%). Mp: 207–209 °C. λ_{max} (DMSO)/nm 432 (ε/dm^3 mol^{-1} cm^{-1} 17,517). ^{1}H NMR (DMSO-*d*$_6$, 400 MHz) δ 3.83 (6H, s, 2x CH$_3$), 6.65 (2H, s, 2x H-4′), 7.38 (2H, d, H-3′, *J* = 4.0 Hz), 7.42 (2H, s, H-4″, H-5″), 8.00 (2H, s, H-3) ppm. MS (ESI) *m/z* (%) = 433 ([M + H]$^+$, 100), 102 (2). HMRS: *m/z* (ESI) found [M + H]$^+$ 433.0965; $C_{22}H_{17}N_4O_4S$ requires 433.0970.

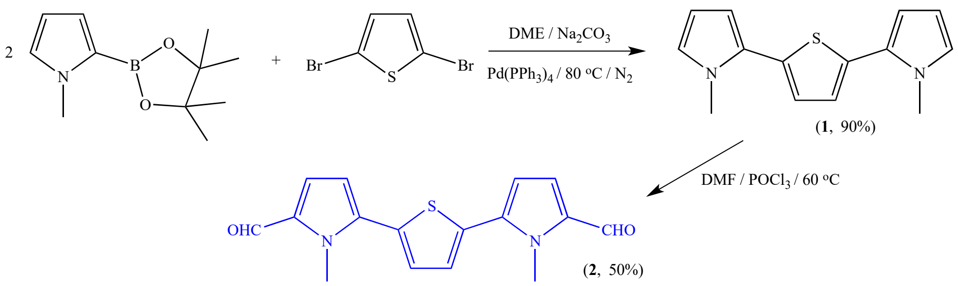
2.3. Preparation and Characterization of DSSCs

The efficacy of new dyes as photosensitizers in DSSCs was assessed. DSSCs were assembled and characterized using procedures described in [50]. Five cells were prepared for each dye and the average parameters are presented.

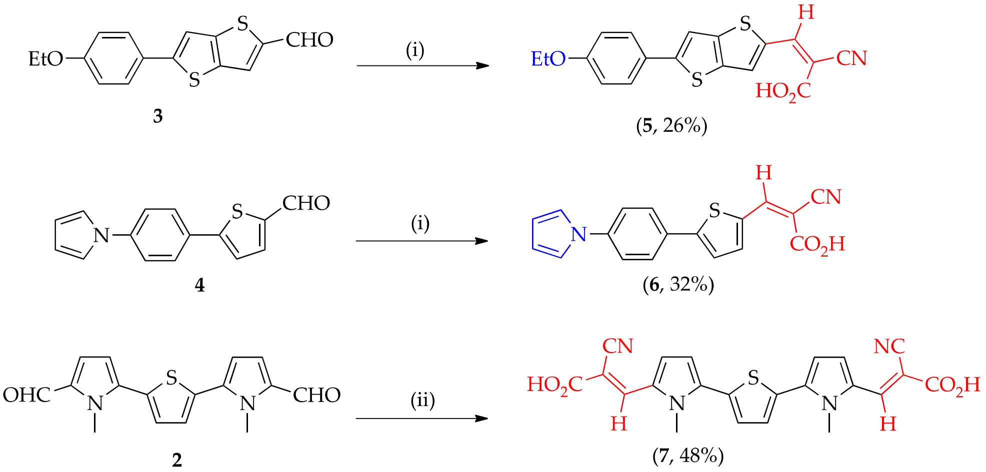
3. Results and Discussion

3.1. Design, Synthesis and Characterization of Dyes **5–7** and for the Aldehyde Precursor 2

Three novel donor-acceptor heterocyclic dyes **5–7** bearing diverse π-spacers constituted by aryl, thiophene and pyrrole nuclei, and different donor groups were produced, keeping in mind the evaluation of their redox, optical and photovoltaic behavior. It is well known that the synthesis and the study of the structure–photovoltaic performance relationship of new metal free organic dyes in DSSCs is of great importance for understanding the prospects of this dyes for application in DSSCs. Moreover, the synthesis and evaluation of novel heterocyclic dyes in which the pyrrole heterocycle is functionalized in positions 1 or 2 performing simultaneously the role of auxiliary electron donor group and π-spacer, are of great interest in order to disclose the best design for application as sensitizers for DSSCs. Therefore, 5-aryl-thieno[3,2-*b*] thiophene **5**, pyrrolylphenylthiophene **6** and *bis*-methylpyrrolylthiophene **7** derivatives, were synthesized and purified through simple synthetic and isolation procedures (Schemes 1 and 2).



Scheme 1. Pyrrole precursors (**1–2**) synthesis by Suzuki-Miyaura coupling and Vilsmeier formylation, respectively.



Scheme 2. Synthesis of dyes **5–7**: (**i**) 2-cyanoacetic acid (1.3 equiv.)/ethanol/piperidine/reflux; (**ii**) 2-cyanoacetic acid (2.5 equiv.)/ethanol/piperidine/reflux.

The aldehyde precursors **2–4** were prepared using several synthetic methodologies developed by our research group. Therefore, aldehyde **2** was synthesized in 50% yield, by Vilsmeier formylation of the precursor 2,5-*bis*(*N*-methyl-1*H*-pyrrol-2-yl)thiophene **1** [74], which in turn was prepared by Suzuki-Myiaura coupling, in 90% yield, of 2,5-

dibromothiophene with 1-methyl-1*H*-pyrrol-2-yl) boronic acid, both commercially available (Scheme 1).

On the other hand, compounds **3** [72] and **4** [41] were prepared directly through Suzuki-Miyaura cross coupling, as described recently by our group of investigation.

Knoevenagel condensation was used for the synthesis of donor-acceptor heterocyclic dyes **5–7** (Scheme 2). Therefore, aldehyde precursors **2–4** and 2-cyanoacetic acid were refluxed for 6 h in ethanol with the addition of four drops of piperidine as a catalyst.

Standard spectroscopic techniques were used to characterize the metal-free organic dyes **5–7** (Table 1). ^{1}H NMR spectra for all compounds showed the characteristic singlet of the vinylic-*H*, which indicates the presence of the ethylenic spacer in these molecules.

Table 1. Reaction yields and data from UV-Vis spectra and ^{1}H NMR for push-pull heterocyclic dyes **5–7**.

Dye	**Yield (%)**	**UV-Vis** [1]		**^{1}H NMR** [2]
		λ_{max} (nm)	**ε ($M^{-1}cm^{-1}$)**	**$H_{vinylic}$ (ppm)**
5	20	399	31,370	8.11
6	32	379	26,858	8.07
7	48	432	17,517	8.00

[1] UV-Vis spectra were performed in ethanol for all compounds, except for compound **7**, where DMSO was used.
[2] For all compounds, NMR spectra were recorded in DMSO-d_6.

Absorption spectra in the UV-Vis range for the four push-pull heterocyclic dyes synthesized was recorded, at room temperature, in an ethanol solution for dyes **5** and **6**, and in a DMSO solution for dye **7** due to solubility issues in other solvents (Figure 2). All compounds exhibit a strong and broad absorption band, with the maximum absorption dependent on the electronic properties of the donor group, strength for electron withdraw of the anchoring group and overall π-conjugation of the molecule. Dye **6** exhibited the shorter wavelength of 379 nm, which might be attributed to the presence of the pyrrole heterocycle as the donor moiety; this is because the nitrogen electron pair is not available for delocalization in the push-pull system due to its involvement in the aromatic system, resulting in a higher electronic band gap [41,46,69,75]. Additionally, this dye has a small conjugation due to its π-spacer constituted by an arylthiophene unit [52]. Dye **7** showed an absorption band centered at 432 nm. An additional absorption band in the long wavelengths manifests itself with an absorption peak at 698 nm. The band with a peak at 432 nm is originated from π-π* transition in the conjugated system; the band centered at 698 nm could be assigned to the absorption by 2,5-*bis*(*N*-methyl-1*H*-pyrrol-2-yl)thiophene moiety.

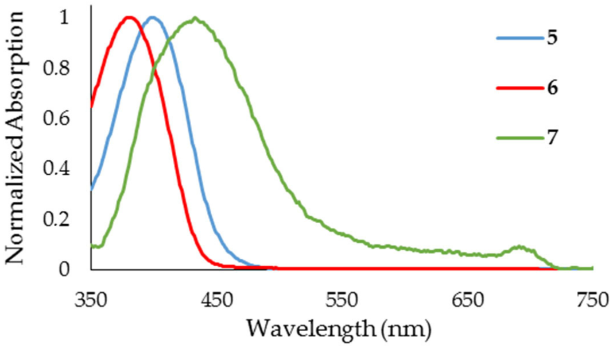


Figure 2. Absorption spectra of push-pull heterocyclic dyes **5** and **6** in ethanol and dye **7** in DMSO, at room temperature.

3.2. Electrochemical Study

The energy levels of the LUMO and HOMO of the dye play an important role for sensitization of DSSCs. For electron injection from the LUMO of a dye into TiO_2 its energy level should be higher than the conduction band edge of semiconductor. Oxidized form of the dye is regenerated only when the energy level of HOMO is below equilibrium potential of the redox couple used. Cyclic voltammetry provided information on the oxidation and reduction potentials for dyes **5–7**, HOMO and LUMO energies [76] and their band gaps calculated as $E_{LUMO}-E_{HOMO}$ [77] (Table 2).

Table 2. Reduction and oxidation potentials; HOMO and LUMO energies and band gaps for dyes **5–7**.

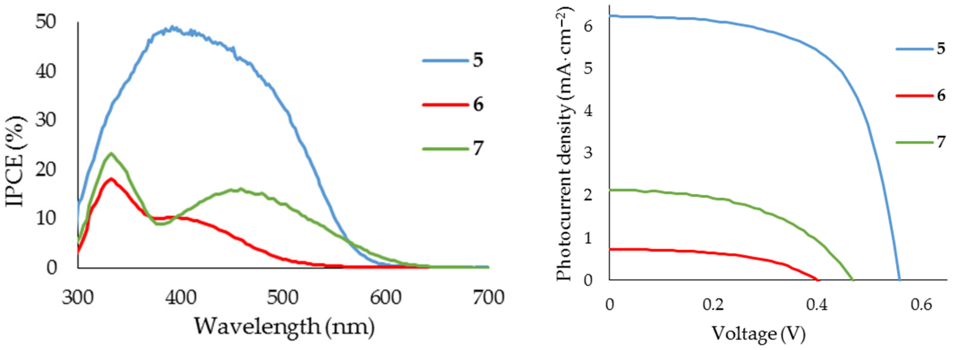
Dye	Reduction [1] (V)	Oxidation [1] (V)	E_{HOMO} [2] (eV)	E_{LUMO} [2] (eV)	Band Gap [3] (eV)
5	−1.65	0.83	−5.22	−2.74	2.48
6	−1.96	0.53	−4.92	−2.43	2.49
7	−1.91	0.25	−4.64	−2.48	2.16

[1] Measured in 1.0 mM solution of the dye in dry DMF with the addition of 0.1 M of $[NBu_4][BF_4]$. Scan rate of potential 0.1 V s^{-1}. Potentials (E) are given vs. Fc^+/Fc redox coupl. [2] $E_{LUMO} = -(E_{red} + 4.39)$ (eV) and $E_{LUMO} = -(4.39 + E_{ox})$ (eV) [46,73,76]. [3] Calculated as $E_{LUMO}-E_{HOMO}$ [77].

The reduction potential for all dyes **5–7** is at −1.65, −1.96 and −1.91 V, respectively (for details, please see the Figures S1–S3), which is less than the TiO_2 conduction band energy (−0.50 V), meaning that the injection of electrons from LUMO of the dye into TiO_2 is permitted energetically [78]. The equilibrium potential of $I_3^-/3I^-$ redox pair is 0.42 V, which indicates that dyes **5** and **6**, with oxidation potentials of 0.83 and 0.53 V, respectively, will accept electrons from I^-, and thus, return to their initial state. Dye **5** has higher oxidation potential than dye **6** and it is regenerated easier. The oxidation potential of dye **7** (0.25 V) is much lower than that of the $I_3^-/3I^-$ redox pair. Therefore, dye regeneration is thermodynamically unfavorable.

3.3. Evaluation of DSSCs Performance

Figure 3a presents photocurrent-voltage (*I–V*) curves of the DSSCs employing as sensitizers the dyes **5–7**. All the DSSCs show typical photodiode behavior. From *I–V* curves, the key parameters of photovoltaic performance (efficiency, η; fill factor, *FF*; short-circuit current density, J_{SC} and open circuit voltage, V_{OC}) of the DSSCs were calculated and presented in Table 3.



(**a**) (**b**)

Figure 3. *I–V* curves (**a**) and IPCE (**b**) of the DSSCs prepared using dyes **5–7**.

Table 3. Photovoltaic parameters of DSSCs sensitized with molecules **5–7**.

Dye	V_{OC} (V)	J_{SC} (mA·cm^{-2})	*FF* (%)	η (%)
5	0.56	6.24	0.63	2.21
6	0.37	0.64	0.50	0.13
7	0.44	1.74	0.49	0.40

The lowest efficiency of DSSCs was observed for the cell sensitized with dye **6** (0.13%). The lowest values of open circuit voltage (0.37 V) and short-circuit current density (0.64 mA·cm^{-2}) were also observed for the DSSC sensitized with dye **6**. This is in accordance with data obtained by cyclic voltammetry—the regeneration of the dye to its fundamental state being inefficient will hinder the injection of electrons into the semiconductor. Quantum yield of the photocurrent in the DSSC sensitized with dye **6** is less than 10% in spectral region above 370 nm (Figure 3b), confirming the low ability of photoexcited dye to inject electrons into TiO_2.

Dye **7** exhibited an intermediate performance as a sensitizer with a DSSC photovoltaic efficiency of 0.40%. The best efficiency of this series of DSSCs, 2.21%, was achieved using dye **5**. The IPCE response of this cells is significantly higher and broads up to 580 nm. Such a feature is attributed to the strong anchoring and electron withdrawing ability of the 2-cyanoacetic acid, long π-conjugation of the heterocyclic system and the high molar extinction coefficient of the dye (31,370 M^{-1}cm^{-1}).

4. Conclusions

Three donor-acceptor heterocyclic dyes **5–7** bearing diverse π-spacers (aryl, thiophene, pyrrole), and different number of anchoring groups, were prepared having in mind the evaluation of the redox and optical properties as well as the photovoltaic performance in DSSCs. All heterocyclic dyes were synthesized by a combination of several methodologies, such as Suzuki-Miyaura cross coupling, Vilsmeier formylation, and Knoevenagel condensation, and characterized using standard spectroscopic techniques.

The absorption spectroscopy study of all compounds exhibited strong and broad bands of absorption, with the wavelength of maximum absorption dependent on the ability for donation of electrons of the donor group, the strength of the acceptor/anchoring group to withdraw electrons, and on the overall π-conjugation of the dye.

The prepared dyes were used as sensitizers in nanocrystalline TiO_2 DSSCs, revealing photovoltaic conversion efficiencies in the range of 0.13%–2.21%. Dye **5**, based on aryl-thieno[3,2-*b*]thiophene spacer, functionalized with an ethoxyl donor group and a cyanoacetic acid anchoring moiety/electron acceptor group, exhibited the highest overall conversion efficiency (2.21%) as sensitizer, which is ascribed to long π-conjugation of the heterocyclic system, higher oxidation potential, higher molar extinction coefficient and strong withdrawing of electrons and anchoring ability of the cyanoacetic acid. Electrochemical study of dyes **5–7** by cyclic voltammetry revealed that for dye **7**, the oxidation potential is lower than that of the redox couple I^-/I_3^-, indicating an inefficient regeneration of this dye from its oxidized state.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/coatings12010034/s1. Figure S1. Cyclic voltammetry plots of compound 2-cyano-3-(5′-(4″-ethoxyphenyl)thieno[3,2-b]thiophen-2′-yl)acetic acid (5), in dry DMF (C = 10^{-4} M); Figure S2. Cyclic voltammetry plots of compound 2-cyano-3-(5′-(4″-(1H-pyrrol-1‴-yl)phenyl)thiophen-2′-yl)acetic acid (6), in dry DMF (C = 10^{-4} M); Figure S3. Cyclic voltammetry plots of compound 3,3-(thiophene-2″,5″-diyl-bis(1′-methyl-1H-pyrrole-5′,2′-diyl))-bis(2-cyanoacetic acid) (7), in dry DMF (C = 10^{-4} M). All the experiments were performed using glassy carbon as working electrode, a platinum wire as counter electrode, and acetonitrile Ag/Ag^+ electrode as reference. [NBu4][BF4] (0.1 M) was used as supporting electrolyte and the collected data were referenced to the potential of Fc/Fc^+ couple.

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