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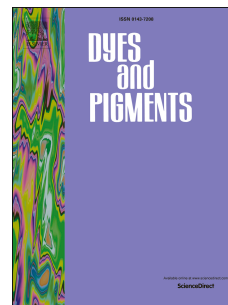
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# Accepted Manuscript

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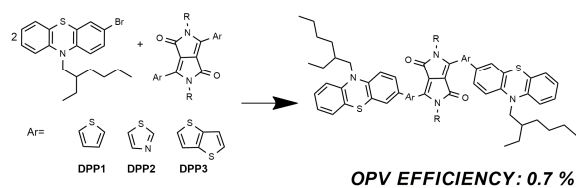
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**DIRECT HETEROARYLATION**

**Novel low bandgap phenothiazine functionalized DPP derivatives prepared by direct heteroarylation: application in bulk heterojunction organic solar cells**

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**Abstract**

The synthesis by direct heteroarylation of three novel low bandgap donor-acceptor-donor molecules is reported herein. The molecules are based on three different diketopyrrolo-pyrrole (DPP) electron deficient cores, functionalized with different electron rich heteroarenes, (thiophene, thiazole and thienothiophene) and symmetrically linked to two terminal donor phenothiazine rings. The optical properties of the synthesized dyes have been measured both in solution and as thin film and a focus has been given on the study of optoelectronic properties as a function of the different heteroarenes (thiophene, thiazole or thienothiophene) functionalizing the DPP core. Bandgap values as small as 1.55 eV have been observed. The energy of the Frontier orbitals has been estimated by means of electrochemical characterization. The electronic properties of the reported molecules have been investigated more in details by computational analysis performed at the DFT level. The new dyes

were used as donor materials in BHJ solar cells and the photovoltaic characterization of these devices led to a maximum power conversion efficiency of 0.7 %.

**Keywords:** phenothiazine, diketopyrrolopyrrole, direct heteroarylation reaction, organic solar cells.

## 1. Introduction

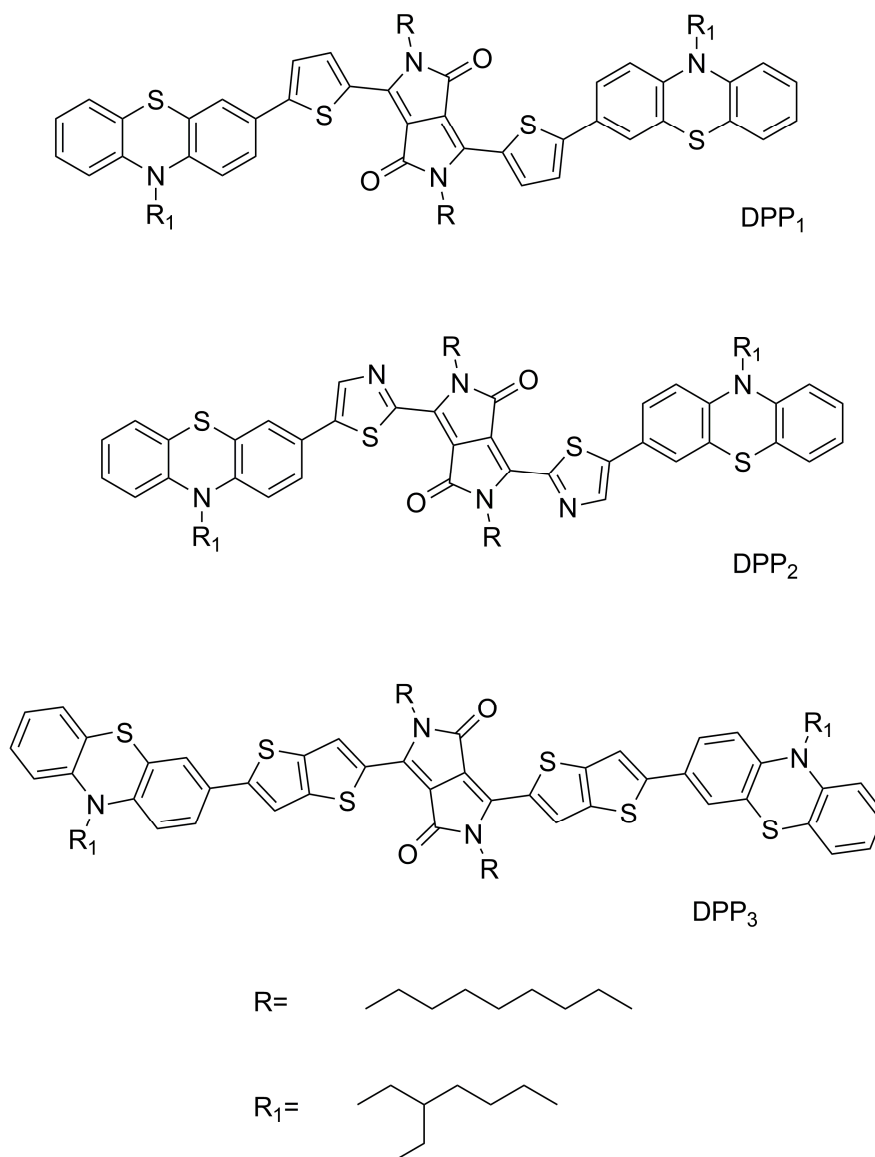
In the past 20 years, bulk-heterojunction (BHJ) solar cells have been mostly based on polymeric donor materials because they offer, upon proper processing conditions, optimal phase separation in blends with fullerene acceptor derivatives.[1–8] The intense study on this class of materials has led to a considerable enhancement of power conversion efficiency (PCE), up to values approaching 12 %.[9,10] Small molecules have been relatively less investigated, mainly because of their lower film forming ability and lower conversion performances. More recently, a growing interest has been observed in solution process BHJ solar cells based on small molecules,[11–14] principally because of an intrinsic limitation of polymeric donor materials: the same polymer prepared in different batches can in fact show different molecular weight and polydispersity index and therefore, slightly different properties influencing device performances. In contrast, small molecules can offer a defined molecular structure, a controlled purity and also, by using specific solution-based deposition techniques, a higher charge carrier mobility.[15,16]

Small molecules should fulfill several features to be good candidates as active layer donor materials in BHJ solar cells, among which a good film forming ability, good charge transport, matched electronic levels and, not least, the ability to widely absorb solar radiation. The largest part of solar photons is emitted between 400 and 800 nm; most of  $\pi$ -conjugated organic systems absorb only in the visible part of spectrum and so, molecules able to absorb also in the 600-800 nm region are highly desirable in order to harvest higher fractions of solar photons. To obtain such moderate to low bandgap materials, one of the strategies is to insert in the conjugated molecular backbone, an

alternation of electron deficient and electron-rich units,[17] following an approach successfully used for other classes of advanced materials, such as optoelectronic compounds.[18,19] This alternation is generally achieved by coupling electron deficient and rich blocks through palladium catalyzed C-C coupling reactions, in which, typically, one arene endowed with a proper leaving group (Br or I, for example) reacts with a second arene functionalized with organometallic groups ( $\text{SnR}_3$ ,  $\text{B(OR)}_3$ ,  $\text{MgX}$ , etc.).[20–22] More recently, direct heteroarylation has emerged as an efficient alternative synthetic tool for C-C coupling:[23–25] The advantage of this type of reaction is that no organometallic derivative is required so that the overall cost and toxicity of the synthetic procedure are noticeably reduced. Despite the recent progress made on the design of molecular systems for organic photovoltaic devices, there is still a need for development of new conjugated building blocks, able to bring new physical-chemical optoelectronic properties. Phenothiazine rings for instance has been relatively scarcely investigated in the organic photovoltaic field. The phenothiazine ring contains electron-rich nitrogen and sulfur atoms and can be considered as an electron-rich building block; it has been widely used, in combination with electron deficient groups, for the realization of low band gap push-pull dyes employed as photosensitizers in dye sensitized solar cells,[26–29] leading to high efficiencies up to 8 %. Phenothiazine containing polymers are also reported in the literature for applications in the field of OLED,[30,31] as NIR emitting materials,[32] and BHJ solar cells, as donor materials.[33–35] To the best of our knowledge, there are only two paper dealing with phenothiazine-based small molecules for use as donor material in BHJ solar cells.[36,37] In ref. 36, two phenothiazine moieties functionalized a pyran electron acceptor core and a power conversion efficiency of 0.28 % was obtained. This last result prompted us to design novel molecules with a similar structure but using a stronger electron-acceptor group as diketopyrrolopyrrole: in particular we report here novel molecules where electron-rich phenothiazine units are symmetrically coupled, as end-capping groups, to several diketopyrrolopyrrole (DPP) derivatives, acting as an electron-deficient moiety. The new dyes are obtained by palladium-catalyzed direct heteroarylation of DPP derivatives with 3-bromo-*N*-

alkylphenothiazine. The structures of the new compounds are shown in Figure 1. DPP is an electron-deficient building block, characterized by a planar geometry favorable for  $\pi$ - $\pi$  stacking interactions, widely used in the synthesis of both low bandgap polymers and small molecules that have been used as organic semiconductors in different electronic devices such as organic field effect transistors (OFET), organic light emitting (OLED) and organic photovoltaic (OPV) devices.[38–48] DPP is structurally based on 2,5-dihydropyrrolo[4,3-*c*]pyrrole-1,4-dione, functionalized in position 3 and 6 with aromatic substituents. DPP derivatives functionalized with electron-rich aromatic groups have proved as efficient platform for direct heteroarylation coupling reactions:[49,50] the strong electron withdrawing ability of DPP is in fact able to activate the protons in position 5 of the heteroaromatic rings.

The synthesized molecules have been optically characterized and their frontier orbitals' energies, calculated from electrochemical measurements. The electronic structures of the molecules have been investigated more in details by DFT calculations. The charge mobility of the new dyes was investigated by realizing and characterizing organic field effect transistors (OFETs). The synthesized materials have then been used as donor materials in the fabrication of BHJ solar cells, in combination with PC<sub>71</sub>BM as electron acceptor material. The fabricated cells efficiencies were measured under normalized simulated solar radiation.



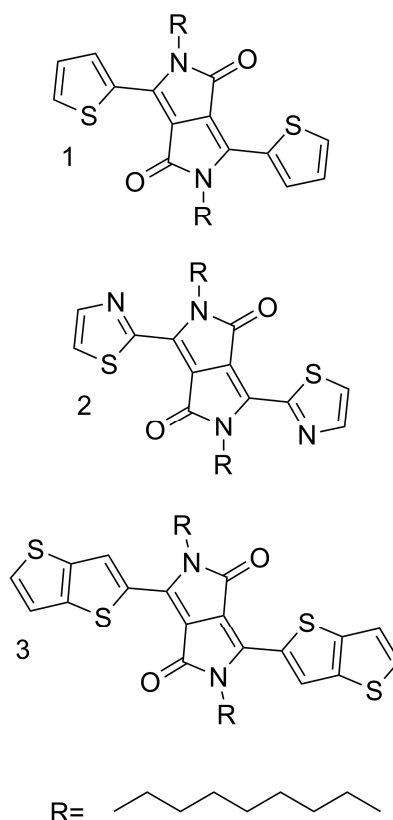
**Figure 1.** Chemical structures of the synthesized molecules

## 2. Materials and methods

### 2.1 Synthesis

All reagents and chemicals were purchased from commercial sources and used without further purification. Diketopyrrolopyrrole precursors, **1**, **2** and **3** (shown in Figure 2) were prepared according to reported procedures.[38,51]





**Figure 2.** Chemical structures of the diketopyrrolopyrrole precursors

#### **9-(2-Ethylhexyl)-9H-phenothiazine (4)**

NaH (60% wt in mineral oil, 1.2 eq., 4.80 g, 120 mmol) was suspended in anhydrous DMF (70 mL) at 0°C and stirred under nitrogen atmosphere. After 10 min, phenothiazine (1.0 eq., 20.0 g, 100 mmol) dissolved in anhydrous DMF (30 mL) was added. The system was kept under stirring in an ice bath. After 1 h, 2-ethylhexylbromide (1.0 eq., 23.17 g, 120 mmol) was added dropwise in the system, the ice bath was removed and the reaction was left overnight at room temperature. The mixture was then quenched with ammonium chloride dilute aqueous solution (200 mL) and extracted with petroleum ether (3x100 mL). The organic phase was then washed with brine and water, dried over  $\text{Na}_2\text{SO}_4$  anhydrous and the solvent removed at reduced pressure. The resulting crude oil was purified by silica gel liquid chromatography (petroleum ether, PE).

A colorless oil was obtained. Yield: 78%.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  = 0.79 (m, 6H); 1.32 (m, 8H); 1.78 (m, 1H); 3.88 (d, 2H,  $J$  = 8.0 Hz); 6.77 (d, 2H,  $J$  = 8.4 Hz); 6.90 (t, 2H,  $J$  = 7.6 Hz); 7.10-7.12 (m, 4H).

<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$  = 10.4; 13.9; 22.9; 23.9; 28.5; 30.7; 35.7; 50.9; 115.8; 122.2; 125.6; 127.0; 127.4; 145.7.

### ***3-Bromo-9-(2-ethylhexyl)-9H-phenothiazine (5)***

Compound **4** (1.0 eq., 10 g, 32.1 mmol) was solved in dry DMF (20 mL); a solution of N-bromosuccinimide (1.0 eq., 5.71 g, 32.1 mmol) in dry DMF (25 mL) was then poured dropwise in the phenothiazine solution. The system reacted overnight at room temperature, in the dark. The solution was then poured in water (200 mL) and extracted with diethyl ether (3x100 mL). The organic phase was washed with brine and water, dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent removed at reduced pressure. The resulting crude oil was purified by silica gel liquid chromatography (PE). A colorless oil was obtained. Yield: 49%.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  = 0.78 (m, 6H); 1.31 (m, 8H); 1.76 (m, 1H); 3.87 (d, 2H,  $J$  = 8.0 Hz); 7.11 (m, 5H); 7.78 (s, 2H).

<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$  = 129.7; 127.6; 127.3; 122.7; 117.0; 116.0; 114.4; 77.4; 77.0; 76.5; 51.3; 35.9; 30.6; 28.6; 24.1; 23.1; 13.9; 10.5.

### ***3,6-Bis(5-(10-(2-ethylhexyl)-10H-phenothiazin-3-yl)thiophen-2-yl)-2,5-dioctyl-2,5-dihydropyrrolo-[3,4-c]pyrrole-1,4-dione (DPP1)***

In a Schlenk system, **1** (1.0 eq., 158 mg, 0.30 mmol) was solved in dry toluene (1.4 mL) and mixed with a solution of compound **5** (2.4 eq., 281 mg, 0.72 mmol) dissolved in dry toluene (1.6 mL). Cs<sub>2</sub>CO<sub>3</sub> (2.4 eq., 235 mg, 0.72 mmol), 2,2-Dimethylpropionic acid (0.4 eq., 12 mg, 0.12 mmol), *trans*-Bis(acetato)bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II) (Herrmann Beller catalyst, 8 mol%, 22 mg, 0.024 mmol), Tris(*o*-methoxyphenyl)phosphine (16 mol%, 0.017 g, 0.048 mmol) were then added in the mixture reaction. The system reacted during 16 h at 120°C, in the dark,

under inert environment. The resulting product was purified by silica gel liquid chromatography (CH<sub>2</sub>Cl<sub>2</sub>:PE / 50:50). A blue solid was recovered. mp: 170 °C. Yield 52%.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ = 0.88-0.93 (m, 18H, -CH<sub>3</sub>); 1.31-1.49 (m, 36H, -CH<sub>2</sub>); 1.74-1.84 (m, 4H, -CH<sub>2</sub>); 1.92-2.00 (m, 2H, -CH<sub>2</sub>); 3.76-3.78 (d, 4H, -NCH<sub>2</sub>, *J* = 7.2 Hz); 4.09-4.14 (t, 4H, -NCH<sub>2</sub>, *J* = 7.5 Hz); 6.87-6.99 (m, 6H, Ar-H); 7.17-7.22 (m, 4H, Ar-H); 7.35-7.36 (d, 2H, HTh, *J* = 4.2 Hz); 7.45-7.46 (m, 4H, Ar-H); 8.95-8.96 (d, 2H, HTh, *J* = 4.2 Hz).

<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75 MHz): δ = 161.4; 149.1; 146.4; 145.1; 139.1; 136.8; 127.6; 126.8; 125.1; 124.8; 122.9; 116.1; 107.9; 51.3; 31.8; 30.8; 30.1; 28.6; 27.0; 24.1; 23.1; 22.6; 14.1; 14.0; 10.5.

ATR-FTIR (neat, cm<sup>-1</sup>): 2926; 2856; 1656; 1557; 1457; 1394; 1327; 1249; 1223; 1155; 1099; 1042; 871; 805; 747; 732.

HRMS ESI-TOF *m/z* calculated for C<sub>70</sub>H<sub>86</sub>N<sub>4</sub>O<sub>2</sub>S<sub>4</sub> [M]: 1142.5638; found: 1142.5695.

***3,6-Bis(5-(10-(2-ethylhexyl)-10H-phenothiazin-3-yl)thiazol-2-yl)-2,5-dioctyl-2,5 dihydropyrrolo-[3,4-c]pyrrole-1,4-dione (DPP2)***

The synthetic procedure was the same used for **DPP1** synthesis with **2** used as **DPP** precursor. The resulting product was purified by silica gel liquid chromatography (CH<sub>2</sub>Cl<sub>2</sub>:PE:Toluene / 20:70:10). The silica gel has previously been deactivated with triethylamine 10%. A blue solid was obtained. mp: 168°C. Yield 70%.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ = 0.78-0.84 (m, 18H, -CH<sub>3</sub>); 1.20-1.42 (m, 36H, -CH<sub>2</sub>); 1.62-1.72 (m, 4H, -CH<sub>2</sub>); 1.82-1.90 (m, 2H, -CH<sub>2</sub>); 3.69-3.70 (d, 4H, -NCH<sub>2</sub>, *J* = 5.4 Hz); 4.34 (t, 4H, -NCH<sub>2</sub>, *J* = 7.2 Hz); 6.76-6.91 (m, 6H, Ar-H); 7.08-7.13 (m, 4H, Ar-H); 7.39-7.42 (m, 4H, Ar-H); 8.04 (s, 2H, HTz).

<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75 MHz): δ = 161.0; 153.0; 146.8; 144.9; 143.8; 139.4; 136.8; 126.8; 126.4; 125.8; 125.1; 124.7; 123.0; 116.3; 116.1; 110.4; 51.3; 42.9; 36.0; 31.9; 30.6; 29.8; 29.3; 27.0; 24.1; 23.0; 22.6; 14.1; 14.0; 10.6.

ATR-FTIR (neat,  $\text{cm}^{-1}$ ): 2955; 2923; 2854; 1678; 1583; 1574; 1479; 1455; 1250; 1219; 1095; 871; 853; 813; 746; 728.

HRMS ESI-TOF  $m/z$  calculated for  $\text{C}_{68}\text{H}_{84}\text{N}_6\text{O}_2\text{S}_4$  [M]: 1145.5539; found: 1144.5550.

**3-(5-(10-(2-Ethylhexyl)-10H-phenothiazin-3-yl)thieno[3,2-b]thiophen-2-yl)-6-(5-(10-(2-ethylhexyl)-10H-phenothiazin-3-yl)thieno[3,2-b]thiophen-3-yl)-2,5-dioctyl-2,5-dihydropyrrolo-[3,4-c]pyrrole-1,4-dione (DPP3)**

The synthetic procedure was the same used for **DPP1** synthesis with **3** used as **DPP** precursor. The resulting product was purified by silica gel liquid chromatography ( $\text{CH}_2\text{Cl}_2$ :PE / 50:50). A blue solid was recovered. mp: 180°C. Yield 15%.

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  = 0.78-0.84 (m, 18H,  $-\text{CH}_3$ ); 1.18-1.41 (m, 36H,  $-\text{CH}_2$ ); 1.68-1.79 (m, 4H,  $-\text{CH}_2$ ); 1.85-1.93 (m, 2H,  $-\text{CH}_2$ ); 3.67-3.69 (d, 4H,  $-\text{NCH}_2$ ,  $J = 6.6$  Hz); 4.04-4.09 (t, 4H,  $-\text{NCH}_2$ ,  $J = 8.1$  Hz); 6.78-6.91 (m, 6H, Ar-H); 7.08-7.13 (m, 4H, Ar-H); 7.34-7.36 (m, 4H, Ar-H); 7.31 (s, 2H, HTh); 9.28 (s, 2H, HTz).

$^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  = 165.1; 145.0; 142.5; 138.2; 134.8; 130.4; 128.1; 127.2; 126.2; 124.6; 123.8; 122.8; 122.2; 119.2; 118.7; 115.0; 63.8; 42.3; 36.4; 34.2; 31.1; 29.3; 27.1; 26.3; 23.0; 22.7; 14.1; 11.6.

ATR-FTIR (neat,  $\text{cm}^{-1}$ ): 2954; 2923; 2853; 1657; 1549; 1455; 1424; 1397; 1329; 1283; 1270; 1249; 1220; 1095; 1038; 870; 804; 745; 731.

HRMS ESI-TOF  $m/z$  calculated for  $\text{C}_{74}\text{H}_{86}\text{N}_4\text{O}_2\text{S}_6$  [M]: 1254.5070; found: 1254.5085.

## 2.2 Chemical Physical characterization

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded with Bruker 300 MHz spectrometers, with  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts reported in  $\delta$  (ppm) relative to  $\text{CDCl}_3$  (7.26 and 77.16 respectively). DSC analyses were performed with a TA Instruments Q1000 instrument, operating at a scanning rate of 5°C/min

on heating and on cooling. Solution and thin film UV-Visible spectra were recorded using a Shimadzu UV-3600 dual-beam grating spectrophotometer with a 1 cm quartz cell. Thin films of small molecules were prepared by drop casting from a dichloromethane (DCM) solution on glass substrates. FTIR spectra were recorded in the attenuated total reflectance (ATR) mode on a Nicolet 380 FTIR spectrometer, in the range  $400 - 4000 \text{ cm}^{-1}$ , as the average of 64 scans with  $4 \text{ cm}^{-1}$  resolution. The samples were directly deposited on the ATR crystal and carefully pressed to ensure a good contact. The background was recorded with the empty ATR crystal in air. HRMS measurements have been recorded on a Bruker micrOTOF-Q mass spectrometer.

### 2.3 Electrochemical characterization

Redox potentials of the dyes were determined by cyclic voltammetry in deoxygenated DCM solutions, containing 0.1 M tetrabutylammonium hexafluorophosphate, at a concentration range of about 1 mM and at rt. Potentials are given versus the saturated calomel electrode (SCE) and standardized vs ferrocene (Fc) as internal reference. The scan rate is of  $100 \text{ mV}\cdot\text{s}^{-1}$ . For all the investigated molecules, the peak potentials onset is considered.

### 2.4 Computational analysis

Density functional theory (DFT) calculations have been performed using SPARTAN 10 ([www.wavefun.com](http://www.wavefun.com)) at the B3LYP/6-311+G\* level of theory in vacuum. Alkyl side-chains were replaced by methyl groups for the calculations to keep a reasonable calculation time. The frontier orbital calculations were performed in the optimized geometry.

### 2.5 BHJ solar cells fabrication

Bulk heterojunction devices were elaborated using the different small molecules synthesized as electron-donor and PC<sub>71</sub>BM as electron-acceptor. Chlorobenzene (CB) was used as solvent with small molecule concentrations ranging from 4 to 5 mg/mL. The standard device structure was as follows: ITO/PEDOT:PSS(40nm)/electron-donor molecule:PC<sub>71</sub>BM/Al(120 nm). Indium tin oxide (surface resistance lower than  $20 \text{ }\Omega/\text{sq}$ ) coated glass was used as a transparent substrate. Substrates

were cleaned sequentially by ultrasonic treatment in acetone, isopropyl alcohol, and deionized water for 15 minutes each. After an additional cleaning for 30 minutes under ultra-violet generated ozone, PEDOT-PSS was spin coated at 1500 rpm for 60s. PEDOT-PSS was then thermally annealed for 30 minutes at 140°C under nitrogen atmosphere. The chlorobenzene dye:PC<sub>71</sub>BM solutions were stirred for at least 24 hours at 50 °C before spin-coating. The small molecules:PC<sub>71</sub>BM weight ratio was set to 1:2. All active layers have been spin-coated in the following conditions: a first 120 seconds step (speed: 2000 rpm, acceleration: 600 rpm/s) followed by a second 60 seconds step (speed: 2500 rpm, acceleration: 600 rpm/s). A post-deposition thermal annealing process (for 5 or 10 minutes from 100 to 120°C) was performed after the electrode (Al) thermal evaporation. Each device contained four 12 mm<sup>2</sup> diodes, the surface of each diode being carefully defined by a shadow mask. The photovoltaic device elaboration and their characterizations were performed in glove boxes. Current versus Voltage (J-V) characteristics were measured using a source measurement unit Keithley 2400 under darkness and under AM1.5G (100 mW·cm<sup>-2</sup>) illumination. The standard illumination was provided by a Class A Lot Oriel solar simulator (550 W filtered Xe lamp) and the illumination power was calibrated using a reference silicon solar cell.

## 2.6 Field effect mobility measurements.

Bottom contact field-effect transistors (FETs) were elaborated on commercially available pre-patterned test structures whose source and drain contacts were composed of a 30 nm thick gold layer on top of a 10 nm thick Indium Tin Oxide (ITO) layer. A 230 nm thick silicon oxide was used as gate dielectric and n-doped ( $3 \times 10^{17} \text{ cm}^{-3}$ ) silicon crystal as gate electrode. The channel length and channel width were 20  $\mu\text{m}$  and 10 mm, respectively. The test structures were cleaned in acetone and isopropyl alcohol and subsequently for 30 minutes in an ultra-violet ozone system. Then, hexamethyldisilazane (HMDS) was spin coated (500 rpm for 5 s and then 4000 rpm for 50 s) under a nitrogen atmosphere and followed by an annealing step at 130°C for 10 minutes. Finally, 5

mg/mL anhydrous chloroform solutions of the dyes **DPP1**, **DPP2** and **DPP3** were spin coated (1250 rpm for 60s and 2250 rpm for 60s) to complete the FET devices. The samples were then left overnight under vacuum ( $<10^{-6}$  mbar) to remove residual solvent traces. Both, the FET elaboration and characterizations were performed under a nitrogen atmosphere. The transistor output and transfer characteristics were recorded using a Keithley 4200 semiconductor characterization system. The charge carrier mobility was extracted in the linear regime using the usual formalism on FET devices annealed at the same temperature as the optimized photovoltaic devices.

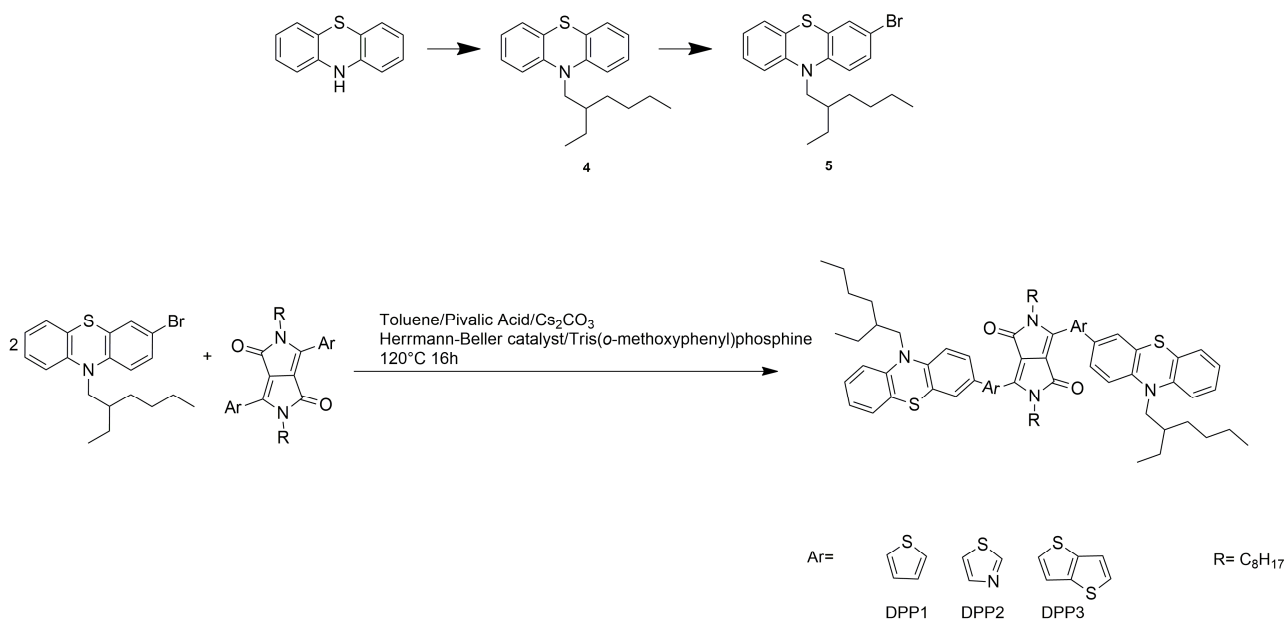
### 3. Results and discussion

#### 3.1 Synthesis

The **DPP** core was synthesized through a well established synthetic procedure which is based on a double condensation and cyclization of cyanoarenes on diesters of succinic acid.[38,51]

The donor part of the molecules has been synthesized starting from phenothiazine that has been alkylated as the first step and successively brominated in position 3 by means of *N*-bromosuccinimide (see Scheme 1).

The phenothiazine derivatives and the **DPP** core have been then coupled by means of a direct heteroarylation reaction, as shown in Scheme 1. The reaction was performed in dry toluene at 120°C for 16 h using Herrmann-Beller catalyst and tris(*o*-methoxyphenyl)phosphine, Cs<sub>2</sub>CO<sub>3</sub> as base and pivalic acid as additive (see Scheme 1).[52]



**Scheme 1.** Synthetic pathway to the **DPPn** molecules

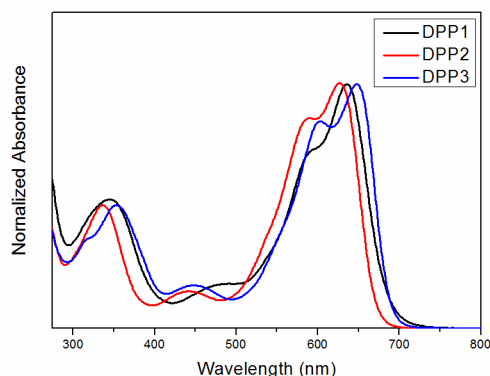
### 3.2 Optical and electrochemical analysis

The optical properties of the compounds were investigated by UV-Vis analysis performed in dichloromethane (DCM) solution and in thin film. Optical spectra in solution are shown in Figure 3.

All the molecules present, in the high wavelength region of the visible spectra, a main peak corresponding to the lowest energy  $\pi-\pi^*$  transition ( $S_0 \rightarrow S_1$ ) with a marked shoulder at higher energy corresponding to the typical vibronic structure well known in DPP derivatives.[39]

Qualitatively, the heteroaromatic rings that functionalize **DPP** core have a slight but clear influence on the optical spectra of molecules: the higher is the electron donor strength of the heteroarenes, the more red shifted is the optical absorbance of the molecule.





**Figure 3.** Normalized absorption spectra of **DPPn** in dichloromethane

In particular, the wavelengths of the two mentioned absorption features shifts from the values of 590/627 nm for **DPP2**, containing the thiazole ring, to 597/636 nm for **DPP1** containing thiophene and 602/648 nm for **DPP3**, the molecule containing the thienothiophene, the stronger electron donor moiety. All molecules have a high molar extinction coefficient ( $\epsilon$ ), up to about  $9 \times 10^4 \text{ M}^{-1} \cdot \text{cm}^{-1}$ , as shown in Table 1.

**Table 1.** Optical properties of small molecules synthesized

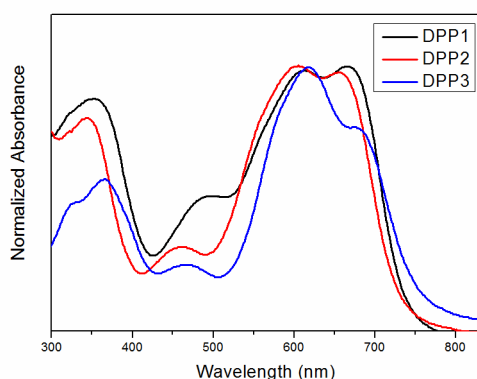
Samples	$\lambda_{\text{max}}$ (nm) <sup>a</sup>	$\epsilon$ ( $\text{M}^{-1} \cdot \text{cm}^{-1}$ ) <sup>a</sup>	$\lambda_{\text{max}}^{\text{film}}$ (nm)	$E_{\text{g}}^{\text{optical}}$ (eV)
<b>DPP1</b>	597/636	$6,0 \times 10^4$	614/664	1,69
<b>DPP2</b>	590/627	$7,8 \times 10^4$	606/655	1,67
<b>DPP3</b>	602/648	$8,7 \times 10^4$	618/677	1,55

a) in dichloromethane solution,  $\epsilon$  is referred to the higher wavelength absorption maximum

Thin films of the synthesized molecules have been prepared and their absorption spectra are shown in Figure 4. The trend observed for the maxima absorption wavelength of the molecules in solution, holds also in solid phase so that **DPP3** is the molecule that absorbs at higher wavelengths. In addition, all molecules show, in solid state, a bathochromic shift of their absorbance as compared to

their spectrum in solution. Such a standard behavior is expected due to higher intermolecular  $\pi$ -stacking in the solid state.

From the film optical absorption spectra it was possible to measure the optical bandgap of the **DPPn** compounds, by applying the Tauc extrapolation:[53] low bandgap values ranging from 1.55 eV (**DPP3**) to 1.69 eV (**DPP1**) were determined. Such bandgap values are particularly desired in OPV applications, determining in fact a better matching with the solar emission spectrum.



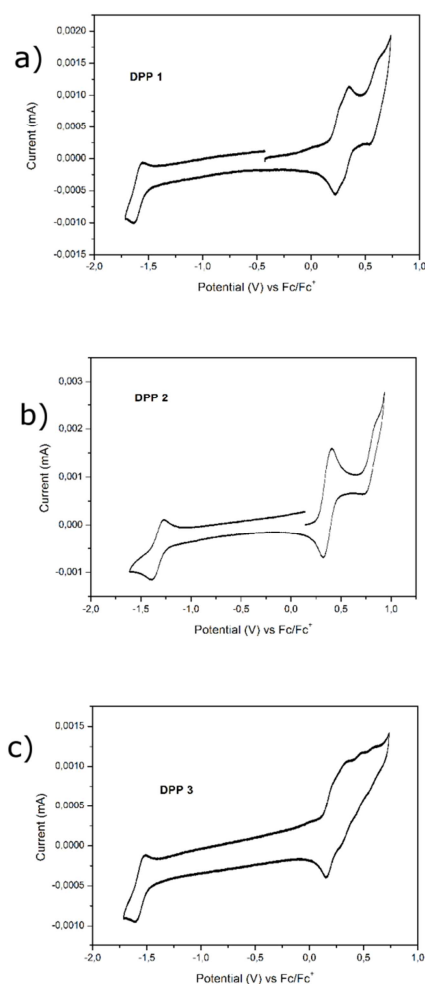
**Figure 4.** Solid state absorption spectra of **DPPn** molecules

More information about the energy of the frontier orbitals was obtained by the electrochemical analysis. Oxidation and reduction potentials of small molecules have been measured by means of cyclic voltammetry (Figure 5), using the redox couple ferrocene/ferrocinium ( $\text{Fc}/\text{Fc}^+$ ) as standard. From the voltammograms, shown in Figure 3, HOMO and LUMO energies have been determined by applying the formula:[54]

$$E_{\text{HOMO}} = - (E_{\text{onset, ox}} - E_{\text{Fc}/\text{Fc}^+} + 4.8)$$

$$E_{\text{LUMO}} = - (E_{\text{onset, red}} - E_{\text{Fc}/\text{Fc}^+} + 4.8)$$

Electrochemical data are reported in Table 2: it is possible to observe that the strength of the electron-rich rings functionalizing the **DPP** core has a clear influence on the oxidation potentials of the molecules: the higher is the donor activity of the heteroaromatic groups, the lower is the corresponding oxidation potential and, consequently, the less stable is the HOMO of the system. As already observed, the thiophene replacement by thiazole unit leads to a down-shifting of both oxidation and reduction potentials from 0.1 to 0.2 V approximately.[55,56,57]As a consequence, both HOMO and LUMO levels of **DPP2** are down-shifted from the same values as compared to the thiophene-based **DPP1** molecule



**Figure 5.** Voltammograms of the **DPP<sub>n</sub>** molecules

**Table 2.** *Electrochemical properties of the synthesized compounds*

Samples	$E_{\text{ox vs Fc/Fc}^+}$ (V)	HOMO (eV)	LUMO (eV)	$E_g^{\text{ec}}$ (eV)
<b>DPP1</b>	0.169	-4.96	-3.29	1.68
<b>DPP2</b>	0.278	-5.07	-3.56	1.50
<b>DPP3</b>	0.121	-4.91	-3.32	1.60

All the molecules present a LUMO energy level higher than that related to fullerene ( $\approx -4.0$  eV[58]) and hence they can act as donor materials in a BHJ solar cells in a blend with fullerene. From this combined optical electro-chemical analysis, it is possible to conclude that the donor strength of the heteroaromatics functionalizing the **DPP** core has an influence on the bandgap of the molecules mainly because it affects the stability of the HOMO orbitals.

### 3.3 Computational analysis

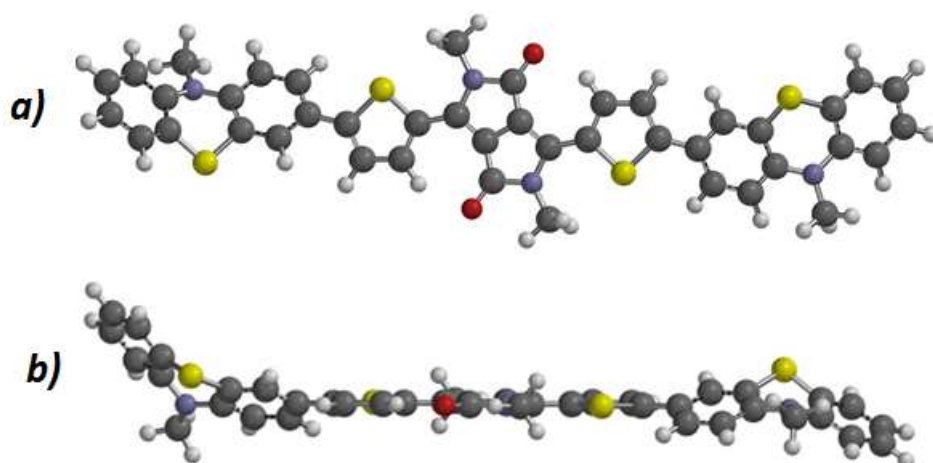
Density functional theory (DFT) calculations have been performed using SPARTAN 10 at the B3LYP/6-311+G\* level of theory in vacuum both on the final dyes and on the precursors. The computed frontier molecular orbital's (FMO) energies are reported in Table 3. In general, it appears that the LUMO energy level differences between phenothiazine and DPP derivatives are larger than their HOMO energy levels offset. Therefore, hybridization between HOMO levels is more pronounced than that of their LUMO counterparts. The calculated levels for the final dyes, shown in Table 3, are consistent with expectations. The theoretical band-gap evolution trend is in good agreement with the optical band gap measurements. The experimental optical and electrochemical frontier energy levels, described in the previous section, are consistent with the performed computational analysis.

**Table 3.** HOMO and LUMO energies calculated by DFT

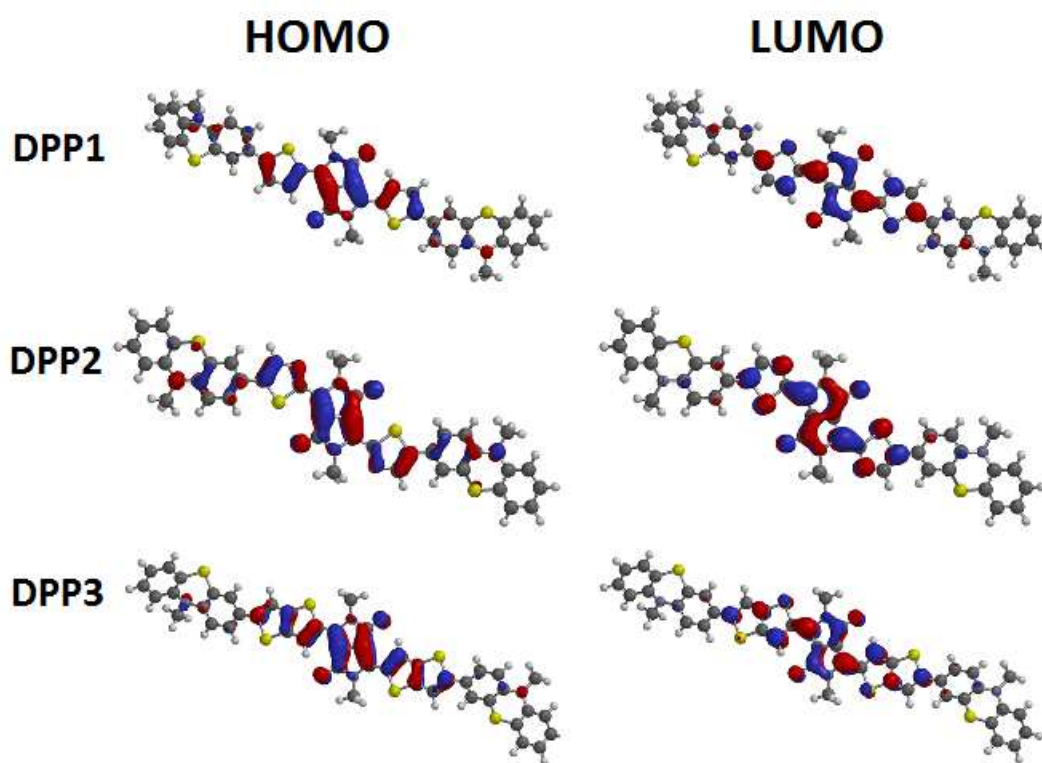
Compound	HOMO (eV)	LUMO (eV)	Bandgap (eV)
<b>N-methyl phenothiazine</b>	-5.04	-0.31	4.73
<b>1</b>	-4.97	-2.51	2.46
<b>2</b>	-5.33	-2.91	2.42
<b>3</b>	-4.89	-2.62	2.27
<b>DPP1</b>	-4.63	-2.48	2.15
<b>DPP2</b>	-4.91	-2.79	2.12
<b>DPP3</b>	-4.64	-2.56	2.08

The optimized geometry for **DPP1** is reported in Figure 6. The molecules adopt a non-planar conformation with a butterfly shape arrangement of the phenothiazine and with a significant dihedral angle between the planar central-core and the adjacent ring of the phenothiazine moiety. This dihedral angle is smaller for **DPP2** (21 to 23°) than for **DPP1** (24 to 26°) and it reaches 26 to 30° for the thienothiophene containing dye.

The non-planarity of all dyes limits the extension of the conjugation, and so of the HOMO and LUMO frontier energy distributions, over the molecular backbone, as shown in Figure 7.



**Figure 6.** Face view (a) and side-view (b) of the optimized molecular geometry for the *DPP1* dye.



**Figure 7.** HOMOs (left) and LUMOs (right) frontier energy distributions for *DPP1*, *DPP2* and *DPP3*.

In agreement with the calculated dihedral angles, the HOMO extension on the phenothiazine moiety is more pronounced for **DPP2** than for **DPP1** and almost no extension is observed for **DPP3** (with also a wider central core).

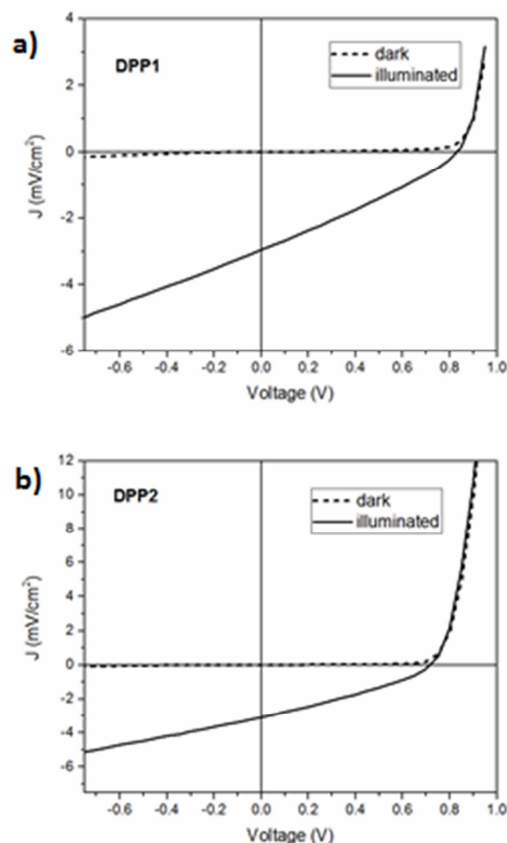
### 3.4 Photovoltaic measurements

Photovoltaic devices have been fabricated using **DPP1** or **DPP2** as donor materials in blends with PC<sub>71</sub>BM in a BHJ architecture. It was not possible to realize any device with **DPP3** because of its very bad film forming ability, probably due to its lower solubility. Chlorobenzene (CB) was used as solvent for the deposition of the active blend: **DPP** molecules concentration ranged from 4 to 5 mg/mL. The J/V curve of best performing devices are shown in Figure 8 while the corresponding photovoltaic parameters are reported in Table 4.

**Table 4.** *Electrical parameters of the best performing BHJ solar cells based on **DPP** donor molecules*

Active layers	V <sub>oc</sub> (mV)	J <sub>sc</sub> (mA·cm <sup>-2</sup> )	FF (%)	η (%)
<b>DPP1/PC<sub>71</sub>BM<sup>a</sup></b>	0.84	2.9	29	0.71
<b>DPP2/PC<sub>71</sub>BM<sup>a</sup></b>	0.73	3.1	31	0.70

a) DPP<sub>n</sub>/PC<sub>71</sub>BM: ratio 1/2 in weight.



**Figure 8.** Representative  $J/V$  curves in the dark and under simulated solar radiation for BJJ solar cells based on (a) **DPP1** and (b) **DPP2**.

All the devices feature a moderate power conversion efficiency that does not improve by annealing the devices (at 80 and 100 °C for 5 minutes) after the preparation. The devices are characterized by a good value of  $V_{oc}$ . In particular, open circuit voltage for the device based on **DPP1** is unexpectedly higher than that measured for the device based on **DPP2**. Indeed, the  $V_{oc}$  scales linearly with the energy difference between the electron-donor (**DPP1-2**) HOMO and the PC<sub>71</sub>BM LUMO[59] and therefore, a 0.1 V higher  $V_{oc}$  was expected for **DPP2**. LUMO On the other hand, it is well known that efficient charge-carrier recombination impacts strongly the  $V_{oc}$  values[60] and both devices show poor FF and low  $J_{sc}$  values. In practice, charge-carriers are hardly extracted from



the devices, as shown by the strong dependence of the current-density on the voltage for negative voltages (Fig.6).

To clarify why charge-carriers are inefficiently extracted from the devices, the **DPP1-3** hole mobilities have been determined by analyzing the characteristics of OFETs. Low values of hole mobility in the order of  $10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  have been measured in-line with the low FF and  $J_{\text{sc}}$  values measured in the photovoltaic devices. The low hole-mobility could in turn be a consequence of the non-planar structure of the molecular systems, as shown in the DFT analysis. Indeed, the non-planar molecular conformation could affect the packing of the molecules in the solid state resulting in reduced charge transport properties. At the same time, DFT analysis suggested a limited length of conjugation due to a near interruption of conjugation because of the phenothiazine bending that could be another reason for the low charge transport properties of the molecule.

#### 4. Conclusions

A class of small molecules based on a diketopyrrolopyrrole core (**DPP** series) has been synthesized. **DPP** molecules have been synthesized by direct heteroarylation of three different **DPP** derivatives with 3-bromo-*N*-alkylphenothiazine. All the molecules were optically characterized: heteroaromatic rings (thiophene, thiazole and thienothiophene) functionalizing the **DPP** core have a clear influence on the optical spectra of the molecules. The higher is the electron donor strength of the heteroarenes, the more red shifted the absorbance spectrum of the molecules. In particular, the wavelength of the absorption maximum shifts from the 627 nm for **DPP2**, containing the thiazole, to 636 nm for **DPP1** containing thiophene and 658 nm for **DPP3**, containing the thienothiophene, the latter being a stronger electron donor. All molecules have a high molar extinction coefficient ( $\epsilon$ ), up to about  $9 \times 10^4 \text{ M}^{-1} \cdot \text{cm}^{-1}$ , making them good candidates for opto-electronic applications. By the optical analysis in the solid phase it has been possible to measure the optical band-gap of the new dyes, with values from 1.55 to 1.69 eV.

**DPP1** and **DPP2** have been used as donor materials in the fabrication of BHJ solar cells, in combination with PC<sub>71</sub>BM as electron acceptor material. All the devices feature moderate power conversion efficiencies with values of about 0.7 %. The devices are characterized by a good value of open-circuit voltage  $V_{oc}$  (around 0.8 V). This behavior is consistent with the high stability of the HOMO orbitals characterizing **DPP1** and **DPP2**, as evaluated by electrochemical measurements. The devices show instead poor values for the fill-factor FF and the short-circuit current density  $J_{sc}$ . Low values of hole mobility for field-effect transistors, in the order of  $10^{-6} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$  have been measured that can explain the low FF and  $J_{sc}$  values due to poor charge-extraction. The low hole-mobility could in turn be a consequence of the non-planar structure of the molecular systems that was suggested by density functional theory calculations on the reported structures.

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**Highlights**

- Synthesis of low bandgap small molecules by direct heteroarylation
- The dyes are based on diketopyrrolopyrrole core and end-capped with phenothiazine
- Optical and electrochemical characterization along with computational investigation
- Fabrication of solar cells based on the reported dyes with efficiency up to 0.7%.

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