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Pyrrolo[3,2-*b*]pyrrole as Electron-Donor Central Core for Solution-Processed Organic Solar Cells

Rocío Domínguez,^[a] Núria F. Montcada,^{*[b]} Pilar de la Cruz,^[a] Emilio Palomares^[b,c] and Fernando Langa^{*[a]}

Abstract: A series of three acceptor-donor-acceptor (A-D-A) small molecules using a tetraaryl-1,4-dihydropyrrolo[3,2-*b*]pyrrole in their central building block were synthesized and fully characterized. These molecules present high thermal stability and suitable HOMO-LUMO energy levels making them feasible electron donor materials in Bulk Heterojunction Organic Solar Cells (BHJ-OSC). Moreover, theoretical work was also performed obtaining a prediction of a lack of planarity and no p-p stacking, furthermore, the probability of the Highest Occupied Molecular Orbital (HOMO) is distributed on the pyrrole-pyrrole moiety and the probability of the Lowest Unoccupied Molecular Orbital (LUMO) is delocalized, on the contrary, on the phenyl groups. The organic solar cells deliver an open-circuit voltage of 0.99V. However, the overall efficiency is limited due to the low charge mobility measured for holes, $10^{-9} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

Introduction

Bulk heterojunction solar cells based on organic conjugated semiconductors as electron-donor materials blended with fullerene derivatives as electron-acceptor materials are technologically appealing for light-weight, flexible, low-cost and roll-to-roll solar cells. Either semiconductor polymers or small molecule donor materials have been widely studied in organic solar cells (OSC) achieving efficiencies above 10%.^[1] Small organic semiconductor molecules were the first choice for organic solar cells^[2], however, a breakthrough was carried out with semiconducting polymers which hindered the use of solution processed small organic molecules in solar cells until the solar-to-energy conversion efficiency reached values close to 5% at 1 sun.^[3] The well-defined molecular structures with monodisperse nature and negligible batch-to-batch variations makes small molecules of particular interest for solar cell

applications. Moreover, these molecules can be easily tuned combining different donor and acceptors and bridge elements in order to widen their absorption overlap with the solar spectrum, better control of the HOMO and LUMO energy levels and improve charge-carrier mobilities and transport pathways to the electrodes. All of these advantages have been widely explored finally reaching the same efficiencies as polymer-based solar cells. For instance, electron-donor central cores moieties has been studied and reported, and fused-ring derivatives have been the most used moieties to obtain the highest efficiencies.^[4] Regarding this, heteropentalenes (10 π -electron aromatic compounds) such as thieno[3,2-*b*]thiophenes and thieno[3,2-*b*]pyrroles are considered a promising candidates as electron donor moieties for BHJSCs that can be easily modified by the introduction of fused rings as a structural element,^[5] achieving in the first case efficiencies up to 8.1%.^[6]

On the other hand, families of furo-, thieno-, and seleno[3,2-*b*]pyrroles are also well-known in the scientific literature and their chemistry has been well studied.^[7] In contrast, the electronic properties of 1,4-dihydropyrrolo[3,2-*b*]pyrroles are almost unknown, probably due to its quite higher complex synthesis compared to others.^[8] Nevertheless, a three components direct synthesis of this 1,4-dihydropyrrolo[3,2-*b*]pyrrole^[9] made this core accessible and viable to be studied and included as possible donor moiety in BHJOSC. Moreover, the synthesis and optical properties of new pentaaryl- and hexaaryl-1,4-dihydropyrrolo[3,2-*b*]pyrroles prepared via direct arylation from tetraaryl-1,4-dihydropyrrolo[3,2-*b*]pyrroles were reported by D. T. Gryko and co-workers.^[10] These new derivatives exhibited interesting optical properties, such as strong blue fluorescence, moderate to large Stokes shifts and fluorescence quantum yields up to 88%, making them a good candidates for many optoelectronic applications.

Taking this into account, we present herein the synthesis and characterization of a new series of acceptor-donor-acceptor (A-D-A) small molecules (**1-3**) based on tetraaryl-1,4-dihydropyrrolo[3,2-*b*]pyrrole and their possibility to be used as electron-donor central building block in solution-processed BHJ-OSCs.

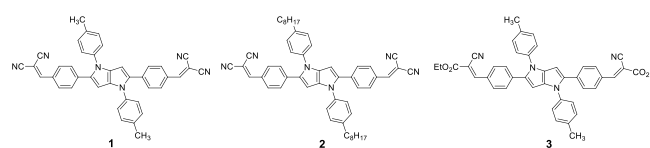


Figure 1. Chemical structure of **1**, **2** and **3** pyrrole-based small molecules.

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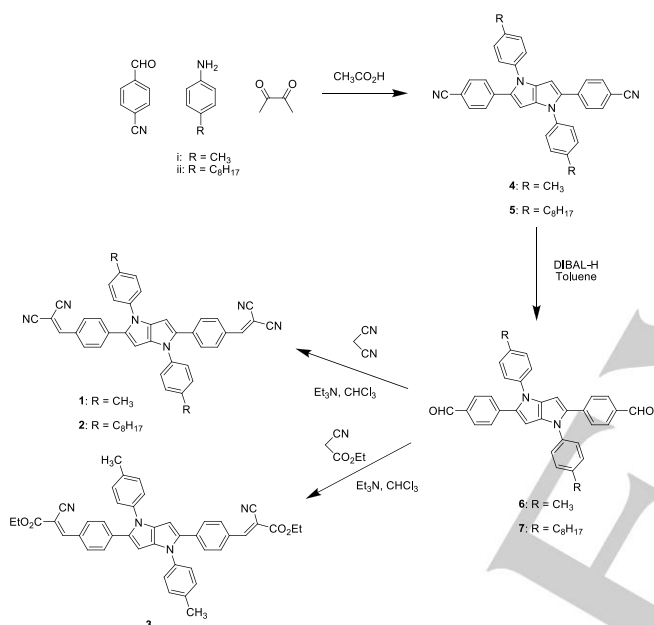
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Results and Discussion

Synthesis and thermal properties

The synthetic route for preparing the new family of small molecules (**1-3**) is outlined in Scheme 1. First, 2,6-di(4-cyanophenyl)-1,5-di(4-methylphenyl)-3,4-dihydropyrrolo[3,2-*b*]pyrrole (**4**)^[9] and 2,6-di(4-cyanophenyl)-1,5-di(4-octylphenyl)-3,4-dihydropyrrolo[3,2-*b*]pyrrole (**5**) were synthesized by a Debus-Radziszewski reaction. Cyano groups were then reduced to the corresponding aldehydes by treatment with diisobutylaluminium hydride (DIBAL-H) in anhydrous toluene at 0 °C, affording derivatives **6** and **7** in excellent yields (95% and 98%, respectively). Finally, the target molecules **1-3** were obtained by Knoevenagel reaction using malononitrile (for **1** and **2**) or ethyl cyanoacetate (for **3**), triethylamine as base and chloroform as solvent at room temperature.

Scheme 1. Synthetic route to **1-3**.

All new compounds were characterized by ¹H-NMR, ¹³C-NMR, FT-IR and MALDI-TOF MS in order to confirm the expected structures (see Supporting Information). While **1** is rather insoluble, **2** and **3** show good solubility in organic solvents.

Thermogravimetric (TGA) and differential scanning calorimetry (DSC) analyses were used in order to investigate the thermal properties of the molecules. The decomposition temperature was estimated from the TGA, as 390 °C for **1**, 374 °C for **3** and 450 °C for **2** (Figure 2 (left)).

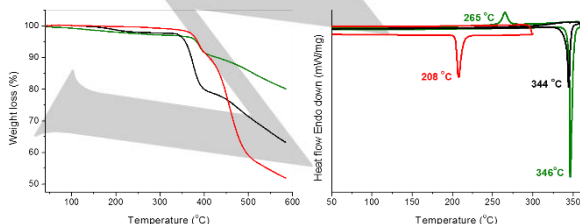


Figure 2. (Left) TGA curves of derivatives **1** (green), **2** (red) and **3** (black) under nitrogen atmosphere (scan rate of 10 °C min⁻¹); (right) DSC curves of derivatives **1** (green), **2** (red) and **3** (black) under nitrogen atmosphere.

For the DSC experiments, the samples were heated from 25 to 360 °C and then cooled to -10 °C with a heating rate of 20 °C/min and a cooling rate of 10 °C/min under nitrogen flow. **1** showed an endothermic peak at 346 °C corresponding to the melting point of the molecule and an exothermic peak at 265 °C associated to a crystallization process. Similarly, molecules **2** and **3** exhibited an endothermic peak at 208 °C and 344 °C, respectively, ascribed to its corresponding melting point. Nevertheless, no exothermic processes were found when samples **2** and **3** were cooled (Figure 2 (right)). These results show that the new family of molecules displays high thermal stability and good enough for optoelectronic applications.

Optical properties

The absorption and emission properties of the new family of sensitizers **1-3** have been investigated by UV-Visible and fluorescence spectroscopy. Absorption spectra in dichloromethane solution and on film are shown in Figure 3, and the most relevant data are summarized in Table 1. Absorption spectra of **1-3** sensitizers are dominated by an intense band around 450-650 nm assigned to the intra-molecular charge transfer (ICT) transition as consequence of the interplay of the donor-acceptor architecture between the electron-rich inner part of the molecule (tetraaryl-1,4-dihydropyrrolo-[3,2-*b*]pyrrole) and the electron-deficient peripheral part (dicyanovinylene or ethyl cyanoacetatevinylene). The maximum in **3** is blue-shifted respecting to **1** and **2** as ethyl cyanoacetatevinylene acceptor group exhibits less electrophilic character than dicyanovinylene.

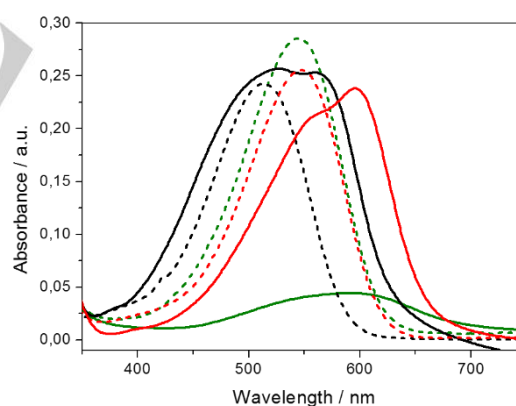


Figure 3. UV-Vis absorption spectra of derivatives **1** (green), **2** (red) and **3** (black) in dichloromethane solution ($c \approx 3 \times 10^{-6}$ M at 25 °C) (dashed lines) and on film (solid lines).

The UV-Visible absorption spectra recorded on film showed, in all cases, a bathochromic shift on the maximum absorption wavelength and broader absorption bands compared to the spectra registered in solution owing to higher order of the molecules in solid state. Additionally, the spectra recorded on film exhibited a new absorption band at longer wavelengths (especially in **2** and **3**) due to the aggregation triggered on film. An increase of the planarity is shown in **2** due to the presence of larger alkyl chains.^[11] In case of molecule **3**, the film present a

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certain degree of molecular order due to the reduction of the molecular distances for the film formation, however the widening of the spectra also indicate the formation of different packing domains. For molecule **1** an important decrease of the absorption intensity is shown, an indication of a totally amorphous domains formation.^[12]

The emission spectra were also recorded in diluted dichloromethane solution ($c \approx 3 \times 10^{-6}$ M at 25°C) by excitation at the corresponding maximum wavelength (see Figure S20, Supporting Information). As expected, the emission wavelength of derivatives **1** and **2** (with dicyanovinylene moiety) is higher than that of dye **3** (Table 1).

Electrochemical properties

The Cyclic voltammetry (CV) and Osteryoung square wave voltammetry (OSWV) experiments were carried out in order to determine the oxidation and reduction potentials, as an approach to estimate the HOMO and LUMO energy levels since the alignment of the HOMO values is very important in order to achieve high open circuit voltage (V_{OC}) (this energy is closely related to the energy difference between the HOMO of the electron-donor and the LUMO of the electron-acceptor materials). The relevant electrochemical data is listed in Table 1. All derivatives revealed two reversible oxidation waves with similar intensities (determined by CV measurements) and an irreversible one at higher voltage (see Figure S21-23 Supporting Information).

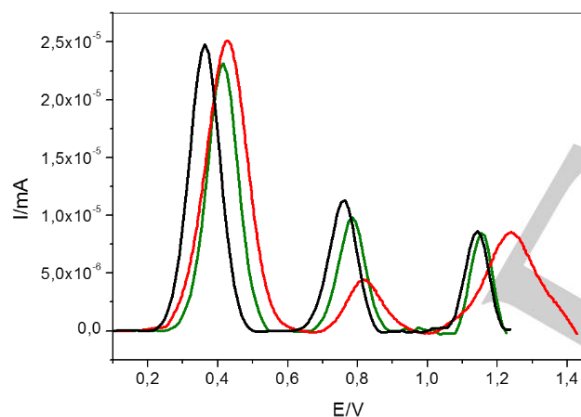


Figure 4. OSWV plots of derivatives **1** (green), **2** (red) and **3** (black) (referred to Fc/Fc^+).

These oxidation processes were ascribed to the central electron-donor building block (tetraaryl-1,4-dihydropyrrolo-[3,2-*b*]pyrrole), whereas the unique reduction process observed in the observation window was associated to the acceptor groups (Figure 4).

The molecule **3** (cyanoacetatevinylene-based derivative) displayed slightly lower first oxidation potential than **1** and **2** (DCV-based derivatives) because ethyl cyanoacetatevinylene acceptor group is less electrophile than dicyanovinylene group. The HOMO and LUMO energy levels were calculated from the first oxidation and reduction potentials according to equations $E_{\text{HOMO}} = -5.1 - E_{\text{OX1(OSWV)}} \text{ (eV)}$ and $E_{\text{LUMO}} = -5.1 - E_{\text{RED1(OSWV)}} \text{ (eV)}$, respectively. **1-3** sensitizers showed relatively low electrochemical band gap (calculated according to equation $E_0^{\text{elec}} = E_{\text{LUMO}} - E_{\text{HOMO}} \text{ (eV)}$) and suitable HOMO-LUMO energy values, enabling their use as electron-donor and using PC_{61}BM or PC_{71}BM as acceptor materials (Figure 5). It is worth emphasizing that the low HOMO levels exhibited by this series of molecules predict relatively high V_{OC} , particularly for **1** and **2**.

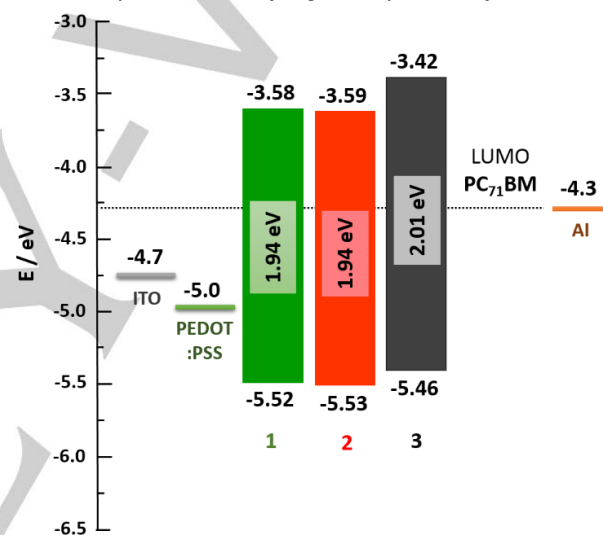


Figure 5. FMO energy levels and band gap of dyes **1-3** and the components that form the studied BHJ devices.

Table 1. Optical and electrochemical data of **1-3** resulted from UV-Vis absorption spectrum, emission spectrum and Osteryoung square wave voltammetry (OSWV) curves.

	$\lambda_{\text{max}}^{\text{sol}}$ (nm)	λ_{em} (nm)	$\log \epsilon$	$\lambda_{\text{max}}^{\text{film}}$ (nm)	$E_{\text{ox1(OSWV)}}$ (V)	$E_{\text{red1(OSWV)}}$ (V)	$E_{\text{HOMO}}^{\text{a}}$ (eV)	$E_{\text{LUMO}}^{\text{a}}$ (eV)	$E_0^{\text{elec b}}$ (eV)
1	545	655	4.83	593	0.42	-1.52	-5.52	-3.58	1.94
2	548	654	4.90	596	0.43	-1.51	-5.53	-3.59	1.94
3	513	639	4.82	527	0.36	-1.68	-5.46	-3.42	2.01

[a] Solution in 0.1 M in ODCB/Acetonitrile 4:1/ $n\text{-Bu}_4\text{NClO}_4$ versus ferrocenium/ferrocene. HOMO and LUMO energy levels were estimated from OSWV oxidation and reduction curves, respectively, assuming the absolute energy level of ferrocene/ferrocenium to be 5.1 eV below vacuum. [b] E_0^{elec} (eV) = $E_{\text{LUMO}} - E_{\text{HOMO}}$.

Theoretical calculations

Ground-state geometry of the new family of sensitizers was fully optimized by density functional theory (DFT) at the B3LYP 6-

31G* level *in vacuo* with Gaussian 09W. As expected, these molecules displayed two different molecular planes: that one formed between the pyrrole-pyrrole unit and the phenyl groups

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linked to position 2, and that between the pyrrole-pyrrole unit and the phenyl groups linked to position 1 with a dihedral angle around 30° (Figure 6). Thereby, the lack of planarity hinders the π - π stacking between molecules, which is inexistent for **1** as observed in the UV-Vis spectra (Figure 3).

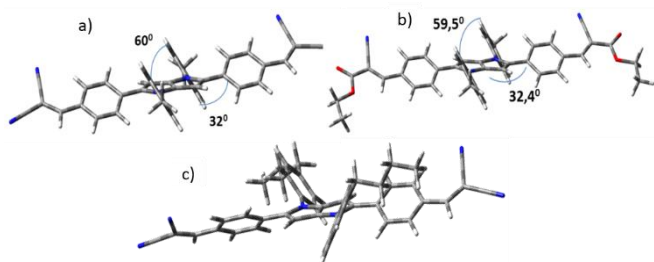


Figure 6. Optimized ground-state geometries of a) **1**, b) **3** and c) **2**.

Electronic distribution of the HOMO and LUMO energy levels was also calculated by quantum chemical calculations, revealing that the electron density of the HOMO in these molecules is mainly distributed on the pyrrole-pyrrole moiety, whereas the electron density of the LUMO is mainly delocalized on the phenyl groups linked by position 2 to the pyrrole-pyrrole unit and on the acceptor groups (Figure 7). Phenyl groups linked by position 1 to the pyrrole-pyrrole unit practically do not contribute to the electronic distribution of the HOMO and LUMO energy levels.

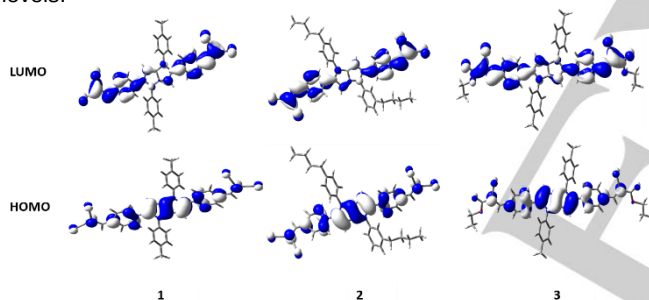


Figure 7. Electronic distribution of the HOMO and LUMO energy levels in derivatives **1-3**.

The theoretical HOMO and LUMO energy levels are similar to the experimental values (see Table S1, Supporting Information), also following the same trend; both energy levels are lower (in absolute terms) for **3** than those of **1** and **2** due to the lower electrophilic character of the ethyl cyanoacetatevinylene acceptor group.

Photovoltaic performance

All complete devices were fabricated using the ITO/PEDOT:PSS/sm(**1,2** or **3**):PC₇₁BM/AI configuration and for hole only devices ITO/PEDOT:PSS/**2**:PC₇₁BM/Au. The fabrication methods are described in the experimental section. In Figure 8 the J-V curves of **1,2** and **3** based complete devices are shown and the main performance parameters are listed in Table 2. The performance parameters obtained in the device optimization before and after SVA process are collected in Table S2 (Supporting Information). The **1**, **2** and **3** devices without any SVA treatment shown low device photocurrent efficiencies in all cases, limited in the three cases for the lower J_{SC} (short-circuit

current density) and a poor FF (fill factor). From the solar cells parameters, we can observe an outstanding Voc for **2**-based devices of 0.99V as it was predicted from the theoretical energetics (the difference between the PCBM LUMO energy and the **2** HOMO energy value), however for **1** and **3** the Voc is decreased drastically respecting to the predicted value, indicating an important charge loss maybe due to faster charge recombination kinetics. In addition, the low J_{SC} obtained in case of **1**-based devices is due to the combination of two factors: on the one hand, the apparent lower light harvesting properties in film as shown previously (Figure 3) and, on the other hand, the extended trap points due to the amorphous domains, that provoked an increase in transport resistance and, thus, a leakage of J_{sc} by recombination. The lower FF also was in agreement with this last point, where the resistance throughout the film increase noticeably. Moreover, the deficient measured Voc in device **1** emphasize a strong resistance at the interfaces induced also by the higher lack of crystallinity of the active layer. On the contrary, for device **3**, it is evidence that there is no limitation over the light harvesting properties (Figure 3), however even the molecule becomes more crystalline in film than using molecule **1**, the intercalation with fullene were clearly not proper creating larger donor domains, greater than the diffusion length, and the charges are not able to reach the donor-acceptor interface, producing also a drastic drop of the FF.^[12]

With the aim to improve the unfavorable molecular packing, solvent vapor annealing was carried out, obtaining only a favorable result for **2**-based devices reaching 1.06%; in this case the FF was increased from 31 to 46 % indicating and improvement on the nanomorphology which lead to less resistance to the charge transport to the electrodes and, thus, we found also an 82% increase of the photocurrent (from 1.4 to 2.5 mA/cm²) but a slight decrease of the V_{oc} to 0.92 V, in good agreement with previous reports that used solvent annealing to improve the solar cell performance.^[13-14]

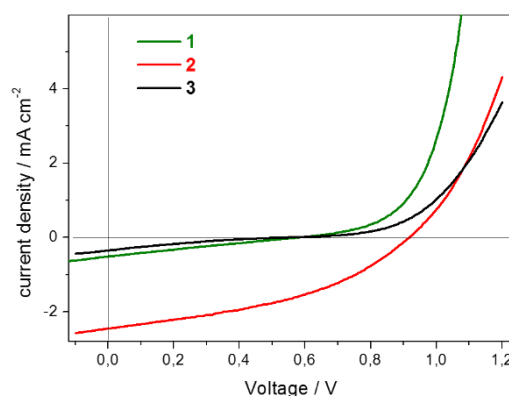


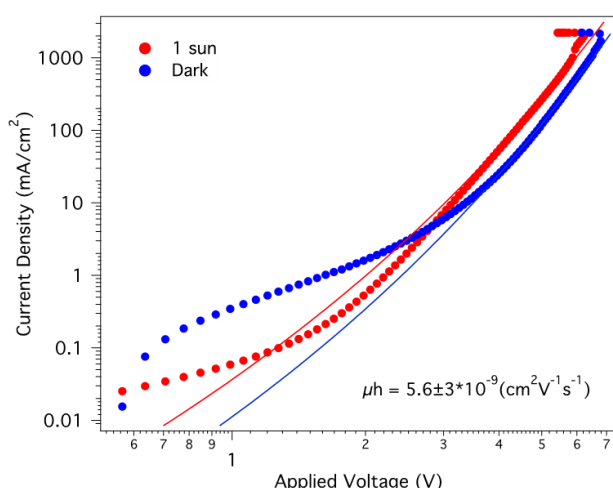
Figure 8. Photocurrent density vs. voltage (J-V) curves for optimized **1-3**:PC₇₁BM solar cells at 1 sun (sun simulated 100 mW cm⁻² light intensity).

Based on the results shown before, we will focus the characterization study on complete devices using molecule **2** as this is the most promising molecule among the others.

The hole mobility of the **2**-based devices was calculated using the space charge limited current method (SCLC). The hole only devices are forced to work at higher potentials as can be seen in Figure 9, at 7 V in this case.

Table 2. Main performance parameters of 1-3-based devices after SVA process.

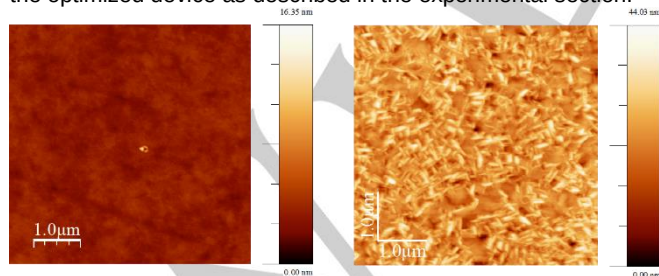
Device	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
1	0.43	0.12	28	0.01
2	2.5	0.92	46	1.06
3	0.044	0.52	19	0.004

**Figure 9.** Representative J-V curves for a hole only device of 2 at 1 sun (Red) and dark (Blue); the solid lines represents the fitting to the SCLC equation. The measured mobility is an average value of 27 independent diodes.

The mobility average for this molecule was $10^{-9} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. That is clearly the major loss mechanism for this devices and the main cause for the limited efficiencies.

Surface morphology characterization

The surface morphology of 2:PC₇₁BM blend film was investigated by atomic force microscopy (AFM, tapping mode). The sample was prepared reproducing the photoactive layer of the optimized device as described in the experimental section.

**Figure 10.** AFM topography images of 2:PC₇₁BM thin films on PEDOT:PSS-coated ITO substrates, (left) before SVA and (right) after SVA.

The topography roughness of the blend films was obtained from the height images. The surface morphology before SVA displayed a smooth roughness of around 2 nm (Figure 10 (left)). Nevertheless, after solvent vapor annealing process, a notable

change was observed (Figure 10 (right)) that is a result of a higher reorganization of the photoactive domains. The roughness increased up to 20 nm and a flake-form nanomorphology was achieved, resulting in a better phase separation and more distinct network of donor/acceptor domains.

Conclusions

To summarize, a series of novel symmetrical A-D-A sensitizers, 1-3, based on tetraphenyl-1,4-dihydropyrrole-[3,2-*b*]pyrrole as electron-donor central building block and different aliphatic chain lengths and acceptor groups has been successfully synthesized and characterized. These derivatives are soluble in common organic solvents (except 1 that displays lower solubility), exhibit wide absorption in a broad part of the solar spectrum (range 400 - 650 nm) and show thermal stability and good miscibility with PC₇₁BM. The 2-based devices display high V_{oc} reaching values up to 0.92 V under standard sun-simulated conditions of AM 1.5G 100 mW cm⁻² after SVA post-treatment, however a low J_{sc} (2.5 mA cm⁻²) and moderate FF (46%) were obtained and therefore a limited PCE of 1.06%. The hole mobility was measured obtaining values in the order of $10^{-9} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ that is clearly one of the main limitation of the device. According to the theoretical calculations, the conjugation could be increased through the groups linked to the pyrrolic nitrogen atoms, thus enhancing and shifting the absorption to higher wavelengths but maintaining the voltage since the HOMO energy level of the molecules is not electronically involved. In addition, all the molecules of this set present lack of planarity that do not favors the electron hopping to the acceptor and efficient charge transport to the contacts. In case of the 2-based devices the improvement after the SVA treatment points out to a higher reorganization of the nanodomains that makes this molecule the best candidate to be further optimized work in the future focused on optimizing the charge mobility.

Experimental Section

Materials and instruments

The synthetic routes for the preparation of 1-3 derivatives are shown in Scheme 1. 4-formylbenzonitrile, 4-methylaniline, 4-octylaniline, butane-2,3-dione, DIBAL-H, malononitrile and ethyl cyanoacetate were purchased from commercial sources (Aldrich, Acros). All other solvents and chemicals used in this work were analytical grade and used without further purification. Column chromatography was performed on silica gel 60, 0.06 - 0.2 mm (70 - 230 mesh ASTM) or 0.04 - 0.06 mm (230 - 400 mesh ASTM) from Scharlau.

¹H NMR and ¹³C NMR spectra were recorded on a Bruker TopSpin AV-400 (400 MHz) spectrometer. The reported chemical shifts were against 7.27 ppm in ¹H NMR experiments and against 77.0 ppm in ¹³C NMR experiments (CDCl₃). Mass spectra were achieved from a VOYAGER DE™ STR mass spectrometer (MALDI-TOF) using dithranol as matrix. FT-IR spectra were recorded in a Fourier Transform IR spectrometer Avatar 370 Thermo Nicolet, using pellets of dispersed samples of the corresponding compounds in dried KBr or ATR accessory. TGA analyses were performed using a TGA/DSC Linea Excellent instrument by Mettler-Toledo and collected under inert atmosphere of nitrogen with a rate of 10°C min⁻¹. Weight changes were recorded as a function of temperature. DSC analyses were performed using a DSC Linea Excellent instrument

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by Mettler-Toledo and collected under inert atmosphere of nitrogen at a heating rate of 20 K min⁻¹ and cooling rate of 10 K min⁻¹. Melting points were taken from the DSC experiments. AFM images were acquired in tapping mode using a Multimode V8.10 (Veeco Instruments, Santa Barbara, USA). Silicon cantilevers were used (RTESP from Bruker Probes) with a resonance frequency of 300 kHz and a nominal force constant of 40 N m⁻¹.

Optical and electrochemical measurements

UV-Vis absorption measurements were carried out in a Shimadzu UV 3600 spectrophotometer using 1 cm standard quartz cuvettes. Fluorescence spectra were recorded in a Cary Eclipse fluorescence spectrophotometer using 1 cm standard quartz cuvettes.

Cyclic voltammetry (CV) and Osteryoung square wave voltammetry (OSWV) experiments were carried out in a potentiostat/galvanostat AUTOLAB using a one-compartment cell equipped with a glassy working electrode ($\varnothing = 2$ mm) and a platinum wire counter electrode. An Ag/AgNO₃ (0.01 M in the supporting electrolyte) electrode was used as reference and checked against the ferrocene/ferrocenium couple (Fc/Fc⁺) before each experiment. Measurements were performed in *o*-dichlorobenzene/acetonitrile 4:1 solutions and tetrabutylammonium perchlorate (purchased from Sigma-Aldrich and used without purification) (0.1 M) as background electrolyte. Solutions were deoxygenated by argon bubbling prior to each experiment, which runs under argon atmosphere.

Device fabrication and characterization

The ITO coated glass substrates (5 Ω /cm²) were ultrasonically cleaned consecutively in acetone, aqueous detergent, de-ionized water and isopropyl alcohol, and finally dried under ambient conditions, the substrates were treated in a UV-ozone cleaner for 20 min in order to remove remaining organic particles and water. An aqueous solution of PEDOT:PSS (HC StarckBaytron P.) was spin-coated over the ITO substrates to obtain a film obtaining thickness of 25 nm (30 seconds at 4500 rpm and 30 seconds at 3500 rpm). The PEDOT:PSS film was subsequently dried at 120°C 15 minutes. Initially, the donor:acceptor ratio (w/w) was varied from 1:3 to 2:1 in order to identify the most suitable ratio for the system using PC₆₁BM and PC₇₁BM. The fabrication conditions were further explored by varying the concentration and solvent of the donor:acceptor solution, and spin-coating rates. Among all conditions, the optimal performance was observed by using 20 mg mL⁻¹ blend solutions in chloroform as solvent for **1** and **3** derivatives and in chlorobenzene for **2**. 1:1 donor:acceptor ratio provided the higher results for DCV-based sensitizers (**1** and **2**) whereas 2:1 D:A ratio yielded the best results for **3**-based devices. Subsequently, the solution of the sensitizer was spin-coated over the PEDOT layer at 2000 rpm obtaining a thickness of approximately 100 nm, the solvent annealing was carried out immediately after the active layer deposition, this treatment was performed by exposing the films to a saturated vapor atmosphere of dichloromethane (10 mL) in a controlled volume closed vessel (100 mL) for different periods of time. Finally 80 nm of aluminum (Al) top electrode was thermally deposited on the active layer using a high vacuum thermal evaporator (1.10⁻⁶ mbar) through a 0.09 cm² shadow mask. For hole only devices a 150 nm of Au electrode were evaporated instead.

The *J-V* curves were measured using a Sun 2000 Solar Simulator (150 W, ABET Technologies) at 100 mW cm⁻² calibrated silicon photodiode (NREL) simulating the AM 1.5G spectrum. The applied potential and cell current were measured with a Keithley 2400 digital source meter. The thickness of the films was measured with a stylus profilometer Ambios Tech. XP-1.

Synthesis of target molecules

The synthetic details of dyes **1-3** are described as follows.

Synthesis of **5**

4-Octylaniline (800 mg, 3.90 mmol, 2 eq) and 4-formylbenzonitrile (511 mg, 3.90 mmol, 2 eq) were stirred in glacial acetic acid (6 mL) at 100 °C for 30 min. Then butane-2,3-dione (0.2 mL, 1.95 mmol, 1 eq) was added and the resulting mixture was stirred at 100 °C for 3h. After cooling, the solvent was removed under reduced pressure. The crude product was purified by chromatography column (silica-flash, CH₂Cl₂) and recrystallization from hexane. **5** was achieved in 18 % of yield (240 mg, 0.35 mmol) as a dark yellow solid. ¹H-NMR (400 MHz, CDCl₃) δ /ppm: 7.49 (d, 4H, ³J = 8.2 Hz), 7.29 (d, 4H, ³J = 8.2 Hz), 7.24 (d, 4H, ³J = 8.2 Hz), 7.18 (d, 4H, ³J = 8.2 Hz), 6.49 (s, 2H), 2.67 (t, 4H, ³J = 7.7 Hz), 1.67-1.65 (m, 4H), 1.36-1.31 (m, 20H), 0.93-0.90 (m, 6H); ¹³C-NMR (100 MHz, CDCl₃) δ /ppm: 141.6, 137.7, 136.9, 135.0, 133.4, 131.9, 129.4, 127.8, 125.2, 119.1, 109.0, 95.9, 35.5, 31.9, 31.3, 29.4, 29.3, 29.2, 22.7, 14.1; FT-IR (KBr) ν /cm⁻¹: UV-Vis (CH₂Cl₂) λ_{max} /nm (log ϵ): 408 (4.85); MS (*m/z*) (MALDI-TOF): calculated C₄₈H₅₂N₄: 684.42; found: 684.58 (M⁺).

General procedure for the synthesis of **6** and **7**

The corresponding cyano derivative (**4** or **5**) (1 eq) was dissolved in anhydrous toluene and cooled to 0 °C. DIBAL-H (1.2 M in toluene, 2.1 eq) was added dropwise under Ar. The solution was stirred for 8 h at 0 °C. A 20 mL sample of chloroform was then added followed by 30 mL of 10 % HCl, and the solution was stirred at room temperature for 15 min. The organic layer was separated and dried over anhydrous MgSO₄. The solvent was removed under *vacuo* and the crude product was purified by chromatography column (silica flash, CH₂Cl₂).

6, 1.35 g of **4** (2.76 mmol) in 90 mL of toluene. Yellow solid, 95% yield (1.3 g, 2.63 mmol). ¹H-NMR (400 MHz, CDCl₃) δ /ppm: 9.93 (s, 2H), 7.72 (d, 4H, ³J = 8.1 Hz), 7.36 (d, 4H, ³J = 8.1 Hz), 7.22 (d, 4H, ³J = 8.1 Hz), 7.18 (d, 4H, ³J = 8.1 Hz), 6.52 (s, 2H), 2.41 (s, 6H); ¹³C-NMR (100 MHz, CDCl₃) δ /ppm: 191.6, 139.3, 137.0, 136.4, 135.7, 133.8, 133.6, 130.1, 129.7, 127.8, 125.2, 96.0, 21.1; UV-Vis (CH₂Cl₂) λ_{max} /nm (log ϵ): 435 (4.62); FT-IR (KBr) ν /cm⁻¹: 2920, 2816, 2733, 1693, 1599, 1512, 1458, 1375, 1215, 1167, 839, 737; MS (*m/z*) (MALDI-TOF): calculated C₃₄H₂₆N₂O₂: 494.20; found: 494.35 (M⁺).

7, 0.24 g of **5** (0.35 mmol) in 30 mL of toluene. Yellow solid, 98% yield (0.24 g, 0.34 mmol). ¹H-NMR (400 MHz, CDCl₃) δ /ppm: 9.93 (s, 2H), 7.72 (d, 4H, ³J = 8.2 Hz), 7.36 (d, 4H, ³J = 8.2 Hz), 7.23-7.18 (m, 8H), 6.54 (s, 2H), 2.65 (t, 4H, ³J = 7.7 Hz), 1.66-1.64 (m, 4H), 1.35-1.30 (m, 20H), 0.91-0.88 (m, 6H); ¹³C-NMR (100 MHz, CDCl₃) δ /ppm: 191.6, 141.4, 139.3, 137.1, 135.7, 133.7, 133.6, 129.7, 129.4, 127.8, 125.2, 96.0, 35.5, 31.9, 31.4, 29.5, 29.4, 29.3, 22.7, 14.2; FT-IR (KBr) ν /cm⁻¹: UV-Vis (CH₂Cl₂) λ_{max} /nm (log ϵ): 436 (4.75), 252 (4.58); MS (*m/z*) (MALDI-TOF): calculated C₄₈H₅₄N₂O₂: 690.42; found: 690.59 (M⁺).

General procedure for the synthesis of **1** and **2**

In a round-bottomed flask under argon atmosphere, three drops of Et₃N were added to a solution of malononitrile (**5** eq) and the corresponding dialdehyde (**6** or **7**) (1 eq) in CHCl₃. The reaction mixture was stirred overnight at 80 °C and treated with brine after consumption of the starting material (monitored by TLC). The organic phase was dried over MgSO₄ and the crude product was purified by chromatography column (silica gel, CH₂Cl₂) and recrystallization from methanol and hexane.

1, 0.21 g of **6** (0.42 mmol) in 50 mL of CHCl₃. Purple solid, 24% yield (58 mg, 0.098 mmol). ¹H-NMR (400 MHz, TCE-d₂) δ /ppm: 7.11 (d, 4H, ³J = 8.1 Hz), 7.01 (s, 2H), 6.70 (d, 4H, ³J = 8.1 Hz), 6.62 (d, 4H, ³J = 8.1 Hz), 3.55 (d, 4H, ³J = 8.1 Hz), 5.94 (s, 2H), 1.79 (s, 6H); ¹³C-NMR (100 MHz, TCE-d₂) δ /ppm: low solubility; UV-Vis (CH₂Cl₂) λ_{max} /nm (log ϵ): 545 (4.83); FT-IR (KBr) ν /cm⁻¹: 3113, 3032, 2922, 2224, 1599, 1572, 1541, 1516, 1417, 1379, 1188, 1144, 825; MS (*m/z*) (MALDI-TOF): calculated C₄₀H₂₆N₆: 590.22; found: 590.88 (M⁺).

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2, 0.27 g of **7** (0.39 mmol) in 20 mL of CHCl₃. Purple solid, 81% yield (0.25 g, 0.32 mmol). ¹H-NMR (400 MHz, CDCl₃) δ/ppm: 7.76 (d, 4H, ³J = 8.1 Hz), 7.63 (s, 2H), 7.34 (d, 4H, ³J = 8.1 Hz), 7.27 (d, 4H, ³J = 8.1 Hz), 7.21 (d, 4H, ³J = 8.1 Hz), 6.57 (s, 2H), 2.69 (t, 4H, ³J = 7.7 Hz), 1.71-1.67 (m, 4H), 1.37-1.30 (m, 20H), 0.93-0.90 (m, 6H); ¹³C-NMR (100 MHz, CDCl₃) δ/ppm: 158.6, 142.0, 139.4, 136.8, 136.2, 134.8, 131.0, 129.6, 128.3, 127.8, 125.3, 114.3, 113.2, 96.7, 80.0, 35.5, 31.9, 31.3, 29.5, 29.4, 29.3, 22.7, 14.2; UV-Vis (CH₂Cl₂) λ_{max}/nm (log ε): 548 (4.90); FT-IR (KBr) ν/cm⁻¹: 2953, 2924, 2852, 2224, 1601, 1574, 1516, 1456, 1419, 1379, 1182, 835, 781, 611, 532; MS (*m/z*) (MALDI-TOF): calculated C₅₄H₅₄N₆: 786.44; found: 786.44 (M⁺). Melting point: 208 °C.

Synthesis of **3**

In a round-bottomed flask under argon atmosphere, three drops of Et₃N were added to a solution of ethyl cyanoacetate (5 eq) and **6** (0.53 g, 1.07 mmol, 1 eq) in 100 mL of CHCl₃. The reaction mixture was stirred overnight at 80 °C and treated with brine after consumption of the starting material (monitored by TLC). The organic phase was dried over MgSO₄ and the crude product was purified by chromatography column (silica gel, CHCl₃) and recrystallization from hexane. Pure product **3** was obtained as red solid in 79% of yield (0.58 g, 0.85 mmol). ¹H-NMR (400 MHz, CDCl₃) δ/ppm: 8.15(s, 2H), 7.86 (d, 4H, ³J = 8.1 Hz), 7.31 (d, 4H, ³J = 8.1 Hz), 7.26-7.19 (m, 8H), 6.52 (s, 2H), 4.38 (q, 4H, ³J = 7 Hz), 2.43 (s, 6H), 1.40 (t, 6H, ³J = 7 Hz); ¹³C-NMR (100 MHz, CDCl₃) δ/ppm: 162.9, 154.3, 138.2, 136.9, 136.7, 136.1, 134.1, 131.4, 130.2, 128.8, 127.7, 125.3, 116.1, 100.7, 96.1, 62.6, 21.1, 14.2; UV-Vis (CH₂Cl₂) λ_{max}/nm (log ε): 513 (4.82); FT-IR (KBr) ν/cm⁻¹: 3026, 2983, 2926, 2218, 1722, 1581, 1514, 1460, 1379, 1265, 1192, 827, 768; MS (*m/z*) (MALDI-TOF): calculated C₄₄H₃₆N₄O₄: 684.27; found: 684.40 (M⁺).

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Keywords: bulk heterojunction solar cells · heteropentalenes · sensitizers · fused-ring systems

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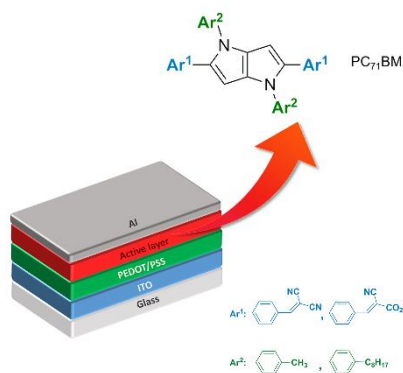
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Small Molecules for Organic Solar

Cells: Three new acceptor-donor-acceptor (A-D-A) small molecules using a tetraaryl-1,4-dihydropyrrolo[3,2-*b*]pyrrole in their central building block were synthesized and fully characterized. These molecules present high thermal stability and suitable HOMO-LUMO energy levels. The bulk heterojunction organic solar cells deliver an open-circuit voltage of 0.99V.



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Pyrrolo[3,2-*b*]pyrrole as Electron-Donor Central Core for Solution-Processed Organic Solar Cells