

Weak Donor-Strong Acceptor Thienopyrazine Based Polymers for Fine Tune of LUMO Levels as Suitable Materials for Energy and Storage Solutions †

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Abstract: A single paragraph of about 100 words to give a brief introduction to your work.

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1. Introduction

The increasing global energy request and the necessity to shift from fossil fuels to renewable energy sources impose to change energy production and storage solutions.

Conjugated semiconducting materials, in between conjugated polymers, may be the protagonists of this epochal change of paradigm because they can be low-cost, lightweight, flexible, derived from raw abundant materials, with low toxicity and reduced environmental impact and able to answer to circular chemistry requests [1–7].

Additionally, a wide range of electronic properties can be accessed through well-developed synthetic organic chemistry. This has allowed conjugated polymers to address optical and electronic properties for many applications, such as light-emitting diodes (OLEDs), organic photovoltaics (OPVs), field-effect transistors (OFETs), biosensors, and energy storage devices [8–15].

As far as p-type materials are concerned, satisfactory results have already been obtained while there is still much to be done on n-type materials [16–18]. The development of new n type materials is fundamental for the improvement of organic solar cells with efficiencies exceeding 10% but it is also revealing particularly significant for pseudocapacitors based on to conjugated polymers [19]. In fact, most of these conjugated polymers are only capable of storing charge in a 'positive' potential range, which results in low operating voltages and limited energy and power densities due to the lacking of stable n type redox active materials [20].

The D-A approach with the repeating units consisting in an electron-donating (Donor) and an electron-withdrawing (Acceptor) moiety has been successfully proposed for developing this class of materials [21–24], specifically donor-acceptor copolymers are a combination of an electron donor and an acceptor unit copolymerized via traditional organometallic coupling [25]. As shown in Figure 1, hybridization of frontier molecular orbitals (HOMO and LUMO) of donor and acceptor units yields a low bandgap material with extend absorption into the near-IR region, which has made these systems popular in OPVs active layer. Moreover polymers for solar cells need to maintain a low HOMO

energy level in order to maximize the open circuit voltage (V_{oc}) beside a small band gap in order to maximize the short circuit current (J_{sh}) [26–28]: alternating “weak” donor and “strong” acceptor will maintain a low HOMO energy level thanks to the the weak donor, and reduce the band gap via Intramolecular Charge transfer (ICT) thanks to the “strong” acceptor [29,30].

Very recently [31] it has been proposed for the development of n-type copolymers the use of proquinoidal acceptors strategy able to promote strong π -electron correlations, extensive delocalization, a very narrow bandgap. An aromatic moiety can in fact be described as “proquinoidal” if it has an important resonance contribution from the quinoidal form and the proquinoidal character can be improved by fusing additional aromatic rings [32]. Notable examples of proquinoidal–aromatic copolymers with proquinoidal building blocks, including thieno[3,4-b]pyrazine (TP) [33] have been developed as active materials for organic field-effect transistors, photovoltaics, organic light-emitting diodes, and many other applications [34].

The TP structure is an isomer of the well-known 2,1,3-Benzothiadiazole (BT) [35] successfully employed as OPV active material achieving PCEs over 18% [36,37]. In addition, TP unit compared to BT (Figure 1) has an important resonance contribution from the quinoidal form in the resonance structures forming a six membered aromatic sextet, and thus additionally lowering the band gap of conjugated polymers with respect to BT [38]. Another potential advantage of TP in conjugated polymers is that the TP moiety provides a more planar backbone between repeating units owing to decreased steric hindrance of the thiophene ring compared to the benzene ring in BT based copolymers

TP-based materials have been developed for OPV applications moreover they possess many attributes that are advantageous to pseudo capacitors, such as the ability to reversibly store negative charge [19,39].

By miming the well-known poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT) we have synthesized the analogue Poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2 thieno[3,4-e]pyrazines)] and the random copolymer between 9-(9-Heptadecanyl)-9H-carbazole-2,7-diboronic acid bis(pinacol) ester with 4,7-Bis(2-bromo-5-thienyl)-2,1,3-benzothiadiazole and 4,7-Bis(2-bromo-5-thienyl)- 2 Thieno[3,4-e]pyrazines]. In our polymers, there is significant internal charge transfer character between electron-rich (donor) and electron-deficient (acceptor) components furthermore, they maintained the ability to reversibly store negative charge and the random copolymer approaches [40] seem to be effective for the fine modulation of HOMO-LUMO levels, finally the polymers are highly soluble in organic solvents and can be processed by solution deposition approaches, rendering them versatile and scalable.

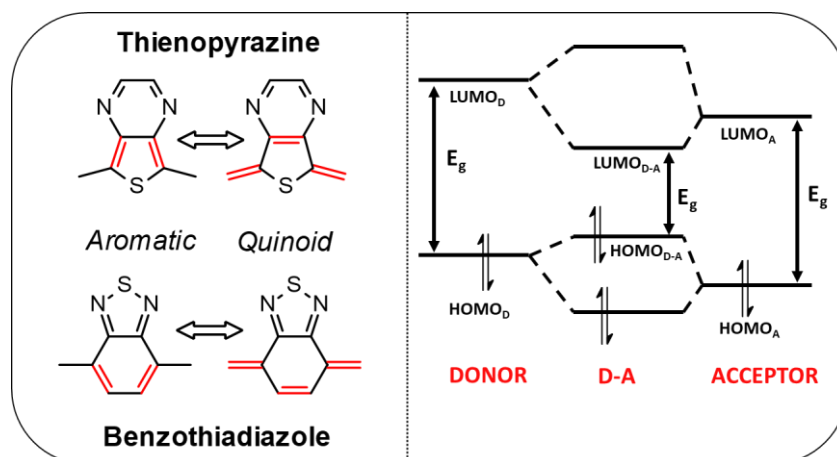


Figure 1. Aromatic and quinoid resonance structure of thienopyrazine and benzothiadiazole unit (left). Hybridization of frontier molecular orbital (HOMO and LUMO) of donor and acceptor unit (right).

2. Materials and Methods

General Information for synthesis. Unless specifically mentioned, all reagents were purchased from commercial source and used without further purification. Toluene was freshly distilled prior to use according to literature procedure. All reaction were carried out in inert atmosphere. Compound M1 was prepared according to the procedures reported in the literature [41,42].

PCDTBT was purchased from 1-Materials. PC₇₀BM (99.5% purity) was purchased from Solenne BV.

Electrochemistry. Electrochemistry was performed at room temperature in acetonitrile under nitrogen in three electrode cells. The counter electrode was platinum; reference electrode was Ag/Ag⁺ (0.1 m AgNO₃ in acetonitrile, 0.34 V vs. SCE, -4.73 V vs. vacuum), supporting electrolyte was 0.1 m tetrabutylammonium perchlorate (TBAP). PCDTBT, PCDTTB and PC(DTTP)_{0.5}(DTBT)_{0.5} films were casted onto electrodes at 80–90 °C from CHCl₃ solution, respectively. The voltammetric apparatus was Metrohm Autolab 128N potentiostat/galvanostat. The working electrode for cyclic voltammetry (CV) was a glassy-carbon (CG) minidisc electrode (0.2 cm²). HOMO and LUMO levels were estimated according to the equation $E_{\text{HOMO}} = -(E_{\text{OX}} + 4.39 + 0.34)$ [43].

Size Exclusion Chromatography (SEC). The molecular weight distribution (MWD) of all samples was obtained by an integrated high-temperature (HT) size exclusion chromatography (SEC) system. The chromatographic system consisted of a GPCV2000 system from Waters (USA) equipped on-line with a differential refractometer (DRI) as concentration detector.

Experimental Conditions: column set constituted by 3 Shodex HT from Showa Denko (Japan); mobile phase: o-dichlorobenzene (o-DCB); flow rate: 0.8 mL/min; temperature: 135 °C.

Nuclear Magnetic Resonance (NMR). ¹H NMR and ¹³C NMR spectra were recorded with Bruker DRX 600 MHz spectrometer.

Synthesis of compound M2. Compound M1 (1 40 mg, 0.47 mmol, 1 eq.) was dissolved in dry chloroform (CHCl₃, 25 mL) and cooled down at 0 °C. Then N-bromosuccinimide (NBS; 174 mg, 0.98 mmol, 2.1 eq.) and glacial acetic acid (CH₃COOH, 25 mL) were added. The reaction was allowed to reach room temperature in the dark by shielding the flask with aluminum foil. After 1 h at room temperature, the crude product was diluted with CHCl₃ and washed 3 times with saturated sodium bicarbonate (NaHCO₃) solution. The organic solvent was removed under reduced pressure and the product was purified by silica gel chromatography and recrystallized from hexane/dichloromethane (143 mg, 66% yield) ¹H NMR (CDCl₃) δ (ppm): 8.51 (s, 2H), 7.31 (d, 2H), 7.1(d, 2H).

Synthesis of polymer PCDTTP. A mixture of monomer M2(65 mg, 0.142 mmol, 1 eq.), 9-(9-Heptadecanyl)-9H-carbazole-2,7-diboronic acid bis(pinacol) ester (93 mg, 0.142 mmol, 1 eq.), Tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄) (3.3 mg, 2% mmol), tetrabutylammonium bromide (TEBAB) were added in a predegassed schlenk, followed by three vacuum/nitrogen cycles. Then dry toluene (4 mL) and degassed potassium carbonate aqueous (2 mL) solution were added. The mixture was stirred at 110 °C. After 5 h, there was the precipitation of the polymer and the reaction was quenched. The crude was precipitated in methanol. The polymer was washed on Soxhlet apparatus with methanol, hexane and chloroform. The chloroform fraction was evaporated under reduced pressure and the polymer was precipitated in methanol, filtered and dried under high vacuum, providing a dark solid (25 mg, 35% yield), ¹H NMR (CDCl₃) δ (ppm) 8.6 (broad, 2H), 8.1–8.0 (broad, 2H), 7.9–7.7 (broad, 4H), 7.58 (broad, 2H), 7.4 (broad, 2H), 4.1 (broad, 1H) 1.2–1.1 (broad, 26H), 0.8 (broad, 8H); MW = 3.7 kDa, MN = 8.1 kDa, PD = 2.22).

Synthesis of polymer PC(DTTP)_{0.5}(DTBT)_{0.5}. A mixture of monomer M2 (58 mg, 0.126 mmol, 0.5 eq.), 4,7-Bis(5-bromo-2-thienyl)-2,1,3-benzothiadiazole (58 mg, 0.126 mmol, 0.5 eq.), 9-(9-Heptadecanyl)-9H-carbazole-2,7-diboronic acid bis(pinacol) ester) (166 mg, 0.253 mmol, 1 eq.), Tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄) (6 mg, 2% mol), tetrabutylammonium bromide (TEBAB) were added in a predegassed schlenk, followed by three vacuum/nitrogen cycles. Then dry toluene (6 mL) and degassed potassium carbonate aqueous solution (3 mL) were added. The mixture was stirred at 110 °C. After 6 h, the polymer started to precipitate and the reaction was quenched. The crude was precipitated in methanol. The polymer was washed on Soxhlet apparatus with methanol, hexane and chloroform. The chloroform fraction was evaporated under reduced pressure and the polymer was precipitated in methanol, filtered and dried under high vacuum, providing a dark solid (95 mg, 46% yield) ¹H NMR (CDCl₃) δ (ppm):) 8.54 (broad, 2H), 8.2–8.1 (broad, 4H), 7.9–7.7 (broad, 6H), 7.6–7.4 (broad, 4H), 7.2–7.0 (broad, 2H), 4.8–4.7 (broad, 1H) 1.2–1.1 (broad, 26 H), 0.8 (broad, 8H). (MW = 3.2 kDa, MN = 6.1 kDa, PD = 1.81).

Device Fabrication and Photovoltaic Characterization

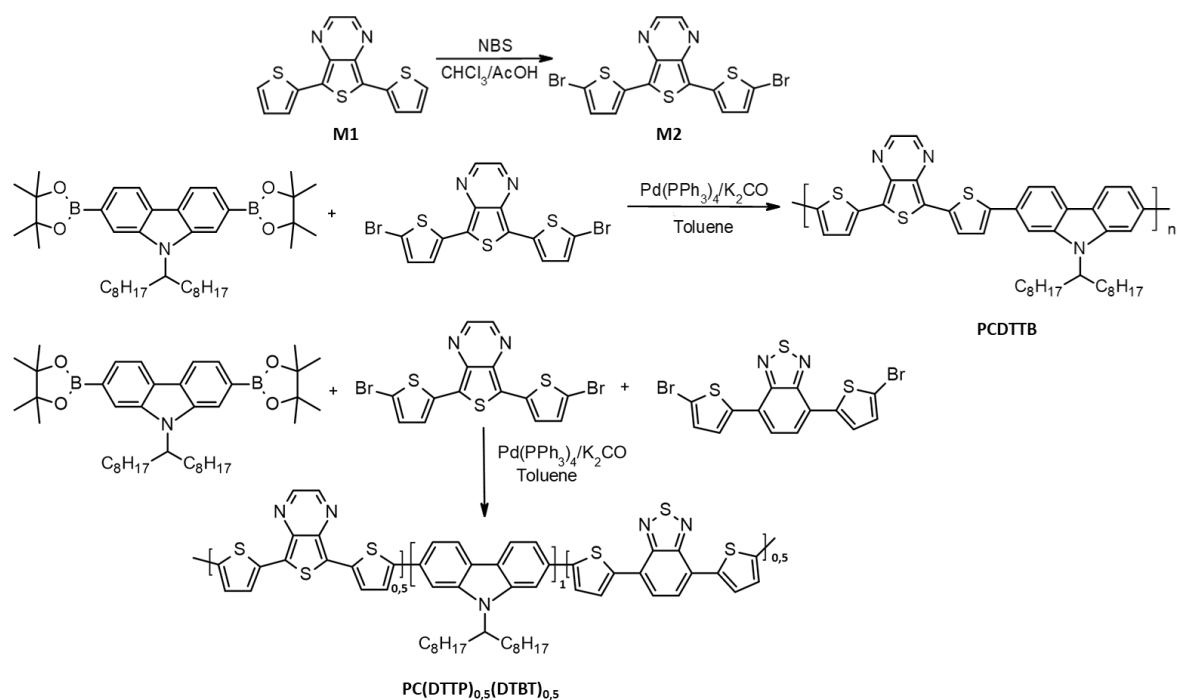
Direct Geometry devices fabrication. Solar cells were assembled with the conventional structure Glass/ITO/PEDOT:PSS/PCDTTP:PC₇₀BM/Ca/Al. Glass ITO (Kintec) 15 Ω/sq substrates were mechanically cleaned with peeling tape and paper with acetone and then were washed in a sonic bath at 50 °C for 10 min sequentially with water, acetone, and isopropanol. After drying with compressed nitrogen flow, 10 min plasma treatment in the air was used to enhance ITO wettability for the next deposition. PEDOT:PSS (AI VP 8030 from Heraeus) was filtered on a 0.45 μm nylon filter, spin-coated in the air at 2500 rpm for 50 s. The device assembly was then performed in glovebox. The active layer was composed by a blend dissolved at 1:4 wt/wt of PCDTTP:PC₇₀BM solution in a 1,2-dichlorobenzene:chlorobenzene 3:1 v:v mixture at a total concentration of 30 mg/mL. The solution was stirred for 12 h on a hotplate in glovebox at 60 °C. The active layer was spin-coated from the warm solution at 1000 rpm for 60 s, which results in a thickness of 95 nm, at 1200 rpm for 60 s, which results in a thickness of 85 and at 1500 rpm for 60 s, which results in a thickness of 70 nm. Finally, the substrates were stored in a glovebox and annealed at 70 °C for 15 min. Finally, 10 nm of Calcium and 100 nm-thick aluminium electrode was evaporated on the top of the device through a shadow mask under a pressure of 2 × 10⁻⁶ mbar. The deposition rate was 0.5 nm/s. There were six devices on a single substrate, each with an active area of 6.1 mm².

Device characterization and measurements. The devices were characterized through current density–voltage and external quantum efficiency characterization. Current density–voltage measurements were performed directly in the glovebox where the solar cells were assembled, with a Keithley 2602 source meter, under AM 1.5G solar simulator (ABET 2000). The incident power, measured with a calibrated photodiode (Si cell + KG5 filter), was 100 mW/cm². The EQE spectral responses were recorded by dispersing an Xe lamp through a monochromator, using an Si solar cell with a calibrated spectral response to measure the incident light power intensity at each wavelength. The devices were taken outside the glovebox for the EQE measurements, after mounting them on a sealed cell to avoid moisture and oxygen exposure.

3. Results and Discussions

3.1. Chemical Characterization

Polymers PCDTTP and PC(DTTP)_{0.5}(DTBT)_{0.5} were synthesized through Suzuki cross-coupling of a dibromide of the acceptor units and the bis-boronic ester of carbazole, with Pd(PPh₃)₄ as a catalyst and K₂CO₃ as a base in degassed toluene as solvent (Scheme 1). Both polymers show low molecular weight due to the poor solubility of the growing chain during polymerization.



Scheme 1. Synthesis of compound M2, polymer PCDTTB and polymer PC(DTTP)_{0.5}(DTBT)_{0.5}.

We decided to use a non-substituted TP derivative in order to have a direct comparison with the well-known PCDTBT copolymer. Moreover the strategy of donor-acceptor conjugated polymers with minimally substituted acceptor moieties [44] has been revealed particularly useful in order to understand the electronic role of the acceptor and the impact of the steric hindrance of the acceptor can be clarified in future studies by inserting linear or branched lateral alkyl chains on TP or thienyl moieties. For this reason, it was not possible to use Palladium-Catalyzed Direct C–H Arylation coupling due to the formation of cross-linked byproducts on the unsubstituted positions [45].

The ¹H NMR spectra of the two synthesized polymers confirmed the presence of the polymers, the peaks are large and broad compatibly with the polydispersity and poor solubility of the materials in room temperature CDCl₃. The FT-IR spectra showed the characteristic aliphatic and aromatic C–H bending between 3000 and 2700 cm⁻¹, and the characteristic aromatic C=C and C=N stretching of aromatic compound.

3.2. Optoelectronic Characterization

The absorption spectra in thin films and CHCl₃ solution of the synthesized polymers PCDTTP and PC(DTTP)_{0.5}(DTBT)_{0.5} and the purchased PCDTB were recorded. The polymers showed two major absorption peaks, a common feature for alternating D–A copolymers and the two new polymers showed a red shifted absorption compared to PCDTBT. In particular the random copolymer PC(DTTP)_{0.5}(DTBT)_{0.5} showed a panchromatic absorption spectrum from 450 nm to 700 nm (Figure 2) and the low energy peak, ascribed to intramolecular charge transfer (ICT), showed the two contributions of the precursor copolymers.

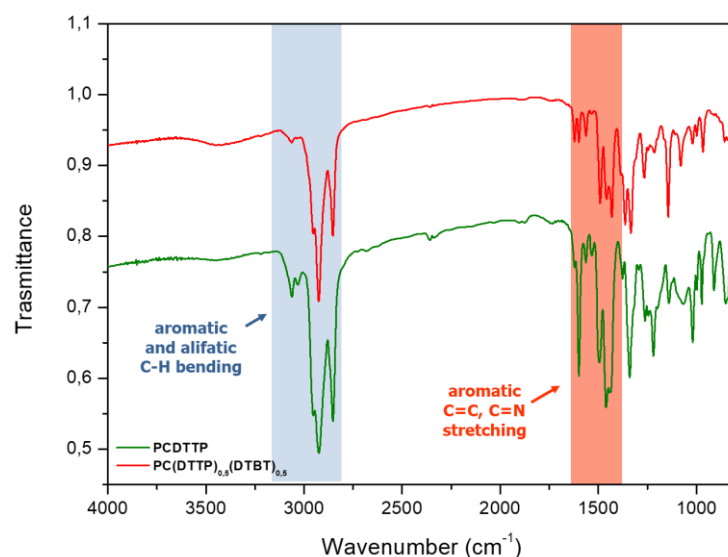


Figure 2. FT-IR spectra of polymers PCDTTP and PC(DTTP)_{0.5}(DTBT)_{0.5}.

The optical energy gap (Table 1) was calculated from the onset of the solid-state absorption spectra: the two new polymers have a similar energy gap (1.60 eV), smaller than the PCDBT polymer (1.89 eV).

Cyclic Voltammetry (CV) determinations (Figure 2b) showed that PCDTBT and PCDTTP presented one irreversible oxidation process, at 0.589 V and 0.627 V, respectively, that probably interests their electron-donating (donor) moieties. In PC(DTTP)_{0.5}(DTBT)_{0.5}, the oxidation process splitted into two reversible ones separated by ca. 0.24 V (see Table 1). The latter could be a solid-state effect which may be accounted for by the formation of mixed-valence states analogous to those found in TTF polymers [46]. All samples presented a single reversible reduction process, that is probably localized on the electron-withdrawing (acceptor) moieties of the molecules.

It is important to underline a lowering of the electrochemical E_g going from PCDTBT to PCDTTP up to PC(DTTP)_{0.5}(DTBT)_{0.5}. This behavior can be attributed to the greater contribution of the quinoid form in the polymer containing the TP unit additionally lowering the band gap. Furthermore, the presence of the TP moiety resulted in an increased backbone planarity thanks to the decreased steric hindrance of the five membered thiophenic ring compared to the six membered benzenic ring. The further decrease in electrochemical E_g in the random copolymer can be attributed to the increase in the mean length of conjugation in the D-A segments.

Table 1. Optoelectronic properties of polymers PCDTBT, PCDTTP, PC(DTTP)_{0.5}(DTBT)_{0.5}.

Polymer	Solution [nm] ^a	Film [nm] ^b		E_g^{opt} [eV] ^c	E_{ox} [eV]	E_{red} [eV]	HOMO [eV] ^d	LUMO [eV]	E_g^{cv} [eV] ^e
	λ_{max}	λ_{max}	λ_{onset}						
PCDTBT	560	581	656	1.89	0.53	-1.70	-5.27	-3.03	2.24
PCDTTP	635	655	775	1.61	0.35	-1.56	-5.08	-3.17	1.91
PC(DTTP) _{0.5} (DTBT) _{0.5}	518, 611	550, 640	766	1.60	0.20	-1.51	-4.93	-3.23	1.7

^a Polymer deluted solution in CHCl₃; ^b Thin film on glass; ^c Estimated from the absorption band edge in film, $E_g^{\text{opt}} = 1240/\lambda_{\text{onset}}$ (eV); ^d $E_{\text{HOMO}} = -4.39 - (E_{\text{ox}} + 0.34)$ eV; $E_{\text{LUMO}} = -4.39 - (E_{\text{red}} + 0.34)$ eV; ^e $E_g^{\text{cv}} = E_{\text{LUMO}} - E_{\text{HOMO}}$.

The absorption spectra and photoluminescence (PL) spectra of PCDTTP and PC(DTTP)_{0.5}(DTBT)_{0.5} were also recorded in solvent with different polarity.

As show in Figure 3 the absorption spectra are not affected by the different nature of the solvent, while the emission maxima result redshifted in polar solvents. The linear

correlation observed between Stokes shift and solvent polarity (E_T^N) (Figure 3e) can be ascribed to a the stabilization of the highly polar charge-transfer excited states in more polar solvents, typical of donor-acceptor emitter [47,48].

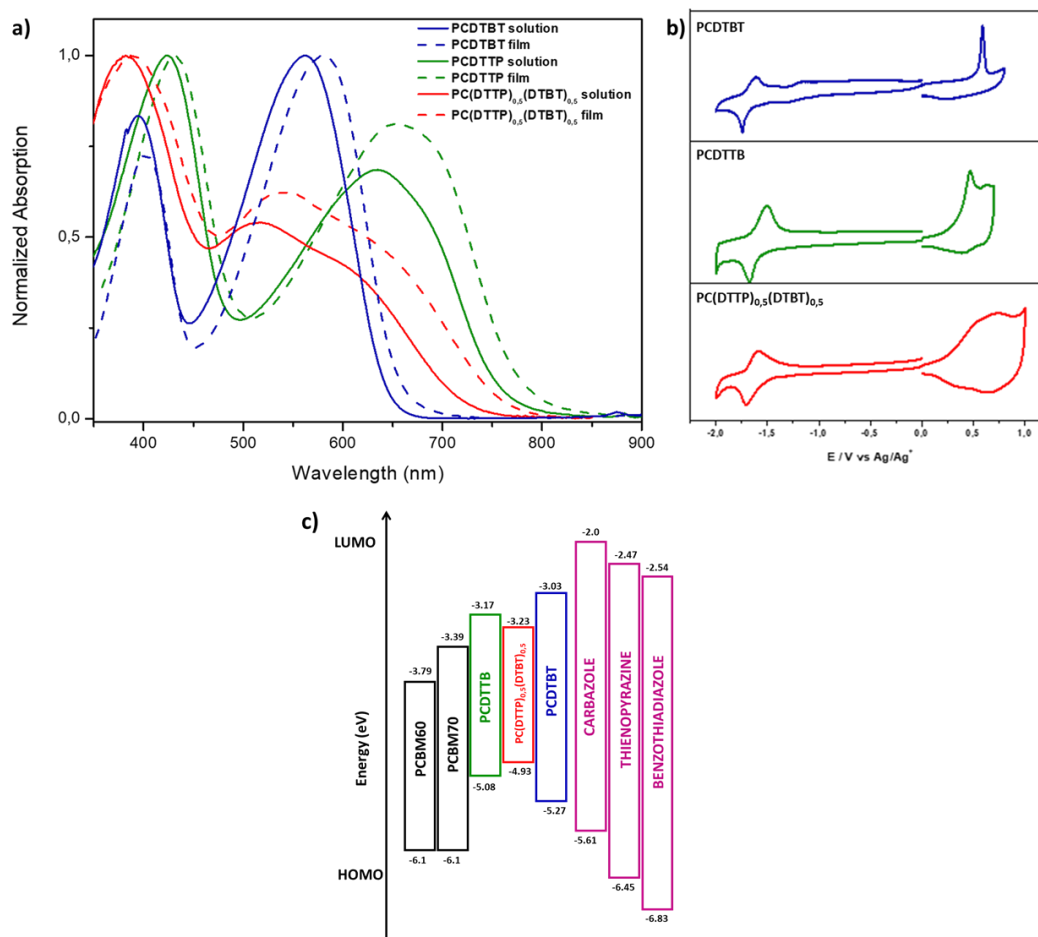


Figure 3. (a) Absorption spectra in CHCl₃ solution and solid state of polymers PCDTBT, PCDTTP, PC(DTTP)_{0.5}(DTBT)_{0.5}. (b) Voltammograms of polymers PCDTBT, PCDTTP, PC(DTTP)_{0.5}(DTBT)_{0.5}. (c) Energy levels digram.

3.3. Photovoltaic CHARACTERIZATION

The photovoltaic characteristics were investigated upon blending PCDTTP with PC71BM in bulk heterojunction devices. The current density-voltage curves (J-V) of devices with different active layer thicknesses under AM1.5 simulated solar light illumination (100 mW/cm²) are shown in Figure 4a and the corresponding photovoltaic parameters are depicted in Table 2. The power conversion efficiency (η) obtained with PCDTTP are reaching 1.24%, which is in line to the reported values in the literature for other TP based polymers OPV devices [39]. The PCDTTP devices exhibit an open circuit voltage (V_{oc}) of 0.58 V which is about 0.2–0.3 V lower than the benchmark PCDTBT solar cells reported in the literature [49]. Such reduction of the V_{oc} could result from the upward shift of the HOMO level of PCDTTP displayed in Figure 2 [26]. In addition the short circuit current density J_{sc} reaching 5.5 mA/cm² in PCDTTP devices is about a half of the typical values reported in the benchmark PCDTBT cells [49] (DOI: 10.1039/c3ta12420g). One of the reasons that may eventually contribute to the relatively lower J_{sc} and EQE values, could be the lower LUMO energy levels offset among the polymer and fullerene component that may limit the charge photogeneration yield[50]. The relatively low FF of 0.39 suggests a non optimal charge separation or transport to the electrodes. Interestingly, the EQE spectra displayed in Figure 4b exhibits an onset at 780 nm (1.59 eV), which is red

shifted when compared to PCDTBT devices [51]. This is consistent with the reduced optical energy gap of PCDTTP displayed in Table 1.

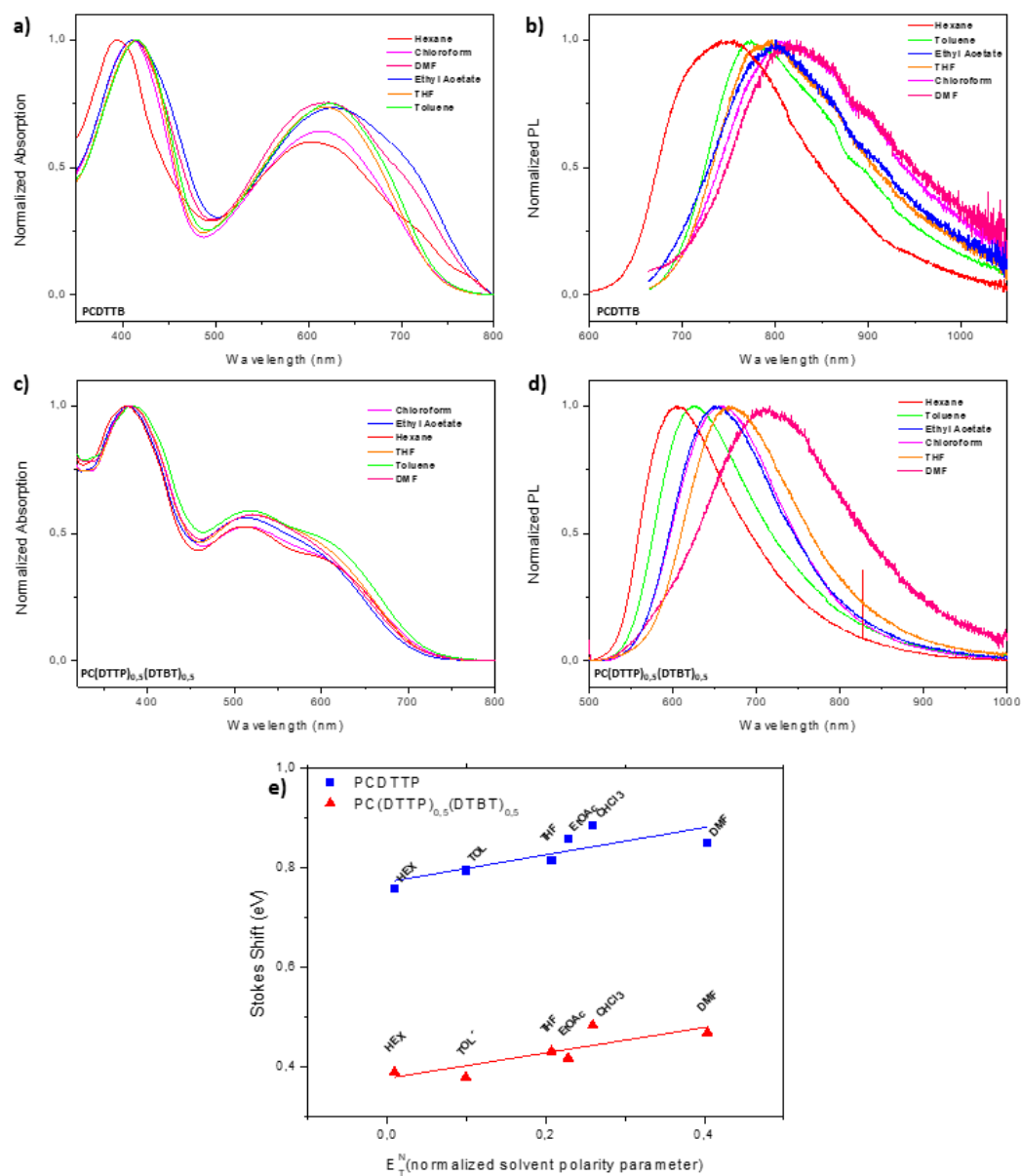


Figure 4. Absorption and emission spectra of polymers PCDTTP (a,b) and PC(DTTP)_{0.5}(DTBT)_{0.5} (c,d) in different solvents (hexane, toluene, chloroform, tetrahydrofuran, N,N-dimethylformamide, ethyl acetate). (e) Stokes shift against normalized solvent polarity parameter.

Table 2. Summary of the photovoltaic parameters.

Thickness	V _{oc} [V]	FF [–]	J _{sc} [mAcm ⁻²]	η [–]	J _{sc} ^{EQE} [mAcm ⁻²] ^a
70	1.89	0.53	–5.27	–3.03	2.24
75	1.61	0.35	–5.08	–3.17	1.91
95	1.60	0.20	–4.93	–3.23	1.7

^a Calculated from the AM1.5G and EQE spectra.

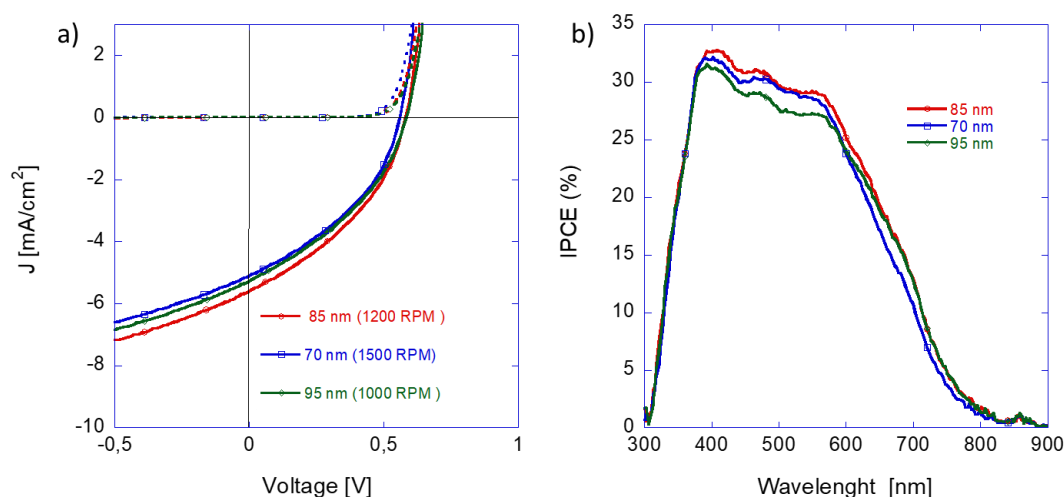


Figure 5. (a) Current density-voltage curves vs. active layer thicknesses of PCDTTP:PC71BM devices. Continuous lines: under 1 sun of AM1.5G solar simulation (100 mW/cm^2); dotted lines: dark curves. (b) EQE spectra vs. active layer thicknesses of PCDTTP:PC71BM devices.

4. Conclusions

In summary, we synthesized an alternating Donor–Acceptor copolymer via Suzuki coupling based on 9'-heptadecanyl-2,7-carbazole as Donor and 2-thienyl-2 thieno[3,4-e]pyrazines as Acceptor and the random terpolymer from the same donor unit and two different acceptors unit namely the 2-thienyl-2 thieno[3,4-e]pyrazines and its isomeric 2-thienyl-2',1',3'-benzothiadiazole. The polymers were chemically characterized and their optical, electrochemical, and photovoltaic properties were discussed also in comparison with the well-known PCDTBT.

The TP based copolymer showed a red shifted absorption and emission both in solution and thin film with respect to the isomeric BT based copolymer reasonably due to the greater contribution of the quinoid form in the presence of TP. The random terpolymer showed extended absorption and lowered electrochemical E_g compared to the parent polymers and this behavior could be ascribed to the increased delocalization of the system due to the presence of two acceptors with different strength as previously observed [40].

This work will help guide the synthetic design of n-type materials that can be applied as acceptor in OPV devices but also will give a contribute for long-standing challenge of finding a stable n-type material for supercapacitors for energy storage. Specifically, we showed that it is possible lowering the LUMO levels by using the random tercopolymer approaches with two different acceptor units maintaining the electrochemical reversibility of the reduction.

Author Contributions: B.M.S. performed the synthesis of materials; E.L. contributed to OPV preparation and characterization; C.B. was responsible for PL spectra; S.L. contributed to the discussion of PV results; B.V. was responsible for CV; S.Z. was responsible for SEC and FT-IR characterization; M.P. and B.S. designed the idea plan, discussed the data and prepared the manuscript. All authors have read and agreed to the published version of the manuscript.

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