

Tuning the HOMO energy levels in quinoline and biquinoline based donor-acceptor polymers

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Abstract Four donor-acceptor type polymers based on quinoline and biquinoline have been synthesized by Pd catalyzed direct C-H (hetero)arylation reaction. Polymers **P1** and **P2** are alternate copolymers of thiophene-benzothiadiazole-thiophene (TBTT) unit with quinoline and biquinoline unit, respectively. **P3** is a random copolymer containing cyclopentadithiophene (CPDT), benzothiadiazole and quinoline moieties in the backbone whereas **P4** contains CPDT unit with randomly distributed benzothiadiazole and biquinoline units. All the polymers show good thermal stability and solubility in common organic solvents. CPDT based polymers **P3** and **P4** exhibit higher absorbance maxima, higher lying Highest Occupied Molecular Orbital (HOMO) energy levels and smaller band gap as compared to thiophene based polymers **P1** and **P2** as a result of better electron-donating ability of the former leading to stronger intramolecular charge transfer. Also, quinoline based polymers **P1** and **P3** show a red-shift in the absorbance maxima compared to biquinoline based polymers **P2** and **P4**, respectively due to non-planar transoid conformation of the two quinoline rings in the biquinoline unit. It is found that the use of N-heterocycle based comonomers allows the tuning of the HOMO level over a remarkably wide range (~0.8 eV). Additionally, the use of quinoline or biquinoline along the conjugated chain leads to deeper lying

HOMO levels suggesting good oxidative stability for this class of materials.

Keywords Quinoline · Biquinoline · Donor-acceptor · Cyclopentadithiophene · 2,1,3-benzothiadiazole · Optical properties

Introduction

In the last few decades, fabrication of a variety of optoelectronic devices such as organic photovoltaic devices (OPVs), organic light emitting diodes (OLEDs), and organic field effect transistors (OFETs) have attracted considerable interest. [1–4] The active layer in all these devices is a conjugated organic material. In recent years, low band gap donor-acceptor (DA) polymers consisting of alternating electron-donating and electron-withdrawing building blocks along the polymer backbone has been widely used as an active layer in OPVs. [5–7] Apart from providing low band gap to maximize light harvesting, DA concept leads to tuning of the HOMO and Lowest Unoccupied Molecular Orbital (LUMO) energy levels by varying the electron-donating ability of the donor and electron-accepting ability of the acceptor. [8, 9] The internal charge transfer (ICT) between the donor and acceptor moiety leads to enhanced double bond character between the repeating units leading to more planar configuration of the polymer backbone thus facilitating π -electron delocalization which subsequently leads to smaller band gap and promotes high charge mobility. Therefore, a large number of DA polymers with various donor and acceptor units have been designed, synthesized and applied in the fabrication of photovoltaic devices and has played an important role in improving the device performance. [10–17].

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Due to the presence of electron rich sulphur atom both thiophene and CPDT act as efficient electron-donating moieties and numerous conjugated polymers containing thiophene and CPDT as donor with various acceptor units with improved device performance have been designed and synthesized. [18–21] 2,1,3-Benzothiadiazole is the most widely investigated electron-accepting unit and its copolymers with various electron-donating species such as fluorene, thiophene, carbazole, CPDT etc. have been synthesized and applied in the fabrication of photovoltaic devices. [22–24] Polymers containing thiophene-benzothiadiazole-thiophene (TBTT) segment with various aromatic moieties such as fluorene, carbazole and thiophene exhibit broad absorption in the region of 300–700 nm. [25–29].

Quinoline based copolymers show n-type electrically conducting properties due to the presence of electron-withdrawing aromatic ring containing imine-nitrogen. [30–32] Polyquinolines possess outstanding oxidative and thermal stability, high glass transition temperature, low moisture absorption and good film forming properties. [33–36] In our previous work, it was shown that the introduction of electron-deficient quinoline unit in polyfluorene backbone results in low lying LUMO energy levels in the resulting polymers. [37].

In the present study, four novel DA polymers poly[(quinoline-5,8-diyl)-alt-(4,7-bis-(4-octylthiophene-2-yl)-2,1,3-benzothiadiazole-5,5 -diyl)] **P1**, poly[(8,8-biquinoline-5,5 -diyl)-alt-(4,7-bis-(4-octylthiophene-2-yl)-2,1,3-benzothiadiazole-5,5 -diyl)] **P2**, poly{[2-(quinoline-5-yl)-4,4 -dioctylcyclopenta[2,1-b:3,4-b]dithiophene-8,6 -diyl]-co-[2-(2,1,3-benzothiadiazole-4-yl)-4,4 -dioctylcyclopenta[2,1-b:3,4-b]dithiophene-7,6 -diyl]} **P3** and poly{[2-(8,8 -biquinoline-5-yl)-4,4 -dioctylcyclopenta[2,1-b:3,4-b]dithiophene-5,6 -diyl]-co-[2-(2,1,3-benzothiadiazole-4-yl)-4,4 -dioctylcyclopenta[2,1-b:3,4-b]dithiophene-7,6 -diyl]} **P4** have been synthesized (Fig. 1). **P1** and **P2** are alternating copolymers where **P1** contains alternate TBTT and quinoline unit in the polymer backbone and **P2** is a copolymer containing TBTT and biquinoline. **P3** and **P4** are random polymers having CPDT moiety as donor and randomly distributed 2,1,3-benzothiadiazole and either quinoline (**P3**) or biquinoline (**P4**) unit as acceptor in the polymer chain. All the four polymers have been synthesized by Pd catalyzed direct-arylation polymerization reaction and have been analyzed for their optical, thermal, electrochemical properties.

Experimental

Materials

The precursors 4,7-bis(4-octylthiophen-2-yl)-benzothiadiazole [23] (**1**), 5,8-dibromoquinoline [37] (**2**), 5,5 dibromo-8,8 -biquinoline [38] (**3**), 4,4-dioctylcyclopenta[2,1-b:3,4-b

]dithiophene [39] (**4**) and 4,7-dibromobenzothiadiazole [40] (**5**) were prepared according to the literature procedures. Pivalic acid was purchased from Sigma Aldrich. Potassium carbonate (K_2CO_3) and dimethylacetamide (DMAc) were purchased from Spectrochem and used without further purification. All the reactions were carried out using dry solvents under a nitrogen atmosphere unless specified otherwise.

Instrumentation and methods

1H NMR spectra were recorded on a Bruker 300 MHz spectrometer in $CDCl_3$ with TMS as an internal standard. Analytical Thin Layer Chromatography (TLC) was conducted using Merck silica gel precoated aluminium plates. The UV/Visible spectra for polymer solutions and films were obtained with a T90+ UV/Visible spectrophotometer and Perkin Elmer, Lambda 1050 UV/VIS/NIR Spectrometer, respectively. Cyclic Voltammetry (CV) measurements were carried out on an Autolab 30 at a scan rate of 50 mVs^{-1} . Tetrabutylammoniumperchlorate (Bu_4NClO_4) in acetonitrile (0.1 M) was used as supporting electrolyte. A three electrode cell was used with Ag/AgCl electrode as the reference electrode and platinum (Pt) wires as both the working and counter electrodes. The films for electrochemical measurement were prepared on a Pt electrode by dipping in a viscous solution of the polymer in chloroform. Thermogravimetric traces for the polymers were recorded on a Q-50 TGA instrument from TA instruments. The experiment was carried out under nitrogen atmosphere at a heating rate of $20\text{ }^\circ\text{Cmin}^{-1}$ with 5 ± 1 mg sample. DSC analysis was carried on a TA Instruments DSC Q200 instrument under nitrogen atmosphere at a heating/cooling rate of $10\text{ }^\circ\text{Cmin}^{-1}$. Molecular weights were measured using a Gel permeation chromatograph (GPC) containing a PLgel column at a flow rate of 1 mL/min against polystyrene standards in chloroform.

OFET fabrication

Field effect transistors using the polymers were made on cleaned glass substrates, in bottom gate-top contact geometry (BG-TC). 40 nm Aluminium gate electrodes were deposited on the glass substrates by thermal evaporation of pure aluminium at 5×10^{-6} mbar pressure, at a rate of $1\text{ A}^\circ/\text{s}$. PMMA (poly(methyl methacrylate)) solution prepared in propylene carbonate solution (80 mg/mL) was spin coated on the gate electrode at 800 rpm and baked at $110\text{ }^\circ\text{C}$ for 1 h in inert atmosphere. Polymer solute on (10 mg/mL concentration in chlorobenzene) was spin coated at 600 rpm and annealed at $100\text{ }^\circ\text{C}$ in N_2 filled glove box for 1 h. 40 nm thick gold top contacts were evaporated using thermal evaporation method at 5×10^{-6} mbar pressure, maintaining a deposition rate of $0.1\text{ A}^\circ/\text{s}$.

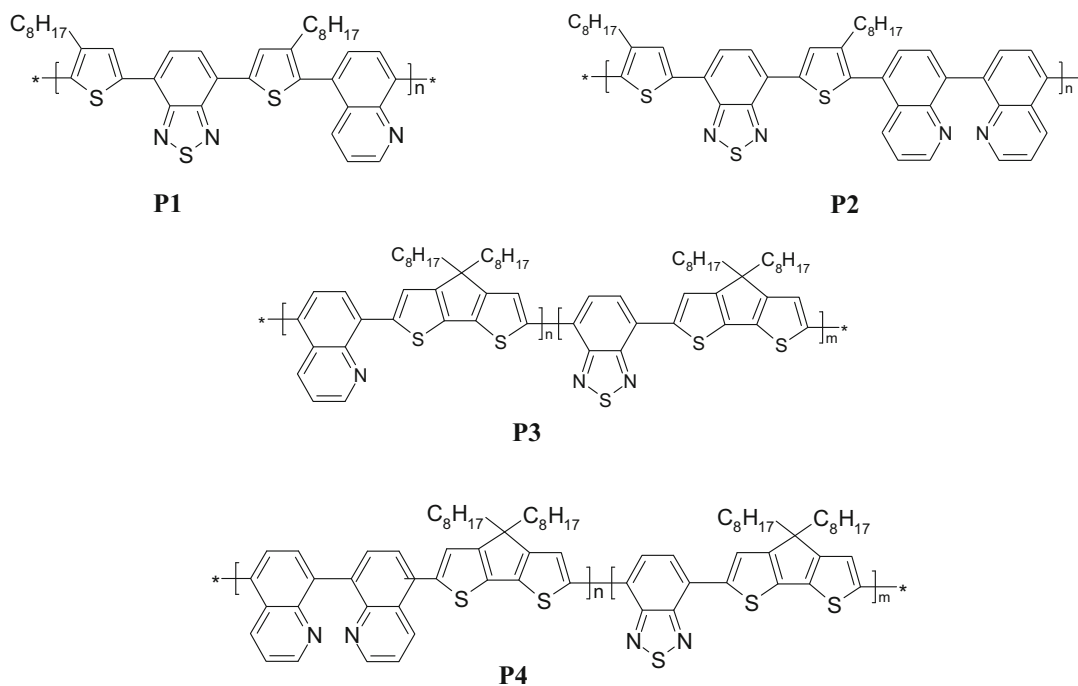


Fig. 1 Structure of polymers **P1-P4**

Electronic characterization of hence prepared organic field effect transistors were carried out using a Keithley 4200-SCS system, while keeping the devices in vacuum (10^{-2} mbar). Mobility of transistors was calculated using standard transistor equation in saturation regime

$$I_{ds} = \frac{\mu_{FET}^{sat} C_{ox} W}{2L} (V_G - V_t)^2$$

Where I_{ds} is the saturation current, μ_{FET}^{sat} is the saturation mobility, C_{ox} is the capacitance per unit area of dielectric, W is the width of channel, V_G is the gate voltage, V_t is the threshold voltage and L is the length of the channel.

Synthetic procedures

Synthesis of poly[(quinoline-5,8-diyl)-alt-(4,7-bis-(4-octylthiophene-2-yl)-2,1,3-benzothiadiazole-5,5 -diyl)] P1

A mixture of $\text{Pd}(\text{OAc})_2$ (3 mg, 0.013 mmol), K_2CO_3 (96 mg, 0.69 mmol), pivalic acid (8.4 mg, 0.083 mmol), **1** (146 mg, 0.279 mmol) and **2** (80 mg, 0.279 mmol) was stirred in DMAc (5.5 mL) at 80 °C for 12 h under a nitrogen atmosphere. It was then cooled to room temperature, the polymer was precipitated in methanol, filtered, washed with EDTA and purified by soxhlet extraction with acetone and chloroform. The chloroform portion was concentrated and reprecipitated in methanol, filtered and dried. The product was obtained as a red solid (175 mg, 96 %). $^1\text{H NMR}$ (300 MHz, CDCl_3): δ

8.87–8.73 (m, 1H), 8.56–8.33 (m, 2H), 8.08–7.58 (m, 6H), 2.79 (bm, 4H), 1.55–0.79 (m, 30H). $M_n = 3.6 \times 10^3 \text{ gmol}^{-1}$, $M_w = 7.56 \times 10^3 \text{ gmol}^{-1}$, $M_w/M_n = 2.1$.

Synthesis of poly[(8,8-biquinolin-5,5 -diyl)-alt-(4,7-bis-(4-octylthiophene-2-yl)-2,1,3-benzothiadiazole-5,5 -diyl)] P2

P2 was synthesized according to the procedure followed for **P1** using $\text{Pd}(\text{OAc})_2$ (3 mg, 0.013 mmol), K_2CO_3 (96 mg, 0.69 mmol), pivalic acid (8.4 mg, 0.083 mmol) **1** (146 mg, 0.279 mmol) and **3** (115 mg, 0.279 mmol) in DMAc (5.5 mL) at 80 °C for 12 h. The product was obtained as a red solid (185 mg, 85 %). $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 8.86 (bs, 2H), 8.35–8.20 (m, 3H), 8.10–7.8 (m, 7H), 7.39 (bs, 2H), 2.68–2.55 (4H), 1.66–0.82 (m, 30H). $M_n = 5.03 \times 10^3 \text{ gmol}^{-1}$, $M_w = 7.94 \times 10^3 \text{ gmol}^{-1}$, $M_w/M_n = 1.58$.

Synthesis of poly{[2-(quinoline-5-yl)-4,4 -dioctylcyclopenta[2,1-b:3,4-b]dithiophene-8,6 -diyl]-co-[2-(2,1,3-benzothiadiazole-4-yl)-4,4 -dioctylcyclopenta[2,1-b:3,4-b]dithiophene-7,6 -diyl]} P3

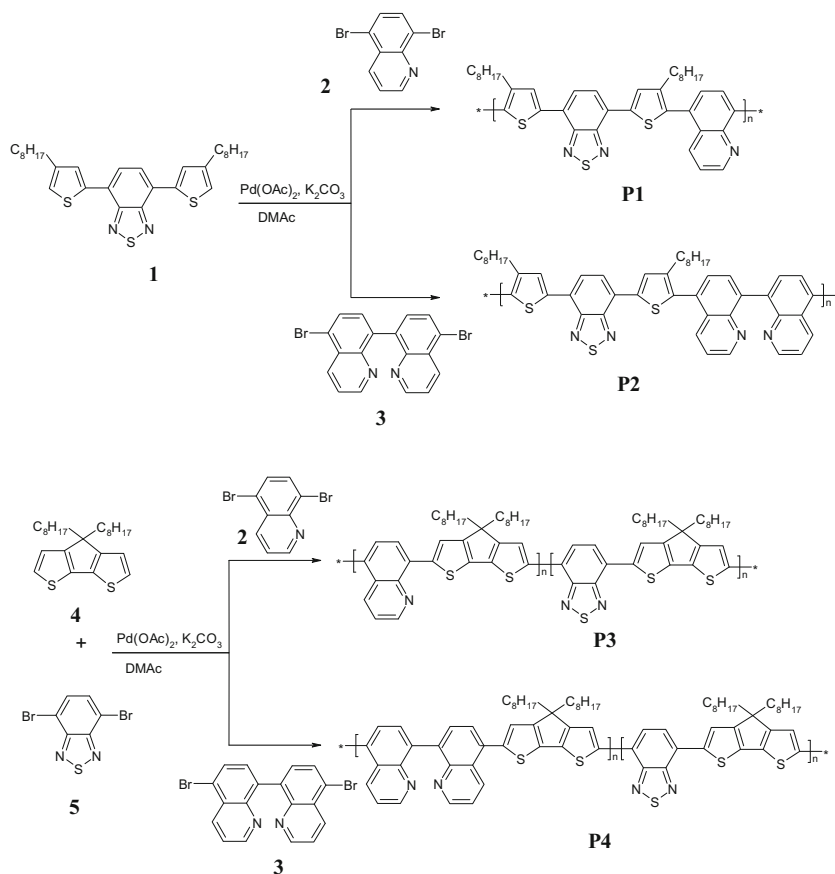
P3 was synthesized according to the procedure followed for **P1** using $\text{Pd}(\text{OAc})_2$ (8.3 mg, 0.03 mmol), K_2CO_3 (257 mg, 1.864 mmol), pivalic acid (22 mg, 0.22 mmol), **4** (300 mg, 0.746 mmol), **5** (109 mg, 0.373 mmol) and **2** (106 mg, 0.373 mmol) in DMAc (3.3 mL) at 80 °C for 24 h. The product was obtained as a dark solid (290 mg, 73 %). $^1\text{H NMR}$

(300 MHz, CDCl_3): δ 9.10 (bs, ArH), 8.71 (bd, ArH), 8.10 (bs, ArH), 7.87 (bm, ArH), 7.55 (bs, ArH), 7.13 (m, ArH), 2.01 (bs, 8H $\alpha\text{-CH}_2$), 1.56–0.83 (m, 60H). $M_n = 5.3 \times 10^3 \text{ gmol}^{-1}$, $M_w = 9.43 \times 10^3 \text{ gmol}^{-1}$, $M_w/M_n = 1.78$.

2.3.4 synthesis of poly{[2-(8,8-biquinoline-5-yl)-4,4-dioctylcyclopenta[2,1-b:3,4-b]dithiophene-5,6-diyl]-co-[2-(2,1,3-benzothiadiazole-4-yl)-4,4-dioctylcyclopenta[2,1-b:3,4-b]dithiophene-7,6-diyl]}
P4

P4 was synthesized according to the procedure followed for **P1** using $\text{Pd}(\text{OAc})_2$ (8.3 mg, 0.03 mmol), K_2CO_3 (257 mg, 1.864 mmol), pivalic acid (22 mg, 0.22 mmol), **1** (300 mg, 0.746 mmol), **5** (109 mg, 0.373 mmol) and **3** (154 mg, 0.373 mmol) in DMAc (3.3 mL) at 80 °C for 24 h. The product was obtained as a dark solid (340 mg, 76.5 %). ^1H NMR (300 MHz, CDCl_3): δ 8.88 (bs, ArH), 8.77 (bs, ArH), 8.10 (bd, ArH), 7.87 (bs, ArH), 7.44 (bs, ArH), 7.00 (bs, ArH), 2.03 (bd, 8H $\alpha\text{-CH}_2$), 1.21–0.84 (m, 60H). $M_n = 7.6 \times 10^3 \text{ gmol}^{-1}$, $M_w = 1.29 \times 10^4 \text{ gmol}^{-1}$, $M_w/M_n = 1.71$.

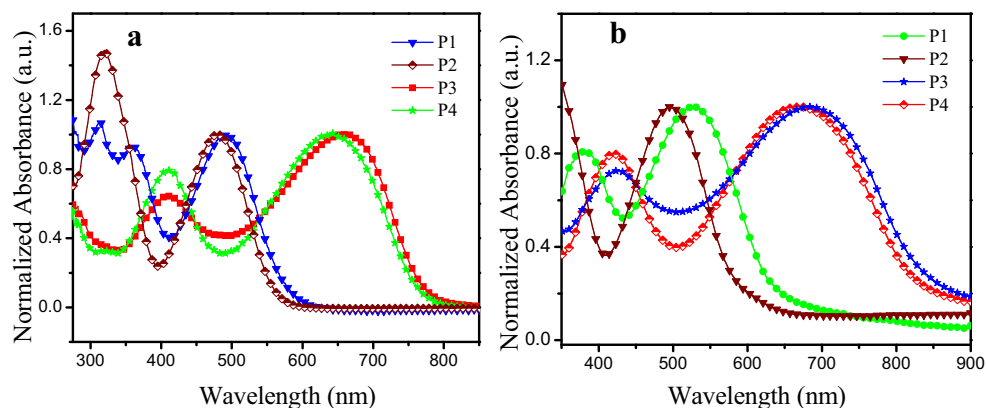
Scheme 1 Schematic for the synthesis of polymers **P1**, **P2**, **P3** and **P4**



Results and discussion

The synthetic pathway for polymers **P1-P4** is outlined in Scheme 1. All the polymers were synthesized using Pd catalyzed direct-arylation polycondensation reaction by heating corresponding monomers with $\text{Pd}(\text{OAc})_2$, Pivalic acid and DMAc at 80 °C under nitrogen atmosphere. All the monomers **1**, **2**, **3**, **4** and **5** were synthesized based on literature procedures. [23, 37–40] Alternate polymers **P1** and **P2** were obtained by reacting **1** with **2** and **3**, respectively. Random polymer **P3** was obtained by reacting **4** with an equimolar mixture of the dibromides, **5** and **2** whereas **P4** was prepared using **3** instead of **2**. Comparison of **P1** and **P3** with **P2** and **P4** provides an insight how the optical and electrochemical properties are affected by replacing quinoline unit with biquinoline unit. Also, comparing **P1** and **P2** with **P3** and **P4** show the effect of replacing thiophene unit by CPDT unit. This method gave the desired polymers in greater than 72 % yield. All the polymers showed good solubility in common organic solvents and gel permeation chromatography (GPC) measurements against polystyrene standards showed the

Fig. 2 Normalized absorption spectra of polymers **P1-P4** in chloroform solution **a** and in thin film **b**



number-average molecular weight to be 3.6×10^3 g mol^{-1} , 5.03×10^3 g mol^{-1} , 5.3×10^3 g mol^{-1} and 7.6×10^3 g mol^{-1} for **P1**, **P2**, **P3** and **P4**, respectively.

Optical properties

The UV-vis absorption spectra of the polymers **P1-P4** in dilute chloroform solution and spin coated films are shown in Fig. 2. The absorption maxima and estimated optical band gaps are summarized in Table 1. The absorption spectra of all the polymers are characterized by two major absorption peaks, which is a common feature of alternating DA copolymers. The low wavelength absorption peak can be attributed to the higher energy π - π^* transitions and long wavelength absorption peak can be attributed to the intermolecular charge-transfer transition (ICT) between the donor moiety and the acceptor unit. **P1**, **P2**, **P3** and **P4** showed their absorbance maxima at 494 nm, 481 nm, 664 nm and 649 nm, respectively. Absorbance maxima for polymers **P1** and **P3** containing quinoline unit in the backbone is red-shifted by 13 nm and 15 nm as compared to biquinoline based polymers **P2** and **P4**, respectively. The higher value of absorbance maxima for **P1** and **P3** is most likely due to more efficient electron delocalization resulting from a more planar structure.[38, 37] **P3** and **P4** display a strongly red-shifted absorption

band when compared to **P1** and **P2** indicating stronger ICT between the donor CPDT and acceptor unit due to more electron-donating nature of CPDT in comparison with thiophene.

Going from solution to solid state, a red-shifted and comparatively broader absorption bands for **P1**, **P2**, **P3** and **P4** were observed with absorbance maxima centered at 530 nm, 497 nm, 684 nm and 672 nm, respectively. A strong tailing effect in the solid state was observed making the determination of onset difficult. The optical band gap estimated from the thin film absorption onsets are 1.92 eV, 2.03 eV, 1.44 eV and 1.45 eV for **P1**, **P2**, **P3** and **P4**, respectively. The optical band gap of polymers containing thiophene unit (**P1** and **P2**) is higher than that of polymers having CPDT moiety (**P3** and **P4**) due to more effective ICT in **P3** and **P4**.

Electrochemical properties

The electrochemical properties of the polymers films were investigated using cyclic voltammetry. The positions of the HOMO energy levels and LUMO energy levels were estimated from the onset oxidation potential ($E_{\text{ox}}^{\text{onset}}$) and onset reduction potential ($E_{\text{red}}^{\text{onset}}$) respectively, using the equations $\text{HOMO} = - (E_{\text{ox}}^{\text{onset}} + 4.4)$ eV and $\text{LUMO} = - (E_{\text{red}}^{\text{onset}} + 4.4)$ eV. Cyclic voltammograms of the synthesized polymers are shown in

Table 1 Optical and electrochemical properties of polymers **P1-P4**

Polymer	$\lambda_{\text{max}}^{\text{soln}}$ (nm)	$\lambda_{\text{max}}^{\text{film}}$ (nm)	$E_{\text{g}}^{\text{opt}}$ (eV) ^a	HOMO (eV) ^b	LUMO (eV) ^c	E_{g}^{ec} (eV) ^d
P1	494	530	1.92	-5.82	-3.84	1.98
P2	481	497	2.03	-5.75	-3.87	1.87
P3	664	684	1.44	-5.19	-3.79	1.40
P4	649	672	1.45	-5.03	-3.83	1.20

^a The optical band gap calculated from absorption edge of solution UV of the copolymers

^b Estimated from $\text{HOMO} = - (E_{\text{ox}}^{\text{onset}} + 4.4)$ eV

^c Estimated from $\text{LUMO} = - (E_{\text{red}}^{\text{onset}} + 4.4)$ eV

^d Electrochemical band gap estimated from $E_{\text{g}}^{\text{ec}} = \text{HOMO} - \text{LUMO}$

Fig. 3 Cyclic voltammograms of **P1** (a), **P2** (b), **P3** (c) and **P4** (d) in thin films on a Pt electrode in 0.1 mol/L $\text{Bu}_4\text{NClO}_4/\text{acetonitrile}$ solution

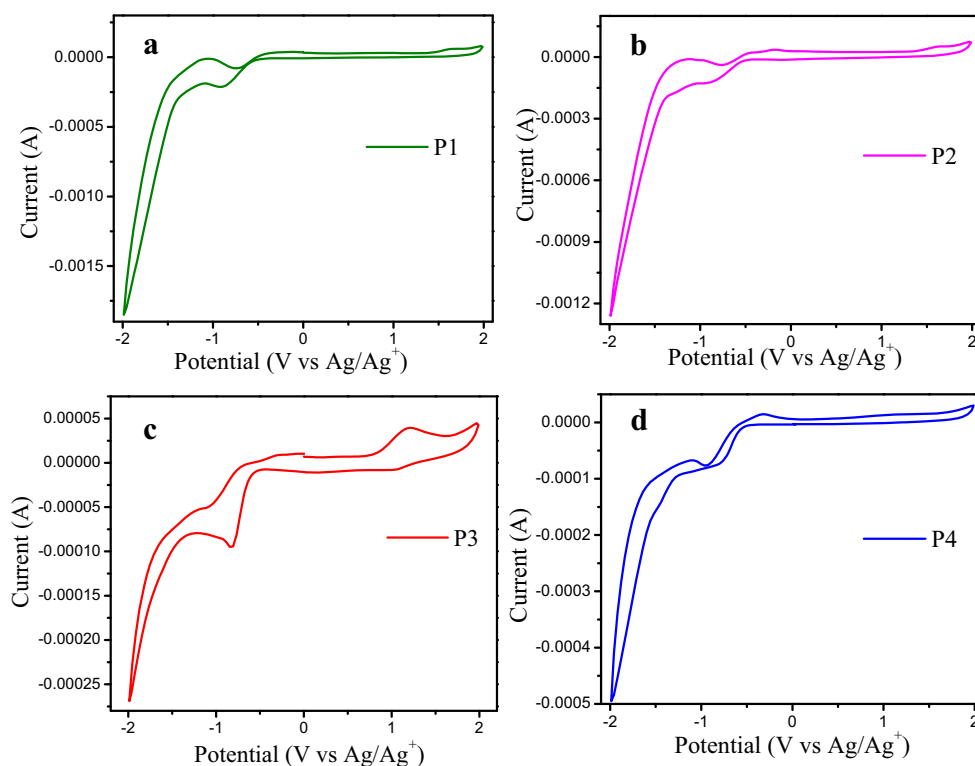


Fig. 3 and the electrochemical properties estimated from cyclic voltammetry are summarized in Table 1.

The estimated HOMO energy levels for polymers **P1**–**P4** lie in the range of -5.82 eV and -5.03 eV. The HOMO energy levels for **P1** and **P2** are -5.82 eV and -5.75 eV, respectively whereas the HOMO energy levels of **P3** and **P4** are positioned at -5.19 eV and -5.03 eV, respectively (Energy level diagram shown in Fig. 4). The HOMO energy levels of DA polymers are essentially dominated by the electron-donating unit and are affected by the electron-donating ability of the donor. Thus, the introduction of highly donating CPDT

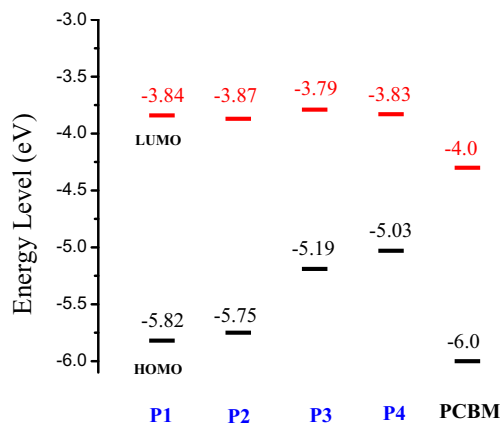
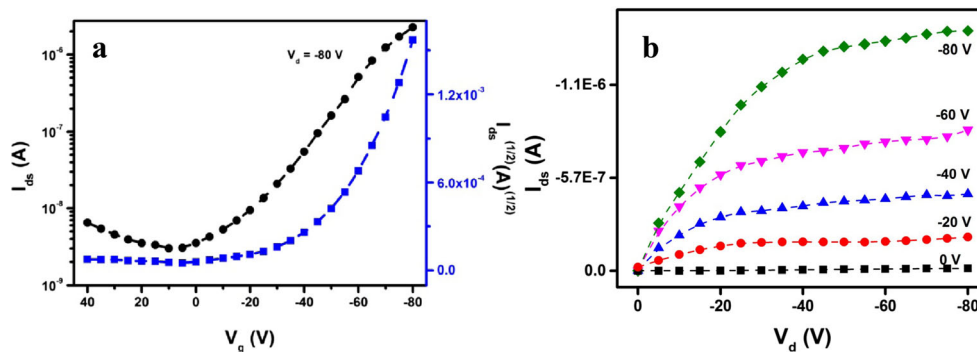


Fig. 4 Energy level diagram of **P1**–**P4** and PCBM

moiety in **P3** and **P4** by replacing thiophene unit in **P1** and **P2** results in higher HOMO energy levels. The deeper lying HOMO levels suggest that the incorporation of quinoline or biquinoline can help in designing conjugated materials with improved oxidative stability. The estimated LUMO energy levels for **P1**, **P2**, **P3** and **P4** are -3.84 eV, -3.87 eV, -3.79 eV and -3.83 eV, respectively. The LUMO energy levels of the polymers are essentially dominated by the acceptor unit (here BT and either quinoline or biquinoline unit) which explains the low and similar reduction potential and LUMO energy levels for all the four polymers. The reduction potential for polymers containing biquinoline unit in the backbone is slightly less than that of polymers containing quinoline unit. The ease in reduction of **P2** and **P4** compared to **P1** and **P3** shows that the introduction of biquinoline unit imparts better electron-accepting property to the polymer but the effect is small due to steric hindrance between the two quinoline units. Electrochemical band gap (E_g^{ec}) for **P1**, **P2**, **P3** and **P4** estimated from difference between the HOMO energy level and LUMO energy level were found out to be 1.98 eV, 1.87 eV, 1.40 eV and 1.20 eV, respectively. Biquinoline based polymers, **P2** and **P4** show smaller electrochemical band gap as compared to quinoline containing polymers **P1** and **P3**, respectively. A slight difference in the electrochemical band gap and optical band gap is observed for all the polymers since the

Fig. 5 **a** Transfer and **b** output characteristics measured for a transistor based on **P3**



determination of oxidation or reduction potential using cyclic voltammetry requires removal or addition of electrons, respectively, whereas optical band gap is the energy difference for intramolecular excitonic state. [41].

Field effect transistors

FET characteristics of these semiconductors were studied. The transfer characteristics and the output characteristics for transistor based on **P3** and **P4** are shown in Figs. 5 and 6, respectively. It is to be noted that apart from the interfacial mobility, the varying HOMO levels of the different polymers also play a decisive factor and the presence of sizable electrode-semiconductor barrier can dominate the I-V characteristics. It was observed that in all the devices tested, CPDT based random copolymers **P3** and **P4** exhibit hole-type transport with average mobility values (10 sample average) $11 \times 10^{-3} \text{ cm}^2/\text{Vs}$ and $6 \times 10^{-3} \text{ cm}^2/\text{Vs}$ respectively. On the other hand, the polymers TBTT based **P1** and **P2** did not exhibit typical FET characteristics. This can be attributed to the existence of a dominant contact resistance and/or to transport parameters arising from reduced planarity and double bond character prevailing in **P1** and **P2** systems.

Thermal properties

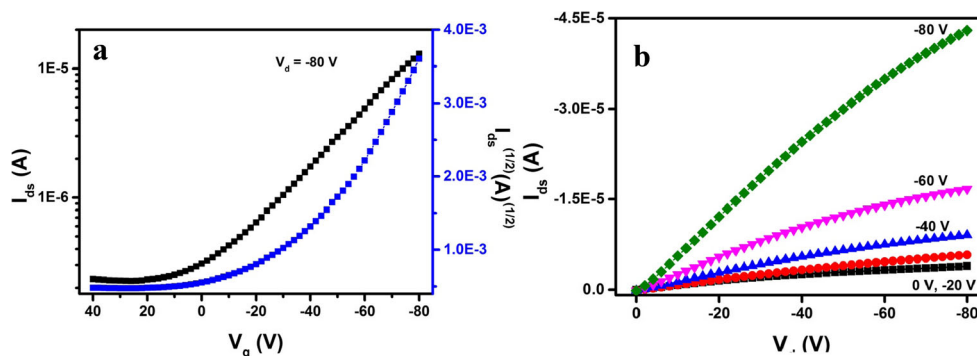
The 5 % weight loss temperatures for the polymers **P1-P4** were found to be between 350 C and 405 C, with no weight loss up to approximately 300 C, indicating that all the four

polymers are thermally stable. **P2**, **P3** and **P4** show clear glass transitions at 90 C, 81 C and 85 C, respectively whereas **P1** does not show any clear transition. The insertion of biquinoline unit in the backbone increased the thermal stability and the glass transition temperature of the polymer.

Conclusions

A series of DA polymers based on quinoline and biquinoline unit in the backbone have been designed and synthesized by palladium catalyzed direct-arylation polycondensation reaction. Two alternating polymers containing TBTT segment and either quinoline (**P1**) or biquinoline (**P2**) unit and two random polymers incorporating donor CPDT moiety and randomly distributed 2,1,3-benzothiadiazole and either quinoline (**P3**) or biquinoline (**P4**) unit were synthesized and their thermal, optical and electrochemical properties of the synthesized polymers were investigated. Quinoline based polymers **P1** and **P3** show absorbance maxima centered at longer wavelength as compared to biquinoline based polymers **P2** and **P4**. The HOMO energy levels of polymers containing thiophene as donor (**P1** = -5.82 eV, **P2** = -5.75 eV) are deeper lying as compared to CPDT based polymers (**P3** = -5.19 eV, **P4** = -5.03 eV). Also, the absorbance maxima for polymers **P3** and **P4** are red-shifted as compared to **P1** and **P2** due to the more electron-donating nature of CPDT compared to thiophene leading to stronger ICT. The estimated electrochemical

Fig. 6 **a** Transfer and **b** output characteristics measured for a transistor based on **P4**



band gap for **P1**, **P2**, **P3** and **P4** are 1.98 eV, 1.87 eV, 1.4 eV and 1.2 eV, respectively. The deeper lying HOMO levels suggest high oxidative stability for this class of polymers and all of them showed thermal stability greater than 300 °C. Field effect transistors made using **P3** and **P4** polymers exhibited hole type charge transport, whereas those made using **P1** and **P2** does not showed any device characteristics.

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