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Vinylidenedithiophenmethyleneoxindole: a centrosymmetric building block for donor–acceptor copolymers†

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Further development of new building blocks is crucial for realizing next-generation, high-performance organic semiconducting materials. In the paper, the design and synthesis of a novel π-extended analogue of isoindigo, vinylidenedithiophenmethyleneoxindole (**VDTOI**), and two **VDTOI**-based copolymers is reported. The centrosymmetric **VDTOI** unit possesses a special acceptor–donor–acceptor structure and contains a highly planar conjugated backbone because of the presence of S···O conformational locks. Of special importance is the fact that the **VDTOI** unit has the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital and energy levels of −5.35 eV/−3.42 eV, which are similar properties to those of the thiophene-flanked diketopyrrolopyrrole building block. The previously mentioned structural features indicate that **VDTOI** might be a potential building block for constructing polymeric semiconductors. As a trial, two **VDTOI**-based copolymers were synthesized, namely **P1** and **P2**. The two copolymers show good thermal stability and broad absorption spectra ranging from 330 to 740 nm. Their HOMO energy levels of around −5.40 eV match well with the work function (5.13 eV) of a gold (Au) electrode, which is indicative of effective hole injections from the Au electrodes to polymer semiconductor films. Both the **P1**- and **P2**-based field-effect transistors exhibited typical p-type transport characteristics. The highest mobility of 0.35 $cm^2 V^{-1} s^{-1}$ was achieved in **P1**-based devices.

Introduction

The third-generation polymers, donor–acceptor (D–A) copolymers, have been widely investigated because of their intriguing and adjustable electronic and optoelectronic properties for potential application in printable opto-electronic devices.[1–3] During the past few years, significant progress in polymeric light-emitting diodes,[4–6] organic photovoltaics,[7–9] and organic field-effect transistors (OFETs)[10–14] has encouraged the continued designing and discovering of new building blocks for constructing new polymers with high thermal stability, broad and intense absorption, and prompt and efficient charge transport. Up to the present time, however, most of the record high mobilities are still limited to several versatile electron-donating or electron-withdrawing building blocks derived from D–A type copolymers. These building blocks include diketopyrrolopyrrole (**DPP**),[15–18] naphthalene diimide,[19–21] isoindigo (**II**),[22–24] benzothiadiazole,[25] benzobisthiadiazole,[26] thieno[3,2-*b*]thiophene,[27] (*E*)-1,2-di(thiophen-2-yl)ethene (**VT**), and (*E*)-1,2-di(selenophen-2-yl)ethene (**VS**), and benzodithiophenes,[28,29] and so on. Therefore, designing more novel building blocks is of equal importance as developing high-performance, polymeric semiconductors and determining the inherent relationship between molecular structures and opto-electronic properties for realizing next-generation, printable electronics.

Since J. G. Mei presented the method for the synthesis of **II** unit, various **II**-based polymers have been synthesized and investigated for opto-electronic applications.[30] For example, the highest power conversion efficiency of 8.2% was obtained in **II**-based polymer/fullerene bulk heterojunction solar cells, whereas a high hole mobility of over 3.0 $cm^2 V^{-1} s^{-1}$ was given by **II**-based polymer FETs.[22,24a] Encouraged by these achievements, great efforts have been paid to developing **II** derived building blocks and related polymeric semiconductors.[31–33] For example, to obtain high planarity, the outer phenyl rings of **II** were replaced by thiophene rings which gave a new building block, thienoisoindigo, which has an enhanced planar conjugated backbone because of the elimination of steric

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repulsion between the protons on the phenyl rings and the carbonyl oxygens of the oxindoles. Furthermore, because of the disappearance of α-H on the phenyl rings, thienoisoindigo endows the copolymers with thiophene–thiophene links with optimized planarity, thus maximizing conjugation and further enhancing attractive interchain interactions. In another example, a novel **II** derived building block, benzodifurandione-based oligo(*p*-phenylene vinylene) (BDOPV), in which oxindoles are bridged by a strong electron-deficient benzodifurandione moiety was also developed.[34] The resulting BDOPV has the lowest unoccupied molecular orbital (LUMO) energy level of −4.2 eV, compared to −3.5 eV for **II**. As result, the corresponding polymers exhibited enhanced electron transport performance and device stability under ambient conditions.

In recent years, the concept of conformational locks has been put forward and applied in developing high-performance semiconducting polymers. Conformational locks refer to weak noncovalent interactions such as S···O, O···H, F···H, and so on, which are considered to be favorable for conjugated backbone planarity, and/or acquiring strong intra- and inter-molecular interactions between neighboring molecules. In previous work, novel oxindole-based oligomers had been synthesized.[34] Solution-processed OFETs based on the oligomers were obtained which exhibited a hole mobility of 0.045–0.075 $cm^2\ V^{-1}\ s^{-1}$. The promising results made this attractive for developing further oxindole-based building blocks for D–A copolymers. In the research reported in this paper, a novel π-extended analogue of **II**, vinylidenedithiophenmethyleneoxindole (**VDTOI**, Fig. 1), was developed. The new **VDTOI** unit has a linear and planar conjugated system with centrosymmetric acceptor–donor–acceptor (A–D–A) geometry. Because of the centrosymmetric structure, the **VDTOI** unit is easily synthesized and, more importantly, is beneficial for **VDTOI**-based derivatives forming ordered molecular packing in the solid state. With the introduction of a π-extended VS unit, the steric repulsion of O···H occurring in the **II** unit has been eliminated. Meanwhile, the **VDTOI** unit possesses S···O noncovalent interactions, which could bring additional intra- and inter-molecular interactions in **VDTOI**-based copolymers. In addition, the solubility of the **VDTOI**-based derivatives can easily be tuned by changing the alkyl side chains. Furthermore, the **VDTOI** unit has similar strong electron-deficient properties to those of the thiophene-flanked DPP unit, rather than the **II** unit. These structural features indicate that **VDTOI** might be a potential building block for constructing high-performance polymeric semiconductors. As a trial, two **VDTOI**-based copolymers **P1** and **P2**, in which the VT or VS building block acts as donor unit, were synthesized (Fig. 1). The copolymers display good solution processability and broad absorption profiles throughout the visible spectra with the optical bandgap of approximately 1.70 eV. Solution-processed OFETs based on **P1** exhibited a maximum hole mobility of 0.35 $cm^2\ V^{-1}\ s^{-1}$ and an average hole mobility of 0.21 $cm^2\ V^{-1}\ s^{-1}$ with a high on/off current ratio of 10^6–10^7.

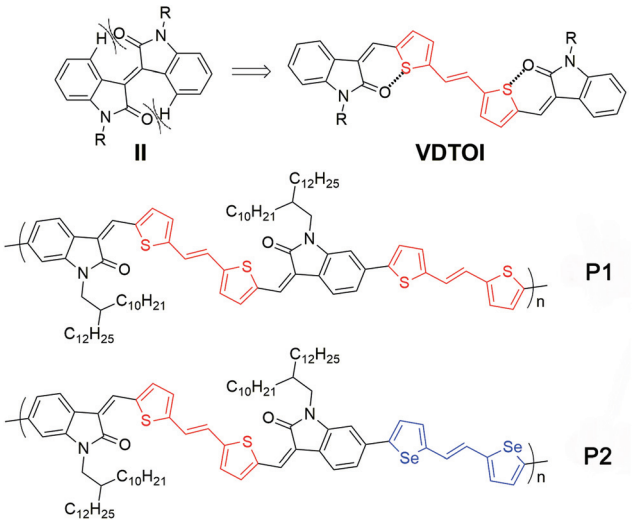

Fig. 1 Design strategy for the **VDTOI** building blocks and the chemical structures of **VDTOI**-based copolymers.

Experimental section

General procedures and requirements

The catalysts and chemicals such as *n*-butyllithium (*n*BuLi), 6-bromoindolin-2-one and 11-(bromomethyl)tricosane, and solvents were purchased from commercial sources, and used as received without further purification. Tetrahydrofuran (THF) was freshly distilled over sodium and benzophenone, and *N*,*N*-dimethylformamide (DMF) was distilled over calcium hydride under nitrogen before use. The (*E*)-1,2-di(thiophen-2-yl)ethene, (*E*)-1,2-bis(5-(trimethylstannyl)thiophen-2-yl)-ethene, and (*E*)-1,2-bis(5-(trimethylstannyl)selenophen-2-yl)-ethene, were synthesized according to a previously established method.[15a]

Measurements and characterization

Proton nuclear magnetic resonance spectroscopy (^{1}H-NMR) and ^{13}C-NMR spectra were recorded on a Bruker 300 MHz NMR spectrometer and the chemical shifts were reported in parts per million (ppm). ^{1}H-NMR chemical shifts were referenced to internal tetramethylsilane (0 ppm), deuterated tetrachloroethane ($CDCl_2CDCl_2$, 6.0 ppm) and ^{13}C-NMR chemical shifts were referenced to deuterated chloroform ($CDCl_3$, 77 ppm). High resolution mass spectrometry (HRMS) was performed using a Bruker APEX II or Bruker 9.4T SolariX Fourier-transform – ion cyclotron resonance mass spectrometers. Elemental analysis was carried out using a Vario EL III CHNOS Elemental Analyzer. Ultraviolet-visible (UV-vis) absorption spectra in chloroform solution and the absorption of the thin films was recorded using an Hitachi U-3010 spectrophotometer. The film absorption measurement samples were prepared by spin-coating polymer solution in chloroform onto quartz glass. Cyclic voltammetry (CV) was carried out on an electrochemistry workstation with a traditional three electro-

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lyte configuration in dry acetonitrile at room temperature. The measurements used 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte, a platinum (Pt) rod as the working electrode, Pt wire as the counter electrode, and silver/silver chloride (Ag/AgCl) as the reference electrode with a scan rate of 50 mV s^{-1}. Thermogravimetric analyses (TGA) were determined on a PerkinElmer series 7 thermal analysis system under nitrogen (N_2) at a heating rate of 10 °C min^{-1}. High temperature gel permeation chromatography (GPC) analysis was performed on a Polymer Labs PL-GPC 220 system using a refractive index detector at 150 °C and using 1,2,4-trichlorobenzene as the eluent with various polystyrenes used as standards. Thin film morphology were investigated in air using a Digital Instruments Nanoscope V atomic force microscope (AFM) operated in tapping mode, and the samples were identical to those used in field-effect performance analysis. The polymeric packing mode in the solid state was studied using grazing incidence X-ray diffraction (GIXRD) at a constant incidence angle of 0.2°.

(*E*)-5,5′-(Ethene-1,2-diyl)bis(thiophene-2-carbaldehyde) 2. To a dry 250 mL two-necked flask containing (*E*)-1,2-di(thiophen-2-yl)ethane, **1** (2.88 g, 15 mmol) and dry THF (150 mL) was added dropwise 2.5 M of *n*BuLi (15 mL, 37.5 mmol) under N_2 at −78 °C. The mixture was stirred for 1 h at −78 °C, then warmed to 0 °C and stirred for 5 min. After cooling to −78 °C, dry DMF (3.0 g, 40 mmol) was quickly added in one portion. The mixture was stirred for 0.5 h at −78 °C, then naturally warmed to room temperature and stirred for another 1 h. The reaction mixture was poured into water, and the resulting yellow solid was filtered, washed with deionized water, and dried in a vacuum at room temperature to give the title product (**2**, 3.0 g, 81%). ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 9.89 (s, 2H), 7.69 (d, J = 3.9 Hz, 2H), 7.24 (s, 2H), 7.23 (d, J = 3.9 Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$, δ) 182.6, 150.2, 142.8, 136.9, 128.2, 124.5. HRMS [electron ionisation]: Calculated for $C_{12}H_8O_2S_2$: 247.9966; Found: 247.9970.

(3*Z*,3′*Z*)-3,3′-((5,5′-((*E*)-Ethene-1,2-diyl)bis(thiophene-5,2-diyl))-bis(methanylylidene))bis(6-bromoindolin-2-one) 3. To a dry 250 mL two-necked flask containing **2** (2.48 g, 10 mmol), 6-bromooxindole (4.24 g, 20 mmol) and methanol (100 mL), piperidine (4 mL) was added under N_2. After heating to reflux with stirring overnight, the reaction mixture was allowed to cool to room temperature. The resulting precipitate was filtered, washed with methanol, and dried in a vacuum to give the title product in crude form as a black solid (6.1 g). The product was directly used in the next reaction without further purification. HRMS [matrix assisted laser desorption/ionisation – time of flight (MALDI-TOF)]: Calculated for $C_{28}H_{16}Br_2N_2O_2S_2Na$: 656.8909; Found: 656.8912.

3*Z*,3′*Z*)-3,3′-((5,5′-((*E*)-Ethene-1,2-diyl)bis(thiophene-5,2-diyl))-bis(methanylylidene))bis(6-bromo-1-(2-decyltetradecyl)indolin-2-one) 4. To a suspension of **3** (2.5 g) and potassium carbonate (1.2 g, 9.0 mmol) in DMF (50 mL) was added 11-(bromomethyl)tricosane (3.0 g, 7.2 mmol) under N_2. The mixture was stirred for 24 h at 100 °C, then poured into water, extracted with dichloromethane, and then dried over anhydrous sodium sulfate. After removing the solvent in a vacuum, the resulting residue was purified using silica gel chromatography and recrystallized several times with chloroform/methanol to give the title product as a metallic film-like solid (1.7 g, 32%). ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 7.59 (m, 4H), 7.34 (m, 4H), 7.17 (d, J = 8.1 Hz, 2H), 7.09 (d, J = 3.6 Hz, 2H), 6.94 (s, 2H), 3.67 (d, J = 7.5 Hz, 4H), 1.85–1.97 (m, 4H), 1.32–1.23 (m, 80H), 0.89–0.84 (m, 12H). ^{13}C-NMR (75 MHz, $CDCl_3$, δ) 166.4, 150.3, 142.9, 138.7, 137.4, 128.1, 127.8, 124.3, 123.9, 122.9, 121.8, 120.1, 119.7, 117.8, 44.6, 36.2, 31.9, 31.6, 30.0, 29.7, 29.7, 29.6, 29.38, 29.36, 26.5, 22.7, 14.1. HRMS (MALDI-TOF): Calculated for $C_{76}H_{112}Br_2N_2O_2S_2Na$: 1329.6418; Found: 1329.6424.

General procedures for Stille polymerization and polymer purification

P1: An N_2-saturated Schlenk tube containing **4** (261.9 mg, 0.20 mmol), (*E*)-1,2-bis(5-(trimethylstannyl)thiophen-2-yl)-ethene (103.6 mg, 0.20 mmol), tris(dibenzylideneacetone)-dipalladium(0) ($Pd_2(dba)_3$; 6 mg), tri(*o*-tolyl)phosphine [P(*o*-tol)$_3$; 17 mg] and chlorobenzene (6 mL) was heated to 115 °C and stirred for 24 h under a N_2 atmosphere. After cooling down to room temperature, the reaction mixture was poured into 200 mL of methanol containing 10 mL of hydrochloric acid, and stirred for 2 h. The resulting blue-purple coloured, crude copolymer was collected by filtration and subjected to Soxhlet extraction for two days in methanol, acetone, and hexane for the removal of the low molecular weight fraction of the material and residual catalytic impurities. The residue was finally collected with chlorobenzene to obtain the desired polymer (250 mg, 93%). ^{1}H-NMR (300 MHz, $CDCl_2CDCl_2$, δ): 7.66–6.83 (br, 16H), 3.86–3.42 (br, 4H), 2.57–2.33 (br, 2H), 1.61–0.87 (br, 92H). GPC: number average molecular weight (M_n) = 36.8 kDa, molecular weight (M_w) = 66.9 kDa, polydispersity index (PDI) = 1.82. Elemental Analysis: Calculated for $C_{86}H_{120}N_2O_2S_4$: C 76.96, H 9.01, N 2.09; Found: C 76.31, H 8.40, N 2.06.

P2: The synthesis of **P2** is similar to that **P1**, as described previously using **4** (261.9 mg, 0.20 mmol), (*E*)-1,2-bis(5-(trimethylstannyl)selenophen-2-yl)ethene (122.3 mg, 0.20 mmol) to give the desired polymer (258 mg, 90%). ^{1}H-NMR (300 MHz, $CDCl_2CDCl_2$, δ): 7.64–6.85 (br, 16H), 3.83–3.42 (br, 4H), 2.57–2.37 (br, 2H), 1.62–0.87 (br. 92H). GPC: M_n = 24.6 kDa, M_w = 46.1 kDa, PDI = 1.90. Elemental Analysis: Calculated for $C_{86}H_{120}N_2O_2S_2Se_2$: C 71.93, H 8.42, N 1.95; Found: C 70.20, H 7.97, N 1.93.

Device fabrication and characterization

Polymer FETs were fabricated with a bottom-contact/bottom-gate configuration. Heavily doped silicon wafers covered with 300 nm thick silicon dioxide (SiO_2) layers were used as the gate electrode and gate dielectric. Gold was used as the source and drain electrodes. The substrates were subjected to cleaning using ultrasonication in acetone, deionized water, and isopropanol. After drying under vacuum at 80 °C, the substrates were treated with plasma for 15 min, then modified with phenyltrichlorosilane (PTS). Thin films of the polymer were

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deposited on the treated substrates by spin coating using a polymer solution (4 mg mL^{-1}) in *o*-dichlorobenzene at 2000 rpm for 60 s. The annealing process was performed in an ambient atmosphere at 140 °C for 5 min. The FET devices had a channel length of 10 μm and a channel width of 1400 μm.

The evaluations of the polymer FET devices were accomplished using a Keithley 4200 SCS semiconductor parameter analyser on a probe stage. The charge carrier mobility, μ was calculated from the data in the saturated regime according to the equation:

$$I_{DS} = (W/2L)C_i\mu(V_{GS} - V_{th})^2$$

where I_{SD} is the drain current in the saturated regime, W/L is the channel width/length, C_i is the gate dielectric layer capacitance per unit area, and V_{GS} and V_{th} are the gate voltage and threshold voltage, respectively.

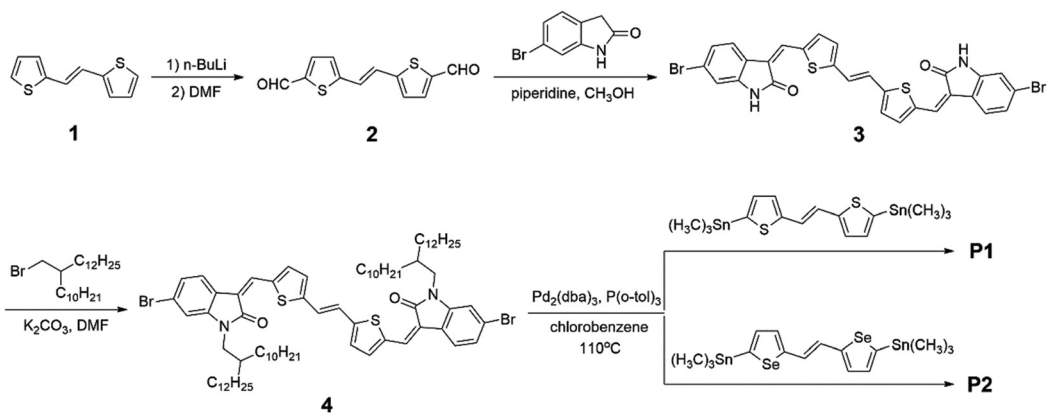
Results and discussion

Synthesis and thermal stability

The synthetic routes of the **VDTOI**-based monomer **4**, and copolymers **P1** and **P2** are shown in Scheme 1. Briefly, (*E*)-1,2-di(thiophen-2-yl)ethene, **1** reacted with *n*BuLi, then quenched with DMF at low temperature giving carbaldehyde **2** as a yellow solid with a high yield of 81%.[35] Knoevenagel reaction of **2** and 6-bromoindolin-2-one in the presence of piperidine gave the key intermediate **3** as a black solid, which is insoluble in common organic solvents. Without further purification, intermediate **3** was *N*-alkylated with 11-(bromomethyl)tricosane to give the black-purple coloured crude solid. After further purification using silica gel chromatography, and recrystallization from chloroform/methanol, the desired **VDTOI**-based monomer **4** with single *Z*,*E*,*Z* configuration was obtained as a metallic solid in a moderate yield of 32% yield. The characterization of monomer **4** was performed using ^{1}H-NMR, ^{13}C-NMR, and HRMS. Frontier molecular orbitals and optimized molecular structures of the monomer **4** were also computed with B3LYP 6-31+G(d,p) levels (alkyl side chains were simplified to methyl groups) (Fig. 2). Computational results reveal that monomer **4** assumes almost planar conjugated backbones. Stille polymerizations of (*E*)-1,2-bis(5-(trimethylstannyl)thiophen-2-yl)ethene or (*E*)-1,2-bis(5-(trimethylstannyl)-selenophen-2-yl)ethene, and monomer **4** were carried out in chlorobenzene at 110 °C to give copolymers **P1** and **P2**, respectively. After the residual catalytic metal and low molecular weight oligomers of the resultant polymer were removed through a standard procedure given in the literature,[11] the two desired copolymers were obtained as a black-purple, film-like solid in excellent yields of 90–93%. The two polymers exhibited good solubility in common solvents such as chloroform, chlorobenzene and dichlorobenzene and so on. The polymers were characterized by ^{1}H-NMR and high temperature GPC (Table 1). **P1** and **P2** display high M_n of 36.8 and 24.6 kDa, respectively, and a PDI of 1.82 and 1.90, respectively. TGA showed that the **VDTOI**-based monomer and copolymers all have good thermal stability. The high decomposition temperatures (T_d) with 5% weight less were obtained at 360 °C for monomer **4**, 390 °C for **P1**, and 402 °C for **P2** (Fig. S1†). Differential scanning calorimetry measurements were performed to determine the thermal transitions for each polymer below the highest annealing temperature see Fig. S2.† Unfortunately, no obvious endothermic transitions and glass transitions were observed for the two copolymers at temperatures ranging from 50 to 250 °C. These observations imply that a successive morphology change would take place in the thin films of the two copolymers.

Optical and electrochemical properties of the monomer and copolymers

The optical properties of **VDTOI**-based monomer and copolymers were studied using UV-vis absorption spectroscopy (Fig. 3, 4 and S3,† and Table 1). As shown in Fig. 3a, monomer **4** in chloroform shows a single band absorption spectrum ranging from 350 to 600 nm with the maximum absorption wavelength at 536 nm. The two **VDTOI**-based copolymers in chloroform have similar and broad absorption profiles band ranging from approximately 330 to 740 nm with the maximum



Scheme 1 Route of synthesis of **VDTOI**-based monomer and its conjugated copolymers.

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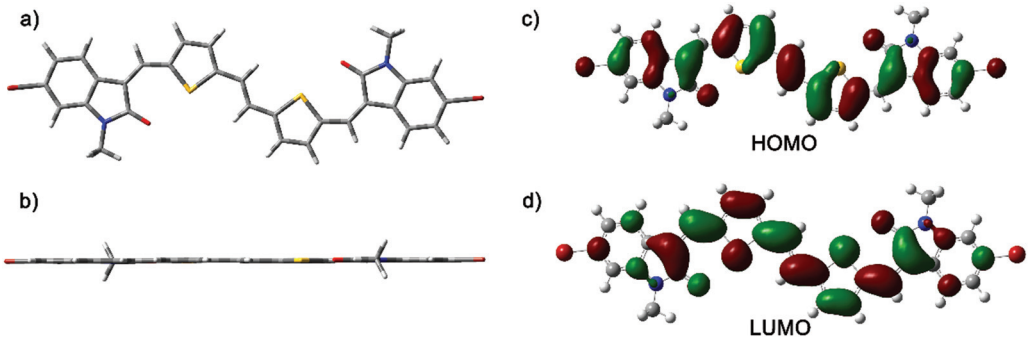

Fig. 2 The optimized molecular structure and frontier molecular orbitals of the **VDTOI**-based monomer. (a) Side view and (b) top view of molecular structure, molecular orbital amplitude plots of (c) HOMO and (d) LUMO.

Table 1 Molecular weights, optical, thermal, and electrochemical properties of **VDTOI**-based monomer **4** and copolymers

Compound	M_n/M_w [a] (kDa)	PDI[a]	T_d [b] (°C)	λ_{max} (nm)	E_g^{opt} [e] (eV)	E_{onset}^{ox} [f] (V)	E_{onset}^{red} [f] (V)	HOMO[f] (eV)	LUMO[f] (eV)
4	—		360	536[c]/636[d]	1.84	0.95	−0.98	−5.35	−3.42
P1	36.8/66.9	1.82	390	600[c]/606[d]	1.72	1.01	−1.06	−5.41	−3.34
P2	24.6/46.1	1.90	402	600[c]/626[d]	1.68	1.00	−0.78	−5.40	−3.62

[a] Molecular weights were determined by GPC at 150 °C. [b] T_d were measured by TGA under N_2. [c] In chloroform solutions. [d] Thin films. [e] Calculated from thin film absorption cut-off values. [f] Determined by CV. HOMO = $-(4.4 + E_{onset}^{ox})$ eV. LUMO = $-(4.4 + E_{onset}^{red})$ eV.

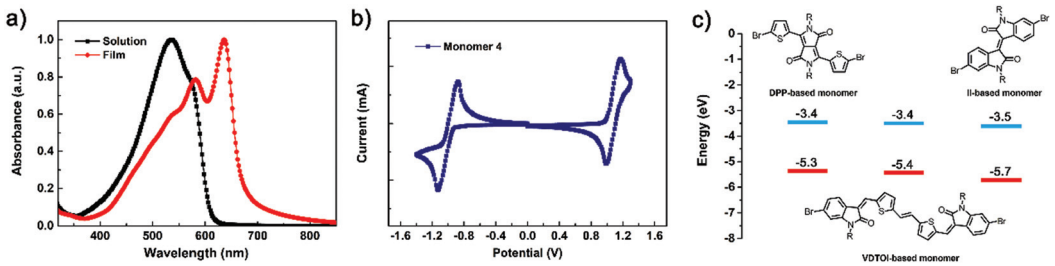

Fig. 3 The optical and electrochemical properties of **VDTOI**-based monomer **4**. (a) UV–vis absorption spectra in chloroform and thin film. (b) CV curve in dichloromethane. (c) The HOMO/LUMO energy levels of **VDTOI**, thiophene-flanked DPP and **II** units.

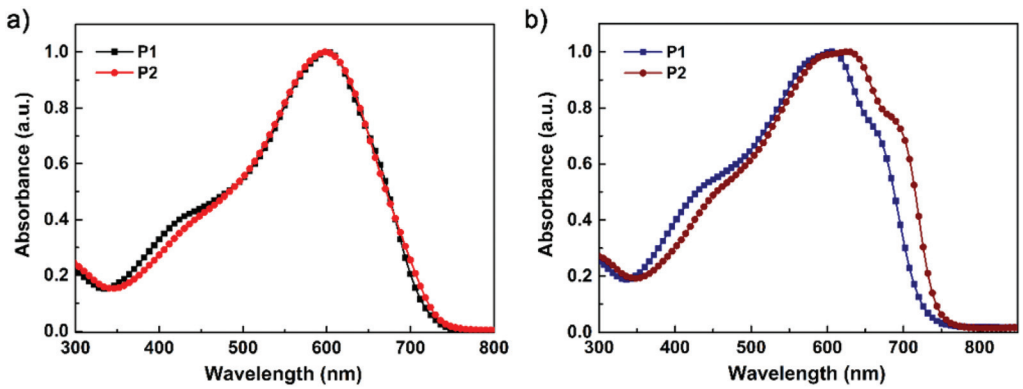

Fig. 4 UV–vis absorption spectra of **P1** and **P2** in (a) chloroform and (b) thin film.

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absorption peaks at approximately 600 nm. These observations indicate that strong intramolecular charge transfer exists in three π-conjugated systems because of strong D–A interactions.[36a] Monomer **4** thin film shows a broader and red-shifted absorption spectrum containing two bands with peaks at 582 and 630 nm. The high energy band is attributed to effective intramolecular charge transfer, while the lower energy band could be assigned to aggregation or orderly packing of the conjugated polymer main chains in the solid films.[7b] The lower energy bands are obviously stronger compared to other polymers reported.[22,23] Further investigations are in progress to fully define the compounds. Nevertheless, it is speculated that the decrease of steric twisting on the conjugated backbone in the thin film results in the enhanced absorption behaviour in the lower energy band.[36b,c] Based on the absorption edge of 680 nm, the optical bandgap of monomer **4** was estimated to be 1.84 eV. It is interesting to note that the **P2** thin film exhibits markedly red-shifted absorption behavior and there was clearly a shoulder peak when the spectra were compared to that of **P1** thin film. The red-shifted absorption is ascribed to the fact that the selenium atoms induce stronger interchain interactions leading to denser chain packing, which was revealed in several papers in the literature.[15b,16b,25b] The selenium effect was thought to be originating from the more mobile lone electron pairs of the selenium atoms.[25b] On the basis of the absorption cut off values, the optical bandgaps of **P1** and **P2** were estimated to be 1.72 and 1.68 eV, respectively.

The electrochemical properties of the **VDTOI**-based monomer and copolymers were investigated using CV. As shown in Fig. 3b, the monomer displayed strong reversible redox peaks with the highest occupied molecular orbit (HOMO)/LUMO energy levels of −5.35/−3.42 eV, which are similar to those obtained for thiophene-flanked **DPP**, rather than **II**. The calculated results show that the frontier orbitals of monomer **4** are highly delocalized all over the conjugated backbones (Fig. 2c and d), and the HOMO/LUMO energy level was calculated to be −5.11/−2.83 eV. The previous results indicate that **VDTOI** might be a potential building block as electron-accepting units in constructing new D–A copolymers. Based on the E^{ox}_{onset} values of 1.00 and 1.01 V, the HOMO energy levels were estimated to be −5.41 for **P1** and −5.40 eV for **P2**. Meanwhile, on the basis of the E^{red}_{onset} values of −1.06 and −0.78 V, the LUMO energy levels of **P1** and **P2** were estimated to be −3.34 and −3.62 eV, respectively (Fig. S3†). The electrochemical data are shown in Table 1. It is worth noting that the HOMO/LUMO behaviours of **VDTOI**-based copolymers seem a little different from the common view that the LUMO level of an acceptor unit and HOMO level of a donor unit generally affect LUMO and HOMO levels of polymers in D–A polymers. The changes are supposed to have arisen from the more complex intramolecular charge transfer in **P1** and **P2** with A–D–A–D′ geometry.

Properties of a field-effect transistor

The field-effect properties of **VDTOI**-based copolymers were measured in bottom contact/bottom gate FET devices, where the SiO_2 surface was modified with a PTS layer. The semiconducting layers of **P1** and **P2** were fabricated by spin-coating a polymer solution in dichlorobenzene (15 mg mL^{-1}). Both copolymers show typical p-type transport characteristics. The representative output and transfer plots are presented in Fig. 5a and b, and the corresponding data are shown in Table 2. The pristine film of **P1** only gave a low hole mobility of 0.11 $cm^2 V^{-1} s^{-1}$; however, the annealed films (140 °C for 5 min) exhibited a maximum mobility of up to 0.35 $cm^2 V^{-1} s^{-1}$ and average values of 0.21 $cm^2 V^{-1} s^{-1}$ (based on 15 devices), with a high on/off current ratio of 10^6–10^7. The great improvements in charge mobility reveal that strong molecular self-assembly actions occurred in the annealing process. Unexpectedly, the annealed thin film of **P2** only displayed a maximum mobility of 0.037 $cm^2 V^{-1} s^{-1}$ and an average mobility of 0.021 $cm^2 V^{-1} s^{-1}$ (based on 15 devices), which are an order of magnitude lower than those of **P1** in the same conditions (Fig. S4 and S5†). In addition, no large difference in mobility was observed between its as-fabricated and annealed **P2** films. The lower mobility of **P2** may be ascribed to the introduction of selenium atoms, with larger van der Waals radius than those of sulfur atoms which may induce less efficient packing of polymer chains and suppresses intermolecular charge hopping.[37a,b]

Thin film microstructural characterization

Tapping-mode AFM and GIXRD were used to investigate the film morphology and molecular packing of **VDTOI**-based copolymers. As shown in Fig. 5c and S6,† the as-fabricated **P1** thin film displays obvious grain boundaries, which are unfavorable for charge carrier transport. However, the annealed film exhibits a highly smooth and uniform morphology and network structure, which is composed of small polymer fibers. The morphology difference is correlated well with the changes in mobility as previously mentioned. For **P2**, however, no such great improvement in thin film morphology was observed when the annealing temperature was elevated (Fig. S7†). When annealed at 140 °C, **P2** thin film has better crystallinity than that of the as-fabricated thin film; however, the grain boundaries also become greater. The 2D GIXRD images of the two copolymers that were collected, are shown in Fig. 5d and S8.† For the **P1** thin film, the peaks of (100), (200), and (300) all display in its out-of-plane diffractions. According to the location of the (100) peak, the d–d distance was estimated to be 21.5 Å. Meanwhile, the peak of (010) corresponding to π–π stacking was also observed in in-plane diffractions. Based on the 2θ of 19.5°, the π–π stacking distance was estimated to be 3.71 Å. These results hint that a highly ordered layer-to-layer molecular packing exists in the **P1** thin film. In addition, because these (h00) peaks are not seen in the in-plane patterns, it can be concluded that **P1** takes a predominantly edge-on orientation in respect to the substrates. However, no apparent (h00) and (010) peaks were found in the **P2** thin film even after many optimizations. The AFM and GIXRD images suggested that the presence of thiophene units endows **P1** with highly ordered molecular packing, good thin film

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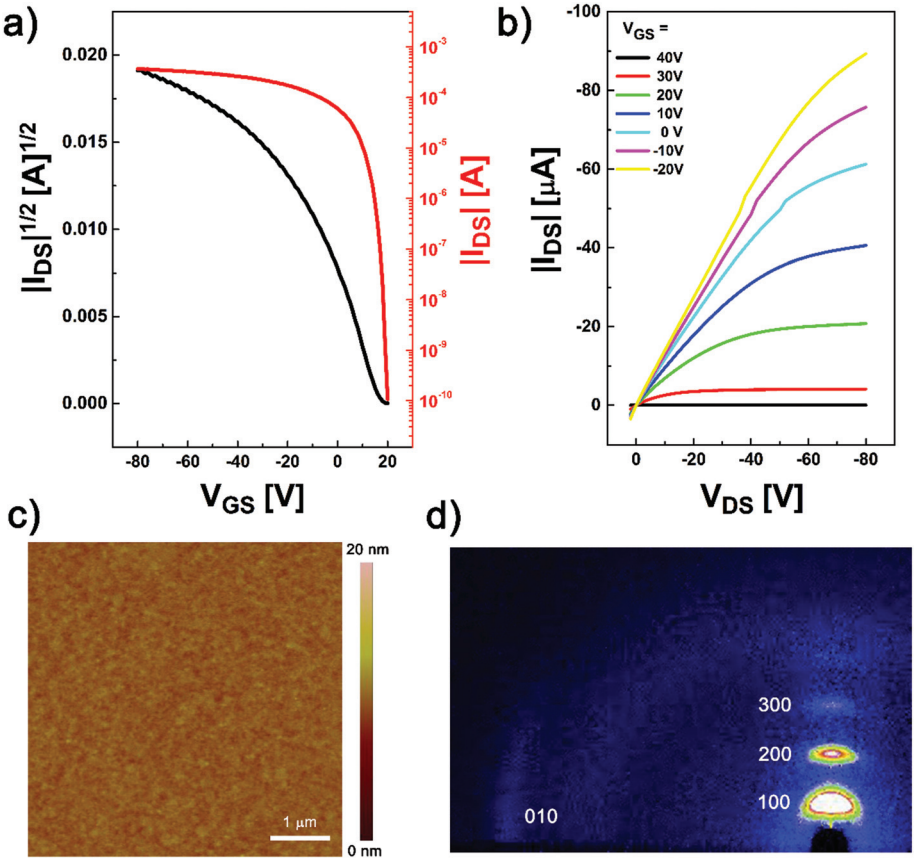

Fig. 5 The device performance of **P1**-based FETs, film morphology and molecular packing of **P1** in the solid state. Typical (a) transfer and (b) output characteristics. (c) AFM topography image (5 μm × 5 μm in size), and (d) two-dimensional (2D)-GIXRD pattern of **P1** thin films on PTS-modified SiO_2/Si substrates after annealing at 140 °C for 5 min.

Table 2 FET device performance of **VDTOI**-based copolymers

Copolymers	Temperature [°C]	μ^b (μ_{max}) [$cm^2\ V^{-1}\ s^{-1}$]	$I_{on}/I_{off}{}^b$	$V_{th}{}^c$ [V]	π–π^d [Å]	d–d^d [Å]
P1	RT	0.08 (0.11)	10^6–10^7	10.51	—	—
	140[a]	0.21 (0.35)	10^6–10^7	8.55	3.71	21.5
P2	RT	0.010 (0.015)	10^6–10^7	2.10	—	—
	140[a]	0.021 (0.037)	10^6–10^7	1.20	—	—

[a] Optimal annealing temperature. [b] Mobility, on/off current ratio, and the threshold voltage are summarized from results obtained from 15 devices for each copolymer. [c] Obtained in the device with μ_{max}. [d] Calculated from GIXRD experiments.

morphology, and crystallinity than those of the thin film of **P2** with selenophene units. Therefore, smaller π–π distance and largely improved crystallinity could result in the higher hole mobility obtained in **P1**-based OFET devices compared to that of the **P2**-based counterparts. This type of selenophene effect matches well with papers in the literature reported previously.[37a,b]

Conclusions

In summary, a new π-extended analogue of isoindigo, centrosymmetric **VDTOI** with A–D–A geometry, was successfully synthesized. The **VDTOI** unit has similar HOMO/LUMO energy levels to those of a thiophene-flanked DPP unit, implying that **VDTOI** also has strong electron-deficient properties and so it could be utilized as electron-accepting building blocks of D–A polymers. In a preliminary attempt, two **VDTOI**-based D–A copolymers were synthesized, **P1** and **P2**. Solution-processed OFETs based on **P1** gave the highest hole mobility of up to 0.35 $cm^2\ V^{-1}\ s^{-1}$ with an on/off current ratio of 10^6–10^7. The results show that **VDTOI** is a promising building block for developing high-performance semiconducting polymers for fabricating various opto-electronic devices.

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