Vinylidenedithiophenmethyleneoxindole: A Centrosymmetric Building block for Donor−Acceptor Copolymers

Journal:	*Polymer Chemistry*
Manuscript ID	PY-ART-09-2015-001500.R2
Article Type:	Paper
Date Submitted by the Author:	31-Dec-2015
Complete List of Authors:	Zhang, Weifeng; Institute of Chemistry, Chinese Academy of Sciences zheng, naihang; Institute of Chemistry, Chinese Academy of Sciences, Wei, Congyuan; Institute of Chemistry, Chinese Academy of Sciences, Huang, Jianyao; Institute of Chemistry, Chinese Academy of Sciences, Beijing, Gao, Dong; Institute of Chemistry, Chinese Academy of Sciences, Shi, Keli; Institute of Chemistry, Chinese Academy of Sciences Xu, Jie; Institute of Chemistry, Chinese Academy of Sciences, Yan, Donghang; Changchun Institute of Applied Chemistry, State Key Lab of Polymer Physics and Chemistry Han, Yanchun; Changchun Institute of Applied Chemistry, State Key Lab of Polymer Physics and Chemistry Yu, Gui; Institute of Chemistry, Chinese Academy of Sciences,

Vinylidenedithiophenmethyleneoxindole: A Centrosymmetric Building block for Donor−Acceptor Copolymers

Weifeng Zhang,[a,#] Naihang Zheng,[a,#] Congyuan Wei,[a] Jianyao Huang,[a] Dong Gao,[a] Keli Shi,[a] Jie Xu,[a] Donghang Yan,[b] Yanchun Han,[b] and Gui Yu[a,*]

[a]Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China

[b]State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

Keywords: Field-Effect Transistors, Copolymers, Building blocks, Vinylidenedithiophenmethyleneoxindoles, Donor−Acceptor Structure

ABSTRACT: Further developing new building blocks is crucial for realizing next-generation high-performance organic semiconducting materials. In the paper, we report the design and synthesis of a novel π-extended analogue of isoindigo, vinylidenedithiophenmethyleneoxindole (**VDTOI**), and two VDTOI-based copolymers. The centrosymmetric VDTOI unit possesses a special acceptor-donor-acceptor structure and contains a highly planar conjugated backbone due to the presence of S···O conformational locks. Especially, VDTOI unit owns the highest occupied molecular orbital and lowest unoccupied molecular orbital (HOMO and LUMO) energy levels of –5.35 eV/–3.42 eV, which are similar to those of thiophene-flanked diketopyrrolopyrrole building block. The aforementioned structural features indicate that VDTOI might be a potential building block for constructing polymeric semiconductors. As a trial, we synthesized two VDTOI-based copolymers, 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 Au electrode, indicative of effective hole injections from Au electrodes to polymer semiconductor films. Both the P1- and P2-based field-effect transistors exhibit 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 due to their intriguing and adjustable electronic and optoelectronic properties for potential application in printable opto-electronic devices.[1–3] During the past decades, significant progress in polymeric light-emitting diodes,[4–6] organic photovoltaics,[7–9] and organic field-effect transistors (OFETs),[10–14] encourages the continued designing and discovering of new buliding blocks for constructing new polymers with high thermal stability, broad and intense absorption, and prompt and efficient charge transport. Up to date, however, most of record high mobilities still limit in several versatile electron-donating or electron-withdrawing building blocks derived 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] *etc*. Therefore, further designing novel building blocks is of equal importance as developing high-performance polymeric semiconductors and digging inherent relationship between molecular structures and opto-electronic properties for realizing next-generation printable electronics.

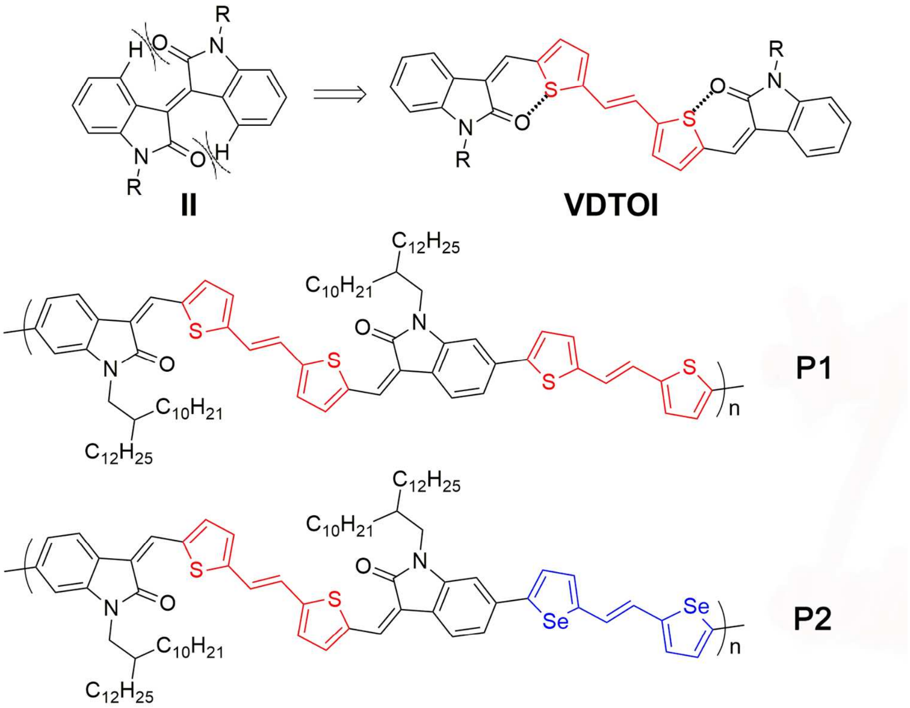


Figure 1. Design strategy of **VDTOI** building block and the chemical structures of **VDTOI**-based copolymers.

Since Reynolds et al. presented 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, while high hole mobility of over 3.0 cm^2 V^{-1} s^{-1} was afforded by II-based polymer field-effect transistors.[22a,24a] Encouraged by these achievements, great efforts have been paid on developing II derived building blocks and related polymeric semiconductors.[31–33] For example, with the aim of obtaining high planarity, the outer phenyl rings of II were replaced by thiophene rings affording new building block, thienoisoindigo, which own an enhanced planar conjugated backbone due to the elimination of steric repulsion between the protons on the phenyl rings and the carbonyl oxygens of the oxindoles. Moreover, because of the disappearance of α-H on phenyl rings, thienoisoindigo would endow the copolymers with thiophene-thiophene links with optimized planarity, thus maximizing conjugated and further enhancing attractive interchain interactions. For another example, a novel II derived building block, BDOPV, in which oxindoles are bridged by strong electron-deficient benzodifurandione moiety were also developed.[34] The resulting BDOPV has lower the lowest unoccupied molecular orbital (LUMO) energy level of −4.2 eV, than −3.5 eV of those of II. As result, the corresponding polymers exhibited enhanced electron transport performance and device stability under ambient conditions.

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

EXPERIMENTAL SECTION

General procedures and requirements. The catalysts and chemicals such as *n*-butyllithium, 6-bromoindolin-2-one and 11-(bromomethyl)tricosane, and solvents were purchased from commercial sources, and used as received without further purification. Tetrahydrofuran was freshly distilled over sodium and benzophenone, and *N*,*N*-dimethylformamide was distilled over CaH_2 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. ^1H and ^{13}C NMR spectra were recorded on a Bruker-300 NMR spectrometer and the chemical shifts were reported in parts per million (ppm). ^1H NMR chemical shifts were referenced to internal tetramethylsilane (TMS, 0 ppm), $CDCl_2CDCl_2$ (6.0 ppm) and ^{13}C NMR chemical shifts were referenced to $CDCl_3$ (77 ppm). HRMS were collected on Bruker APEXII or 9.4T Solarix FT-ICR mass spectrometers. Elemental Analysis was carried on Varlo ELIII Elemental Analyzer. UV-vis absorption spectra in chloroform solution and thin films were recorded using a Hitachi U-3010 spectrophotometer. The film absorption measurement samples were prepared by spin-coating polymer solution in chloroform onto quartz glass. Cyclic voltammetry was carried on an electrochemistry workstation with traditional three-electrolyte configuration in dry acetonitrile at room temperature. The measurements were used 0.1 M n-Bu_4NPF_6 as a supporting electrolyte, platinum rod as the working, platinum wire as counter electrode, and Ag/AgCl as the reference electrode with a scan rate of 50 mV s^{-1}. Thermal gravity analyses (TGA) were determined on a Perkin–Elmer series 7 thermal analysis system under 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 220 system using a refractive index detector at 150 °C and using 1,2,4-trichlorobenzene as the eluent with polystyrenes as standards. Thin film morphology were investigated in air using a Digital Instruments Nanoscope V atomic force microscope operated in tapping mode, and the samples were identical to those used in field-effect performance analysis. The polymeric packing mode in solid state was studied by grazing incidence X-ray diffraction (GXRD) 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-neck 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*-butyllithium (15 mL, 37.5 mmol) under nitrogen at –78 ^{o}C. The mixture was stirred for 1 h at –78 ^{o}C, then warmed to 0 ^{o}C and stirred for 5 mins. After cooled to –78 ^{o}C, dry *N*,*N*-dimethylformamide (3.0 g, 40 mmol) was quickly added in one portion. The mixture was stirred for 0.5 h at –78 ^{o}C, then naturally warmed to r.t and stirred for another 1 h. The reaction mixture was poured into water, and the resulting yellow solid was filtered, washed with deionized water, dried in vacuum at r.t to give the title product (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 (EI): Calcd. 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-neck flask containing **2** (2.48 g, 10 mmol), 6-bromooxindole (4.24 g, 20 mmol) and methanol (100 mL) was added piperidine (4 mL) under nitrogen. After heated to reflux and stirred overnight, the reaction mixture was allowed to cool to r.t. The resulting precipitate was filtered, washed with methanol, and dried in vacuum affording the title crude product as a black solid (6.1 g). The product was directly used in the next reaction without further purification. HRMS (MALDI-TOF): Calcd. 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 *N*,*N*-dimethylformamide (50 mL) was added 11-(bromomethyl)tricosane (3.0 g, 7.2 mmol) under nitrogen. The mixture was stirred for 24 h at 100 °C, then poured into water, extracted with dichloromethane, dried over anhydrous Na_2SO_4. After removing the solvent in vacuum, the resulting residue was purified by silica gel chromatography and recrystallization with chloroform/methanol several times to give the title product as 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): Calcd. for $C_{76}H_{112}Br_2N_2O_2S_2Na$: 1329.6418; Found: 1329.6424.

General Procedures for Stille Polymerization and Polymer Purification.

P1: Nitrogen-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), $Pd_2(dba)_3$ (6 mg), P(*o*-tol)$_3$ (17 mg) and chlorobenzene (6 mL) was heated to 115 ^{o}C and stirred for 24 h under nitrogen 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 crude copolymer was collected by filtration and subjected to Soxhlet extraction for 2 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 obtaining 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: M_n = 36.8 *kDa*, M_w = 66.9 *kDa*, PDI = 1.82. Elemental Anal.: Calcd. 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 as described above using **4** (261.9 mg, 0.20 mmol), (*E*)-1,2-bis(5-(trimethylstannyl)selenophen-2-yl)ethene (122.3 mg, 0.20 mmol) affording 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 Anal.: Calcd. 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.

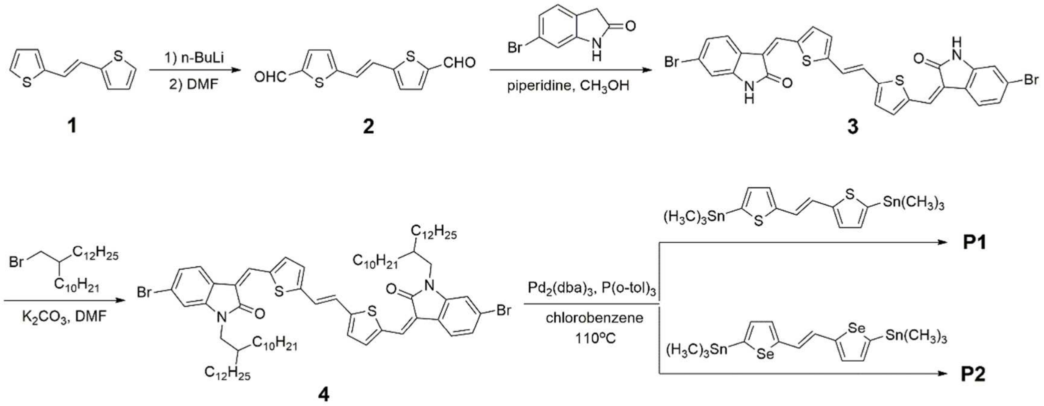
Device Fabrication and Characterization. Polymer field-effect transistors were fabricated with bottom-contact/bottom-gate configuration. Heavily doped silicon wafers covered with 300 nm thick silicon dioxide layers were used as the gate electrode and gate dielectric. Gold was used as source and drain electrodes. The substrates were subjected to cleaning using ultrasonication in acetone, deionized water, and *iso*-propanol. After dried under vacuum at 80 ^{o}C, the substrates were treated with plasma for 15 min, then modified with phenyltrichlorosilane (PTS). Thin films of the polymer were deposited on the treated substrates by spin coating using a polymer solution (4 mg/mL) in *o*-dichlorobenzene at 2000 rpm for 60 s. The annealing process was performed at ambient atmosphere at 140 °C for 5 mins. The FET devices have a channel length of 10 μm and channel width of 1400 μm.

The evaluations of the PFET 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



Scheme 1. Synthetic Route of **VDTOI**-based Monomer and Conjugated Copolymers.

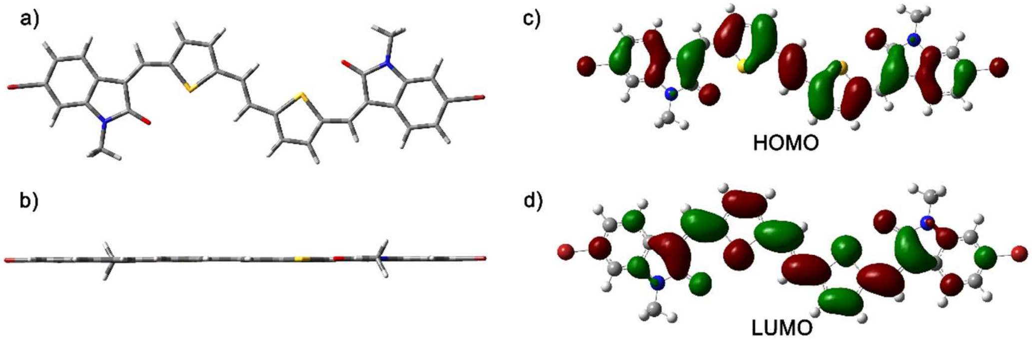


Figure 2. The optimized molecular structure and frontier molecular orbitals of **VDTOI**-based monomer. (a) Side view and (b) top view of molecular structure, Molecular orbital amplitude plots of c) HOMO and (d) LUMO.

Synthesis and Thermal Stability. The synthetic routes of VDTOI-based monomer

4, and copolymers P1 and P2 are shown in Scheme 1. (*E*)-1,2-di(thiophen-2-yl)ethene, 1 reacted with *n*-butyllithium, then quenched with *N*,*N*-dimethylformamide at low temperature giving carbaldehyde 2 as a yellow solid in high yield of 81%.[35] Knoevenagel reaction of 2 and 6-bromoindolin-2-one in the presence of piperidine afforded 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 crude black-purple crude solid. After further purification by 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 moderate yield of 32% yield. The characterization of monomer 4 was preformed through ^{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) (**Figure 2**). Computational results reveal that the 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 the monomer 4 were carried out in chlorobenzene at 110 ^{o}C affording the 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 as depicted in literatures,[11] we obtained the desired two copolymers as black-purple, film-like solid in excellent yields of 90-93%. The two polymers exhibit good solubility in common solvents such as chloroform, chlorobenzene and dichlorobenzene etc. The polymers were characterized by ^{1}H NMR and high temperature GPC (**Table 1**). P1 and P2 display high number-average molecular weights (M_n) of 36.8 and 24.6 kDa, and polydispersity index (PDI) of 1.82 and 1.90, respectively. Thermaogravimetric analyses (TGA) show 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 the monomer 4, 390 °C for P1, and 402 °C for P2 (**Figures S1**). Differential scanning calorimetry (DSC) measurements were performed to determine the thermal transitions for each polymer below the highest annealing temperature discussed hereinafter (**Figures S2**). It is pity that no obvious endothermic transitions and glass transitions were observed for the two copolymers in the temperatures ranging from 50 to 250 °C. The observations imply that a successive morphology change would take place in respective thin films of the two copolymers.

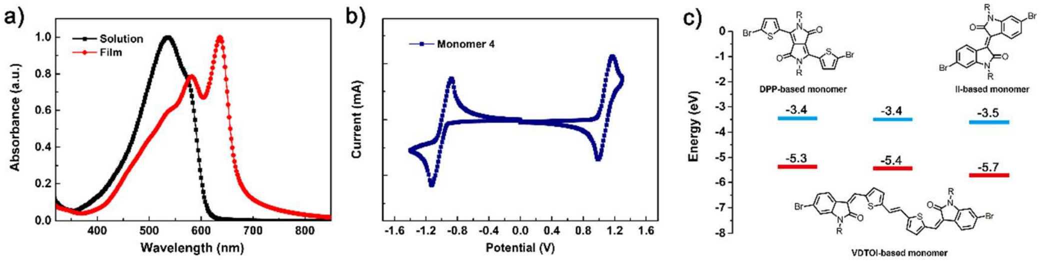


Figure 3. The optical and electrochemical properties of **VDTOI**-based monomer **4**. (a) UV–Vis absorption spectra in chloroform and thin film. (b) CV curve in dichloromethane. (c) The HOMO/LUMO energy levels of VDTOI, thiophene-flanked DPP and II units.

Optical and Electrochemical Properties of the Monomer and Copolymers. The optical properties of VDTOI-based monomer and copolymers were studied by UV-Vis absorption spectroscopy (**Figures 3,4** and **S3**, and **Table 1**). As shown in Figure 3a, the 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 ca. 330 to 740 nm with the maximum absorption peaks at ca. 600 nm. These observations indicate that strong intramolecular charge transfer (ICT) exist in three π-conjugated systems due to strong D–A interactions.[36a] Monomer 4 thin film owns a broader and red-shifted absorption spectrum containing two bands with peaks at 582 and 630 nm, respectively. 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 is obviously stronger compared to other polymers reported.[22,23] Further defining investigation are in progress. Nevertheless, we speculate that the decrease of steric twisting on the conjugated backbone in thin film result in the enhanced absorption behaviour in lower energy band.[36b,c] Based on the absorption edge of 680 nm, the optical bandgap of the monomer 4 was estimated to be 1.84 eV. It is interesting to note that P2 thin film exhibits markedly red-shifted absorption behavior and clearly shoulder peak compared to that of P1 thin film. The red-shifted absorption is ascribed to that selenium atoms induce to stronger interchain interactions leading to denser chain packing, which was revealed in several literatures.[15b,16b,25b] The selenium effect was thought to be originating from the more mobile lone electron pairs of selenium atoms.[25b] On the basis of absorption cut off values, the optical bandgaps of P1 and P2 were estimated to be 1.72 and 1.68 eV, respectively.

We investigated the electrochemical properties of VDTOI-based monomer and copolymers by cyclic voltammetry (CV). As shown in Figure 3b, the monomer displayed strong reversible redox peaks with the HOMO/LUMO energy levels of −5.35/−3.42 eV, which are similar to those of thiophene-flanked **DPP**, rather than II. Calculated results show that the frontier orbitals of monomer 4 are highly delocalized all over conjugated backbones (**Figure 2c** and **2d**). And the HOMO/LUMO energy level was calculated to be −5.11/−2.83 eV. The above results indicate that VDTOI might be a potential building block as electron-accepting units in constructing new D-A copolymers. Based on the E_{onset}^{ox} values of 1.00 and 1.01 V, the HOMO energy

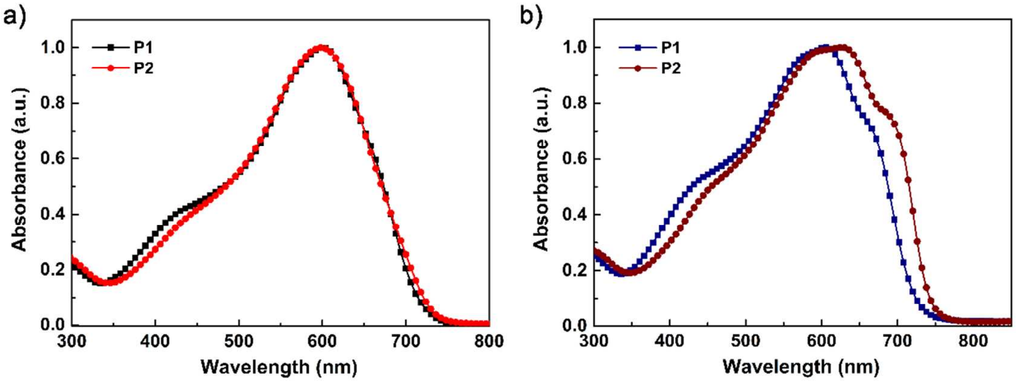


Figure 4. UV–Vis absorption spectra of **P1** and **P2** in (a) chloroform and (b) thin film.

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} (eV) [e]	E_{onset}^{ox} (V) [f]	E_{onset}^{red} (V) [f]	HOMO (eV) [f]	LUMO (eV) [f]
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 cutoff values. [f] Determined by CV. HOMO = – (4.4 + E_{onset}^{ox}) eV. LUMO = – (4.4 +E_{onset}^{red}) eV.

levels were estimated to be –5.41 for P1 and –5.40 eV for P2. Meanwhile, on the basis of $\boldsymbol{E_{onset}^{red}}$ 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 (Figure S3). The electrochemical data were collected in Table 1. It is worth to 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 has arisen from the more complex intramolecular charge transfer in P1 and P2 with A-D-A-D' geometry.

Properties of 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 phenyltrichlorosilane (PTS) layer. The semiconducting layers of P1 and P2 were fabricated by spin-coating a polymer solution in dichlorobenzene (15 mg/mL). Both copolymers show typical *p*–type transport characteristics. The representative output and transfer plots are presented in

Figure 5a and 5b, and the corresponding data are collected in Table 2. The pristine film of P1 only afforded low hole mobility of 0.11 $cm^2 V^{-1} s^{-1}$, however, the annealed films (140 ^oC for 5 mins) exhibited a maximum mobility of up to 0.35 $cm^2 V^{-1} s^{-1}$ and an 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-assemble 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 (**Figures 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, whose larger van der Waals radius of Se atoms than those of S atoms may induces less efficient packing of polymer chains and suppresses intermolecular charge hopping.[37a,b]

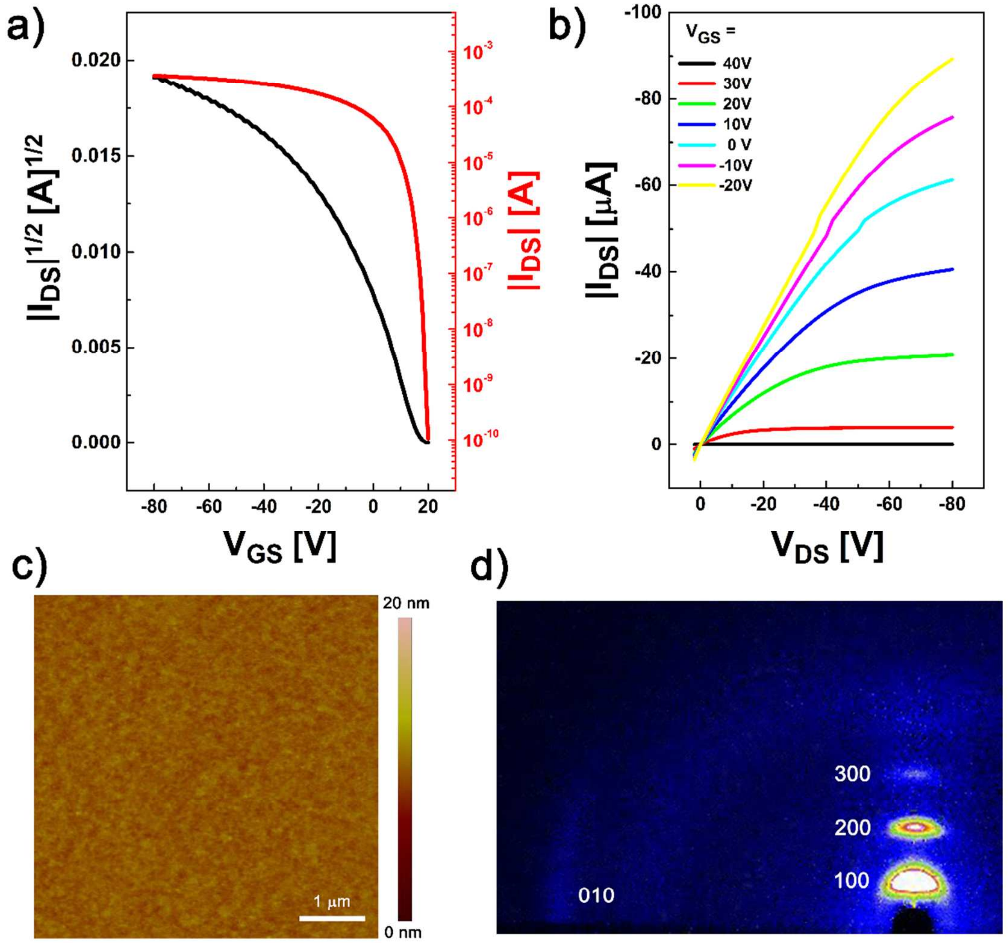


Figure 5. The device performance of **P1**-based FETs, film morphology and molecular packing of **P1** in solid state. Typical a) transfer and b) output characteristics. c) AFM topography image (5 μm × 5μm in size), and d) 2D-GXRD pattern of of **P1** thin films on PTS-modified SiO_2/Si substrates after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

Table 2. FET devices 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 were summarized from 15 devices for each copolymers. [c] Obtained in the device with μ_{max}. [d] Calculated from GIXRD experiments.

Thin Film Microstructural Characterization. Tapping-mode atomic force microscopy (AFM) and grazing incidence X-ray diffraction (GXRD) were used to inverstigate the film morphology and molecular packing of VDTOI-based copolymers. As shown in Figures 5c and and S6, the as-fabricated P1 thin film displays obvious grain boundaries, which is 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 aforementioned. For P2, however, no such great improvement in thin film morphology was observed with the annealing temperature elevated (**Figure S7**). When annealed at 140 °C, P2 thin film becomes better crystallinity than that of as-fabricated thin film, however, the grain boundaries also become greater. The 2D GXRD images of the two copolymers were collected in Figures 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 (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 degree, 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, we can conclude that

P1 take predominantly edge-on oriented respective to the substrates. However, no apparent (*h*00) and (010) peaks was found in P2 thin film even after many optimazations. The AFM and GXRD images suggested that the presence of thiophene units endows P1 with highly ordered molecular packing, good thin film 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 higher hole mobility obtained in P1-based OFET devices than that of P2-based counterparts. The kind of selenophene effect matches well with the literatures reported before.[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 owns similar HOMO/LUMO energy levels as those of thiophene-flanked DPP unit, implying that VDTOI has also strong electron-deficient properties and could be utilized as electron-accepting building blocks of D-A polymers. In a preliminary attempt, we synthesized two VDTOI-based D–A copolymers, P1 and P2. Solution-processed OFETs based on P1 afforded the highest hole mobility of up to 0.35 $cm^2 V^{-1} s^{-1}$ with on/off current ratio of 10^6–10^7. The results show that VDTOI is a promising building block in developing high-performance semiconducting polymers for fabricating various opto-electronic devices.

AUTHOR INFORMATION

Corresponding Author

* E-mail: yugui@iccas.ac.cn (G. Y.)

Acknowledgments

This work was financially support by the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB12030100), the National Science Foundation of China (21474116 and 51233006), and Open Research Fund of State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences. The GXRD results were tested at 23A1 Station of National Synchrotron Radiation Research Center (NSRRC, Taiwan), 1W1A Station of Beijing Synchrotron Radiation Facility, and BL16B1 Station of Shanghai Synchrotron Radiation Facility (SSRF).The authors gratefully thank the assistance of scientists from the stations during the experiments.

Notes and references

[#]Authors W. F. Zhang and N. H. Zheng contributed equally to this work

1. (a) A. J. Heeger, *Chem. Soc. Rev.,* 2010, **39**, 2354; (b) C. Li, M. Liu, N. G. Pschirer, M. Baumgarten, K. Müllen, *Chem. Rev.,* 2010, **110**, 6817; (c) J. D. Yuen, Fred. Wudl, *Energy Environ. Sci.,* 2013, **6**, 392.
2. (a) P. M. Beaujuge, J. M. J. Fréchet, *J. Am. Chem. Soc.,* 2011, **133**, 20009; (b) C. L. Wang, H. L. Dong, W. P. Hu, Y. Q. Liu, D. B. Zhu, *Chem. Rev.,* 2012, **112**, 2208.
3. (a) H. Bronstein, Z. Y. Chen, R. S. Ashraf, W. M. Zhang, J. P. Du, J. R. Durrant, P. S. Tuladhar, K. Song, S. E. Watkins, Y. Geerts, M. M. Wienk, R. A. J. Janssen, T.

Anthopoulos, H. Sirringhaus, M. Heeney, I. McCulloch, *J. Am. Chem. Soc.,* 2011, **133**, 3272; (b) W. F. Zhang, Y. Q. Liu, G. Yu, *Adv. Mater.,* 2014, **26**, 6898.

4. J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, A. B. Holmes, *Nature* 1990, **347**, 539.
5. A. C. Grimsdale, K. L. Chan, R. E. Martin, P. G. Jokisz, A. B. Holmes, *Chem. Rev.,* 2009, **109**, 897.
6. S. Welter, K. Brunner, J. W. Hofstraat, L. De Cola, *Nature,* 2003, **421**, 54.
7. (a) Y. F. Deng, J. Liu, J. T. Wang, L. H. Liu, W. L. Li, H. K. Tian, X. J. Zhang, Z. Y. Xie, Y. H. Geng, F. S. Wang, *Adv. Mater.,* 2014, **26**, 471; (b) E. G. Wang, Z. Ma, Z. Zhang, K. Vandewal, P. Henriksson, O. Ingans, F. Zhang, M. R. Andersson, *J. Am. Chem. Soc.,* 2011, **133**, 14244.
8. (a) Z. A. Tan, W. Q. Zhang, Z. G. Zhang, D. P. Qian, Y. Huang, J. H. Hou, Y. F. Li, *Adv. Mater.,* 2012, **24**, 1476; (b) Y. H. Liu, J. B. Zhao, Z. K. Li, C. Mu, W. Ma, H. W. Hu, K. Jiang, H. R. Lin, H. Ade, H. Yan, *Nat. Commun.,* 2014, **5**, 5293.
9. (a) J.-D. Chen, C. Cui, Y.-Q. Li, L. Zhou, Q.-D. Ou, C. Li, Y. Li, J.-X. Tang, *Adv. Mater.,* 2015, **27**, 1035; (b) X. W. Zhan, Z. A. Tan, B. Domercq, Z. S. An, X. Zhang, S. Barlow, Y. F. Li, D. B. Zhu, B. Kippelen, S. R. Marder, *J. Am. Chem. Soc.,* 2007, **129**, 7246.
10. (a) H. Yan, Z. H. Chen, Y. Zheng, C. Newman, J. R. Quinn, F. Dötz, M. Kastler, A. Facchetti, *Nature,* 2009, **457**, 679; (b) Y. G. Wen, Y. Q. Liu, Y. L. Guo, G. Yu, W. P. Hu, *Chem. Rev.,* 2011, **111**, 3358.
11. (a) H. Sirringhaus, T. Kawase, R. H. Friend, T. Shimoda, M. Inbasekaran, W. Wu,

E. P. Woo, *Science,* 2000, **290**, 2123; (b) X. T. Liu, Y. L. Guo, Y. Q. Ma, H. J. Chen, Z. P. Mao, H. L. Wang, G. Yu, Y. Q. Liu, *Adv. Mater.,* 2014, **26**, 3631.

12. (a) J. G. Mei, D. H. Kim, A. L. Ayzner, M. F. Toney, Z. N. Bao, *J. Am. Chem. Soc.,* 2011, **133**, 20130; (b) T. Lei, J.-Y. Wang, J. Pei, *Acc. Chem. Res.,* 2014, **47**, 1117.
13. Z. Y. Yi, X. N. Sun, Y. Zhao, Y. L. Guo, X. G. Chen, J. G. Qin, G. Yu, Y. Q. Liu, *Chem Mater.,* 2012, **24**, 4350.
14. W.-H. Lee, S. K. Son, K. Kim, S. K. Lee, W. S. Shin, S.-J. Moon, I.-N. Kang, *Macromolecules* **2012**, *45*, 1303.
15. (a) H. J. Chen, Y. L. Guo, G. Yu, Y. Zhao, J. Zhang, D. Gao, H. T. Liu, Y. Q. Liu, *Adv. Mater.,* 2012, **24**, 4618; (b) I. Kang, H. J. Yun, D. S. Chung, S. K. Kwon, Y. H. Kim, J. *Am. Chem. Soc*., 2013, **135**, 14896; (c) J. Li, Y. Zhao, H. S. Tan, Y. L. Guo, C. A. Di, G. Yu, Y. Q. Liu, M. Lin, S. H. Lim, Y. H. Zhou, H. B. Su, B. S. Ong, *Sci. Rep.,* 2012, **2**, 754.
16. a) J. C. Bijleveld, A. P. Zoombelt, S. G. J. Mathijssen, M. M. Wienk, M. Turbiez, D. M. DeLeeuw, R. A. J. Janssen, *J. Am. Chem. Soc.,* 2009, **131**, 16616; b) I. Kang, T. K. An, J.-a. Hong, H.-J. Yun, R. Kim, D. Su. Chung, C. E. Park, Y.-H. Kim, S.-K. Kwon, *Adv. Mater.,* 2013, **25**, 524
17. S. Qu, W. Wu, J. Hua, C. Kong, Y. Long, H. Tian, *J. Phys. Chem. C,* 2010, **114**, 1343.
18. T. L. Nelson, T. M. Young, J. Liu, S. P. Mishra, J. A. Belot, C. L. Balliet, A. E. Javier, T. Kowalewski, R. D. McCullough, *Adv. Mater.,* 2010, **22**, 4617.

19. (a) Z. H. Chen, Y. Zheng, H. Yan, A. Facchetti, *J. Am. Chem. Soc.,* 2009, **131**, 8; (b) X. Zhan, A. Facchetti, S.; Barlow, T. J. Marks, M. A. Ratner, M. R. Wasielewski, S. R. Marder, *Adv. Mater.,* 2011, **23**, 268.
20. H. J. Chen, Y. L. Guo, Z. P. Mao, G. Yu, J. Y. Huang, Y. Zhao, Y. Q. Liu, *Chem. Mater.,* 2013, **25**, 3589.
21. H. Huang, Z. H. Chen, R. P. Ortiz, C. Newman, H. Usta, S. Lou, J. Youn, Y. Y. Noh, K. J. Baeg, L. X. Chen, A. Facchetti, *J. Am. Chem. Soc.,* 2012, **134**, 10966.
22. T. Lei, J. H. Dou, J. Pei, *Adv. Mater.,* 2012, **24**, 6457.
23. (a) R. Stadler, J. Mei, J. R. Reynolds, *Macromolecules,* 2010, **43**, 8348; (b) B. Liu, Y. P. Zou, B. Peng, B. Zhao, K. L. Huang, Y. H. He, C. Y. Pan, *Polym. Chem.,* 2011, **2**, 1156.
24. (a) G. Zhang, Y. Fu, Z. Xie, Q. Zhang, *Macromolecules,* 2011, **44**, 1414; (b) R. Stalder, J. Mei, J. Subbiah, C. Grand, L. A. Estrada, F. So, J. R. Reynolds, *Macromolecules,* 2011, **44**, 6303; (c) E. Wang, Z. Ma, Z. Zhang, P. Henriksson, O. Inganas, F. Zhang, M. R. Andersson, *Chem. Commun.,* 2011, **47**, 4908.
25. (a) P. Sonar, S. P. Singh, Y. N. Li, M. S. Soh, A. Dodabalapur, *Adv. Mater.,* 2010, **22**, 5409; (b) A. J. Kronemeijer, E. Gili, M. Shahid, J. Rivnay, A. Salleo, M. Heeney, H. A. Sirringhaus, *Adv. Mater.,* 2012, **24**, 1558.
26. (a) J. D. Yuen, J. Fan, J. Seifter, B. Lim, R. Hufschmid, A. J. Heeger, F. Wudl, *J. Am. Chem. Soc.,* 2011, **133**, 20799; b) J. Fan, J. D. Yuen, M.; J. Wang, Seifter, J. H. Seo, A. R. Mohebbi, D. Zakhidov, A. J. Heeger, F. Wudl, *Adv. Mater.,* 2012, **24**, 2186.

27. Y. N. Li, S. P. Singh, P. Sonar, *Adv. Mater.,* 2010, **22**, 4862.
28. (a) L. Ye, S. Q. Zhang, L. J. Huo, M. J. Zhang, J. H. Hou, *Acc. Chem. Res.,* 2014, **47**, 1595; (b) G. Z. Zuo, Z. J. Li, M. J. Zhang, X. Guo, Y. Wu, S. Q. Zhang, B. Peng, W. Wei, J. H. Hou, *Polym. Chem.,* 2014, **5**, 1976.
29. (a) B. Wang, S.-W. Tsang, W. F. Zhang, Y. Tao, M. S. Wong, *Chem. Commun.,* 2011, **47**, 9471; (b) B. Wang, J. Zhang, H. L. Tam, B. Wu, W. F. Zhang, M. S. Chan, F. Pan, G. Yu, F. R. Zhu, M. S. Wong, *Polym. Chem.,* 2014, **5**, 836.
30. J. G. Mei, K. R. Graham, R. Stalder, J. R. Reynolds, *Org. Lett.,* 2010, **12**, 660.
31. (a) R. S. Ashraf, A. J. Kronemeijer, D. I. James, H. Sirringhaus, I. McCulloch, *Chem. Commun.,* 2012, **48**, 3939; (b) G. W. P. Van Pruissen, F. Gholamrezaie, M. M. Wienk, R. A. J. Janssen, *J. Mater. Chem.,* 2012, **22**, 20387; (c) Y. Koizumi, M. Ide, A. Saeki, C. Vijayakumar, B. Balan, M. Kawamoto, S. Seki, *Polym. Chem.,* 2013, **4**, 484.
32. M. Karakawa, Y. Aso, *RSC Adv.,* 2013, **3**, 16259.
33. T. Lei, J. H. Dou, X. Y. Cao, J. Y. Wang, J. Pei, *J. Am. Chem. Soc.,* 2013, **135**, 12168; (b) Z. Yan, B. Sun, Y. N. Li, *Chem Commun.,* 2013, **49**, 3790.
34. T. Wu, C. M. Yu, Y. L. Guo, H. T. Liu, G. Yu, Y. Fang, Y. Q. Liu, *J. Phys. Chem.* C, 2012, **116**, 22655.
35. J. X. Zhang, P. Dubois, R. Jérôme, *J. Chem. Soc., Perkin Trans. 2*, **1997**, 1209.
36. a) J. S. Ha, K. H. Kim, D. H. Choi, *J. Am. Chem. Soc.,* 2011, **133**, 10364; b) A. Zen, J. Pflaum, S. Hirschmann, W. Zhuang, F. Jaiser, U. Asawapirom, J. P. Rabe, U. Scherf, D. Neher, *Adv. Funct. Mater.,* 2004, **14**, 757; c) H. H. Jaffé, M. Orchin,

Theory and Applications of Ultra Violet Spectroscopy; Wiley: New York, 1962.

37. a) Z. Zhang, Y. Qin, *ACS Macro Lett.,* 2015, **4**, 679; b) K. H. Park, K. H. Cheon, Y. J. Lee, D. S. Chung, S. K. Kwon and Y. H. Kim, *Chem. Commun.,* 2015, **51**, 8120.

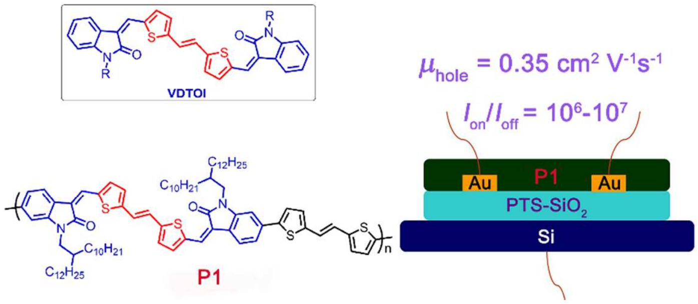
The table of contents:

Vinylidenedithiophenmethyleneoxindole: A Centrosymmetric Building block for Donor−Acceptor Copolymers

Weifeng Zhang,[a,#] Naihang Zheng,[a,#] Congyuan Wei,[a] Jianyao Huang,[a] Dong Gao,[a] Keli Shi,[a] Jie Xu,[a] Donghang Yan,[b] Yanchun Han,[b] and Gui Yu[a,*]

[a]Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China

[b]State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China



A novel building block (VDTOI) were designed and synthesized. VDTOI-based copolymers exhibit a high mobility of $0.35\ cm^2\ V^{-1}\ s^{-1}$.