Alkylated Selenophene-Based Ladder-Type Monomers via a Facile Route for High-Performance Thin-Film Transistor Applications

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ABSTRACT: We report the synthesis of two new selenophene-containing ladder-type monomers, cyclopentadiselenophene (CPDS) and indacenodiselenophene (IDSe), via a 2-fold and 4-fold Pd-catalyzed coupling with a 1,1-diborylmethane derivative. Copolymers with benzothiadiazole were prepared in high yield by Suzuki polymerization to afford materials which exhibited excellent solubility in a range of nonchlorinated solvents. The CPDS copolymer exhibited a band gap of just 1.18 eV, which is among the lowest reported for donor–acceptor polymers. Thin-film transistors were fabricated using environmentally benign, nonchlorinated solvents, with the CPDS and IDSe copolymers exhibiting hole mobility up to 0.15 and 6.4 cm2 V−1 s−1, respectively. This high performance was achieved without the undesirable peak in mobility often observed at low gate voltages due to parasitic contact resistance.

INTRODUCTION

The past three decades has seen tremendous effort devoted to the development of conjugated small molecules and polymers for low-cost, flexible, and large-area electronics.1,2 A variety of building blocks have been developed and incorporated into conjugated architectures for high-performance organic thin-film transistor (OTFTs) and organic photovoltaic (OPV) applications.3–6 Among these building blocks, ladder-type fused aromatic monomers have attracted much interest because of their unique structures and intriguing electrical properties. Covalently flanked adjacent aromatic units force the ladder-type monomer to adopt a nearly coplanar rigid conformation.7,8 The use of this kind of coplanar building block can potentially elongate the effective conjugation length, facilitating π-electron delocalization and decreasing the reorganizational energy, thus enhancing the intrinsic charge carrier mobility.9–11 Many of the high-performance ladder-type monomers reported to date are thiophene-based, in which the thiophene units have been bridged by a variety of heteroatoms. In addition to their electronic effects, these bridging atoms are typically utilized to incorporate solubilizing groups to enable processability. For example, many polymers and small molecules based on cyclopentadithiophene (CDT) and indacenodithiophene (IDT) with carbon as the bridging atom exhibit promising performance in solution-processed high-performance OTFTs12–16 and OPVs.3 Different strategies have been employed to modify the structure of the ladder-type units to adjust the electronic energy levels and aggregation state of the resulting semiconductor, for example, replacing the bridging carbon with a Si or Ge atom, or further extending the conjugation length by flanking with fused aromatic rings.

Replacing the sulfur atom in the thiophene ring is another approach to control the properties of semiconducting molecules. The larger size of Se over S reduces overlap with the adjacent π-system, and the resulting reduction in aromaticity of selenophene compared to thiophene increases the quinoidal character of the polymer backbone, which usually results in a reduced band gap.17,18 The more polarizable Se can also enhance intermolecular interactions of conjugated backbones in some cases, and many different selenophene-containing conjugated polymers have been reported to give improved device performance, especially charge carrier mobility, over their thiophene-containing analogues.18–34 One consequence of these changes is that selenophene-containing polymers are often poorly soluble, and those that are soluble
typically require the use of highly chlorinated, high-boiling-point solvents such as 1,2-dichlorobenzene. However, such solvents are very unattractive for processing due to their detrimental environmental impact and health hazards.35 In this respect, we were interested to develop new fused ladder-type selenophene monomers, since the bridging position could be utilized to promote solubility in nonchlorinated solvents via the use of very long alkyl side chains. However, until now, there have been few examples of selenophene-based ladder-type building blocks reported, possibly due to the difficulty in the functionalization of selenophene compared to thiophene.20,36 Of the limited selenophene-containing ladder-type building blocks reported, it is noticeable that carbon-bridged examples always incorporate a bridging phenylalkyl or phenylalkoxy group as the solubilizing group. This is likely due to synthetic reasons, since Friedel–Crafts-type ring-closing reactions are utilized from the corresponding (stable) triaryl cations. However, in many cases it is undesirable for device applications to utilize aromatic groups directly on the bridging carbon because of the rather large steric hindrance compared to that of simple linear alkyl groups. This can inhibit close packing of the polymer backbones, resulting in reduced device performance, particularly for transistor applications.

Here we report a facile route for the first reported preparation of the alkylated selenophene-based fused-ring ladder monomers cyclopentadiselenophene (CPDS) and indacenodiselenophene (IDSe). We report their corresponding polymerization with an electron acceptor unit, 2,1,3-benzothiadiazole-4,7-bis(diethyl)bis(trimethylsilane) (DETSi) was puriﬁed by recrystallization from hexane before use. (3,3'),5,5'-dicyanobenzene-2,2'-biscyclohexane (DCA) was synthesized by the reported method.102,103 The resulting polymers exhibit excellent solubility in nonchlorinated solvents such as tetralin, and organic thin-ﬁlm transistors fabricated from these solutions exhibit a saturated mobility up to 6.4 cm² V⁻¹ s⁻¹. This is among the highest hole mobility values reported for devices fabricated from nonchlorinated solvents.37 Importantly, all optimized devices show clean transistor behavior without the ﬂuctuations in the derived carrier mobility at low gate voltages that are apparent in numerous previous reports of high-mobility polymers.41,42

## EXPERIMENTAL SECTION

### General Procedures

All reactions were carried out in oven-dried glassware under Ar using solvents and reagents as commercially supplied, unless otherwise stated. 2,1,3-Benzothiadiazole-5,5'-dicyanobenzene (DCA) was synthesized by the reported method.102,103 The resulting polymers exhibit excellent solubility in nonchlorinated solvents such as tetralin, and organic thin-ﬁlm transistors fabricated from these solutions exhibit a saturated mobility up to 6.4 cm² V⁻¹ s⁻¹. This is among the highest hole mobility values reported for devices fabricated from nonchlorinated solvents.37 Importantly, all optimized devices show clean transistor behavior without the ﬂuctuations in the derived carrier mobility at low gate voltages that are apparent in numerous previous reports of high-mobility polymers.41,42

A solution of polymer was prepared by dissolving the polymer in tetralin at a concentration of 10 mg/mL. Transistors were prepared by first thermally evaporating Au (40 nm) onto glass substrates through a shadow mask to form bottom-source/drain (S/D) electrodes, which were then treated with a self-assembled monolayer (SAM) of pentafluorobenzenethiol (PFBT) to improve the work function. The SAM treatment step was carried out by immersing the substrates with patterned Au electrodes in a solution containing a 1:1000 ratio of PFBT in ethanol for 30 min before rinsing them off with plenty of ethanol to remove the excess materials and annealing at 100 °C for 15 min.

Copper(I) thiocyanate (CuSCN) was dissolved in diethyl sulfoxide to a concentration of 5 mg/mL and spin cast onto the substrates with prepatterned Au electrodes at 5000 rpm for 30 s. The resulting CuSCN thin ﬁlms were annealed at 100 °C for 30 min under nitrogen. The polymer solution was then spin cast and annealed following the same procedures as for PFBT-treated devices.

The deep trap densities (N_d) of OTFTs were determined from the subthreshold swing (S) according to the following equation:

\[ N_d = \frac{C_i C_s}{e^2 kT \ln(10)^2} \]

where \( e \) is the elementary charge, \( C_i \) the geometric capacitance of the gate dielectric, \( V_{on} \) the onset voltage, \( k \) the Boltzmann constant, and \( T \) the measuring temperature.

The dielectric constant of CuSCN was determined with capacitance–frequency (C–F) measurements performed on a parallel plate capacitor structure using an impedance analyzer (Solartron1260). The data yielded a value for the dielectric constant of 2.14, which is in good agreement with the manufacturer’s specification (2.0–2.1). The \( C_i \) of CuSCN was then determined to be 2.10 ± 0.09 nF cm⁻² according to the following equation:

\[ C_i = \frac{1}{kT \ln(10)^2} \]

**Journal of the American Chemical Society**

DOI: 10.1021/jacs.7b03099

J. Am. Chem. Soc. 2017, 139, 8552–8561

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where $\varepsilon$ is the dielectric constant of CYTOP ($\varepsilon = 2.14$), $v$ the vacuum permittivity, and $d$ the thickness of the CYTOP dielectric layer (~900 nm).

**Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS)**
GIWAXS measurements were performed at the small-angle X-ray scattering/wide-angle X-ray scattering (SAXS/WAXS) beamline at the Australian Synchrotron. Two-dimensional scattering patterns were recorded on a Dectris Pilatus 1M detector with 11 keV photons used to probe the samples. An angle of incidence close to the critical angle (~0.13°) was used. The total exposure time was 3 s, with the reported images a composite of three separate 1 s exposures taken with different lateral detector offsets to fill in the regions missed by gaps in the detector. A silver behenate standard was used to calibrate the sample-to-detector distance. The results were analyzed using NIKADA implemented in IgorPro.

**Synthesis of 4H-Cyclopenta[2′,1-b:3′,4-b]diselenophene (2).**

4,4-Dihexadecyl-4H-cyclopenta[2′,1-b:3′,4-b]diselenophene (3). (3.3'-Dimbromo-2′,2′-biselenophene-5,5'-diyl)bis(trimethylsilane) (4.3 g, 7.6 mmol), bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (3.07 g, 11.5 mmol), and bis(tri-tert-butylphosphine)palladium (0.4 g, 0.76 mmol) were added into a 100 mL two-neck round-bottom flask under argon. Then predegassed dioxane (40 mL) and 8 M KOH (1.44 mL, 11.5 mmol) were added. The mixture was thoroughly degassed under argon and stirred for 24 h at 30 °C. Additional KOH (2.88 mL, 23.0 mmol) was added to the mixture, and the reaction was heated for 24 h at 60 °C. Water (30 mL) was added and the mixture extracted (3 × 50 mL of dichloromethane (DCM)). The combined organics were dried by MgSO4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (eluent hexane) to afford a pale yellow solid (1.21 g). To the resulting solid in THF (30 mL) was added tetraethylammonium fluoride (TFAB) (5.7 mL of a 1 M solution in THF, 5.7 mmol) dropwise at 0 °C. After being stirred at this temperature for 5 min, the mixture was passed through a silica gel plug (5 cm × 5 cm) (elucent hexane). The solvent was removed under vacuum and the residue was purified by silica gel chromatography (eluent hexane) to afford a pale yellow solid (0.77 g, yield 37%).

1H NMR (CDCl3, 400 MHz): δ (ppm) 7.85 (d, J = 5.3 Hz, 2H), 7.34 (d, J = 5.3 Hz, 2H), 3.47 (s, 2H).

13C NMR (CDCl3, 100 MHz): δ (ppm) 150.8, 143.6, 129.3, 125.3, 34.6. HRMS (EI+): calcd for C20H22Br4Se2: 878.8; found: 878.8. MALDI-TOF: 878.8 (M+).

C. After being cooled to room temperature, the mixture was poured into a mixture of methanol (50 mL) and concentrated HCl (3 M) and the precipitant was filtered through a Soxlet thimble. The polymer was purified by Soxlet extraction with methanol, acetone, hexane, and chloroform. The chloroform solution was concentrated and precipitated into methanol, and the precipitant was filtered and dried under vacuum to afford PCPDSBT as a dark green solid (72 mg, yield 83%). GPC (chlorobenzene, 80 °C): $M_w$ = 75000 g/mol, $M_n$ = 158000 g/mol; $\Delta_{\text{cv}}/\Delta_{\text{v}}$ (film) = 860 nm. 1H NMR (d-1,2,2-trichloroethane, 80 °C, 130 °C): δ (ppm) 8.16 (s, br, 2H), 7.93 (s, br, 2H), 2.13 (s, br, 4H), 1.39–1.30 (s, br, 2H), 0.98–0.95 (s, br, 1H). Anal. Calcd for (C47H70N2SSe2)2: C, 66.17; H, 8.27; N, 3.28. Found: C, 65.05; H, 8.16; N, 3.65.

**Diselenophene-5,5′-diyl(2,5-Dibromo-1,4-phenylene)bis(trimethylsilane) (6).** To a solution of 2,5-dibromophenol (10.8 g, 37.3 mmol) in THF (100 mL) at −78 °C was added a solution of n-BuLi (15.7 mL of a 2.5 M solution in hexane, 39.2 mmol) dropwise. After the resulting mixture was stirred for 20 min at this temperature, chlorotrimethylsilane (8.2 mmol) was added. The mixture was allowed to warm to room temperature, water (100 mL) was added, and the mixture was extracted (3 × 100 mL of hexane). The combined organics were dried by MgSO4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (elucent hexane) to afford a pale yellow oil (8.6 g, yield 82%). 1H NMR (CDCl3, 400 MHz): δ (ppm) 7.30 (dd, J = 3.7, 1.2 Hz, 2H), 7.22 (dd, J = 3.7, 1.2 Hz, 2H), 0.33 (s, 9H). 13C NMR (CDCl3, 100 MHz): δ (ppm) 152.0, 136.4, 134.6, 119.8, 0.17. HRMS (EI+): calcd for C44H34Br2Se2Si: 818.8979; found, 818.8968.

**Diselenophene-5,5′-diyl(5,5′-Dibromo-4,4′-phenylene)bis(4-bromoselenophene-5,2-diyl)bis(trimethylsilane) (8).** To a solution of (5-bromoselenophen-2-yl)trimethylsilane (3.6 g, 12.8 mmol) in THF (100 mL) at −78 °C was added a solution of lithium diisopropylamide (LDA) (7.7 mL of a 2 M solution in THF/heptanes/ethylbenzene, 15.4 mmol) dropwise. The mixture was stirred for 1 h at this temperature and then warmed to −40 °C for 20 min. ZnCl2 (24 mL of 0.7 M in THF, 16.8 mmol) was added dropwise and the resulting mixture was stirred at this temperature for 30 min. Then the mixture was allowed to warm to 0 °C for 1 h and the reaction was repeated for 30 min. 1,4-Dibromo-2,5-diodobenzene (2.5 g, 5.1 mmol) and Pd(PPh3)4 (295 mg, 0.26 mmol) were added, and the mixture was heated to 65 °C overnight. The mixture was cooled and passed directly through a silica gel plug (5 cm × 5 cm) (elucent THF). The solvent was removed under reduced pressure, and the residue was purified by silica gel chromatography (elucent hexane and then DCM/hexane = 1/1), followed by recrystallization from ethyl acetate to afford a white solid (2.5 g, yield 62%). 1H NMR (CDCl3, 400 MHz): δ (ppm) 7.68 (s, 2H), 7.46 (s, 2H), 7.36 (s, 18H). 13C NMR (CDCl3, 100 MHz): δ (ppm) 150.6, 143.8, 138.8, 138.0, 135.7, 122.5, 113.3, 0.03. Anal. Calcd for C57H38Br2Se2Si4: C, 53.67; H, 4.67; Se, 22.37. Found: C, 51.78; H, 4.52; Se, 22.14.
mmol) were added. The mixture was thoroughly degassed under argon and stirred for 24 h at 30 °C. Additional KOH (6.2 mL, 49.6 mmol) was added to the mixture, and the reaction was heated 24 h at 60 °C. Water (100 mL) was added and the mixture extracted (3 × 150 mL of DCM). The combined organics were dried by MgSO4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (eluents DCM/hexane = 1/2) to afford an off-white solid (2.1 g, yield 91%). 1H NMR (CDCl3, 400 MHz): δ (ppm) 2.83 (s, 2H), 2.75 (s, 2H), 0.83 (s, 2H), 0.39 (s, 18H), 0.29 (s, 18H), and 0.09 (s, 18H). 13C NMR (CDCl3, 100 MHz): δ (ppm) 155.2, 151.2, 145.2, 138.0, 127.5, 115.0, 113.3, 55.8, 39.0, 31.9, 29.8, 29.6 (overlapping C), 29.4, 23.9, 22.7, 14.1. MALDI-TOF: 1417.9 (M+).

To a solution of 2,7-bis(trimethylsilyl)-4,9-dihydro-s-indaceno[1,2-b:5,6-b′-]bis(selenophene) (0.51 g, 1.0 mmol) in anhydrous DMSO (40 mL) was added sodium tert-butoxide (0.58 g, 6.0 mmol). The mixture was stirred at 70 °C for 30 min before 1-bromohexadecane (1.9 g, 6.2 mmol) was added dropwise. The mixture was heated to 80 °C overnight and poured into ice-water (150 mL). The precipitant was filtered, washed by water and methanol, and dried under vacuum, followed by recrystallization from hexane to afford a pale yellow solid (1.1 g, yield 61%). 1H NMR (CDCl3, 400 MHz): δ (ppm) 7.89 (d, J = 5.3 Hz, 2H), 7.23 (t, J = 2.2 Hz, 2H), 7.18 (d, J = 5.3 Hz, 2H), 1.99–1.83 (m, 8H), 1.31–1.08 (m, 104H), 0.89–0.78 (m, 20H), 1.1C NMR (CDCl3, 100 MHz): δ (ppm) 156.8, 152.2, 144.4, 138.0, 130.6, 124.2, 113.4, 54.9, 39.1, 31.9, 29.7, 29.7–29.6 (overlapping C), 29.4, 22.7, 14.1. MALDI-TOF: 1259.9 (M+).

**RESULTS AND DISCUSSION**

**Synthesis and Characterization.** The most common routes to alkylated thiophene-based ladder monomers of cyclopentadithiophene (CDT) and indacenodithiophene (IDT) usually involve alkylation of the methylene (–CH2–) bridged precursor. However, the synthesis of this key intermediate often involves relatively harsh reaction conditions, for example, an acid-catalyzed Friedel–Crafts acylation, followed by reduction of the resulting ketone.31−34 Such sequences are usually low yielding for thiophene-based materials, due to the high reactivity of thiophene under acetic conditions and due to difficulties in purifying the poorly soluble fused ketone intermediates. These routes thus appeared even more unattractive for the selenophene analogues, particularly given the higher reactivity of selenophene over thiophene. We therefore developed a route directly to the methylene-bridged intermediates that avoided acidic conditions (Scheme 1) and utilized a Suzuki ring closing of a suitable di- or tetrabromo derivative with bis(4,4,5,5-tetramethyl-1,3,5-dioxaborolan-2-yl)-methane.44,55−58

Hence, previously unknown cyclopentadiselenolene (CPDS, 2) was isolated in 37% yield from 1, following ring closure with Pd[P-(t-Bu)4]2 in a mixture of dioxane/aqueous KOH with Pd[P-(t-Bu)4]2. In this case the crude product was directly desilylated with TBAF before isolation to avoid complications with partial loss of the trimethylsilyl groups during chromatography. Subsequent alkylation with 1-bromohexadecane followed by boration with NBS afforded monomer material 4 in 66% yield over the two steps. Gratifyingly, such an approach was even successful for the more challenging 4-fold cross-coupling of tetrabromo derivative 8 (itself prepared from 2,5-dibromoselenophene in three steps in 51% yield) to afford the new 4,9-dihydro-s-indaceno[1,2-b:5,6-b′]-bis(selenophene) (IDSe) in 51% yield. The higher yield compared to that of CPDS, despite the 4-fold coupling, is likely related to the very electron rich nature of 1 compared to 8. This different electron densities of the ring-closed monomers is also reflected in the fact that the silylated IDSe was stable during chromatography, unlike CPDS, which was partially desilylated. The IDSe was readily alkylated with hexadecyl side chains and bminated in an overall yield of 58%.

Our initial attempts to prepare the copolymer of dibrominated CPDS (4) and 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester) under standard Suzuki polymerization conditions with Pd[PPh3]4 or Pd2dba3/P-(o-tol), as the catalyst were unsuccessful. Only very low weight oligomer material was formed. We believed this related to problems with the oxidative addition of the catalyst to the very electron rich CPDS. Therefore, use of the more reactive catalyst Pd[P-(t-Bu)4]2 enabled the successful isolation of polymeric material. Unlike PCPDSBT, PIDSeBT was readily prepared by Pd2dba3/P-(o-tol), as the catalyst under standard Suzuki polymerization conditions. Both polymers were purified by precipitation into acidic methanol followed by Soxhlet extraction with methanol, acetone, hexane, and chloroform. The chloroform solution was concentrated and precipitated into methanol, and the precipitant was filtered and dried under vacuum to afford PIDSeBT as a dark green solid (476 g, yield 86%). GPC (chlorobenzene, 80 °C): Mn = 119000 g/mol, Mw = 303000 g/mol; ηmax(film) = 725 nm. 1H NMR (d-d, 1,1,2,2-tetrachloroethane, 400 MHz, 130 °C): δ (ppm) 8.17 (s, br, 2H), 7.97 (s, br, 2H), 7.45 (s, br, 2H), 2.18–2.10 (m, br, 8H), 1.40–1.26 (m, 104H), 0.97–0.94 (m, br, 20H). Anal. Calcd for C86H138N2SSe2: C, 74.31; H, 10.01; N, 2.02. Found: C, 74.15; H, 10.15; N, 2.14.

### Physical and Optoelectronic Properties

Both PCPDSBT and PIDSeBT exhibited good thermal stabilities, as evaluated by thermal gravimetric analysis (TGA) (Figure 8555). DOI: 10.1021/jacs.7b03099 J. Am. Chem. Soc. 2017, 139, 8552−8561
S1a, Supporting Information), with a 5% weight loss at temperatures of 390 and 410 °C under nitrogen, respectively. Differential scanning calorimetry (DSC) curves (Figure S1b) of both polymers showed no obvious thermal transitions upon cycling between 0 and 300 °C, suggesting, in agreement with many ladder polymers, that the backbone melting temperature is above 300 °C. DFT calculations of trimers of PCPDSBT and PIDSeBT were modeled using Gaussian at the B3LYP/6-31G* level, with the side chains modified to an ethyl group for simplifying the calculations. The minimum-energy conformations of the CPDSBT and IDSeBT trimers both show the polymers adopt almost coplanar backbones (Figure 1), potentially minimizing torsional disorder along the backbone.59 The minimum-energy conformation of CPDSBT also shows PCPDSBT has a slightly flexural geometry, which potentially hinders the charge transport along the backbone.60,61 However, that of IDSeBT exhibits a more linear geometry, which may facilitate charge transport. Both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of PCPDSBT are predicted to be delocalized over the entire backbones, while the HOMO of PIDSeBT is delocalized and the LUMO is mainly localized on the acceptor unit (Figures S2 and S3, Supporting Information).
The UV−vis absorption spectra of PCPDSBT and PIDSeBT in dilute tetralin and as thin films are shown in Figure 2 and the data summarized in Table 1. PCPDSBT exhibits two main broad absorption bands in dilute tetralin, with a peak of 443 nm in the high-energy region which is assigned to $\pi-\pi^*$ transitions of the main backbone and a peak of 860 nm with a shoulder of 806 nm in the low-energy region which we attribute to an intramolecular charge transfer (ICT) from the CPDS donor to the BT acceptor. In the film, the main peaks of PCPDSBT are red-shifted to 455 and 885 nm, suggestive of backbone planarization and ordering in the solid state. The long-wavelength peak is red-shifted by around 135 nm compared to that of its thiophene analogue CDT−BT,62 further demonstrating the significant impact of selenophene substitution on the optical spectra.17,27,63 The absorption onset of PCPDSBT in the solid state is around 1050 nm, corresponding to an optical band gap of 1.18 eV, which is among the lowest reported for donor−acceptor polymers.70−75

PIDSeBT also exhibits two main bands with peaks at 426, 650, and 705 nm in tetralin solution and 434, 663, and 725 nm in the solid state. The absorption onset of PIDSeBT in the solid state is 780 nm, corresponding to an optical band gap of 1.59 eV. The band gap of PCPDSBT is much smaller than that of PIDSeBT, which can be attributed to enhanced ICT from the stronger donor unit CPDS to the BT acceptor unit. The ionization potentials (IPs) of thin films of PCPDSBT and PIDSeBT were measured by PESA to be 4.85 and 5.22 eV, respectively. The IP of PIDSeBT is around 0.18 eV smaller than that of the thiophene analogue measured by the same technique.54

Thin-Film Transistor Properties. The charge transport properties of both polymers were assessed in bottom-contact/top-gate (BC/TG) TFTs. Importantly, both polymers were deposited from tetralin solutions, thereby avoiding the use of hazardous chlorinated solvents. Polymers were spin coated onto glass substrates equipped with prepatterned Au source/drain electrodes, which were treated with the PFBT self-assembling monolayer to improve hole injection, followed by annealing at 200 °C. Both PCPDSBT and PIDSeBT displayed dominant p-type behavior, with negligible hysteresis between

| Property                  | PCPDSBT | PIDSeBT |
|--------------------------|---------|---------|
| $M_n$ (KDa)              | 75      | 119     |
| $M_w$ (KDa)              | 158     | 303     |
| $\mathcal{D}$            | 2.1     | 2.5     |
| UV(sol) peaks (nm)       | 443, 806, 860 | 426, 650, 705 |
| UV(film) peaks (nm)      | 455, 885 | 434, 663, 725 |
| Onset (nm)               | 1050    | 780     |
| $E_{g,opt}$ (eV)         | 1.18    | 1.59    |
| IP (eV)                  | 4.85    | 5.22    |

*Measured using gel permeation chromatography (against polystyrene standards) in chlorobenzene at 80 °C. Optical band gap estimated from the low-energy band edge in the optical spectrum. Ionization potential measured by UV−PESA (error ±0.05 eV).
the forward and reverse bias transfer characteristics (Figure 3; Figure S4, Supporting Information). PCPDSBT exhibited the lower performance of the two polymers with average linear and saturation mobilities of 0.10 and 0.14 cm² V⁻¹ s⁻¹, respectively. Although these values are lower than those reported previously for the best performing thiophene analogues, we note that these were only achieved with carefully optimized processing (chain alignment techniques) and molecular weight. In comparison, transistors based on PIDSeBT performed significantly better, with average linear and saturation mobility values of 0.56 and 1.6 cm² V⁻¹ s⁻¹, respectively.

On the basis of these initial results, we further optimized the PIDSeBT transistors via a combination of postdeposition thermal treatment and interfacial layer engineering. The use of a higher annealing temperature of 270 °C was found to enhance the performance (Table 2; Figure S5, Supporting Information). We note that the mobility values obtained here are among the highest reported to date for polymers processed via spin-coating from a nonchlorinated solvent without the use of any special alignment techniques. Most importantly, optimized devices exhibit excellent transfer characteristics without the undesirable peak in mobility often observed at low gate voltages due to parasitic contact resistance.

The subthreshold regime of the devices was also investigated to determine whether the performance improvement was due to decreasing trap density within the bulk film as a result of thermal annealing or the employment of the hole injection layer. The deep trap density in the bulk film displayed a negligible difference for all PIDSeBT-based devices, in the range of (0.9−1.3) × 10¹¹ eV⁻¹ cm⁻³ (Table S1, Supporting Information). Thus, the increase in mobility is most likely attributed to local changes at the semiconductor/dielectric interface and/or molecular rearrangement and the improved hole injection characteristics.

### Table 2. OTFT Device Performance of PCPDSBT and PIDSeBT in Bottom-Gate/Top-Contact Devices

| polymer² | μ<sub>sat(average)</sub> (cm² V⁻¹ s⁻¹) | μ<sub>sat(max)</sub> (cm² V⁻¹ s⁻¹) | V<sub>th</sub> (V) | I<sub>on</sub>/I<sub>off</sub> |
|----------|-----------------|-----------------|----------|-------------|
| PIDSeBT/PFBTN₃₀₀ | 2.8 (3.2) | 0.58 | −34.0 | 10⁵−10⁶ |
| PIDSeBT/CuSCN₇₀₀ | 4.4 (6.4) | 1.8 | −24.8 | 10⁵−10⁶ |
| PIDSeBT/PFBTN₂₀₀ | 1.6 (1.7) | 0.56 | −26.9 | 10⁵−10⁶ |
| PIDSeBT/CuSCN₇₀₀ | 1.8 (2.0) | 1.1 | −21.3 | 10⁵−10⁶ |
| PCPDSBT/PFBTN₂₀₀ | 0.14 (0.15) | 0.10 | −5.0 | ∼10² |

“²The compound after the slash indicates the monolayer material, and the number after the underscore indicates the annealing temperature (°C).

Figure 4. Typical transfer characteristics of the BC/TG configuration OTFT device with PIDSeBT/CuSCN annealed at 200 °C (a) and 270 °C (b). (c) Device structure employed.
consistent with values reported for CDT−BT.81,82 The scattering pattern of PCPDSBT also shows a broad feature located at \( q \approx 14 \text{ nm}^{-1} \) that is most intense at \( (q_{xy}, q_{z}) = (10 \text{ nm}^{-1}, 10 \text{ nm}^{-1}) \), which is associated with the ordered stacking of the side chains.83 Thus, PCPDSBT is very similar in its packing to CDT−BT, with the exchange of sulfur atoms for selenium atoms only slightly perturbing the microstructure. The lower OTFT performance of PCPDSBT observed here compared to values previously reported for CDT−BT may be due to suboptimal processing,52 with the mixture of face-on and edge-on components seen here less than ideal. Table 3 summarizes the crystallographic spacings and coherence lengths determined from the GIWAXS data.

In contrast to PCPDSBT, PIDS\( \text{e} \)BT shows a very different molecular packing. The 2D GIWAXS images of the PIDS\( \text{e} \)BT films are characterized by a prominent backbone stacking (001) peak located in-plane at \( q = 3.95 \text{ nm}^{-1} \). This peak is distinguished from an alkyl stacking peak by its narrow, vertical shape and corresponds to a backbone repeat distance of 1.59 nm. A weak alkyl stacking peak is seen in the out-of-plane direction, corresponding to a \( d \)-spacing of \( \sim 1.8 \text{ nm} \), which is very different from the much larger spacing seen for PCPDSBT. The \( \pi-\pi \) stacking distance of PIDS\( \text{e} \)BT is found to be \( \sim 0.42 \text{ nm} \), slightly larger than the value measured for IDT−BT.55 The shorter lamellar spacing and larger \( \pi-\pi \) spacing of PIDS\( \text{e} \)BT compared to PCPDSBT indicate that PIDS\( \text{e} \)BT adopts a completely different side-chain-packing geometry. Indeed, the rigid, planar nature of the PIDS\( \text{e} \)BT backbone promotes backbone ordering over side-chain ordering. High degrees of order in lamellar stacking have been shown not to be necessary for high charge transport mobility, with polymers such as IDT−BT demonstrating exceptionally low degrees of energetic disorder attributed to their backbone planarity.59 With the increase in annealing temperature from 200 to 270 °C, the crystalline features of PIDS\( \text{e} \)BT become sharper, notably the backbone stacking peak, which helps to understand the increase in mobility with annealing in terms of improved order along the polymer backbone.

To probe the surface microstructures, the morphologies of the polymer semiconductor films were characterized by tapping mode AFM. Sample films were prepared under conditions identical to those of OTFT fabrication except that no dielectric or gate electrodes were deposited. The topography and phase images of polymer films processed under different conditions are shown in Figures 6 and S7 (Supporting Information). PCPDSBT forms a continuous and smooth film with fine fibrillar structures, affording surface roughness (root-mean-square, rms) of 0.649 nm after annealing at 200 °C. PIDS\( \text{e} \)BT yielded films with less pronounced microstructural features, and a similar rms of 0.748 nm. The film turned modestly smoother after annealing at a higher temperature of 270 °C, with an rms of 0.560 nm. Films cast atop CuSCN and annealed at 200 °C were rougher than those without an interfacial layer, with an rms of 1.326 nm, due to the rather rough surface of crystallized CuSCN.83 The surface roughness decreased to 0.582 nm after annealing at 270 °C, in agreement with the increase in transistor performance.

### Table 3. Crystallographic Spacings and Coherence Lengths Determined from the GIWAXS Data

| polymer            | (100) \( d \)-spacing (nm) | (100) coherence length (nm) | (010) \( d \)-spacing (nm) | (010) coherence length (nm) | (001) \( d \)-spacing (nm) | (001) coherence length (nm) |
|--------------------|-----------------------------|------------------------------|-----------------------------|------------------------------|-----------------------------|------------------------------|
| PCPDSBT            | 2.60                        | 13.4                         | 0.38                        | 9.1                          | 0.42                        | 2                            |
| PIDS\( \text{e} \)BT (200 °C) | 1.79                        | 10.6                         | 0.42                        | 2                            | 1.59                        | 18.8                         |
| PIDS\( \text{e} \)BT (270 °C) | 1.79                        | 10.6                         | 0.42                        | 2                            | 1.59                        | 21.6                         |

**CONCLUSION**

In conclusion, we have reported the synthesis of two novel selenophene-containing ladder monomers by a 2-fold and 4-fold Pd-catalyzed ring-closing reaction between bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethane and the di- and tetrabrominated aryl precursors. This route, which avoids the necessity for harsh acidic or reducing conditions, allows the preparation of unalkylated cyclopentadiselenophene (CPDS) and indacenodiselenophene (IDS\( \text{e} \)) for the first time. Subsequent alkylation with long hexadecyl side chains affords highly soluble monomeric materials, which were copolymerized with the electron acceptor benzothiadiazole. The resulting polymers PCPDSBT and PIDS\( \text{e} \)BT exhibit highly planar backbones in combination with excellent solubility in a range of nonchlorinated solvents. The optical band gap of PCPDSBT exhibits a significant red shift compared to that of the well-investigated thiophene analogue, with a small optical band gap of 1.18 eV, one of the lowest reported for a donor−acceptor copolymer. Thin-film transistors fabricated from tetralin solutions of both polymers exhibited p-type behavior, with PIDS\( \text{e} \)BT exhibiting a hole mobility up to 6.4 cm² V⁻¹ s⁻¹ after

Figure 5. Two-dimensional GIWAXS images of PCPDSBT annealed at 200 °C (a), PIDS\( \text{e} \)BT annealed at 200 °C (b), and PIDS\( \text{e} \)BT annealed at 270 °C (c). Also shown are one-dimensional scattering profiles taken along the in-plane (d, f) and out-of-plane (e, g) directions for PCPDSBT (d, e) and PIDS\( \text{e} \)BT (f, g).

DOI: 10.1021/jacs.7b03099
J. Am. Chem. Soc. 2017, 139, 8552–8561
device optimization. This is among the best reported transistor performances for a polymer fabricated from a nonchlorinated solvent. Importantly, these devices exhibited excellent transfer characteristics without the undesirable peak in mobility often observed at low gate voltages due to parasitic contact resistance. These results demonstrate that the incorporation of selenophene into ladder-type structures is a possible route to improve the performance of the materials. In particular, given the interest in ladder-type monomers for non-fullerene acceptor materials, we believe that this synthetic approach will be of further interest for the development of new types of acceptor backbones.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/jacs.7b03099.

TGA plots, DSC traces, modeling, transistor plots, and AFM data (PDF)

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Notes

The authors declare no competing financial interest. Additional data relating to the paper can be found at dx.doi.org/10.6084/m9.figshare.5001965.

ACKNOWLEDGMENTS

We thank the British Council (Grant No. 173601536) and Engineering and Physical Sciences Research Council (EPSRC) (Grant No. EP/L016702/1) for support. C.R.M. acknowledges support from the Australian Research Council (Grant No. DP130102616). This research was undertaken in part on the SAXS/WAXS beamline at the Australian Synchrotron, Victoria, Australia.

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