ARTICLE TYPE

A low band gap co-polymer of dithienogermole and 2,1,3-benzothiadiazole by Suzuki polycondensation and its application in transistor and photovoltaic cells.

Zhuping Fei[a], Jong Soo Kim[b], Jeremy Smith[b], Ester Buchaca Domingo[c], Thomas D. Anthopoulos[b],
5 Natalie Stingelin[c], Scott E Watkins[d], Ji-Seon Kim*[b], Martin Heeney*[a]

We report the preparation of a 4,4-bis(2-ethylhexyl)dithieno[3,2-*b*:2',3'-*d*]germole monomer and its
polymerisation with 2,1,3-benzothiadiazole. Unlike the analogous dithienosilole, the dithienogermole is
10 sufficiently stable under basic conditions to enable Suzuki polycondensation. The resulting high
molecular weight polymer exhibits a high propensity to order in the solid state and demonstrates charge
carrier mobilities up to 0.11 cm^2/Vs in field effect transistors. A PGeBTBT based BHJ solar cell device
achieved a PCE of 4.5% with remarkably a high J$_{sc}$ of 18.6 mA cm^{-2}.

.

15 Introduction

Low band gap semiconducting polymers containing silicon bridging heteroatoms have been the subject of much recent interest for organic field effect transistor (FET) and photovoltaic cell (OPV) applications. Several studies have
20 demonstrated that the electronic properties of the polymer backbone can be modified by interaction of the low lying σ* orbitals of the silicon atom with π* orbitals of the conjugated system, primarily resulting in stabilisation of the polymer LUMO in comparison to the carbon bridged analogues.[1]
25 Furthermore studies by Yang[2, 3], Morana[4] and Scharber[5] et al. have directly compared the properties of a silole-containing polymer, poly{[4,4'-bis(2-ethylhexyl)dithieno[3,2-*b*;2',3'-*d*]silole]-2,6-diyl-*alt*-(2,1,3-benzothidiazole)-4,7-diyl}
(**PSBTBT**), a copolymer of dithienosilole and BT, with those of
30 the carbon analogue poly{[4,4-bis(2-ethylhexyl)-cyclopenta[2,1-*b*;3,4-*b'*)dithiophene]-2,6-diyl-alt-(2,1,3-benzothiadiazole)-4,7-diyl} (**PCPDTBT**) (fig 1). They found significant differences in the crystallinity and thin film morphology of the two polymers, which were rationalised on the basis of detailed modelling that
35 the longer carbon-silicon bond in **PSBTBT** resulted in a reduction of steric hindrance between the solubilising alkyl groups and adjacent thiophene rings. The improved crystalline structure of **PSBTBT** resulted in a higher charge carrier mobility and improved solar cell performance in blends with fullerene
40 derivatives. Low band gap co-polymers containing silafluorene[6], dithieno[3,2-*b*:2',3'-*d*]silole[2, 7] and silaindacenodithiophene[8] have recently demonstrated promising FET and solar cell performance, with dithienosilole co-polymers exhibiting FET mobilities up to 0.08 cm^2/Vs[9] and solar cell power conversion efficiencies up to
45 7.3%[6].

However to date there has been little work on the properties of polymers containing related germanium bridged systems.[10] Germanium sits below silicon in the periodic table, but due to the d-block contraction (or 'scandide' contraction), both
50 elements exhibit similar covalent radii, with an average C-Ge bond being only slightly longer than a C-Si bond (1.96 versus 1.88 Å respectively).[11] Thus the introduction of Ge bridging groups may be expected to exhibit subtle effects on molecular packing and morphology compared to Si. In addition the same
55 d-block contraction renders the electronegativity of Ge much closer to C than that of Si,[12] reducing the polarisation of the C-Ge bond and rendering arylgermanes much more stable towards bases and nucleophiles than the corresponding aryl silanes.[13] We were particularly interested to explore the potential
60 of dithienogermoles in this context, since all dithienosilole co-polymers reported to date have been prepared by Stille cross-coupling rather than the more environmentally benign Suzuki cross-coupling. Furthermore the purification of the required bis-stannyl dithienosiloles to the levels necessary to obtain high
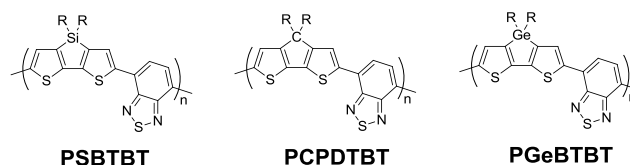65 molecular weights is difficult due to the ready cleavage of the tin groups.[14]

PSBTBT   **PCPDTBT**   **PGeBTBT**

Fig. 1. Structure of bridged bithiophene co-polymers

Herein, we report the synthesis of a 4,4-bis(2-
70 ethylhexyl)dithieno[3,2-*b*:2',3'-*d*]germole monomer and its co-polymerisation with an electron accepting 2,1,3-

benzothiadiazole-4,7-bis(boronic acid pinacol ester) by Suzuki polycondensation reaction. The resulting high molecular weight polymer, poly[(4,4'-bis(2-ethylhexyl)dithieno[3,2-*b*:2',3'-*d*]germole)-2,6-diyl-alt-(2,1,3-benzothiadiazole)-4,7-diyl]

[5] (**PGeBTBT**), is shown to be a promising materials for both FET and OPV applications. During the writing of this manuscript, an indentical polymer has been reported by Ohshita et al.[15] In contrast to our work, they prepare PGeBTBT by a Stille polycondensation reaction between the stannylated

[10] dithienogermole and dibrominated benzothiadiazole to afford a polymer of relatively low molecular weight. A co-polymer of dithienogermole and N-octylthienopyrrolodione has also just been reported by Reynolds and So, which achieved solar cell efficiencies of over 7% in blends with $PC_{70}BM$.[16]

[15] ## Experimental

All reactions were carried out under Ar using solvents and reagents as commercially supplied, unless otherwise stated. 3,3'-Dibromo-5,5'-bis(trimethylsilyl)-2,2'-bithiophene was synthesized by the reported method.[2] Commercial 2,1,3-

[20] benzothiadiazole-4,7-bis(boronic acid pinacol ester) was purified by chromatography over silica gel (eluent: 3% ethyl acetate in hexane), followed by recrystallisation from hexane before use.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-400 (400 MHz), using the residual solvent resonance of $CDCl_3$ or

[25] TMS as an internal reference and are given in ppm. Number-average (Mn) and Weight-average (Mw) were determined by Agilent Technologies 1200 series GPC running in chlorobenzene at 80°C, using two PL mixed B columns in series, and calibrated against narrow polydispersity polystyrene standards. Electrospray

[30] mass spectrometry was performed with a Thermo Electron Corporation DSQII mass spectrometer. UV-vis spectra were recorded on a UV-1601 Shimadzu UV-vis spectrometer. Flash chromatography (FC) was performed on silica gel (Merck Kieselgel 60 F254 230-400 mesh). Photo Electron Spectroscopy

[35] in Air (PESA) measurements were recorded with a Riken Keiki AC-2 PESA spectrometer with a power setting of 5nW and a power number of 0.5. Samples for PESA were prepared on glass substrates by spin-coating. X-ray diffraction (XRD) measurements were carried out with a PANALYTICAL X'

[40] PERT-PRO MRD diffractometer equipped with a nickel-filtered Cu-Kα1 beam and X' CELERATOR detector, using current I = 40 mA and accelerating voltage U = 40kv. Samples were prepared by drop casting.

Top-gate, bottom-contact OFETs were fabricated on glass

[45] substrates using gold source-drain electrodes and CYTOP dielectric. Electrodes were treated with a pentafluorobenzene thiol SAM to increase the work function. The channel width and length of the transistors are 1 mm and 50 μm, respectively. The polymer was dissolved in dichlorobenzene (5 mg/ml) and spin

[50] cast at 2000 rpm from a hot solution before being annealed at 140°C for 30 min. V varied from 10 to -60 V in 1 V steps and V_D set at -5 (linear) and -60 V (saturation).

Bottom-gate, bottom-contact OFETs were fabricated on Si/SiO₂ substrates with photolithographically patterned gold

[55] electrodes. The electrodes were again treated with the pentafluorobenzene thiol SAM and the SiO_2 was treated with an octadecyltrichlorosilane SAM. The channel width and length of

the transistors are 10mm and 10 μm, respectively. The polymer was dissolved in dichlorobenzene (5 mg/ml) and spin cast at 2000

[60] rpm from a hot solution before being annealed at 140°C for 30 min. V_G varied from 20 to -40 V in 1 V steps and V_D set at -5 (linear) and -40 V (saturation).

Organic photovoltaic devices were fabricated using PGeBTBT and [6,6]-phenyl C71 butyric acid methyl ester ($PC_{71}BM$,

[65] purchased from Nano C Inc.) as the donor and acceptor materials. Devices were fabricated onto the indium tin oxide (ITO) coated substrates with the device structure ITO/PDEOT: PSS/PGeBTBT: $PC_{71}BM$/Ca/Al. After sequential cleaning of the ITO with the detergent (Mucasol), acetone and isopropyl alcohol,

[70] thepoly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT:PSS, Baytron P TP AI 4083, Bayer AG) was spin coated onto a layer with a thickness of 30 nm and baked at 120 °C for 30 minutes. PGeBTBT:$PC_{71}BM$ solutions in chlorobenzene (CB) at different weight ratios were stirred

[75] overnight at 100 °C with or without a small amount of 1-chloronaphthalene (CN, 3%). The best devices were prepared from 1:1 solutions (24 mg/mL) by spin coating onto PEDOT: PSS coated ITO substrate (1500 rpm, 2 min) with a hot (100°C) metal chuck. The thickness of the active layer was ~150 nm.

[80] After spin coating of the active layers, films were thermally treated at 140°C for 20 minutes. For the power conversion efficiency (PCE) measurement of OPV devices, we used the thermally deposited Ca (20 nm)/Al (100 nm) cathode. Electrical characteristics were measured by Keithley 236 source/measure

[85] units under AM 1.5 solar illumination (Oriel 300 W solar simulator) at an intensity of 100 mW/cm² with a device area of 0.045 cm². All electrical measurements of OPVs were executed in the inert N₂ purged devices chamber.

[90] **Diphenylbis(2-ethylhexyl) germane (1):**

In a dry three neck 100 mL round bottom flask, diphenylgermanium dichloride (2.5 g, 8.3 mmol) was dissolved in dry THF (20 mL) and cooled to -40°C. (2-Ethylhexyl) magnesium bromide solution (25 ml of a 1 M solution in diethyl

[95] ether, 25 mmol) was added dropwise. The reaction mixture was allowed to warm to RT and stirred for 0.5 h at RT, and then heated to 60 °C for 2 h. The reaction was cooled and the mixture was poured to hexane (40 mL) and filtered. The precipitated salts were washed with hexane. The combined filtrates were

[100] concentrated under reduced pressure. The crude product was purified by silica gel chromatography (eluent: hexane) to obtain **1** as a colourless liquid (3.35 g, yield: 88%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.48-7.46 (m, 4H), 7.36-7.34 (m, 6H), 1.48-1.43 (m, 2H), 1.31-1.11 (m, 20H), 0.84-0.76 (m, 12H). ^{13}C NMR

[105] ($CDCl_3$, 100 MHz), δ (ppm): 140.0, 134.6, 128.2, 127.8, 36.0, 35.4, 28.6, 28.6, 23.0, 19.5, 14.1, 10.7. MS: CI $[M+NH_4]^+$ Calculated for $C_{28}H_{48}NGe$: 472.2999; found: 472.3004.

Dibromobis(2-ethylhexyl) germane (2):

[110] In a 100 mL three neck round bottom flask, diphenyl-di-(2-ethylhexyl) germane (**1**) (3.38 g, 7.5 mmol) was dissolved in dry 1,2-dichlorethane (30 mL). Bromine (0.81 mL, 15.7 mmol) in 1,2-dichloroethane (15 mL) was added dropwise to the solution in the absence of light. The reaction mixture was heated at reflux for

[115] 5 h, cooled and the solvent was removed under reduced pressure.

The resulting oil was dried under high vacuum to afford **2** as a pale yellow oil (3.42 g, yield: 98%). ^{1}H NMR (CDCl$_3$, 400 MHz), δ (ppm): 1.83-1.80 (m, 6H), 1.43-1.26 (m, 16H), 0.93-0.88 (m, 12H). ^{13}C NMR (CDCl$_3$, 100 MHz), δ (ppm): 36.2, 34.8, 34.5, 28.5, 27.7, 22.9, 14.1, 10.5. EI: m/z = 458.

4,4'-Bis(2-ethyl-hexyl)-5,5'-dibromo-dithieno[3,2-*b*:2',3'-*d*]germole (4):

A solution of n-BuLi (2.8 mL of a 2.5 M solution in hexanes, 7.0 mmol) was added dropwise to a solution of 3,3'-dibromo-5,5'-bis(trimethylsilyl)-2,2'-bithiophene (1.51 g, 3.2 mmol) in THF (15 mL) at -78 °C. After stirring for 15 min at -78 °C, dibromo-di-(2-ethylhexyl) germane (**2**) (1.78 g, 3.9 mmol) was added in one portion. The cooling bath was removed and the reactant was allowed to warm to RT, followed by stirring for 0.5 h at RT. Water (50 mL) was added, and the mixture extracted (3 x 30 mL hexane). The combined organics were dried (MgSO$_4$), filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography (eluent: hexane) to afford a pale yellow oil.

To the resulting oil in THF (40 mL) was added NBS (1.20 g, 6.5 mmol) in one portion. The mixture was stirred for 2 h at RT in the absence of light. An aqueous solution of Na$_2$SO$_3$ (40 mL) was added to to quench this reaction. Then the mixture was extracted by hexane (3 x 30 mL). The combined organics were dried (MgSO$_4$), filtered and the solvent removed solvent under reduced pressure. The residue was purified by silica gel chromatography (eluent: hexane) to afford **4** as a pale yellow oil (1.32 g, yield: 66%). ^{1}H NMR (CDCl$_3$, 400MHz), δ (ppm): 6.97 (s, 2H), 1.47-1.41 (m, 2H), 1.23-1.08 (m, 20H), 0.90-0.77 (m, 12H). ^{13}C NMR (CDCl$_3$, 100MHz), δ (ppm): 146.2, 143.1, 132.3, 111.0, 36.9, 35.4, 28.9, 28.7, 23.0, 20.8, 14.1, 10.9. MS (EI)+ Calculated for C$_{24}$H$_{36}$Br$_2$GeS$_2$: 619.9837; found: 619.9826.

Poly[(4,4'-bis(2-ethylhexyl)dithieno[3,2-b:2',3'-d]germole)-2,6-diyl-alt-(2,1,3-benzothiadiazole)-4,7-diyl] (PGeBTBT):

In a 20 mL high pressure microwave reactor tube, equipped with a sealed septum was added compound **4** (328.4 mg, 0.53 mmol), 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester) (204.9 mg, 0.53 mmol), and Pd(PPh3)$_4$ (12.2 mg, 0.011 mmol). The tube was sealed and flushed with Ar, and then degassed toluene (8 mL), degassed aqueous 1M Na$_2$CO$_3$ (2 mL) and 2 drops of Aliquat 336 were added. The solution was thoroughly degassed under Argon, and then the Argon inlet was removed and the reaction heated 3 days at 120°C (oil bath temperature). After cooling to RT, the polymer was precipitated into methanol (100 mL), and filtered through a Soxhlet thimble. The polymer was extracted (Soxhlet) with methanol, acetone, hexane, chloroform and chlorobenzene. The chlorobenzene solution was concentrated and precipitated into methanol, and the precipitant was filtered and dried under vacuum to afford **PGeBTBT**, as a purple solid (228 mg, yield: 72%). ^{1}H NMR (1,1,2,2-tetrachloroethane-d$_4$, 130°C, 400MHz), δ (ppm): 8.26 (broad, 2H), 7.95 (broad, 2H), 1.71-1.38 (broad, 22H), 1.04-0.97 (broad, 12H). Anal. Calcd.: C, 60.51; H, 6.43; N, 4.70. Found: C, 60.21; H, 6.47; N, 4.71. GPC: M$_n$ =31,000 g/mol, M$_w$ =98,000 g/mol.

A second batch prepared under similar conditions using 217.8 mg

of **4** was isolated in 70% yield. GPC: M$_n$ =25,000 g/mol, M$_w$ =75,000 g/mol

Results and Discussion

Design and Synthesis

The first synthesis of dithienogermole was reported by Yabusaki and co-workers in 2010 by a palladium catalysed reaction between 3,3'-diiodo-2,2'-bithiophene and a dialkylgermane in low yield.[17] The resulting molecules demonstrated interesting solid state fluorescence properties. Our synthesis of dithienogermole, and its subsequent polymerisation to afford **PGeBTBT** is shown in Scheme 1. Here bulky 2-ethylhexyl side chains were employed as the bridging groups in order to enhance the polymer solubility. Dibromobis(2-ethylhexyl) germane (**2**) was synthesized by a two-step route following a procedure similar to that reported by Leclerc.[10] Thus commerically available diphenyl germanium dichloride was reacted with 2-2-ethylhexylmagnesium bromide to afford diphenylbis(2-ethylhexyl) germane (**1**) in 88% yield. Treatment with bromine in refluxing dichloroethane afforded dibromobis(2-ethylhexyl)germane (**2**) in a yield of 98%. The dithieno[3,2-*b*:2',3'-*d*]germole was prepared by dilithiation of the known **3**[2] at -78°C, followed by addition of the dibromogermane **2**. Purification of the resultant heterocycle was complicated by the tendency of the trimethylsilyl groups to protodesilylate, especially during flash chromatography. We therefore developed a protocol in which the crude heterocycle was rapidly filtered through silica, and the resultant mixture containing dithienogermole with 2, 1 or 0 trimethylsilyl groups was brominated directly with excess NBS. The final monomer **4** was thereby isolated in a yield of 66% from **3.**
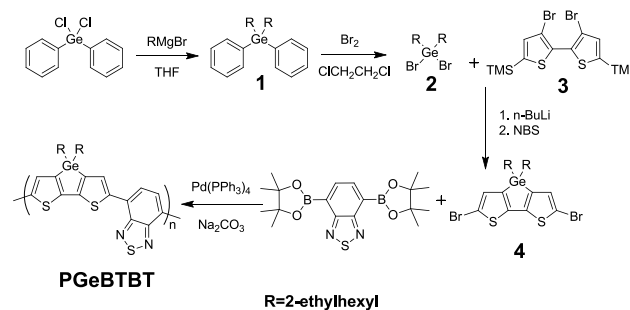
Scheme 1 Synthetic route to **PGeBTBT**

Suzuki polymerisation of **4** with 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester) was carried out in a biphasic system (toluene/aqueous Na$_2$CO$_3$) with Pd(PPh$_3$)$_4$ as the catalyst and aliquot 336 as the phase transfer catalyst. After precipitation and solvent extraction to remove lower weight oligomers and catalyst residues, **PGeBTBT** was obtained as a purple solid in typical yield of 70-75%. The good stability of the diethienogermole under the reaction conditions was confirmed by the respectable molecular weights produced. Two batches of polymer were synthesised under these conditions, showing good reproducability (Mn 31 KDa, PD 3.2 and Mn 25 KDa, PD 3). Here we note that determination of the molecular weight by gel permeation chromatography against polystyrene standards was complicated by the tendency for the polymer to aggregate in

solution, especially at room temperature and at typical GPC concentrations (ca. 0.2 mg/ml). We therefore heated dilute solutions to 80°C just before injection into the GPC. We also note that these molecular weights are significantly higher than those obtained by Ohshita et al by Stille polymerisation, in which they obtained Mn 8 KDa (PD 1.4).[15] By preparative GPC they were also able to separate a higher weight fraction of Mn 15 KDa (PD 1.7).

Optoelectronic Properties

The UV-vis absoption spectra of **PGeBTBT** in dilute dichlorobenzene (DCB), hot DCB and as a thin film are shown in Fig. 2. No differences were observed between the two molecular weight batches, indicating that the molecular weight of both batches was above the effective conjugation limit. In solution the polymer shows a broad absorption with a maxima at 756 nm and a distinct shoulder peak at shorter wavelenth (700 nm). Heating the solution did not significantly alter the absorption wavelengths, although the peak at 700 nm increased in intensity with respect to the peak at 756 nm, possibly indicating that the longer wavelength peak is related to aggregation effects in solution, similar to the silicon bridged analogues.[3, 14] Upon film formation there is a small red shift in the both the shoulder (714 nm) and absorption maxima (778 nm), which are suggestive of enhanced backbone planarisation and ordering compared to the solution state. Nevertheless it is apparent that the polymer exhibits appreciable aggregation in solution even upon heating, in agreement with our GPC results. Interestingly we find that the lower MW PGeBTBT reported by Ohshita exhibits significantly different optical properties, with a blue shift in solution absorbance to 651 nm in chloroform, whilst the thin film has a maxima at 687 nm with a shoulder at 740 nm.[15] This suggests that the lower MW polymer is not at the effective conjugation limit for these polymers, and also exhibits a reduced tendency to aggregate in solution.

The absoption onset in the solid state is 843 nm, corresponding to an optical band gap of 1.47 eV, which is similar to the silicon analogue.[2] The ionization potential of a thin film was measured by photo electron spectroscopy in air (PESA) to be 4.78 eV. PESA uses a low-power, tunable UV source to generate photoelectrons that ionize oxygen molecules that are in turn detected by an open counter.[18] It has previously been shown that ionization potentials determined by PESA are comparable with those obtained by other techniques.[19]
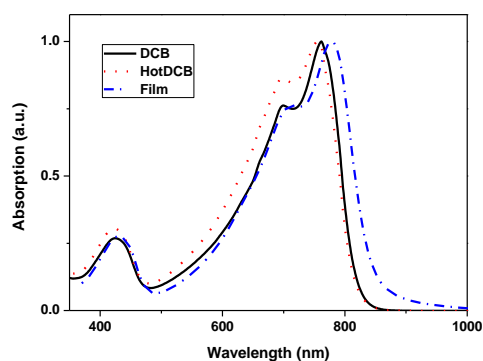
Fig. 2. UV-Vis spectra of **PGeBTBT** in dilute dichlorobenzene (black line), hot dichlorobenzene (red line) and in thin film (blue line).

Thin Film Morphology

The ordering of thin films of **PGeBTBT** was investigated by wide angle X-ray scattering (WAXS). The WAXS patterns of films prepared under different conditions are shown in Fig. 3. Films were prepared by drop casting hot chlorobenzene solutions onto substrates at either RT or 80°C, followed by annealing at 140°C. All four films showed a strong diffraction peak at 25.4 degree (2θ) corresponding to a *d*-spacing of 3.51 Å, which we attribute to the π-π stacking distance of **PGeBTBT** backbones. This is similar to that observed in the Si analogue,[3] but significantly smaller than the typical distances of 3.7-3.8 Å observed for thiophene polymers like P3HT.[20] The films also show a pronounced peak around 5° attributable to lamellar packing of the polymer backbones. Here subtle differences were observed according to the deposition conditions, with films drop cast onto hot substrates exhibiting a peak at 5.02° (17.6 Å), which did not change upon subsequent thermal annealing, whilst those films drop cast onto RT substrates exhibited a peak at 5.22° (16.93 Å), which changed to 5.12° (17.26 Å) upon annealing. The reduced lamellar distance may be indicative of more amorphous sidechains (less all trans gauche arrangements of the alkyl chains). Films drop cast onto hot substrates also exhibited narrower diffraction peaks, alluding to more pronounced long range order in the film. These results suggest the rapid cooling of the hot solutions (by drop casting onto RT substrates) results in rapid precipitation of the polymer and a more disordered film, whereas the hot substrate keeps the polymer in solution longer, enabling the growth of crystalline domains during solvent evaporation. It is also apparent that some thermal annealing of the less ordered films does not result in the same degree of order as that for solutions cast hot.
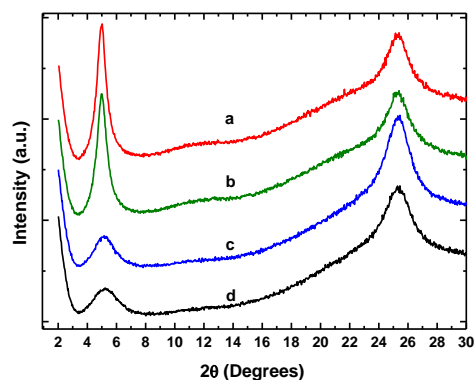
Fig. 3. X-ray diffraction pattern of **PGeBTBT-HW** films. Drop cast from hot chlorobenzene solution onto 80°C substrate with annealing at 140°C for 15 min (a) and without annealing (b); Drop cast from hot chlorobenzene solution to RT substrate with annealing at 140°C for 15 min (c) and without annealing (d).

Electrical Properties

The charge transport behaviour of **PGeBTBT** was investigated in both bottom contact, top gate (TG) and bottom gate (BG) transistor devices. Bottom gate devices used heavily doped Si[++]

substrates as the gate electrode and a 200 nm thermally oxidised SiO_2 layer as the gate dielectric. The SiO_2 layer was treated with octadecyltrichlorosilane (OTS) before use, and the Au source drain electrodes were treated with pentafluorobenzene thiol before use to afford a reliable work function. Devices were fabricated by spin coating hot 1,2-dichlorobenzene solutions followed by annealing of the devices at 140°C. The transfer and output characteristics of a typical BG device are shown in fig. 4. The polymer exhibited promising saturated and linear hole mobilities of 0.11 and 0.08 cm^2/Vs respectively, with low hysteresis between the forward and reverse sweeps. This is almost one order of magnitude higher than the Si containing analogue in the same device geometry.[5] In the saturated regime the drain current starts to increase again at positive gate voltages, possibly indicative of some electron transport occurring. Such ambipolar behaviour has been observed in the analogous carbon bridged polymer **PCPDTBT**, although the electron mobility, on the order of 10^{-5} cm^2/Vs, was two orders of magnitude lower than the hole mobility.[21] However attempts to measure electron transport characteristics at positive gates voltages indicated a large amount of trapping and injection issues, which may be due to the large workfunction mismatch between the SAM treated Au electrodes and the LUMO of the polymer, or by electron trapping at the SiO_2 interface due to free silanol surface groups as a result of incomplete OTS coverage.[221]
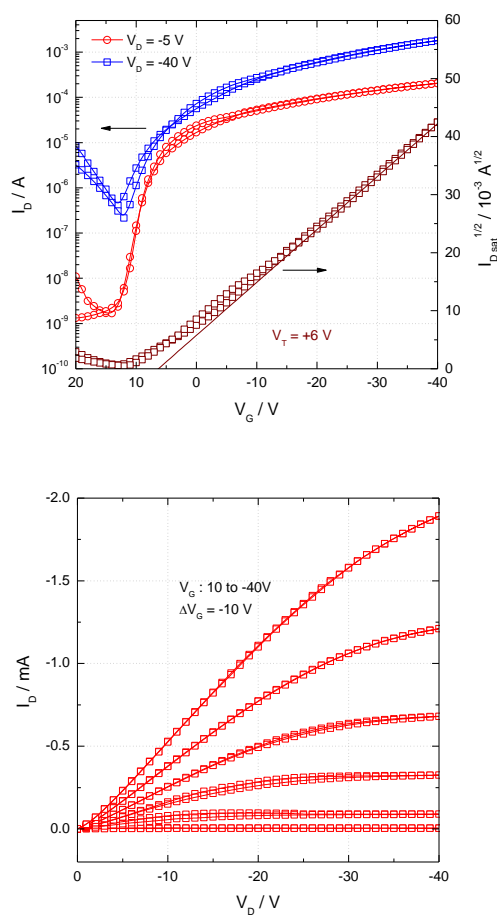

channel length = 10 μm and channel width = 10 mm at room temperature under N_2

Previously it has been demonstrated that top gate device transistor geometries using non-polar dielectrics that contain few hydrophilic trapping sites can result in improved electron transport.[22] Therefore top gate device were investigated using a fluorinated dielectric, Cytop, as the gate insulator (see SI). The average saturated and linear hole mobilities from four devices were 0.08 cm^2/Vs, with a standard deviation of 0.005 cm^2/Vs, demonstrating that the polymer was relatively insensitive to the device geometry used. However even in this geometry we were not able to observe clean electron transport, possibly due to a combination of injection issues and traps present in the semiconductor.

Photovoltaic Properties

The photovoltaic performance of **PGeBTBT** was investigated in devices using a standard configuration of ITO/PEDOT:PSS/polymer blend/Ca/Al, and measured under 100 mW cm^2 AM 1.5 illumination. The active layers were prepared by spin coating from hot chlorobenzene onto heated substrates. $PC_{70}BM$ was used as the acceptor because of the complementary absorption in the low wavelength region of the polymer spectrum.[23] Initial investigations were based upon spun cast blends of 1:1, 1:2, 1:3 and 1:4 polymer:fullerene in chlorobenzene at constant loadings. A heated (100°C) substrate was used for spin coating in order to prevent premature precipitation of the solution. Nevertheless the as-spun performance was rather low in all cases, with power conversion efficiencies (PCE) around 1-1.5%. Therefore all devices were annealed at 120°C for 10 minutes, which resulted in significant devices improvement. The J-V characteristics are shown in figure 5a, and show that the 1:1 blend exhibited the best performance, with average devices (average over 6 cells) exhibiting an open circuit voltage (V_{oc}) of 0.56 V, a short circuit current (J_{sc}) of 11. 6 mA/cm^2 and a fill factor of 0.43 leading to a PCE of 2.85%. Higher loadings of fullerene resulted in a systematic reduction of photocurrent, as the percentage of light absorbing polymer within the active layer was reduced.

Based upon these initial results, the performance of the 1:1 blend was further investigated as a function of solvent additives. Solvent additives have been shown to dramatically influence the phase segregation of the blend film. We investigated two common additives, 1,8-octanedithiol[24], and 1-chloronaphthalene[25], which have both been shown to enhance device performance. In our hands the addition of 3% chloronaphthalene gave the highest efficiency devices. Figure 5 shows the J – V curve of the best device with 1-chloronaphthalene under illumination of AM1.5 (100 mW/cm^2), both before and after annealing. As spun devices exhibited poor performance, with a PCE of less than 1%. However, after annealing at 140°C devices reached a PCE of 4.5%, with 18.6 mA/cm^2 of photocurrent density (J_{sc}), 0.57 V of V_{oc} and 0.43 of FF. Average performance, based upon 6 devices was V_{oc} 0.56 ± 0.003 (standard deviation) V, J_{sc} 18.4 ± 0.81 mA/cm^2, FF 0.42 ± 0.01 and PCE 4.32 ± 0.24.

Devices showed a broad spectral response covering 350-800

Fig. 4. Transfer (top) and output (bottom) characteristics of bottom-gate, bottom contact (BG, BC) organic field-effect transistor (OFET) with

nm, with external quantum efficiencies up to 65% (fig 5 inset). The EQE had a rather reactangular shape across this region, in common with the silicon based analogues.[2, 14] The promising performance is mainly a result of the remarkably high photocurrent, which is significantly higher than that observed in the analogous Si polymer[2] (12.7 mA/cm^2), although we note that the Si bridged co-polymer substitued with n-dodecyl sidechains also demonstrates high photocurrents (17.3 mA/cm^2).[14] The high photocurrent is consistent with the high charge carrier mobilities observed in field effect transistors. However the overall efficiency is currently limited by both a low FF and low V_{oc}.
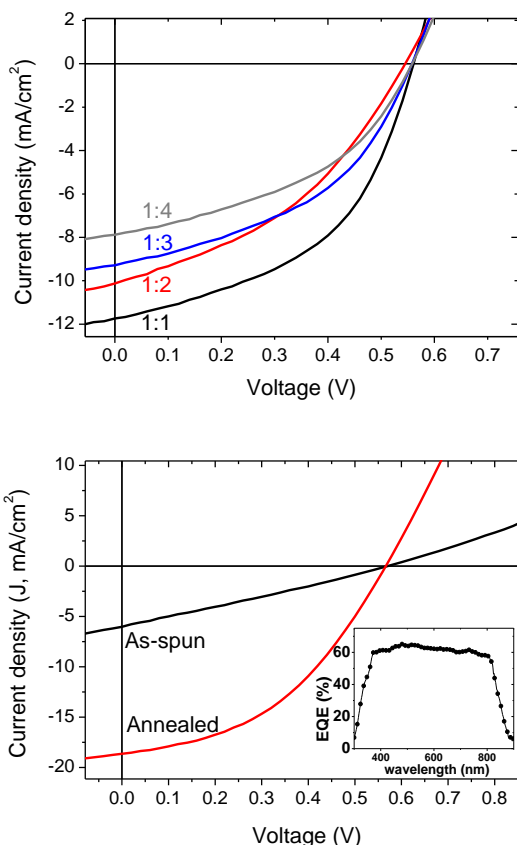

Fig. 3. (top) I-V curve of **PGeBTBT:**$PC_{70}BM$ at various blends ratios after annealing at 120°C (bottom) I-V curve of optimised device prepared from chlorobenzene containing chloronaphthalene (inset) EQE curve for this device.

The V_{oc} is lower than that observed for blends of $PC_{70}BM$ with the analogous silicon polymer, which varies between 0.68 V[2] to 0.58 V[4, 5], and is consistent with the relatively low ionisation potential measured by PESA. Reynolds and So have also reported that the dithienogermole-*co*-N-octylthienopyrrolodione polymer exhibits a lower V_{oc} than the analogous silicon bridged polymer by 0.05 V, and has a correspondingly smaller ionisation potential.[16] Our results corroborate those of Reynolds that dithienogermole containing polymers are slightly easier to oxidise than the analogous diethienosilole polymers.

The second factor limiting efficiency is low FF, which is generally indicative of a non-optimal blend morphology. This may be related to the high tendency of the polymer to aggregate in solution resulting in poor intermixing of the polymer and

fullerene phase.[26] Further investigations into the control of blend morphology via mixed solvent systems, and the influence of polymer molecular weight are in progress.

It is also instructive to compare our OPV results with those of Ohshita and co-workers who fabricated photovoltaic cells with lower weight (Mn 15 KDa) PGeBTBT:$PC_{70}BM$ in a 1:3.6 ratio, in a similar device structure except LiF/Al was used as the cathode. Devices exhibited a PCE of 1.2%, with a V_{oc} of 0.61 V, J_{sc} of 4.68 mA/cm^2 and FF of 0.43. The slightly higher V_{oc} reported may be related to the lower molecular weight polymer used, since the UV spectra demonstrate the effective conjugation was less than in the high MW polymer reported here. The use of a LiF/Al cathode in these devices instead of the Ca/Al used in our devices has also been shown to increase V_{oc}.[27] The low photocurrents compared to our devices may be explained by the blue shift in absorption for the lower MW polymer, in combination with the increased fullerene loading. Therefore it appears that the molecular weight of the **PGeBTBT** donor polymer has a significant impact on device performance.

Conclusions

We have reported the synthesis of dithienogermole monomers and have demonstrated, unlike the analogous dithienosiloles, they are sufficiently stable in the presence of aqueous base to participate in a Suzuki polymerisation to afford high molecular weight polymers. This is significant because purification of the corresponding stannyl monomers required for the preparation of high molecular polymers by Stille polymerisation is problematic due to the ready decomposition of the monomer. The resulting polymers form semicrystalline thin films which display high charge carrier mobilities in field effect devices. These high mobilities are reflected in photovoltaic blend devices exhibiting very high photocurrents and overall power conversion efficiencies of 4.5%. Efforts are ongoing to further improve the efficiency of photovoltaic devices by optimisation of the molecular weight and film formation conditions.

Notes and references

^{a} *Dept. Chemistry and Centre for Plastic Electronics, Imperial College London, London SW7 2AZ, U.K.*
E-mail: m.heeney@imperial.ac.uk; ji-seon.kim@imperial.ac.uk
^{b} *Dept. Physics & Centre for Plastic Electronics, Imperial College..*
^{c} *Dept. Materials & Centre for Plastic Electronics, Imperial College..*
^{d} *CSIRO, Molecular and Health Technologies, VIC 3169, Australia*
† Electronic Supplementary Information (ESI) available: [top gate transistor transfer and output plots; GPC traces]. See DOI: 10.1039/b000000x/

1.   J. Ohshita, *Macromol. Chem. Phys.*, 2009, **210**, 1360.

2.   J. H. Hou, H. Y. Chen, S. Q. Zhang, G. Li and Y. Yang, *J. Am. Chem. Soc.*, 2008, **130**, 16144.

3.   H. Y. Chen, J. H. Hou, A. E. Hayden, H. Yang, K. N. Houk and Y. Yang, *Adv. Mater.*, 2010, **22**, 371.

4.   M. Morana, H. Azimi, G. Dennler, H.-J. Egelhaaf, M. Scharber, K. Forberich, J. Hauch, R. Gaudiana, D. Waller, Z. Zhu, K. Hingerl, B. S. S. van, J. Loos and C. J. Brabec, *Adv.*

Funct. Mater., 2010, **20**, 1180.

5. M. C. Scharber, M. Koppe, J. Gao, F. Cordella, M. A. Loi, P. Denk, M. Morana, H. J. Egelhaaf, K. Forberich, G. Dennler, R. Gaudiana, D. Waller, Z. G. Zhu, X. B. Shi and C. J. Brabec, *Adv. Mater.*, 2010, **22**, 367.

6. E. G. Wang, L. Wang, L. F. Lan, C. Luo, W. L. Zhuang, J. B. Peng and Y. Cao, *Appl. Phys. Lett.*, 2008, **92**, 033307.

7. T.-Y. Chu, J. Lu, S. Beaupré, Y. Zhang, J.-R. m. Pouliot, S. Wakim, J. Zhou, M. Leclerc, Z. Li, J. Ding and Y. Tao, *J. Am. Chem. Soc.*, 2011, **133**, 4250; Y. R. Hong, H. K. Wong, L. C. H. Moh, H. S. Tan and Z. K. Chen, *Chem. Commun.*, 2011, **47**, 4920; M. J. Zhang, H. J. Fan, X. Cuo, Y. J. He, Z. G. Zhang, J. Min, J. Zhang, G. J. Zhao, X. W. Zhan and Y. F. Li, *Macromolecules*, 2010, **43**, 5706; J. F. Ding, N. H. Song and Z. Li, *Chem. Commun.*, 2010, **46**, 8668; J. Ohshita, K. Kimura, K. H. Lee, A. Kunai, Y. W. Kwak, E. C. Son and Y. Kunug, *J. Polym. Sci. Pol. Chem.*, 2007, **45**, 4588.

8. R. S. Ashraf, Z. Y. Chen, D. S. Leem, H. Bronstein, W. M. Zhang, B. Schroeder, Y. Geerts, J. Smith, S. Watkins, T. D. Anthopoulos, H. Sirringhaus, J. C. de Mello, M. Heeney and I. McCulloch, *Chem. Mat.*, 2011, **23**, 768; J. Y. Wang, S. K. Hau, H. L. Yip, J. A. Davies, K. S. Chen, Y. Zhang, Y. Sun and A. K. Y. Jen, *Chem. Mat.*, 2011, **23**, 765.

9. G. Lu, H. Usta, C. Risko, L. Wang, A. Facchetti, M. A. Ratner and T. J. Marks, *J. Am. Chem. Soc.*, 2008, **130**, 7670; H. Usta, G. Lu, A. Facchetti and T. J. Marks, *J. Am. Chem. Soc.*, 2006, **128**, 9034.

10. N. Allard, R. B. Aich, D. Gendron, P. L. T. Boudreault, C. Tessier, S. Alem, S. C. Tse, Y. Tao and M. Leclerc, *Macromolecules*, 2010, **43**, 2328.

11. A. Karnezis, R. A. J. O'Hair and J. M. White, *Organometallics*, 2009, **28**, 6480; S. Yamaguchi, Y. Itami and K. Tamao, *Organometallics*, 1998, **17**, 4910.

12. A. C. Spivey, C. J. G. Gripton and J. P. Hannah, *Curr. Org. Synth.*, 2004, **1**, 211.

13. A. C. Spivey, D. J. Turner, M. L. Turner and S. Yeates, *Synlett*, 2004, 111; A. C. Spivey, C. C. Tseng, J. P. Hannah, C. J. G. Gripton, P. de Fraine, N. J. Parr and J. J. Scicinski, *Chem. Commun.*, 2007, 2926.

14. R. C. Coffin, J. Peet, J. Rogers and G. C. Bazan, *Nat. Chem.*, 2009, **1**, 657.

15. J. Ohshita, Y. M. Hwang, T. Mizumo, H. Yoshida, Y. Ooyama, Y. Harima and Y. Kunugi, *Organometallics*, 2011, **30**, 3233.

16. C. M. Amb, S. Chen, K. R. Graham, J. Subbiah, C. E. Small, F. So and J. R. Reynolds, *J. Am. Chem. Soc.*, 2011, **133**, 10062.

17. Y. Yabusaki, N. Ohshima, H. Kondo, T. Kusamoto, Y. Yamanio and H. Nishihara, *Chem. Eur. J.*, 2010, **16**, 5581.

18. H. Kirihata and M. Uda, *Rev. Sci. Instr.*, 1980, **52**, 68.

19. R. J. Davis, M. T. Lloyd, S. R. Ferreira, M. J. Bruzek, S. E. Watkins, M. Fahlman, J. E. Anthony and J. W. P. Hsu, *J. Mater. Chem*, 2011, **21**, 1721.

20. A. Salleo, R. J. Kline, D. M. DeLongchamp and M. L. Chanbinyc, *Adv. Mater.*, 2010, **22**, 3812.

21. M. Morana, M. Wegscheider, A. Bonanni, N. Kopidakis, S. Shaheen, M. Scharber, Z. Zhu, D. Waller, R. Gaudiana and C. Brabec, *Adv. Funct. Mater.*, 2008, **18**, 1757.

22. L.-L. Chua, J. Zaumseil, J. F. Chang, E. C.-W. Ou, P. K.-H. Ho, H. Sirringhaus and R. H. Friend, *Nature*, 2005, **434**, 194.

23. M. M. Wienk, J. M. Kroon, W. J. H. Verhees, J. Knol, J. C. Hummelen, P. A. van Hal and R. A. J. Janssen, *Angew. Chem. Int. Ed.*, 2003, **42**, 3371.

24. J. K. Lee, W. L. Ma, C. J. Brabec, J. Yuen, J. S. Moon, J. Y. Kim, K. Lee, G. C. Bazan and A. J. Heeger, *J. Am. Chem. Soc.*, 2008, **130**, 3619.

25. F.-C. Chen, H.-C. Tseng and C.-J. Ko, *Appl. Phys. Lett.*, 2008, **92**, 103316.

26. C. J. Brabec, M. Heeney, I. McCulloch and J. Nelson, *Chem. Soc. Rev.*, 2011, **40**, 1185.

27. C. J. Brabec, S. E. Shaheen, C. Winder, N. S. Sariciftci and P. Denk, *Appl. Phys. Lett.*, 2002, **80**, 1288.