ChemComm

COMMUNICATION

Germaindacenodithiophene based low band gap polymers for organic solar cells†

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We report the first synthesis of a fused germaindacenodithiophene monomer and its polymerisation with 2,1,3-benzothiadiazole by Suzuki polycondensation. The resulting polymer, PGeTPTBT, is semicrystalline, despite the presence of four bulky 2-ethylhexyl groups. Blends with $P_{70}CBM$ afford solar cells with efficiencies of 5.02%.
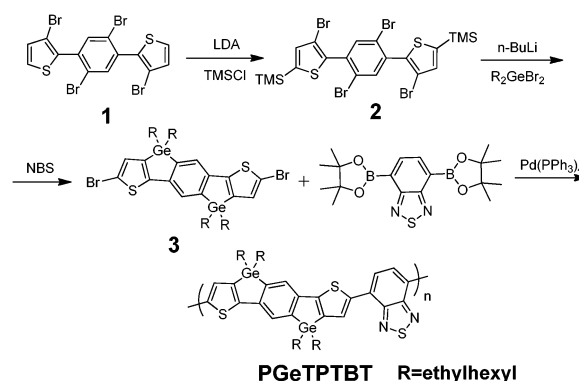
There has been tremendous progress in recent years in the development of low band gap conjugated polymers for use in photovoltaic devices or field effect transistors.[1] One promising class of polymer is the so-called ladder type, in which linked aromatic units such as thiophene or benzene are forced to be co-planar by the use of bridging heteroatoms. In addition to serving as a point of attachment for solubilising side chains, the bridging atom also plays an important role in modifying the electronic properties of the system. Systems containing bridging atoms from group 14 (C, Si and to a lesser extent Ge) have been the subject of much interest, partly due to the fact that two solubilising side chains can be attached to the bridge, facilitating solubility and self-assembly.[2–6] Moreover it has been demonstrated that the electronic properties of the polymer backbone itself can be modified by changing the bridging heteroatom. Thus changing C to Si can result in stabilisation of the LUMO by interaction of the low lying σ^* orbital of the silicon atoms with the π^* orbital of the conjugated system.[7]

The choice of bridging heteroatom has also been shown to have a significant effect on the crystallinity of the polymer. For example in comparing the benzothiadiazole co-polymers of a 2,2′-bithiophene bridged with either C, Si or Ge containing two branched ethylhexyl groups, it was found that the C bridged co-polymer was amorphous whereas the Si[8,9] and Ge[5,10] bridged co-polymers were semicrystalline. The crystalline polymers demonstrated higher charge carrier mobilities ideal for a number

of applications including bulk heterojunction solar cells. The improved crystallinity has been rationalised on the basis of the longer C–Si bond length compared to the C–C bond, which changes the geometry of the fused ring allowing stronger π–π interactions to occur.[8]

As part of our investigations into ladder type polymers we have recently shown that alternating copolymers of indaceno-dithiophene (**IDT**)[11] and silaindacenodithiophene (**SiIDT**)[3] with benzothiadiazole exhibit promising photovoltaic and FET properties. In an effort to enhance polymer crystallinity and performance further, we were interested to investigate the affects of introducing bridging Ge atoms into the system. Here we report the synthesis of a novel germaindacenodithiophene monomer and its co-polymerisation with an electron accepting 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester) by Suzuki polycondensation reaction. We show the resulting polymer **PGeTPTBT** is semicrystalline and demonstrates promising solar cell device performance.

The synthesis of **PGeTPTBT** is shown in Scheme 1. Here bulky 2-ethylhexyl side chains were employed as the bridging groups in order to enhance the polymer solubility and processability. The synthesis of the key intermediate **2** has been reported by Jen et al.[6] Here we adopted another route for the synthesis of **2** via the lithiation of **1**[3] with lithium diisopropylamide (LDA) and subsequent quenching with chlorotrimethylsilane (TMSCl) to afford **2** in a yield of 85%. The bridged monomer **3** was prepared by the lithiation of **2** with four equivalents of n-BuLi

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Scheme 1 Synthetic route to **PGeTPTBT**.

at −78 °C, followed by addition of the dibromo-di-(2-ethylhexyl) germane. Purification of the resultant compound was complicated by the tendency of the trimethylsilyl groups to protodesilylate, especially during flash chromatography. Therefore the crude product was rapidly filtered through silica, and the resultant mixture containing germaindacenodithiophene with 2, 1 or 0 trimethylsilyl groups was brominated directly with NBS to afford **3** in a yield of 33%.

In our investigations of silaindacenodithiophene we found that the monomer was unstable under the basic conditions required for Suzuki cross-coupling, which necessitated the use of Stille polymerisation with stannylated silaindacenodithiophene. Unfortunately the tin monomer was difficult to purify due to its tendency to readily protodestannylate, especially during chromatography. Thus only moderate molecular weights could be obtained for the polymer. Encouraged by our recent finding that dithienogermoles were stable to the basic conditions of Suzuki coupling,[5] we found that **3** could be readily polymerised under Suzuki conditions. We attribute the higher stability in base to the reduced polarisation of the C–Ge bond over the C–Si bond. Polymerisation with 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester) was carried out in a biphasic system (toluene/aqueous Na_2CO_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, **PGeTPTBT** was obtained as a purple solid in a typical yield of 82%. As a result of the four branched alkyl chains, the polymer exhibited good solubility in common organic solvents such as chloroform, THF and chlorobenzene. The number average molecular weight (Mn) of **PGeTPTBT** by GPC in hot chlorobenzene (80 °C) was found to be 32 KDa with a PDI of 2.3.

The UV-vis absorption spectra of **PGeTPTBT** in dilute chlorobenzene (CB) and as a thin film are shown in Fig. 1. In solution the polymer exhibits an absorption maximum at 630 nm, whereas in the solid the polymer shows a main absorption peak at 644 nm with a shoulder at 596 nm. The 14 nm red-shift of the main absorption peak and the broadening of the absorption from solution to solid state indicate some aggregation in the solid state. This is in contrast to the C-bridged polymer (**IDTBT**) with identical branched side chains, in which the solution and thin film spectra are very similar with a maximum at 660 nm,[11] suggesting that the introduction of Ge results in an increase in solid state aggregation. The absorption onset in solid state is 712 nm, corresponding to an 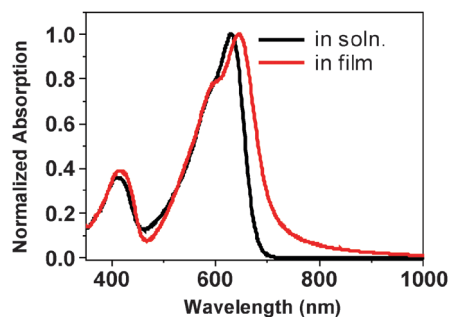optical band gap of 1.74 eV, which is slightly wider than **IDTBT** (1.7 eV), but narrower than the Si bridged polymer **SiIDTBT** (1.8 eV) with n-octyl sidechains.

The ordering of spin cast thin films of **PGeTPTBT** was investigated by grazing incidence wide angle X-ray scattering (GIWAXS). The 2D WAXS patterns of **PGeTPTBT** films both before and after annealing at 140 °C, are shown in Fig. 2, with the 1D out-of-plane and in-plane profiles shown in Fig. S2.† In contrast to the carbon analogue IDT-BT which lacks any obvious crystallinity,[11] the results clearly indicate that the Ge polymer forms semi-crystalline thin films, despite the inclusion of the four bulky ethylhexyl groups. Two orders of (h00) scatterings are apparent in the out-of-plane direction, indicating the formation of lamellar like sheets of polymer with a d-spacing of 14.5 Å before annealing, and 14.0 Å after annealing. The arcing apparent in the 2D profiles implies that the lamellar sheets are not well aligned with respect to the substrate, but have a relatively broad distribution of orientations. The π–π stacking distance, as measured by the in-plane profile is 3.93 Å. Annealing resulted in a modest improvement of film crystallinity of about 30%. More quantitative information about changes in crystallinity and orientation were obtained from pole figures, focussing on the distribution of the (100) peak as a function of ω, the angle between crystallite and the substrate normal (Fig. S3).[12] We find that increase in crystallinity is mainly driven by an increase in the crystallinity of the misorientated domains (those not aligned normal to the substrate), whereas the crystallinity of the aligned domains is relatively unchanged.

In order to investigate the influence of the germanium bridge on charge carrier mobility, field effect transistors were fabricated in the top gate, bottom contact configuration using Cytop as the gate dielectric (Fig. S1). The polymer exhibited as-cast saturated and linear mobilities of 0.013 and 0.005 cm^2/Vs. Annealing the film did not result in any significant device improvement, in agreement with the XRD results which suggest little change in the crystallinity of the polymers in
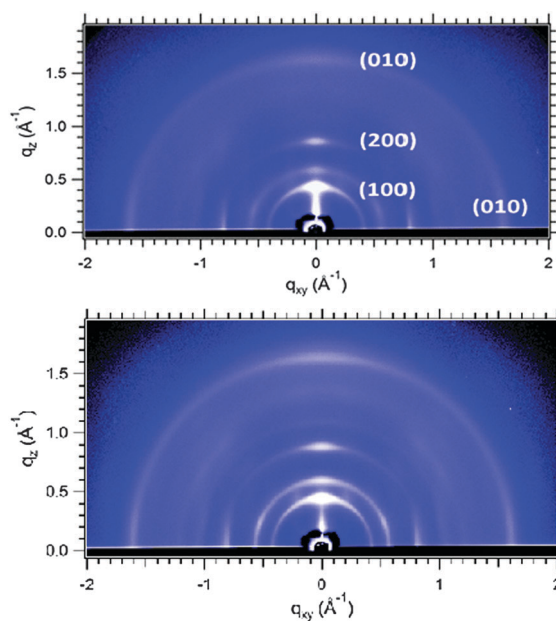

Fig. 1 UV-Vis spectra of **PGeTPTBT** in dilute chlorobenzene (black line) and in thin film (red line).

Fig. 2 GIXD detector images of (top) as-cast thin film of **PGeTPTBT** and (bottom) after annealing at 140 °C.
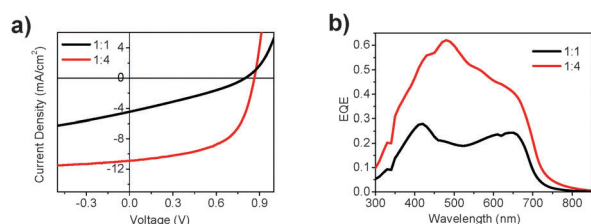
Fig. 3 (a) *J-V* curves and (b) EQE curves of polymer solar cell based on different blend ratio of **PGeTPTBT** : PC$_{71}$BM.

the transport direction. These values are slightly higher than those measured for the **SiIDTBT** bridged polymer containing n-octyl sidechains in the same device configuration. However they are significantly lower than analogous **IDT-BT** polymer, despite the lack of any obvious crystallinity in **IDT-BT**. This surprising result may indicate that transport in **PGeTPTBT** is limited by grain boundaries and misaligned domains, and that optimisation of the coating and annealing conditions may result in further performance enhancements.

The photovoltaic properties were investigated in solar cells with a device structure of ITO/PEDOT:PSS/**PGeTPTBT**:PC$_{71}$BM/ Ca/Al. The active layers were spin-coated from dichlorobenzene (DCB) with different blend ratios of **PGeTPTBT**:PC$_{71}$BM from 1 : 1 to 1 : 4 (w/w). In common with other ladder type donor polymers, we found the optimal polymer:fullerene ratio was around 1 : 4, with significant differences in the device performance of the 1 : 1 blend and the 1 : 4 blend. The *I–V* curve of typical devices under illumination of AM1.5 are shown in Fig. 3, with 1 : 1 devices having a PCE of 1.1% with 4.5 mA cm^{-2} of photocurrent density (J$_{sc}$), 0.80 V of V$_{oc}$ and 0.3 of FF, whereas the 1 : 4 devices reached a PCE of 5.02%, with 10.1 mA cm^{-2} of photocurrent density (J$_{sc}$), 0.86 V of V$_{oc}$ and 0.58 of FF. The promising performance is mainly a factor of the high voltage, which is significantly higher than that observed in **IDTBT** blends (0.79 V), but slightly lower than that of **SiIDTBT** (0.88 eV).

Fig. 3b shows the external quantum efficiency (EQE) spectra of the best devices of each blend ratio as a function of wavelength. These devices exhibited broad EQE responses extending from 300 to 750 nm, which maps well with the polymer absorption, and had a maximum intensity ranging between 400 and 500 nm. We attribute their higher EQE responses in the visible region to the corresponding higher absorbance of the blend, resulting from both the intrinsic absorption of the polymer and the presence of a high content of PC$_{71}$BM, which also absorbs significantly at 400–500 nm.

In conclusion we have prepared the first example of a germaindacenodithiophene monomer and report its polymerisation with benzothiadiazole to afford a low band gap polymer. Unlike the analogous silaindacenodithiophene the germanium bridged monomer is stable under basic conditions facilitating polymerisation by Suzuki polycondensation. The resulting polymer forms semicrystalline thin films, despite the presence of four bulky ethylhexyl groups and is found to exhibit initial power conversion efficiencies of 5.02% in bulk heterojunction solar cells without thermal annealing. We are currently investigating the use of additives and co-solvents in an effort to further increase device efficiency.

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