Germaindacenodithiophene based low band gap polymer for Organic Solar Cells

Zhuping Fei[‡a], Raja Shahid Ashraf[‡a], Zhengang Huang[a], Jeremy Smith[b], R. Joseph Kline[c], Pasquale D'Angelo[b], Thomas D. Anthopoulos[b], James R. Durrant[a], Iain McCulloch[a], Martin Heeney*[a]

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General Procedures

Reagents and chemicals were purchased from Aldrich and Acros unless otherwise noted. 2,2'-(2,5-dibromo-1,4-phenylene)bis(3-bromothiophene) (**1**)[1] and dibromo-di-(2-ethylhexyl) germane[2] were synthesized by the reported method. Commercial 2,1,3-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.

All reactions were carried out under Ar using solvents and reagents as commercially supplied, unless otherwise stated. ^{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 TMS as an internal reference and are given in ppm.[3] 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 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 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. Compounds were named according to the ACD/IUPAC name generated using the ACD/I-Lab service via the Chemical Database Service at Daresbury.[5]

X-Ray diffraction measurements

Grazing-incidence wide angle X-ray scattering (GIWAXS) was done at beam line 11-3 at Stanford Synchrotron Radiation Laboratory. The beam energy was 12.715 keV and the incidence angle was 0.12°. Samples were measured in a helium environment to minimize air scattering and beam damage. Data was collected with a MAR2300 image plate. The detector image was calibrated using a LaB_6 crystal standard. Full pole figures were made by combining GIWAXS measurement with a local specular measurement following the procedure of Baker et al.[4] The diffraction measurements identified significantly more scattering peaks than observed for P3HT or pBTTT as shown in table S1. The peaks do not fit simple models of unit cells. This could be due to either a complex triclinic cell or the coexistence of multiple crystal structures or orientations. The complete indexing is beyond the scope of this manuscript.

OFET (organic field effect transistors) devices fabrication:

Top-gate, bottom-contact devices were fabricated on glass with Au-PFBT electrodes, CYTOP dielectric (900 nm) and Al gate. The channel width and length of the transistors are 1 mm and 50 µm, respectively. Films were formed from hot solutions (5 mg/ml in o-DCB) by spin coating at 2000 rpm for 30 sec. Films were then annealed at 140 °C for 15 min. V_G varied from 10 to -60 V in 1 V steps and V_D set at -5 (linear) and -60 V (saturation).

OPV fabrication and characterization:

ITO-coated glass substrates were cleaned with acetone and isopropyl alcohol, followed by drying and oxygen plasma treatment. A 30 nm layer of PEDOT:PSS (Al4083) was spin-coated onto the plasma-treated ITO substrate and annealed at 150 oC for 30 min. An 80-100 nm active layer consisting of blends (1:1 and 1:4) of PGeTPTBT (12 mg mL-1) and [70]PCBM, Solenne) dissolved in o-dichlorobenzene (ODCB) was spin-coated on the PEDOT:PSS layer and then Ca (30 nm)/Al (100 nm) cathode was finally deposited by thermal evaporation under high vacuum (10-6 mbar) through a shadow mask. The pixel size, defined by the spatial overlap of the ITO anode and Ca/Al cathode, was 0.045 cm^2. The device characteristics were obtained using a xenon lamp at AM1.5 solar illumination (Oriel Instruments).

Synthesis:

Preparation of [(2,5-dibromo-1,4-phenylene)bis(4-bromothiene-5,2-diyl)]bis(trimethylsilane) ***2****:*

In a dry three neck 100 mL round bottom flask, 2,2'-(2,5-dibromo-1,4-phenylene)bis(3-bromothiophene, **1)** (3.0 g, 5.4 mmol) was dissolved in dry THF (120 mL) and cooled to -78 °C. Lithium diisopropylamide (LDA) (7.2 mL of a 1.8 M solution in THF/heptanes/ethylbenzene, 13.0 mmol) was added dropwise. After stirring for 1 h at -78 °C, chlorotrimethylsilane (1.7 mL, 13.4 mmol) was added. The reaction mixture was allowed to warm to RT and stirred for 0.5 h at RT, and then purified by chromatography (SiO_2, eluent: THF). The solvent was removed under reduced pressure, and then the crude product was recrystallization from ethyl acetate to afford **2** as a white crystal. (3.3 g, yield: 85%). ^1H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.69 (s, 2H), 7.16 (s, 2H), 0.36 (s, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm): 142.4, 139.9, 136.5, 136.3, 136.2, 123.0, 112.6, 0.31. MS (EI): m/z = 702.

*Preparation of 5,5,10,10-tetrakis(2-ethylhexyl)-5,10-dihydrothieno[3'',2'':4',5']germolo[2',3': 5,6][1]benzogermolo[2,3-b]thiophene (****3****):*

A solution of n-BuLi (2.9 mL of a 2.5 M solution in hexanes, 7.3 mmol) was added dropwise to a solution of **2** (1.05 g, 1.45 mmol) in THF (40 mL) at -78°C, and the reactant was stirred for 1 h at that temperature. Then the cooling bath was removed and the reactant was stirred at RT for another 1 h. After cooling to -78 °C, dibromo-di-(2-ethylhexyl) germane (2.0 g, 4.4 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 (0.52 g, 2.9 mmol) in one portion. The mixture was stirred for 1 h at RT in the absence of light. An aqueous solution of Na_2SO_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 under reduced pressure. The residue was purified by silica gel chromatography (eluent: hexane) to afford **3** as a pale yellow oil (0.48 g, yield: 33%). ^1H NMR ($CDCl_3$, 400MHz), δ (ppm): 7.47 (s, 2H), 7.04 (s, 2H), 1.50-1.44 (m, 4H), 1.27-1.15 (m, 40H), 0.83-0.76 (m, 24H). ^{13}C NMR ($CDCl_3$, 100MHz), δ (ppm): 154.0, 142.0, 140.8, 132.7, 125.6, 111.6, 36.9, 35.5, 35.5, 28.8, 20.8, 14.1, 10.9, 10.8. MS (EI): m/z = 994.

Synthesis of ***PGeTPTBT****:*

In a 20 mL high pressure microwave reactor tube, equipped with a sealed septum was added compound **3** (260.0 mg, 0.26 mmol), 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester) (101.5 mg, 0.26 mmol), and $Pd(PPh3)_4$ (6.0 mg, 0.005 mmol). The tube was sealed and flushed with Ar, and then degassed toluene (3.5 mL), degassed aqueous 1M Na_2CO_3 (0.7 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 and, chloroform. The chloroform solution was concentrated and precipitated into methanol, and the precipitant was filtered and dried under vacuum to get **PGeTPTBT**, as a brown solid (182 mg, yield: 82%). ^{1}H NMR ($CDCl_3$, 400MHz), δ (ppm): 8.26 (broad, 2H), 7.94 (broad, 2H), 7.79 (broad, 2H), 1.63-1.61 (broad, 4H), 1.47-1.25 (broad, 40H), 0.88-0.80 (broad, 24H). Anal. Calcd.: $(C_{52}H_{74}Ge_2N_2S_3)n$: C, 64.48; H, 7.70; N, 2.89. Found: C, 64.47; H, 7.83; N, 2.99. GPC: M_n =32,000 g/mol, M_w = 75,000 g/mol.

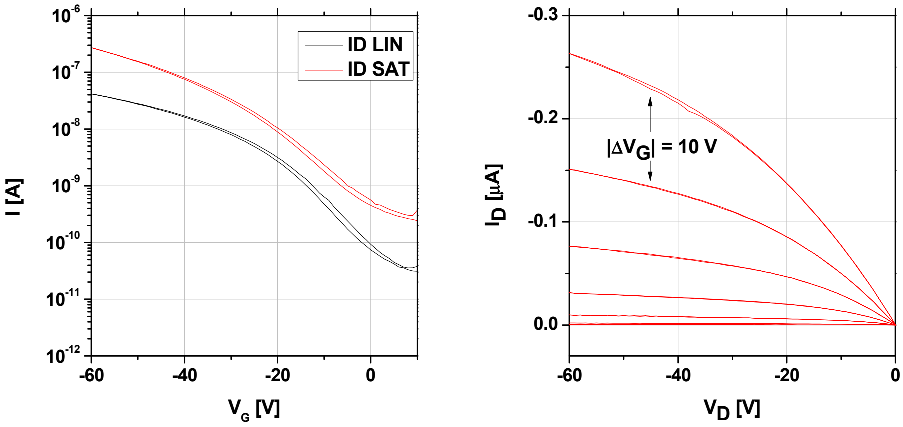

Fig. S1. Transfer (left) and output (right) characteristics of top-gate, bottom contact organic field-effect transistor (OFET) with channel length = 50 µm and channel width = 1mm at room temperature under N_2.

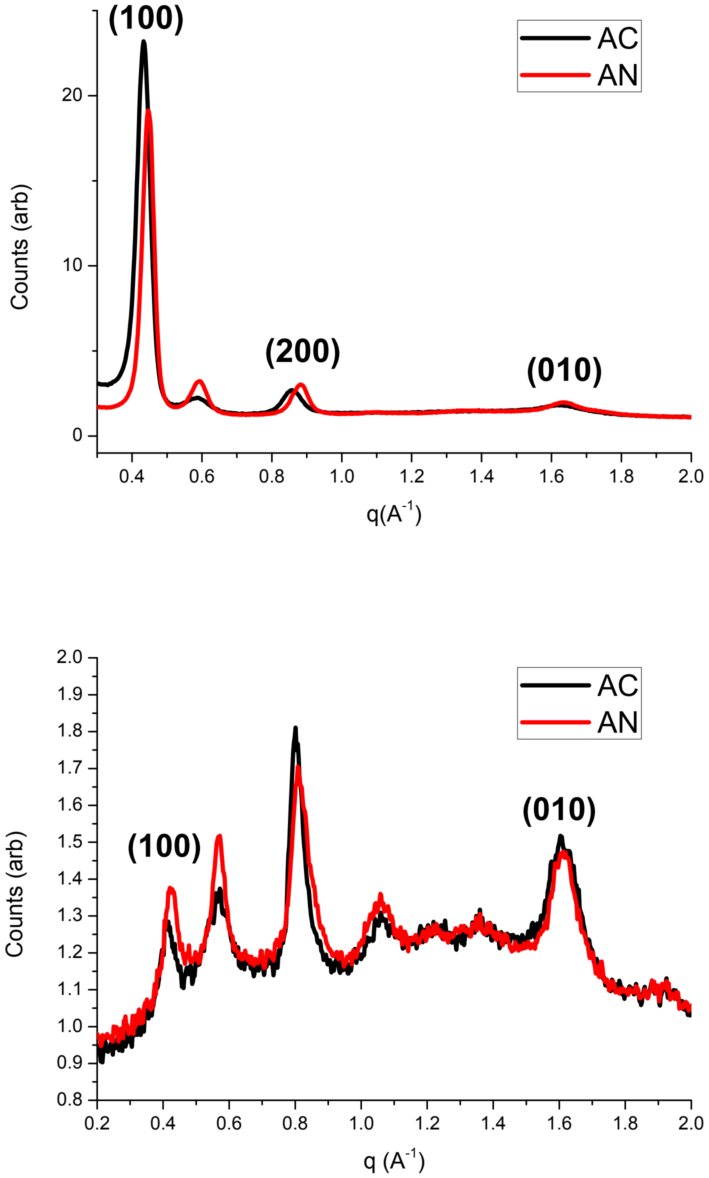

Fig S2. Out-of-plane (a) and in-plane (b) diffraction of as-case (AC) and annealed (AN) thin films of PGeTPTBT

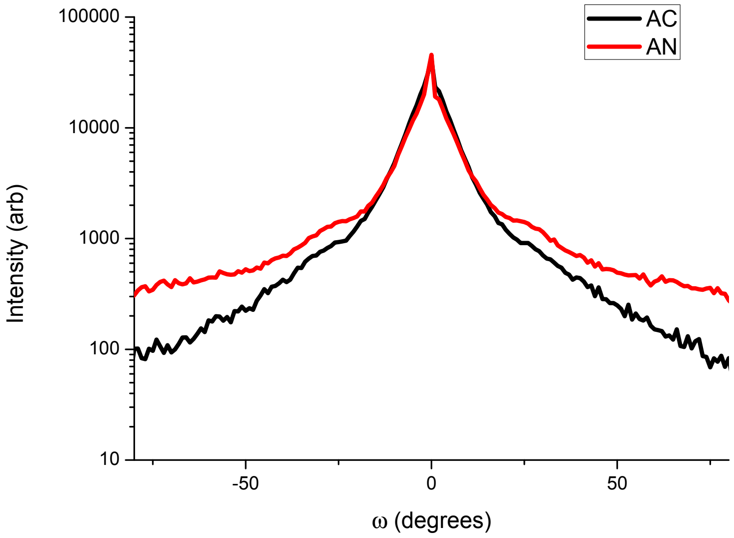

Fig S3. Radial pole figure for the (100) diffraction for as-cast (AC) and annealed (AN) films of pGeTPTBT

	Out of plane			**In plane**	
peak	**q (Å^{-1})**	**d (Å)**	**peak**	**q (Å^{-1})**	**d (Å)**
1	0.448	14.02497	1	0.421	14.92443
2	0.591	10.63145	2	0.572	10.98459
3	0.882	7.123793	3	0.808	7.776219
4	1.09	5.76439	4	1.06	5.927533
5	1.34	4.688944	5	1.22	5.150152
6	1.64	3.831211	6	1.36	4.619989
			7	1.61	3.9026
			8	1.92	3.272492
			9	2.2	2.855993

Table S1. GIXD peaks and corresponding *d*-spacings for the annealed film

References for SI

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3. Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

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5. D. A. Fletcher, R. F. McMeeking and D. J. Parkin, *J. Chem. Inf. Comput. Sci.,* 1996, ***36***, 746-749.