

Supporting Information

for

Incorporation of Benzocborane into Conjugated Polymer Systems; Synthesis, Characterisation and OFET Device Performance

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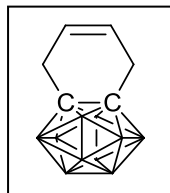
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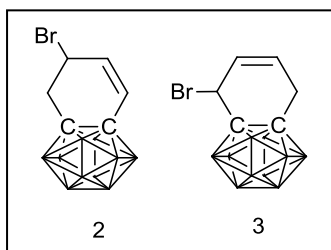
1. Experimental procedures

1.1 1,4-dihydrobenzocarborane (1)



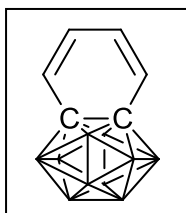
Following the synthesis described by Matteson et al.,¹ to a solution of freshly sublimed ortho-carborane (9.99 g, 70 mmol) in anhydrous diethyl ether (300 mL) was added n-BuLi (62.5 mL, 2.5 M in hexanes, 156 mmol), dropwise. The resulting solution was stirred at room temperature for 2 hours before heating to reflux. To this was added cis-1,4-dichloro-2-butene (7.35 mL, 70 mmol) over the course of 1 hour. Reflux was maintained for a further 16 hours. After cooling to room temperature, the reaction was quenched by the addition of methanol (100 mL), washed with water, brine and dried over magnesium sulphate. Purification by column chromatography (eluent: hexane) afforded **1** (10.9 g, 56 mmol, 79%) as colourless crystals. ¹H {¹¹B} NMR (400 MHz, CDCl₃): δ 5.66 (t, 2H), 3.00 (d, 4H), 2.40-1.79 (m, 10H); ¹³C NMR (100 MHz, CDCl₃) δ 119.0, 69.9, 33.1. Melting Point 104 °C (lit 100-110°C).¹

1.2 Bromodihydrobenzocarborane (2 and 3)



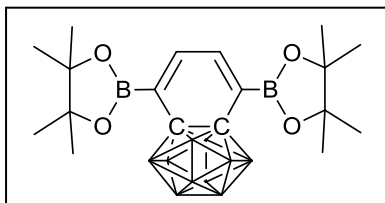
1,4-dihydrobenzocarborane (10.8 g, 56 mmol) and N-bromosuccinimide (10.4 g, 58 mmol) were dissolved in carbon tetrachloride (200 mL) and heated to 80 °C. To this rapidly stirring mixture was added benzoyl peroxide (900 mg, 5.6 mmol) in two equal portions, at 0 h and 3 h from the commencement of heating. The mixture was refluxed overnight before being allowed to cool to room temperature, filtered and extracted with water. The remaining organic layer was washed with brine, dried over magnesium sulphate, filtered and concentrated under reduced pressure. Purification by column chromatography (eluent: hexane) yielded the product as a mixture of two isomers (2-bromo-1,2-dihydrobenzocarborane (**2**) and 1-bromo-1,4-dihydrobenzocarborane (**3**)) as an off-white solid (9.6 g, 35 mmol, 62%, ratio of 2:3 ~ 5:2). ¹H NMR (400 MHz, CDCl₃): **2**: δ 6.09 (dd, 1H), 5.99 (dd, 1H), 5.66 (t, 1H), 4.70 (d, 2H), 3.20-1.80 (m, 10H). **3**: δ 6.33 (m, 1H), 5.75-5.65 (m, 2H), 5.19 (m, 2H), 3.20-1.80 (m, 10H).

1.3 Benzocarborane (4)



The mixture of isomers of bromodihydrobenzocarborane (9.5 g, 35 mmol) was dissolved in anhydrous DMF (200 mL) and the resulting solution was heated to 150 °C for 20 mins. After cooling to room temperature, the solution was diluted with water and extracted with n-pentane. The organic fractions were combined and washed with water and brine before being dried over magnesium sulphate. After filtration and concentration under reduced pressure the residue was purified by column chromatography (eluent: hexane) followed by recrystallisation from ethanol to afford **3** as a colourless solid (3.5 g, 18 mmol, 51%). ¹H NMR (400 MHz, CDCl₃): δ 6.50 (dd, 2H), 6.32 (dd, 2H), 3.02-1.68 (m, 10H); ¹³C NMR (100 MHz, CDCl₃): δ 129.2, 122.9, 119.9. Melting point 118°C (lit: 121-123°C).¹

1.4 Bis-1,4-(pinacol)-boronic acid-benzocarborane



Benzocarborane (1g, 5.2 mmol) and anhydrous N,N,N',N'-tetramethylethane-1,2-diamine (1.7 g, 14.6 mmol) were dissolved in anhydrous THF (30 mL) and cooled to -78°C. To this solution was added n-BuLi (1.6 M in hexanes, 7.1 mL, 11.3 mmol) slowly

before the mixture was allowed to warm to room temperature and stirred for 30 minutes. Following re-cooling to -78°C , isopropoxyboronic acid pinacol ester (2.7 mL, 15.9 mmol) was added and the solution was allowed to warm to room temperature overnight. The reaction mixture was diluted with water and extracted with diethyl ether. The organic layers were combined, washed with brine and dried over anhydrous magnesium sulphate before being concentrated under reduced pressure. Column chromatography (hexane eluent) afforded the desired product as a flaky white solid (1.7 g, 71%). ^1H { ^{11}B } NMR (400 MHz, CDCl_3): δ 6.90 (s, 2H), 2.66-1.68 (m, 10H), 1.31 (s, 24H) ^{13}C NMR (100 MHz, CDCl_3): δ 24.80, 84.83, 133.36. ^{11}B { ^1H } NMR (400 MHz, CDCl_3): δ 29.16, -6.58, -9.30, -12.53. Melting point 233°C . MS (EI): $m/z = 448.49$ (M $^{+}$)

1.5 Poly[(4,4-bis(dodecyl)-4H-cyclopenta-[2,1-b:3,4-b']-dithiophene-2,6-diyl)-alt-benzene-1,4-diyl (pB-CDT)]

A glass vial was charged with 1,4-benzenediboronic acid bis (pinacol) ester (82.5 mg, 0.25 mmol), 2,6-dibromo-4,4'-bis(2-dodecyl)-4H-cyclopenta[1,2-*b*:5,4-*b'*]dithiophene (167.6 mg, 0.25 mmol), $\text{Pd}_2(\text{dba})_3$ (4.4 mg, 4.8×10^{-3} mmol), (*o*-tol) $_3\text{P}$ (5.8 mg, 0.02 mmol), Aliquat 336 (1 drop) and toluene (5 mL). This mixture was degassed with argon for 30 mins, followed by the addition of degassed Na_2CO_3 solution (1.0 M, 1.0 mL). The resultant mixture was degassed for a further 10 minutes then sealed and heated to 120°C for 48 h. Following cooling to room temperature, the resultant mixture was precipitated from methanol and collected by filtration. The polymer was further purified by Soxhlet extraction first in methanol (24h), acetone (24h), *n*-hexane (24h) and chloroform (24h). The chloroform extract was stirred at 50°C in the presence of an aqueous sodium diethyldicarbamate trihydrate for 2 h. After cooling to room temperature the organic layer was separated and washed with water, dried and concentrated under reduced pressure. Final purification was by preparative size exclusion chromatography. The desired polymer was afforded following concentration under reduced pressure and precipitation in methanol (116 mg, 79%) as a dark red solid. GPC (chlorobenzene): Mn 12 KDa, Mw 19 KDa, PDI 1.6. ^1H NMR (400 MHz, CDCl_3) δ 7.62 (b, 4H), 7.23 (b, 2H), 1.89 (b, 4H) 1.24 (b, 40 H), 0.87 (b, 6H).

2. Physical Spectra and Measurements

2.1 Transistor Fabrication.

2.1.1 Top Gate Devices.

All film preparation steps were carried out under an inert atmosphere. The 2×2 cm glass slides were cleaned in a DECON90 deionized (DI) water solution in an ultrasonic bath twice for 10 min and then rinsed with DI water. To help with the adhesion of the gold on the glass substrate, 5 nm of aluminum was evaporated prior to the evaporation of 25 nm of gold. Polymeric chlorobenzene solution and substrates were heated to processing temperature followed by spin-coating for 10 s at 500 rpm followed by 30–60 s at 2000 rpm. The films were then dried at 100°C for 5 min. A perfluorinated polymer (commercial name CYTOP from Ashani Glass) was used as gate dielectric and applied via spin-coating for 60 s at 2000 rpm and cured at 100°C for 90 min. 50 nm aluminium was evaporated on top of the dielectric as a gate electrode.

2.1.2 Bottom Gate Devices.

Photolithographically pre-patterned bottom gate bottom contact (200 nm SiO_2 over Si^{+}) substrates with gold electrodes were used. Substrates were cleaned in an ultrasonic bath (acetone 10 min and isopropanol 10 min). The devices were spun from same solution concentrations and processing parameters as described for top gate devices

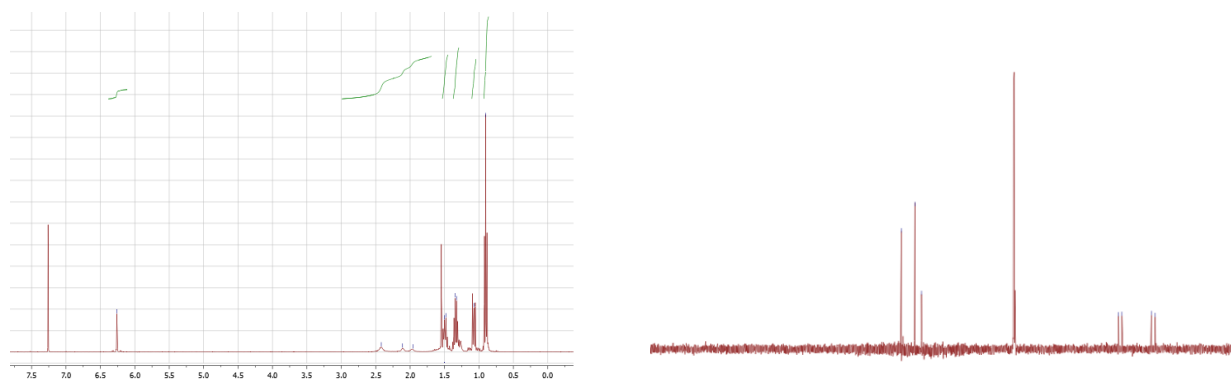


Fig. S1 ^1H and ^{13}C NMR spectra of bis(1,4-tributylstannyl)benzocarborane

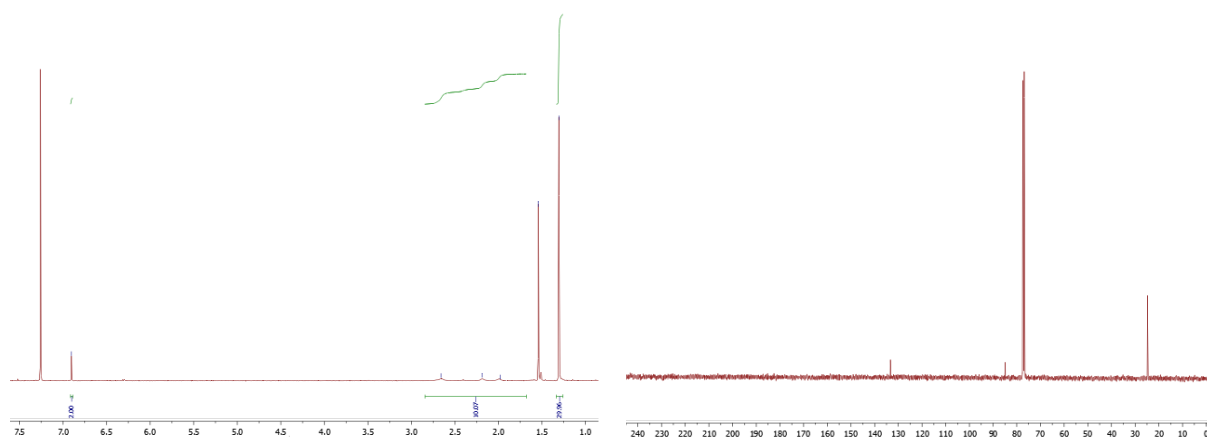


Fig. S2 ^1H and ^{13}C spectrum of bis-1,4-(pinacol)-boronic acid-benzocarborane

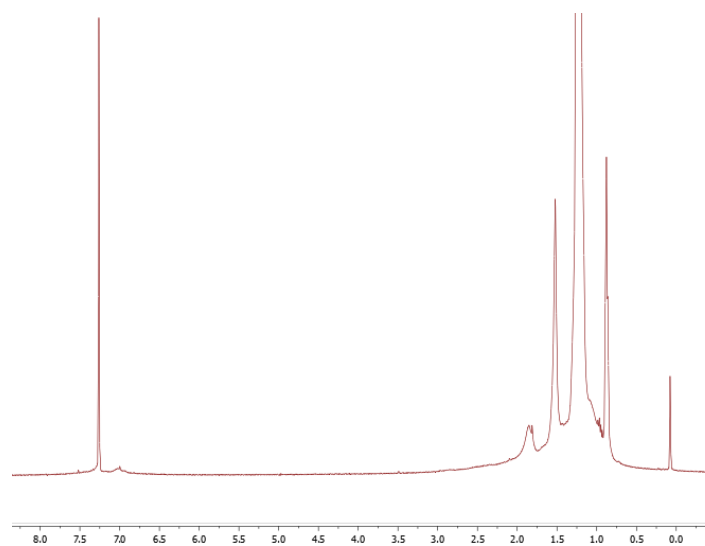


Fig S3. $^1\text{H}\{^{11}\text{B}\}$ NMR of pBZ-CDT

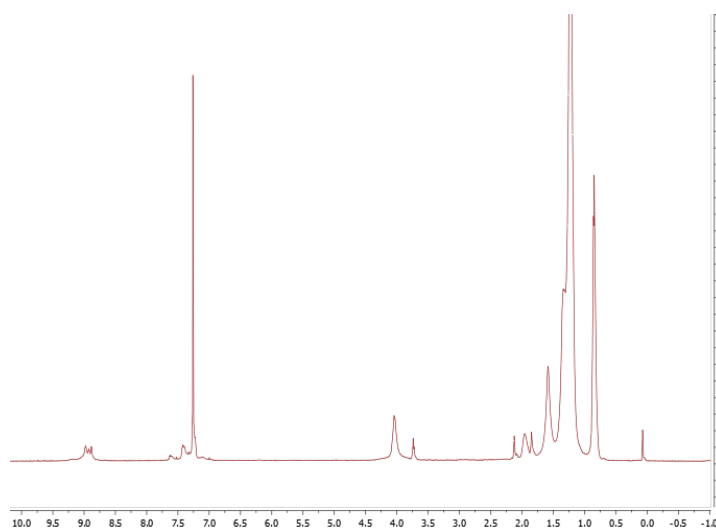


Fig S4. $^1\text{H}\{^{11}\text{B}\}$ NMR of pBZ-DPP

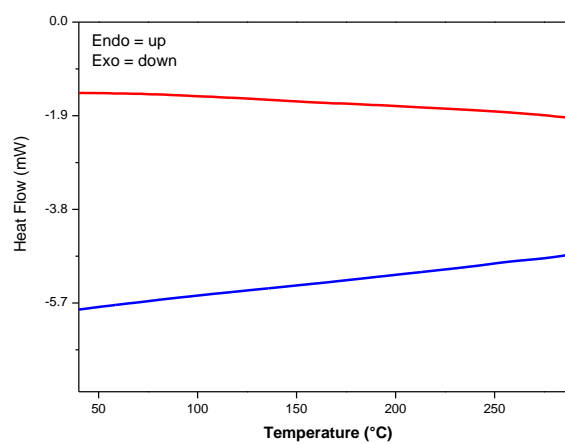


Fig S5. Second heating/cooling cycle DSC of pBZ-CDT (10C/min)

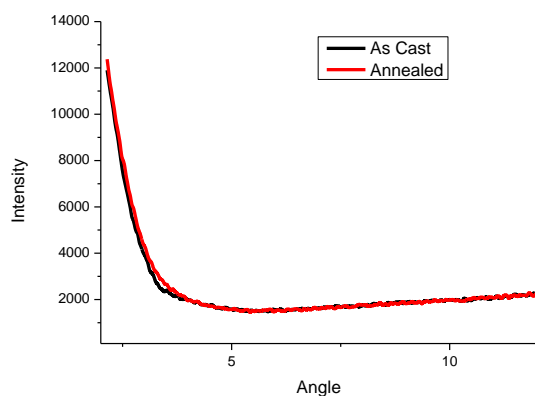


Fig S6. XRD of pBZ-CDT

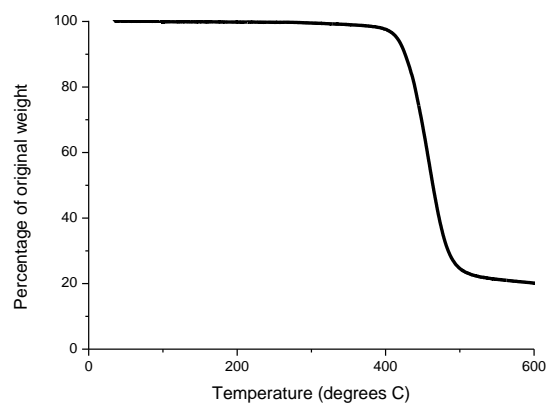


Fig. S7 TGA of pBZ-CDT under nitrogen

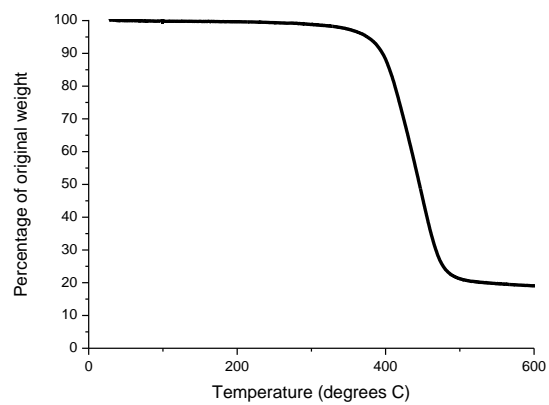


Fig. S8 TGA of pBZ-DPP under nitrogen

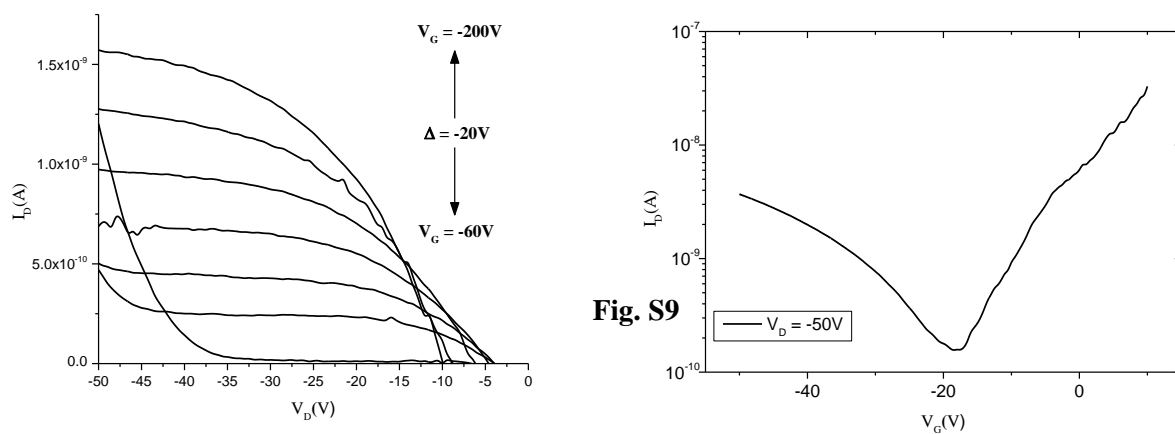


Figure S9. Output and transfer plots of pBZ-CDT in top gate devices

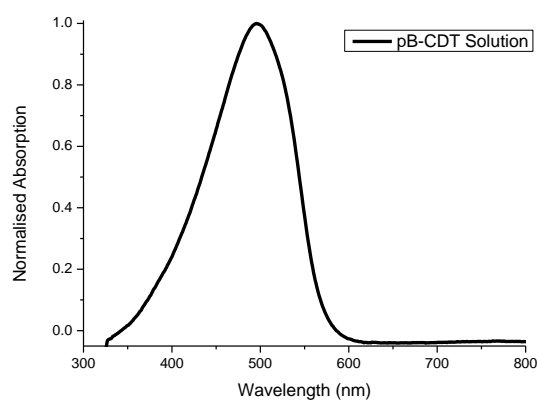


Figure S10. UV-Vis absorption spectrum for pB-CDT in Chloroform solution at RT.

1. D. S. Matteson and N. K. Hota, *J. Am. Chem. Soc.*, 1971, **93**, 2893–2897.
2. M. Horie, J. Kettle, C.-Y. Yu, L. a. Majewski, S.-W. Chang, J. Kirkpatrick, S. M. Tuladhar, J. Nelson, B. R. Saunders, and M. L. Turner, *J. Mat. Chem.*, 2012, **22**, 381.