**N-type polymer semiconductors incorporating *para*, *meta*, and *ortho*-carborane in the conjugated backbone†**

†In commemoration of Nobel Laurate, the late Sir Geoffrey Wilkinson, on the occasion of his centenary birthday.

*Filip Aniés,1 Zhuoran Qiao,1 Mohamad Insan Nugraha,2 Aniruddha Basu,2 Thomas D. Anthopoulos,2 Nicola Gasparini,1 Martin Heeney1\**

1 Department of Chemistry and Centre for Processable Electronics, Imperial College London, Molecular Sciences Research Hub, 80 Wood Lane, London, W12 0BZ, UK

2 KAUST Solar Center (KSC), Physical Science and Engineering Division (PSE), King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia

**ToC graphic**



**Keywords:**

Carborane; Polymer Semiconductor; Organic Thin-Film Transistor; Organic Photovoltaics

**Abstract**

We report on three novel n-type conjugated polymer semiconductors incorporating carborane in the polymer backbone and demonstrate their applicability in optoelectronic devices. Comparing the optoelectronic properties of *para*-, *meta*-, and *ortho*-carborane isomers revealed similar energetic characteristics between the different polymers, with the carborane unit acting as a “conjugation breaker”, confining electron delocalisation to the conjugated moieties. The fabrication of all-polymer organic photovoltaic (OPV) devices and thin-film transistors (TFTs) revealed some differences in device performance between the polymers, with the *meta*-carborane based polymer exhibiting superior performance in both OPV and TFT devices.

**1. Introduction**

Carboranes are polyhedral clusters made of hydrogen substituted boron and carbon atoms, held together by three-centre, two-electron bonds in an unusual σ-conjugated fashion. The icosahedral C2B10H12 carborane exists as either the *para* (*p*), *meta* (*m*), or *ortho* (*o*) isomer, with an increasing polarity and electron withdrawing nature as the carbon atoms are positioned closer to each other.[1] The unique “3D aromaticity” of carboranes typically results in chemical species with high thermal and electrochemical durability, lending itself to a wide range of specialised applications, including the formation of heat-resistant and flame-retardant materials.[2–5] Such examples include carborane-containing polysiloxanes, cyanate esters, polyimides, epoxy resin, and others.[6–10] Carborane derivatives are also highly relevant for medical applications, particularly for potential cancer treatments via boron neutron capture therapy (BNCT) due to their high concentration of 10B.[11–13] Furthermore, many aryl-substituted *o*-carborane species have been developed due to their unusual luminescent properties.[14] Over the past decade, the use of carboranes has received increasing attention within the scope of functional polymeric frameworks, such as conjugated polymers, macrocycles, and metal organic frameworks.[15,16]

Conjugated polymers comprise a diverse mix of materials, with their semiconducting properties utilised in various optoelectronic applications, such as thin-film transistors (TFTs), organic photovoltaics (OPVs), and organic light-emitting diodes (OLEDs).[17] Within this context, a range of carborane-containing polymers have been demonstrated in literature. Early examples focussed mainly on the synthesis and characterisation of carborane containing thiophenes and pyrroles and their subsequent electropolymerisation, whilst their optoelectronic applications and properties were rarely investigated in detail.[5,18–20] Later years have seen an increase in the interest of conjugated polymers incorporating carborane in the polymer backbone, mainly thanks to their intriguing emissive properties. In particular, Carter and co-workers have studied the emissive properties of polyfluorene with *o*-carborane incorporated into the backbone.[21] For example, they showed that the emission wavelength of the polymer in the solid state was influenced by exposure to vapours of common laboratory solvents, enabling it for sensing applications.[22] The strong solvatochromism of the polymer was traced to the impact of solvent polarity on the rate of intramolecular charge transfer (ICT) between the fluorene and carborane unit upon excitation, and its subsequent radiative or non-radiative decay.[23] The polymer was also successfully applied as the light-emitting layer in polymer light-emitting diodes (PLEDs).[24] Carter and co-workers also demonstrated the synthesis of a polyfluorene containing the isomeric *p*-carborane in the backbone.[25] Whilst this was photoluminescent in solution, no solvatochromism was reported.

Another sub-set of conjugated polymers incorporating carborane into the backbone has been explored by Chujo and co-workers, focussing on diphenyl-*m*/*o*-carboranes with various aromatic co-monomers, many of which demonstrated aggregation induced emission (AIE) behaviour.[26–28] The AIE behaviour was only observed in the *o*-carborane materials, with such properties absent in corresponding *m*-carborane or B-substituted polymers.[27,29,30] Importantly, the insertion of carborane into polymer backbones has, thus far, been noted not to extend the conjugation between conjugated units, although it may have an effect on bandgap energies and absorption spectra through other mechanisms, e.g. through its electron-withdrawing nature.[25,29]

Additional strategies to incorporate carboranes into conjugated polymers have also been demonstrated. Several groups have reported monomers containing annelated *o*-carborane derivatives such as benzocarborane or benzocarboranodithiophene, which could partake in the overall extended conjugation of the polymer, albeit via the fused ring rather than the carborane.[31–33] Pendant carboranes have also been introduced to polythiophenes and polyfluorene.[34–36] In the case of polythiophene with sidechains consisting of *p*-, *m*-, or *o*-carborane linked via vinylene groups, the inductively electron-withdrawing effect of the various carborane isomers had a slight impact on frontier molecular orbital (FMO) energy levels.[35]

Only a handful of examples exist where carborane-containing conjugated polymers have been employed in optoelectronic devices. In addition to the aforementioned PLED application of a fluorene derived polymer, it was also successfully used in TFTs, with a hole carrier mobility at ≈10-5 cm2V-1s-1.[24] Polymers incorporating fused *o*-carborane monomers were also used in TFTs, with the polymer pBZTT-DPP demonstrating ambipolar behaviour, with hole and electron carrier mobilities of 1×10-3 and 1×10-4 cm2V-1s-1 respectively.[31,32] Finally, polythiophenes with pendant carboranes demonstrated hole mobilities of ≈10-4 cm2V-1s-1, and were also tested in organic photovoltaic devices with PC70BM, achieving power conversion efficiencies (PCEs) of up to 2 %.[35] However to the best of our knowledge, the influence of the carborane isomer on the charge transport behaviour and solar cell performance has not been investigated for conjugated polymers containing the carborane in the mainchain. Motivated by their electron-withdrawing character, we proposed that the incorporation of carborane into the backbone of an n-type polymer would offer an interesting opportunity to systematically study the isomer influence.

In this work, we present a series of prototypical n-type conjugated polymer semiconductors incorporating carborane directly into the polymer backbone, namely poly{[N,N'-bis(2-octyldodecyl)naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-*alt*-5,5’-[1,12/7/2-bis(5-thiophen-2-yl)-*para*/*meta*/*ortho*-carborane]} (*p*CbT2-NDI, *m*CbT2-NDI, and *o*CbT2-NDI, respectively). Polymers were prepared by coupling bis(thiophenyl)carborane monomers with a naphthalenediimide (NDI) monomer via Stille polymerisation, forming a carborane containing analogue of the well-known polymer NDI2OD-T2 (also known as N2200).[37] All resulting polymers demonstrated excellent thermal stability. In terms of optical and electronic properties, we found that the polymers were relatively similar, with such properties being dependent mainly on the conjugated units. However, in their device performance in both TFTs and as OPVs, the nature of the carborane isomer had a strong impact on device performance. Whilst functional OPV devices could be fabricated with all polymers, devices made with *m*CbT2-NDI showed the highest performance. Furthermore, the kinked structure of *o*CbT2-NDI prevented the observation of semiconducting behaviour in TFT devices.

**2. Experimental**

**2.1 Synthesis and characterisation**

The synthetic route is outlined in Scheme 1 and described in further detail in the Supplementary Information. Details of synthetic, analytical, and characterisation equipment and procedures, and theoretical calculations, are also outlined in the Supplementary Information.

**2.2 Device fabrication and measurement**

TFTs were fabricated with a bottom-contact top-gate structure, employing gold source/drain electrodes, a Cytop dielectric, and an aluminium gate electrode. Polymers were deposited by spin coating from a chlorobenzene solution and annealed for 30 min at 100 °C. Channel lengths and widths were 30 µm and 1000 µm respectively. OPVs were fabricated with an inverted structure with the configuration glass/ITO/ZnO/active layer/MoO3/Ag. The active layer was deposited by spin coating from a 10 mg/mL chlorobenzene solution of PM6 with respective n-type polymer in a 2:1 wt/wt ratio. Full fabrication and characterisation details can be found in the Supplementary Information.

**3. Results and discussion**

**3.1 Polymer synthesis and characterisation**

The synthetic route to all target polymers is outlined in Scheme 1. In the first step, dithiophenyl carboranes were synthesised, using *para*, *meta*, or *ortho*-carborane as starting material. The *para* (**1**) and *meta* (**2**) compounds were obtained following previously reported synthetic procedures via an Ullmann-type reaction.[5,20,38,39] Thus the carboranes were dilithiated by treatment with n-BuLi, followed by reaction of the resulting species with 2-iodothiophene in the presence of copper iodide in stoichiometric amounts, to afford a mixture of mono- and di-substituted products.[5,20,38,39] When attempting this approach with *ortho*-carborane, only the mono-substituted product was obtained. We initially speculated that the reason behind this may be an unfavourable dilithiation of adjacent carbon atoms on the *o*-carborane. To test this hypothesis, we reacted the mono-substituted product under the same conditions, which should allow for a second addition on the unsubstituted carbon. However, we were only able to recover the unreacted mono-substituted species. This led us to conclude that this behaviour is caused by steric limitations, rather than issues with the dilithiation.

Instead, a Kumada-type reaction was performed, inspired by similar approaches to other diaryl species.[40–43] To the best of our knowledge, this has never before been reported with a thiophene compound. Thus ortho-carborane was treated with a slight excess of the lithium chloride salt of iso-propylmagnesium chloride (i.e. ‘turbo’ Grignard) and the resulting di-magnesium species was reacted with 2-bromothiophene in the presence of catalytic nickel(II) chloride, resulting in the formation of the target compound (**3**), albeit in low yield. By increasing the amount of 2-bromothiophene from 2.5 to 4 eq., the yield was doubled, from 7 to 15 %, which was sufficient for our purposes. We note that the reaction of decaborane with a disubstituted alkyne is often a higher yielding approach to 1,2-diaryl-*ortho*-carboranes.[5,20]

With the thiophene substituted carboranes in hand, all materials were stannylated by treatment with a slight excess of n-BuLi, followed by trapping of the resulting dianion with trimethyltin chloride. The resulting compounds were purified by preparative gel permeation chromatography to avoid issues with destannylation known to occur during conventional chromatography of tin compounds.[44] The dibrominated NDI unit was prepared following literature procedures.[45]

Polymerisations were performed under microwave heating using catalytic Pd2(dba)3 in the presence of P(o-tol)3.[46] The resulting polymers were purified by Soxhlet extraction with methanol, acetone, hexane, and chloroform, in that order. This revealed a difference in solubility between the polymers, as the majority of the *p*CbT2-NDI and *m*CbT2-NDI dissolved only in the chloroform fraction, whilst *o*CbT2-NDI was extracted with the hexane fraction. This is possibly caused by the higher exposure of the carborane units to the solvent environment as a result of the kinked polymer backbone conformation of *o*CbT2-NDI, as discussed in further detail under Section 3.2, although the different molecular weights may also play a role. Furthermore, analytical gel-permeation chromatography (GPC) performed in chlorobenzene at 80 °C pointed towards a strong correlation between monomer shape and molecular weights of the resulting polymers, with number average molecular weights (Mn) decreasing from 36 to 18 to 5 kDa, for *para*, *meta*, and *ortho* species respectively (Table 1). The same observation can be made from literature, where *meta*- and *para*-carborane monomers resulted in higher molecular weights than *ortho*-carborane monomers in the cases of Yamamoto and Sonogashira-Hagihara polymerisations respectively.[21,25,26,29]

Differential scanning calorimetry (DSC) was performed to investigate the thermal properties of the polymers, but revealed no features between 25 and 350 °C over three heating cycles, indicating a disordered amorphous packing of the polymers (Figure S1). This conclusion was reinforced by both X-ray diffraction (XRD) and atomic force microscopy (AFM), which were measured for both pristine and annealed films. XRD measurements resulted in featureless broad patterns in all films, with no significant difference before and after annealing (Figure S2). Likewise, AFM images show amorphous topographies of all films, with no obvious trends in root mean square (RMS) roughness between polymers or pristine/annealed films (Figure S3).

Thermal gravimetric analysis (TGA) was also performed to study the thermal stability of the polymers (Figure S4). Scans were run from 50 to 750 °C at 5 °C/min under nitrogen. All polymers exhibited excellent thermal stability, with degradation temperatures Td around 450 °C corresponding to a 5 % weight loss. Whilst this is very similar to the degradation temperature of NDI2OD-T2 (Figure S4), the carborane polymers exhibited a much higher residual mass RW at 700 °C, with values of 45, 49, and 56 % for *p*CbT2-NDI, *m*CbT2-NDI, and *o*CbT2-NDI respectively, compared to 32 % of NDI2OD-T2. The general improvement in Rw upon the inclusion of carborane, whilst Td remains largely unaffected, has been observed for many other polymer examples.[8,10,47]



**Scheme 1.** Synthetic route to the polymers featured in this work.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Polymer | Mn (kDa) | Mw (kDa) | *Đ* | Td,5% (°C) | Rw,700°C (%) |
| *p*CbT2-NDI | 36 | 53 | 1.47 | 450 | 45 |
| *m*CbT2-NDI | 18 | 29 | 1.59 | 449 | 49 |
| *o*CbT2-NDI | 5 | 9 | 1.73 | 445 | 56 |

**Table 1.** Polymer weights by GPC against polystyrene standards, degradation temperatures, and residual masses of respective polymer.

**3.2 Optical and electronic properties**

Absorption spectra were measured of each polymer, both in chloroform solution and as thin films, and emission spectra were measured in chloroform, as depicted in Figure 1. The spectra of the different polymers were largely unaffected by the nature of the carborane isomer, although there was a slight shift of the lowest energy peak, with λmax shifting from 493 to 486 to 468 nm for *p*CbT2-NDI, *m*CbT2-NDI and *o*CbT2-NDI solutions respectively. The absorption maxima are all significantly blue-shifted compared to NDI2OD-T2, which exhibits a low energy peak at 620 nm in chloronaphthalene, a solvent in which it does not show appreciable aggregation.[48] This suggest that all carborane isomers effectively prevent delocalisation between the adjacent T-NDI-T segments. Indeed, the spectra are similar to those reported for NDI-TET co-polymers in which conjugation is deliberately impeded by the inclusion of a non-conjugated ethane linker.[49]

Time-dependent density functional theory (TD-DFT) calculations were performed on the B3LYP/6-31G\*\* level to understand the origin of the absorption around 480 nm. The calculations demonstrate that the peak corresponds mainly to HOMO→LUMO and HOMO-1→LUMO+1 transitions, with additional HOMO→LUMO+1 and HOMO→LUMO+2 contributions in the case of *o*CbT2-NDI (Figure S5). The λmax of the emission peak follows the opposite trend to absorption, with a red-shift from 567 to 578 to 586 nm for *p*-, *m*-, and *o*-carborane containing polymers respectively, with an increasing Stokes shift of 74, 92, and 118 nm respectively. Thin film absorption spectra were very similar to those measured in solution, with a very slight red-shift of the main peak, and a decreasing intensity of the peaks around 380 and 365 nm. The absence of a peak shoulder or an additional low-energy peak – otherwise typical for ordered conjugated polymers – once again suggests disordered amorphous films.[50]

**Figure 1.** Normalised absorption (solid lines) and emission (dashed lines, λex = 375 nm) spectra of respective polymer in chloroform (solution) or spun-cast thin film.

Bandgap energies were estimated from the thin film λonset of each polymer (Table 2), revealing relatively wide bandgaps, at 2.14 eV for *p*CbT2-NDI and *m*CbT2-NDI and slightly wider at 2.21 eV for *o*CbT2-NDI. To further investigate the energetic properties of the polymers, DFT calculations were performed for trimers of each polymer at the B3LYP/6-311G\*\* level. These calculations resulted in similar bandgap energies between all polymers, in agreement with the experimental observation, although the absolute band gap values were ≈0.5 eV wider than those estimated from the λonset (Table 2).

To further investigate the energetic properties of the polymers, cyclic voltammetry (CV) was used to measure the redox potentials of polymer films. CV was performed with 0.1 M tetrabutylammonium hexaﬂuorophosphate electrolyte in acetonitrile, using a Pt counter electrode and Ag/Ag+ reference electrode, and films were drop cast directly onto a glassy carbon working electrode. Using ferrocene as an internal reference (added at the end of measurements), redox potentials could be detected with respect to the ferrocene/ferrocenium redox couple at 4.8 V. All polymers exhibited two reversible reduction peaks (Figure S6), with the absence of oxidation peaks within the electroactive window of the setup supporting their n-type character. The shape and position of the observed reduction peaks are reminiscent of those of other polymeric NDI species reported in literature, suggesting these reductions are associated with the NDI unit. [49,51] Electrochemical studies on substituted carboranes have reported that reduction occurs at much lower potentials, and that there are significant differences between the isomers.[2] As such it appears that reductions are centred on the NDI units. The reduction potentials provide a good estimate of the lowest unoccupied molecular orbital (LUMO) energy levels and were derived from the first reduction peak onset. Estimated LUMO energies were found to be very similar for all polymers, with values around -4.06 eV. We note this is slightly deeper than the value for N2200 (usually -3.9 to -4.0 eV[31,51]), or the related NDI-TET polymer in which conjugation is inhibited (-3.9 eV[49]), suggesting that the carborane may be exerting an inductively withdrawing effect. The experimental values are in reasonable agreement with DFT calculated values, which resulted in a range between -3.71 to -3.98 eV, as detailed in Table 2.

The DFT optimised structures of trimers, as shown in Figure 2, show the expectedly increasing kinked polymer backbone as carborane isomers move from *para* to *meta* to *ortho*. This also results in less planar conformations between adjacent NDI moieties. Furthermore, population analysis shows that the FMOs are heavily centred around the conjugated T-NDI-T segments, with little or no wavefunction concentrated on the carborane units. The highest occupied molecular orbitals (HOMOs) are localised more on the thiophenes, and LUMOs are centralised around the NDI units, as is also typical for the non-carborane analogue NDI2OD-T2.[52] Overall, this means that the carborane moieties act as “conjugation breakers”, with electron delocalisation limited to each π-conjugated T-NDI-T unit, rather than being delocalised across the entire polymer backbone. This means that, despite carborane having a σ-conjugated system of its own, this does not overlap with the π-conjugated systems of adjacent aromatic units. Similar behaviour has been observed for carboranes coupled to aromatic substituents and has been seen also for other polymers incorporating various carborane isomers in the polymer backbone.[25,29] The limited conjugation may explain the wide bandgap of these polymers, as an extended conjugation would have resulted in a narrowing of the band gap. Again, this can be compared to the non-carborane, fully conjugated analogue NDI2OD-T2, which has a ≈0.6V narrower bandgap, comparing to both calculated and UV-vis derived values.[51,52]

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Polymer | HOMO (eV) | LUMO (eV) | | Bandgap (eV) | |
| DFT | DFT | CV[a] | DFT | UV-vis[b] |
| *p*CbT2-NDI | -6.30 | -3.71 | -4.05 | 2.59 | 2.14 |
| *m*CbT2-NDI | -6.42 | -3.76 | -4.06 | 2.66 | 2.14 |
| *o*CbT2-NDI | -6.70 | -3.98 | -4.06 | 2.72 | 2.21 |

**Table 2.** Energy levels and bandgaps of respective polymers as calculated using DFT, or measured with CV and UV-vis spectroscopy. [a]Estimated from the reduction potential at the peak onset. [b]Estimated from the absorption peak onset.

**Chart, scatter chart

Description automatically generated**

**Figure 2.** Optimised trimer structure and HOMO and LUMO distribution of the polymers featured in this work, as calculated with DFT on the B3LYP/6-311G\*\* level. Alkyl chains have been replaced with methyl groups.

**3.3 Transistor and Photovoltaic device performance**

Bottom-contact, top-gate TFTs were fabricated to evaluate the charge transport properties of all three polymers. The active layers were deposited by spin-coating followed by thermal annealing at 100 °C to remove traces of solvent, prior to deposition of the gate dielectric. Both *p*CbT2-NDI and *m*CbT2-NDI exhibited typical n-type behaviour, with little hysteresis between the forward and reverse sweeps. The transfer and output curves are depicted in Figure 3, and performance indicators are summarised in Table 3. Devices made with *o*CbT2-NDI did not show any semiconducting character (Figure S7). The electron saturation mobility (μ) was approximately three times higher for *m*CbT2-NDI than for *p*CbT2-NDI, at 1.22×10-3 cm2V-1s-1, with threshold voltages (Vth) and on/off current ratios (Ion/Ioff) at similar levels.

In comparison to NDI2OD-T2, which typically achieves an electron mobility around 0.1 cm2V-1s-1 in our set-up, the inclusion of the carborane clearly has a detrimental effect on overall device performance.[53] Because π-conjugation is localised at each individual conjugated T-NDI-T moiety, rather than delocalised fully along the polymer backbone (as discussed under Section 3.2), we believe that charge transport is predominantly intermolecular, and thereby limiting the charge transport mobility. Furthermore, this may be an important contributing factor as to why devices made with *o*CbT2-NDI do not exhibit any semiconducting behaviour, as both the extremely kinked polymer backbone and out-of-plane conjugated units may prevent efficient π-π overlap between polymers. Consequently, this would prevent any intermolecular charge transport, which would be detrimental to the semiconducting properties of any material dependent on such charge transport mechanisms. Whilst the overall performance is lower than the fully conjugated NDI2OD-T2, these are nevertheless the first examples of electron transporting behaviour in a polymer incorporating carborane directly in the main chain, to the best of our knowledge. Furthermore, they compare reasonably in terms of charge transport in comparison to other classes of fully amorphous polymers, for example p-type poly(aryl)amines which exhibit hole mobilities on the order of 5×10-3 cm2V-1s-1 in TFT devices.[53]

Shape, arrow

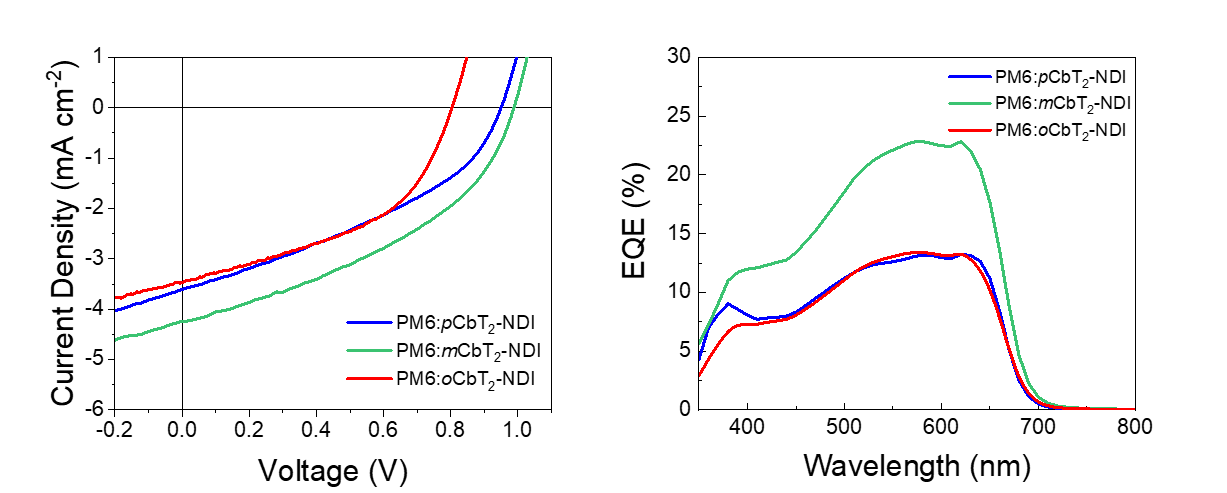
Description automatically generated

**Figure 3.** Transfer (left) and output (right) curves of spin-coated TFTs employing *p*CbT2-NDI (top) and *m*CbT2-NDI (bottom) in the semiconductor layer. Channel widths/lengths are 30/1000 µm respectively.

|  |  |  |  |
| --- | --- | --- | --- |
| **Polymer** | **μ (cm2V-1s-1)** | **Vth (V)** | **Ion/Ioff** |
| *p*CbT2-NDI | 4.2×10-4 | 7.0 | 4×103 |
| *m*CbT2-NDI | 1.22×10-3 | 10.4 | 7×103 |

**Table 3.** TFT characteristics of devices employing *m*CbT2-NDI and *p*CbT2-NDI in the semiconductor layer.

In addition to TFT devices, each polymer was also employed as the electron accepting material in all-polymer organic photovoltaic (OPV) devices.[54,55] We utilised PM6 as the donor material, since that had previously been demonstrated as a compatible donor for bulk heterojunction (BHJ) blends with NDI2OD-T2, and likewise has the structurally similar polymer PBDB-T (also known as PCE12).[56–58] Thus devices were fabricated using an inverted structure of glass/ITO/ZnO/active layer/MoO3/Ag utilising a 2:1 donor:acceptor ratio as optimised for NDI2OD-T2. Gratifyingly, all devices exhibited typical photovoltaic behaviour under one equivalent illumination (AM1.5G), as depicted in Figure 4, with OPV parameters of the optimised devices summarised in Table 4. Similar to the TFT devices, *m*CbT2-NDI achieved the highest overall performance, with an average PCE of 1.8 %, compared to 1.3 % for both *p*CbT2-NDI and *o*CbT2-NDI, respectively, due to higher short circuit current density (JSC) and open circuit voltage (VOC). To confirm the higher Jsc in mCbT2-NDI based devices, we carried out external quantum efficiency (EQE) measurements. As depicted in Figure 4, we obtained the highest light-to-current conversion in PM6:*m*CbT2-NDI devices. Regarding device optimisation, solar cells were measured either as-cast or after annealing the BHJ layer at 120 °C for 10 min (Figure S8, Table S1). However, annealing only had a marginal effect on device performance, reflecting the largely unchanged morphology of the polymers upon annealing, as discussed under Section 3.1.

Curiously, devices employing *o*CbT2-NDI were fully functional, despite the lack of semiconducting behaviour in TFT devices. OPV devices made with *o*CbT2-NDI also exhibited a higher fill factor (FF) than the other polymers, which is partially related to the charge transport mobility of the blend. We ascribe this partly to the different direction of charge transport in the two devices, with TFT probing in-plane two-dimensional charge transport, whereas in OPV devices the charge direction is the out-of-plane lateral direction. While the overall performance is modest in comparison to N2200, the high thermal stability and glass transition of many carborane containing polymers suggest that such polymers may be useful additives in ternary OPV devices,[59] and future work will investigate this direction further.****

**Figure 4.** J-V plots of optimised photovoltaic devices using each polymer as acceptor material (left), and corresponding EQE (right).

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Polymer** | **Voc (V)** | **Jsc (mA cm-2)** | **FF (%)** | **PCE (%)** |
| *p*CbT2-NDI | 0.95 | 3.60 | 0.37 | 1.3 |
| *m*CbT2-NDI | 0.99 | 4.24 | 0.41 | 1.8 |
| *o*CbT2-NDI | 0.80 | 3.47 | 0.46 | 1.3 |

**Table 4**. Photovoltaic parameters of highest performing optimised devices employing each polymer as the electron acceptor material in a 2:1 blend with PM6.

**4. Conclusion**

In summary, we report three new n-type co-polymer semiconductors, incorporating each of the *para­*-, *meta*-, and *ortho*-carborane directly in the polymer backbone, namely *p*CbT2-NDI, *m*CbT2-NDI, and *o*CbT2-NDI. Stille polymerisation afforded polymeric materials in all cases, although the ortho-carborane containing polymer had a noticeably lower molecular weight, possibly due to increased steric effects. All three polymers exhibit high thermal stability. Optical and electronic properties were largely unaffected by the choice of carborane isomer, as seen through absorption and emission measurements, cyclic voltammetry, and DFT calculations. This is explained by the fact that conjugated systems are localised on the aromatic (T-NDI-T) segments with the carboranes acting as “conjugation breakers”, minimising their impact on the frontier molecular orbitals of the polymers, and preventing full electron delocalisation across the polymer backbone but exerting an inductive, electron withdrawing effect. Nevertheless, both *p*CbT2-NDI and *m*CbT2-NDI showed n-type semiconductor behaviour in thin-film transistor devices, with reasonable mobility values of up to 1.22×10-3 cm2V-1s-1for fully amorphous films. Furthermore, all three polymers could be used as the acceptor material in all-polymer organic photovoltaics, with power conversion efficiencies of up to 1.8 %. This is, to the best of our knowledge, the first comparison of all three carborane isomers incorporated directly into the backbone of conjugated polymers, in the context of their optoelectronic properties and applications. These results suggest that the inclusion of such borane clusters can be useful to tune mechanical and semiconducting behaviour in such materials

**Acknowledgements**

The authors thank the Engineering and Physical Sciences Research Council (EPSRC) (EP/L016702/1 and EP/T028513/1), the Royal Society and the Wolfson Foundation (Royal Society Wolfson Fellowship), The Wilkinson Charitable Foundation, and King Abdullah University of Science and Technology (KAUST) Office of Sponsored Research (OSR) under Award No. OSR-2019-CRG8-4095.3, No. OSR-2020-CRG8-4095.2, and No. OSR-2018-CARF/CCF-3079 for funding. The authors also thank Charlotte Rapley for her assistance in obtaining thermal measurements data.

**Declaration of competing interest**

The authors have no competing interests to declare.

**CRediT authorship contribution statement**

Filip Aniés (Conceptualization, Methodology, Investigation, Formal analysis, Writing - Original Draft), Zhuoran Qiao (Investigation, Formal analysis), Mohamad Insan Nugraha (Investigation, Formal analysis, Writing - Review & Editing), Aniruddha Basu (Investigation, Formal analysis), Thomas D. Anthopoulos (Supervision), Nicola Gasparini (Investigation, Formal analysis, Supervision, Writing - Review & Editing), Martin Heeney (Conceptualization, Methodology, Supervision, Writing - Review & Editing)

**5. References**

[1] R.N. Grimes, Carboranes, 3rd ed., Academic Press, 2016. https://doi.org/10.1016/C2014-0-01334-2.

[2] R. Núñez, M. Tarrés, A. Ferrer-Ugalde, F.F. de Biani, F. Teixidor, Electrochemistry and Photoluminescence of Icosahedral Carboranes, Boranes, Metallacarboranes, and Their Derivatives, Chemical Reviews. 116 (2016) 14307–14378. https://doi.org/10.1021/acs.chemrev.6b00198.

[3] R. Núñez, I. Romero, F. Teixidor, C. Viñas, Icosahedral boron clusters: a perfect tool for the enhancement of polymer features, Chemical Society Reviews. 45 (2016) 5147–5173. https://doi.org/10.1039/C6CS00159A.

[4] S.-Y. Lu, I. Hamerton, Recent developments in the chemistry of halogen-free flame retardant polymers, Progress in Polymer Science. 27 (2002) 1661–1712. https://doi.org/10.1016/S0079-6700(02)00018-7.

[5] E. Hao, B. Fabre, F.R. Fronczek, M.G.H. Vicente, Poly[di(2-thiophenyl)carborane]s: conducting polymers with high electrochemical and thermal resistance, Chemical Communications. (2007) 4387. https://doi.org/10.1039/b710375a.

[6] A.A. Anisimov, A. v. Zaitsev, V.A. Ol’shevskaya, M.I. Buzin, V.G. Vasil’ev, O.I. Shchegolikhina, A.M. Muzafarov, Carborane–Siloxanes: Synthesis and Properties. New Possibilities for Structure Control, INEOS OPEN. 1 (2018) 71–84. https://doi.org/10.32931/io1806r.

[7] E.N. Peters, The development of carborane-siloxane polymers, Industrial & Engineering Chemistry Product Research and Development. 23 (1984) 28–32. https://doi.org/10.1021/i300013a006.

[8] S. Goyal, M.J. Forrester, D. Coverdell, S. Torres, M.W. Lee, E.W. Cochran, High-Temperature-Performance Cyanate Ester Composites with Carboranes, Macromolecules. 54 (2021) 9155–9164. https://doi.org/10.1021/acs.macromol.1c01410.

[9] T. Xing, K. Zhang, Syntheses of novel soluble carborane polyimides with ultrahigh thermal stability, Polymer International. 64 (2015) 1715–1721. https://doi.org/10.1002/pi.4971.

[10] M. Cui, L. Zhang, P. Lou, X. Zhang, X. Han, Z. Zhang, S. Zhu, Study on thermal degradation mechanism of heat-resistant epoxy resin modified with carboranes, Polymer Degradation and Stability. 176 (2020) 109143. https://doi.org/10.1016/j.polymdegradstab.2020.109143.

[11] P. Stockmann, M. Gozzi, R. Kuhnert, M.B. Sárosi, E. Hey-Hawkins, New keys for old locks: carborane-containing drugs as platforms for mechanism-based therapies, Chemical Society Reviews. 48 (2019) 3497–3512. https://doi.org/10.1039/C9CS00197B.

[12] F. Ali, N. S Hosmane, Y. Zhu, Boron Chemistry for Medical Applications, Molecules. 25 (2020) 828. https://doi.org/10.3390/molecules25040828.

[13] A. Pitto-Barry, Polymers and boron neutron capture therapy (BNCT): a potent combination, Polymer Chemistry. 12 (2021) 2035–2044. https://doi.org/10.1039/D0PY01392G.

[14] J. Ochi, K. Tanaka, Y. Chujo, Recent Progress in the Development of Solid‐State Luminescent o ‐Carboranes with Stimuli Responsivity , Angewandte Chemie. 132 (2020) 9925–9939. https://doi.org/10.1002/ange.201916666.

[15] J. Yan, W. Yang, Q. Zhang, Y. Yan, Introducing borane clusters into polymeric frameworks: architecture, synthesis, and applications, Chemical Communications. 56 (2020) 11720–11734. https://doi.org/10.1039/D0CC04709K.

[16] C.E. Housecroft, Carboranes as guests, counterions and linkers in coordination polymers and networks This review is dedicated to Russ Grimes, a true pioneer in carborane (carbaborane) cluster chemistry, on the occasion of his 80th birthday., Journal of Organometallic Chemistry. 798 (2015) 218–228. https://doi.org/10.1016/j.jorganchem.2015.04.047.

[17] H. Bronstein, C.B. Nielsen, B.C. Schroeder, I. McCulloch, The role of chemical design in the performance of organic semiconductors, Nature Reviews Chemistry. 4 (2020) 66–77. https://doi.org/10.1038/s41570-019-0152-9.

[18] B. Fabre, S. Chayer, M.G.H. Vicente, First conducting polymer functionalized with covalently linked carborane units, Electrochemistry Communications. 5 (2003) 431–434. https://doi.org/10.1016/S1388-2481(03)00095-X.

[19] E. Hao, B. Fabre, F.R. Fronczek, M.G.H. Vicente, Syntheses and Electropolymerization of Carboranyl-Functionalized Pyrroles and Thiophenes, Chemistry of Materials. 19 (2007) 6195–6205. https://doi.org/10.1021/cm701935n.

[20] F. Barrière, B. Fabre, E. Hao, Z.M. LeJeune, E. Hwang, J.C. Garno, E.E. Nesterov, M.G.H. Vicente, Electropolymerizable 2,2′-Carboranyldithiophenes. Structure−Property Investigations of the Corresponding Conducting Polymer Films by Electrochemistry, UV−Visible Spectroscopy and Conducting Probe Atomic Force Microscopy, Macromolecules. 42 (2009) 2981–2987. https://doi.org/10.1021/ma802369z.

[21] J.J. Peterson, M. Werre, Y.C. Simon, E.B. Coughlin, K.R. Carter, Carborane-Containing Polyfluorene: o- Carborane in the Main Chain, Macromolecules. 42 (2009) 8594–8598. https://doi.org/10.1021/ma901703r.

[22] J.J. Peterson, A.R. Davis, M. Werre, E.B. Coughlin, K.R. Carter, Carborane-Containing Poly(fluorene): Response to Solvent Vapors and Amines, ACS Applied Materials & Interfaces. 3 (2011) 1796–1799. https://doi.org/10.1021/am2000856.

[23] K.L. Martin, A. Krishnamurthy, J. Strahan, E.R. Young, K.R. Carter, Excited State Characterization of Carborane-Containing Poly(dihexyl fluorene)s, The Journal of Physical Chemistry A. 123 (2019) 1701–1709. https://doi.org/10.1021/acs.jpca.8b07955.

[24] A.R. Davis, J.J. Peterson, K.R. Carter, Effect of o-carborane on the optoelectronic and device-level properties of poly(fluorene)s, ACS Macro Letters. 1 (2012) 469–472. https://doi.org/10.1021/mz300037u.

[25] J.J. Peterson, Y.C. Simon, E.B. Coughlin, K.R. Carter, Polyfluorene with p-carborane in the backbone, Chemical Communications. (2009) 4950–4952. https://doi.org/10.1039/b908131c.

[26] K. Kokado, Y. Chujo, Emission via Aggregation of Alternating Polymers with o -Carborane and p -Phenylene−Ethynylene Sequences, Macromolecules. 42 (2009) 1418–1420. https://doi.org/10.1021/ma8027358.

[27] K. Kokado, Y. Tokoro, Y. Chujo, Luminescent and Axially Chiral π-Conjugated Polymers Linked by Carboranes in the Main Chain, Macromolecules. 42 (2009) 9238–9242. https://doi.org/10.1021/ma902094u.

[28] K. Kokado, Y. Chujo, Polymer reaction of poly(p-phenylene–ethynylene) by addition of decaborane: modulation of luminescence and heat resistance, Polymer Journal. 42 (2010) 363–367. https://doi.org/10.1038/pj.2010.13.

[29] K. Kokado, Y. Tokoro, Y. Chujo, Luminescent m -Carborane-Based π-Conjugated Polymer, Macromolecules. 42 (2009) 2925–2930. https://doi.org/10.1021/ma900174j.

[30] M. Tominaga, Y. Morisaki, H. Naito, Y. Chujo, Synthesis and characterization of an alternating copolymer with 1,2-disubstituted and 9,12-disubstituted o-carborane units, Polymer Journal. 46 (2014) 740–744. https://doi.org/10.1038/pj.2014.60.

[31] J. Marshall, Z. Fei, C.P. Yau, N. Yaacobi-Gross, S. Rossbauer, T.D. Anthopoulos, S.E. Watkins, P. Beavis, M. Heeney, Incorporation of benzocarborane into conjugated polymer systems: Synthesis, characterisation and optoelectronic properties, Journal of Materials Chemistry C. 2 (2014) 232–239. https://doi.org/10.1039/c3tc31663g.

[32] J. Marshall, B.C. Schroeder, H. Bronstein, I. Meager, S. Rossbauer, N. Yaacobi-Gross, E. Buchaca-Domingo, T.D. Anthopoulos, N. Stingelin, P. Beavis, M. Heeney, Benzocarborano[2,1- b :3,4- b ′]dithiophene Containing Conjugated Polymers: Synthesis, Characterization, and Optoelectronic Properties, Macromolecules. 47 (2014) 89–96. https://doi.org/10.1021/ma402273w.

[33] K. Kokado, M. Tominaga, Y. Chujo, Aromatic ring-fused carborane-based luminescent π-conjugated polymers, Macromolecular Rapid Communications. 31 (2010) 1389–1394. https://doi.org/10.1002/marc.201000160.

[34] Y.C. Simon, J.J. Peterson, C. Mangold, K.R. Carter, E.B. Coughlin, Synthesis of Polyfluorenes with Pendant Silylcarboranes, Macromolecules. 42 (2009) 512–516. https://doi.org/10.1021/ma8018816.

[35] J. Marshall, J. Hooton, Y. Han, A. Creamer, R.S. Ashraf, Y. Porte, T.D. Anthopoulos, P.N. Stavrinou, M.A. McLachlan, H. Bronstein, P. Beavis, M. Heeney, Polythiophenes with vinylene linked ortho , meta and para -carborane sidechains, Polym. Chem. 5 (2014) 6190–6199. https://doi.org/10.1039/C4PY00767K.

[36] Y. Morisaki, M. Tominaga, Y. Chujo, Synthesis and Properties of Thiophene-Fused Benzocarborane, Chemistry - A European Journal. 18 (2012) 11251–11257. https://doi.org/10.1002/chem.201201513.

[37] N. Zhou, A. Facchetti, Naphthalenediimide (NDI) polymers for all-polymer photovoltaics, Materials Today. 21 (2018) 377–390. https://doi.org/10.1016/j.mattod.2018.02.003.

[38] R. Coult, M.A. Fox, W.R. Gill, P.L. Herbertson, J.A.H. MacBride, K. Wade, C-arylation and C-heteroarylation of icosahedral carboranes via their copper(I) derivatives, Journal of Organometallic Chemistry. 462 (1993) 19–29. https://doi.org/10.1016/0022-328X(93)83337-U.

[39] A. v. Marsh, M.J. Dyson, N.J. Cheetham, M. Bidwell, M. Little, A.J.P. White, C.N. Warriner, A.C. Swain, I. McCulloch, P.N. Stavrinou, S.C.J. Meskers, M. Heeney, Correlating the Structural and Photophysical Properties of Ortho, Meta, and Para-Carboranyl–Anthracene Dyads, Advanced Electronic Materials. 6 (2020). https://doi.org/10.1002/aelm.202000312.

[40] C. Tang, Z. Xie, Nickel-Catalyzed Cross-Coupling Reactions of o -Carboranyl with Aryl Iodides: Facile Synthesis of 1-Aryl- o -Carboranes and 1,2-Diaryl- o -Carboranes, Angewandte Chemie International Edition. 54 (2015) 7662–7665. https://doi.org/10.1002/anie.201502502.

[41] Y. Chen, J. Guo, X. Wu, D. Jia, F. Tong, Color-tuning aggregation-induced emission of o -Carborane-bis(1,3,5-triaryl-2-pyrazoline) triads: Preparation and investigation of the photophysics, Dyes and Pigments. 148 (2018) 180–188. https://doi.org/10.1016/j.dyepig.2017.09.011.

[42] X. Wu, J. Guo, J. Zhao, Y. Che, D. Jia, Y. Chen, Multifunctional luminescent molecules of o -carborane-pyrene dyad/triad: flexible synthesis and study of the photophysical properties, Dyes and Pigments. 154 (2018) 44–51. https://doi.org/10.1016/j.dyepig.2018.02.035.

[43] X. Wu, J. Guo, Y. Lv, D. Jia, J. Zhao, H. Shan, X. Jin, Y. Ma, Aggregation-induced emission characteristics of o -carborane-functionalized fluorene and its heteroanalogs: the influence of heteroatoms on photoluminescence, Materials Chemistry Frontiers. 4 (2020) 257–267. https://doi.org/10.1039/C9QM00621D.

[44] Z. Fei, M. Shahid, N. Yaacobi-Gross, S. Rossbauer, H. Zhong, S.E. Watkins, T.D. Anthopoulos, M. Heeney, Thiophene fluorination to enhance photovoltaic performance in low band gap donor–acceptor polymers, Chemical Communications. 48 (2012) 11130. https://doi.org/10.1039/c2cc35079c.

[45] Z. Chen, Y. Zheng, H. Yan, A. Facchetti, Naphthalenedicarboximide- vs Perylenedicarboximide-Based Copolymers. Synthesis and Semiconducting Properties in Bottom-Gate N-Channel Organic Transistors, Journal of the American Chemical Society. 131 (2009) 8–9. https://doi.org/10.1021/ja805407g.

[46] S. Tierney, M. Heeney, I. McCulloch, Microwave-assisted synthesis of polythiophenes via the Stille coupling, Synthetic Metals. 148 (2005) 195–198. https://doi.org/10.1016/j.synthmet.2004.09.015.

[47] Y. Wu, G. Chen, C. Feng, J. Yang, High T g and Thermo-Oxidatively Stable Thermosetting Polyimides Derived from a Carborane-Containing Diamine, Macromolecular Rapid Communications. 39 (2018) 1800484. https://doi.org/10.1002/marc.201800484.

[48] R. Steyrleuthner, M. Schubert, I. Howard, B. Klaumünzer, K. Schilling, Z. Chen, P. Saalfrank, F. Laquai, A. Facchetti, D. Neher, Aggregation in a High-Mobility n-Type Low-Bandgap Copolymer with Implications on Semicrystalline Morphology, Journal of the American Chemical Society. 134 (2012) 18303–18317. https://doi.org/10.1021/ja306844f.

[49] T. Erdmann, S. Fabiano, B. Milián‐Medina, D. Hanifi, Z. Chen, M. Berggren, J. Gierschner, A. Salleo, A. Kiriy, B. Voit, A. Facchetti, Naphthalenediimide Polymers with Finely Tuned In‐Chain π‐Conjugation: Electronic Structure, Film Microstructure, and Charge Transport Properties, Advanced Materials. 28 (2016) 9169–9174. https://doi.org/10.1002/adma.201602923.

[50] F. Aniés, S. Wang, T. Hodsden, J. Panidi, Z. Fei, X. Jiao, Y.H.C. Wong, C.R. McNeill, T.D. Anthopoulos, M. Heeney, A Structurally Simple but High‐Performing Donor–Acceptor Polymer for Field‐Effect Transistor Applications, Advanced Electronic Materials. 6 (2020) 2000490. https://doi.org/10.1002/aelm.202000490.

[51] S. Brixi, O.A. Melville, B. Mirka, Y. He, A.D. Hendsbee, H. Meng, Y. Li, B.H. Lessard, Air and temperature sensitivity of n-type polymer materials to meet and exceed the standard of N2200, Scientific Reports. 10 (2020) 4014. https://doi.org/10.1038/s41598-020-60812-x.

[52] G. Wen, X. Zou, R. Hu, J. Peng, Z. Chen, X. He, G. Dong, W. Zhang, Ground- and excited-state characteristics in photovoltaic polymer N2200, RSC Advances. 11 (2021) 20191–20199. https://doi.org/10.1039/D1RA01474A.

[53] W. Zhang, J. Smith, R. Hamilton, M. Heeney, J. Kirkpatrick, K. Song, S.E. Watkins, T. Anthopoulos, I. McCulloch, Systematic Improvement in Charge Carrier Mobility of Air Stable Triarylamine Copolymers, Journal of the American Chemical Society. 131 (2009) 10814–10815. https://doi.org/10.1021/ja9034818.

[54] G. Wang, F.S. Melkonyan, A. Facchetti, T.J. Marks, All‐Polymer Solar Cells: Recent Progress, Challenges, and Prospects, Angewandte Chemie International Edition. 58 (2019) 4129–4142. https://doi.org/10.1002/anie.201808976.

[55] C. Lee, S. Lee, G.-U. Kim, W. Lee, B.J. Kim, Recent Advances, Design Guidelines, and Prospects of All-Polymer Solar Cells, Chemical Reviews. 119 (2019) 8028–8086. https://doi.org/10.1021/acs.chemrev.9b00044.

[56] Q. Fan, W. Su, S. Chen, W. Kim, X. Chen, B. Lee, T. Liu, U.A. Méndez-Romero, R. Ma, T. Yang, W. Zhuang, Y. Li, Y. Li, T.-S. Kim, L. Hou, C. Yang, H. Yan, D. Yu, E. Wang, Mechanically Robust All-Polymer Solar Cells from Narrow Band Gap Acceptors with Hetero-Bridging Atoms, Joule. 4 (2020) 658–672. https://doi.org/10.1016/j.joule.2020.01.014.

[57] S. Huang, Z. Huai, J. Ren, Y. Sun, X. Zhao, L. Wang, W. Kong, G. Fu, S. Yang, Improved Morphology and Interfacial Contact of PBDB-T:N2200-Based All-Polymer Solar Cells by Using the Solvent Additive *p* -Anisaldehyde, ACS Applied Energy Materials. 3 (2020) 358–365. https://doi.org/10.1021/acsaem.9b01624.

[58] M. Zhang, X. Guo, W. Ma, H. Ade, J. Hou, A Large-Bandgap Conjugated Polymer for Versatile Photovoltaic Applications with High Performance, Advanced Materials. 27 (2015) 4655–4660. <https://doi.org/10.1002/adma.201502110>.

[59] N. Gasparine, S. H. K. Paleti, J. Bertrandie, G. Cai, G. Zhang, A. Wadsworth, X. Lu, H.-L. Yip, I. McCulloch, D. Baran Exploiting ternary blends for improved photostability in high-efficiency organic solar cells ACS Energy Lett. 5 (2020) 1371-1379. https://pubs.acs.org/doi/abs/10.1021/acsenergylett.0c00604