# Effect of *o*-Carborane on the Optoelectronic and Device-Level Properties of Poly(fluorene)s

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S *Supporting Information*

ABSTRACT: Carboranes have been previously noted to distinctively affect the luminescent properties of semiconducting polymers when incorporated into the conjugated backbone. In this report, we use carborane-based poly(fluorene) derivatives as active materials for polymer light-emitting diodes and transistors. Optoelectronic analysis unequivocally shows that carborane does not participate in the π-conjugated network, yet their presence causes major red-shifting in device electroluminescence as well as in thin film photoluminescence. In field effect transistors, they also improve charge carrier mobility by an order of magnitude despite disrupting π-conjugation. This use of carborane-containing conjugated polymers in active devices holds promise as new responsive materials in electronic polymer applications.
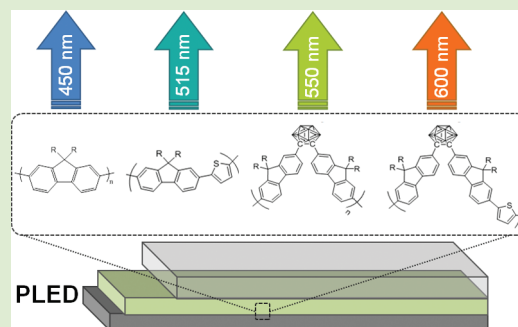
Icosahedral carboranes ($C_2B_{10}H_{12}$) have been the subject of investigation for decades due to a number of attributes including their thermal and chemical stability, unusual geometry, interesting electronics, and high neutron capture cross-section.[1,2] The variable carbon−carbon bond length in *ortho*-carboranes has also been an issue of considerable interest.[3] Many of these factors can largely be attributed to the three-center two-electron bonding scheme within carborane cages which simultaneously provides them with aspects of 3D σ-aromaticity and electron-deficiency. Evidence of their potentially unique electronic and structural effects on conjugated polymers has been shown in recent work via the incorporation of carboranes into poly(fluorene)s by our group[4] and into the backbone of phenylene-ethynylene-based molecules by Chujo and co-workers.[5] In these reports, one of the most prominent effects of bonding *o*-carborane directly to the conjugated π-system of luminescent semiconducting polymers is the observation of aggregation-induced emission (AIE), where luminescence is enhanced and often color-shifted in solutions of high concentration or in thin film regimes. Similarly, we recently observed that carborane-containing conjugated polymers can act as colorimetric sensors when exposed to various organic solvents.[6]

Despite the progress being made to understand these systems, the use of carborane in sensing and detecting applications has been limited to photoluminescent and colorimetric observations. No reports exist on incorporating carborane-containing conjugated polymers in organic electronic device architectures (such as light-emitting diodes and thin film transistors) whose response could provide further insight into the effect of carboranes on conjugated systems.[7] In this report, we fabricate the first electronic devices made from semiconducting polymers with carborane incorporated directly into the backbone, which show that carborane disrupts conjugation but allows for low-energy emissive modes possibly due to energy transfer. We show the cages' effect on the electroluminescence of polymer light-emitting diodes (PLEDs) and on the charge transport properties of thin film transistors (TFTs) and rationalize their behavior based on the effect on the polymers' highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels.

Figure 1 shows the synthetic scheme and nomenclature of the poly(fluorene) derivatives studied in this report. The syntheses of *o*-carborane-containing poly(fluorene) (PF-*o*-carb) and its monomer **2** have been described previously.[4] However, the fluorene-thiophene copolymer incorporating *o*-carborane (PFT-*o*-carb) has not been reported. The synthesis of PFT-*o*-carb is very similar to PF-*o*-carb, accomplished via Stille coupling of the dibromo fluorene-carborane monomer **2** and 2,5-bis(tributylstannyl)-thiophene **3**. PFT was likewise synthesized to serve as a control. PFT and PFT-*o*-carb polymers were characterized using conventional techniques (Figures S1−S5 of the Supporting Information, SI). Glass transition temperatures were found to be similar between PF and PFT (102 and 101 °C, respectively) and likewise between PF-*o*-carb and PFT-*o*-carb (128 and 129 °C, respectively), highlighting the chain rigidifying effects of the carborane linkage. While the PFT repeat structure is perhaps an imperfect analogue to PFT-*o*-carb repeat structure, we expect that general comparisons between the two can still be insightful for illuminating the carborane cage's effect on optoelectronic properties, especially noting
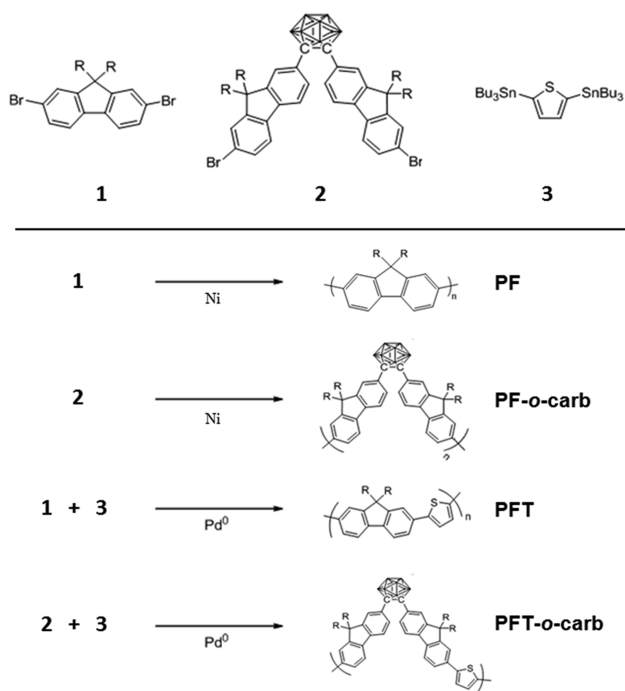
Figure 1. Synthetic scheme and nomenclatures of the poly(fluorene) derivatives investigated. R = hexyl. B−H hydrogens at carborane cage vertices are omitted for clarity.

previous data showing only slight consequences of increased fluorene−thiophene ratios in copolymers (much greater consequences are expected for an increase of *adjacent* thiophene units, which is not occurring here).[8]

The UV−vis absorption of the polymers is shown in Figure 2. As expected, PFT copolymer is red-shifted in absorption
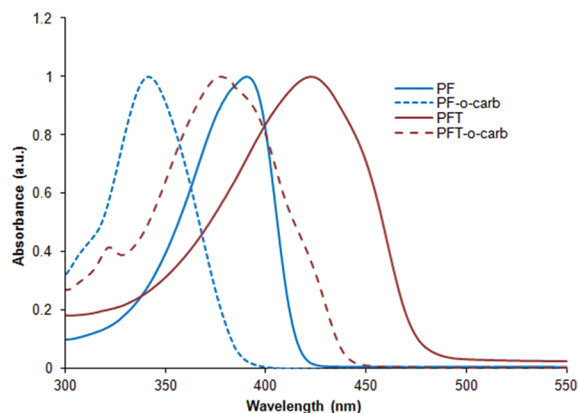

Figure 2. UV−vis spectra of poly(fluorene) derivatives.

compared to PF homopolymer, attributed to the lower band gap of thiophene as well as to the likelihood of increased backbone planarization.[9] In both PF and PFT systems, adding *o*-carborane into the conjugated backbone leads to a dramatic blue-shift (>50 nm) in the absorption onset and peak absorption values, characteristic of decreased conjugation length. Similar effects on absorption are well-known for oligomeric conjugated materials compared to their higher molecular weight analogues.[10] Comparative blue-shifting, also observed for fully conjugated *ortho* linkages, has been attributed to out-of-plane sterically induced twisting of the polymer

backbone which decreases the effective conjugation length.[7,11] To corroborate this argument of decreased conjugation length, cyclic voltammetry (CV) was used to measure the onset of electrochemical oxidation of the polymers and calculate their HOMO energies (Figure S6 of the SI). LUMO levels were then approximated using the optical band gaps measured from the UV−vis data. Results are summarized in Figure 3 (and in Table
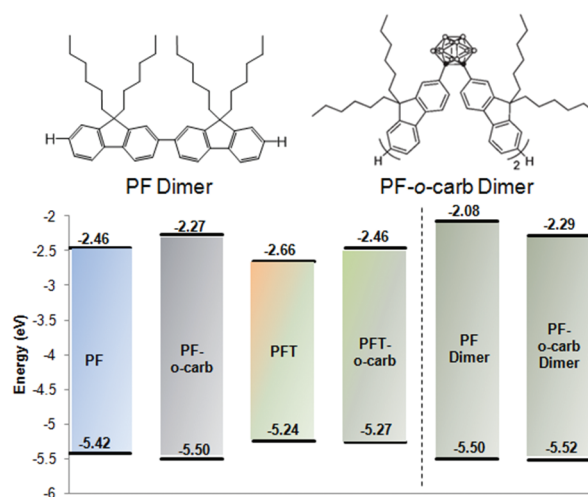

Figure 3. Energy level diagram showing the estimated HOMO/LUMO levels of the poly(fluorene) derivatives calculated from UV−vis and cyclic voltammetry data. Dimer structures are illustrated above.

S7 of the SI). As suggested from the UV−vis absorption, the carborane-containing derivatives show increased band gaps compared to their PF and PFT analogues.

A comparison of the HOMO/LUMO levels of the PF-*o*-carb polymer to its corresponding dimer further supports the argument of shorter effective conjugation length imposed by the carborane moiety (dimer structure illustrated in Figure 3). If conjugation extends along the backbone, a significant decrease in band gap would be expected from the polymer compared to the dimer. This is clearly evident for dihexyl fluorene where a 0.4 eV decrease in the band gap was observed between the dimer and the fully polymerized PF. A similar decrease was entirely absent for the *o*-carborane dimer/polymer pair. Instead, the band gaps of the *o*-carborane dimer/polymer pair were found to remain effectively constant at approximately 3.2 eV, indicating that the *o*-carborane linkages do not extend π-conjugation throughout the polymer chain. The *o*-carborane segment does seem to offer some electronic effect, however, as observed by comparing the optical band gap for the two dimers. A decrease of approximately 0.2 eV in the LUMO after incorporation of *o*-carborane in the dimer is consistent with descriptions of the electron-withdrawing nature of *ortho*-connected carboranes.[1]

There have been relatively few reports on the spatial modeling of the HOMO/LUMO localizations of *o*-carborane bonded to conjugated segments. It may be possible that localization of the HOMO and LUMO to fluorene and carborane, respectively, could account for the lack of red-shifting upon chain extension, but there are no data currently to support this. Kokado et al. have suggested that both the HOMO and the LUMO are localized to the conjugated organic segments in a phenylene-ethynelene-based system,[5d] but more studies would be needed to provide a definitive explanation.

Photoluminescence (PL) and electroluminescence (EL) of PF, PFT, and their carborane-containing derivatives are shown in Figure 4. PL was measured in solution (Figure 4a) and solid
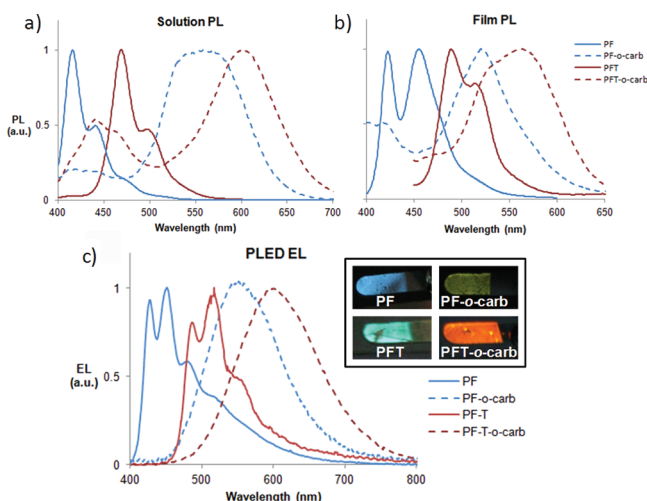

Figure 4. (a) CHCl$_3$ solution and (b) thin-film photoluminescence (PL) of poly(fluorene) derivatives. Electroluminescence (EL) spectra (c) are from PLEDs with the general device structure: ITO/PEDOT:PSS/emissive polymer/Ba/Al. The inset shows digital photographs of operating PLEDs.

state thin films (Figure 4b). Starting with PL, PFT peak emission was found to red-shift relative to PF due to decreased band gap, and both samples showed band broadening and red-shifting when in the solid films, as expected from the likely formation of lower energy aggregate states. However, a much more significant red-shifting of emission was observed when o-carborane was incorporated into these samples. This much lower energy emission (shifted by approximately 140 nm) is clearly not a result of reduced band gap. If anything, a higher energy blue-shifted emission might be expected given the larger HOMO/LUMO gap discussed above. The exact nature of this red-shifting is still a subject of much interest but seems likely due to energy transfer or formation of low energy aggregate structures. Furthermore, both carborane-containing polymers counterintuitively showed blue-shifted emission in the solid state compared to the solution state. We had previously observed this effect with PF-o-carb,[4c] and its observation in

PFT-o-carb now confirms that it is a direct consequence of the incorporation of the carborane cage. Since the solid state PF-o-carb emission peak at ~520 nm corresponds nicely to known low-energy green emissive modes of poly(fluorene) homopolymer,[12] we attribute its cause to forced aggregation of adjacent fluorene segments.

Polymer light-emitting diodes (PLEDs) were fabricated from each of the polymers with the general device architecture of ITO/PEDOT:PSS/(emissive polymer)/Ba/Al. To our knowledge, these are the first reported opto-electronic devices with carborane directly incorporated into the emissive conjugated network. Figure 4c shows the electroluminescence (EL) of these devices which is comparable to the PL of the polymer films, again showing large red-shifting of PF-o-carb and PFT-o-carb emission compared to the polymers without carborane. Peak EL emissions for PF-o-carb and PFT-o-carb surprisingly correlate more closely with the peak *solution* PL than the peak *thin film* PL (numerical data shown in Table S8, SI). These results are a continued source of interest to us.

Current density—voltage—luminance (J—V—L) data for the PLEDs are shown in Figure 5. We quickly observed that PLEDs using the carborane-containing polymers required much higher voltages to turn on, while PF and PFT each showed visible electroluminescence at a respectable applied bias of 4 V. In contrast, PLEDs made from PF-o-carb and PFT-o-carb required over 10 V to observe any emission. We explain the increased turn-on voltage by considering the long-known behavior of decreased device performance with misaligned energy levels.[13] For PF and PF-o-carb, the work function of the Ba cathode (2.5 eV) aligns much more closely with the PF LUMO (2.46 eV) than with the PF-o-carb LUMO (2.27 eV). Thus electrons are more easily injected into PF than PF-o-carb, leading to the large observed difference in J—V—L behavior between the two. The difference in J—V—L behavior between PFT and PFT-o-carb is not as pronounced due to LUMO levels (2.46 and 2.66 eV, respectively) that are both relatively close to the Ba work function. The larger barrier for electron injection into PFT-o-carb correlates to the observed J—V—L curve. Even so, the brightness of the carborane-containing PLEDs is low (especially for PFT-o-carb), and more detailed photophysical studies would likely provide further insight into the charge injection and recombination behavior of these polymers.

A brief study of device-level charge carrier behavior was then conducted by fabricating bottom-contact thin film transistors
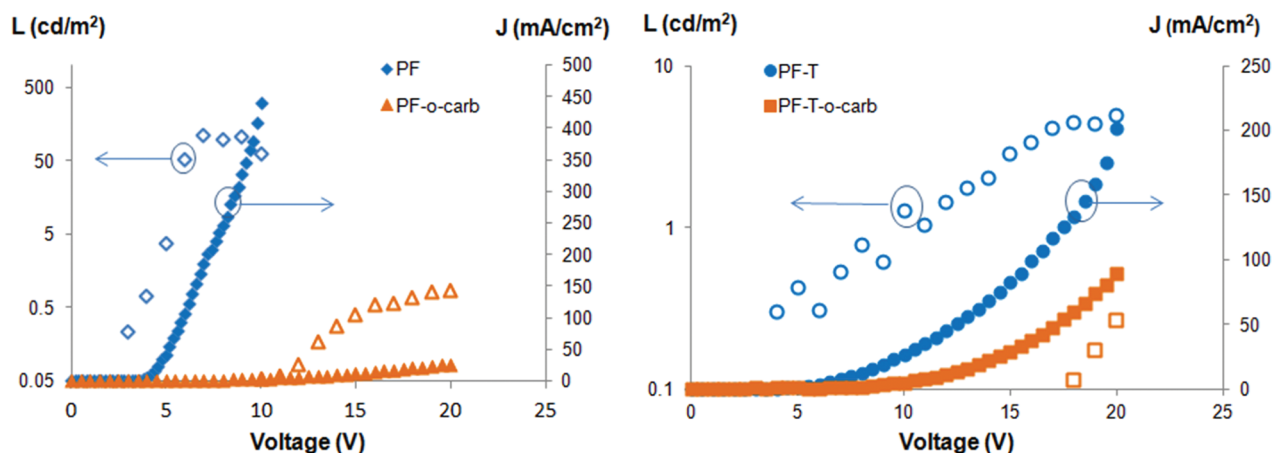

Figure 5. Current density—voltage—luminance (J—V—L) curves for poly(fluorene) derivative PLEDs.

(TFTs) from PFT and PFT-*o*-carb (Figure S9, SI). The devices are clearly not optimized, as evidenced by large threshold voltages and low on/off current ratios, but the comparison between the two identically prepared systems is still insightful. Field-effect hole mobilities were then calculated in the saturation regime. The calculated hole mobility of the PFT-*o*-carb TFT (1.5×10^{-5} cm^2 V^{-1} s^{-1}) was found to be an order of magnitude greater than that of the PFT devices (1.2×10^{-6} cm^2 V^{-1} s^{-1}), and I_{on}/I_{off} also increased (~ 70 and ~ 20, respectively). While this result was not initially expected, given the evidence that carborane cages disrupt extended π-conjugation, it may be that the geometric effects of the carborane cage improve efficient packing of the conjugated segments. The suggestion from the luminescence data is that the *o*-carborane moiety could force aggregation in the polymer chains which may be causing the improved charge carrier transport in these TFTs. The exact nature of PFT-*o*-carb chain alignment and packing is a subject of continued research. Given the relatively sensitive nature of TFT current to external stimuli (i.e., current can change by orders of magnitude with small changes in gate voltage or active layer morphology), this initial evidence that carborane does not degrade TFT performance is encouraging for the future of high sensitivity carborane-based sensing and detection applications.

By incorporating *o*-carborane directly into the conjugated backbone of two different semiconducting polymer systems (PF and PFT), we have achieved further insight into the effect of the cages' effect on conjugated polymer systems. The cages were shown to clearly disrupt extended π-conjugation along the polymer chain, as evident by CV and UV−vis analysis, with band gaps of fully polymerized carborane polymers effectively identical to their corresponding dimers. Very large red-shifting of the polymer emissions upon carborane incorporation suggests the existence of a still unidentified low energy excimer or charge transfer state. Furthermore, we have demonstrated the first reported electronic devices (PLEDs and TFTs) made from conjugated polymers incorporating carborane directly in the polymer backbone. Their successful use in current-carrying applications is particularly promising for the development of more sensitive carborane-containing sensors. We anticipate that future studies will uncover more details of the packing and aggregation behavior of these carborane-containing polymers.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures for polymer synthesis and characterization, device fabrication, and additional characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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