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COMMUNICATION TO THE EDITOR

Carborane-Containing Polyfluorene: *o*-Carborane in the Main Chain

Joseph J. Peterson, Mathias Werre, Yoan C. Simon, E. Bryan Coughlin,* and Kenneth R. Carter*

Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003

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Icosahedral carboranes have been investigated for their thermal stability, chemical resistance, unique geometry, and the high neutron capture cross-section of the ^{10}B nucleus.[1,2] Whereas carboranes have been widely incorporated into small molecules, metal complexes, and polymer systems,[3−6] relatively little work exists relating their unique properties to systems with extended conjugation. The incorporation of carborane cages into the conjugated backbone of semiconducting polymers may provide a unique perspective into the behavior of these boron cages, and the properties they impart could lead to new classes of hybrid organic−inorganic conjugated systems for polymer-based electronics. Derivatives of the icosahedral carborane cages ($C_2B_{10}H_{12}$) are thermally and chemically stable. They have somewhat nontraditional bonding structures, with three-center $2e^-$ bonds,[1] creating extremely electron-deficient cage systems that possess aspects of σ-aromaticity, making them attractive targets for incorporation into conjugated polymeric systems. The C−C bond of *o*-carborane is particularly interesting in that it presents itself as an unusual bond displaying both σ- and π-characteristics.[7] A small number of previous reports have discussed the incorporation of carboranes into conjugated polymer systems including pyrroles[8] and thiophenes,[9] polyphenylenes,[10] and polyfluorenes.[11,12] Recently, work by Chujo and coworkers described the introduction of *o*- and *m*-carborane into the backbone of phenylene−ethynylene-based polymers and showed that the boron cages interacted with the aromatic π-conjugation and influenced emission properties.[13] They reported that the incorporation of *o*-carborane induced aggregation-based emission resulting from its unique geometry, whereas the variable C−C bond acted to quench photoluminescence from the phenylene−ethynylene segments.[13] In this communication, we report the synthesis of polyfluorene with *o*-carborane in the backbone. Polyfluorenes have been widely investigated as active materials for polymer light-emitting diodes, sensors, and detector applications,[14,15] including examples of boron-containing polyfluorene systems.[16] This body of knowledge makes polyfluorene-based conjugated polymers an ideal platform for studying the influence of carborane cages. In addition to extending the conjugation length of the aromatic segments and promoting aggregation-based emissions, the *o*-carborane cages were found to influence the photoluminescence behavior of polyfluorene greatly; the incorporation of *o*-carborane gave rise to a new lower energy emission in addition to the blue fluorene emission and green aggregation emission. Photoluminescence changes observed after chemically disrupting the carborane cage structures gave direct insight into their interactions with the fluorene segments and could pave the way toward carborane-conjugated polymer hybrid materials for devices.

The synthesis of the *o*-carborane fluorene monomer **M1** began with the synthesis of 2-bromo-7-iodo-9,9-dihexylfluorene. Fluorene was first brominated with 1 equiv of *N*-bromosuccinimide to give 2-bromofluorene, which was subsequently iodinated using iodine and potassium iodate in acidic media to yield 2-bromo-7-iodofluorene. Alkylation with 1-bromohexane was accomplished through deprotonation with sodium hydroxide in DMSO, aided by a phase-transfer catalyst to give 2-bromo-7-iodo-9,9-dihexylfluorene, **1**. A Sonogashira coupling of **1** to trimethylsilylacetylene gave a TMS-protected ethynylfluorene, **2**. A facile deprotection of the acetylene with potassium hydroxide in methanol/THF gave **3** nearly quantitatively, which was then coupled to a second equivalent of **1**, again using a Sonogashira coupling to obtain 1,2-bis(7-bromo-9,9-dihexyl-9*H*-fluoren-2-yl)-ethyne, **4**. Following a literature precedent,[17] we reacted the adduct of decaborane and dimethylsulfide with our acetylene **4** to form, in situ, the *o*-carborane monomer **M1**. (Scheme 1) The closing of the cage to obtain *o*-carborane monomer **M1** proceeds in modest yields of ∼45%. With an overall yield of ∼12% (seven steps), the synthesis of **M1** can be carried out on a multigram scale with little difficulty.

Polymerization of **M1** was performed following the widely used Ni(0) dehalogenative Yamamoto-type polymerization.[18] Using bis(1,5-cyclooctadiene)nickel(0) (Ni(COD)$_2$), bipyridine, and 1,5-cyclooctadiene (1,5-COD) in a mixture of toluene and dimethylformamide (4:1), **M1** was polymerized to the *o*-carborane polymer **P1**. Kokado and Chujo's recent work on *o*-carborane systems described difficulty in forming high-molecular-weight polymers, possibly because of the bent conformation of *o*-carborane monomers.[13] Similarly, the polymerization of **M1** did not display typical fluorene polymerization behavior and tended to give lower MW products ($M_n \approx 2.4-10$ kg/mol) with multimodal distributions, as shown in GPC. Thermal analysis of the polymerization product showed a T_g of 128 °C. Interestingly, a sharp, low-MW peak was observed in the GPC at the same elution volume for several different reactions. To investigate the nature of the polymerization, we initiated a short trial to observe the effects of heating conditions and concentration. (See the Supporting Information.) We found that reaction temperature had little effect on the polymerization, as monitored by GPC. Microwave heating, previously shown to improve some Yamamoto polymerizations,[19] also appeared to have little effect on the reaction. We hypothesized that the low-MW species might be the result of intramolecular effects due to the kinked, hindered conformation of the *o*-carborane monomer. To test this, we ran the polymerization at various concentrations. The GPC traces showed a decreased intensity of the low-MW peak and a significant increase in higher MW fractions with increasing concentration, although the complete elimination of the low-MW peak was not achieved. The addition of a comonomer should serve to reduce the number of chain ends being hindered during polymerization as a result of the monomer geometry; copolymerization of **M1** with 2,7-dibromo-9,9-dihexylfluorene was found to promote higher MW fractions and reduce low-MW product formation. These results appear to indicate that the polymerization of **M1** is somehow intramolecularly limiting. We synthesized a discrete dimer, **D1**, (Scheme 2) to compare to the unknown low-MW species. The unknown species displaced a larger hydrodynamic radius than both **M1** and **D1**, as shown by

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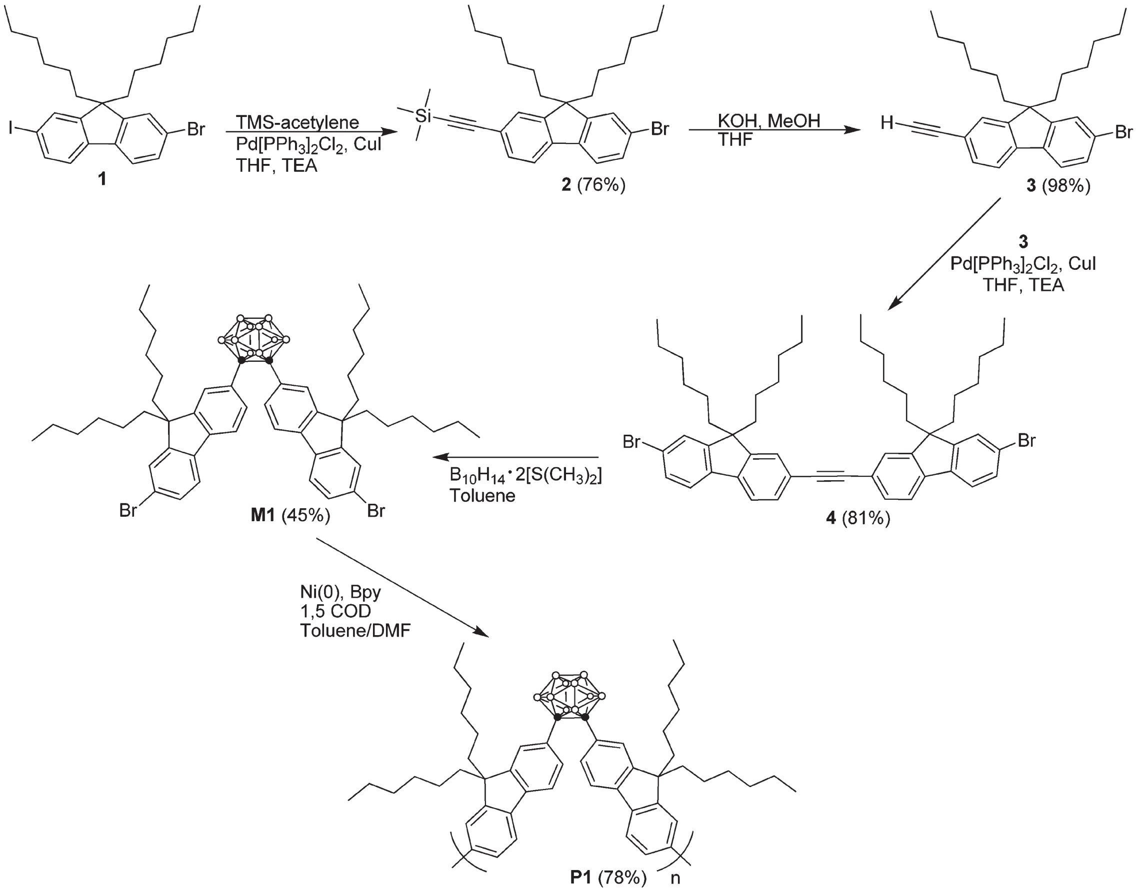
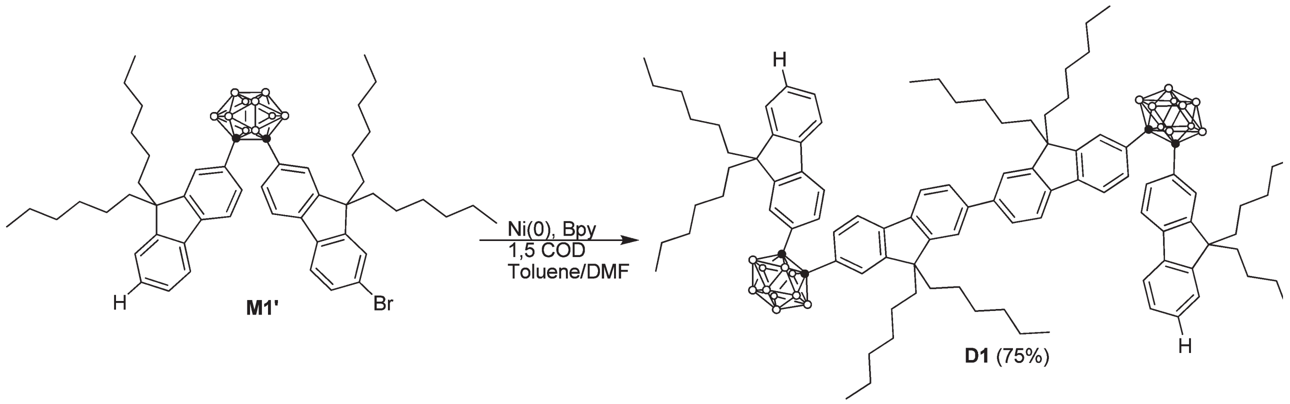
*Corresponding authors. E-mail: coughlin@mail.pse.umass.edu (E.B.C.); krcarter@polysci.umass.edu (K.R.C.).

Scheme 1. Synthetic Route to *o*-Carborane Monomer M1 and Polymer P1



Scheme 2. Synthetic Route to *o*-Carborane Dimer D1



their elution times from GPC. (See the Supporting Information.) We suspect that the unknown species may be a trimer whose ends are brought close together and are sterically hindered because of the conformations driven by the *o*-carborane linkages. On the basis of the proposed mechanism of the Yamamoto polymerization, which requires a disproportionation between two aryl–nickel species, a bent monomer structure should be less reactive toward polymerization. It may be possible that this situation promotes cyclization into macrocycles, because these have been reported for both fluorene- and carborane-based systems,[20–22] but we cannot yet rule out simple impedance due to conformational crowding on the basis of our data, and further study into this topic is ongoing. In either case, the polymer and the discrete dimer provide sufficient conjugation lengths to observe any effects the *o*-carborane may have on the optical behavior of the material.

The wide interest in polyfluorenes as a luminescent material provides a path for investigating the influence of the carborane cages; there exists a large body of previous work on the fluorescence and UV–vis spectroscopy of fluorenes with which to compare our materials.[23] We observed that the incorporation of *o*-carborane caused a 30 nm bathochromic shift in the fluorescence emission and a 14 nm shift in the UV absorption compared with a dihexylfluorene dimer, the repeat structure between the cage units. This suggests that the incorporation of carborane is extending the conjugation length of the fluorene segments between the cages (Figure 1). A red shift upon incorporation of carborane into a conjugated system is consistent with

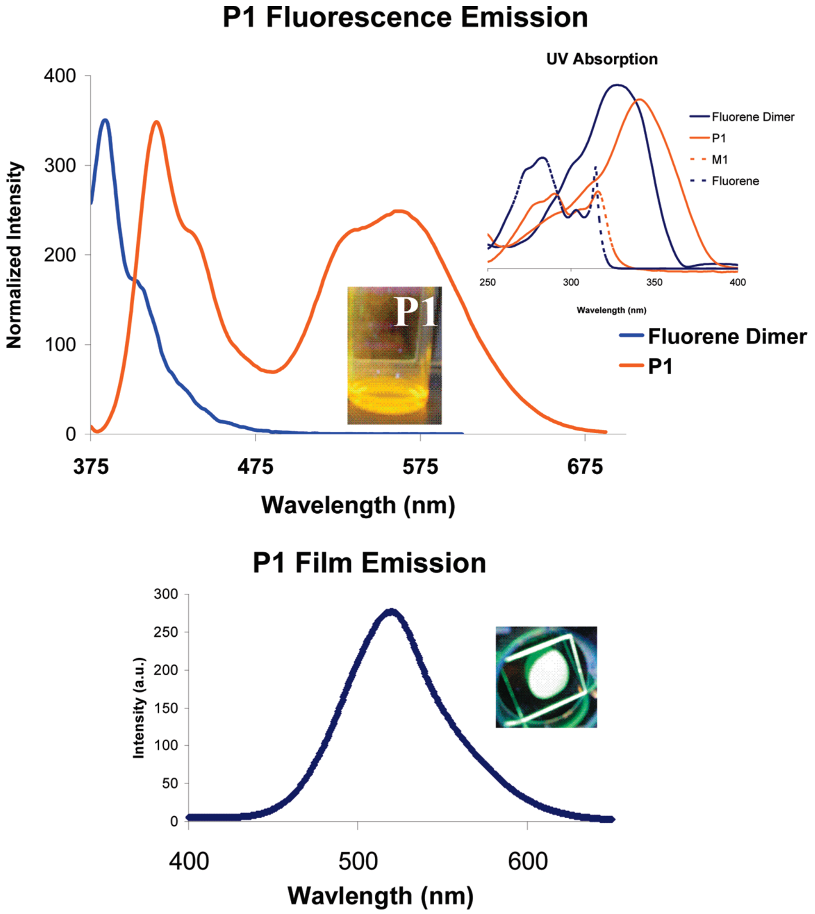


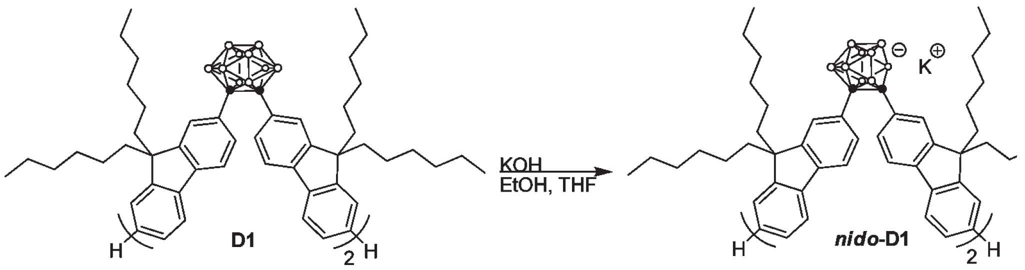
Figure 1. Top: Solution fluorescence in $CHCl_3$ of *o*-carborane polymer **P1** and a dimer of dihexylfluorene for comparison. Inset shows the UV absorption of the *o*-carborane polymer **P1** and a fluorene dimer for comparison. Bottom: Film fluorescence of **P1** film. The dimer **D1** shows a similar solid-state emission.

the recent reports on *o*- and *m*- carborane in phenylene−ethynylene systems.[12]

Perhaps more interesting, the incorporation of *o*-carborane into both the dimer **D1** and the polymer **P1** gave rise to new lower energy emissions in the solution fluorescence spectrum in the region of 565 nm in addition to the blue emission from the fluorene units, resulting in a solution that appeared orange under UV irradiation (Figure 1). This behavior is similar to that reported for other polyfluorene structures containing conjugated, electron-withdrawing groups such as benzothiadiazoles, in which energy absorbed by the fluorene units is transferred to the electron-withdrawing groups and emitted at a lower energy.[24] The solid-state spectrum of **P1** displays a single well-defined green emission centered around 520 nm. (Figure 1) Whereas this is also observed in fluorene copolymers with electron-withdrawing groups because the efficiency of energy transfer increases as the chains are packed closer together, this new single peak is also in the same region that green emissions are commonly observed for annealed polyfluorene films that are thought to be due, at least in part, to excimer formation due to aggregation.[15,24] The recent report of aggregation-induced emission (AIE) of conjugated *o*-carborane backbone structures lends support for aggregation-induced phenomenon. In Chujo and coworkers' phenylene−ethynylene-based system, direct $\pi-\pi$ stacking was not necessary to observe AIE.[13] It is possible that in **P1**, a combination of energy transfer to the carborane units and aggregation-based phenomena between the fluorene segments is observed. Solution fluorescence excitation experiments revealed that the 565 nm emission of the *o*-carborane polymer has a peak excitation wavelength of 380 nm, whereas the peak excitation for the emission at 415 nm occurs at 390 nm, with significant overlap of the two. Additionally, the monomer **M1** showed no lower energy fluorescence emission. This suggests that the *o*-carborane segments are likely being excited through an energy transfer process rather than being directly excited by the ~415 nm emission of the fluorenyl units. Regardless, the solution spectrum of the *o*-carborane polymer in chloroform suggests that *o*-carborane is in conjugation with the backbone system, or at least strongly affecting its behavior. The solid-state green emission was also found to be thermally stable; after annealing in air at 180 °C for 2 h, the films showed no shift in the emission wavelength and actually increased in intensity, which is likely a result of increased aggregation from rearrangements above T_g. Spectral stability and lifetime are important for light-emitting applications, and the incorporation of carborane may be one route toward generating more spectrally stable active materials.

Finally, the effects of cage degradation on our conjugated system were explored. We hypothesized that if the cages were in direct conjugation with the polymer backbone, then changes in the cage bonding structure should directly affect the properties of the polymer system. Whereas carboranes are generally thought to be chemically and thermally stable species, *o*-carborane is susceptible to nucleophilic bases, which open the cage to the anionic *nido*-species (Scheme 3). With this in mind, the *o*-carborane dimer **D1** species was exposed to hydroxide ions in an ethanol/THF mixture, and the fluorescence was monitored. We observed a decreasing intensity of the peak near 570 nm and a simultaneous large increase in intensity near 430 nm with increasing concentration of hydroxide ions, visibly changing the fluorescence from orange to bright blue. (Figure 2) The formation of *nido*-cage

Scheme 3. Partial Cage Degradation to the *nido*-Dimer



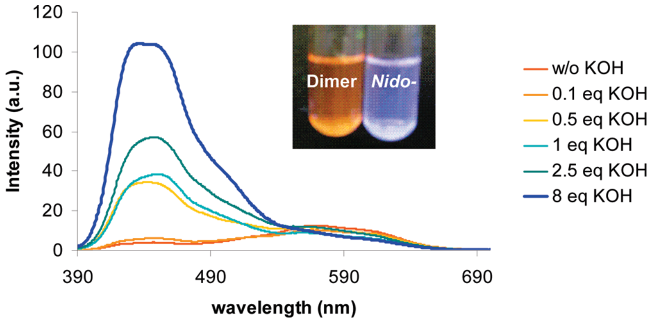


Figure 2. Solution fluorescence in EtOH/THF of *o*-carborane dimer **D1** treated with increasing amounts of KOH to degrade the cages to the *nido*-species.

species can be observed in NMR by the proton bridging the borons on the open face of the cage, giving rise to a signal at -1.5 ppm relative to TMS.[25] (See the Supporting Information) Whereas it has been shown that the introduction of ionic species to the structure of polyfluorene can alter color and properties,[26] we observed that even after neutralization of the anion, the fluorescence spectra of the *nido*-species remained virtually unchanged. This would suggest that the observed intensity changes are due to the changing bonding structure of the cage and not simply the introduction of charged species to the system. Whereas others have reported small wavelength shifts upon cage opening in luminescent species,[25] the dramatic changes observed upon cage opening in this work clearly point to strong electronic interactions between the *o*-carborane cages and the conjugated fluorene segments in the polymer. Interestingly, when the *nido*-species solutions were drop cast into films, the characteristic green color returned when placed under UV light. This may be further evidence of multiple influences on fluorescence being at work; whereas the conjugation with the cage appears to influence the solution fluorescence, enhanced aggregation due to the bent structure of the backbone may remain dominant in the solid state even after cage opening begins to disrupt the emission resulting from energy transfer to the electron deficient cage units.

In conclusion, we have synthesized a new *o*-carborane-containing fluorene monomer and polymerized it to create a conjugated hybrid carborane−fluorene polymer. The nature of the polymerization of the *o*-carborane fluorene monomer was investigated and found to be self-limiting, most likely because of its bent conformational structure. The incorporation of *o*-carborane contributed to the conjugation of the system and gave rise to a new lower-energy emission in the solution state. In the solid state, the *o*-carborane materials are stable pure-green emitters. The degradation of the *o*-carborane cages was found to influence the solution fluorescence spectra significantly, leading to the conclusion that the bonding structure of the cage can directly influence the conjugation of the polymer system. The incorporation of carborane into the backbone of conjugated polymers provides an important route to new materials for sensors and light-emitting devices while at the same time serving as a platform for further study of the nature of carborane cages.

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Supporting Information Available: Complete experimental details and data files containing ^{1}H and ^{13}C NMR, FT-IR, DSC, and fluorescence measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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