

Polyfluorene with *p*-carborane in the backbone†

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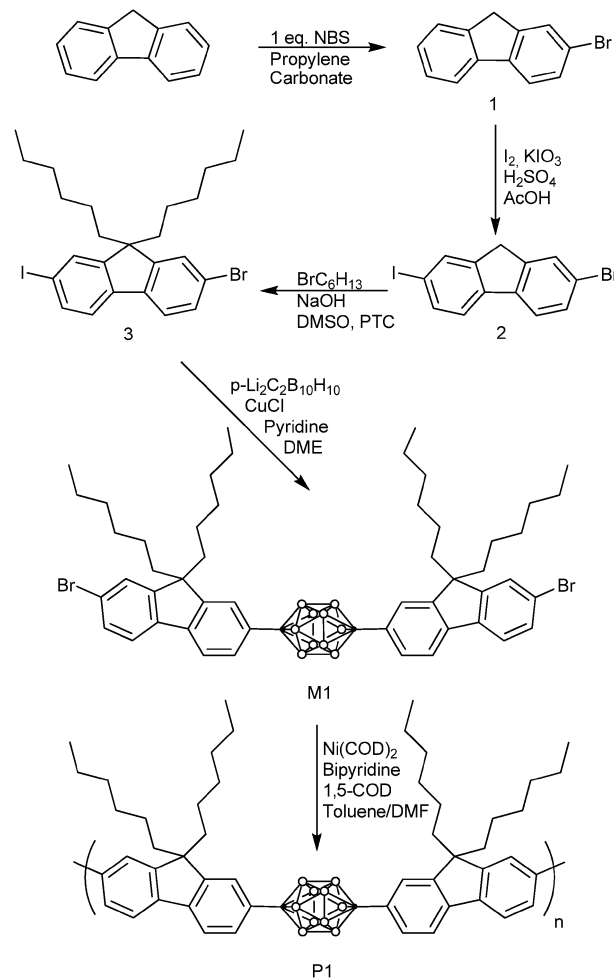
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Polyfluorene with *p*-carborane in the backbone was synthesized from the new monomer 1,12-bis(7-bromo-9,9-dihexyl-9H-fluorene-2-yl)-*closo*-1,12-dicarbodecaborane to give a high MW, soluble, blue-emitting material characterized by NMR, UV-vis, and fluorescence spectroscopy.

The incorporation of boron into conjugated polymer systems is a promising approach to improving, and tuning, materials for organic electronics. Boron atoms, with the ability to conjugate through their empty *p*-orbital, have been incorporated into side groups and backbones of conjugated systems in order to develop emissive materials and sensors.^{1–5} Carborane cages present an alternate route to incorporate boron into polymeric systems. *p*-Carborane, a C₂B₁₀H₁₂ icosahedron with carbons at opposite vertices,⁶ represents an electron deficient boron containing unit that can be incorporated into conjugated polymers without disrupting their linear rigid rod behavior. While there have been many reports on carboranes in polymeric systems, there have been relatively few examples of conjugated polymers with covalently attached carboranes in the backbone.^{7–10} Excellent thermal and chemical stability along with their electron deficient σ -aromatic bonding scheme make carboranes an attractive structural unit for use in conjugated polymers.¹¹ Blue-emitting polyfluorenes are interesting candidates for carborane incorporation because they often suffer from stability problems under device conditions¹² and may benefit from carboranes' unique properties. We report the synthesis of a polyfluorene based conjugated polymer with *p*-carborane in the backbone.

The monomer, 1,12-bis(7-bromo-9,9-dihexyl-9H-fluorene-2-yl)-*closo*-1,12-dicarbodecaborane **M1**, was synthesized as shown in Scheme 1. Fluorene was brominated, iodinated, and alkylated in three steps to give 2-bromo-9,9-dihexyl-7-iodo-9H-fluorene **3** in 45% yield. The effort to create an aryl iodide bromide rather than a dibromo species was necessary to promote the attachment of the carborane cage at the iodo-position and preserve the less active bromides for subsequent polymerization. *p*-Carborane was deprotonated using 2 equiv. of *n*-butyllithium and subsequently reacted with CuCl to give Cu₂[C₂B₁₀H₁₀] which was stabilized with pyridine and reacted with two equivalents of **3** in an Ullmann-type coupling to give the monomer **M1** in 10% yield.¹³ The structure was confirmed by ¹H NMR, where the characteristic broad carborane B–H signals were observed



Scheme 1 Synthesis of *p*-carborane monomer **M1** and polymer **P1**.

from δ 1.4–4.1 ppm, and by ¹³C NMR where the carbons residing at the 1,12 cage positions give a single resonance at δ 83.21 ppm. High resolution mass spectrometry gave final structure confirmation. The yield in the final step may be a consequence of the poor solubility of the copper species and the hindered nature of the fluorene–carborane coupling partners.

Polymerization of **M1** was accomplished using a Yamamoto-type Ni(0) dehalogenative polymerization as shown in Scheme 1.¹⁴ The polymerization was carried out in a mixture of toluene–DMF (4:1) under an inert atmosphere for 24 h. ¹H NMR of the polymer matched the expected structure and FT-IR showed B–H stretches at \sim 2600 cm^{–1} in addition to the aromatic and aliphatic C–H signals. The polymer product was soluble in chloroform, THF, and toluene. The molecular

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weight was found to be 50 kg mol^{-1} with a PDI of 2.3 by GPC (THF vs. PS standards), typical of step growth Ni(0) polymerizations of aryl bromides. Differential scanning calorimetry showed a glass transition temperature (T_g) of $137 \text{ }^\circ\text{C}$ compared to $102 \text{ }^\circ\text{C}$ for poly(dihexylfluorene) of similar MW and synthesized under analogous conditions. In addition to a T_g , an exotherm was noted on the first heating cycle at $215 \text{ }^\circ\text{C}$, possibly as a result of the formation of a new crystalline state.

Previous reports on *p*-carboranes suggest that there may be some electronic communication between the carbon centers in *p*-carborane, though data suggest that it is not truly conjugated in the traditional sense.¹⁵ To help investigate the behavior of **P1**, we used small molecule analogs of the fluorene units in our materials. To represent the fluorene units in the monomer **M1**, we chose a dibromodihexylfluorene molecule to mimic the structure on either side of the carborane cage. For the polymer, which has a repeat structure of a carborane cage followed by two fluorene units, we synthesized a discrete dimer of dihexylfluorene to represent the two fluorene units between each carborane cage along the backbone.

The polymer was photoluminescent under UV light, giving a bright blue emission. Fluorescence spectroscopy in chloroform revealed a peak emission at 400 nm for **P1**, a 15 nm bathochromic shift compared to the fluorene dimer. (Fig. 1) A 20 nm bathochromic shift was observed in the UV

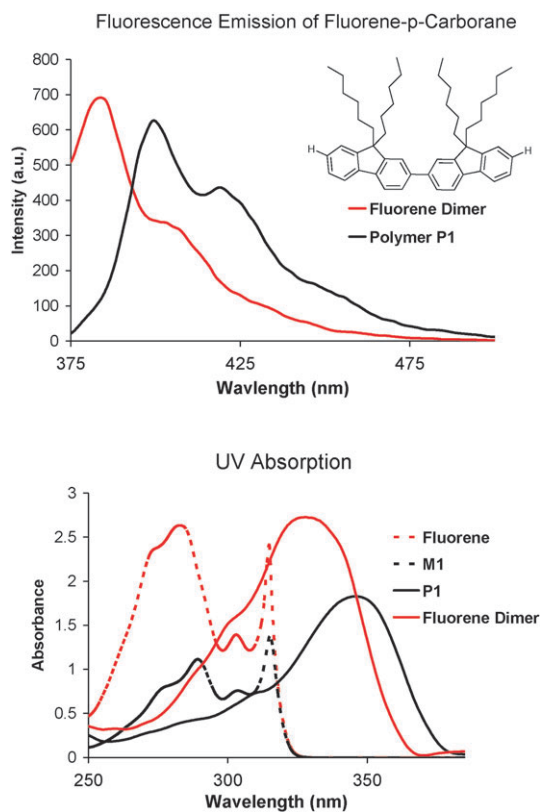


Fig. 1 Fluorescence (top) of **P1** and a dihexylfluorene dimer and UV-vis (bottom) spectra of dihexylfluorene, **M1**, a dihexylfluorene dimer, and **P1** in CHCl_3 solutions. Excitation λ for fluorescence was 350 nm .

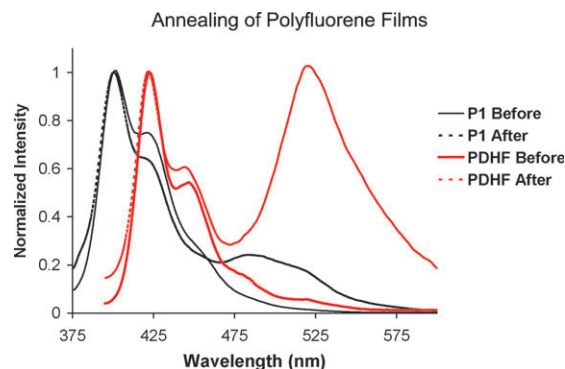


Fig. 2 Fluorescence spectra of **P1** before and after annealing in air at $180 \text{ }^\circ\text{C}$ for 2 h, and poly(dihexylfluorene) before and after annealing in air at $150 \text{ }^\circ\text{C}$ for 1 h. Excitation λ for fluorescence was 365 nm .

absorption of the polymer **P1** compared to the fluorene dimer, while the monomer **M1** and a single fluorene unit display strikingly similar absorbances (Fig. 1). The UV and fluorescence peaks would be expected to red-shift with an increase in the effective conjugation length in polyfluorene systems.¹⁶ The observed shifts in the UV absorption and fluorescence emission indicate that the *p*-carborane cages are extending the conjugation length of each fluorene dimer unit of the polymer backbone. Recent work on conjugated polymers containing *m*-carborane in the backbone suggests that, while the carborane cages extended the conjugation length of the aromatic units between the cages, there was little conjugation between the aromatic segments through the cages.^{9b} Similarly, the shifts observed for **P1** could be due to the electron deficient nature of carboranes and some extension of the aromatic conjugation into the cages, but the similarity of **M1** to a single fluorene unit in the UV spectra suggests that the carborane cage limits effective conjugation between the fluorene segments.

Nevertheless, the excellent thermal properties of the carborane cages impart stability to the polyfluorene structure. Previously we have shown that pendant carborane cages improve the thermal stability of polyfluorene, increasing T_g and spectral integrity during annealing.¹⁷ Annealing studies on films of **P1** showed a minimal rise in green emission after heating to $180 \text{ }^\circ\text{C}$ in air for 2 h. This is in marked contrast to poly(dihexylfluorene) which shows a pronounced green emission after heating to $150 \text{ }^\circ\text{C}$ for only an hour. (Fig. 2) The carborane cages act to effectively suppress the green emission that commonly plagues blue-emitting polyfluorene systems, due in part to aggregation based excimer formation. Color stable blue emitters are crucial for polymer LED's as performance and lifetime could limit their wide adoption compared to traditional display materials.

In summary, we have synthesized a new carborane containing fluorene monomer and successfully polymerized it to provide a polyfluorene based polymer with *p*-carborane directly in the conjugated backbone. The *p*-carborane cage acts to increase T_g and thermal properties while still being solution processable, creating a stable blue-emitter that has potential applications for light emitting devices and sensors.

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