

Carborane-Containing Poly(fluorene): Response to Solvent Vapors and Amines

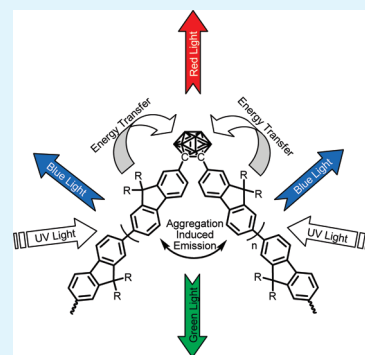
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S Supporting Information

ABSTRACT: Hybrid conjugated polymers containing carborane directly bonded in the aromatic backbone repeat structure have interesting electronic bonding structures and are potentially useful new materials in organic electronics. Conjugated polymers based on *o*-carborane are particularly interesting for applications in sensing and detection because of the cage's unique bonding scheme and its bent geometry. Poly(fluorene) containing *o*-carborane displays multiple emission pathways that can be modulated through interactions with small molecules. In this paper, we report that films of poly(fluorene) with *o*-carborane in the backbone function as vapochromatic photoluminescent sensors toward volatile organic molecules.

KEYWORDS: Carborane, poly(fluorene), solvatochromism, fluorescence, conjugated polymer, sensors



INTRODUCTION

Conjugated organic systems containing boron are interesting as emissive materials and active materials for sensors and devices.¹ Boron has been incorporated into many conjugated and fluorescent systems and shows excellent potential for tuning the behavior of the materials.^{2–6} Incorporation of boron atoms has also been shown to be effective in modulating the emissive behavior of conjugated polymers based on their response to chemical species. Chemosensitive behavior has been described previously for several boron containing conjugated polymers: poly(fluorene) has been combined with boron to show sensitivity to fluoride ions,⁷ and a thiophene-based, boron-containing polymer has recently been shown to be sensitive to the vapors of certain amines.⁸ Carboranes are another approach toward boron-containing conjugated polymers, and the literature shows a surge in current research activity on these materials.^{9–13} The C₂B₁₀ cages provide interesting building units for conjugated systems, due to their unique electronic structure and geometry. Recently we described the synthesis of poly(fluorene)s containing *p*- and *o*-carborane in the conjugated backbone.^{14,15} Incorporation of *o*-carborane into poly(fluorene) imparted new emissive behavior. Based on these previous results, we hypothesized that the unique behavior of the *o*-carborane polymer system could be harnessed as a sensor or detector. The *o*-carborane system provides a unique system in which several possible routes toward sensing are available in a single material. Three potential emissive modes were observed to be possible with the *o*-carborane conjugated polymer in previous studies.¹⁵ (Figure 1) Under UV excitation of dilute polymer solutions in chloroform, typical blue emission was observed from the fluorene segments near 420 nm, a green emission from aggregation-induced phenomena between fluorene segments was observed near 525 nm, and a lower energy orange/red

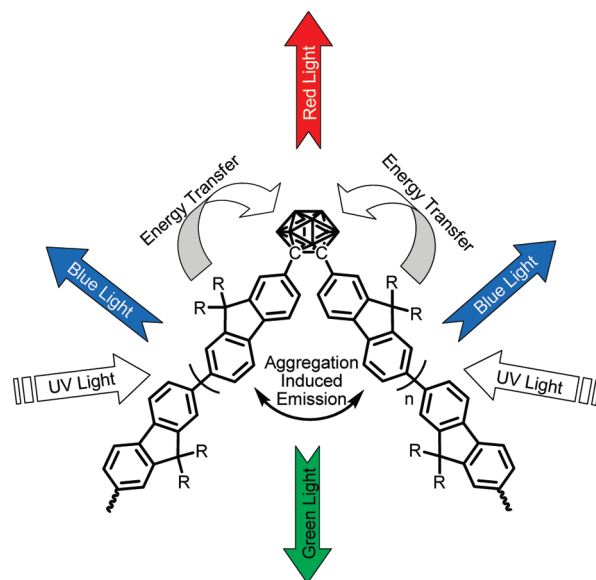


Figure 1. Repeat structure of the *o*-carborane poly(fluorene) and the possible photoluminescence pathways upon excitation of the fluorene segments with UV light. Cage vertices represent boron atoms, with hydrogens omitted for clarity. R = *n*-hexyl.

emission was observed near 570 nm (see the Supporting Information). Modulation of these emissions using small molecules provides a new route toward conjugated polymer sensors.

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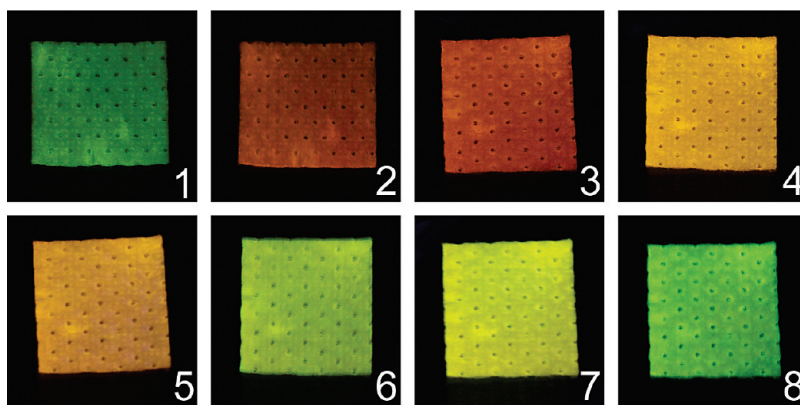


Figure 2. Optical images under UV light of the pristine polymer (1) and in the presence of tetrahydrofuran, ethyl acetate, methylene chloride, acetone, methanol, toluene, and hexanes vapors (2–8, respectively) (the polymer is coated onto squares of laboratory wipes, $\sim 2\text{ cm} \times 2\text{ cm}$).

Photoluminescence Emission During Exposure to Vapors

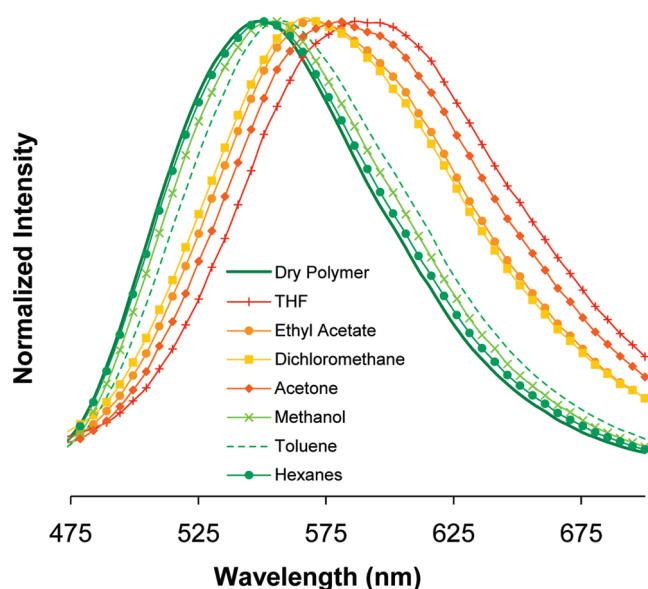


Figure 3. Photoluminescence spectra of the pristine polymer and after exposure to various vapors.

o-Caborane units can promote aggregation induced emission (AIE) in conjugated polymer systems. This has been recently described in work by Kokado et al., which focused on polymers based on an arylene–ethynylene backbone synthesized via Sonohashira couplings.^{11,16,17} Widely investigated for blue light emission,^{18,19} poly(fluorene)s are often plagued by lower energy green emissions due to aggregation and/or fluorenone defects. The problem is frequently dealt with through the use of bulky side groups or end-cappers to help prevent efficient chain packing in thin films.^{20–23} Our poly(fluorene)-based *o*-caborane polymer were found to display AIE behavior, displaying green photoluminescence in the solid state resulting from the AIE of the fluorene segments adjacent to the caborane cages.¹⁵ This phenomenon is dependent on the proximity and packing of the fluorene segments in the polymer. In solution, where solvent molecules generally help to partially suppress chain aggregation, the *o*-caborane units in our polymer can also give rise to lower energy orange/red emissions, likely a result of energy transfer

Emission During Solvent Exposure Cycles

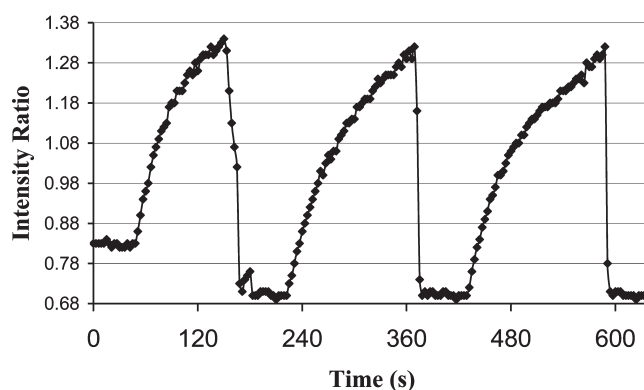


Figure 4. Ratio of the intensity of the photoemissions at 585 nm vs 550 nm over time as the sample is exposed to CH_2Cl_2 then removed from exposure.

from the excited fluorene units to the electron deficient cages.¹⁷ In the solid state, a green AIE appears to be dominant, suppressing other emissions. This opens the door to sensor behavior.

EXPERIMENTAL SECTION

All solvents and reagents were reagent grade, purchased from commercial sources, and used as received. Poly(fluorene-*o*-caborane) was synthesized as previously described.¹⁵ The polymer was reprecipitated from THF into methanol three times and dried under vacuum for 24 hrs. For solid sample vapor exposure, an $\sim 2 \times 2\text{ cm}$ square of a composite laboratory wipe (thermally bonded polypropylene and cellulose, ITW Texwipe Betawipes TX 2009) was dipped in a 0.5 mg/mL methylene chloride solution of the polymer and dried under a stream of nitrogen to yield a polymer impregnated sample that fluoresced green under UV light. The sample was then placed in a Petri dish on an angled microscope slide so that the sample was not in contact with the bottom of the dish. One mL of the organic solvent or amine was then placed in the bottom, and the dish was covered with a lid. After 5 min, the sample was irradiated with UV light from a hand-held lamp while an optical picture or fluorescence spectrum was taken through the Petri dish lid.

For fluorescence spectra, samples were irradiated with 365 nm UV light from an Entela UVGL-25 and the emission was recorded with an Ocean Optics USB4000 UV–vis spectrometer. Optical images were taken under using an Olympus E-420 digital camera.

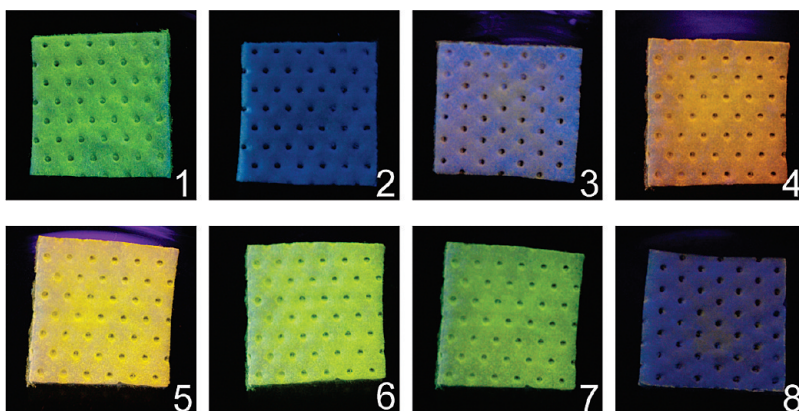


Figure 5. Emission under UV light of the pristine polymer (1) and in the presence of triethylamine, diisopropylamine, *n*-butylamine, pyridine, DBU, aniline, and piperidine (2–8, respectively) (the blue color is the observed color of the composite wipe under UV light, not an emission from the fluorene segments).

RESULTS AND DISCUSSION

If the emissions can be moderated through interactions of small molecules with the polymer in the solid state, then the lower energy emissions may become competitive with the green AIE and lead to a color change. Indeed, the *o*-carborane poly(fluorene) in the solid state was found to undergo a shift in its emission wavelength upon exposure to organic solvent liquid or vapors, changing from bright green to shades of yellow, orange or red under UV light depending on the vapors. The shift appears to correlate most closely to the polarity of the solvent, with more polar solvents producing greater red-shifts, similar to solvochromatic shifts observed for fluorescent molecules in the solution phase.^{17,24} Exposure to the vapors also appeared to decrease emission intensity and is likely related to the fact that the AIE of *o*-carborane systems can be quenched to a large extent in solution^{17,25} (see the Supporting Information). To illustrate this phenomenon, we fabricated a simple test “sensor” by coating the polymer onto small squares of laboratory wipes by dip coating. Coated onto the substrate, the polymer fluoresced at 550 nm under a hand-held UV longwave lamp. The solid state samples of the polymer were then exposed to a number of solvent vapors. (Figure 2, 3) The various solvents affected a range of color changes on the emission of the polymer, which was monitored using a portable spectrometer.

Upon exposure to ambient air, the samples regained their previous green emission as the vapors dissipated and could be used repeatedly with different solvents without any apparent negative effects. As an example, a plot of the intensity ratio of the photoemissions at 585 nm vs 550 nm as a sample is exposed to dichloromethane illustrates the time scale at which these changes are occurring (Figure 4). Color changes can be observed with the naked eye after several seconds and saturate after several minutes. Upon removal of the sample from solvent vapor exposure, the color returns quickly to its original green emission in ~1–2 s.

The unique electronic nature of the carborane cage structure might also be utilized for sensing behavior through its influence on the conjugated polymer backbone. Carboranes possess aspects of σ -aromaticity and can interact with π -conjugated systems. *o*-Carborane cages can be opened to the *nido*-species through deboronation by nucleophilic bases, commonly ethanolic hydroxide solutions, amine bases, and fluoride ions.^{26,27} Opening of the cages by deboronation disrupts the 3D aromaticity

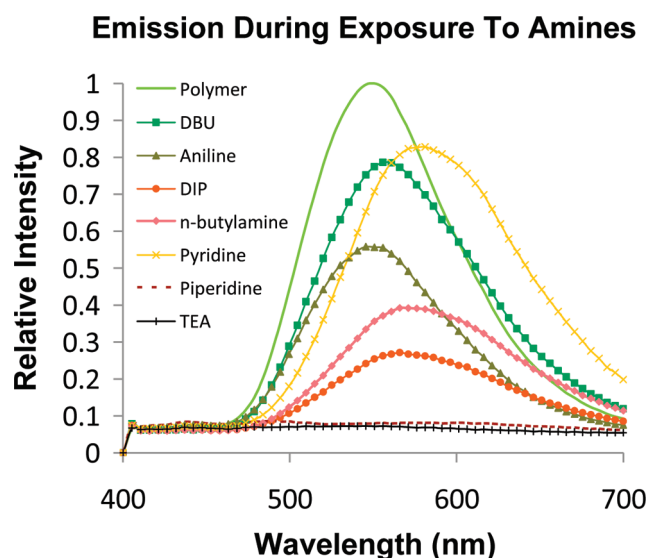


Figure 6. Photoluminescence emission of the polymer and during exposure to amine vapors.

and directly affects the photoluminescent properties of the polymer system. In our previous studies we observed that this disruption of the 3D cage structures led to an orange to blue color change in solution.¹⁵ This was attributed to the disruption of the energy transfer from the fluorene segments to the carborane cages; with the cage effects moderated and solvent molecules helping to suppress aggregation, the fluorene segments were then able to emit in the blue.

However, for sensor applications it is probably not desirable, or necessary, to completely open the cages via deboronation using such harsh conditions. Other reported sensor systems utilize boron in conjugated polymers,⁸ under the principle that the Lewis acidic boron atoms influence the conjugated polymer, and can in turn be influenced by Lewis basic molecules interactions with the empty p-orbital. Although the *o*-carborane cages cannot interact via empty p-orbitals, amines are known to react with the cages during deboronation reactions.²⁶ This is thought to occur via the amine attacking the boron adjacent to the C–C bond, which is the most electron deficient. There has been some postulating on whether or not some initial amine adduct is

formed during these reactions which might influence the polymer system.^{28–31} When solid films of the *o*-carborane based poly(fluorene) were exposed to vapors of amines, the fluorescence emissions were red-shifted, reduced in intensity, or largely quenched, in the case of triethylamine and piperidine, which have been reported to deboronate *o*-carborane in solution reactions.²⁶ (Figure S,6) The amines appear to be able to influence the AIE, much as the solvent molecules do, and have the added possibility of further quenching the emissions.

It is interesting to note that the blue emission from the fluorene units appears to remain largely quenched. In our previous studies we found that chemically opening the cages in solution restored the characteristic blue emission from the fluorene segments. The amine sensing behavior is also quickly reversible upon removal from the vapors. It may be that the cages remain intact during the short, room-temperature exposure to amine during the experiment in which the amines only loosely interact with the cages, or there may be quenching via another mechanism.^{32,33} Further work is needed to better understand these results.

CONCLUSIONS

o-Carborane based conjugated polymers are a new and promising class of materials for sensor applications. Poly(fluorene-*o*-carborane) was shown to act as a reversible colorimetric sensor for volatile nitrogen containing molecules based on their modulation of one or more of the material's possible photoluminescence emission pathways. Exposure to common laboratory solvent vapors led to a color change in the film's emission under UV light via a disruption of the green aggregation based emission, shifting the observed color toward the red. Exposure to certain amines quenched emission completely by both disrupting the AIE and interacting with the Lewis acidic boron cages. As has been shown for other conjugated polymer sensors, the structure of the conjugated segments between the carborane cages could be tuned to promote specific interactions with analyte molecules. We foresee potential applications for carborane-based conjugated polymer sensors for detecting explosives, fissile materials, or perhaps even biological species, and work toward these applications is currently underway in our laboratories.

ACKNOWLEDGMENT

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ASSOCIATED CONTENT

S Supporting Information. Plots of un-normalized fluorescence spectra for solvent exposure, emission intensity time-course during cyclical exposure to triethylamine vapor, and fluorescence spectrum of polymer in dilute chloroform solution (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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