

Perfluorocyclobutyl-Linked Hexa-*peri*-hexabenzocoronene Networks

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In the quest for improved materials for photonics, the design and synthesis of polyaromatic systems are increasingly important considerations.¹ One such class of recent interest are hexa-*peri*-hexabenzocoronene (HBC) derivatives, pioneered by Müllen and others.^{2–4} HBCs can exhibit liquid crystalline properties and hole transport capabilities, and they can emit light over a broad range of wavelengths.

To date, substituents on HBC systems have been limited primarily to long alkyl chains or phenyl groups due to solubility and reactivity constraints. Although the synthesis of hexakisalkoxy-substituted HBCs using a monolayer precursor on Cu 111 surfaces has been reported,⁴ undesired side products result under standard oxidation conditions, which has precluded their general preparation.

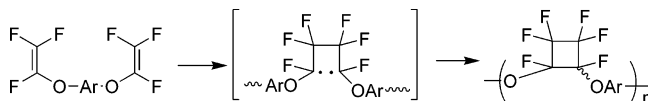
Here we report the first synthesis of a hexa-*peri*-hexabenzocoronene compound containing trifluorovinyl ether substituents able to undergo thermal cyclopolymerization and copolymerization to perfluorocyclobutyl (PFCB) networks. Polymers containing the PFCB linkage have been established for high-performance optical applications.^{5,6} Vinyl ether or perfluorovinyl ether substitutions on HBC structures were not known previously.

Trifluorovinyl ether-substituted arenes, in general, undergo thermal cyclopolymerization when heated above 150 °C to form fluorinated cyclobutyl rings, as shown in Scheme 1. These unique semi-fluorinated polymers have shown great promise as components in optical devices due to their excellent processability and transparency at telecommunication wavelengths.⁵

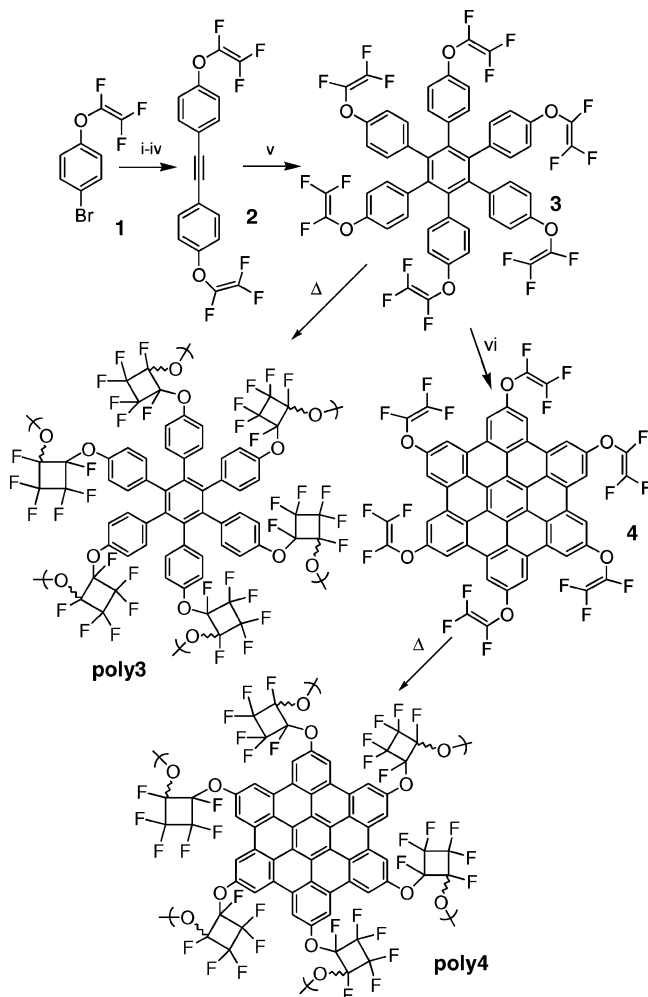
The syntheses of hexaphenylbenzenes have traditionally been accomplished by Diels–Alder reaction⁷ of tetraphenylcyclopentadienones with a diphenylacetylene or, alternatively, cobalt-catalyzed cyclotrimerization of diphenylacetylenes.⁸ Thermal sensitivity of the aryl trifluorovinyl ether group restricted our approach to the cobalt route, as shown in Scheme 2. Bromo aromatic **1** was converted to the iodo analogue and subsequently to new bisaryl acetylene **2** via Sonogashira chemistry. Hexakis intermediate **3** was obtained in 40% yield, and its X-ray crystal structure is shown in Figure 1, the morphology of which resembles that of other hexaphenylbenzene compounds.⁹

Benzene derivative **3** underwent standard oxidative ring fusion¹⁰ with FeCl₃ to give hexa-*peri*-hexabenzocoronene **4** and the first hexakisalkoxy-substituted HBC by this route. Sparingly soluble monomer **4** was characterized by MALDI-TOF-MS as similarly reported for other insoluble benzocoronenes.¹¹ The spectrum clearly indicates the loss of 12 DA from **3**. Solid-state FTIR (–OCF=CF₂, 1831 cm^{–1}) and ¹⁹F NMR (sparingly soluble in pyridine-*d*₅, δ –122.5 (dd), –129.8 (dd), –138.4 (dd)) confirmed the presence of trifluorovinyl ether substitution.¹² Modulated differential scanning calorimetry (MDSC) of **4** exhibited an exothermic peak with an onset temperature of 190 °C and a peak at 215 °C, characteristic

Scheme 1. General Cyclopolymerization to Perfluorocyclobutyl (PFCB) Polymers



Scheme 2. Synthesis of Compounds **1–4** and **Poly3** and **Poly4**^a



^a Reagents and conditions: (i) *t*-BuLi, I₂; (ii) CuI, trimethylsilylacetylene, Pd(II), NEt₃; (iii) KOH, MeOH; (iv) CuI, Pd(II), NEt₃; (v) Co₂(CO)₈, 1,4 dioxane; (vi) CH₂Cl₂, MeNO₂, FeCl₃.

of trifluorovinyl ether cyclodimerization. Disappearance of the fluoroolefin and formation of the PFCB linkage (960 cm^{–1}) were confirmed by FTIR of **poly4**. Alternatively, monomer **3** can be polymerized upon melting at 162 °C with a similar DSC profile.

The wide-angle X-ray diffraction pattern of **4** powder is shown in Figure 2. The first peak, centered at 16.7 Å, is attributed to the

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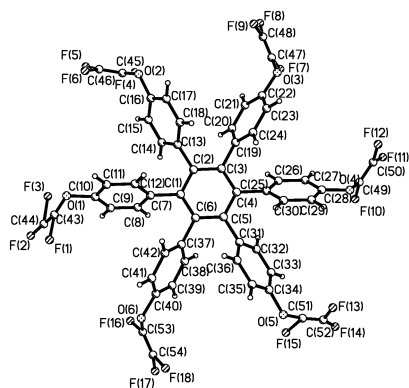


Figure 1. X-ray crystal structure of **3**.

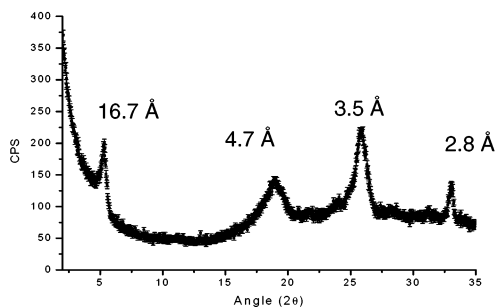


Figure 2. WAXD of monomer **4** powder.

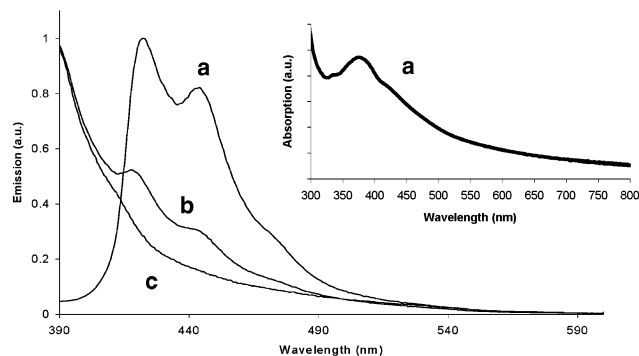


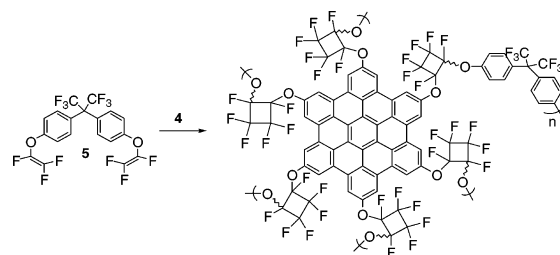
Figure 3. Emission and absorption spectra (inset): (a) **4**, (b) **poly4-co-5**, and (c) **poly5**.

molecular diameter, while the peaks at 4.7 and 3.5 Å are assigned to stacking of the vinyl ether groups and the cores, respectively.¹³ The final peak, at 2.8 Å, is assigned to the diameter of the aromatic core edge. After thermal polymerization at 150 °C for 12 h, diffraction peaks at these dimensions disappear.

A dispersion of monomer **4** (in CH₂Cl₂) exhibited an absorbance λ_{\max} at 374 nm (Figure 3, inset). The photoluminescence spectra revealed two peaks at 425 and 445 nm in addition to a plateau from 520 to 580 nm. The broad emission from 520 to 580 nm is due to excimer formation in coronene aggregates, as similarly observed for other coronene derivatives.¹⁴ Filtration of the dispersion and subsequent fluorescence measurements resulted in disappearance of the plateau peak; however, the peaks at 425 and 445 nm remained as the true solution fluorescence of monomer **4** (Figure 3a), as similarly observed for unsubstituted coronenes.¹⁴

Monomer **4** was further mixed, via sonication, with other trifluorovinyl ether monomers such as monomer **5**.⁵ Upon copolymerization at 150 °C, monomer **4** adducts became soluble, resulting in a new PFCB copolymer (Scheme 3). Cyclopolymerization to PFCB copolymer was confirmed by FTIR and ¹⁹F NMR. Gel permeation chromatography results confirmed copolymerization by

Scheme 3. Copolymerization of **4** with **5**



the presence of HBC absorption peaks as a function of elution volume (see Supporting Information). The copolymer emission spectrum revealed HBC luminescence in addition to the 360 nm emission of the homopolymer **poly5** (Figure 3b,c).

The first synthesis and polymerization of trifluorovinyl ether-substituted hexa-*peri*-hexabenzocoronene to perfluorocyclobutyl polymers and copolymers has been demonstrated. Unlike hydrocarbon ethers, fluorovinyl ethers are stable under HBC oxidation conditions. Discrete HBC units in PFCB polymers provide access to potentially processable HBC optical materials.

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Supporting Information Available: Detailed synthetic procedures for **1–4** and characterization data of **3** and **4** including, MALDI, DSC, excitation, emission, WAXD, and GPC data (PDF). Crystallographic data, including bond angles and distances (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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