Synthesis and Electrochemistry of Carboranylpyrroles. Toward the Preparation of Electrochemically and Thermally Resistant Conjugated Polymers

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ABSTRACT: Pyrrole derivatives covalently linked to a neutral *ortho*- or anionic *nido*-carborane cage via a methylene or ethylene spacer arm have been synthesized. Their electrochemical study showed that only the neutral compounds yielded anodically conducting 3-substituted polypyrrole films. In contrast, the anodic oxidation of the anionic derivatives underwent the passivation of the electrode surface. The pyrrole with a two-carbon linkage was the most efficiently electropolymerized, and the relevant polymer films exhibited the best electroactive and conducting properties. These were resistant to highly positive potentials owing to the hydrophobic nature and the electron-withdrawing character of the attached carborane cage. Moreover, this material was more thermally stable than unsubstituted polypyrrole.

Introduction

Owing to the exceptional characteristics exhibited by the carboranes in their neutral and anionic forms, such as low nucleophilicity, unparalleled chemical inertness, electron-withdrawing properties having highly polarizable σ-aromatic character, and high hydrophobicity,[1,2] their incorporation in organic materials appears very attractive. Indeed, such functional groups could confer on the host matrix novel properties, such as a thermal and/or chemical stability, optoelectronic characteristics, and an ordered structure. For instance, numerous polymers in which the icosahedral carboranes were linked by aromatic units (generally benzene) have been synthesized and characterized.[3−6] These macromolecular systems showed either an extreme resistance to combustion[3,6] or a two-dimensional grid-shaped structure using the boron cage as a molecular connector.[4] Other poly(carborane−siloxane) elastomers incorporating acetylenic units showed also remarkable thermal and oxidative stabilities.[7]

Recently, Teixidor's group and ourselves have synthesized conducting polypyrrole films functionalized by a neutral *o*-carborane[8] or a Co(III) complex of anionic dicarbollide moieties.[9−11] The boron cage was either electrostatically entrapped[9,10] or covalently bound to the polymer backbone via a spacer of appropriate length.[8,11] These redox-active polymers exhibited an electrochemical stability largely higher than unsubstituted polypyrrole which could be of great interest for some applications, such as electrochromic and energy storage devices. Moreover, these functionalized materials were electrochemically generated from the anodic oxidation of the precursor pyrrole. The interest of the electrochemical method is that the polymer is obtained fastly in one step as a film deposited on the electrode surface from the oxidation of the corresponding monomer in solution. The film thickness can be easily controlled from the electrical charge consumed during the electropolymerization reaction. So, some nanometers to several micrometer-thick films can be electrodeposited on macroelectrodes but also on ultramicroelectrodes. Furthermore, the electrochemical route allows also the deposition of uniform films onto electrode surfaces of different shapes and geometries (sheet, disk, cylinder, drop, or felt). Another advantage for some applications is the possibility of micro- and nanopatterning conducting polymers using relatively simple processes.[12−15] In our previous paper,[8] the choice of pyrrole 3-substituted by the carborane unit as the starting monomer has been motivated by its easier electropolymerization (comparatively to N-substituted pyrroles) and to the better electroactive and conducting properties of the resulting conducting polymer films.[16,17]

In the pursuit of our investigations, we present herein the synthesis and the electrochemical study of novel pyrrole derivatives covalently linked to a neutral *ortho*- or anionic *nido*-carborane cage via a methylene or ethylene spacer arm.[18,19] The goal of this work was to analyze the effects of the spacer length and the charge of the boron cluster on the electropolymerization efficiency and the properties of the resulting conducting polymer films.

Experimental Section

Synthesis of Carboranylpyrroles. General. All experiments were performed under an inert argon atmosphere using a Schlenk line. Melting points were measured with an Electrothermal melting point apparatus. The ^{1}H NMR spectra were obtained using either a Bruker ARX 300 MHz or a DPX 250 MHz instrument. The reactions were monitored by silica gel thin-layer chromatography (TLC) plates from Sorbent Technologies (precoated sheets, 0.2 mm thick). 1-Methyl-*o*-carborane was purchased from Dexsil, and all other starting materials were purchased from Sigma-Aldrich and used without further purification. Silica gel for column chromatography was purchased from Sorbent Technologies (60 Å, 40−75 μm). All solvents were purchased from Fisher Scientific. Dichloromethane was distilled over CaH_2, and tetrahydrofuran (THF) was first distilled over $LiAlH_4$ and then sodium/benzophenone. The low-resolution FAB-MS measurements were performed on a Finnigan MAT 900 instrument and the HRMS on a an Applied Biosystems Q Star XL electrospray. The elemental analyses were performed by Midwest Microlab, LLC.

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1-(3-Butenyl)-2-methyl-*o*-carborane (1). 1-Methyl-*o*-carborane (1.00 g, 6.36 mmol) was dissolved in freshly distilled THF (60 mL) in a 250 mL round-bottom flask (RBF) equipped with magnetic stirring and cooled to 0 °C with an ice bath. *n*-Butyllithium (*n*-BuLi, 3.05 mL of a 2.5 M solution in hexane, 7.63 mmol) was added slowly to the cooled solution, and the color turned yellow. The solution was warmed to room temperature (RT), stirred for 1 h, and then cooled to −78 °C. 4-Bromo-1-butene (1.12 g, 8.27 mmol) dissolved in THF (20 mL) and LiI (0.17 g, 1.27 mmol) were added to the solution at −78 °C, and the final mixture was slowly warmed to RT and stirred for 36 h. Aqueous saturated NaCl (20 mL) and distilled H_2O (30 mL) were added, and the reaction mixture was stirred for an additional 5 min. The aqueous layer was extracted with ethyl acetate (3 × 100 mL), dried over $MgSO_4$, and purified by column chromatography on silica gel, using 90% hexanes:10% ethyl acetate for elution. The title compound was obtained as a white solid (1.00 g) in 74% yield; mp = 70−71 °C. MS (FAB) *m*/*z* 211.2 ($M + H^+$). ^{1}H NMR (250 MHz, $CDCl_3$, δ ppm): 5.84−5.68 (m, 1H), 5.13−5.08 (m, 1H), 5.08−5.03 (m, 1H), 2.44−2.41 (m, 4H), 2.02 (s, 3H), 3.67−0.95 (br, 10H, BH).

2-Methyl-1-(3-phenylthio-4-chlorobutyl)-*o*-carborane (2). *N*-Chlorosuccinimide (NCS, 1.95 g, 14.6 mmol) was added to a three-neck 250 mL RBF equipped with magnetic stirring and dried under reduced pressure. Dichloromethane (30 mL) was added via syringe, and the suspension was heated to reflux. Four drops of benzenethiol (PhSH) were added to initiate the reaction, and the remainder PhSH (0.62 g, 5.63 mmol) was slowly added via syringe while maintaining the reflux. The resulting mixture was stirred for 2 h and then cooled to −78 °C. Compound **1** (1.03 g, 4.85 mmol) dissolved in dichloromethane (20 mL) was added via syringe, and the final mixture was stirred for 10 min before being warmed to RT. The excess NCS was removed by filtration on a plug of silica gel using 85% hexanes:15% ethyl acetate, and the filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography using 85% hexanes:15% ethyl acetate for elution, followed by recrystallization from hexanes yielding the title compound as a white solid (1.60 g) in 92% yield; mp = 65−66 °C. MS (FAB) *m*/*z* 357.2 ($M + H^+$). ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 7.42−7.36 (m, 2H, Ph−H), 7.36−7.32 (m, 3H, Ph−H), 3.75 (dd, 1H, J = 11, 4 Hz), 3.47 (dd, 1H, J = 11, 11 Hz), 3.01−3.20 (m, 1H), 2.85−2.52 (m, 2H), 2.37−2.25 (m, 2H), 2.05 (s, 3H), 3.10−1.10 (br m, 10H, BH).

2-Methyl-1-(3-phenylsulfonyl-4-chlorobutyl)-*o*-carborane (3). Compound **2** (0.334 g, 0.936 mmol) was dissolved in dichloromethane (5 mL) in a 50 mL RBF equipped with magnetic stirring and cooled to 0 °C. A solution of vacuum-dried *m*-chloroperoxybenzoic acid (mCPBA, 1.61 g, 9.33 mmol) in dichloromethane (10 mL) was added dropwise. A white precipitate formed a few minutes after the addition of mCPBA, and TLC indicated that the reaction was complete. After removal of the solvent under vacuum, ethyl acetate was added and the solution was washed with aqueous saturated Na_2SO_3 (3 × 100 mL), $NaHCO_3$ (3 × 100 mL), and finally with aqueous saturated NaCl (1 × 100 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure to yield a oily solid, which was recrystallized from ethanol to give the title compound as fluffy white crystals (0.343 g) in 94% yield; mp = 125−127 °C. HRMS (ESI) for $C_{13}H_{26}O_2SB_{10}C_{11}$ 390.2337 (calcd 390.2332). ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 7.89−7.86 (m, 2H, Ph−H), 7.75−7.73 (m, 1H, Ph−H), 7.66−7.61 (m, 2H, Ph−H), 3.83 (dd, 1H, J = 4, 12 Hz), 3.58 (dd, 1H, J = 12, 10 Hz), 3.28−3.16 (m, 1H), 2.50−2.40 (m, 2H), 2.30−2.10 (m, 2H), 2.03 (s, 3H), 3.10−1.00 (br m, 10H, BH).

2-Methyl-1-(3-phenylsulfonyl-3-butenyl)-*o*-carborane (4). Compound **3** (1.80 g, 4.63 mmol) was dissolved in freshly distilled THF (20 mL) in a 100 mL RBF and cooled to 0 °C. A solution of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 0.670 g, 4.40 mmol) in THF (5 mL) was added dropwise. A precipitate formed immediately, and the reaction was complete (TLC) in a just a few minutes. The reaction mixture was filtered through a plug of silica gel to remove the precipitate, and ethyl acetate (100 mL) was added to the filtrate. The solution was washed with distilled H_2O (1 × 100 mL), and the aqueous layer was extracted with ethyl acetate (2 × 100 mL). The organic layer was dried over $MgSO_4$, concentrated under reduced pressure, and recrystallized from ethanol to yield the title compound as a white solid (1.47 g) in 90% yield; mp = 145−147 °C. HRMS (ESI) for $C_{13}H_{25}O_2SB_{10}$ 353.2579 (calcd 353.2585). ^{1}H NMR (250 MHz, $CDCl_3$, δ ppm): 7.89−7.85 (m, 2H, Ph−H), 7.59−7.73 (m, 3H, Ph−H), 6.41 (d, 1H, J = 1 Hz), 5.81 (d, 1H, J = 1 Hz), 2.46−2.41 (m, 4H), 1.99 (s, 3H), 3.60−1.05 (br, 10H, BH).

4-(2-Methyl-*o*-carboranyl)ethyl-1*H*-pyrrole-2-carboxylic Acid *tert*-Butyl Ester (5). Carborane **4** (0.244 g, 0.69 mmol) and *tert*-butyl isocyanoacetate (0.097 g, 0.68 mmol) were dissolved in THF (20 mL) in a 250 mL RBF equipped with magnetic stirring and fitted with a reflux condenser. The mixture was heated to reflux, and a solution of sodium *tert*-butoxide (NaO^tBu, 0.066 g, 0.69 mmol) in THF (80 mL) was added. The solution immediately turned yellow. The reaction mixture was refluxed for 4 h and allowed to stir at RT for an additional 12 h. Ethyl acetate (50 mL), aqueous saturated NaCl (50 mL), and H_2O (100 mL) were added to the flask, and the mixture was stirred for 15 min. The aqueous layer was extracted with ethyl acetate (3 × 100 mL), and the combined organic layers were dried over $MgSO_4$, concentrated under reduced pressure, and purified by silica gel column chromatography using 70% hexanes:30% ethyl acetate for elution. The title compound was obtained as a white solid (0.222 g) in 92% yield; mp = 208−209 °C. MS (FAB) *m*/*z* 296.2 [$M + H^+ - {}^t$Bu]. ^{1}H NMR (250 MHz, $CDCl_3$, δ ppm): 9.44 (br s, 1H, NH), 6.77−6.71 (m, 1H) 6.68−6.62 (m, 1H), 2.78−2.68 (m, 2H), 2.48−2.37 (m, 2H), 2.03 (s, 3H), 1.57 (s, 9H), 3.78−1.90 (br m, 10H, BH). Anal. Calcd for $C_{14}H_{29}B_{10}NO_2$: C, 47.83; H, 8.33; N, 3.99. Found: C, 48.27; H, 8.34; N, 3.75.

3-(2-Methyl-*o*-carboranyl)ethyl-1*H*-pyrrole (6). Pyrrole *tert*-butyl ester **5** (0.100 g, 0.284 mmol) was dissolved in trifluoroacetic acid (TFA, 5 mL) and gently warmed with stirring for 5 min. Aqueous saturated Na_2SO_3 (10 mL) was added, followed by ethyl acetate (50 mL). The organic layer was washed with $NaHCO_3$ until the washes were basic, then dried over $MgSO_4$, filtered through Celite, and concentrated under reduced pressure. The resulting crude product was dissolved in 80% hexanes:20% ethyl acetate and filtered through a plug of silica gel. The product was collected and concentrated under vacuum to yield the title compound as an off-white solid (0.067 g) in 94% yield; mp = 67−69 °C. HRMS (ESI) for $C_9H_{22}B_{10}N$ 252.2767 (calcd 252.2759). ^{1}H NMR (250 MHz, $CDCl_3$, δ ppm): 8.10 (br s, 1H, NH), 6.76 (dd, 1H, J = 2, 3 Hz) 6.63−6.59 (m, 1H), 6.09 (dd, 1H, J = 2, 3 Hz), 2.89−2.65 (m, 2H), 2.50−2.37 (m, 2H), 2.08 (s, 3H), 3.78−1.90 (br m, 10H, BH).

Tetrabutylammonium 3-(*nido*-2-Methyl-*o*-carboranyl)ethyl-1*H*-pyrrole (7). Pyrrole **6** (0.150 g, 0.60 mmol) was dissolved in 2.98 mL of a 1.0 M solution of tetrabutylammonium fluoride (TBAF) and distilled H_2O (0.43 mL). The solution was heated to a gentle reflux for 30 min. Dichloromethane (100 mL) was added to the mixture, and the organic layer was washed with H_2O (3 × 100 mL), dried over $MgSO_4$, filtered through Celite, and concentrated under reduced pressure. The resulting oily solid was recrystallized from ethanol to yield the title compound as off-white crystals (0.240 g) in 86% yield; mp = 152−153 °C. MS (MALDI) *m*/*z* 240.8 ($M - NBu_4^+$). ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 8.15 (br s, 1H, NH), 6.68 (d, 1H, J = 2 Hz), 6.54 (s, 1H), 6.08−6.02 (m, 1H), 3.15−3.05 (m, 8H), 2.75−2.55 (m, 2H), 2.05−1.90 (m, 2H), 1.60−1.55 (m, 8H), 1.50 (s, 3H), 1.42 (q, 8H, J = 7 Hz), 1.02 (t, 12H, J = 7 Hz), 2.50−0.50 (br m, 9H, BH), −2.44 (br s, 1H, B−H−B).

2-Methyl-1-(2-propenyl)-*o*-carborane (8). 1-Methyl-*o*-carborane (2.50 g, 15.9 mmol) was dissolved in THF (40 mL) in a three-neck RBF equipped with magnetic stirring and cooled to 0 °C. *n*-BuLi (11.1 mL of a 2.5 M solution in hexanes, 27.8 mmol) was added, and the final solution was warmed to RT, stirred for 30 min, and then cooled to −78 °C. Allyl bromide (2.89 g, 23.9 mmol) dissolved THF (20 mL) was added via syringe. The solution was allowed to react for only 1.5 h at −78 °C to minimize isomerization to the more stable internal alkene. After warming to RT, aqueous

saturated NaCl (20 mL) and distilled H_2O (30 mL) were added to the reaction mixture, and stirring continued for 5 min. The mixture was extracted with ethyl acetate (3 × 100 mL), dried over $MgSO_4$, and purified by column chromatography on silica gel using 90% hexanes:10% ethyl acetate for elution. The title compound was obtained as a clear oil (2.63 g) in 84% yield. MS (ESI) *m*/*z* 197.06 (M^+). ^{1}H NMR (250 MHz, $CDCl_3$, δ ppm): 5.84−5.73 (m, 1H), 5.23−5.08 (m, 2H), 2.96 (d, 2H, J = 7.5), 2.03 (s, 3H), 1.03−3.20 (br m, 10H, BH).

2-Methyl-1-(2-phenylthio-3-chloropropyl)-*o*-carborane (9). Dried NCS (2.56 g, 19.17 mmol) was dissolved in freshly distilled dichloromethane (30 mL) and heated to reflux. PhSH (1.56 g, 14.18 mmol) was added dropwise via syringe. Upon the addition of one drop of PhSH, the solution became bright yellow, and after further addition, it turned amber. The resulting solution was refluxed for 20 min, then cooled to RT, and stirred for 2 h. Carborane **8** (2.56 g, 12.9 mmol), was added in one portion dissolved in 10 mL of dichloromethane at −78 °C. The final mixture was stirred for 1 h at −78 °C before being warmed to RT. The mixture was filtered through a plug of silica gel and concentrated under reduced pressure to afford a reddish oily residue. Recrystallization from hot ethanol gave the title compound as white crystals (3.97 g) in 90% yield; mp = 89−92 °C. MS (FAB) *m*/*z* 343.1 ($M + H^+$). ^{1}H NMR (250 MHz, $CDCl_3$, δ ppm): 7.49−7.37 (m, 5H, Ph−H), 3.76 (dd, 1H, J = 11, 3 Hz), 3.49 (dd, 1H, J = 9, 11 Hz), 3.47−3.40 (m, 1H), 2.90 (dd, 1H, J = 3, 16 Hz), 2.28 (dd, 1H, J = 8, 16 Hz), 2.05 (s, 3H), 1.20−3.50 (br m, 10H, BH).

2-Methyl-1-(2-phenylsulfonyl-3-chloropropyl)-*o*-carborane (10). Carborane **9** (1.75 g, 5.10 mmol) was dissolved in dichloromethane (15 mL) and cooled to 0 °C with constant stirring. A solution of mCPBA (3.51 g, 20.3 mmol) in dichloromethane (50 mL) was added dropwise, and the final mixture was stirred for 5 min. The excess mCPBA was removed by filtration on a silica gel plug. The dichloromethane layer was washed with aqueous saturated Na_2SO_3 (3 × 100 mL), once with $NaHCO_3$ (100 mL), and once with aqueous saturated NaCl (100 mL). The organic layer was dried over $MgSO_4$ and concentrated to yield a oily solid, which was recrystallized from hot methanol to give the title compound as white crystals (1.81 g) in 95% yield; mp = 124−126 °C. MS (FAB) *m*/*z* 374.2 ($M + H^+$). ^{1}H NMR (250 MHz, $CDCl_3$, δ ppm): 7.94−7.90 (m, 2H, Ph−H) 7.75−7.61 (m, 3H, Ph−H), 4.48−4.34 (m, 1H), 3.57−3.41 (m, 2H), 2.67 (dd, 2H, J = 16, 9 Hz), 2.11 (s, 3H), 3.50−1.20 (br m, 10H, BH).

2-Methyl-1-(2-phenylsulfonyl-2-propenyl)-*o*-carborane (11). Sulfone **10** (0.27 g, 0.72 mmol) was dissolved in THF (25 mL) and cooled to 0 °C with constant stirring. A solution of DBU (0.091 g, 0.60 mmol) in THF (10 mL) was added via syringe, and the final mixture was stirred for 10 min at 0 °C. The precipitate formed was removed by filtration, and the filtrate was concentrated under reduced pressure. The product was purified by column chromatography on silica gel using 80% hexanes:20% ethyl acetate for elution. The title compound was obtained as a white solid (0.246 g) in 97% yield; mp = 138−140 °C. MS (FAB) *m*/*z* 339.0 ($M + H^+$). ^{1}H NMR (250 MHz, $CDCl_3$, δ ppm): 7.87−7.83 (m, 2H, Ph−H), 7.71−7.61 (m, 3H, Ph−H), 6.09 (quint, 1H, J = 7.5 Hz), 5.73 (d, 1H, J = 15 Hz), 3.86 (dd, 2H, J = 8, 1 Hz), 1.83 (s, 3H), 1.20−3.18 (m, 10H, BH).

4-(2-Methyl-*o*-carboranyl)methyl-1*H*-pyrrole-2-carboxylic Acid *tert*-Butyl ester (12). Carborane **11** (0.350 g, 1.03 mmol) and *tert*-butyl isocyanoacetate (0.169 g, 1.19 mmol) were dissolved in THF (60 mL) and heated to reflux. A solution of NaO^{t}Bu (0.114 g, 1.19 mmol) in 40 mL of THF was added, and the final mixture was stirred at RT overnight. Aqueous saturated NaCl (40 mL) and distilled H_2O (40 mL) were added, and the mixture was stirred for 20 min. The aqueous layer was extracted with ethyl acetate (3 × 100 mL), dried over $MgSO_4$, and concentrated under vacuum. The residue was dissolved in dichloromethane (20 mL), activated carbon was added, and the mixture was heated to reflux. The carbon was removed by filtration through Celite, and the crude product was further purified by recrystallization from hot methanol to yield the title compound as fine needles (0.334 g) in 91% yield; mp = 156−158 °C. MS (FAB) *m*/*z* = 337.5 ($M - Bu^+$). ^{1}H NMR (250 MHz, $CDCl_3$, δ ppm): 9.25 (br s, 1H, NH), 6.79−6.75 (m, 1H), 6.68−6.65 (m, 1H), 3.37 (s, 2H), 2.12 (s, 3H), 1.57 (s, 9H), 3.60−0.1.00 (br m, 10H, BH). Anal. Calcd for $C_{13}H_{27}B_{10}NO_2$: C, 46.26; H, 8.08; N, 4.15. Found: C, 46.52; H, 7.95; N, 4.08.

3-(2-Methyl-*o*-carboranyl)methyl-1*H*-pyrrole (13). Pyrrole **12** (0.130 g, 0.385 mmol) was dissolved in a small amount of TFA (∼5 mL) and stirred for 2.5 h at RT. Aqueous saturated NaCl (25 mL), distilled H_2O (50 mL), and ethyl acetate (50 mL) were added to the reaction mixture, and stirring continued for 20 min. The organic layer was washed with aqueous saturated Na_2SO_3 (3 × 100 mL), $NaHCO_3$ (2 × 100 mL), and aqueous saturated NaCl (100 mL), before being dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was a light brown oil, which was dissolved in 20% ethyl acetate:80% hexanes and filtered through a plug of silica gel to afford the title compound (0.091 g) as an oil in 100% yield. MS (FAB) *m*/*z* 237.4 ($M + H^+$). ^{1}H NMR (250 MHz, $CDCl_3$, δ ppm): 8.20 (broad s, 1H, NH), 6.79−6.70 (m, 1H), 6.70−6.61 (m, 1H), 6.14−6.05 (m, 1H), 3.40 (s, 2H), 2.11 (s, 3H), 3.67−0.77 (br m, 10H, BH).

Tetrabutylammonium 3-(*nido*-2-Methyl-*o*-carboranyl)methyl-1*H*-pyrrole (14). Pyrrole **13** (0.150 g, 0.66 mmol) was dissolved in TBAF (2.98 mL of a 1.0 M solution) and distilled H_2O (0.43 mL) and heated to a gentle reflux for 30 min. Dichloromethane (100 mL) was added to the reaction mixture, the organic layer washed with distilled H_2O (3 × 100 mL), then dried over $MgSO_4$, filtered through Celite, and concentrated under vacuum. The resulting oily solid was recrystallized from ethanol, yielding the title compound as off-white crystals (0.240 g) in 86% yield; mp = 98−100 °C. MS (ESI) *m*/*z* 227.27 ($M^+ - NBu_4$). ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 8.15 (br s, 1H, NH), 6.78−6.74 (m, 1H), 6.68−6.65 (m, 1H), 6.18−6.14 (m, 1H), 3.25−3.10 (m, 8H), 2.96 (s, 2H), 1.68−1.52 (m, 8H), 1.44 (s, 3H), 1.50−1.36 (m, 8H), 1.01 (t, 12H, J = 7 Hz), 2.50−0.50 (br m, 9H, BH), −2.35 (br s, 1H, B−H−B). Anal. Calcd for $C_{14}H_{29}B_{10}NO_2$: C, 61.46; H, 11.84; N, 5.97. Found: C, 60.91; H, 12.42; N, 5.55.

Electrochemical Characterizations. Tetra-*n*-butylammonium hexafluorophosphate Bu_4NPF_6 was purchased from Fluka (puriss, electrochemical grade). Acetonitrile (Merck) was freshly distilled over calcium hydride prior to use. The electrolytic medium was dried in situ over activated, neutral alumina from Aldrich. Alumina was previously activated at 450 °C under vacuum for several hours.

Linear potential sweep cyclic voltammetry experiments were performed with an Autolab PGSTAT 20 potentiostat from Eco Chemie B.V., equipped with General Purpose Electrochemical System GPES software (version 4.5 for Windows). The working electrode was a 1 mm diameter platinum disk (area: 0.8 mm^2), and the counter electrode was a glassy carbon rod. Potentials were relative to the system 10^{-2} M $Ag^+|Ag$ in acetonitrile (+0.29 V vs aqueous SCE). Solution resistance was compensated by positive feedback. All electrochemical measurements were carried out at room temperature (20 ± 2 °C) and under a constant flow of argon.

UV−vis Spectroelectrochemistry. UV−vis absorption spectra were recorded on a Shimadzu Multispec-1501 spectrophotometer (190−1100 nm scan range) interfaced with a microcomputer for data acquisition, and quartz Suprasil cells from Hellma (1 cm path length) were used. The polymer films were grown on an indium tin oxide (ITO) coated glass slide electrode.

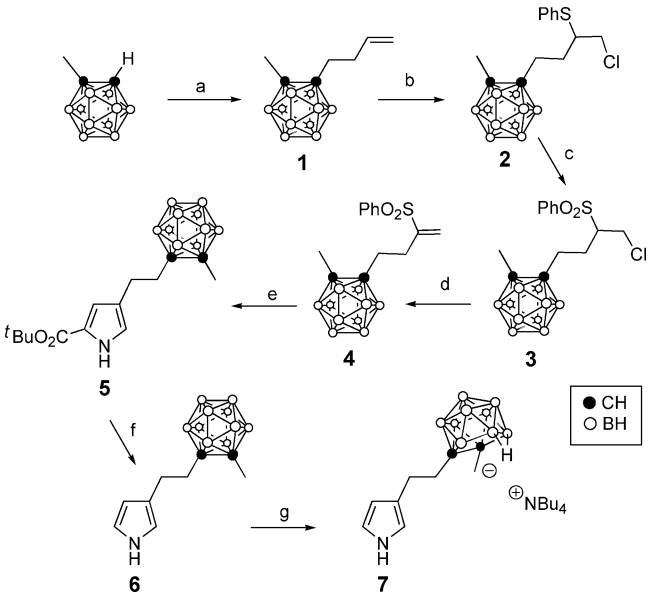
Each spectrum was recorded after the application of a potential for 10 s and kept at this value during the recording.

Scanning Electron Microscopy. SEM pictures were taken with a JSM-6301 F JEOL microscope. The polymer samples were electrogenerated on an array of platinum interdigitated microelectrodes (IMEs). The device used in this study was purchased from AAI-ABTECH and consisted of two buses of 50 10 μm wide platinum lines separated by 10 μm spaces (model 1050 series).

Results and Discussion

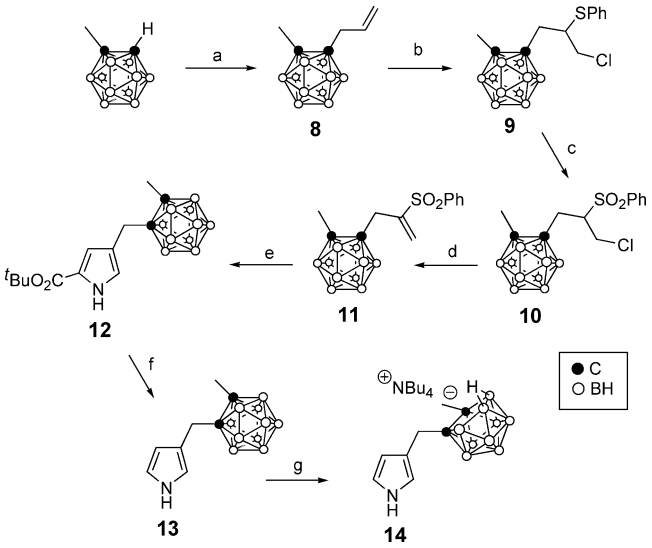
Synthesis of Carboranylpyrroles. Pyrroles **6**, **7**, **13**, and **14** were prepared from commercially available 1-methyl-*o*-carbo-

Scheme 1. Reagents and Conditions[a]



[a] (a) ^{n}Butyllithium, LiI, 4-bromo-1-butene, THF, −78 °C (74%); (b) PhSCl, CH_2Cl_2, −78 °C (92%); (c) *m*CPBA, CH_2Cl_2, 0 °C (94%); (d) DBU (1 equiv), THF, 0 °C (90%); (e) $CNCH_2CO_2{}^t$Bu, NaO^{t}Bu, THF (92%); (f) TFA, CH_2Cl_2 (94%).; (g) TBAF, H_2O, THF, reflux (86%).

Scheme 2. Reagents and Conditions[a]



[a] (a) ^{n}Butyllithium, allylic bromide, THF, −78 °C (84%); (b) PhSCl, CH_2Cl_2, −78 °C (90%); (c) *m*CPBA, CH_2Cl_2, 0 °C (95%); (d) DBU, THF, 0 °C (97%); (e) $CNCH_2CO_2{}^t$Bu, NaO^{t}Bu, THF (91%); (f) TFA, CH_2Cl_2 (100%).; (g) TBAF, H_2O, THF, reflux (86%).

rane using similar synthetic routes, as shown in Schemes 1 and 2.[18,19] Alkylation of 1-methyl-*o*-carborane with an alkenyl bromide at −78 °C gave moderate yields of the corresponding alkylated products, which could be increased to 74−84% upon addition of LiI.[20] The anti-Markovnikov addition of in situ generated phenylsulfenyl chloride to alkenes **1** and **8** proceed smoothly at low temperature, producing **2** and **9** exclusively, in >90% yields.[21] These yields decreased significantly when the reaction was carried out at temperatures higher than −78 °C due to the concomitant formation of the Markovnikov product. The oxidation of sulfides **2** and **9** to the corresponding sulfones was achieved in very high yields using mCPBA at 0 °C; these reactions were completed in only a few minutes. Dehydrochlorination to the α,β-unsaturated sulfones **4** and **11** was achieved with 1 equiv of DBU as base at 0 °C, in 90−

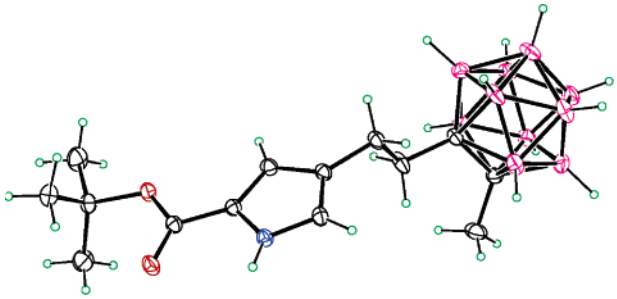


Figure 1. X-ray crystal structure of carboranylpyrrole **5**.[19]

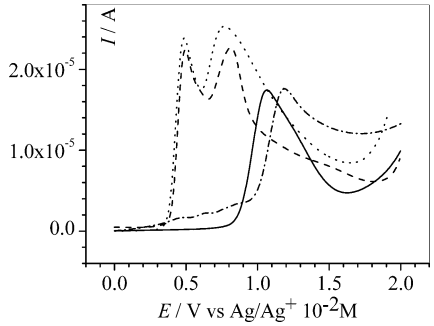


Figure 2. Linear sweep voltammograms of (solid line) **6**, (dashed line) **7**, (dashed dotted line) **13**, and (dotted line) **14** at 10^{-2} M in CH_3CN + 10^{-1} M Bu_4NPF_6. Potential scan rate: 0.1 V s^{-1}.

97% yields. A slight excess of base decreased the yield of these reactions due to competitive elimination[19] and isomerization[18] side reactions. Pyrroles **5** and **12** were obtained in high yields under Barton−Zard conditions,[22] using *tert*-butyl isocyanoacetate and sodium *tert*-butoxide in THF. Cleavage of the *tert*-butyl esters and decarboxylation were achieved in a single step using TFA, affording the neutral *o*-carboranylpyrroles **6** and **13** in >94% yields. The anionic *nido*-carboranylpyrroles **7** and **14** were obtained in high yield by fluoride-induced deboronation of the *closo*-carborane cages using tetrabutylammonium fluoride.[23] Unlike **6** and **13**, pyrroles **7** and **14** are highly soluble in polar organic solvents such as CH_3CN, DMF, and DMSO.

Electrochemistry of Carboranylpyrroles. Cyclic voltammetry study of neutral carboranylpyrroles **6** and **13** at 10^{-2} M in thoroughly dried CH_3CN + 10^{-1} M Bu_4NPF_6 revealed a single irreversible oxidation peak at 1.06_5 and 1.20 V vs Ag/Ag^+ 10^{-2} M (0.1 V s^{-1}), respectively, corresponding to the oxidation of the pyrrole ring (Figure 2). Under the same conditions, unsubstituted pyrrole displayed an anodic peak at 1.04 V. The more difficult oxidation of **13** can be explained by the electron-withdrawing character of the covalently bound carborane unit, whereas the introduction of an ethyl spacer in **6** contributed to strongly attenuate the electronic effects of the carborane. These two compounds could be anodically electropolymerized using either cyclic voltammetry or electrolysis at constant potential. However, **6** was found to be more efficiently and easily electropolymerized than **13**.[8] Typical multiple voltammetric scans of **6** between −0.5 and 1.0 V show the emergence of a new reversible system at less oxidizing potentials, attributable to the p-doping/undoping process of the electrogenerated conducting polymer (Figure 3). Further information on the deposition mechanism was provided from the chronoamperometric curves monitored during the potentiostatic electrodeposition experiments. As illustrated in Figure 4, the current−time profiles observed for poly(**6**) and unsubstituted polypyrrole PPy reveal that the transient period (i.e., before the stabilization of the electropolymerization current) is much shorter in the case of PPy. This result indicates that the

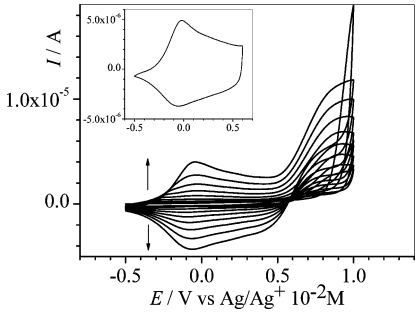


Figure 3. Successive cyclic voltammograms of **6** at 10^{-2} M in $CH_3CN + 10^{-1}$ M Bu_4NPF_6. (inset) Corresponding electrochemical response of poly(**6**) in the monomer-free electrolytic medium. Potential scan rate: 0.1 V s^{-1}.

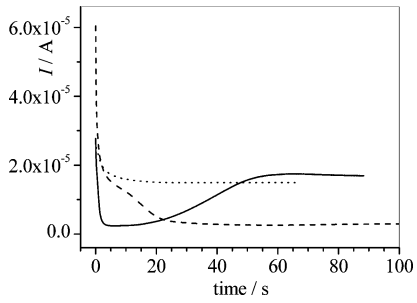


Figure 4. Evolution of the current intensity during potentiostatic deposition on a Pt disk electrode (1 mm diameter) of (solid line) poly(**6**) at 0.90 V, (dashed line) poly(**13**) at 1.20 V, and (dotted line) polypyrrole at 0.90 V from a 2×10^{-2} M solution of monomer in $CH_3CN + 10^{-1}$ M Bu_4NPF_6.

nucleation and growth rates of poly(**6**) are much slower. Moreover, the lower currents observed during poly(**13**) deposition are consistent with an electropolymerization rate slower than poly(**6**).

In contrast to the feasible electropolymerization of the neutral carboranes, the corresponding anionic derivatives **7** and **14** were found to not electropolymerize whatever the tested experimental conditions (namely, monomer concentration, oxidation potential and method, solvent). At 0.1 V s^{-1}, two closely spaced redox processes were seen at 0.50 and 0.82 V for **7** and at 0.48 and 0.75 V for **14** (Figure 2). Within the investigated potential scan rate range (0.05−10 V s^{-1}), these two systems appear to be irreversible. The variation of cyclic voltammograms with v was consistent with two diffusion-controlled irreversible anodic steps involving two and one electrons, respectively (see Supporting Information). At the present time, the nature of these two processes is not fully elucidated. Nevertheless, their position would be consistent with the oxidation of anionic carborane insofar as higher potentials are required to oxidize the pyrrole ring. As already reported for carbon-substituted carboranes,[24,25] the first two-electron component could yield to a neutral product derived from the acetonitrile substitution of a hydride ion on a boron atom. It is obvious that the oxidation of the carborane ion inhibited the oxidation of the pyrrole ring since no oxidation wave was observed for **7** whereas **14** underwent only a small shoulder within the expected potential window, i.e., 1.0−1.2 V. If a repeated scanning was performed until 1.0 V, a passivation phenomenon of the electrode occurred both for **7** and **14** as revealed by the progressive decrease of the current with the number of scans. No visible electroinactive or active film was detected on the electrode surface. Varying the anodic limit from 0.8 to 1.5 V had no effect. Moreover, similar results were obtained in CH_2Cl_2 or if the oxidation was driven potentiostatically. The inability of the anionic derivatives to

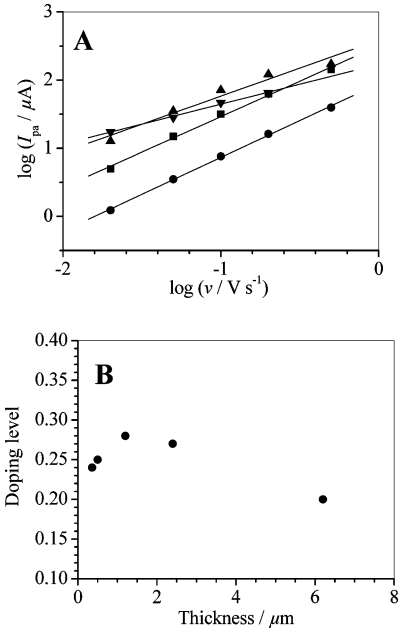


Figure 5. (A) Log I_{pa}−log v plots for poly(**6**) films electrogenerated in $CH_3CN + 10^{-1}$ M Bu_4NPF_6. The thicknesses of the polymer films were estimated from consumed electropolymerization charges: (●) 0.5, (■) 1.2, (▲) 2.4, and (▼) 6.2 μm (see the Supporting Information). (B) Variation of the doping level of poly(**6**) with the film thickness.

electropolymerize contrasts with the ease electropolymerization of the pyrrole derivatives N-substituted by cobalt bisdicarbollide moieties.[11] Such differences can be explained by a longer electronically insulating spacer between the cobalt bisdicarbollide and the pyrrole ring but also by the stabilization of the anionic carboranyl unit when complexed with a metal cation, as proved by the absence of any oxidation process within the potential window 0.0−1.5 V.[11] Indeed, the lengthening of the spacer arm contributes to annihilate the electronic and steric effects of the anionic carborane on the electrochemical oxidation of the pyrrole ring.

Electrochemistry of Poly(6). Among the synthesized carboranylpyrroles, only **6** and **13** were found to yield anodically electronically conducting polymer films. Hereafter, emphasis will be thus placed on poly(**6**) as the results obtained for poly(**13**) have been reported in our previous paper.[8] Following its electrosynthesis, the poly(**6**) film was examined in a monomer-free electrolytic medium. It exhibited a reversible redox system at ca. −0.05 V, the shape and the magnitude of which were not significantly changed over more than 20 cycles (Figure 3). Consistent with the electrochemical data of the monomers, the electronic and steric effects of the carborane substituent on the corresponding polymer response were strongly decreased with the lengthening of the alkyl spacer arm. Compared with poly(**6**), the redox system assigned to PPy was observed at a slightly lower potential, i.e., −0.10 V, whereas that of poly(**13**) was 300 mV positively shifted. To evaluate the mechanism that controls the charge transport in poly(**6**), the anodic peak current intensities (I_{pa}) were plotted as a function of the potential scan rate, v, in a logarithmic form (Figure 5A). The values of the slope for films thinner than ca. 2 μm are 1.0, as expected for surface-immobilized electroactive species.[26] A decrease of the slope from 1.0 to 0.6 was observed upon increasing the film thickness from 2 to 6 μm. Ideally, a slope of 0.5 is obtained for semiinfinite diffusion-controlled process. These results indicate that for thick films the charge transport mechanism is controlled by the diffusion of counteranions, namely PF_6^-, across the polymer film. They are correlated with the variation of the

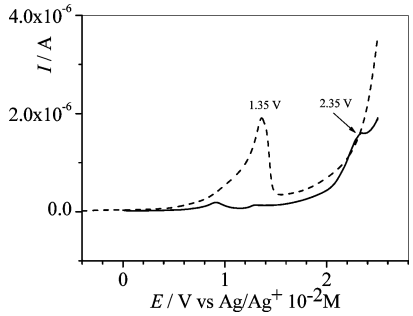


Figure 6. Linear sweep voltammograms at 1 mV s^{-1} of (solid line) poly(**6**) and (dashed line) polypyrrole in $CH_3CN + 10^{-1}$ M Bu_4NPF_6.

doping level of poly(**6**) δ with the film thickness. δ was estimated from the integration of the cyclic voltammetry curve corresponding to the oxidation step of the polymer matrix. As shown in Figure 5B, δ lay in the range 0.25−0.28 positive charge per pyrrole unit for the thinnest films and was significantly decreased for thick films. For example, a value of 0.20 was obtained for a 6 μm thick film. Consistent with these observations, the electron conductivity of poly(**6**) was found to decrease with the film thickness. Conductivities of 1.0 and 0.2 S cm^{-1} were measured at room temperature by the four-probe method for 2 and 10 μm thick PF_6^--doped films, respectively. It must be noted that these values were about 1 order of magnitude higher than that determined for poly(**13**) which demonstrates the benefits of using a longer spacer between the carborane moiety and the pyrrole ring. Experiments to perform in situ conductivity measurements as a function of the potential using interdigitated microelectrodes were unsuccessful. Indeed, the poly(**6**) films were found to be poorly adherent to these microelectrodes and peeled off from them before their interconnection.

Polypyrroles are known to be highly sensitive to overoxidation[27,28] where, at high potentials, the electroactivity and conductivity of the polymer films are degraded as a result of the attack of some nucleophilic species on the pyrrole rings. As a consequence of the presence of the carborane substituent, poly(**6**) was found to be more resistant to highly oxidizing potentials than PPy. To illustrate this increase in the electrochemical stability, we have monitored a single scan voltammogram for PPy and poly(**6**) at a very low scan rate (1 mV s^{-1}). Within the range 0−2.5 V, the overoxidation process of PPy produced a current peak at 1.35 V whereas poly(**6**) was overoxidized at a much higher potential (Figure 6). Such a difference is believed to be ascribed to the highly hydrophobic nature and electron-withdrawing character of the carborane cage which would protect the polymer backbone from nucleophilic attack by OH^- present in solution.

UV−vis Spectroelectrochemical Analysis of Poly(6). To gain further insight on the electronic properties of poly(**6**), a UV−vis spectroscopic analysis was performed at different oxidation states of the polymer. This optoelectrochemical method was also used to elucidate the effect of the carboranyl substituent on the energy of the π electrons. First, in the fully reduced state (−0.80 V), a strong absorption band due to the $\pi \rightarrow \pi^*$ transition of the chain of conjugated pyrrole rings appears at ca. 350 nm together with weak shoulders at 580 and 710 nm (Figure 7A). It must be noted that the carboranyl unit has no absorption beyond ca. 210 nm. The ca. 40 nm hypsochromic shift of the $\pi \rightarrow \pi^*$ transition band compared with neutral PPy[29] indicates that the average length on which the π-electron delocalization occurs is less extended in the poly(**6**) film. Several energetic contributions control the value of the band gap.[30] These

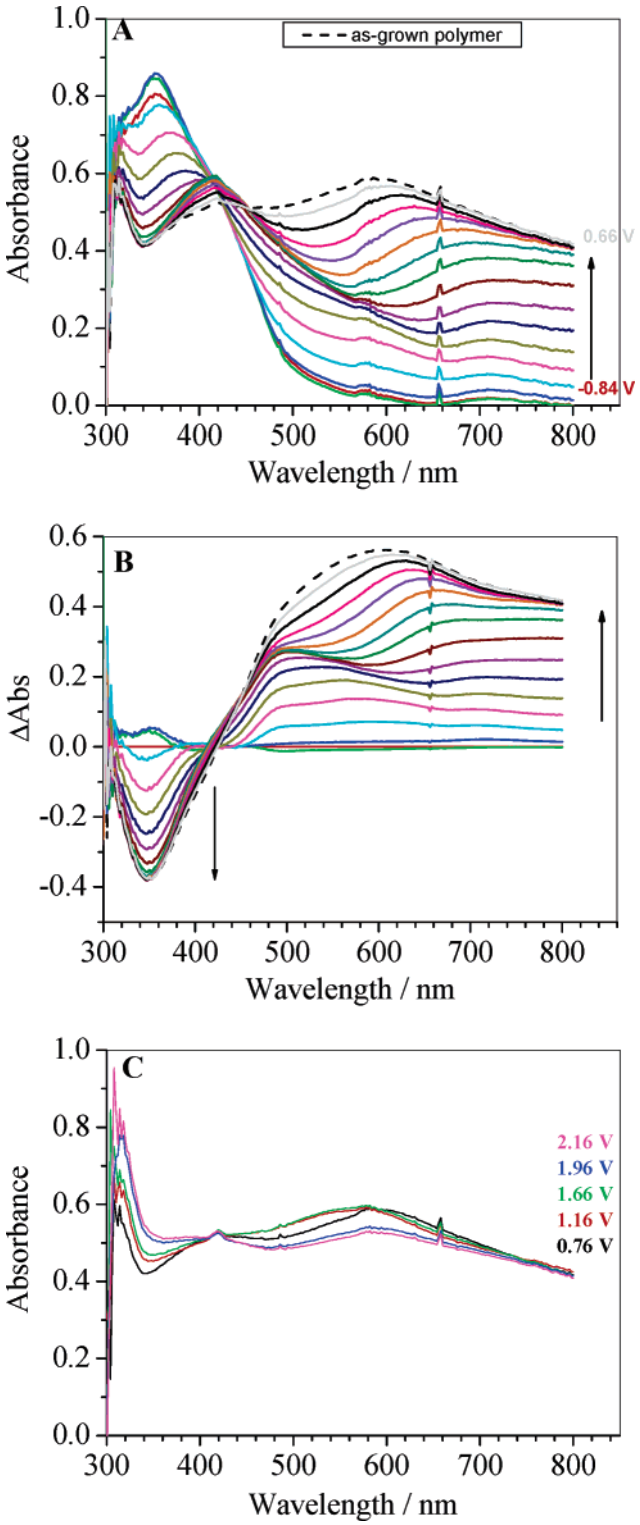


Figure 7. (A) UV−vis spectra of poly(**6**) in $CH_3CN + 10^{-1}$ M Bu_4NPF_6 between −0.84 and 0.66 V vs Ag/Ag^+ 10^{-2} M (one spectrum every 100 mV). (B) Corresponding normalized spectra using the spectrum at −0.84 V as the reference for background subtraction. (C) Effect of a highly oxidizing potential on the spectroelectrochemical response of poly(**6**). The film was electrogenerated onto a ITO electrode at 0.9 V in $CH_3CN + 10^{-1}$ M Bu_4NPF_6 containing **6** at 1.5×10^{-2} M (electropolymerization charge: 30 mC cm^{-2}).

include the energy related to bond length alternation, the mean deviation from planarity, aromatic resonance energy, the inductive or mesomeric electronic effects of substituents, and interchain coupling in the solid state. In the case of poly(**6**), the larger band gap can be explained by the twisting from planarity

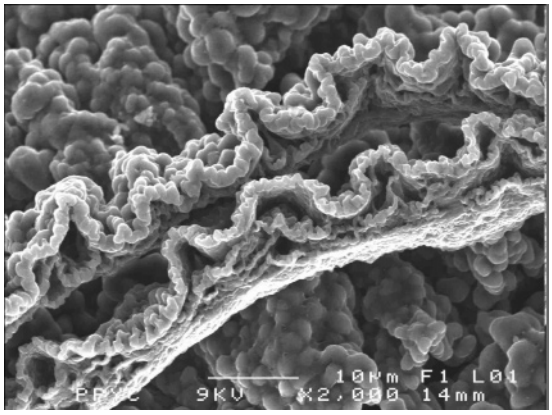


Figure 8. SEM picture of PF_6^--doped poly(**6**).

of the pyrrole rings due to both the electron-withdrawing character and steric constraints induced by the carborane cage.

Upon increasing the potential (and thus, the polymer doping), the following principal trends were observed: (i) the $\pi \rightarrow \pi^*$ transition band was decreased in intensity, (ii) two bands appeared at 494 and 576 nm and merged into a single broad band at ~510 nm from −0.10 V, and (iii) a broad absorption band beyond 700 nm increased in intensity and shifted to ca. 610 nm for potentials larger than 0.0 V (Figure 7A,B). The variation of the spectral response of polypyrrole films with the doping level is usually interpreted in terms of doping induced polaron (radical cation) and bipolaron (dication) formation on the polymer chains.[31] For poly(**6**), the transition at higher wavelengths was ascribed to bipolaronic charge carriers since its intensity increased continuously with potential. In contrast, the band at 510 nm initially increased at moderate potentials and then decreased in intensity for higher potentials. That is consistent with species of intermediate oxidation state, i.e., polarons. Globally, the characteristic optical bands of neutral and doped poly(**6**) are blue-shifted compared with unsubstituted PPy, as expected on the basis of both electronic and steric effects of substitution. Such results are perfectly in line with those reported for other polypyrrole films 3-substituted by alkyl groups.[32] The scanning electron microscopy analysis of a poly(**6**) film revealed a strongly distorted polymer structure which would support the spectroscopic data (Figure 8).

For applied potentials within the range 0.8−1.6 V, the persistency of the 600 nm band suggested that the conducting state of poly(**6**) was retained (Figure 7C). A significant decrease of its intensity was observed for potentials higher than 1.8 V, as a result of the beginning of the overoxidation process. Concomitantly, an absorbance increase was observed below 350 nm which could originate from some oxygen containing groups (e.g., carbonyl) bound to the pyrrole rings.[33] Comparatively, the absorbance of a PPy film beyond 500 nm was strongly decreased upon the application of much less positive potentials.

Thermal Stability of Poly(6). As another consequence of the presence of carborane cages grafted to the polypyrrole chains, poly(**6**) was found to be more thermally stable than PPy. The thermogravimetric analysis of undoped poly(**6**) was performed in air up to 700 °C and compared with TGA of PPy. As displayed in Figure 9, there is an appreciable loss in the mass of poly(**6**), namely 25%, until 360 °C and then an increase above this temperature until ca. 550 °C. This behavior atypical for conducting polymers was ascribed to the oxidation of B−H groups and the formation of more thermally stable B−O−B groups.[34] The total weight loss with respect to the initial state was 15% at 700 °C. For PPy, a continuous loss in the mass was observed to reach 70% at 700 °C, in agreement with other previously reported results.[35]

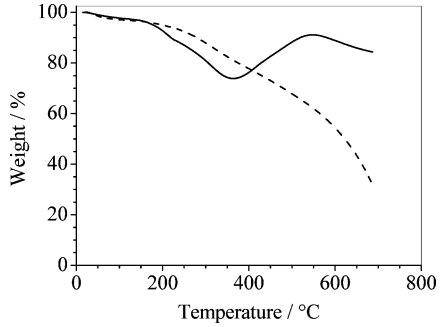


Figure 9. TG analysis of (solid line) undoped poly(**6**) and (dashed line) PPy in air. Amount of polymer: 2 mg; heating rate: 10 °C min^{-1}.

Conclusions

Among the synthesized carboranylpyrroles, only the neutral derivative **6** containing an ethyl spacer between the pyrrole ring and the boron cluster yielded better electroactive and conducting polypyrrole films. As a consequence of the presence of the carborane, the poly(**6**) films were found to be thermally and electrochemically more stable than unsubstituted polypyrrole. This inorganic−organic hybrid polymer could find applications as an advanced material in high-temperature devices or as a polymeric precursor for ceramics. Molecular modeling calculations using DFT methods are currently underway in order to explain the large differences in the electrochemical behavior of the neutral and anionic carboranylpyrroles. Additionally, the synthesis of polypyrroles containing the carborane unit within the polymer backbone is envisioned in order to examine whether the stability can be enhanced appreciably when the boron cage is directly connected to the π-conjugated ring but also if unusual electronic properties can be induced.

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Supporting Information Available: Cyclic voltammetry data of **7** and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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