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Synthesis and Electropolymerization of a series of 2,2'-(*ortho*-Carboranyl)bisthiophenes

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Abstract

A series of 5,5'-functionalized 2,2'-(*ortho*-carboranyl)bisthiophene with bromo, vinyl, trimethylsilylethyne, N-methylpyrrole or thienyl groups was synthesized and all compounds were characterized by NMR, MS, and X-ray analysis. Electrochemical characterizations of **12a,b** and **13a,b** were conducted, and the di(thienyl-N-methylpyrrole)-*o*-carborane **12a** and di(bisthienyl)-*o*-carborane **12b** were successfully electropolymerized on a suitable anode to produce the corresponding conducting polymers. DFT calculations are consistent with the electrochemical data.

Introduction

Carboranes[1] belong to a class of boron clusters that contain carbon and boron atoms. The neutral isomeric carboranes *ortho*-, *meta*-, and *para*-C₂B₁₀H₁₂ and the negatively charged *nido*-C₂B₉H₁₂⁻ and *closo*-CB₁₁H₁₂⁻ carboranes (**1-5**, respectively, shown in Figure 1), possess unique steric, electronic and physicochemical properties, including high hydrophobicity and remarkably high thermal and chemical stabilities, which has led to their wide application in diverse areas, for example in cancer therapy, molecular recognition, catalysis, and in electronics.[1-3] These unique clusters with delocalized electrons, are readily synthesized and functionalized, and the carbon atoms in these clusters make convenient sites for attachment of organic molecules. In particular the synthesis of carborane-containing polymers[4, 5] and their investigation for applications as pre-ceramic,[6] thermally robust,[7, 8] conducting,[9] and luminescent[10, 11] materials, have been an active area of research in recent years.

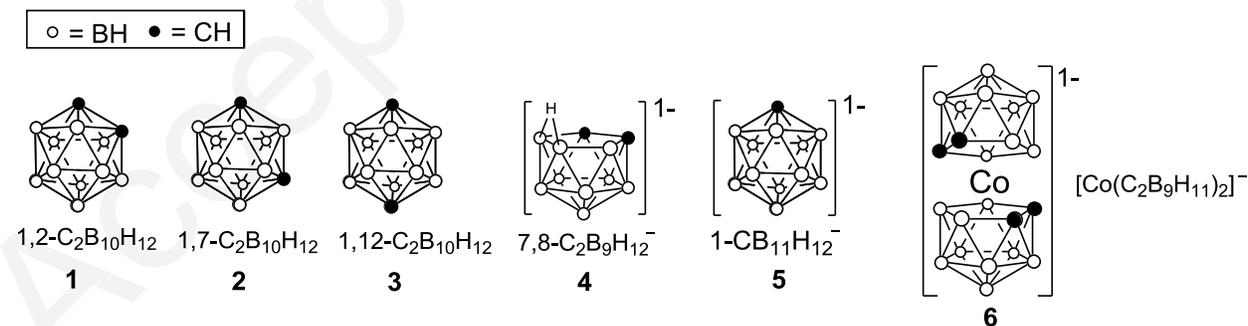


Figure 1: Neutral, anionic *nido* and *closo*- carboranes.

Since conducting polymers were first reported by Heeger, MacDiarmid and Shirakawa in 1977,[12, 13] a large body of research has been dedicated to the synthesis and investigation of conducting polymers, including the polypyrrole (PPy), polythiophene (PTh), and polyaniline

(PANI) types.[14] However, there are several challenges that remain associated with these systems, including their poor thermal and oxidative stabilities in the environment, and short lifetimes during the charge-discharge process, that have hampered the commerciality of conducting polymers.[15] Due to their special properties as mentioned above, carboranes are excellent candidates to be used for the functionalization of both monomers and polymers.

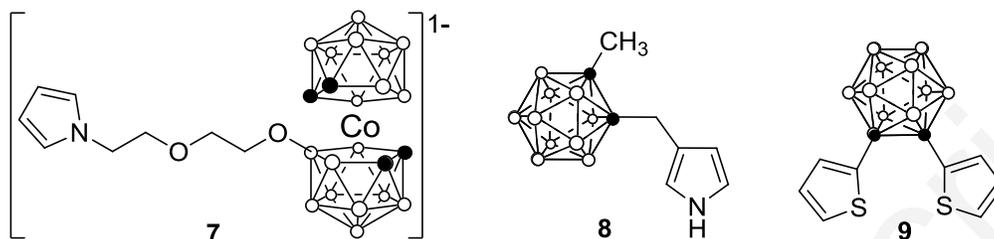


Figure 2: Structures of compounds 7-9.

Several strategies for incorporation of carboranes into polymers have been reported: (i) $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ (**6**) was used as doping agent for the electropolymerization of monomers;[16-19] (ii) pyrrole and thiophene monomers were modified by functionalization at the 2-position[20] and the N-position (e.i. **7**)[21] with anion (**6**), followed by electropolymerization to form the self-doped polymers under suitable conditions; (iii) monomers were modified by using neutral carboranes (*o*-, *m*-, *p*-) at the 2-position[22, 23] and at the 3 and/or 4-positions (e.g. **8**) [24-27] followed by polymerization; and (iv) copolymerization between carborane-containing monomers with α -free monomers (pyrroles or thiophenes) using both chemical[28, 29] and electrochemical[21, 30] methods, for the introduction of carborane groups into the main chain (Figure 2). These carborane groups entrust to the monomers and relevant conducting polymers several desirable properties, including enhanced oxidation potentials, which can help to overcome the “polythiophene paradox”,[31] and high thermal and chemical stabilities. However, several challenges in carborane-functionalized organic polymers remain. Among them, decreased conductivity (e.g. $10^{-2} \text{ S cm}^{-1}$ and 20 S cm^{-1} for poly(**8**)[25] and poly(**9**)[22], respectively, compared with values of up to 200 S cm^{-1} and 100 S cm^{-1} measured for traditional PPy and PTh, respectively[32]), and blue-shifted $\pi - \pi^*$ transition bands from UV-vis spectroscopy analysis, are often observed. These might be due to their less conjugated backbone caused by the electron-withdrawing effect and steric hindrance induced by the carborane groups. Furthermore, some carborane-containing molecules even fail to be successfully electropolymerized when the carborane groups are too close to the aromatic rings.[23, 24, 26, 27]

On the other hand, a wide range of structurally-modified π -conjugated oligomers have been designed, synthesized and polymerized to afford materials with specific properties (e.g. photovoltaic properties and controlled length of the main chain).[33, 34] For example, in the process of electropolymerization of thiophene monomers, oligomers with oxidation potential higher than that of polymers are usually generated.[31] This may lead to a significant degradation of the mechanical and chemical properties of the materials. However, electropolymerization of short-chain oligomers (such as bis- and tetra-thiophenes) can overcome the “polythiophene paradox” and produce better defined polymers, although these might show decreased conductivity.[35-37] Another advantage of using oligomers rather than monomers is the versatility they bring to polymer synthesis by taking advantage of the number and ratio of co-polymers used.[34] In the last two

decades, a large number of thiophene oligomers[34] and pyrrole oligomers[38-40] have been reported.

In that context, we have been interested in the design and synthesis of new electroactive carborane-functionalized oligomers for electropolymerization. Based on our previous work, we observed that poly(**9**) showed high conductivity and lifetime, with high thermal stability and enhanced oxidation resistance.[22] We now report a new series of derivatives of *ortho*-carboranylbi-thiophene **9** bearing vinyl, thienyl or pyrrole groups at the 5- or 5,5'-positions. We anticipated that such modifications could lead to more aerated polymer structures and more conjugated main chains due to decreased steric hindrance and electronic effect induced by the carborane cluster. On the other hand, it has been reported that pyrrolic groups in the oligomers and polymers can promote and stabilize the radical cations formed during electropolymerization, which further promotes the π - π intermolecular dimerizations.[41, 42] Such phenomena may lead to supramolecular π -dimers with enhanced conductivity.[42-44] Therefore, electron-rich *N*-methylpyrrole units were introduced to the 5,5'-positions (**12a**) and this compound was anticipated to be easier to polymerize to form a more conductive material, relative to analogues **12b** and **13a**.

Materials and methods

Synthesis and characterization

General

All the reagents and solvents were purchased from Fisher or Sigma-Aldrich without further purification. All the reactions were monitored by Sorbent TLC using 0.2 mm silica gel or neutral alumina with UV- 254/366 nm. Silica gel (230×400 mesh) and neutral alumina (50-200 μ m, Act. I) for column chromatography were purchased from Sorbent. All NMR spectra were collected using a Bruker AV-400 MHz, AV-500 MHz or DPX-400 MHz NMR spectrometers in CDCl₃ at room temperature. The chemical shifts (δ) are reported in ppm with CDCl₃ (δ = 7.27 ppm for ¹H NMR and 77.0 ppm for ¹³C NMR) as reference. All mass spectra were collected using an Agilent 6210 ESI-TOF MS, Varian Saturn 2000 Ion Trap with CP 3800 GC MS and Applied Biosystems QSTAR for MALDI.

Synthesis

2,2'-o-Carboranyl-bi-thiophene (9) was synthesized using a slightly modified published procedure.[22]

5,5'-Dibromo-2,2'-Co-arboranyl-bi-thiophene (10a).

To a 50 mL flask equipped with a magnetic stirrer were added **9** (630 mg, 2.04 mmol) and NBS (2.18 g, 12.24 mmol). The flask was evacuated and refilled with argon 3 times. Chloroform (15 mL) and acetic acid (10 mL) were added into the flask. The mixture was stirred and refluxed overnight under Ar. The reaction was stopped when starting material disappeared, according to TLC. After cooling to room temperature, the mixture was poured into water. Dichloromethane (30 mL × 3) was used to extract the organic components. The organic layers were combined and washed with saturated aqueous NaHCO₃ and brine. The organic layer was dried using dry sodium sulfate then the solvents were removed under reduced pressure. The residue was purified by silica gel column chromatography using hexane as the eluent, to give **10a** as a white solid product (722.9 mg, 76% yield). mp 99-100 °C. ¹H NMR (400 MHz, CDCl₃) δ 6.94-6.95 (d, *J* = 4.0 Hz, 1H), 6.84-6.85

(d, $J = 4.0$ Hz, 1H), 1.60-3.50 (br, 10 H); ^{13}C NMR (400 MHz, CDCl_3): 135.6, 132.8, 130.3, 116.8, 80.0; MS (GC-MS) m/z $[\text{M}]^+$ 466.0, calculated for $\text{C}_{10}\text{H}_{14}\text{B}_{10}\text{Br}_2\text{S}_2$ 466.0.

5-Bromo-2,2'-o-Carboranyl-bisthiophene (10b).

A similar procedure as that described above was used, starting from **9** (257 mg, 0.83 mmol), NBS (443 mg, 2.49 mmol), chloroform (4 mL), and acetic acid (4 mL). The mixture was stirred and refluxed overnight under Ar. After cooling to room temperature, the mixture was poured into water, extracted with dichloromethane (10 mL \times 3) and the organic layers washed with saturated aqueous NaHCO_3 and brine. The resulting residue was purified by silica gel column chromatography using hexane as the eluent to give **10b** as a white solid (160.8 mg, 50%). mp 107-108 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.23-7.25 (dd, $J = 5.2, 1.2$ Hz, 1H), 7.19-7.20 (dd, $J = 3.7, 1.2$ Hz, 1H), 6.92-6.93 (d, $J = 4.0$ Hz, 1H), 6.85-6.87 (dd, $J = 5.1, 3.8$ Hz, 1H), 6.79-6.80 (d, $J = 4.0$ Hz, 1H), 1.60-3.50 (br, 10H); ^{13}C NMR (CDCl_3 , 400Hz): 135.9, 134.5, 132.7, 132.6, 130.0, 129.7, 127.2, 116.4, 80.8, 80.0; MS (GC-MS) m/z $[\text{M}]^+$ 387.3, calculated for $\text{C}_{10}\text{H}_{15}\text{B}_{10}\text{BrS}_2$ 387.1.

2,2'-o-Carboranyldi(2-trimethylsilylethynylthiophene) (11)

To a 25 mL flask equipped with a magnetic stirrer were added **10a** (92.3 mg, 0.2 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (27 mg, 6 mol%) and CuI (14 mg, 10 mol%). The flask was evacuated and refilled with argon 3 times. Dry diethylamine (DEA) (5 mL) and ethynyltrimethylsilane (58.9 mg, 0.6 mmol) were added into the flask. The mixture was stirred at 60 °C under argon for 2 h. The reaction was stopped when all the starting material disappeared according to TLC. After cooling to room temperature, the solvent was removed under reduced pressure. The catalysts were removed by filtration through a pad of silica gel and washed with dichloromethane. The organic solvents were removed under reduced pressure and the resulting residue was purified by silica gel column chromatography using hexane as the eluent, to give **11** as a white solid (132.6 mg, 80%). mp 140-141 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.00 (d, $J = 3.9$ Hz, 1H), 6.92 (d, $J = 3.9$ Hz, 1H), 1.60-3.50 (10H, br), 0.23 (s, 18H); ^{13}C NMR (400 MHz, CDCl_3): 134.9, 132.3, 132.1, 127.4, 101.7, 96.0, 80.3, -0.3; MS (GC-MS) m/z $[\text{M}]^+$ 500.8, calculated for $\text{C}_{20}\text{H}_{32}\text{B}_{10}\text{Si}_2\text{S}_2$ 501.2.

General procedure for Stille reactions

Into a 100 mL flask equipped with a magnetic stirrer were added **10a** or **10b** (0.1 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (12 mg, 10 mol%). The flask was evacuated and refilled with argon 3 times. Toluene (10 mL) and stannane reagent (3 equiv for the synthesis of **12a,b** and **13a**, or 1.5 equiv for synthesis of **13b**) were added into the flask. The mixture was stirred and refluxed for 2-4 h under nitrogen. The reaction was stopped when starting material disappeared according to TLC. The catalysts were removed by filtration through a pad of celite and washed with dichloromethane. The solvents were removed under reduced pressure. The residue was purified by silica gel column chromatography using hexane/dichloromethane as the eluents to give the desired products.

Di(thienyl-N-methylpyrrole)-o-carborane (12a): 44.3 mg, 95%; mp 152-154 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.14 (d, $J = 3.9$ Hz, 2H), 6.73 (d, $J = 3.9$ Hz, 2H), 6.67 (m, 2H), 6.26 (dd, $J = 3.7, 1.7$ Hz, 2H), 6.11 (dd, $J = 3.6, 2.8$ Hz, 2H), 3.60 (s, 6H), 1.60-3.50 (10H, br); ^{13}C NMR (CDCl_3 , 100Hz): 139.3, 133.0, 132.7, 125.8, 125.1, 124.0, 110.8, 108.2, 81.6, 35.3; HRMS (ESI-TOF) m/z $[\text{M}+\text{H}]^+$ 468.2595, calculated for $\text{C}_{20}\text{H}_{26}\text{N}_2\text{S}_2\text{B}_{10}$ 468.2600.

Di(bisthieryl)-o-carborane (12b): 43.5 mg, 92%; mp 172-174 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.22-7.24 (m, 2H), 7.12-7.13 (m, 2H), 7.09-7.10 (d, $J = 3.9$ Hz, 2H), 6.98-7.00 (dd, $J = 5.0, 3.7$ Hz, 2H), 6.88 (d, $J = 3.9$ Hz, 2H), 1.60-3.50 (br, 10H); ^{13}C NMR (126 MHz, CDCl_3) δ 141.5, 135.8,

133.2, 132.8, 128.0, 125.7, 124.8, 123.3, 81.4; MALDI-TOF m/z $[M+H]^+$ 473.138, calculated for $C_{18}H_{20}S_4B_{10}$ 473.143.

5,5'-Divinyl-2,2'-Carboranyldithiophene (13a): 24.5 mg, 68%; mp 144-147 °C; 1H NMR (400 MHz, $CDCl_3$) δ 7.02-7.03 (d, J = 3.9 Hz, 2H), 6.68-6.69 (d, J = 3.8 Hz, 2H), 6.56-6.63 (dd, J = 17.4, 10.9 Hz, 2H), 5.51-5.56 (d, J = 17.4 Hz, 2H), 5.17-5.20 (d, J = 10.9 Hz, 2H), 1.60-3.50 (br, 10H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.7, 132.9, 132.7, 129.0, 125.4, 115.5, 81.3. MS (GC-MS) m/z $[M]^+$ 360.5, calculated for $C_{14}H_{20}B_{10}S_2$ 360.2.

5-Vinyl-2,2'-Carboranyldithiophene (13b): 25.1 mg, 75%; mp 91-93 °C; 1H NMR ($CDCl_3$, 400 Hz) δ 7.19-7.22 (m, 2H), 7.01-7.02 (d, J = 3.8 Hz, 1H), 6.83-6.85 (dd, J = 5.0, 3.9 Hz, 1H), 6.66-6.67 (d, J = 3.8 Hz, 1H), 6.55-6.62 (dd, J = 17.4, 10.9 Hz, 1H), 5.50-5.54 (d, J = 17.4 Hz, 1H), 5.16-5.19 (d, J = 10.9 Hz, 1H), 1.60-3.50 (br, 10H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 146.6, 134.8, 133.0, 132.7, 132.6, 129.5, 129.0, 127.1, 125.3, 115.5, 81.0; MS (GC-MS) m/z $[M]^+$ 334.3, calculated for $C_{12}H_{18}B_{10}S_2$ 334.2.

X-Ray Diffraction

Diffraction data for **10a**, **10b**, **11**, **12a**, **13a** and **13b** were collected at $T=100K$ on a Brüker Kappa Apex-II DUO diffractometer equipped with $MoK\alpha$ radiation and a Triumph curved monochromator ($CuK\alpha$ radiation from a microfocus source for **13b**). For **12b**, data were from a Nonius KappaCCD diffractometer with $MoK\alpha$ radiation at $T=90K$. In **10a**, there are four independent molecules, and for two of them, disorder exists in the conformation of one of the bromothiophenes. A similar disorder exists for the nonbrominated thiophene of **10b**, and for the terminal thiophenes in **12b**. In **11**, the molecule lies on a crystallographic twofold axis. CIFs are provided as supplementary material. CCDC deposition numbers are 1012320-1012322 for **10a**, **10b**, **11**, and 1484163-1484166 for **12a**, **12b**, **13a**, and **13b**, respectively.

Electrochemical Characterizations

Tetra-*n*-butylammonium hexafluorophosphate Bu_4NPF_6 was purchased from Fluka (puriss, electrochemical grade). Anhydrous dichloromethane (less than 50 ppm water from Merck) and acetonitrile (anhydrous, >99.8%, from Sigma-Aldrich) were used as received. 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 cyclic voltammetry experiments were performed with an Autolab PGSTAT 30 potentiostat from Eco Chemie B.V., equipped with General Purpose Electrochemical System GPES software. The working electrode was a 1 mm-diameter platinum disk (area: 0.8 mm²) and the counter electrode was a glassy carbon rod. Potentials were relative to the system 10^{-2} M $Ag^+ | Ag$ in acetonitrile and the ferrocene/ferrocenium couple in CH_2Cl_2 + 0.2 M Bu_4NPF_6 was observed at $E^{o'}$ = 0.19 V vs this reference. All electrochemical measurements were carried out inside a home-made Faraday cage at room temperature ($20\pm 2^\circ C$) and under a constant flow of argon.

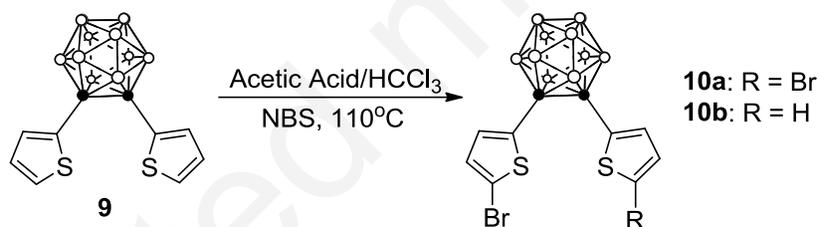
Computer Modeling

The geometries of all structures were optimized without symmetry constraints using B3LYP/6-31+G(d,p) level calculations. The hybrid Becke's Three Parameter DFT Functional was used.[45, 46] The solvent effects were taken into account using the Polarized Continuum Model (PCM).[47, 48] All calculations were performed using the Gaussian 09 program package.[49]

Results and Discussion

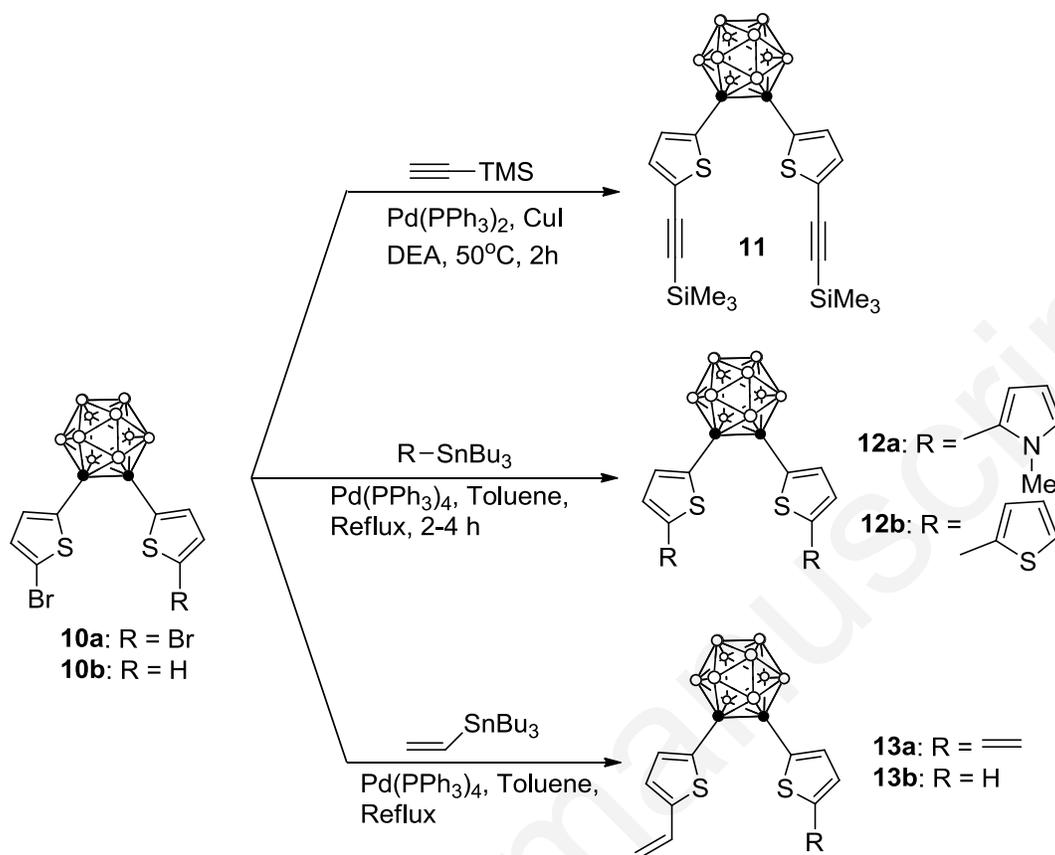
Synthesis of *ortho*-Carboranylbi thiophenes

The key intermediate 2,2'-*o*-carboranyldithiophene **9** was obtained using a slightly modified procedure from that previously published by us,[22, 23] in 30% overall yield. The Sonogashira cross-coupling reaction of commercially available 2-iodothiophene and 2-[(trimethylsilyl)ethynyl]thiophene, deprotected in situ in the presence of 1,8-diazabicycloundec-7-ene (DBU), using bis(triphenylphosphine)-palladium(II) dichloride and copper(I) iodide as catalysts, produced 2,2'-ethylenedithiophene in 87% yield.[50] Reaction of 2,2'-ethylenedithiophene with decaborane and diethyl sulfide gave the key precursor 2,2'-*o*-carboranyldithiophene **9** in 35% yield.[22, 23] Bromination of the two α -positions of 2,2'-carboranyldithiophene **9** was accomplished using 6 equiv of N-bromosuccinimide (NBS) in chloroform and acetic acid (1:1), at 130 °C overnight, producing the dibrominated product **10a** in 76% yield,[51] as shown in Scheme 1. The two α -positions of 2,2'-carboranyldithiophene **9** are deactivated toward bromination due to the electron-withdrawing character of the *ortho*-carborane group, therefore requiring high temperature to proceed. At lower reaction temperature, or using THF, DMF, CCl₄ or pure CHCl₃ as the solvent, no bromination took place. On the other hand, using pure acetic acid as the solvent at 110 °C, produced multiple brominated products in low yields,[51] while using different ratios of chloroform/acetic acid (e.g. 2:1) also decreased the yield of the target product **10a**. The mono-brominated product **10b** was obtained as the main product in 50% yield, along with 15% of **10a**, using only 3 equiv of NBS at lower temperature (110 °C, rather than 130 °C).



Scheme 1. Synthesis of 5-bromo- and 5,5'-dibromo-*o*-carboranyl-bisthiophenes **10a,b**.

The reactivity of the newly generated *o*-carboranylbi thiophenes **10a,b** were investigated under Sonogashira and Stille cross-coupling reactions, as shown in Scheme 2. The Sonogashira coupling reaction between **10a** and ethynyltrimethylsilane, using bis(triphenylphosphine)-palladium(II) dichloride and copper(I) iodide as the catalysts, produced the corresponding diethynyl product **11**, in 80% yield. On the other hand, **10a** reacted with 3 equiv of 2-(tributylstannyl)thiophene, or with 1-methyl-2-(tributylstannyl)pyrrole or with tributyl(vinyl)tin, in the presence of tetrakis(triphenylphosphine)palladium(0) as the catalyst, in refluxing toluene for 2-4 h, to provide di(thienyl-N-methylpyrrole)-*o*-carborane **12a**, di(bisthienyl)-*o*-carborane **12b** and di(2'-vinylthienyl)-*o*-carborane **13a**, respectively, in good to excellent yields (68%-95%), as shown in Scheme 2. In addition, the Stille cross-coupling reaction between **10b** and tributyl(vinyl)tin produced the corresponding mono-vinyl product **13b** in 75% yield. The structures of all new carboranylthiophenes were confirmed by ¹H-NMR, ¹³C-NMR, MS (GC, ESI-TOF or MALDI-TOF), and by X-ray analysis (Figure 3).



Scheme 2. Reactivity of 5-bromo- and 5,5'-dibromo-*o*-carboranyl-bisthiophenes **10a,b** under Pd(0)-catalyzed cross coupling reactions.

X-Ray Analysis

By slow evaporation of hexanes or from hexane/dichloromethane mixed solvents, crystals of *o*-carboranyl-bisthiophene products **10a-b**, **11**, **12a-b**, and **13a-b** suitable for X-ray analysis were obtained, and their structures are shown in Figure 3. Compound **10a** has four independent molecules, two of which have the thiophene S atoms relatively *syn* (approximate C_s symmetry). The dihedral angles formed by the thiophene planes in these two molecules are 63.8 and 72.3°. The other two independent molecules each have one thiophene disordered into both *syn* and *anti* conformations, with the *anti* (approximate symmetry C_2) being the dominant conformer. In the disordered molecules, the two thiophene planes form dihedral angles of 63.5 and 66.2°. The four carborane C-C distances are in the range 1.732(4)-1.734(4) Å. Compound **10b** has disorder in its unsubstituted thiophene, the dihedral angle formed by the substituted and unsubstituted thiophenes is 54.1°, and the carborane C-C distance is 1.737(3) Å. **11** lies on a crystallographic two-fold axis, thus the thiophenes are *anti*, forming a dihedral angle of 54.2°. The C-C distance in the carborane is 1.7338(13) Å, and the alkyne triple bond distance is 1.2130(10) Å. Compound **12a** has approximate C_2 symmetry, with the thiophene planes forming a dihedral angle of 52.6°. The thiophene and N-methylpyrrole rings have their S and N atoms *anti*, with S-C-C-N torsion angles of 151.81(12) and 164.04(11)°. The carborane C-C distance is 1.753(2) Å. Compound **12b** also has approximate C_2 symmetry, with the carborane-bound thiophene planes forming a dihedral angle of 61.6°. Both terminal thiophenes are disordered, such that both *syn* and *anti* bisthiophenes are present. The carborane C-C distance is 1.730(11) Å. Compound **13a** has approximate C_2 symmetry, with the thiophene planes forming a dihedral angle of 63.3° and the vinyl groups *syn* to thiophene S. The carborane C-C distance is 1.7364(14) Å. In **13b**, the

thiophene rings are *anti* and form a 58.6° dihedral angle, the vinyl group is *syn* to the thiophene S, and the carborane C-C distance is 1.740(2) Å.

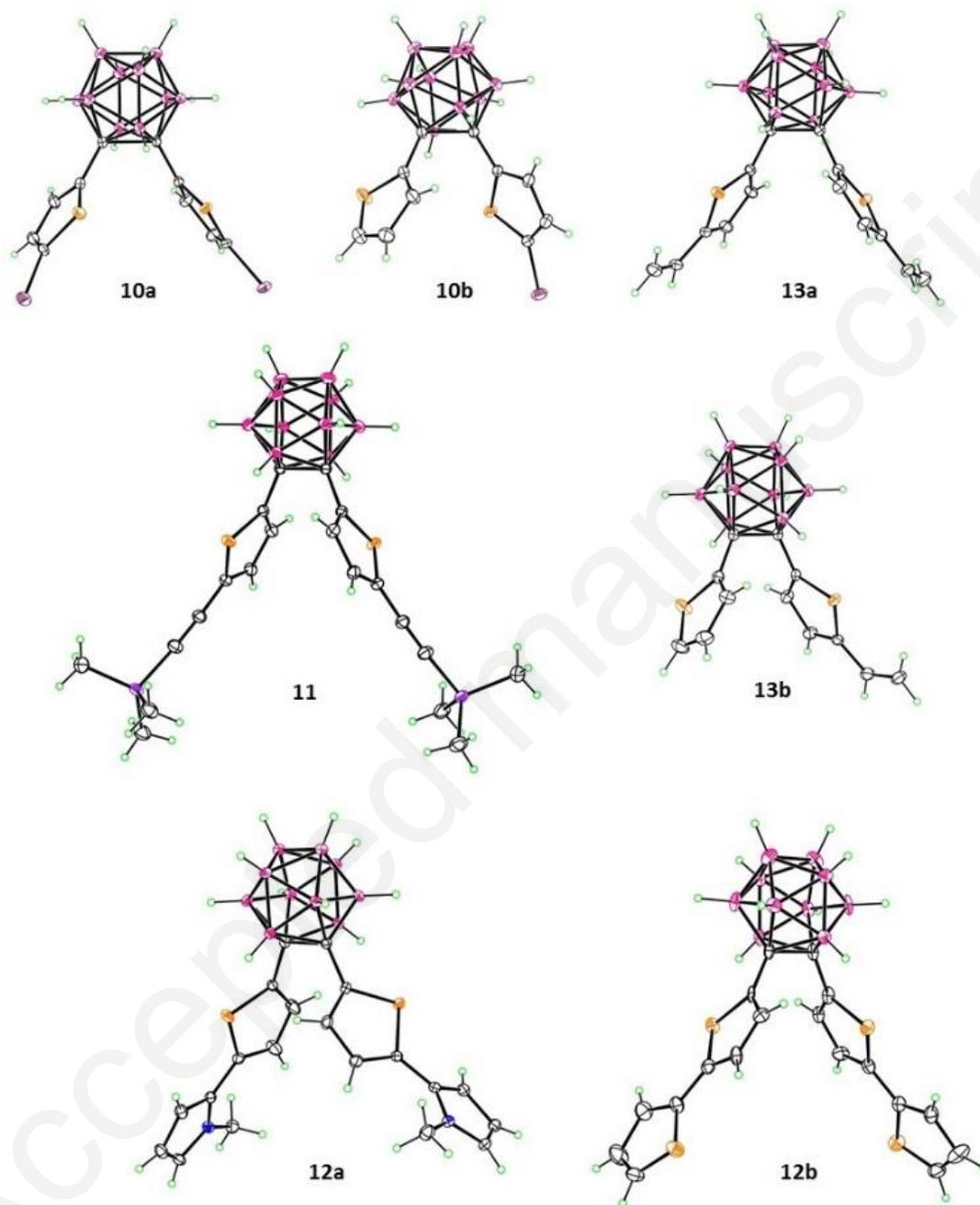


Figure 3. Crystal structures of monomers **10a-b**, **11**, **12a-b**, and **13a-b**, with 50% ellipsoids. Only the major conformer is shown for disordered thiophene rings.

Electrochemistry of the Monomers and their Corresponding Conducting Polymer Films

The cyclic voltammetry characterization of the *o*-carboranes derivatives at 5 mM in thoroughly dried $\text{CH}_2\text{Cl}_2 + 2 \times 10^{-1} \text{ M Bu}_4\text{NPF}_6$ (except for **12a** examined in $\text{CH}_3\text{CN} + 0.1 \text{ M Bu}_4\text{NPF}_6$) revealed two irreversible oxidation peaks when cycled between 0.0 and 2.2 V vs Ag/Ag^+

10⁻² M (Figure 4a and Table 1). Since unsubstituted carboranes are not oxidized under these electrolytic conditions, these can be assigned to the oxidation of the aromatic rings into radical cation species. Furthermore, the anodic potentials of these systems were found to increase in the order **12a** < **12b** < **13a** ≈ **13b**, in perfect line with the trend observed for the electrochemical oxidation of the aromatic rings substituting the carborane, namely 2-(2-thienyl)-1*H*-pyrrole[52, 53] < bithiophene[54] < 2-vinylthiophene.[55] For **12a**, both oxidation processes at 0.74 and 1.30 V can be assigned to the oxidation of the pyrrole and thiophene rings, respectively.

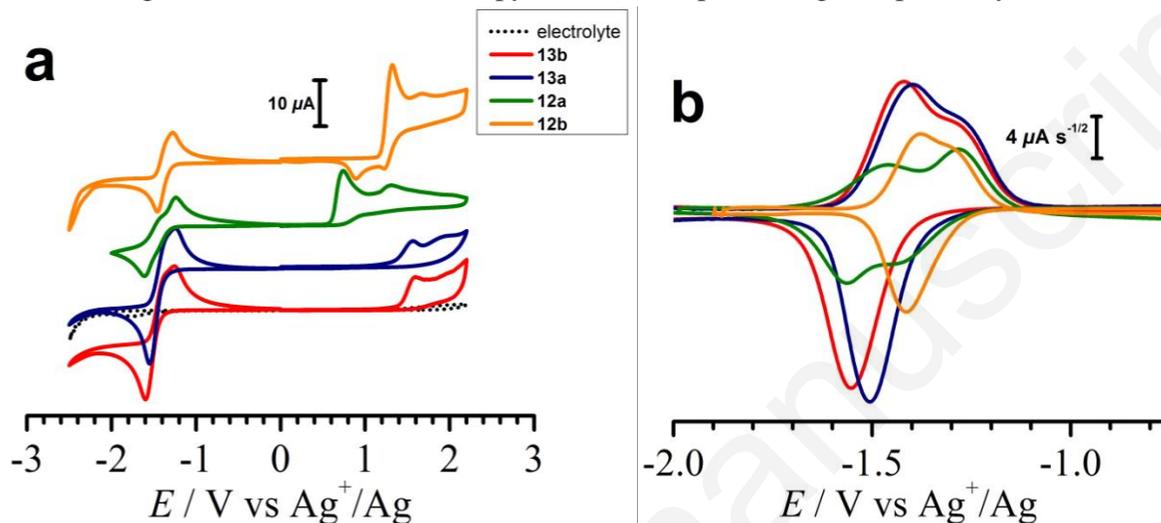


Figure 4. (a) Cyclic voltammograms at 0.1 V s⁻¹ of different *o*-carborane derivatives at 5 mM in CH₂Cl₂ + 0.2 M Bu₄NPF₆ (for **12b**, **13a** and **13b**) or CH₃CN + 0.1 M Bu₄NPF₆ (for **12a**). (b) Corresponding time semi-derivative voltammograms for the cathodic region.

Table 1. Cyclic voltammetry data of the *o*-carboranyl derivatives at 5 mM in CH₂Cl₂ or CH₃CN medium. Potential scan rate: 0.1 V s⁻¹. All potentials are reported vs. 10⁻²M Ag⁺/Ag.

	Monomer		Polymer	
	E_{ox} / V^a	E_{red} / V^b	E_{ox} / V^c	E_{red} / V^d
13b^e	1.58; 1.96	-1.43	— ^g	— ^g
13a^e	1.56; 1.93	-1.40	— ^g	— ^g
12a^f	0.74; 1.30	-1.42	0.40; 0.75	-1.50
12b^e	1.32; 1.68	-1.39	0.95; 1.30	-1.36

^aIrreversible anodic peak potentials corresponding to the monomer oxidation. ^b Formal potential corresponding to the quasi-reversible reduction step. ^c Formal potential corresponding to the reversible *p*-doping/undoping of the electrogenerated polymer (average of anodic and cathodic peak potentials). ^d Formal potential corresponding to the reduction of the carborane (average of anodic and cathodic peak potentials). ^e in CH₂Cl₂ + 0.2 M Bu₄NPF₆. ^f in CH₃CN + 0.1 M Bu₄NPF₆. ^g No conducting polymer film was electrogenerated; electrode passivation was observed.

We now turn towards the electrochemical behavior of these systems when the potential is scanned towards negative potentials. As shown in Figure 4, their reduction gives rise to two quasi-reversible closely spaced systems around -1.40 V which can be clearly evidenced on the backward scans of the corresponding time semi-derivative curves (Figure 4b). These are ascribed to the formation of radical anion and dianion species of carborane,[56, 57] respectively. Studies with analogous diaryl-substituted *ortho*-carborane systems have suggested that the electronic charge was located within the carborane cage.[57] Moreover, the fact that this cathodic process is observed at approximately the same potential for the four molecules is not surprising in so far as both the geometry of these molecules and the nature of the substituents in close proximity to the carborane are similar. Among these carboranes, only the electrochemical oxidation of **12a** and **12b** led to the formation of a conducting polymer deposit on the electrode surface. Such films could be electrogenerated either potentiodynamically or potentiostatically with no significant effect of the electropolymerization method on their respective electrochemical responses. Representative cyclic voltammograms corresponding to the potentiodynamical electropolymerization of these compounds are shown in Figure 5. As can be seen, the progressive increase of both anodic and cathodic currents with the number of scans indicates the regular growth of a conducting deposit onto the electrode surface. In contrast to the facile electropolymerization of **12a** and **12b**, **13a** and **13b** did not yield a conducting polymer deposit under various tested experimental conditions (monomer concentration, oxidation potential, solvent and electrochemical method). Instead, a poorly electroactive film was electrogenerated yielding the progressive passivation of the electrode surface. Such a result can be explained by the inhibition of the electropolymerization process owing to the substitution of the α -position of the thiophene rings by vinyl units.

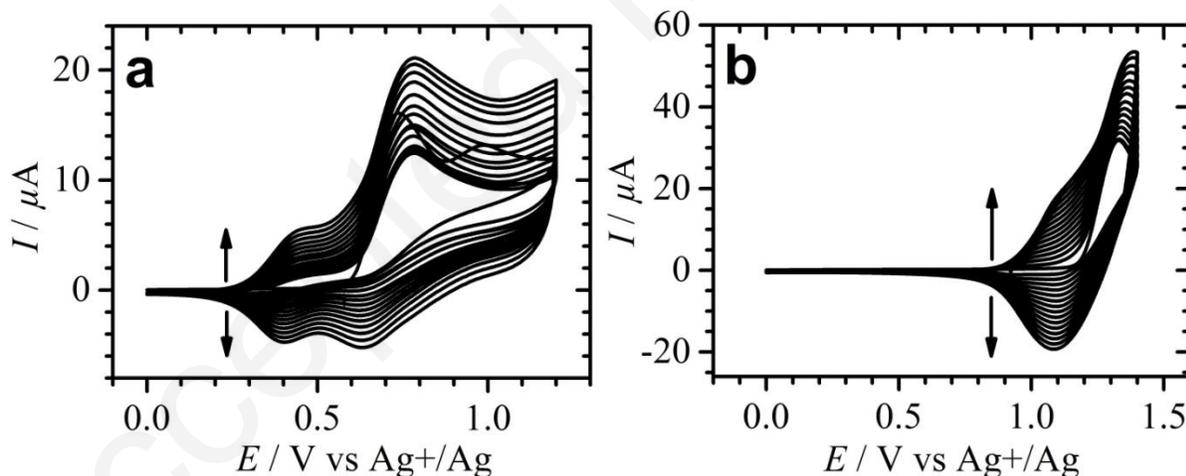


Figure 5. Successive cyclic voltammograms of **12a** (a) and **12b** (b) at 5 mM in $\text{CH}_3\text{CN} + 0.1 \text{ M Bu}_4\text{NPF}_6$ (a) or $\text{CH}_2\text{Cl}_2 + 0.2 \text{ M Bu}_4\text{NPF}_6$ (b). Potential scan rate: 0.1 V s^{-1} .

Following their electrosynthesis, the polymer films, namely poly(**12a**) and poly(**12b**), were examined in a monomer-free electrolytic medium (Figure 6). In the anodic range, their electrochemical response was characterized by two broad reversible redox processes corresponding to the *p*-doping/undoping of the expected conjugated segments (Table 1), namely 2,2'-bi-1*H*-pyrrole, 1,1'-dimethyl-1,6-di-2-thienyl and quaterthienyl units for poly(**12a**) and poly(**12b**), respectively. As expected for surface-immobilized electroactive species,[58] the anodic peak current intensities corresponding to these two

systems (I_{pa}^1 and I_{pa}^2) were found to vary linearly with the potential scan rate ν . Moreover, the doping level δ [59] of poly(**12a**) and poly(**12b**) were estimated respectively at 0.10-0.15 and 0.15-0.20 positive charge per monomer unit. Compared with unsubstituted poly(2-(2-thienyl)-1*H*-pyrrole)[52] and polythiophene,[37] the oxidation level of both polymers is lower, which demonstrates the prominent role of the incorporated carborane on the ion transport in these films. In the cathodic potential range, poly(**12a**) and poly(**12b**) showed a reversible system at -1.50 and -1.36 V, respectively, corresponding to the reduction of the carborane incorporated between two conjugated segments of the polymer (Figure 6). As for the polymer redox process, the peak currents ascribed to this system varied linearly with ν . Nevertheless, upon increasing the film thickness from the anodic charge consumed during the electropolymerization reaction, the redox signature of the carborane became less and less visible. Such intriguing effects of the film thickness on the electroactivity of the surface-confined reducible couple have already been reported by us with polythiophenes containing in-chain cobaltabisdicarbollide centers.[20] It must be kept in mind that the cathodic process occurs within a potential range where the polymer is in its neutral reduced state, i.e. in its electronically insulating state. Consequently, the reduction of the carborane in the insulating polymer matrix is expected to occur by electron hopping until the electrode surface and therefore involves cation migration through the film in order to ensure the electroneutrality of the material. For thick films, it is very likely that a large amount of carborane within the film is not electrochemically addressable because electrolyte cations can not migrate until them.

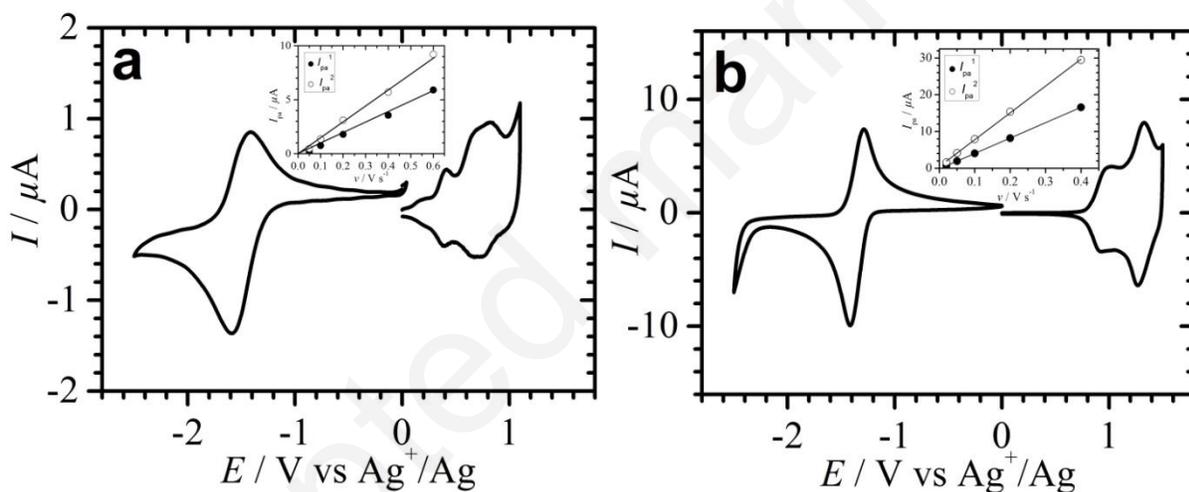


Figure 6. Electrochemical responses of the electrogenerated poly(**12a**) (a) and poly(**12b**) (b) films at 0.1 V s^{-1} with the corresponding $I_{pa} - \nu$ plots for the two anodic processes (insets). Electrolyte: $\text{CH}_3\text{CN} + 0.1 \text{ M Bu}_4\text{NPF}_6$ (a) or $\text{CH}_2\text{Cl}_2 + 0.2 \text{ M Bu}_4\text{NPF}_6$ (b). The consumed electropolymerization charges are 20 (a) and 64 mC cm^{-2} (b).

Computer Modeling

To gain insights into their properties, the monomers and the dimers of carboranyl-bisthiophenes **12a,b** and **13a,b** were modeled computationally. Figure 7 shows the shape and the energies of their frontier molecular orbitals. The HOMO and LUMO of 2,2'-carboranyldithiophene **9** are also given for comparison purposes. In general, the orbitals look similar for all compounds: both HOMO and LUMO show almost no contribution from the carborane cage. The HOMO has C-C π -bonding character and mostly non-bonding character for the remaining of the atoms in the backbone, while the LUMO shows bonding character between the carborane cage and the adjacent thiophene units. Substitution with N-methylpyrrole, thienyl, and vinyl groups at the 5- or 5,5'-positions destabilizes the HOMO by 0.5 to 1.4 eV when compared to **9**.

The effect is greatest for the N-methylpyrrole, followed by thienyl and then vinyl. This trend is consistent with the experimentally observed trend in the anodic potentials of these systems. The effect on LUMO is very small, only 0.1-0.4 eV. Thus, the resulting band gaps follow the trend of HOMO destabilization. As can be seen from Table 2, all 5,5'-substituted carboranyl-bisthiophenes exhibit smaller band gaps than **9** with the effect being most pronounced for **12a**: about 1.4 eV.

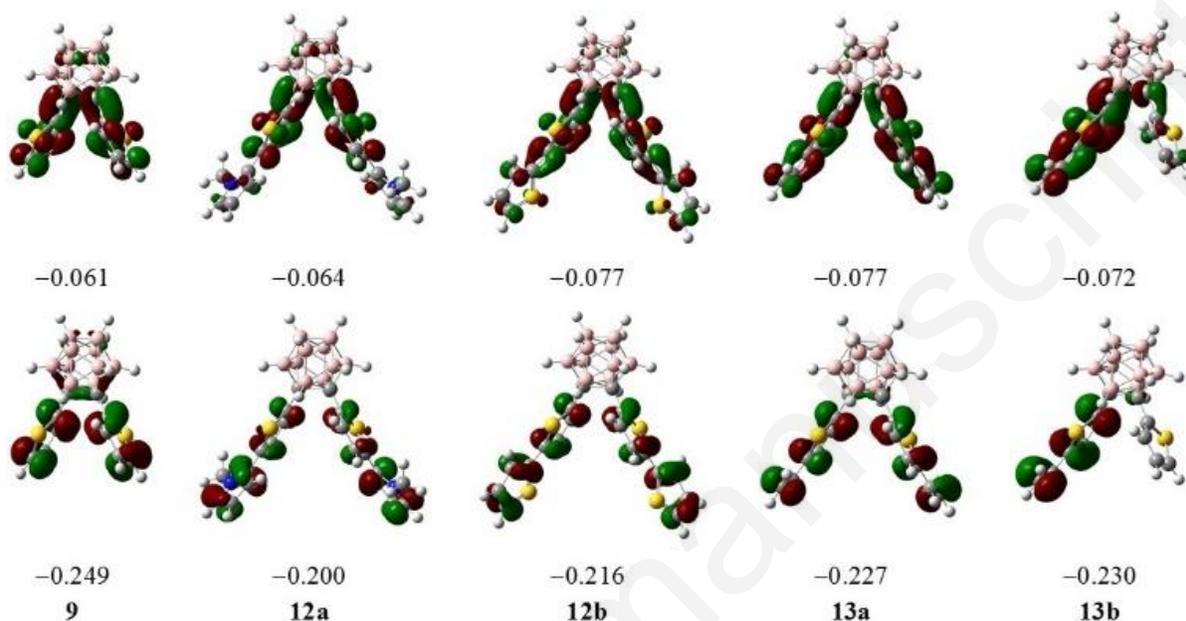


Figure 7. Frontier orbitals of carboranyl-bisthiophenes **9**, **12a,b**, and **13a,b**. Energies in a.u.

Table 2. Band gap energies, syn-anti difference energies, and energies of dimerization and intracyclization for carboranyl-bisthiophenes **9**, **12a-b** and **13a-b**.

Compound	Band Gap (eV)	$\Delta E_{\text{syn-anti}}$ (kcal/mol)	ΔE_{dimer} (kcal/mol)	$\Delta E_{\text{intracycl}}$ (kcal/mol)
9	5.11	0.22	8.36	7.34
12a	3.68	0.27	7.81	8.05
12b	3.78	0.39	8.30	7.93
13a	4.11	0.39	1.53	7.61
13b	4.30	0.25	5.01	7.50

Table 2 also shows the energy difference between the *anti* and *syn* conformers. In agreement with the X-ray Analysis (Figure 3), the *syn* conformer is more stable but the energy difference is very small: less than 0.5 kcal/mol. This finding is also consistent with previously performed calculations on compound **9** and its *meta*, and *para* analogues. Erreur ! Source du renvoi introuvable.

The last two columns of Table 2 list the energies required for formation of the dimer, ΔE_{dimer} , and the energy required for intracyclization, $\Delta E_{\text{intracycl}}$. The energies required for dimerization of **12a** and **12b** are similar to that of **9** and are around 8 kcal/mol. The vinyl substitution has more pronounced effect on the dimerization energy: it appears that each vinyl substitution reduces the required energy and makes the dimer easier to form. In view of these facts, the reason why **13a** and **13b** fail to polymerize is unlikely to be in the difficulty of the formation of the dimer. Another possible mechanism for the polymerization is the previously proposed intramolecular cyclization.^{Erreur ! Source du renvoi introuvable.} The energies required for the intramolecular cyclization are given in the last column of Table 2. All energies are between 7 and 8 kcal/mol without significant differences when pyrrole, thienyl, vinyl, or no substitution is used. All structures are planar, which is in agreement with previously reported data for **9**.^{Erreur ! Source du renvoi introuvable.}

Conclusions

A new series of 2,2'-(*ortho*-carboranyl)-bisthiophenes bearing N-methylpyrrole, vinyl, trimethylsilylethyne, or thienyl groups at the 5,5'-positions were synthesized in good yields via \square -bromination of 2,2'-carboranyldithiophene **9** followed by palladium(0)-catalyzed cross-coupling reactions of the Sonogashira and Stille types. Seven X-ray structures were obtained to confirm the regioselectivity of the reactions, and the solid state characteristics of the new compounds. The electrochemical characterization of these systems showed that their anodic potential increased in the order **12a** < **12b** < **13a** \approx **13b**, which is consistent with the trend observed from DFT calculations. In addition, poly(**12a**) and poly(**12b**) could be electro-generated from new compounds **12a** and **12b** under the suitable conditions. The lower doping levels determined for both electro-generated polymers compared with the parent conducting polymers, suggest the prominent effect of the incorporated carborane clusters. Furthermore, DFT calculations also suggest that low energy is required for the intramolecular cyclization of compounds **12a** and **12b**, which may provide more organized structures for the generated polymers. Therefore, poly(**12a**) and poly(**12b**) are promising candidates for the development of carborane-functionalized conducting materials with enhanced chemical and thermal stabilities.

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