CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.201201513

Synthesis and Properties of Thiophene-Fused Benzocarborane

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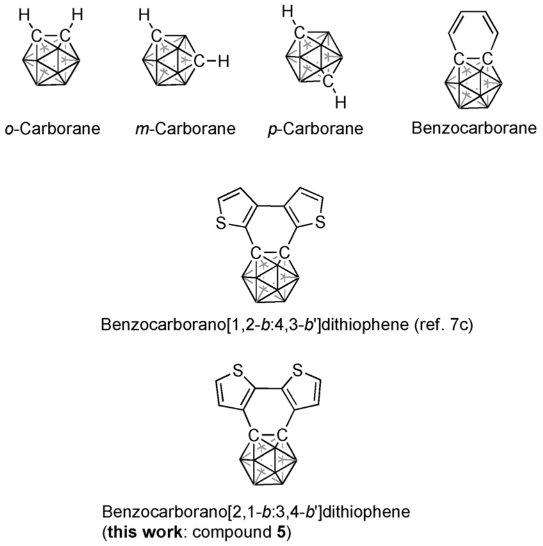
Abstract: The *o*-carborane-based π-conjugated compound, benzocarborano[2,1-*b*:3,4-*b*′]dithiophene was synthesized. Its crystal structure revealed high coplanarity for the two thiophene rings of the 2,2′-bithiophene skeleton, which is fixed in the *cisoid* structure by the *o*-carborane unit. Theoretical calculations indicated non-aromaticity for its center C_6 ring moiety as well as decreased HOMO and LUMO levels. The *o*-carborane moiety provides an electron-withdrawing character to the 2,2′-bithiophene unit through an inductive effect.

Keywords: carboranes · conjugation · electronic structure · fused-ring systems · sulfur heterocycles

Introduction

Carboranes are a class of polyhedral boron cluster compounds containing two carbon atoms in the cluster cage. Representative examples of this class of compound are the icosahedral boron–carbon clusters *o*-, *m*-, and *p*-carborane (*o*-, *m*-, and *p*-$C_2B_{10}H_{12}$, respectively) shown in Scheme 1. They exhibit three-center two-electron bonds as well as three dimensionally conjugated electrons that confer high thermal and chemical stability.[1] Because of these unique properties, such compounds have been widely used in various areas ranging from, for example, heat-resistant polymers[2] for industrial use to boron-neutron capture therapy (BNCT) in the field of health and medical care.[3] Several π-conjugated compounds and polymers in which carboranes are incorporated into the extended π-conjugation systems have been reported. For example, Yamamoto and co-workers synthesized carborane–fullerene as well as carborane–ferrocene conjugated dyads by taking advantage of the strong electron-withdrawing character of carborane, which leads to considerable hyperpolarizability.[4] Tour and co-workers employed carborane as a wheel for their nanocars by exploiting the highly symmetric structural features of carborane rather than the electronic features.[5] A series of carborane-appended 1,3,5-triphenylbenzene and 1,3,5-tris(biphenyl-4-yl)benzene derivatives were synthesized, and their emission behavior was investigated.[6] Moreover, conjugated polymers containing carboranes in their main chains have also been prepared; carboranes have been incorporated into poly(*p*-arylene)[7a] and polythiophene[7b,c] skeletons. In addition, carborane-based luminescent conjugated polymers have been reported independently by two research groups. Coughlin, Carter, and co-workers synthesized *o*- and *p*-carborane-containing polyfluorenes[8] by Yamamoto coupling polymerization[9] and described their application as reversible colorimetric sensors for volatile nitrogen-containing molecules.[8c] Our group has also synthesized *o*- and *m*-carborane-containing poly(*p*-arylene-ethynylene) derivatives[10] by Sonogashira–Hagihara coupling.[11] We found that the *o*-carborane-containing poly(*p*-arylene-ethynylene) materials exhibited aggregation-induced-emission (AIE)[12] in the film or aggregated form, whereas their emission was quenched in solution. This emission behavior stems from the variable carbon–carbon bond in the phenyl-substituted *o*-carborane moiety. Very recently, it was reported that π-electron systems with a *o*-carborane core act as electron acceptors by



Scheme 1. Structures of *o*-, *m*-, *p*-carboranes, and *o*-carborane-based compounds.

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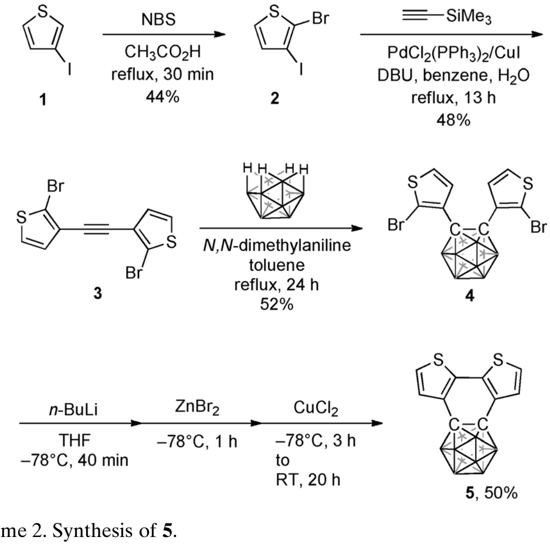
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201201513.

photo-excitation, and their charge-transfer (CT) behavior in the excited state was investigated in detail.[13] Thus, the carborane skeleton is an attractive framework for constructing new high-performance π-conjugated compounds.

Inspired by these results, we extended our work to create *o*-carborane-based π-conjugated molecules. In this study, we focused on benzocarboranes (Scheme 1), in which a benzene ring and the carbon–carbon bond of the *o*-carborane are fused to form a benzenoid ring structure on the carborane cage.[14] Specifically, we prepared benzocarborano[2,1-*b*:3,4-*b*′]dithiophene (Scheme 1), in which the thiophene rings are further fused on the benzenoid unit. Note that the formation of the benzocarborano[1,2-*b*:4,3-*b*′]dithiophene skeleton in the conjugated polymer backbone was implied by the intramolecular β-β′ electrochemical cyclization of di-(2-thienyl)-*o*-carborane.[7c,15] However, there have been no reports on the synthesis or isolation of a series of benzocarboranodithiophene derivatives, and their fundamental properties remain unclear. Here, we report a detailed synthetic procedure for and characteristics of benzocarborano-[2,1-*b*:3,4-*b*′]dithiophene, and we discuss its potential use as a building block for various *o*-carborane-based π-conjugated molecules.

Results and Discussion

The synthetic procedure used to access benzocarborano-[2,1-*b*:3,4-*b*′]dithiophene (**5**) is shown in Scheme 2. 3-Iodothiophene (**1**) was brominated at the 2-position by *N*-bromosuccinimide (NBS) to obtain 2-bromo-3-iodothiophene (**2**) in 44 % yield. Sonogashira–Hagihara coupling reaction of **2** with trimethylsilylacetylene was carried out by using a $[PdCl_2(PPh_3)_2]$/CuI catalytic system with 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) in benzene and H_2O,[16] and the desilylation also proceeded simultaneously to afford **3** in 48 % yield. Treatment of **3** and decaborane with *N*,*N*-dimethylaniline afforded bis[3-(2-bromothienyl)]-*o*-carborane (**4**) in 52 % yield. The bromine–lithium exchange reaction of **4** with *n*BuLi proceeded, and successive treatment with $ZnBr_2$ and $CuCl_2$ provided the target compound **5** in 50 % isolated yield.



Scheme 2. Synthesis of **5**.

Compound **5** was obtained as an air- and moisture-stable white solid, which was characterized by ^{1}H, ^{13}C, and ^{11}B NMR spectroscopic analysis (Figure S6–8 in the Supporting Information), high-resolution mass analysis, and elemental analysis. Single crystals were readily formed from $CHCl_3$ and MeOH solution, and the molecular structure was determined by X-ray crystallography. As shown in Figure 1, the crystal structure of **5** revealed the high planarity of the 2,2′-bithiophene skeleton with a torsion angle (S1-C2-C3-C4) of 179.26° between the two thiophene rings, which was fixed with a *cisoid* structure. From the structure of **5**, it looks as if the 3- and 3′-positions in bithiophene are fastened with a bulldog clip. The C−C bond lengths of the center C_6 ring are found to be 1.376(9) (C1−C2), 1.419(10) (C2−C3), 1.351(10) (C3−C4), 1.494(9) (C4−C5), 1.634(8) (C5−C6), and 1.483(8) Å (C6−C1). In particular, the results show that the C5−C6 bond length (1.634(8) Å) of the carborane cage in **5** is much longer than that in benzene (1.397 Å) and is similar to that for benzocarborane (1.651 Å).[17] In addition, the C1−C2 and C3−C4 bond lengths in **5** (1.376(9) and 1.351(10) Å, respectively) are shorter than the C2−C3 bond length (1.419(10) Å), indicating that the C1-C2-C3-C4 butadiene skeleton consists of localized double bonds and a single bond.[17]

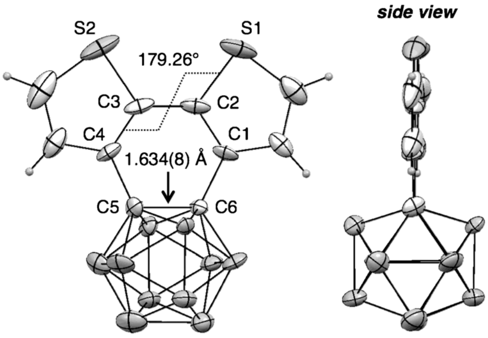


Figure 1. Molecular structures of **5**. Thermal ellipsoids are drawn at the 30 % probability level. Selected bond lengths (Å) are: C1−C2 1.376(9); C2−C3 1.419(10); C3−C4 1.351(10); C4−C5 1.494(9); C5−C6 1.634(8); C6−C1 1.483(8).

From the molecular structure as well as from reports by Matteson[14] and Wade,[17] aromaticity is not expected for the center C_6 ring in **5**. To obtain further insight into the aromaticity, the nucleus-independent chemical shift (NICS) values were calculated at the B3LYP/6-31G(d,p)//B3LYP/6-31G-(d,p) level, together with values for related compounds benzo[2,1-*b*:3,4-*b*′]dithiophene and 4,5-dihydrobenzo[2,1-*b*:3,4-*b*′]dithiophene. As shown in Figure 2, the NICS(1) values of the thiophene rings were estimated to be less than −8.0 for all the compounds, suggesting their aromaticity. The NICS(1) value of the benzene ring in benzo[2,1-*b*:

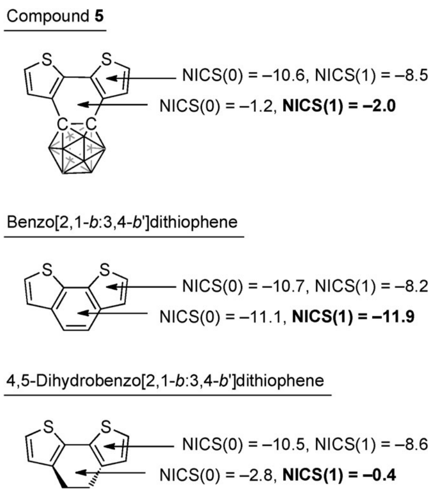
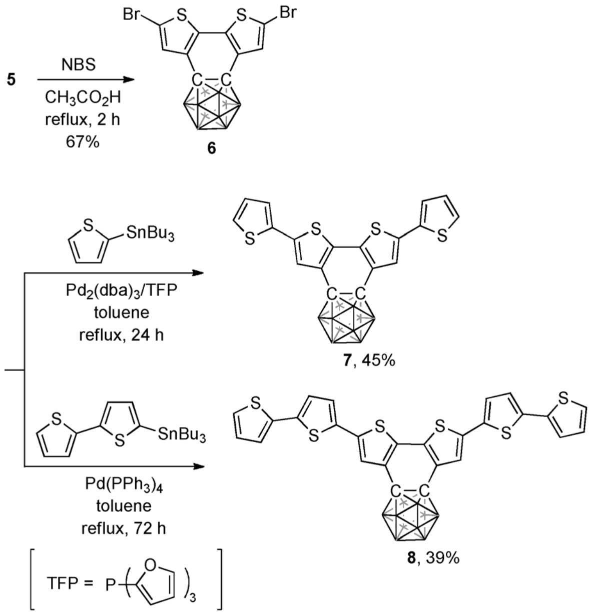


Figure 2. NICS values (ppm) of **5**, benzo[2,1-*b*:3,4-*b*′]dithiophene, and 4,5-dihydrobenzo[2,1-*b*:3,4-*b*′]dithiophene calculated at the B3LYP/6-31G(d,p)//B3LYP/6-31G(d,p) level.

3,4-*b*′]dithiophene was −11.9, whereas those of the C_6 rings in **5** and 4,5-dihydrobenzo[2,1-*b*:3,4-*b*′]dithiophene were −2.0 and −0.4, respectively. Although the NICS(1) value (−2.0) for the center C_6 ring in **5** is smaller than that in 4,5-dihydrobenzo[2,1-*b*:3,4-*b*′]dithiophene (−0.4), this result does not confirm that the C−C bond of the carborane cage in **5** possesses double bond character to express the aromaticity of the center C_6 ring moiety.

The highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) of **5**, benzo[2,1-*b*:3,4-*b*′]dithiophene, and 4,5-dihydrobenzo[2,1-*b*:3,4-*b*′]dithiophene were estimated (Figure 3). The HOMO and LUMO levels of **5** were calculated to be −6.13 and −1.99 eV, respectively. These values are lower than those of benzo[2,1-*b*:3,4-*b*′]dithiophene (−5.76 and −0.97 eV for HOMO and LUMO, respectively) and 4,5-dihydrobenzo[2,1-*b*:3,4-*b*′]dithiophene (−5.21 and −1.09 eV for HOMO and LUMO, respectively), indicating the electron-withdrawing character of the carborane unit. Both the HOMO and LUMO of **5** were centered on the bithiophene moiety, and no overlap of orbitals was observed between bithiophene and *o*-carborane units. For the present fused system, charge-transfer (CT) transition is not expected, and the *o*-carborane moiety acts as an electron-withdrawing group operating through an inductive effect rather than a conjugation effect.

We also constructed extended π-conjugation systems by using compound **5** as a scaffold. As shown in Scheme 3, bromination of **5** by NBS proceeded smoothly to afford **6** in 67 % yield.[18] Treatment of **6** with 2-(tributylstannyl)thiophene and 5-(tributylstannyl)-2,2′-bithiophene in the presence of $[Pd_2(dba)_3]$ with tri-(2-furyl)phosphane (TFP)[19] or $[Pd(PPh_3)_4]$ afforded the corresponding oligothiophenes **7** and **8** in 45 and 39 % isolated yields, respectively, as air-stable powders.[20] UV/Vis absorption spectra and photoluminescence spectra of compounds **5**, **7**, and **8** in $CHCl_3$ (1.0×10^{-5} M) are shown in Figure 4,[21] and their optical properties are summarized in



Scheme 3. Synthesis of **7** and **8**.

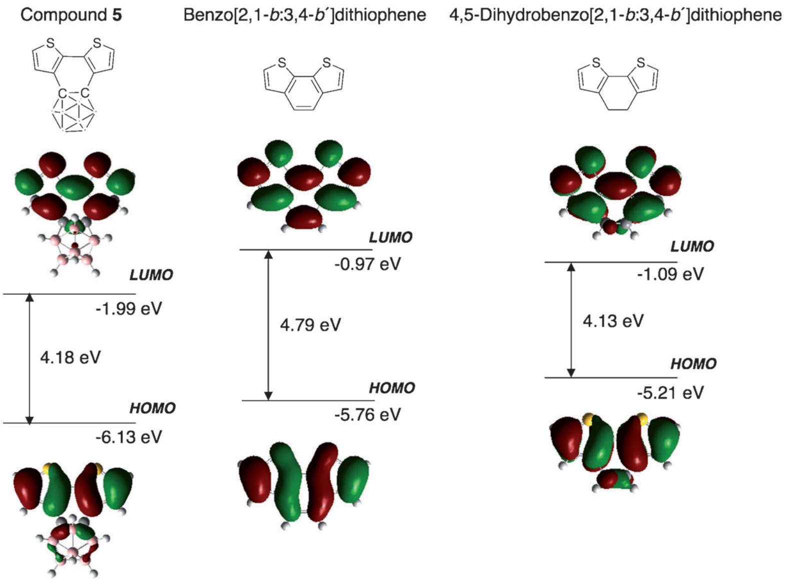


Figure 3. The HOMO and LUMO orbitals and their energy levels calculated at the B3LYP/6-31G(d,p) level of theory for compound **5**, benzo[2,1-*b*:3,4-*b*′]dithiophene, and 4,5-dihydrobenzo[2,1-*b*:3,4-*b*′]dithiophene.

Table 1. Optical and electrochemical data.

Compound	UV/Vis[a]				PL[a,d]		CV[f]			
	$\lambda_{abs,max}$ [nm]	ε [$M^{-1}cm^{-1}$][b]	$\lambda_{abs,edge}$ [nm]	E_g [eV][c]	$\lambda_{pl,max}$ [nm]	Φ_{pl}[e]	$E_{onset}{}^{red}$ [V]	LUMO [eV]	$E_{onset}{}^{ox}$ [V]	HOMO [eV]
5	310, 323, 337	15000	350	3.5	365	0.01	−2.1	−2.7	1.1	−5.9
BT[h]	305	11000	350	3.5	366	0.11	–	−2.3[g]	0.8	−5.6
7	261, 315, 414	47000	475	2.6	460, 489	0.21	−1.8	−3.0	0.6	−5.4
QT[i]	250, 392	39000	460	2.7	459, 488	0.20	–	−2.5[g]	0.4	−5.2
8	265, 320, 380, 458	–	530	2.3	519, 555	0.45	–	–	–	–
ST[j]	255, 324, 422	–	520	2.4	507, 549	0.34	–	–	–	–

[a] In $CHCl_3$ solution (1.0×10^{-5} M) at room temperature. Solubility of **8** and ST was less than 1.0×10^{-5} M in $CHCl_3$; therefore, the data were collected from highly diluted $CHCl_3$ solutions. [b] Molar extinction coefficient. [c] Band gap energy: $E_g = 1240/\lambda_{abs,edge}$. [d] Photoluminescence (excited at each $\lambda_{abs,max}$). [e] Absolute photoluminescence quantum efficiency. [f] In solution (1.0 mM) at room temperature, vs. ferrocene/ferrocenium external reference. See Figure S26 and S27 in the Supporting Information. [g] LUMO = HOMO + E_g. [h] Bithiphene. [i] Quaterthiophene. [j] Sexithiophene.

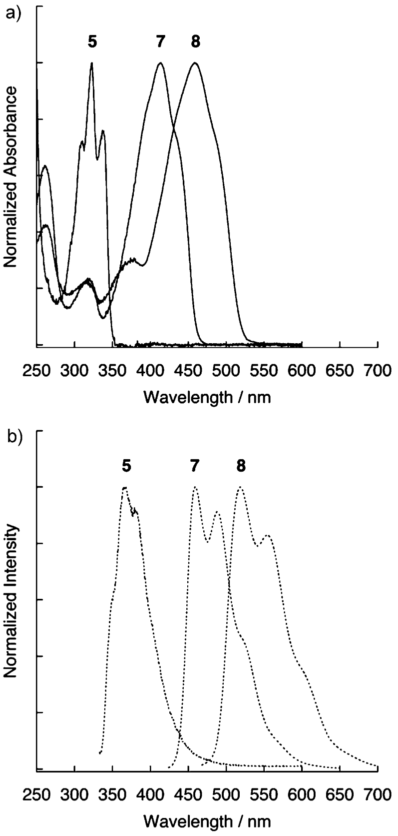
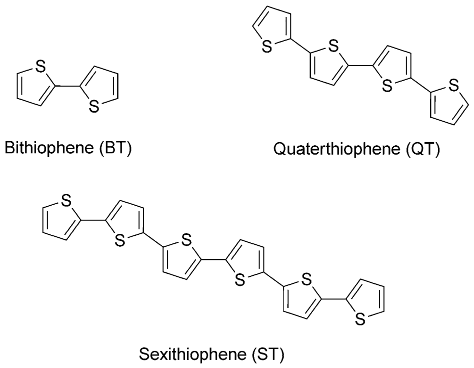


Figure 4. a) UV/Vis absorption spectra of **5**, **7**, and **8** in $CHCl_3$ (1.0×10^{-5} M). b) Photoluminescence spectra of **5**, **7**, and **8** in $CHCl_3$ (1.0×10^{-5} M) excited at each absorption maximum.



Scheme 4. Structures of bithiophene (BT), quaterthiophene (QT), and sexithiophene (ST).

Table 1 together with data[22] for bithiphene (BT), quaterthiophene (QT), and sexithiophene (ST) (Scheme 4). As shown in Figure 4a, the longest absorption bands of **5**, **7**, and **8**, which are ascribed to the π–π* transition, are bathochromically shifted with a concomitant increase in the molar extinction coefficient (ε) (Table 1) in accordance with the extension of the π-conjugation systems.[22,23] The absorption maxima ($\lambda_{abs,max}$) of **5**, **7**, and **8** were observed at longer wavelengths than those of the corresponding oligothiophenes BT, QT, and ST (Table 1). This result is rationalized as being partly the result of suppression of the rotary motion of the two thiophene rings by the *o*-carborane skeleton in **5**, **7**, and **8**, which can also explain the smaller Stokes shifts of **5**, **7**, and **8** compared with those of the series of oligothiophenes (Table 1). As shown in Figure 4b, compounds **5**, **7**, and **8** emitted by photo-excitation (in $CHCl_3$; 1.0×10^{-5} M) absolute photoluminescence quantum efficiencies (Φ_{pl}s) of 0.01, 0.21, and 0.45, respectively. Their spectra also exhibited vibrational structures, as observed in the spectra of the corresponding oligothiophenes BT, QT, and ST (Figure S21–23 in the Supporting Information). In addition, AIE was not observed in **5**, **7**, and **8**. These results imply that the photoluminescence of benzocarborano[2,1-*b*:3,4-*b'*]dithiophene and its derivatives is the common S_1–S_0 emission rather than CT emission due to suppression of the mobility of the carbon–carbon bond in the *o*-carborane cage.

The HOMO–LUMO band gaps for all compounds were estimated from their absorption edges, which are listed in Table 1. In addition, the HOMO and LUMO energy levels were also estimated from the cyclic voltammetry peak onset potentials as well as the band gap energy (Figure 5). Compounds **5** and **7** exhibited both oxidation and reduction peaks, whereas only oxidation peaks were observed in BT and QT. For example, the energy band gaps of **5** and BT were almost identical (3.5 eV according to the absorption spectra as well as 3.2 eV according to the cyclic voltammo-

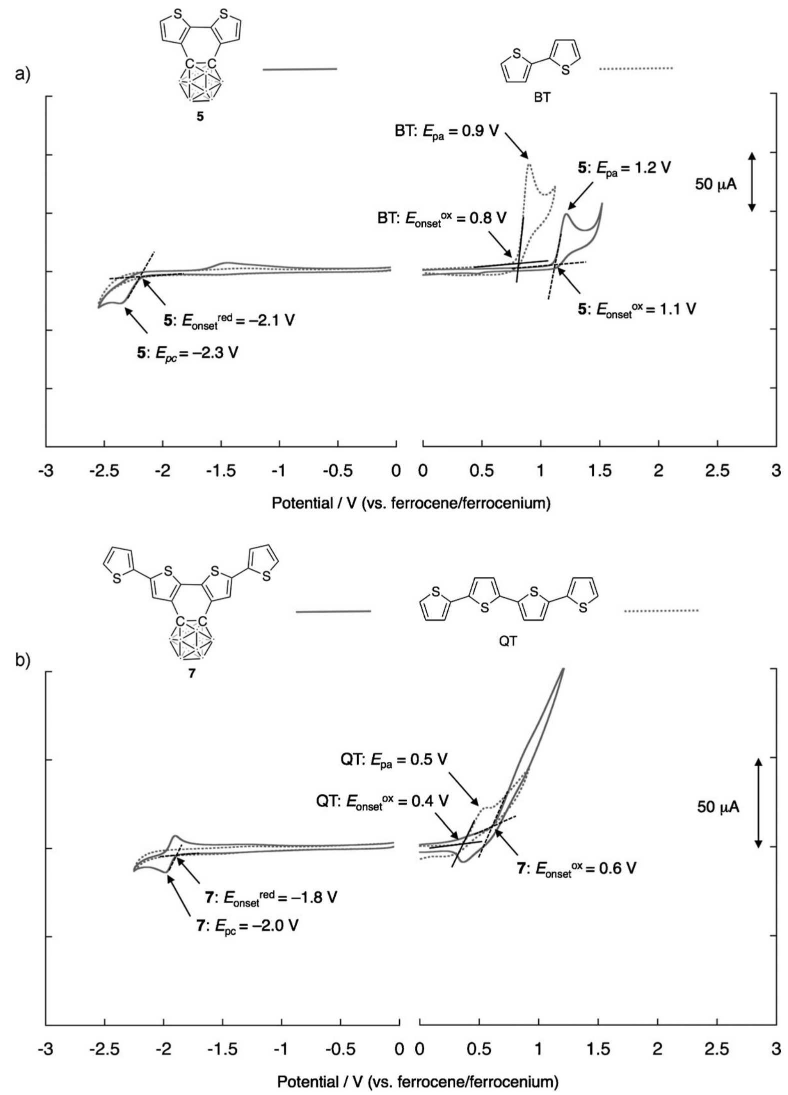
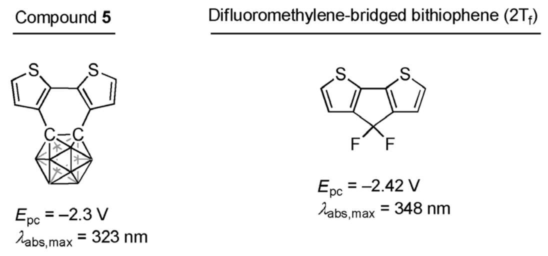


Figure 5. a) Cyclic voltammograms of **5** and BT. In CH_3CN (1.0 mM) containing NBu_4BF_4 (0.1 M) for oxidation and DMF (1.0 mM) containing NBu_4ClO_4 (0.1 M) for reduction using a Pt working electrode, a Pt wire counter electrode, a Ag/AgCl reference electrode, and a ferrocene/ferrocenium external standard at room temperature with a scan rate of 0.1 Vs^{-1} under N_2. b) Cyclic voltammograms of **7** and QT. In THF (1.0 mM) containing NBu_4ClO_4 (0.1 M) for oxidation and DMF (1.0 mM) containing NBu_4ClO_4 (0.1 M) for reduction using a Pt working electrode, a Pt wire counter electrode, a Ag/AgCl reference electrode, and a ferrocene/ferrocenium external standard at room temperature with scan rate of 0.1 Vs^{-1} under N_2.

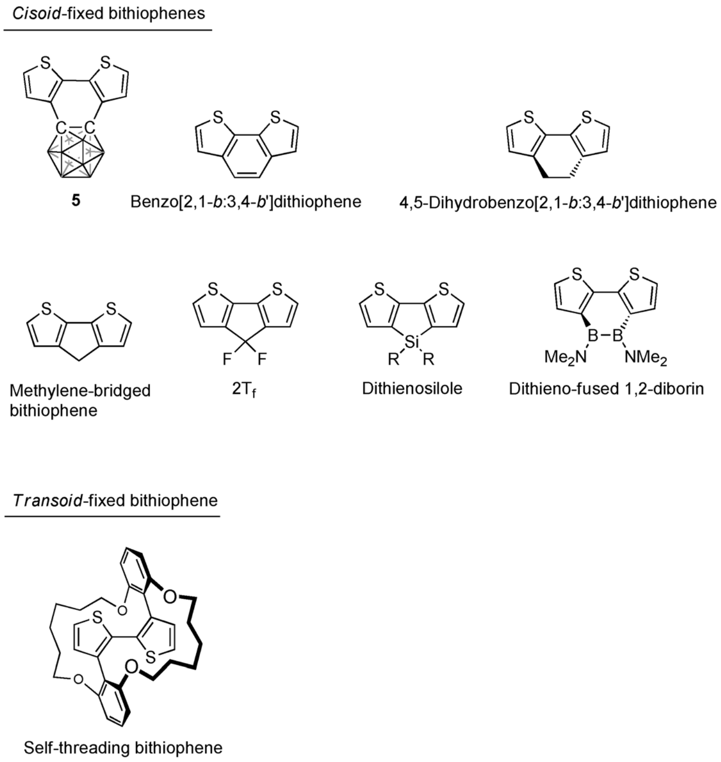
grams in Table 1); however, the HOMO and LUMO levels of **5** were approximately 0.3 eV lower than those of BT. Thus, the carborane moiety acts as an electron-withdrawing group acting through an inductive effect rather than a conjugation effect.

For comparison, we consider the difluoromethylene-bridged bithiophene $2T_f$, in which bithiophene is fixed with the electron-withdrawing -CF_2- group (Scheme 5).[24] Compound $2T_f$ is electronegative with an anodic peak potential E_{pa} of +0.99 V and cathodic peak potential E_{pc} of −2.42 V. The E_{pc} value of **5** (−2.3 V in Figure S26 in the Supporting Information) is slightly larger than that of $2T_f$, indicating that **5** is comparable to $2T_f$ in terms of its electronegativity. The difference between $2T_f$ and **5** is their conjugation system. The C−F bond orbital is conjugated with the bithiophene π-orbital in the LUMO of $2T_f$, indicating that the contribution of the conjugation effect decreases the energy level, in contrast to the inductive effect of **5**. The $\lambda_{abs,max}$ of $2T_f$ is 348 nm, which is longer than that of **5** ($\lambda_{abs,max}$ = 323 nm) due to the conjugation effect.

From the structural viewpoint, the bithiophene unit of **5** adopts the fixed *cisoid* form, in common with, for example, benzo[2,1-*b*:3,4-*b*′]dithiophene, 4,5-dihydrobenzo[2,1-*b*:3,4-*b*′]dithiophene, methylene-bridged bithiophene, difluoromethylene-bridged bithiophene $2T_f$,[24] dithienosilole,[25] and dithieno-fused 1,2-diborin[26] (Scheme 6).[27] However, the conjugation systems of the bithiophene units in benzo[2,1-*b*:3,4-*b*′]dithiophene, $2T_f$, dithienosilole, and dithieno-fused 1,2-diborin are conjugated with their bridge units (-CH=CH-, -CF_2-, -SiR_2-, and -$B(NMe_2)$-$B(NMe_2)$-, respectively). In addition, the bithiophene units in 4,5-dihydrobenzo[2,1-*b*:3,4-*b*′]dithiophene and dithieno-fused 1,2-diborin are twisted by C−C and B−B bridge chains, respectively. Thus, *o*-carborane is regarded as a molecular bulldog clip that fastens biaryls to achieve the high planarity without electronic perturbations in the conjugation systems.



Scheme 5. Structures of compound **5** and difluoromethylene-bridged bithiophene ($2T_f$).



Scheme 6. Structures of *cisoid*-fixed bithiophenes and *transoid*-fixed bithiophene.

Conclusion

This work introduces an *o*-carborane-based π-conjugated compound, benzocarborano[2,1-*b*:3,4-*b′*]dithiophene, in which the 2,2′-bithiophene unit is fixed in the *cisoid* structure by the *o*-carborane unit. Its crystal structure revealed high coplanarity for the two thiophene rings of the 2,2′-bithiophene skeleton and non-aromaticity for the center C_6 ring moiety. The *o*-carborane unit provides an electron-withdrawing character to the 2,2′-bithiophene unit through an inductive effect rather than a conjugation effect; according to UV/Vis absorption spectroscopy and CV, it lowers both the HOMO and LUMO levels of the 2,2′-bithiophene unit without changing the band-gap energy, which was supported by DFT calculations. In the aromatic-ring-fused benzocarborane, the CT state is not formed by photo-excitation, in contrast to the π-electron-system-substituted *o*-carboranes. Finally, the facile transformation of benzocarborano[2,1-*b*:3,4-*b′*]dithiophene enables us to prepare various π-conjugated oligomers and polymers, offering great promise for use as an electronegative π-conjugated building block.

Experimental Section

Synthesis of 3: A 100 mL round-bottom flask with a Teflon-coated magnetic stir bar was fitted with a reflux tube, and dried under vacuum. The flask was purged with dry Ar and charged with [$PdCl_2(PPh_3)_2$] (0.444 g, 0.632 mmol), CuI (0.200 g, 1.05 mmol), and **2** (3.04 g, 10.5 mmol). While stirring, anhydrous benzene (53 mL) was added under an Ar atmosphere by using a syringe. DBU (9.62 g, 63.2 mmol) was added by using a syringe, followed by a purge of the reaction flask with Ar. Ice-chilled trimethylsilylacetylene (0.745 mL, 5.27 mmol) was added by using a syringe, and H_2O (76.0 μL, 40 mol%) was immediately added.[4] The reaction flask was covered in aluminum foil and the reaction mixture was heated to reflux for 13 h, then poured into H_2O and extracted with Et_2O. The organic layer was washed with diluted aqueous HCl, brine, and dried over $MgSO_4$. After $MgSO_4$ was removed, the solvent was reduced under vacuum. The residue was purified by silica gel column chromatography (hexane) to give **3** as a yellow solid (0.885 g, 48%). ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.21$ (d, $J=5.60$ Hz, 2H), 7.03 ppm (d, $J=5.60$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=129.8$, 125.9, 124.2, 117.4, 86.6 ppm; ^1H NMR chemical shifts were in agreement with reported values.[28]

Synthesis of 4: A mixture of **3** (734 mg, 2.11 mmol) and decaborane (296 mg, 2.43 mmol) was dissolved in anhydrous toluene (21 mL) at RT under an Ar atmosphere. *N,N*-Dimethylaniline (481 μL, 3.80 mmol) was added and the mixture was heated to reflux for 24 h. After cooling to RT, the mixture was decanted from the solid residue and evaporated. The crude residue was subjected to silica gel column chromatography with hexane as an eluent ($R_f=0.30$). Recrystallization from $CHCl_3$ and MeOH provided **4** as colorless crystals (593 mg, 52%). ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.03$ (d, $J=6.09$ Hz, 2H), 6.92 (d, $J=6.09$ Hz, 2H), 4.60–1.60 ppm (br, 10H; B-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=131.2$, 127.6, 125.6 (Ar), 116.5, 81.0 ppm (carborane-*C*); ^{11}B NMR (128 MHz, $CDCl_3$): $\delta=-2.15$ (d, $J(B,H)=150.0$ Hz; 2B), −10.2 ppm (overlapping signals, 8B); HRMS (EI^+): *m*/*z* calcd for $C_{10}H_{14}B_{10}Br_2S_2$: 465.9834; found: 465.9850; elemental analysis calcd (%) for $C_{10}H_{14}B_{10}Br_2S_2$: C 25.76, H 3.03; found: C 25.53, H 3.05.

Synthesis of 5: A solution of **4** (187 mg, 0.400 mmol) in THF (4.0 mL) was added slowly to a stirred solution of *n*BuLi (1.60 M in hexane, 530 μL) under an Ar atmosphere at −78 °C by using a syringe, and the mixture was stirred at −78 °C for 40 min. A solution of anhydrous $ZnBr_2$ (180 mg, 0.800 mmol) in THF (1.0 mL) was added dropwise to the stirred solution under an Ar atmosphere at −78 °C by using a syringe, and the mixture was stirred at −78 °C for 1 h. Anhydrous $CuCl_2$ (53.1 mg, 0.400 mmol) was added in one portion with vigorous stirring and the mixture was stirred at −78 °C for 3 h. The reaction mixture was allowed to slowly warm to RT and, after stirring at RT for 20 h, the reaction was quenched by the addition of aqueous ammonia and extracted with $CHCl_3$. The $CHCl_3$ solution was washed with aqueous ammonia and brine, and dried over $MgSO_4$. $MgSO_4$ was removed, and the solvent was evaporated. The residue was purified by silica gel column chromatography with hexane as an eluent ($R_f=0.46$) to obtain **5** as a white solid (56.8 mg, 0.20 mmol, 50%). Single crystals of **5** were obtained by recrystallization from $CHCl_3$ and MeOH (CCDC-874952). ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.29$ (d, $J=5.12$ Hz, 2H), 7.22 (d, $J=5.12$ Hz, 2H), 3.60–0.70 ppm (br, 10H; B-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=131.6$, 129.1, 126.7, 124.5, 73.2 ppm (carborane-*C*); ^{11}B NMR (128 MHz, $CDCl_3$): $\delta=-9.02$ (d, $J(B,H)=151.0$ Hz, 2B), −12.9 ppm (m, overlapping signals, 8B); HRMS (EI^+): *m*/*z* calcd for $C_{10}H_{14}B_{10}S_2$: 308.1468; found: 308.1479; elemental analysis calcd (%) for $C_{10}H_{14}B_{10}S_2$: C 39.19, H 4.60, S 20.93; found: C 38.90, H 4.44, S 20.94. CCDC-874952 (**5**) and CCDC-874593 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

Financial support from The Japan Securities Scholarship Foundation is gratefully acknowledged. M. T. appreciates Research Fellowships from the Japan Society for the Promotion of Science for Young Scientists.

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Received: May 1, 2012

Carboranes

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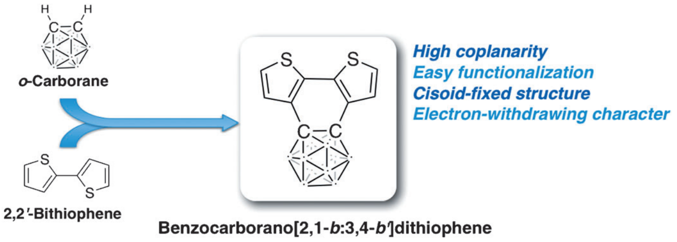
Synthesis and Properties of Thiophene-Fused Benzocarborane



Fused carboranes: The *o*-carborane-based π-conjugated compound, benzocarborano[2,1-*b*:3,4-*b*′]dithiophene was synthesized (see scheme). The 2,2′-bithiophene unit is fixed in the *cisoid* structure with high planarity by the *o*-carborane unit. The *o*-carborane moiety provides an electron-withdrawing character to the 2,2′-bithiophene unit through an inductive effect.