JOC The Journal of Organic Chemistry

Article

pubs.acs.org/joc

Electronic Alteration on Oligothiophenes by *o*-Carborane: Electron Acceptor Character of *o*-Carborane in Oligothiophene Frameworks with Dicyano-Vinyl End-On Group

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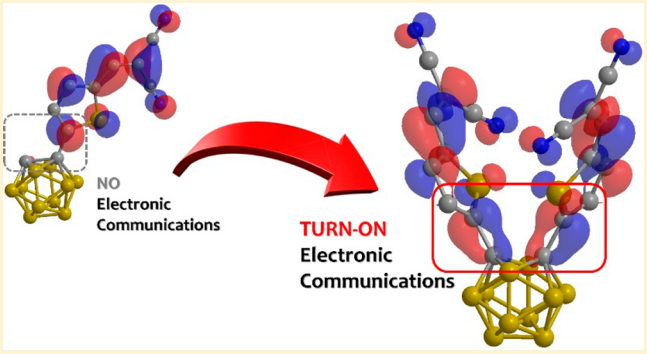
Supporting Information

ABSTRACT: We studied electronic change in oligothiophenes by employing *o*-carborane into a molecular array in which one or both end(s) were substituted by electron-withdrawing dicyano-vinyl group(s). Depending on mono- or bis-substitution at the *o*-carborane, a series of linear A_1-D-A_2 (**1a**−**1c**) or V-shaped A_1-D-A_2-D-A_1 (**2a**−**2c**) oligothiophene chain structures of variable length were prepared; A_1, D, and A_2, represent dicyano-vinyl, oligothiophenyl, and *o*-carboranyl groups, respectively. Among this series, **2a** shows strong electron-acceptor capability of *o*-carborane comparable to that of the dicyano-vinyl substituent, which can be elaborated by a conformational effect driven by cage $\sigma^*-\pi^*$ interaction. As a result, electronic communications between *o*-carborane and dicyano-vinyl groups are successfully achieved in **2a**.



INTRODUCTION

Oligothiophene functionalities show good electron-donor (ED) character, and they have been utilized as *p*-type materials for organic electronic materials.[1] Soon, they became essential ingredients in heterojunction organic solar cells matching properly with C_{60} based *n*-type materials such as phenyl-C_{61}-butyric acid methyl ester (PCBM).[2] Since then, electronic alteration in oligothiophenes thus allowing optimum energy levels as EDs for maximum efficiency has become a major hurdle. One approach to the alteration of oligothiophene energy levels involves the incorporation of electron-withdrawing (EW) units such as a dicyano-vinyl group at either one or both ends of the oligothiophene to achieve the desired charge separation.[3] Electronic perturbation can, therefore, facilitate the resulting electronic property adjustment in oligothiophenes.

Polyhedral carborane clusters are a class of electronically useful molecules[4] and have practical applications in areas such as luminescent materials.[5] Recently, EW character of *o*-carborane was proposed by a $\pi^*-\sigma^*$ conjugation and elaborated by the unique fluorescence behaviors, aggregation-induced emission,[6] and charge transfer.[7] Thus, application of *o*-carborane as a potential EW functional group in oligothiophenes is of special interest for the energy level adjustment.

In this paper, we report the synthesis and electronic properties of a series of linear A_1-D-A_2 (**1a**−**1c**) and V-shaped A_1-D-A_2-D-A_1 (**2a**−**2c**) systems alternating with dicyano-vinyl (A_1), oligothiophenyl (D), and *o*-carboranyl (A_2) units of variable oligothiophenyl length, as depicted in Chart 1. Our primary goal is to determine how efficiently *o*-carborane can function as an electron acceptor (EA) in the presence of strong dicyano-vinyl EW functional groups located at the end(s) of the thiophene. Another motivation of this study is elucidating the mechanism for *o*-carborane electronic control through π-electron channels with the thiophene groups; thiophene is regarded as an aromatic analogue to benzene, but much reduced π-electronic interaction is expected due to the presence of the 3*p* sulfur atom. Since EA character of *o*-carborane was known to be dictated by the orthogonal geometry set by the adjacent aryl units, for structural variation, linear-shaped compound **1a** and V-shaped compound **2a** were prepared.

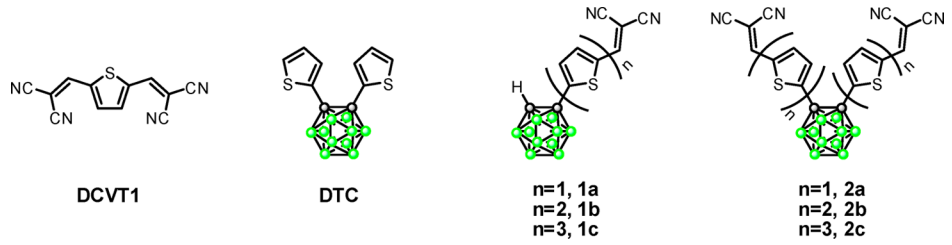
RESULTS AND DISCUSSION

Synthesis and Crystal Structures of 1a and 2a. The synthesis of the target compounds **1a** and **2a** is shown in Scheme 1, and the detailed experimental procedures and characterizations are in the Experimental Section. For **1a**, the starting compound **3** was converted to **4** via palladium-catalyzed coupling of trimethylsilyl acetylene, followed by deprotection of the silyl group. The resulting **4** was reacted with decaborane in the presence of *N*,*N*-dimethylaniline to give

Received: February 25, 2015
Published: April 6, 2015

DOI: 10.1021/acs.joc.5b00336
J. Org. Chem. 2015, 80, 4573−4580

Chart 1. Molecular Structures of DCVT1, DTC, and Dicyano-vinyl-oligothiophenyl-*o*-carboranes, 1a−1c and 2a−2c



5 in modest yield. The acetal group of **5** was then deprotected upon treatment with trifluoroacetic acid (TFA) in 85% yield. Finally, the condensation reaction of **6** with malononitrile in the presence of piperidine gave **1a** as a white crystalline solid in quantitative yield. In the case of **2a**, direct dilithiation of 2,2′-dithiophenylcarborane (**DTC**), followed by addition of DMF, gave **11** in modest yield. The condensation reaction of **11** with malononitrile in the presence of piperidine gave compound **2a** as a yellowish crystalline solid.

The single crystals of **1a** and **2a** were grown from a dichloromethane/*n*-hexane mixed solution, and their crystal structures are shown in Figure 1. The crystal data and collection parameters are summarized in Table S1 in the Supporting Information. **1a** and **2a** were crystallized in the monoclinic crystal system with $P2_1/c$ and $C2/c$ space groups, respectively. In **2a**, two thiophene units adopt a *transoid* orientation of the sulfur atoms in adjacent thiophene rings with "Face-On" conformation upon incorporation into the *o*-carborane cage. The thiophene rings in **2a** are disposed orthogonally to the C−C bond of the carborane cage with dihedral angles of 108.9° for C1′−C1−C2−C3, while the thiophene ring in **1a** shows a relatively parallel structure with a dihedral angle of 30.9° for C2−C1−C3−C4. Furthermore, the C−C bond distance of the *o*-carborane cage of **2a** (1.727 Å) is longer than that of **1a** (1.696 Å; averaged distance of C1 with adjacent five atoms in the cluster was used due to the cluster disorder), which indicates EW character of *o*-carborane in **2a**.[9]

Optical Properties of 1a and 2a. Figure 2 shows the absorption and emission spectra of **1a** and **2a**. Both compounds showed similar absorption spectra with the lowest energy absorption maxima (λ_{max}) at 349 and 340 nm, respectively, which can be assigned to the $\pi-\pi^*$ transition of the thiophene unit. Interestingly, their fluorescence emissions were completely quenched by the introduction of *o*-carboranyl groups. It should be noted that **DCVT1** (see structure in Chart 1) emits its fluorescence at 460 nm,[3a] which indicates that the incorporation of *o*-carborane significantly perturbed the excited-state behavior.

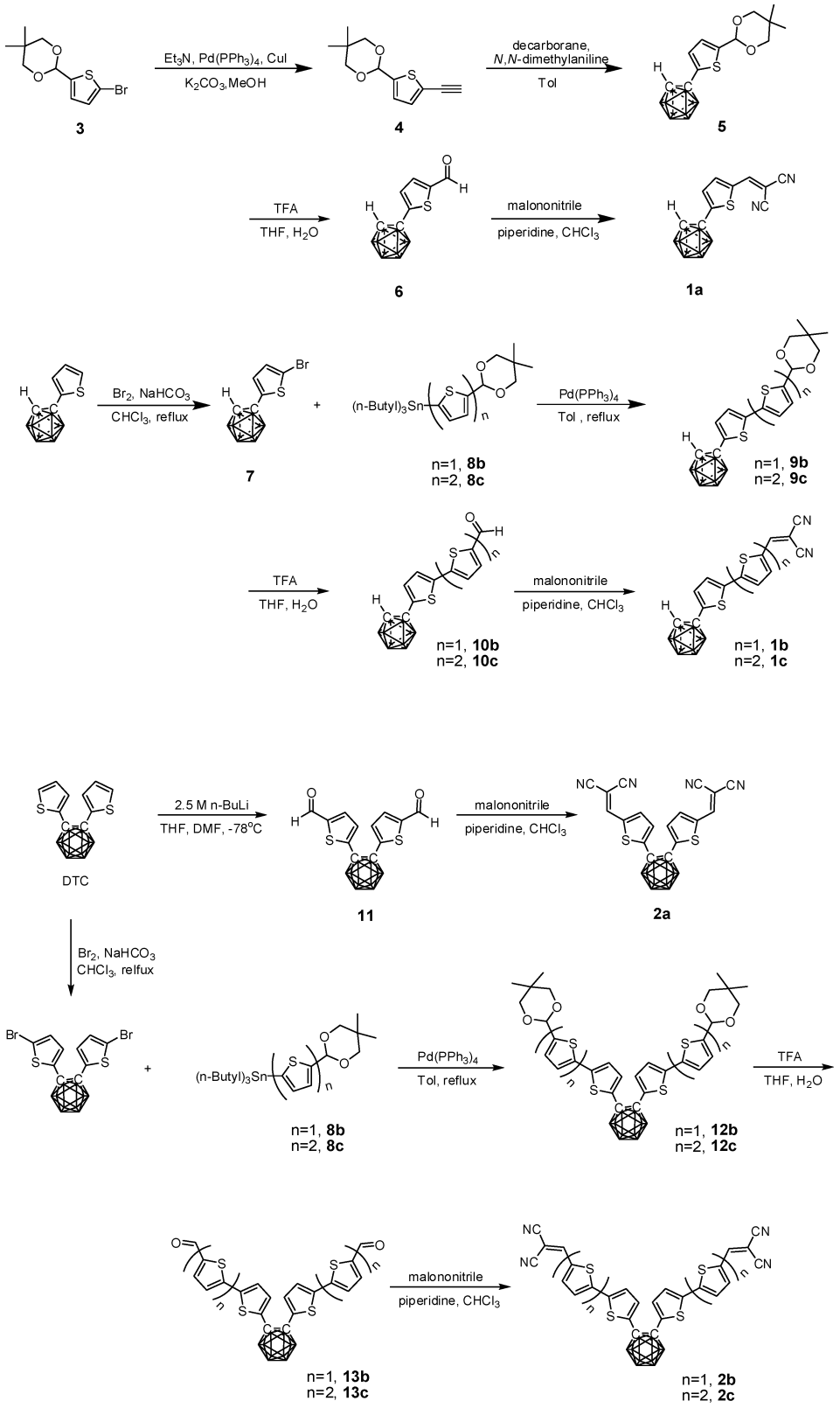
Electrochemical Properties of 1a and 2a. To confirm the electronic states altered by *o*-carboranyl groups, their electrochemical properties were studied by cyclic voltammetry (CV). CVs of **DCVT1** and **DCT** were also measured for comparison. As shown in Figure S5 (Supporting Information), **1a** and **2a** showed significantly different reduction waves. In the case of **1a**, an irreversible reduction peak appeared at E_{pc} = −1.33 V (versus Fc/Fc^+), which can be assigned to the reduction of the dicyano-vinyl group. On the other hand, **2a** showed two reduction peaks, the first one for a reversible reduction peak at E_{pc} = −1.10 V and the second one for a quasi-reversible reduction peak at E_{pc} = −1.76 V. To compare with **DCVT1** and **DTC**, it is clear that the electronic state of dicyano-vinyl groups in **2a** is affected by introducing an *o*-carboranyl group. This result is in good agreement with the obtained crystal structures that **2a** showed an elongated C−C bond of the *o*-carborane cage. It was reported that, when *o*-carborane is linked to two aryl groups orthogonally at the two carbon atoms of the *o*-carborane cage, π-electron channels between *o*-carborane and aryl groups open the function of *o*-carborane as an efficient EA.[10] Therefore, we can conclude that the *o*-carborane can act as an EA when inserted between two dicyano-vinyl thiophenes. It should be noted that the first reduction peak in **2a** maintains reversibility, which indicates that *o*-carboranly and dicyano-vinyl groups are communicating with each other.

Electronic Structure Calculations of 1a and 2a. Further support for this conclusion is provided by DFT (B3LYP/6-31G(d,p)) calculations using the Gaussian 09 package.[11] The specific molecular orbital levels of **1a** and **2a** are shown in Figure 3, and their selected energy levels, orbital contributions, and oscillation strengths are summarized in Table S2 in the Supporting Information. The frontier orbitals of **1a** showed that both HOMO and LUMO are delocalized along the π-conjugated dicyano-vinyl-thiophene unit with little participation of the *o*-carborane cage. The HOMO orbital population of **2a** is similar to that of **1a**, but its LUMO is fully delocalized over the two dicyano-vinyl-thiophene units involving the C−C bond of the *o*-carborane cage. This result is in good agreement with electrochemistry of **2a** that the *o*-carboranly and dicyano-vinyl groups are communicating each other. Furthermore, a simple linear-response method (time-dependent DFT with the same functional and basis set) confirms that the λ_{max} at 338 nm (3.67 eV) of **1a** is associated with a HOMO → LUMO transition (oscillator strength, f = 0.78), while that for **2a** is associated with HOMO → LUMO+1 and HOMO−1 → LUMO transitions calculated at 3.71 eV (oscillator strength, f = 0.88).

Optical Properties of Lengthened System. Further structure−property relationships were investigated in a series of compounds with varying conjugated chain lengths using linear and V-shaped molecules with lengthened thiophene units, **1b**, **1c**, **2b**, and **2c**, as shown in Chart 1. The absorption and emission spectra obtained in DCM are summarized in Table 1. As shown in Figures S3 and S4 (Supporting Information), the absorption spectra showed two conspicuous absorption features. The higher energy absorptions around 300−350 nm are assignable to conventional $\pi-\pi^*$ transitions of oligothiophenes, and the λ_{max} values at 421, 466, 413, and 465 nm for **1b**, **1c**, **2b**, and **2c**, respectively, can be assigned to the intramolecular charge transition (ICT) between the oligothiophene donor and the acceptor groups.[12] Full conjugation of the π-system for lengthened thiophene units, **1b**, **1c**, **2b**, and **2c**, was confirmed by the strong bathochromic shifts of the absorption maximum, λ_{max}, assigned to the $\pi-\pi^*$ transition. As expected, their fluorescence quantum yields were very low due to the ICT character (see Figures S3 and S4 in the Supporting

DOI: 10.1021/acs.joc.5b00336
J. Org. Chem. 2015, 80, 4573−4580

Scheme 1. Synthesis of Series 1 and 2



Information). Among them, however, the lengthened thiophene compounds, **1b**, **1c**, and **2c**, have measurable fluorescence emissions. To quantify emission quenching caused by *o*-carborane, we obtained Mataga−Lippert plots for these compounds. Dipole moment differences between the excited state and ground state for **1b**, **1c**, and **2c** were calculated to be $\Delta\mu$ = 15.9, 24.3, and 27.7 D, respectively. Figure S6 (Supporting Information) shows Mataga−Lippert plots for the solvatochromic shifts of the emissions versus the solvent-polarity parameter (Δf). As expected, the dipole moment of **1c**

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J. Org. Chem. 2015, 80, 4573−4580

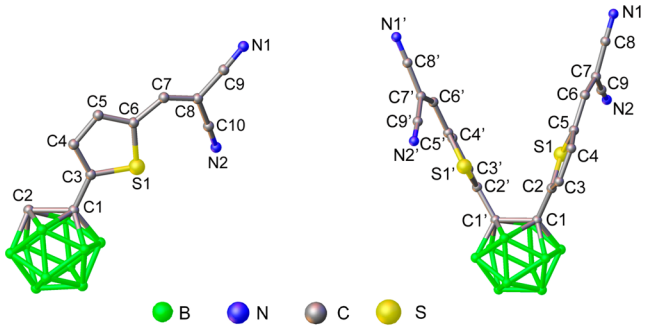


Figure 1. Single crystal structures of **1a** (left) and **2a** (right) drawn by the OLEX2 program.[8] Hydrogen atoms were omitted for clarity.

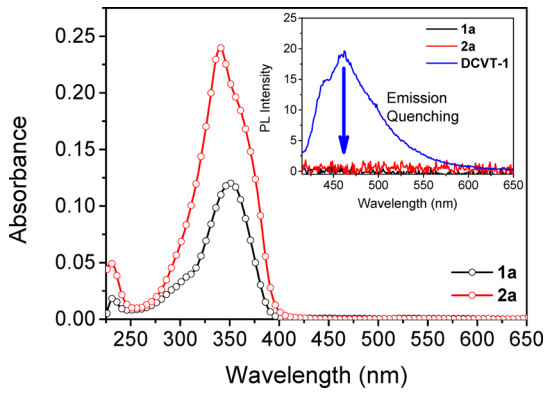


Figure 2. Absorption spectra of **1a** and **2a** in dichloromethane (DCM). Inset: Fluorescence spectra of **DCVT1**, **1a**, and **2a** in 10 μM DCM solution (λ_{ex} = 400 nm).

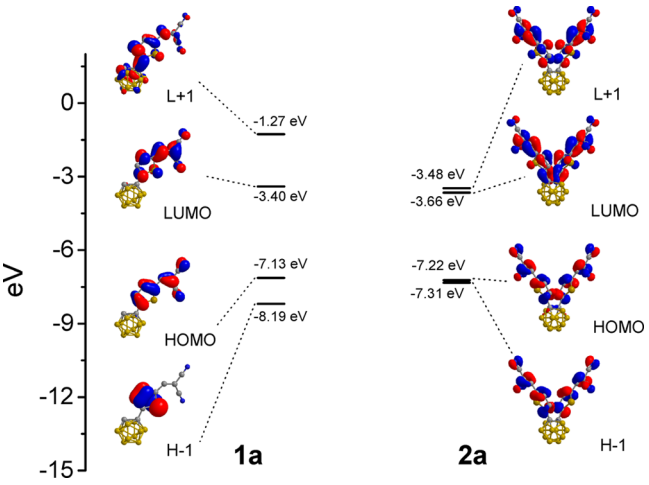


Figure 3. TD-DFT calculation results for **1a** and **2a**. Energy levels and isodensity plots for HOMO−LUMOs are shown.

was larger than that of **1b** because **1c** has a longer distance between the donor (ED) and the acceptor (EA) groups.[13]

Electrochemical Properties of Lengthened System. The electrochemical properties of compounds **1b**, **1c**, **2b**, and **2c** were investigated by cyclic voltammetry (CV). As shown in Figure S5 (Supporting Information), linear-shaped compounds showed only one reduction wave (**1b** at E_{pc} = −1.39 V and **1c** at E_{pc} = −1.42 V), while V-shaped compounds showed two reduction waves (**2b** at E_{pc} = −1.31 and −1.67 V, and **2c** at E_{pc} = −1.36 and −1.64 V). It should be noted that the reduction peaks in **2b** and **2c** lost reversibility, while **2a** maintains reversibility. Thus, we can conclude that electronic communications between *o*-carboranly and dicyano-vinyl groups are not observed in **2b** and **2c**. This phenomenon could be explained by the enhanced dipole moment of the dicyano-vinyl group resulting from the longer distance between donor and acceptor groups as shown above.

Electronic Structure Calculations of Lengthened System. Quantum chemical calculations for **1b**, **1c**, **2b**, and **2c** were performed at the B3LYP/6-31G(d,p) level, and their specific molecular orbital levels are shown in Figures S7 and S8 (Supporting Information). Their HOMO levels are destabilized while LUMO levels are stabilized when they are compared with **1a** and **2a**, resulting in a net reduction in HOMO−LUMO energy upon increasing the length of the oligothiophene. The frontier orbitals of linear-shaped compounds, **1b** and **1c**, showed similar distributions to those of **1a**. On the other hand, the frontier orbitals of V-shaped compounds, **2b** and **2c**, showed significantly different distributions from those found in **2a**. While the HOMOs of all V-shaped compounds **2a**−**2c** are delocalized along the π-conjugated oligothiophene-dicyano-vinyls, the distributions of the LUMOs are dependent on the oligothiophene length. In the case of **2b**, the LUMO is preeminently delocalized in the thiophenyl-dicyanovinyl position with partial contributions from the C−C bond of *o*-carborane. Finally, the LUMO of **2c** is delocalized only along the thiophenyl-dicyanovinyl channels without any contributions from *o*-carborane. These results comply well with the red-shift of the lowest energy absorption values and with the irreversibility of reduction waves.

Structure−Property Relationship. Noting that the most salient feature that enables *o*-carborane to bear EA character comes from a geometrical factor,[10] we compared the dihedral angles of the C−C bonds of the *o*-carborane cage with the C−C bonds in the thiophene ring, as depicted in Table 2. Optimized geometries showed dihedral angles of 42.0, 45.4, 48.4, 104.1, 98.8, and 98.7° for **1a**, **1b**, **1c**, **2a**, **2b**, and **2c**, respectively. The V-shaped compounds, **2a**−**2c**, clearly possess orthogonal geometries comprising the C−C vector of the *o*-carborane to the thiophene rings when they are compared with the linear-shaped compounds, **1a**−**1c**. It should be noted that, even though **2b** and **2c** have ideal geometries for the interaction between the *o*-carborane cage and thiophene rings, *o*-carborane does not behave as a strong EA. This is due to the fact that delocalization of π-electrons is restricted mostly in the thiophene rings in extended aromatic systems rather than spread to the *o*-carboranyl C−C bond. This trend can be clearly seen in Figure S9 (Supporting Information), which shows the calculated LUMO energy level versus dihedral angle.

CONCLUSIONS

In summary, we synthesized a series of linear A_1-D-A_2 and V-shaped A_1-D-A_2-D-A_1 systems and compared their electronic properties by varying the number of oligothiophene donor units in the system. The V-shaped *o*-carborane (**2a**) with two end-on thiophene rings can act as a strong EA due to the efficient electronic perturbation between the π^* orbitals of the thiophene rings and the σ^* orbitals of *o*-carborane carbons even in the presence of strong electron-withdrawing groups, dicyano-vinyl groups. Further investigations of the photovoltaic properties of these compounds in bulk heterojunction solar cells are underway.

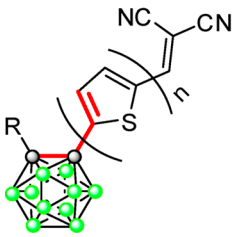
DOI: 10.1021/acs.joc.5b00336
J. Org. Chem. 2015, 80, 4573−4580

Table 1. Photophysical and Electrochemical Properties of 1 and 2[a]

	absorption		emission[b]			
	λ_{max} (nm)	ε (M^{-1} cm^{-1})	λ_{max} (nm)	E_{ox} (V)	E_{red}^1 (V)	E_{red}^2 (V)
1a	349	3.0×10^4		1.80	−1.40	
1b	421	4.8×10^4	486	1.24	−1.35	
1c	466	4.9×10^4	561	0.96	−1.38	
2a	340	6.0×10^4		1.69	−1.26	−1.92
2b	413	5.0×10^4		1.16	−1.50	−1.71
2c	465	5.1×10^4	565	0.78	−1.54	−1.88

[a]All spectra were measured in dichloromethane. [b]Excited at 400 nm.

Table 2. Calculated Dihedral Angles of 1 and 2[a]



1a	**1b**	**1c**
42.0 (30.9)	45.4	48.4
2a	**2b**	**2c**
104.1 (108.9)	98.8	98.7

[a]Values in parentheses are obtained from X-ray structures.

EXPERIMENTAL SECTION

General Procedures. All manipulations were performed either in a dry nitrogen atmosphere using standard Schlenk techniques or in a vacuum atmospheres in a glovebox. Tetrahydrofuran and toluene were distilled over sodium−benzophenone and calcium chloride, respectively, under nitrogen prior to use. Glassware, syringes, magnetic stirring bars, and needles were dried in a convection oven overnight. Reactions were checked with thin-layer chromatography. The spots developed onto TLC were identified under UV light at 254 and 365 nm. Column chromatography was done on silica gel. Synthesized compounds were characterized by ^{1}H NMR, ^{13}C NMR, elemental analyses, and HR-MS (ESI) mass analyses. The ^{1}H and ^{13}C NMR spectra for series **1** compounds and **12c** were recorded operating at 300.1 and 75.4 MHz, respectively, while those for series **2** compounds were recorded operating at 900.2 and 226.4 MHz, respectively, and exclude **12c**. ^{1}H and ^{13}C NMR chemical shifts were measured relative to internal residual peaks from the lock solvent (99.9% $CDCl_3$). The ^{11}B NMR spectra for **1a**, **1b**, and **2a** were recorded operating at 96.3 MHz. ^{11}B NMR spectra for **1c**, **2b**, and **2c** were measured but not reported due to their low solubility. All ^{11}B NMR chemical shifts were referenced to $BF_3{\cdot}O(C_2H_5)_2$ (0.0 ppm), with a negative sign indicating an upfield shift. HR-MS of prepared compounds were measured by using an ion trap mass analyzer. Starting compounds, monothiophenyl-*o*-carborane,[14] dithiophenyl-*o*-carborane (**DTC**),[15] 2,2′-dithiophenyl-5,5′-dibromocarborane,[16] tributyl(5-(5,5-dimethyl-1,3-dioxan-2-yl)-thiophen-2-yl)stannane (**8b**),[17] tributyl(5′-(5,5-dimethyl-1,3-dioxan-2-yl)-[2,2′-bithiophen]-5-yl)stannane (**8c**),[18] and compounds **3**[17] and **4**[19] were prepared according to previously reported procedures. Cyclic voltammetry (CV) measurements were carried out for dichloromethane solutions of 1 mM sample and 0.1 M tetrabutylammonium hexafluorophosphate at room temperature equipped with a Pt working electrode, a platinum wire counter electrode, and a $Ag/AgNO_3$ (0.1 M) reference. All potentials were calibrated against a ferrocenium/ferrocene (Fc^+/Fc) redox couple.

5,5-Dimethyl-2-(5-(*o*-carboranyl)thiophen-2-yl)-1,3-dioxane (5). To a 100 mL two-neck round-bottom flask equipped with a stir bar and a reflux condenser were added **4** (2.04 g, 9.2 mmol), decarborane (1.35 g, 11.0 mmol), *N*,*N*-dimethylaniline (2.5 mL, 20.2 mmol), and 55 mL of toluene. The reaction mixture was heated to reflux for 5 h. After cooling down to room temperature, the volatiles were evaporated under reduced pressure and the residue was treated with 0.1 M HCl to remove unreacted *N*,*N*-dimethylaniline. It was then extracted with dichloromethane (50 mL × 2) and washed with water. The combined organic layer was dried over anhydrous $MgSO_4$ and filtered. The filtrate was evaporated under reduced pressure, and the resulting residue was purified by flash column chromatography on silica gel using *n*-hexane as an eluent to afford **5** as a white solid (Yield: 76%, 2.38 g). ^{1}H NMR (300.1 MHz, $CDCl_3$, ppm): δ 7.08 (d, J = 3.6 Hz, 1H), 6.91 (d, J = 4.2 Hz, 1H), 5.54 (s, 1H), 3.81 (s, 1H), 3.74 (d, J = 11.1 Hz, 2H), 3.61 (d, J = 11.1 Hz, 2H), 1.25 (s, 3H), 0.79 (s, 3H), (broad weak peak from 1.3−3.1 ppm for 10H of B−*H* was not integrated). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm): δ 144.2, 137.0, 129.6, 125.1, 97.7, 72.1, 63.3, 30.4, 23.1, 22.0. HRMS (ESI) calcd for $C_{12}H_{24}B_{10}O_2S$: 342.2428. Found: 342.2434. Anal. Calcd for $C_{12}H_{24}B_{10}O_2S$: C, 42.33; H, 7.10; B, 31.75; O, 9.40; S, 9.42. Found: C, 42.35; H, 7.08.

5-(*o*-Carboranyl)thiophene-2-carbaldehyde (6). To a 50 mL two-neck round-bottom flask equipped with a stir bar and a reflux condenser were added **5** (0.74 g, 2.2 mmol), 10 mL of THF, 5 mL of distilled water, and 5 mL of trifluoroacetic acid (TFA). The reaction mixture was stirred for 5 min at room temperature and then heated to 50 °C for 1 h. After cooling down to room temperature, the reaction was quenched with saturated aqueous sodium bicarbonate, then extracted with dichloromethane (30 mL × 2), and finally washed with aqueous sodium bicarbonate. The combined organic layer was dried over $MgSO_4$ and filtered. The filtrate was evaporated under reduced pressure, and the resulting residue was purified by flash column chromatography on silica gel using a mixed eluent (dichloromethane:*n*-hexane in a 1:1 ratio (v/v)) to afford **6** as a white solid (Yield: 41%, 0.23 g). ^{1}H NMR (300.1 MHz, $CDCl_3$, ppm): δ 9.85 (s, 1H), 7.57 (d, J = 4.2 Hz, 1H), 7.28 (d, J = 4.2 Hz, 1H), 3.91 (s, 1H), (broad weak peak from 1.3−3.2 ppm for 10H of B−*H* was not integrated). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm): δ 182.3, 145.7, 144.9, 135.3, 130.5, 70.7, 62.7. HRMS (ESI) calcd for $C_7H_{14}B_{10}OS$: 256.1696. Found: 256.1699. Anal. Calcd for $C_7H_{14}B_{10}OS$: C, 33.05; H, 5.55; B, 42.50; O, 6.29; S, 12.61. Found: C, 33.07; H, 5.54.

2-((5-(*o*-Carboranyl)thiophen-2-yl)methylene)malononitrile (1a). To a 50 mL two-neck round-bottom flask equipped with a stir bar were added **6** (0.23 g, 0.89 mmol), malononitrile (0.07 g, 1.07 mmol), and 10 mL of chloroform. The reaction mixture was stirred for 10 min at room temperature. A drop of piperidine was then added to the reaction mixture, and stirring was continued for an additional 1 h at room temperature. The reaction mixture was then extracted with chloroform (15 mL × 2) and washed with water. The organic layers were combined, dried over anhydrous $MgSO_4$, and filtered. The filtrate was evaporated under reduced pressure, and the resulting residue was purified by flash column chromatography on silica gel using a mixed eluent (dichloromethane:*n*-hexane in a 1:1 ratio, (v/v)) to afford **1a** as a pale yellow solid (Yield: 51%, 0.09 g). mp: 176−179 °C. ^{1}H NMR (300.1 MHz, $CDCl_3$, ppm): δ 7.74 (s, 1H), 7.59 (d, J = 4.2 Hz, 1H), 7.31 (d, J = 4.2 Hz, 1H), 3.93 (s, 1H), (broad weak peak from 1.4−3.2 ppm for 10H of B−*H* was not integrated). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm): δ 150.0, 146.8, 137.6, 136.4, 130.9, 113.1, 112.4, 81.1, 69.9, 62.6. ^{11}B NMR (96.3 MHz, $CDCl_3$, ppm): δ −5.62, −8.01, −13.18, −14.77, −15.83, −16.71. HRMS (ESI) calcd for $C_{10}H_{14}B_{10}N_2S$: 304.1808. Found: 304.1810. Anal. Calcd for $C_{10}H_{14}B_{10}N_2S$: C, 39.72; H, 4.67; B, 35.75; N, 9.26; S, 10.60. Found: C, 39.73; H, 4.68; N, 9.25.

DOI: 10.1021/acs.joc.5b00336
J. Org. Chem. 2015, 80, 4573−4580

5-Bromo-thiophene-2-yl-carborane (7). To a 500 mL two-neck round-bottom flask equipped with a stir bar were added thiophene-2-yl-carborane (8.85 g, 39.1 mmol), sodium bicarbonate (3.94 g, 46.9 mmol), and 200 mL of chloroform. The reaction temperature was cooled down to 0 °C, and Br_2 was added slowly. After Br_2 addition, the reaction temperature was gradually increased to reflux and the mixture was allowed to reflux overnight. The reaction mixture was then cooled down to 0 °C, followed by the addition of 1 N NaOH. After stirring for an additional 10 min at 0 °C, the crude product was extracted with chloroform (15 mL × 2) and washed with water. The organic layers were combined, dried over anhydrous $MgSO_4$, and filtered. The filtrate was evaporated under reduced pressure, and the resulting residue was purified by flash column chromatography on silica gel using *n*-hexane as an eluent to afford **7** as a white solid (Yield: 58%, 6.92 g). ^{1}H NMR (300.1 MHz, $CDCl_3$, ppm): δ 6.96 (d, J = 4.4 Hz, 1H), 6.89 (d, J = 5.6 Hz, 1H), 3.81 (s, 1H), (broad weak peak from 1.5−3.2 ppm for 10H of B−*H* was not integrated). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm): δ 137.9, 130.3, 128.1, 115.2, 71.4, 63.3. HRMS (ESI) calcd for $C_6H_{13}B_{10}BrS$: 306.0852. Found: 306.0855. Anal. Calcd for $C_6H_{13}B_{10}BrS$: C, 23.61; H, 4.29; B, 35.42; Br, 26.18; S, 10.50. Found: C, 23.62; H, 4.29.

5,5-Dimethyl-2-(5′-(*o*-carboranyl)-2,2′-bithiophen-5-yl)-1,3-dioxane (9b). To a 100 mL two-neck round-bottom flask equipped with a stir bar was added **7** (1.32 g, 4.32 mmol), **8b** (2.32 g, 4.75 mmol), $Pd(PPh_3)_4$ (0.25 g, 0.22 mmol), and 25 mL of toluene. The reaction mixture was heated to reflux for 4 h, cooled down to room temperature, extracted with toluene (20 mL × 2), and washed with water. The organic layers were combined, dried over anhydrous $MgSO_4$, and filtered. The filtrate was evaporated under reduced pressure, and the resulting residue was purified by flash column chromatography using a mixed eluent (dichloromethane:*n*-hexane = 1:1, v/v) to afford **9b** as a white solid (Yield: 58%, 1.06 g). ^{1}H NMR (300.1 MHz, $CDCl_3$, ppm): δ 7.08 (d, J = 3.6 Hz, 1H), 7.03 (s, 2H), 6.91 (d, J = 4.4 Hz, 1H), 5.60 (s, 1H), 3.85 (s, 1H), 3.76 (d, J = 14.8 Hz, 2H), 3.64 (d, J = 14.8 Hz, 2H), 1.28 (s, 3H), 0.80 (s, 3H), (broad weak peak from 1.5−3.2 ppm for 10H of B−*H* was not integrated). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm): δ 141.9, 140.1, 136.0, 135.1, 130.9, 126.1, 124.4, 123.6, 98.1, 72.1, 63.5, 30.4, 23.1, 22.0. HRMS (ESI) calcd for $C_{16}H_{26}B_{10}O_2S_2$: 424.2305. Found: 424.2301. Anal. Calcd for $C_{16}H_{26}B_{10}O_2S_2$: C, 45.47; H, 6.20; B, 25.58; O, 7.57; S, 15.17. Found: C, 45.45; H, 6.22.

5′-(*o*-Carboranyl)-2,2′-bithiophene-5-carbaldehyde (10b). A procedure analogous to the preparation of **6** was used. The reaction was carried out with **9b** (0.92 g, 2.2 mmol), 10 mL of THF, 5 mL of distilled water, and 5 mL of trifluoroacetic acid (TFA). The product was obtained as a yellow solid (Yield: 38%, 0.28 g). ^{1}H NMR (300.1 MHz, $CDCl_3$, ppm): δ 9.88 (s, 1H), 7.68 (d, J = 4.2 Hz, 1H), 7.24 (d, J = 3.6 Hz, 1H), 7.14 (dd, J = 8.3, 4.1 Hz, 2H), 3.88 (s, 1H), (the broad weak peak from 1.4−3.4 ppm for 10H of B−*H* was not integrated). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm): δ 182.6, 149.9, 143.0, 138.4, 137.7, 131.1, 125.8, 116.4, 71.4, 63.3. HRMS (ESI) calcd for $C_{11}H_{16}B_{10}OS_2$: 338.1573. Found: 338.1575. Anal. Calcd for $C_{11}H_{16}B_{10}OS_2$: C, 39.26; H, 4.79; B, 32.13; O, 4.75; S, 19.06. Found: C, 39.27; H, 4.78.

2-((5′-(*o*-Carboranyl)-2,2′-bithiophen-5-yl)methylene)-malononitrile (1b). A procedure analogous to the preparation of **1a** was used. The reaction was carried out with **10b** (2.5 g, 7.48 mmol), malononitrile (1.2 g, 18.5 mmol), piperidine, and 75 mL of chloroform. The product was obtained as an orange solid (Yield: 54%, 1.5 g). mp: 211−216 °C. ^{1}H NMR (300.1 MHz, $CDCl_3$, ppm): δ 7.78 (s, 1H), 7.51 (d, J = 4.2 Hz, 1H), 7.27 (d, J = 4.2 Hz, 1H), 7.18 (dd, J = 7.7, 3.5 Hz, 2H), 3.90 (s, 1H), (the broad weak peak from 1.3−3.4 ppm for 10H of B−*H* was not integrated). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm): δ 150.3, 146.8, 139.9, 138.8, 137.4, 134.7, 131.1, 126.6, 125.6, 113.9, 113.2, 71.1, 63.1. ^{11}B NMR (96.3 MHz, $CDCl_3$, ppm): δ −5.74, −8.34, −13.56, −14.63, −16.01, −16.83. HRMS (ESI) calcd for $C_{14}H_{16}B_{10}N_2S_2$: 386.1685. Found: 386.1689. Anal. Calcd for $C_{14}H_{16}B_{10}N_2S_2$: C, 43.73; H, 4.19; B, 28.11; N, 7.29; S, 16.68. Found: C, 43.71; H, 4.20.

5,5-Dimethyl-2-(5′-(*o*-carboranyl)-2,2′,2″-terthiophen-5-yl)-1,3-dioxane (9c). A procedure analogous to the preparation of **9b** was used. The reaction was carried out with **7** (1.32 g, 5.1 mmol), **8c** (3.17g, 5.6 mmol), $Ph(PPh_3)_4$, and 30 mL of toluene. The product was obtained as a pale yellow solid (Yield: 40%, 4.02 g). ^{1}H NMR (400.1 MHz, $CDCl_3$, ppm): δ 7.09 (d, J = 3.6 Hz, 1H), 7.04−7.06 (m, 4H), 6.92 (d, J = 3.6 Hz, 1H), 5.62 (s, 1H), 3.86 (s, 1H), 3.77 (d, J = 11.1 Hz, 2H), 3.64 (d, J = 11.1 Hz, 2H), 1.29 (s, 3H), 0.81 (s, 3H), (the broad weak peak from 1.3−3.3 ppm for 10H of B−*H* was not integrated). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 138.2, 136.6, 130.9, 130.2, 128.1, 127.4, 124.6, 71.6, 63.5, 63.4, 30.0, 29.5, 27.6, 13.9, 9.0. HRMS (ESI) calcd for $C_{20}H_{28}B_{10}O_2S_3$: 506.2182. Found: 506.2184. Anal. Calcd for $C_{20}H_{28}B_{10}O_2S_3$: C, 47.59; H, 5.59; B, 21.42; O, 6.34; S, 19.06. Found: C, 47.60; H, 5.60.

5′-(*o*-Carboranyl)-2,2′,2″-terthiophene-5-carbaldehyde (10c). A procedure analogous to the preparation of **6** was used. The reaction was carried out with **9c** (1.10 g, 2.2 mmol), 10 mL of THF, 5 mL of distilled water, and 5 mL of trifluoroacetic acid (TFA). The product was obtained as a yellow solid (Yield: 51%, 0.46 g). ^{1}H NMR (300.1 MHz, $CDCl_3$, ppm): δ 9.88 (s, 1H), 7.68 (d, J = 3.6 Hz, 1H), 7.27 (t, J = 5.3 Hz, 2H), 7.12 (d, J = 4.2 Hz, 2H), 6.99 (d, J = 4.2 Hz, 1H), 3.87 (s, 1H), (the broad weak peak from 1.3−3.3 ppm for 10H of B−*H* was not integrated). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm): δ 182.7, 146.3, 142.4, 139.1, 137.5, 137.2, 136.2. 136.0, 131.3, 127.1, 125.9, 124.7, 124.2. HRMS (ESI) calcd for $C_{15}H_{18}B_{10}OS_3$: 420.1450. Found: 420.1452. Anal. Calcd for $C_{15}H_{18}B_{10}OS_3$: C, 43.04; H, 4.33; B, 25.83; O, 3.82; S, 22.98. Found: C, 43.03; H, 4.31.

2-((5′-(*o*-Carboranyl)-2,2′,2″-terthiophen-5-yl)methylene)-malononitrile (1c). A procedure analogous to the preparation of **1a** was used. The reaction was carried out with **10c** (0.2 g, 0.45 mmol), malononitrile (0.07 g, 1.1 mmol), piperidine, and 5 mL of chloroform. The product was obtained as a red solid (Yield: 48%, 0.1 g). mp: 217−220 °C. ^{1}H NMR (300.1 MHz, $CDCl_3$, ppm): δ 7.77 (s, 1H), 7.64 (d, J = 4.2 Hz, 1H), 7.35 (d, J = 4.2 Hz, 1H), 7.27 (d, J = 4.2 Hz, 2H), 7.15 (t, J = 5.0 Hz, 2H), 7.02 (d, J = 3.9 Hz, 1H), 3.87 (s, 1H), (the broad weak peak from 1.2−3.5 ppm for 10H of B−*H* was not integrated). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm): δ 150.1, 140.1, 130.9, 128.1, 124.9, 124.5, 114.2, 31.7, 22.8, 14.3. ^{11}B NMR (96.3 MHz, $CDCl_3$, ppm): δ −5.91, −13.56. HRMS (ESI) calcd for $C_{18}H_{18}B_{10}N_2S_3$: 468.1563. Found: 468.1567. Anal. Calcd for $C_{18}H_{18}B_{10}N_2S_3$: C, 46.33; H, 3.89; B, 23.17; N, 6.00; S, 20.61. Found: C, 46.31; H, 3.90.

5,5′-(*o*-Carboranyl)dithiophene-2-carbaldehyde (11). To a solution of bis(thiophen-2-yl)-*o*-carborane (1.0 g, 3.46 mmol) in THF (15 mL), *n*-BuLi (3.0 mL, 2.5 M in hexanes, 7.6 mmol) was added dropwise over a period of 10 min at −78 °C. The mixture was stirred for 30 min, and then a solution of DMF (1.3 mL, 17.3 mmol) was added dropwise at −78 °C. The reaction mixture was stirred at this temperature for 1 h and an additional 12 h at room temperature. The reaction mixture was poured into water and extracted with CH_2Cl_2. The combined organic layer was dried over anhydrous $MgSO_4$ and filtered. The filtrate was evaporated under reduced pressure, and the residue was purified by silica gel column chromatography using CH_2Cl_2/*n*-hexane as an eluent. Compound **11** was obtained as a white solid (Yield: 37%, 0.43 g). ^{1}H NMR (900 MHz, $CDCl_3$, ppm): δ 9.69 (s, 2H), 7.42 (d, J = 4.5 Hz, 2H), 7.23 (d, J = 3.6 Hz, 2H), (the broad weak peak from 1.4−3.4 ppm for 10H of B−*H* was not integrated). ^{13}C NMR (202 MHz, $CDCl_3$, ppm): δ 182.5, 146.1, 142.5, 134.9, 133.3, 78.8. HRMS (ESI) calcd for $C_{12}H_{16}B_{10}O_2S_2$: 366.1522. Found: 366.1525. Anal. Calcd for $C_{12}H_{16}B_{10}O_2S_2$: C, 39.54; H, 4.42; B, 29.66; O, 8.78; S, 17.59. Found: C, 39.55; H, 4.43.

2,2′-(5,5′-(*o*-Carboranyl)bis(thiophene-5,2-diyl))bis(methan-1-yl-1-ylidene)dimalononitrile (2a). A procedure analogous to the preparation of **1a** was used. The reaction was carried out with **11** (0.4 g, 1.2 mmol), malononitrile (0.20 g, 3.1 mmol), piperidine, and 10 mL of chloroform. The product was obtained as a pale yellow solid (Yield: 41%, 0.24 g). mp: 186−189 °C. ^{1}H NMR (900.2 MHz, $CDCl_3$, ppm): δ 8.03 (s, 2H), 7.54 (d, J = 3.6 Hz, 2H), 7.28 (d, J = 4.5 Hz, 2H), (the broad weak peak from 1.2−3.5 ppm for 10H of B−*H* was not integrated). ^{13}C NMR (226.3 MHz, $CDCl_3$, ppm): δ 149.6, 143.3,

DOI: 10.1021/acs.joc.5b00336
J. Org. Chem. 2015, 80, 4573−4580

137.8, 136.9, 133.7, 112.8, 112.2, 81.8, 78.3. ^{11}B NMR (96.3 MHz, $CDCl_3$, ppm): δ −5.73, −13.86. HRMS (ESI) calcd for $C_{18}H_{16}B_{10}N_4S_2$: 462.1747. Found: 462.1746. Anal. Calcd for $C_{18}H_{16}B_{10}N_4S_2$: C, 46.94; H, 3.50; B, 23.47; N, 12.16; S, 13.92. Found: C, 46.95; H, 3.49.

Bis(5′-(5,5-dimethyl-1,3-dioxan-2-yl)-2,2′-bithiophen-5-yl)-*o*-carborane (12b). A procedure analogous to the preparation of **9b** was used. The reaction was carried out with 2,2′-dithionyl-5,5′-dibromocarborane (1.5 g, 3.2 mmol), **8b** (3.4 g, 7.1 mmol), $Ph(PPh_3)_4$, and 20 mL of toluene. The product was obtained as a yellow solid (Yield: 73%, 1.6 g). ^{1}H NMR (900.2 MHz, $CDCl_3$, ppm): δ 7.01 (d, J = 3.6 Hz, 2H), 6.94 (d, J = 6.3 Hz, 4H), 6.78 (d, J = 4.5 Hz, 2H), 5.53 (s, 2H), 3.68 (d, J = 10.8 Hz, 4H), 3.56 (d, J = 10.8 Hz, 4H), 1.21 (s, 6H), 0.73 (s, 6H), (the broad weak peak from 1.4−3.2 ppm for 10H of B−*H* was not integrated). ^{13}C NMR (226.3 MHz, $CDCl_3$, ppm): δ 141.2, 140.8, 137.5, 136.8, 134.5, 133.3, 132.7, 125.8, 125.4, 124.4, 123.5, 123.2, 98.0,81.5, 77.5, 71.9. HRMS (ESI) calcd for $C_{30}H_{40}B_{10}O_4S_4$: 702.2740. Found: 702.2738. Anal. Calcd for $C_{30}H_{40}B_{10}O_4S_4$: C, 51.40; H, 5.75; B, 15.42; O, 9.13; S, 18.30. Found: C, 51.38; H, 5.76.

5′,5″-(*o*-Carbonyl)di-2,2′-bithiophene-5-carbaldehyde (13b). A procedure analogous to the preparation of **6** was used. The reaction was carried out with **12b** (1.10 g, 2.2 mmol), 10 mL of THF, 5 mL of distilled water, and 5 mL of trifluoroacetic acid (TFA). The product was obtained as a yellow solid (Yield: 85%, 0.96 g). ^{1}H NMR (900.2 MHz, $CDCl_3$, ppm): δ 9.78 (s, 2H), 7.56 (d, J = 4.5 Hz, 2H), 7.12 (d, J = 3.6 Hz, 2H), 7.09 (d, J = 4.5 Hz, 2H), 6.91 (d, J = 6.3 Hz, 2H), (the broad weak peak from 1.5−3.3 ppm for 10H of B−*H* was not integrated). ^{13}C NMR (226.3 MHz, $CDCl_3$, ppm): δ 182.4, 144.7, 142.8, 139.9, 136.9, 135.2, 133.5, 126.5, 125.3, 80.4. HRMS (ESI) calcd for $C_{20}H_{20}B_{10}O_2S_4$: 530.1277. Found: 530.1278. Anal. Calcd for $C_{20}H_{20}B_{10}O_2S_4$: C, 45.43; H, 3.81; B, 20.45; O, 6.05; S, 24.26. Found: C, 45.42; H, 3.80.

2,2′-(5′,5″-(*o*-Carbonyl)bis(2,2′-bithiophene-5′,5-diyl))bis-(methan-1-yl-1-ylidene)dimalononitrile (2b). A procedure analogous to the preparation of **1a** was used. The reaction was carried out with **13b** (0.8 g, 1.5 mmol), malononitrile (0.25 g, 3.7 mmol), piperidine, and 15 mL of chloroform. The product was obtained as an orange solid (Yield: 43%, 0.41 g). mp: 253−256 °C. ^{1}H NMR (900.2 MHz, $CDCl_3$, ppm): δ 7.68 (s, 2H), 7.52 (d, J = 3.6 Hz, 2H), 7.15 (d, J = 4.5 Hz, 2H), 7.12 (d, J = 4.5 Hz, 2H), 7.06 (d, J = 4.5 Hz, 2H), (the broad weak peak from 1.2−3.3 ppm for 10H of B−*H* was not integrated). ^{13}C NMR (226.3 MHz, $CDCl_3$, ppm): δ 150.1, 146.5, 139.7, 138.9, 136.3, 134.6, 133.8, 126.5, 125.6, 113.7, 113.0, 80.0, 78.0. ^{11}B NMR (96.3 MHz, $CDCl_3$, ppm): δ −6.37, −14.83. HRMS (ESI) calcd for $C_{26}H_{20}B_{10}N_4S_4$: 626.1501. Found: 626.1501. Anal. Calcd for $C_{26}H_{20}B_{10}N_4S_4$: C, 49.98; H, 3.23; B, 17.30; N, 8.97; S, 20.53. Found: C, 49.99; H, 3.24.

Bis(5′-(5,5-dimethyl-1,3-dioxan-2-yl)-2,2′,2″-terthiophen-5-yl)-*o*-carborane (12c). A procedure analogous to the preparation of **9b** was used. The reaction was carried out with 2,2′-dithionyl-5,5′-dibromocarborane (1.3 g, 5.1 mmol), **8c** (6.4 g, 11.2 mmol), $Ph(PPh_3)_4$, and 30 mL of toluene. The product was obtained as a yellow solid (Yield: 35%, 1.5 g). ^{1}H NMR (300.1 MHz, $CDCl_3$, ppm): 7.09 (d, J = 4.2 Hz, 2H), 7.01 (s, 8H), 6.85 (d, J = 4.2 Hz, 2H), 5.60 (s, 2H), 3.75 (d, J = 10.0 Hz, 4H), 3.63 (d, J = 10.5 Hz, 4H), 1.27 (s, 6H), 0.80 (s, 6H). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm): δ 141.5, 141.1, 137.8, 137.5, 137.4, 137.1, 134.7, 133.6, 133.5, 132.9, 126.1, 125.9, 125.7, 124.2, 123.7, 123.4, 98.2, 72.1, 30.4, 23.2, 22.0, 21.5. HRMS (ESI) calcd for $C_{38}H_{44}B_{10}O_4S_6$: 866.2494. Found: 866.2496. Anal. Calcd for $C_{38}H_{44}B_{10}O_4S_6$: C, 52.75; H, 5.13; B, 12.49; O, 7.40; S, 22.24. Found: C, 52.74; H, 5.13.

5′,5″-(*o*-Carbonyl)di-2,2′,2″-terthiophene-5-carbaldehyde (13c). A procedure analogous to the preparation of **6** was used. The reaction was carried out with **12c** (1.53 g, 1.8 mmol), 10 mL of THF, 5 mL of distilled water, and 5 mL of trifluoroacetic acid (TFA). The product was obtained as a yellow solid (Yield: 33%, 0.4 g). ^{1}H NMR (900.2 MHz, $CDCl_3$, ppm): δ 9.79 (s, 2H), 7.58 (d, J = 3.6 Hz, 2H), 7.14 (dd, J = 9.9, 3.6 Hz, 4H), 7.06 (d, J = 4.5 Hz, 2H), 7.00 (d, J = 3.6 Hz, 2H), 6.86 (d, J = 4.5 Hz, 2H), (the broad weak peak from 1.3−3.3 ppm for 10H of B−*H* was not integrated). ^{13}C NMR (226.3 MHz, $CDCl_3$, ppm): δ 182.4, 146.0, 142.1, 140.4, 137.2, 137.1, 135.9, 133.6, 133.4, 126.8, 125.7, 124.5, 123.9, 81.0. HRMS (ESI) calcd for $C_{28}H_{24}B_{10}O_2S_6$: 694.1031. Found: 694.1029. Anal. Calcd for $C_{28}H_{24}B_{10}O_2S_6$: C, 48.53; H, 3.49; B, 15.60; O, 4.62; S, 27.76. Found: C, 48.54; H, 3.48.

2,2′-(5′,5″-(*o*-Carbonyl)bis(2,2′,2″-terthiophene-5′,5-diyl))-bis(methan-1-yl-1-ylidene)dimalononitrile (2c). A procedure analogous to the preparation of **1a** was used. The reaction was carried out with **13c** (0.4 g, 0.6 mmol), malononitrile (0.1 g, 1.5 mmol), piperidine, and 6 mL of chloroform. The product was obtained as a red solid (Yield: 44%, 0.2 g). mp: 270−273 °C. ^{1}H NMR (900.2 MHz, $CDCl_3$, ppm): δ 7.67 (s, 2H), 7.54 (d, J = 7.2 Hz, 2H), 7.23 (d, J = 3.6 Hz, 2H), 7.16 (d, J = 3.6 Hz, 2H), 7.08 (d, J = 3.6 Hz, 2H), 7.04 (d, J = 3.6 Hz, 2H), 6.88 (d, J = 4.5 Hz, 2H), (the broad weak peak from 0.6−2.7 ppm for 10H of B−*H* was not integrated). ^{13}C NMR (226.3 MHz, $CDCl_3$, ppm): δ 150.0, 148.1, 140.1, 140.0, 138.3, 134.9, 134.1, 133.9, 133.5, 127.9, 126.0, 124.7, 124.3, 114.0, 113.3, 80.8. ^{11}B NMR (96.3 MHz, $CDCl_3$, ppm): δ −7.56. HRMS (ESI) calcd for $C_{34}H_{24}B_{10}N_4S_6$: 790.1256. Found: 790.1258. Anal. Calcd for $C_{34}H_{24}B_{10}N_4S_6$: C, 51.75; H, 3.07; B, 13.70; N, 7.10; S, 24.38. Found: C, 51.76; H, 3.08.

DFT Calculations. Theoretical calculations for the derivatives were conducted on the Gaussian 09 package.[11] The ground-state geometries of **1a−1c** and **2a−2c** were optimized by using the B3LYP density functional theory (DFT)[20] and 6-31G(d,p) basis set. Time-dependent DFT (TDDFT) calculations were then performed with the same functional and basis set to estimate the energies and oscillator strengths of the derivatives. The contours of the electron density were plotted by using Chem3D ver.10.[21]

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H, ^{11}B, and ^{13}C NMR spectra, absorption and emission spectra of **1a−1c** and **2a−2c**, cyclic voltammograms (CVs) of **1a−1c**, **2a−2c**, **DCVT1**, and **DTC**, and DFT calculated energy levels and isodensity plots for **1b**, **1c**, **2b**, and **2c**. Crystal data, collection parameters, and CIF file for **1a** and **2a** are also available. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by a Korea University research grant 2014.

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