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Synthesis and electron transporting properties of methanofullerene-*o*-carborane dyads in organic field-effect transistors†

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A series of methanofullerene-*o*-carborane dyads (**PCB-Ph-CB**, **PCB-C*n*-CB**, *n* = 1, 3, 6, 11) were synthesized *via* esterification of [6,6]-phenyl-C_{61}-butyric acid (PCBA) with 2-alcohol functionalized *o*-carborane derivatives, 1-(4-*n*-BuC_6H_4)-2-R-1,2-*closo*-$C_2B_{10}H_{10}$ (R = *p*-C_6H_4OH, $(CH_2)_nOH$, *n* = 1, 3, 6, 11). All the dyads are highly soluble in chlorinated and aromatic solvents under ambient conditions. UV–vis absorption and electrochemical reduction of the dyads exhibited features almost identical to each other, as well as to their parent PCBM, suggesting that the electronic properties of the dyads would be dominated by the methanofullerene moiety. Solution-processed field-effect transistors (FETs) incorporating the methanofullerene-*o*-carborane dyads as active layer materials were fabricated and tested. AFM images of all the thin films showed a homogeneous morphology with RMS values of 0.184–0.212 nm. The transport data are shown to be typical of n-channel FETs. Among the devices, the **PCB-C1-CB** FET showed the best performance, with an electron mobility of 1.72×10^{-2} cm^2 V^{-1} s^{-1}, which is similar to that of PCBM. While the device performances gradually decreased with increasing length of the alkyl linker, they are superior to that (6.83×10^{-4} cm^2 V^{-1} s^{-1}) of the physical blend of *o*-carborane and PCBM.

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Introduction

Buckminsterfullerene, C_{60}, has attracted considerable interest as an n-type semiconductor since its first report in 1985:[1] it is considered important for its high electron affinity,[2] excellent electron transporting property,[3] and low reorganization energy.[4] Owing to the poor solubility of the pristine fullerenes in common organic solvents, however, these compounds have been limitedly used in solution-processed optoelectronic device applications. To circumvent this problem, soluble fullerene derivatives such as [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM),[5] which is one of the most widely studied soluble fullerene derivatives as n-type semiconductors for organic photovoltaic cells (OPVs)[6] and field-effect transistors (OFETs),[7] have been actively investigated. A variety of PCBM analogues have recently been reported to modulate the electronic properties of PCBM and thereby improve the performance of OPV[8] and OFET[9] devices. In particular, efforts to enhance electron mobility of PCBM have been the focus of research interest in the field of n-type OFET applications, but the electron mobility of most PCBM derivatives has been found to be similar to or poorer than that of PCBM.[9]

To elaborate on the electron accepting and transporting ability of PCBM, we have been interested in the introduction of a novel electron-accepting auxiliary into the PCBM, which led us to consider the use of an icosahedral carborane ($C_2B_{10}H_{12}$) as a new substituent of PCBM. Due to the existence of three-center, two-electron bonds, the carborane cages possess three-dimensional delocalization of skeletal electrons which results in a highly polarizable σ-aromaticity and electron-deficiency.[10] Because of these interesting electronic properties and excellent thermal and chemical stability, carborane cages have attracted great attention in the fields of materials science,[11] organometallic chemistry,[12] and medicinal chemistry.[13] In particular, we and others have recently demonstrated that the introduction of *o*-carborane (1,2-dicarba-*closo*-dodecaborane) into organic π-systems largely stabilizes the lowest unoccupied molecular orbital (LUMO) level by direct contribution to LUMO delocalization, as well as by a strong inductive electron-withdrawing effect.[14,15] It is also known that *o*-carborane can be utilized as an electron-transfer mediator in electrocatalytic reductions

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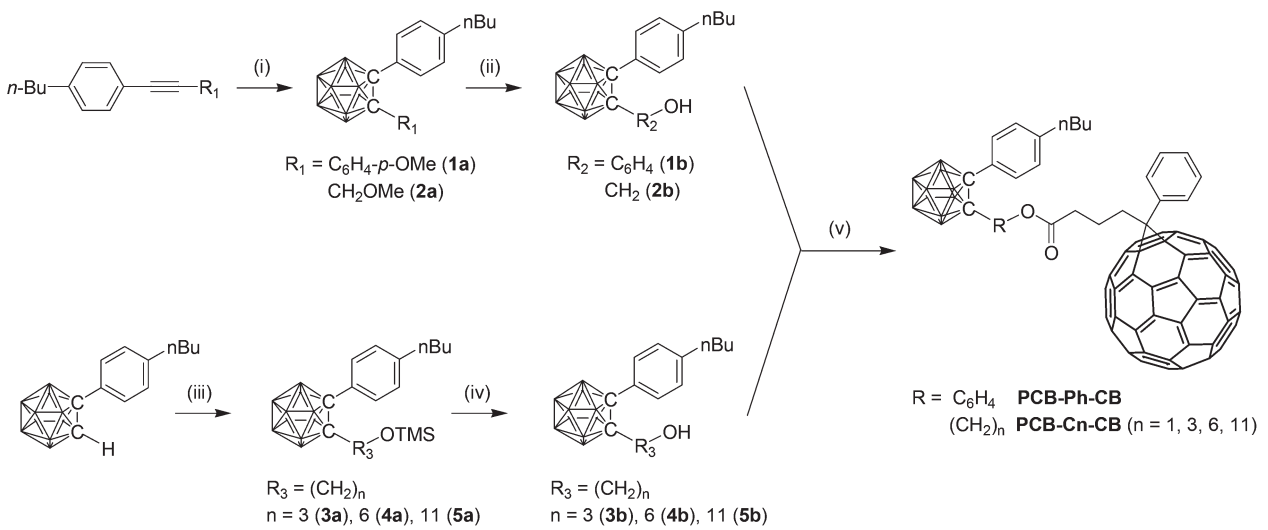
due to its high stability and electron transfer ability.[16] Therefore, it may be intriguing to investigate whether the introduction of *o*-carborane as an electron-accepting and/or transporting auxiliary into PCBM affects the electron transporting properties of PCBM, thereby modulating the electron mobility in fullerene-based n-type OFET devices. It is also worth mentioning that the carborane derivatives have rarely been utilized as electroactive materials in optoelectronic device applications such as organic light-emitting diodes (OLEDs), OPVs, or OFETs,[17] while they have often been incorporated into nonlinear optical systems in the form of C_{60}-π-carborane hybrids.[18] Moreover, there have been no reports so far on the use of *o*-carborane as an electron transporting material in n-type OFET applications.

In this report, we prepared a series of methanofullerene-*o*-carborane dyads *via* covalent-linking of the *o*-carborane derivatives to the ester-functionality of a PCBM moiety and utilized them as the electron-transporting materials in solution-processed OFET devices. The results show that the electron mobility is closely related to the distance between the fullerene moiety and the covalently linked *o*-carborane cage, implying the impact of *o*-carborane on the electron transporting property of PCBM. Details of the synthesis and properties of the methanofullerene-*o*-carborane dyads and their use in the solution-processed, n-type OFETs are described.

Results and discussion

Synthesis and characterization

The *o*-carborane linked PCBM derivatives, methanofullerene-*o*-carborane dyads (**PCB-Ph-CB**, **PCB-C*n*-CB**, n = 1, 3, 6, 11) were designed and synthesized according to Scheme 1. Dyads having a different length of linker (C1, C3, C6, C11, or Ph) were prepared to modulate the distance between the C_{60} moiety and the *o*-carborane cage. An alkyl (*n*-butyl) substituted phenyl ring was introduced at the C1-position of the *o*-carborane to endow better solubility in the organic solvent and electrochemical stability.[16] It was also previously shown that aryl substitution on the carborane cage leads to LUMO stabilization of the carborane moiety,[15] which could be desirable for possible electronic interaction with the fullerene moiety. The reaction of decaborane ($B_{10}H_{14}$) with the acetylene precursors yielded the 1-(4-*n*-BuC_6H_4)-2-substituted-*o*-carborane cages of **1a** and **2a**. In the case of longer alkylene linked derivatives, the lithiation of 1-(4-*n*-BuC_6H_4)-2-*H*-1,2-*closo*-$C_2B_{10}H_{10}$ followed by the reaction with the Br-$(CH_2)_n$-OTMS (n = 3, 6, 11) in the presence of 0.2 equiv. of LiI produced **3a–5a**. Compounds **1a–5a** were further converted into the corresponding alcohols *via* either the demethylation reaction of the methoxy group with BBr_3 (**1b** and **2b**) or the deprotection of the trimethylsilyl group with aqueous HCl (**3b–5b**). The subsequent esterification of **1b–5b** with [6,6]-phenyl-C_{61}-butyric acid (PCBA) led to the formation of the final methanofullerene-*o*-carborane dyads **PCB-Ph-CB** and **PCB-C*n*-CB** (n = 1, 3, 6, 11) as a brown solid. The formation of the dyads was fully characterized by multinuclear NMR spectroscopy, elemental analysis, and MALDI-TOF mass spectrometry. While the ^{1}H and ^{13}C NMR spectra showed the typical signals of a methanofullerene moiety with ester linkage, the two broad ^{11}B NMR signals in the regions of δ −2 to −12 ppm confirm the presence of *o*-carboranyl boron atoms (Fig. S1–S5, ESI†). All the compounds exhibited high solubility in chlorinated and aromatic solvents such as chloroform, toluene, and chlorobenzene under ambient conditions and showed solubility better than that of PCBM, making them suitable for application to solution-processed OFET devices. The increased solubility of dyads was further confirmed in CH_2Cl_2 and tetrahydrofuran (THF) solvents where the



Scheme 1 Conditions and reagents: (i) decaborane ($B_{10}H_{14}$), CH_3CN–toluene (1 : 4, v/v), reflux. (ii) BBr_3, CH_2Cl_2, r.t. (iii) *n*-BuLi, Br-$(CH_2)_n$-OTMS, 0.2 equiv. LiI, THF, −78 °C. (iv) 10% aq. HCl, MeOH–CH_2Cl_2 (2 : 1, v/v), 0 °C. (v) 4-(Dimethylamino)pyridine (DMAP), *N*,*N*′-dicyclohexylcarbodiimide (DCC), PCBA, CH_2Cl_2–CS_2 (1 : 1, v/v), r.t.

solubility of PCBM has been reported to be 10 mg mL^{-1} and 2 mg mL^{-1} at room temperature, respectively.[19] It was shown that **PCB-C1-CB** freely dissolves in CH_2Cl_2 and THF up to at least 2.0 wt% (20 mg mL^{-1}), indicating that the introduction of *o*-carborane may help the processability of fullerene-based materials in a wide range of common solvents.

Optical and electrochemical properties

The UV–vis absorption properties of **PCB-Ph-CB** and **PCB-C*n*-CB** were investigated using a dilute toluene solution (5×10^{-5} M) (Fig. 1). The absorption spectra of all the dyads display features very similar to those of their parent PCBM in the visible region[20] because the carborane cage absorbs light in the UV region only.[14b,21] While a sharp peak at 430 nm reflects the partially broken symmetry (C_{2v}) of the C_{60} moiety when compared to that of the pristine C_{60} (I_h), the small band at 700 nm can be assigned to the [6,6]-addition in the C_{60} moiety. To investigate the LUMO level of the dyads, cyclic voltammetry (CV) measurements were carried out in a mixed solution of toluene–CH_3CN (4 : 1, 5×10^{-4} M) (Fig. 2). For comparison, the cyclic voltammogram of PCBM was also obtained. The cyclic voltammograms of **PCB-Ph-CB** and **PCB-C*n*-CB** show three well-defined, reversible reductions, which are very similar to that for PCBM (Table 1).

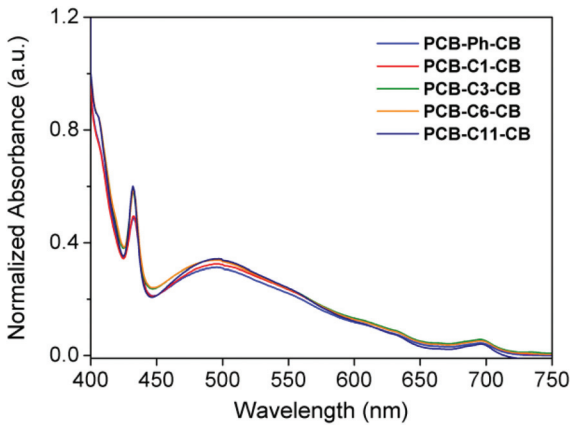


Fig. 1 UV–vis absorption spectra of **PCB-Ph-CB** and **PCB-C*n*-CB** (*n* = 1, 3, 6, 11) in toluene.

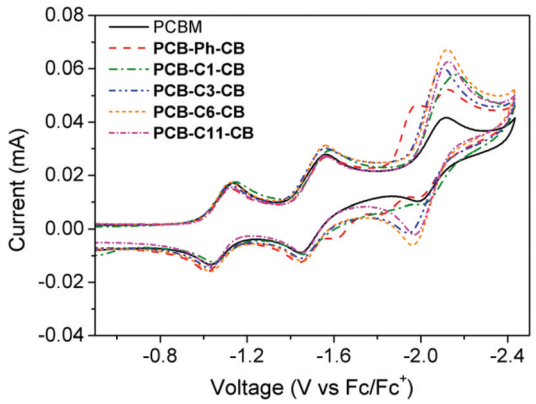


Fig. 2 Cyclic voltammograms of **PCB-Ph-CB** and **PCB-C*n*-CB**.

Table 1 Reduction potentials and LUMO energy levels of **PCB-Ph-CB** and **PCB-C*n*-CB**

Compounds	$E_{1/2}^{1\ red\ a}$ (V)	$E_{1/2}^{2\ red\ a}$ (V)	$E_{1/2}^{3\ red\ a}$ (V)	LUMO[b] (eV)
PCB-Ph-CB	−1.07	−1.50	−1.89, −2.05	−3.73
PCB-C1-CB	−1.10	−1.52	−2.08	−3.70
PCB-C3-CB	−1.07	−1.50	−2.02	−3.73
PCB-C6-CB	−1.08	−1.51	−2.04	−3.72
PCB-C11-CB	−1.08	−1.51	−2.05	−3.72
PCBM	−1.08	−1.50	−2.05	−3.72

[a] Potential values (V) with reference to an Fc/Fc^+ redox couple. [b] LUMO = $-(4.8 + E_{1/2}^{1\ red})$ (eV).

However, inspection of the third reduction of **PCB-Ph-CB** shows an additional well-defined, quasi-reversible peak at $E_{1/2} = -1.89$ V. This peak may be ascribable to the reduction at the 1,2-diaryl-*o*-carborane moiety, which is known to undergo two reversible one-electron reductions or one two-electron reduction depending on a scan rate.[15,16,22] The high intensity of the cathodic peak at −1.98 V with respect to that of the two oxidation peaks at −1.82 and −1.61 V after reduction also supports one two-electron reduction in **PCB-Ph-CB** at a given scan rate of 100 mV s^{-1}. Thus, the CV trace for **PCB-Ph-CB** is considered the sum of the two CV traces of the methanofullerene moiety and the 1,2-diaryl-*o*-carborane moiety. From the first reduction potentials, the LUMO energy levels of the dyads were calculated to be *ca.* −3.70 to −3.73 eV, indicating an essentially identical LUMO level for all dyads (Table 1). Furthermore, the values are almost the same as that of PCBM (−3.72 eV), indicating that the electron accepting and transporting properties of the dyads are dominated by the methanofullerene moiety. The observed absorption and reduction features further suggest that the direct influence of an *o*-carborane cage on the electronic properties of the methanofullerene moiety will be marginal in the present methanofullerene-*o*-carborane dyads, which are covalently linked *via* the ester group of methanofullerene.

Organic field-effect transistors based on the dyads

To investigate the electron transporting properties of the methanofullerene-*o*-carborane dyads, FET devices were fabricated with **PCB-Ph-CB** and **PCB-C*n*-CB** as active layer materials. Fig. 3 shows the transfer characteristics, I_{ds} *vs.* V_{gs}, of the FET devices fabricated with the dyads. Data obtained from similar OFETs based on a physical blend of 1-(4-*n*-BuC_6H_4)-2-Me-1,2-*closo*-$C_2B_{10}H_{10}$ and PCBM are also included for comparison (Fig. 3f). All transport data are typical of n-channel OFETs; the devices turn on with positive gate bias. The FET parameters and results are listed in Table 2.

The saturated electron mobilities of **PCB-Ph-CB** and **PCB-C*n*-CB** were calculated using the saturation current equation: $I_{ds} = (WCi/2L)\,\mu(V_{gs} - V_T)^2$, where W (= 50 μm) is the channel width, L (= 3000 μm) is the channel length of the devices, Ci (= 15 nF cm^{-2}) is the capacitance of the SiO_2

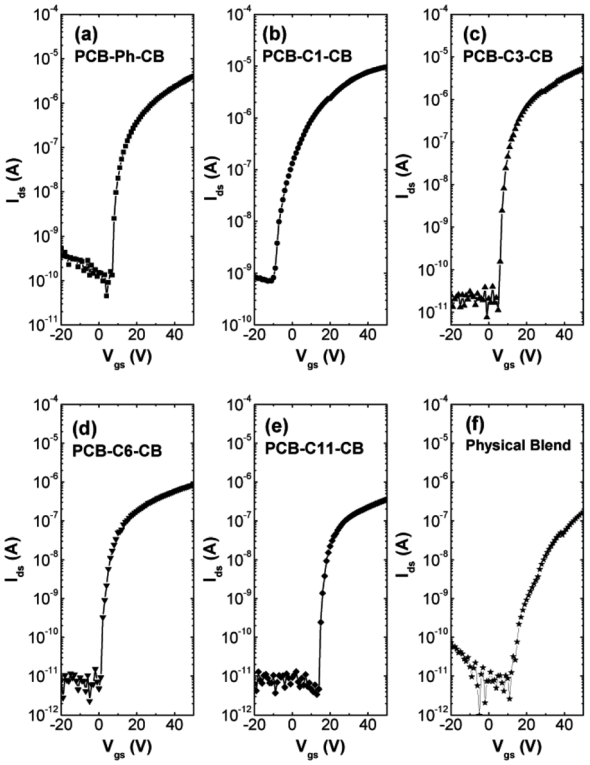


Fig. 3 OFET transfer characteristics of **PCB-Ph-CB** and **PCB-C*n*-CB**.

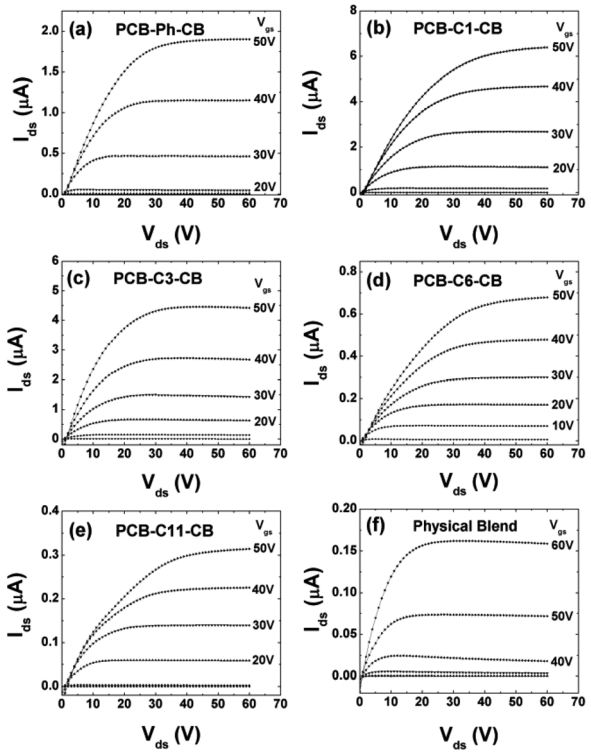


Fig. 4 OFET output characteristics of **PCB-Ph-CB** and **PCB-C*n*-CB**.

Table 2 FET results for **PCB-Ph-CB** and **PCB-C*n*-CB**

	Electron mobility ($cm^2\ V^{-1}\ s^{-1}$)	On/off ratio	V_T (V)
PCB-Ph-CB	9.81×10^{-3}	5×10^5	7.3
PCB-C1-CB	1.72×10^{-2}	3×10^4	−1.2
PCB-C3-CB	1.08×10^{-2}	6×10^5	7.5
PCB-C6-CB	1.14×10^{-3}	1×10^5	−4.2
PCB-C11-CB	7.15×10^{-4}	4×10^4	3.5
PCBM[a]	3.50×10^{-2}	2×10^5	2
Physical blend[b]	6.83×10^{-4}	2×10^4	21

[a] See ref. 9. [b] Spin-casting from a solution of PCBM and 1-(4-*n*-BuC_6H_4)-2-Me-1,2-*closo*-$C_2B_{10}H_{10}$.

dielectric, and V_T is the threshold voltage. The output characteristics, I_{ds} *vs.* V_{ds}, of the FET devices are shown in Fig. 4. The best device performance was obtained from **PCB-C1-CB** FET, with an electron mobility of 1.72×10^{-2} $cm^2\ V^{-1}\ s^{-1}$, which is similar to that of PCBM, reported in previous studies.[9] However, the device performances gradually decreased with increasing length of the alkyl linker.

In the case of **PCB-C11-CB**, which has the longest alkyl linker between PCBM and *o*-carborane, the device performance was lowest and close to that of the FET fabricated with a physical blend of *o*-carborane and PCBM. Note that the data on the performance of the **PCB-Ph-CB** FET are similar to the data obtained from the device fabricated with **PCB-C3-CB**, which has a similar physical distance between PCBM and *o*-carborane. These results indicate that the incorporation of an electron-deficient carborane cage into the methanofullerene moiety in close proximity may have an impact on the electron transporting properties of PCBM, although the direct electron-withdrawing effect of *o*-carborane through an alkyl linker is not apparently observed, as shown in the electrochemical reduction.

Surface morphology of thin films

Since the performance of FET devices often strongly depends on the nanomorphology of the film, we examined the surface morphology of the thin films of the dyads. Fig. 5 shows the height images (2 μm × 2 μm) of **PCB-Ph-CB** and **PCB-C*n*-CB** thin films recorded by tapping mode atomic force microscopy (AFM). All AFM images show a quite homogeneous morphology consisting of fine, regular grains with RMS values of 0.184–0.212 nm. No significant differences were observed in the morphological study.

Therefore, the differences between the FET properties may not have originated from the morphological differences. In the case of the films of a physical blend of *o*-carborane and PCBM (Fig. 5f), however, height images showed a somewhat aggregated morphology with a slightly increased RMS value of 0.360 nm. This aggregated morphology may be attributed to the phase separation of the *o*-carborane and PCBM. Such an undesired phase separation of the two moieties could negatively affect the charge transport pathway, thereby suppressing the electron mobility of an FET device fabricated with a physical blend of *o*-carborane and PCBM.

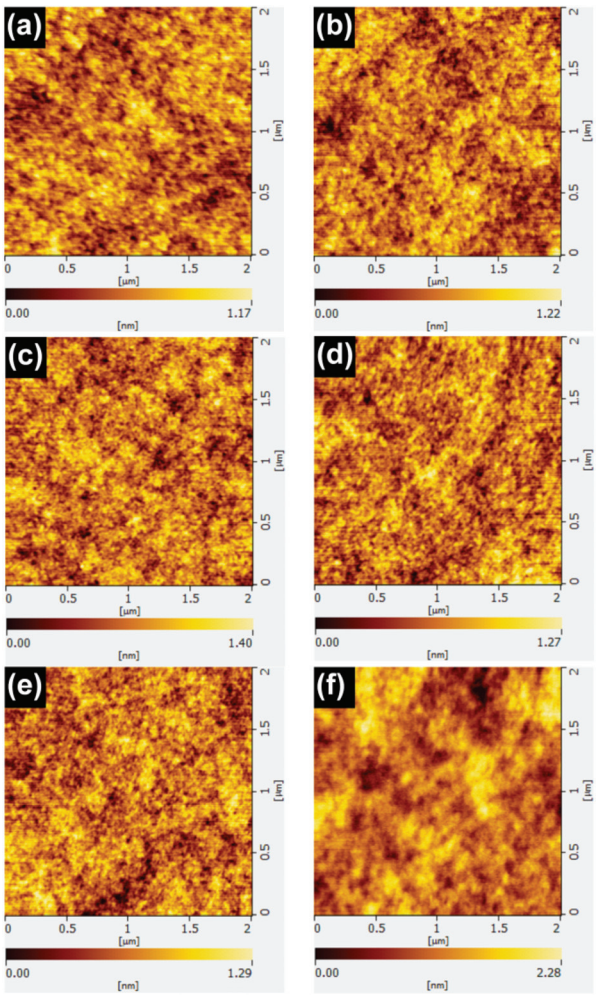


Fig. 5 Topographic AFM images of (a) **PCB-Ph-CB** (RMS = 0.184 nm), (b) **PCB-C1-CB** (RMS = 0.193 nm), (c) **PCB-C3-CB**, (RMS = 0.212 nm), (d) **PCB-C6-CB** (RMS = 0.198 nm), (e) **PCB-C11-CB** (RMS = 0.203 nm), and (f) physical blend of PCBM and 1-(4-*n*-BuC_6H_4)-2-Me-1,2-*closo*-$C_2B_{10}H_{10}$ (RMS = 0.360 nm).

Experimental

General considerations

All operations were performed under an inert nitrogen atmosphere using standard Schlenk and glove box techniques. Anhydrous grade solvents (Aldrich) were dried by passing them through an activated alumina column and stored over activated molecular sieves (5 Å). Spectrophotometric-grade toluene was used as received from J. T. Baker. Commercial reagents were used without any further purification after purchasing from Aldrich (BBr_3 (1.0 M solution in heptane), lithium iodide (LiI), diethyl sulfide (Et_2S), 4-(dimethylamino)pyridine (DMAP), *N*,*N*′-dicyclohexylcarbodiimide (DCC), *n*-BuLi (2.5 M solution in hexane), carbon disulfide (CS_2), TCI (1-butyl-4-ethynylbenzene), and KatChem ($B_{10}H_{14}$, decaborane) and nano-C (PCBM)). 1-(2-(4-Butylphenyl)ethynyl)-4-methoxybenzene and 1-butyl-4-(3-methoxyprop-1-ynyl)benzene (Sonogashira reaction),[23] [6,6]-phenyl-C_{61}-butyric acid (PCBA),[5] and Br-$(CH_2)_n$-OTMS (TMS; trimethylsilyl, the protection reaction of alcohol),[24] and 1-(4-*n*-BuC_6H_4)-2-*H*-1,2-*closo*-$C_2B_{10}H_{10}$ [25] were analogously synthesized according to the published procedures. $CDCl_3$ from Cambridge Isotope Laboratories was used after drying over activated molecular sieves (5 Å). NMR spectra of compounds were recorded on a Bruker Avance 400 spectrometer (400.13 MHz for ^{1}H, 100.62 MHz for ^{13}C, 128.38 MHz for ^{11}B) at ambient temperature. Chemical shifts are given in ppm, and are referenced against external Me_4Si (^{1}H, ^{13}C) and $BF_3{\cdot}Et_2O$ (^{11}B). MALDI-TOF MS was measured with a Voyager DE-STR 4700 proteomics analyzer at the Korea Basic Science Center (KBSC). HR EI-MS measurement (JEOL JMS700) was carried out at KBSC. Elemental analyses were performed using an EA1110 (Fisons Instruments) by the Environmental Analysis Laboratory at KAIST. The UV–vis spectrum was recorded on a Jasco V-530 in a toluene solvent with a 1 cm quartz cuvette at ambient temperature.

Synthesis of 1a

To a stirred solution of decaborane (1.16 g, 9.49 mmol) in toluene (40 mL) was added CH_3CN (10 mL) and the solution was heated to reflux for 3 h. The solution was cooled to room temperature and 1-(2-(4-butylphenyl)ethynyl)-4-methoxybenzene (2.50 g, 9.30 mmol) was added. The reaction mixture was heated at reflux for 16 h and cooled to room temperature. After removal of the solvent, the residue was purified by column chromatography on silica (eluent: *n*-hexane–ethyl acetate = 4/1), which afforded **1a** as a colorless oil (1.53 g, 43%). ^{1}H NMR ($CDCl_3$): δ ppm: 7.33–7.26 (m, 4H), 6.91 (d, J = 8.5 Hz, 2H), 6.62–6.58 (m, 2H), 3.69 (s, 3H), 2.46 (t, J = 7.6 Hz, 2H), 1.51–1.42 (m, 2H), 1.27–1.17 (m, 2H), 0.85 (t, J = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ ppm: 160.76, 145.19, 132.06, 130.54, 128.23, 128.17, 123.17, 113.41, 85.75 (CB-*C*), 85.69 (CB-*C*), 55.26, 34.97, 32.95, 22.16, 13.85. ^{11}B NMR ($CDCl_3$): δ ppm: −2.8 (br s, 3B), −9.2 (br s), −10.8 (br s) (7B). HR EI-MS: *m*/*z* calcd for $C_{19}H_{30}B_{10}O$, 384.3227; found, 384.3229.

Synthesis of 1b

To a solution of **1a** (1.05 g, 2.74 mmol) in CH_2Cl_2 (40 mL) was added dropwise BBr_3 (6.86 mmol) at −78 °C. The solution was allowed to warm to room temperature and stirred overnight. After the addition of MeOH (10 mL) in an ice bath, the solvent was removed by rotary evaporation. The crude product was purified by column chromatography on silica (eluent: *n*-hexane–CH_2Cl_2 = 3/1, then CH_2Cl_2), which afforded **1b** as a light yellow oil (0.86 g, 85%). ^{1}H NMR ($CDCl_3$): δ ppm: 7.32 (t, J = 8.6 Hz, 4H), 6.96 (d, J = 7.7 Hz, 2H), 6.55 (d, J = 8.2 Hz, 2H), 5.16 (s, 1H), 2.50 (t, J = 7.6 Hz, 2H), 1.55–1.45 (m, 2H), 1.32–1.21 (m, 2H), 0.88 (t, J = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ ppm: 145.29, 132.27, 130.47, 128.24, 127.95, 123.40, 114.95, 85.82 (CB-*C*), 85.57 (CB-*C*), 34.90, 32.86, 22.13, 13.81. ^{11}B NMR ($CDCl_3$): δ ppm: −2.8 (br s, 3B), −9.2 (br s), −10.7 (br s) (7B). HR EI-MS: *m*/*z* calcd for $C_{18}H_{28}B_{10}O$, 370.3071; found, 370.3073.

Synthesis of PCB-Ph-CB

A solution of DMAP (64 mg, 0.52 mmol), DCC (0.49 g, 2.37 mmol), and **1b** (0.872 g, 2.37 mmol) in CH_2Cl_2 (150 mL)

was added to a solution of PCBA (0.94 g, 1.05 mmol) in dry carbon disulfide (150 mL) *via* a cannula. The reaction mixture was stirred for 20 h at room temperature. After removal of the solvent, the residue was purified by column chromatography on silica (eluent: toluene–*n*-hexane = 1/2). The obtained solid was precipitated by MeOH and filtered off, which afforded the product as a brown solid (0.54 g, 41%). ^{1}H NMR ($CDCl_3$): δ ppm: 7.92–7.88 (m, 2H), 7.55–7.49 (m, 2H), 7.48–7.42 (m, 1H), 7.41–7.36 (m, 2H), 7.28 (d, J = 8.5 Hz, 2H), 6.92 (d, J = 8.3 Hz, 2H), 6.87–6.82 (m, 2H), 2.97–2.91 (m, 2H), 2.69 (t, J = 7.4 Hz, 2H), 2.46 (t, J = 7.6 Hz, 2H), 2.28–2.18 (m, 2H), 1.52–1.41 (m, 2H), 1.27–1.16 (m, 2H), 0.85 (t, J = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ ppm: 170.62, 151.84, 148.63, 145.77, 145.20, 145.16, 144.99, 144.66, 144.52, 143.73, 143.01, 142.95, 142.16, 142.12, 141.00, 140.76, 137.98, 137.58, 132.04, 131.83, 130.47, 128.49, 128.35, 127.81, 121.10, 85.67 (CB-*C*), 84.34 (CB-*C*), 79.71, 51.58, 34.96, 34.10, 33.88, 22.18, 13.89. ^{11}B NMR ($CDCl_3$): δ ppm: −2.6 (br s, 3B), −10.4 (br s, 7B). MALDI-TOF MS: *m*/*z* calcd for $C_{89}H_{38}B_{10}O_2$, 1248.4; found, 1248.7. Anal. calcd for $C_{89}H_{38}B_{10}O_2$: C 85.70, H 3.07; found: C 85.77, H 2.93.

Synthesis of 2a

A procedure analogous to that for **1a** was employed with decaborane (1.96 g, 16.07 mmol) and 1-butyl-4-(3-methoxyprop-1-ynyl)benzene (3.19 g, 15.75 mmol). Purification by column chromatography on alumina (eluent: toluene) afforded **2a** as a light yellow oil (2.27 g, 45%). ^{1}H NMR ($CDCl_3$): δ ppm: 7.53–7.48 (m, 2H), 7.14 (d, J = 8.6 Hz, 2H), 3.45 (s, 2H), 3.12 (s, 3H), 2.60 (t, J = 7.6 Hz, 2H), 1.62–1.53 (m, 2H), 1.38–1.28 (m, 2H), 0.91 (t, J = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ ppm: 145.90, 130.91, 128.69, 127.76, 82.67 (CB-*C*), 80.33 (CB-*C*), 71.96, 59.40, 35.11, 33.13, 22.32, 13.87. ^{11}B NMR ($CDCl_3$): δ ppm: −2.7 (br s), −3.4 (br s) (3B), −10.5 (br s), −12.1 (br s) (7B). HR EI-MS: *m*/*z* calcd for $C_{14}H_{28}B_{10}O$, 322.3071; found, 322.3067.

Synthesis of 2b

A procedure analogous to that for **1b** was employed with **2a** (1.19 g, 3.72 mmol) and BBr_3 (9.29 mmol). Purification by column chromatography on silica (eluent: CH_2Cl_2) afforded **2b** as a dark yellow oil (1.13 g, 99%). ^{1}H NMR ($CDCl_3$): δ ppm: 7.51 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 8.4 Hz, 2H), 3.75–3.70 (m, 2H), 2.60 (t, J = 7.7 Hz, 2H), 1.86–1.81 (m, 1H), 1.62–1.52 (m, 2H), 1.39–1.28 (m, 2H), 0.91 (t, J = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ ppm: 146.16, 132.27, 130.85, 128.98, 127.54, 82.99 (CB-*C*), 82.53 (CB-*C*), 63.03, 35.10, 33.10, 22.34, 13.86. ^{11}B NMR ($CDCl_3$): δ ppm: −2.8 (br s), −3.4 (br s) (3B), −10.3 (br s), −12.4 (br s) (7B). HR EI-MS: *m*/*z* calcd for $C_{13}H_{26}B_{10}O$, 308.2914; found, 308.2916.

Synthesis of PCB-C1-CB

A procedure analogous to that for **PCB-Ph-CB** was employed with **2b** instead of **1b**. The product was obtained as a brown solid (50%). ^{1}H NMR ($CDCl_3$): δ ppm: 7.93–7.89 (m, 2H), 7.58–7.52 (m, 2H), 7.50–7.44 (m, 3H), 7.14 (d, J = 8.3 Hz, 2H), 4.20 (s, 2H), 2.89–2.83 (m, 2H), 2.59 (t, J = 7.7 Hz, 2H), 2.46 (t, J = 7.5 Hz, 2H), 2.18–2.09 (m, 2H), 1.62–1.53 (m, 2H), 1.39–1.28 (m, 2H), 0.91 (t, J = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ ppm: 171.03, 148.65, 147.62, 145.78, 145.15, 145.04, 144.65, 143.74, 142.99, 142.20, 142.16, 142.12, 142.09, 141.01, 140.76, 137.99, 137.58, 132.03, 130.94, 128.96, 128.53, 127.19, 83.29 (CB-*C*), 79.74, 78.20 (CB-*C*), 62.24, 51.66, 35.13, 33.62, 33.54, 33.06, 22.36, 22.17, 13.92. ^{11}B NMR ($CDCl_3$): δ ppm: −3.5 (br s, 3B), −10.0 (br s, 7B). MALDI-TOF MS: *m*/*z* calcd for $C_{84}H_{36}B_{10}O_2$, 1186.4; found, 1186.5. Anal. calcd for $C_{84}H_{36}B_{10}O_2$: C 85.12, H 3.06; found: C 85.21, H 3.01.

Synthesis of 3a

1-(4-*n*-BuC_6H_4)-2-*H*-1,2-*closo*-$C_2B_{10}H_{10}$ (3.34 g, 12.08 mmol) in THF (40 mL) was treated with one equiv. of *n*-BuLi (4.8 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. To the mixture was slowly added Br-$(CH_2)_3$-OTMS (2.55 g, 12.08 mmol) and LiI (0.32 g, 2.42 mmol) in THF (40 mL) at −78 °C. The reaction mixture was slowly allowed to warm to room temperature and further stirred overnight. The resulting solution was treated with 30 mL of a saturated aqueous solution of NH_4Cl and the organic portion was separated. The aqueous layer was further extracted with diethyl ether (2 × 20 mL). The combined organic portions were dried over $MgSO_4$, filtered, and evaporated to dryness. The residue was purified by column chromatography on silica (eluent: *n*-hexane–CH_2Cl_2 = 2/1), affording **3a** as a colorless oil (3.24 g, 66%). ^{1}H NMR ($CDCl_3$): δ ppm: 7.49 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 8.4 Hz, 2H), 3.35 (t, J = 5.9 Hz, 2H), 2.59 (t, J = 7.8 Hz, 2H), 1.87–1.80 (m, 2H), 1.62–1.52 (m, 4H), 1.39–1.28 (m, 2H), 0.91 (t, J = 7.4 Hz, 3H), −0.07 (s, 9H). ^{13}C NMR ($CDCl_3$): δ ppm: 145.80, 131.04, 128.82, 128.04, 84.13 (CB-*C*), 82.31 (CB-*C*), 61.12, 35.10, 33.16, 32.34, 31.75, 22.35, 13.87, −0.68. ^{11}B NMR ($CDCl_3$): δ ppm: −3.8 (br s, 3B), −10.3 (br s, 7B). HR EI-MS: *m*/*z* calcd for $C_{18}H_{38}B_{10}OSi$, 408.3622; found, 408.3625.

Synthesis of 3b

To a solution of the compound **3a** (2.36 g, 5.81 mmol) in MeOH (40 mL) and CH_2Cl_2 (20 mL) was added 10% aqueous HCl (5 mL) at 0 °C. The reaction mixture was stirred for 1 h at 0 °C. After addition of water (30 mL), the resulting solution was extracted with CH_2Cl_2 (30 mL) and the organic phase was washed with water (2 × 20 mL). The organic portions were dried over $MgSO_4$, filtered, and evaporated to dryness. The residue was purified by column chromatography on silica (eluent: CH_2Cl_2), affording **3b** as a white solid (1.49 g, 77%). ^{1}H NMR ($CDCl_3$): δ ppm: 7.49 (d, J = 8.6 Hz, 2H), 7.15 (d, J = 8.4 Hz, 2H), 3.42 (q, J = 5.8 Hz, 2H), 2.60 (t, J = 7.7 Hz, 2H), 1.91–1.85 (m, 2H), 1.67–1.53 (m, 4H), 1.39–1.28 (m, 2H), 1.12 (t, J = 5.3 Hz, 1H), 0.91 (t, J = 7.4 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ ppm: 145.89, 130.98, 128.86, 127.93, 83.95 (CB-*C*), 82.01 (CB-*C*), 61.48, 35.09, 33.08, 32.34, 31.57, 22.32, 13.87. ^{11}B NMR ($CDCl_3$): δ ppm: −3.7 (br s, 3B), −10.4 (br s, 7B). Anal. calcd for $C_{15}H_{30}B_{10}O$, C 53.86, H 9.04; found, C 53.85, H 9.07.

Synthesis of PCB-C3-CB

A procedure analogous to that for **PCB-Ph-CB** was employed with **3b**. The product was obtained as a brown solid (56%). ^{1}H NMR ($CDCl_3$): δ ppm: 7.92–7.87 (m, 2H), 7.56–7.51 (m, 2H), 7.49–7.44 (m, 3H), 7.15 (d, J = 8.4 Hz, 2H), 3.82 (t, J = 6.2 Hz, 2H), 2.86–2.81 (m, 2H), 2.60 (t, J = 7.7 Hz, 2H), 2.35 (t, J = 7.5 Hz, 2H), 2.13–2.03 (m, 2H), 1.84–1.79 (m, 2H), 1.73–1.65 (m, 2H), 1.63–1.54 (m, 2H), 1.39–1.29 (m, 2H), 0.91 (t, J = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ ppm: 172.62, 148.69, 147.72, 145.81, 145.20, 145.16, 145.05, 145.02, 144.80, 144.66, 144.52, 143.76, 143.01, 142.95, 142.16, 142.13, 141.00, 137.57, 132.05, 131.01, 128.91, 128.47, 127.85, 84.05 (CB-*C*), 81.36 (CB-*C*), 79.78, 62.89, 51.70, 35.15, 33.77, 33.57, 33.15, 31.45, 28.49, 22.40, 22.23, 13.96. ^{11}B NMR ($CDCl_3$): δ ppm: −3.7 (br s, 3B), −10.2 (br s, 7B). MALDI-TOF MS: *m*/*z* calcd for $C_{86}H_{40}B_{10}O_2$, 1214.4; found, 1214.6. Anal. calcd for $C_{86}H_{40}B_{10}O_2$: C 85.13, H 3.32; found: C 85.10, H 3.15.

Synthesis of 4a

A procedure analogous to that for **3a** was employed with Br-$(CH_2)_6$-OTMS, affording **4a** as a colorless oil (74%). ^{1}H NMR ($CDCl_3$): δ ppm: 7.49 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 8.4 Hz, 2H), 3.46 (t, J = 6.6 Hz, 2H), 2.60 (t, J = 7.7 Hz, 2H), 1.76–1.70 (m, 2H), 1.63–1.54 (m, 2H), 1.41–1.30 (m, 6H), 1.19–1.01 (m, 4H), 0.91 (t, J = 7.3 Hz, 3H), −0.06 (s, 9H). ^{13}C NMR ($CDCl_3$): δ ppm: 145.77, 130.98, 128.80, 128.09, 83.80 (CB-*C*), 82.53 (CB-*C*), 62.32, 35.10, 34.90, 33.11, 32.32, 29.37, 28.76, 25.22, 22.33, −0.52. ^{11}B NMR ($CDCl_3$): δ ppm: −3.8 (br s, 3B), −10.4 (br s, 7B). HR EI-MS: *m*/*z* calcd for $C_{21}H_{44}B_{10}OSi$, 450.4092; found, 450.4090.

Synthesis of 4b

A procedure analogous to that for **3b** was employed with **4a**, affording **4b** as a colorless oil (70%). ^{1}H NMR ($CDCl_3$): δ ppm: 7.48 (d, J = 8.5 Hz, 2H), 7.15 (d, J = 8.4 Hz, 2H), 3.53 (t, J = 6.7 Hz, 2H), 2.60 (t, J = 7.7 Hz, 2H), 1.77–1.70 (m, 2H), 1.63–1.53 (m, 2H), 1.45–1.28 (m, 6H), 1.20–1.03 (m, 5H), 0.91 (t, J = 7.4 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ ppm: 145.79, 130.97, 128.79, 128.05, 83.80 (CB-*C*), 82.47 (CB-*C*), 62.65, 35.08, 34.81, 33.09, 32.30, 29.29, 28.68, 25.09, 22.31, 13.86. ^{11}B NMR ($CDCl_3$): δ ppm: −3.8 (br s, 3B), −10.4 (br s, 7B). HR EI-MS: *m*/*z* calcd for $C_{18}H_{36}B_{10}O$, 378.3697; found, 378.3694.

Synthesis of PCB-C6-CB

A procedure analogous to that for **PCB-Ph-CB** was employed with **4b**, affording the product as a brown solid (55%). ^{1}H NMR ($CDCl_3$): δ ppm: 7.92–7.88 (m, 2H), 7.55–7.42 (m, 5H), 7.15 (d, J = 8.4 Hz, 2H), 3.95 (t, J = 6.8 Hz, 2H), 2.91–2.85 (m, 2H), 2.60 (t, J = 7.7 Hz, 2H), 2.47 (t, J = 7.4 Hz, 2H), 2.19–2.10 (m, 2H), 1.75–1.69 (m, 2H), 1.62–1.53 (m, 2H), 1.50–1.42 (m, 2H), 1.40–1.28 (m, 2H), 1.20–1.02 (m, 4H), 0.91 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ ppm: 173.03, 148.78, 147.80, 145.85, 145.20, 145.05, 144.41, 144.01, 143.77, 143.00, 142.95, 142.91, 142.19, 142.14, 142.10, 140.98, 138.01, 137.57, 132.09, 130.99, 128.83, 128.42, 128.25, 83.82 (CB-*C*), 82.34 (CB-*C*), 79.87, 64.33, 51.84, 35.11, 34.85, 34.07, 33.65, 33.10, 29.25, 28.60, 28.23, 25.37, 22.38, 22.35, 13.91. ^{11}B NMR ($CDCl_3$): δ ppm: −3.8 (br s, 3B), −10.4 (br s, 7B). MALDI-TOF MS: *m*/*z* calcd for $C_{89}H_{46}B_{10}O_2$, 1256.4; found, 1256.7. Anal. calcd for $C_{89}H_{46}B_{10}O_2$: C 85.15, H 3.69; found: C 85.05, H 3.60.

Synthesis of 5a

A procedure analogous to that for **3a** was employed with Br-$(CH_2)_{11}$-OTMS, affording **5a** as a colorless oil (76%). ^{1}H NMR ($CDCl_3$): δ ppm: 7.51–7.46 (m, 2H), 7.15 (d, J = 8.5 Hz, 2H), 3.54 (t, J = 6.7 Hz, 2H), 2.60 (t, J = 7.7 Hz, 2H), 1.75–1.69 (m, 2H), 1.62–1.53 (m, 2H), 1.53–1.44 (m, 2H), 1.38–1.29 (m, 4H), 1.29–0.99 (m, 14H), 0.91 (t, J = 7.2 Hz, 3H), −0.09 (s, 9H). ^{13}C NMR ($CDCl_3$): δ ppm: 145.74, 130.99, 128.78, 128.12, 83.79 (CB-*C*), 82.63 (CB-*C*), 62.71, 35.11, 34.91, 33.14, 32.73, 29.51, 29.41, 29.35, 29.25, 28.92, 28.90, 25.80, 22.33, 13.89, −0.46. ^{11}B NMR ($CDCl_3$): δ ppm: −3.8 (br s, 3B), −10.4 (br s, 7B). HR EI-MS: *m*/*z* calcd for $C_{26}H_{54}B_{10}OSi$, 520.4874; found, 520.4877.

Synthesis of 5b

A procedure analogous to that for **3b** was employed with **5a**, affording **5b** as a colorless oil (75%). ^{1}H NMR ($CDCl_3$): δ ppm: 7.48 (d, J = 8.5 Hz, 2H), 7.15 (d, J = 8.4 Hz, 2H), 3.61 (s, 2H), 2.60 (t, J = 7.5 Hz, 2H), 1.75–1.69 (m, 2H), 1.62–1.48 (m, 4H), 1.38–0.97 (m, 19H), 0.91 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ ppm: 145.73, 130.96, 128.76, 128.07, 83.78 (CB-*C*), 82.61 (CB-*C*), 62.99, 35.08, 34.87, 33.10, 32.74, 29.47, 29.36, 29.35, 29.32, 29.21, 28.87, 25.68, 22.30, 13.86. ^{11}B NMR ($CDCl_3$): δ ppm: −3.8 (br s, 3B), −10.4 (br s, 7B). HR EI-MS: *m*/*z* calcd for $C_{23}H_{46}B_{10}O$, 448.4479; found, 448.4482.

Synthesis of PCB-C11-CB

A procedure analogous to that for **PCB-Ph-CB** was employed with **5b**, affording the product as a dark brown solid (51%). ^{1}H NMR ($CDCl_3$): δ ppm: 7.93–7.88 (m, 2H), 7.55–7.42 (m, 5H), 7.15 (d, J = 8.3 Hz, 2H), 4.03 (t, J = 6.7 Hz, 2H), 2.92–2.86 (m, 2H), 2.60 (t, J = 7.7 Hz, 2H), 2.49 (t, J = 7.4 Hz, 2H), 2.21–2.11 (m, 2H), 1.75–1.69 (m, 2H), 1.63–1.53 (m, 4H), 1.39–0.98 (m, 18H), 0.91 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ ppm: 173.09, 148.80, 147.80, 145.84, 145.71, 145.17, 145.12, 145.06, 145.02, 144.77, 144.67, 144.63, 144.48, 144.39, 143.98, 143.74, 143.73, 143.09, 143.01, 142.97, 142.92, 142.89, 142.21, 142.16, 142.11, 142.08, 140.95, 140.72, 138.02, 137.54, 136.73, 132.08, 130.98, 128.78, 128.41, 128.22, 128.09, 83.83 (CB-*C*), 82.59 (CB-*C*), 79.88, 64.73, 51.89, 35.11, 34.91, 34.13, 33.66, 33.12, 29.45, 29.43, 29.38, 29.27, 29.25, 28.95, 28.62, 25.92, 22.41, 22.34, 13.94. ^{11}B NMR ($CDCl_3$): δ ppm: −3.8 (br s, 3B), −10.3 (br s, 7B). MALDI-TOF MS: *m*/*z* calcd for $C_{94}H_{56}B_{10}O_2$, 1326.5; found, 1326.0. Anal. calcd for $C_{94}H_{56}B_{10}O_2$: C 85.17, H 4.26; found: C 85.30, H 4.22.

Cyclic voltammetry

Cyclic voltammetry measurement was carried out with a three-electrode cell configuration consisting of platinum working and counter electrodes and an $Ag/AgNO_3$ (0.01 M in CH_3CN) reference electrode at room temperature. Measurement was

conducted using a solution of PCBM, **PCB-Ph-CB** and **PCB-C*n*-CB** (n = 1, 3, 6, 11) in a mixed solvent of toluene–CH_3CN (4 : 1, 5×10^{-4} M) and 0.1 M tetrabutylammonium hexafluorophosphate (n-Bu_4NPF_6) was used as the supporting electrolyte. The reduction potentials were recorded at a scan rate of 100 mV s^{-1} and reported with reference to the ferrocene/ferrocenium (Fc/Fc^+) redox couple.

Device fabrication

All FETs (with the top contact geometry) were fabricated on heavily doped n-type silicon (Si) wafers each covered with a thermally grown silicon dioxide (SiO_2) layer with a thickness of 200 nm. The active layer was deposited by spin-coating at 2500 rpm. All solutions were prepared at a concentration of 1.0 wt% in chloroform. The thickness of the deposited films was about 70 nm. Before deposition of source–drain electrodes, the films were dried on a hot plate and stabilized at 80 °C for 30 min. All fabrication processes were carried out in a glovebox filled with N_2. An Ag source and drain electrodes were deposited by thermal evaporation using a shadow mask. The thickness of the source and drain electrodes was 75 nm. The channel length (L) and the channel width (W) were 3000 μm and 50 μm, respectively. Electrical characterization was performed using a Keithley semiconductor parametric analyzer (Keithley 4200) under an N_2 atmosphere.

Sample preparation for AFM

Thin film samples for AFM measurements were prepared by spin-coating on a Si wafer covered with 200 nm SiO_2 using the same solution (1.0 wt% in chloroform) used to prepare the FET devices. AFM images were obtained using a multimode microscope with a NanoNavi II (SII nanotechnology).

Conclusions

We have demonstrated that methanofullerene-*o*-carborane dyads can be prepared *via* esterification of [6,6]-phenyl-C_{61}-butyric acid (PCBA) with 2-alcohol functionalized *o*-carborane derivatives, 1-(4-*n*-BuC_6H_4)-2-R-1,2-*closo*-$C_2B_{10}H_{10}$ (R = *p*-C_6H_4OH, $(CH_2)_nOH$, n = 1, 3, 6, 11). It was shown that the dyads can act as active layer materials in n-type FET devices with an electron mobility comparable to that of PCBM. The performances are quite dependent on the length of the alkyl linker between the methanofullerene and the *o*-carborane moieties, and are better than that of the physical blend of *o*-carborane and PCBM. Although the direct influence of an *o*-carborane cage on the electronic properties of the methanofullerene moiety was not apparently observed, the incorporation of an electron-deficient carborane cage into the methanofullerene moiety in close proximity may have an impact on the electron transporting properties of PCBM, suggesting that the methanofullerene-*o*-carborane dyads may constitute a new class of electron transporting materials.

Abbreviations

PCBM	[6,6]-Phenyl-C_{61}-butyric acid methyl ester
PCBA	[6,6]-Phenyl-C_{61}-butyric acid
FET (OFET)	(Organic) Field-effect transistor
OLED	Organic light-emitting diode
OPV	Organic photovoltaic
LUMO	Lowest unoccupied molecular orbital
CV	Cyclic voltammetry
AFM	Atomic force microscopy

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