Electronic Supporting Information for

New Type of Carborane-based Electron-accepting Material

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EXPERIMENTAL SECTION

General Information

All the experimental procedures were performed under a dry nitrogen (N_2) or argon (Ar) atmosphere using standard Schlenk techniques. All solvents were distilled freshly and used under dry nitrogen or argon-purging. Phenylacetylene, TMEDA, copper iodide, copper chloride, NBS, silver nitrate, 2-methyl-3-butyn-2-ol, *n*-butylamine, hydroxylamine hydrochloride, sodium hydroxide, decaborane, *N,N*-dimethylaniline were purchased from Aldrich or TCI and used without further purification. The starting materials, diphenylbutadiyne (1)[1], (bromoethynyl)benzene (2)[2], 2-methyl-6-phenylhexa-3,5-diyn-2-ol (3)[3], phenylbutadiyne (4)[4], and diphenylhexatriyne (5)[5] were prepared according to previously reported procedures. Reference compound **I** was also prepared according to previously reported procedure.[6] ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded using a Bruker Fourier 300 MHz spectrometer operated at 300.1 and 75.4 MHz, respectively. ^{1}H and ^{13}C NMR chemical shifts were measured in $CDCl_3$. Referenced to the relative peaks of $CDCl_3$ are 7.26 ppm for ^{1}H NMR and 77.16 ppm for ^{13}C NMR, respectively. ^{11}B NMR were acquired on 500MHz NMR spectrometer (AVANCE III HD, Bruker, Germany) at KBSI Western Seoul center. Elemental analyses were performed using a Carlo Erba Instruments CHNS-O EA 1108 analyser. A high-resolution mass spectrometry (HR-MS) analysis was performed using a highly sensitive liquid chromatography–multistage MS (LC/MS/MS^n)(n = 10) spectrometer (Thermo Fisher Scientific, LCQ Fleet Hyperbolic Ion Trap MS/MS^n Spectrometer).

Crystal Structures Determination

The structures of the (**II**) and (**III**) single crystal were determined at 223 K using an X-ray diffraction system (Bruker AXS GMBH) at the Korea Basic Science Institute, Seoul Western Centre that was equipped with a sealed-tube X-ray source (50 kV 30 mA); monochromatic Mo $K\alpha$ radiation (λ = 0.71073 Å) corresponding to graphite was obtained from the X-ray source. At this preliminary stage,

the unit cell constants were determined from a set of 45 narrow-frame (0.3° in ω) scans. A double-pass method of scanning was used to exclude any noise. The collected frames were integrated using an orientation matrix, which was developed using narrow frame scans. The *SMART* software package was used for data collection, while the *SAINT* software package[7] was used for frame integration. Final cell constants were determined by conducting global refinement of the *xyz* centroids of the reflections, which were harvested from the entire data set. The structural solution and refinement were carried out using *SHELXTL PLUS* software package.[8] The crystal structures of II and III have been deposited in the CCDC database (deposit numbers 1986098 and 1986099).

Absorption and Fluorescence Measurements

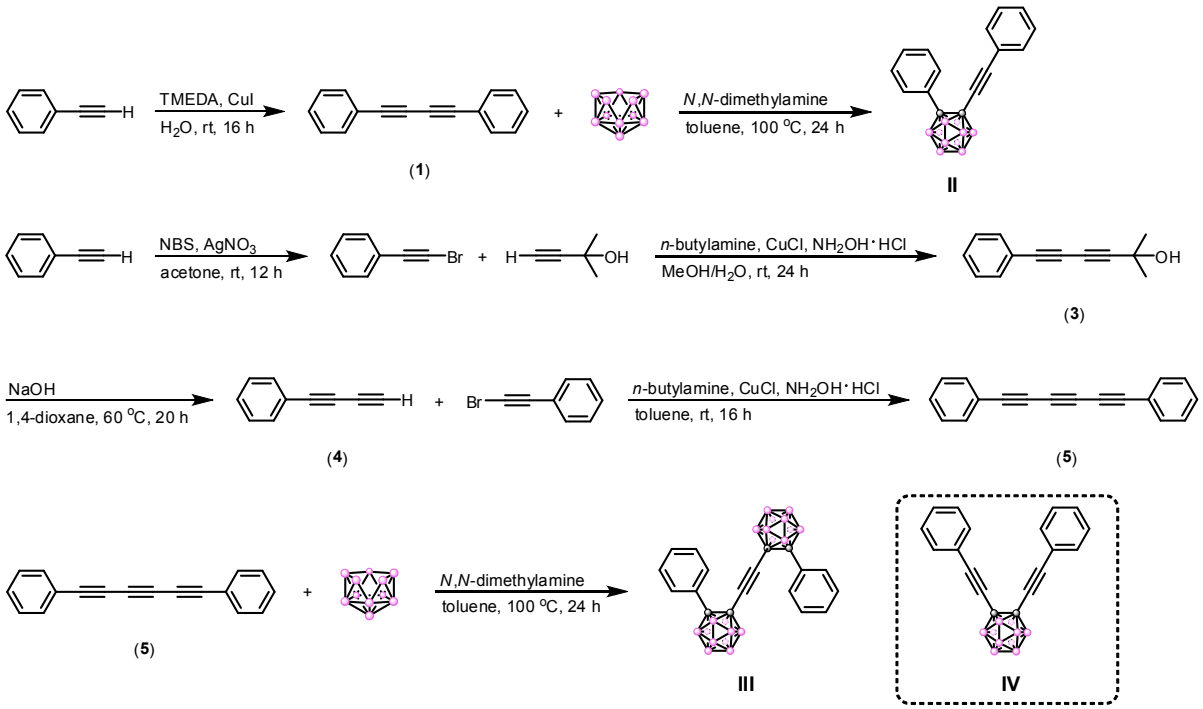
Absorption spectra were recorded using a Shimadzu (UV-3101PC) scanning spectrophotometer (Japan). Emission and excitation spectra were measured by using a Varian fluorescence spectrophotometer (Cary Eclipse) (Scinco, Korea).

DFT Calculations

Theoretical calculations for all complexes were conducted by the *Gaussian 16* Package.[9] The ground-state geometries of **I**−**III** were optimised by using the B3LYP density functional theory (DFT) and 6-31G(d,p) basis set. The contours of the electron density were plotted by using *Chem3D version.10.0.*[10]

Cyclic Voltammetry Measurements

Cyclic voltammetry (CV) was performed in an electrolytic solution prepared using 0.1 M tetra-butyl ammonium hexafluorophosphate (NBu_4PF_6) at room temperature under an atmosphere of argon. For this purpose, CHI600E (CH Instrument, Inc., USA) was used. Glassy carbon, platinum wire, and $Ag/AgNO_3$ (0.1 M) were used as the working, counter, and reference electrodes, respectively. All the potentials were calibrated to the ferrocene/ferrocenium (Fc/Fc^+) redox couple.



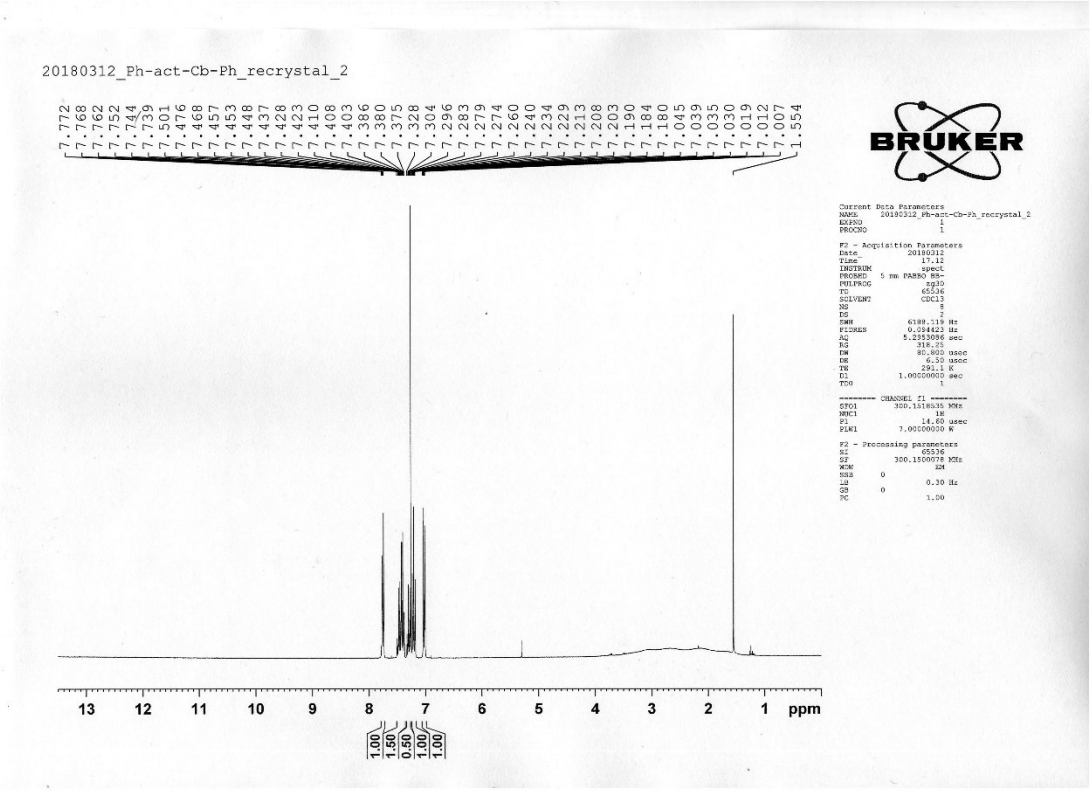
Scheme S1. Synthetic procedures for **II** and **III**.

Synthesis

1-(Phenylethynyl)-2-phenyl-*o*-carborane (II) A mixture of decaborane (0.39 g, 3.21 mmol), diphenylbutadiyne (1) (0.65 g, 1.63 mmol), and *N*,*N*-dimethylaniline (0.9 mL, 7.11 mmol) in toluene (15 mL) was stirred at 100 °C for 17 h under argon atmosphere. After cooling to room temperature, the mixture was filtered by vacuum filtration, washed with 1 M HCl aqueous solution and extracted with dichloromethane (DCM). The combined organic layers were dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was purified via recrystallisation with DCM and methanol after silica-gel column chromatography using toluene:hexane (*v*:*v*=1:1) as an eluent. White crystal; Yield: 74%; ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.76 (dt, J = 7.2 Hz, 1.5 Hz, 2H), 7.50–7.38 (m, 3H), 7.33-7.28 (m, 1H), 7.23-7.18 (m, 2H), 7.02 (dt, J = 6.9 Hz, 1.5 Hz), 3.85-1.40 (br, 10H); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 131.96, 131.22, 130.70, 129.78, 128.58, 128.42, 120.07, 85.44, 82.45, 82.12, 69.65; ^{11}B NMR (500 MHz, $CDCl_3$, δ): −2.1, −3.9, −9.2, −9.8. HRMS (FAB) calcd for $C_{16}H_{20}B_{10}$: 322.2496, found 322.2494; Elem. anal. calcd for $C_{16}H_{20}B_{10}$: C, 59.97; H, 6.29; B, 33.74 Found: C, 59.96; H, 6.27.

1,2-bis(2-Phenylcarboranyl)ethyne (III) A mixture of decaborane (0.107 g, 0.88 mmol), diphenylhexatriyne (5) (0.2 g, 0.88 mmol), and *N*,*N*-dimethylaniline (0.25 mL, 1.95 mmol) in toluene (5 mL) was stirred at 100 °C for 17 h under argon atmosphere. After cooling to room temperature, the mixture was filtered by vacuum filtration, washed with 1 M HCl aqueous solution and extracted with ethylacetate and DCM. The combined organic layers were dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was purified via recrystallisation with DCM and methanol after silica-gel column chromatography using toluene:hexane (*v*:*v*=1:1) as an eluent. White transparent crystal; Yield: 53%; ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.56-7.51 (m, 2H), 7.44-1.37 (m, 8H), 3.90-1.20 (br, 10H); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 131.14, 130.89, 130.35, 128.83, 128.60, 128.44; ^{11}B NMR (500 MHz, $CDCl_3$, δ): −1.1, −3.9, −9.8. HRMS (FAB) calcd for $C_{18}H_{20}B_{10}$: 346.2496, found 346.2495; Elem. anal. calcd for $C_{18}H_{20}B_{10}$: C, 62.76; H, 5.85; B, 31.39; Found: C, 62.74; H, 5.84.

(a)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7.035
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7.019
7.012
7.007
1.554
BRUKER
13
12
11
10
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(b)

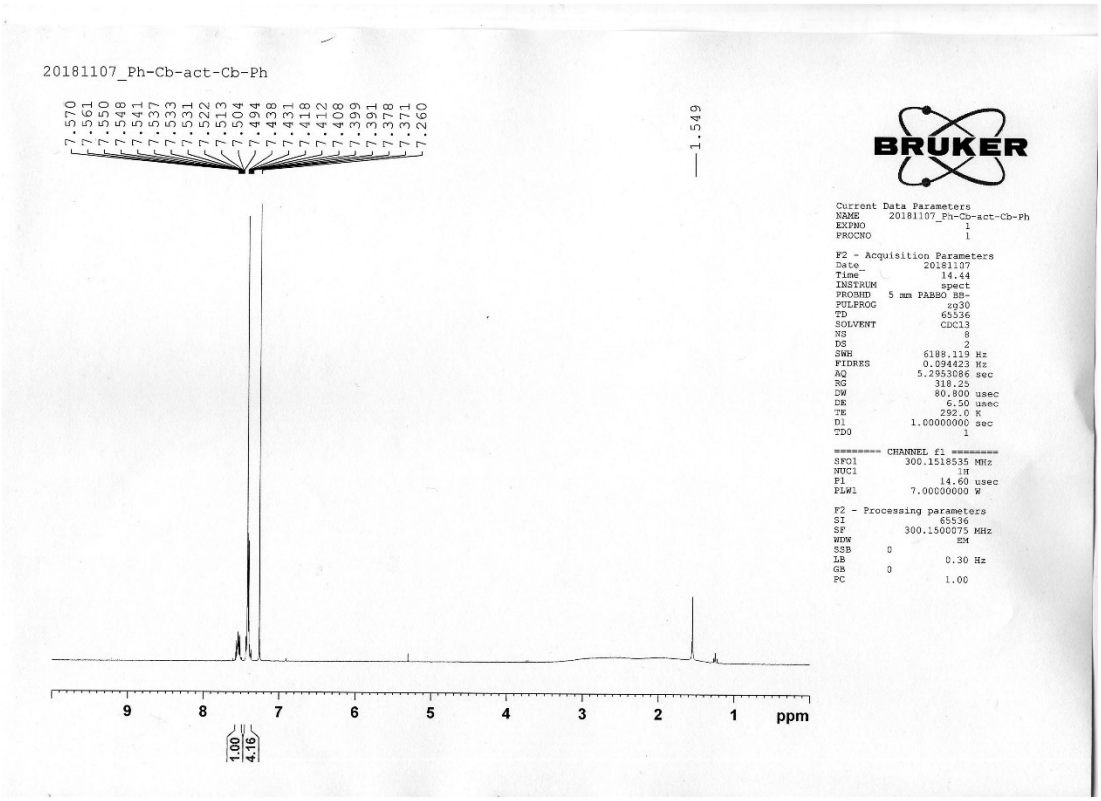
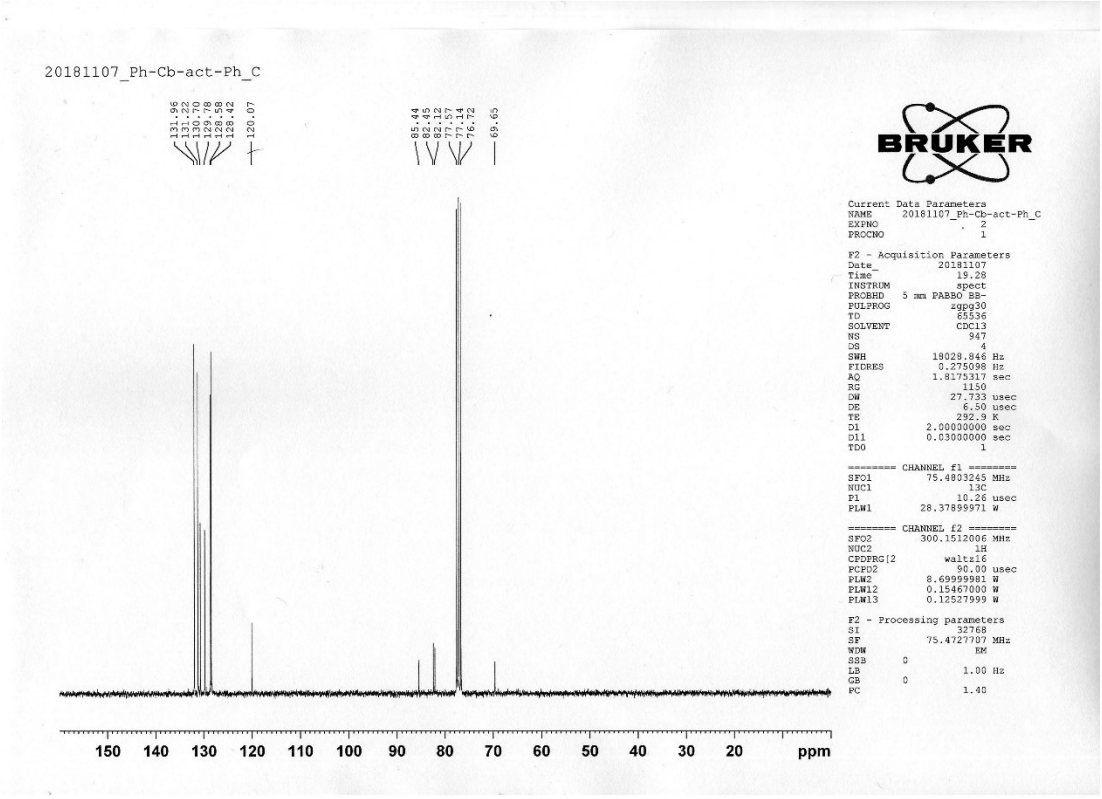


Figure S1. ^{1}H NMR spectra for (a) **II** and (b) **III** in $CDCl_3$.

(a)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82.12
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77.14
76.72
69.65
BRUKER
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EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
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Time 19.28
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PULPROG zgpg30
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SOLVENT CDCl3
NS 947
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175317 sec
RG 1150
DW 27.733 usec
DE 6.50 usec
TE 292.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
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NUC1 13C
P1 10.26 usec
PLW1 28.37899971 W
======== CHANNEL f2 ========
SFO2 300.1512006 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 8.69999981 W
PLW12 0.15467000 W
PLW13 0.12527999 W
F2 - Processing parameters
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150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

(b)

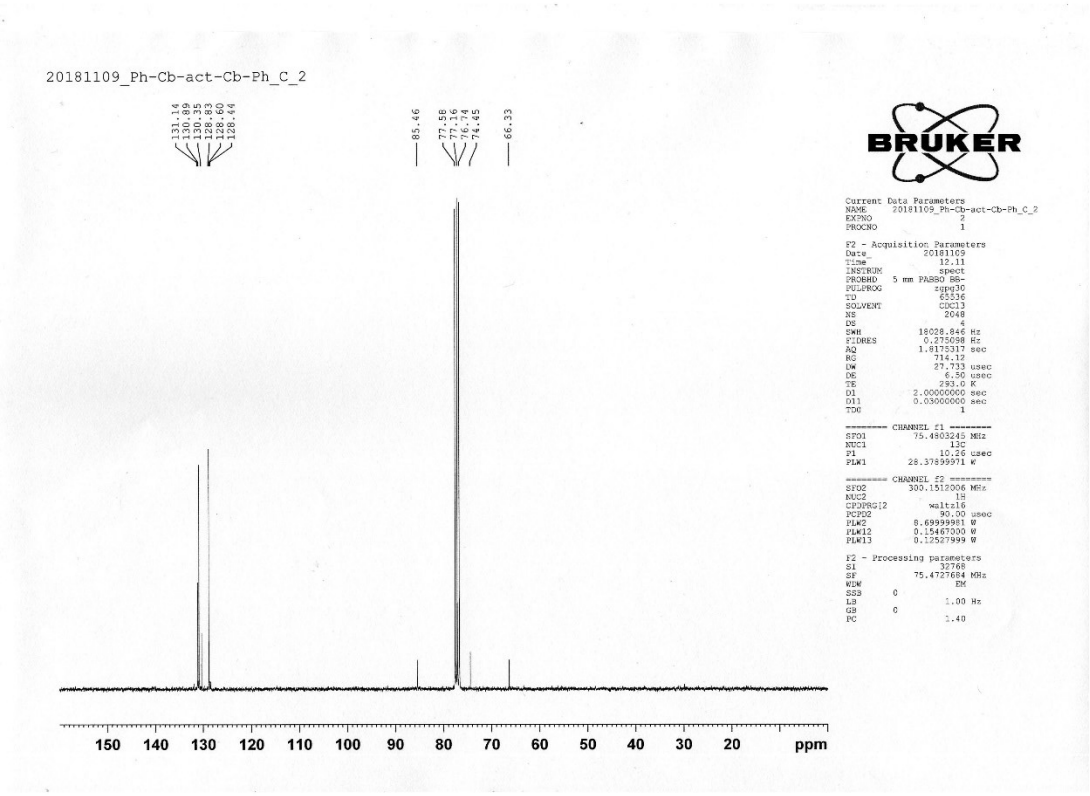
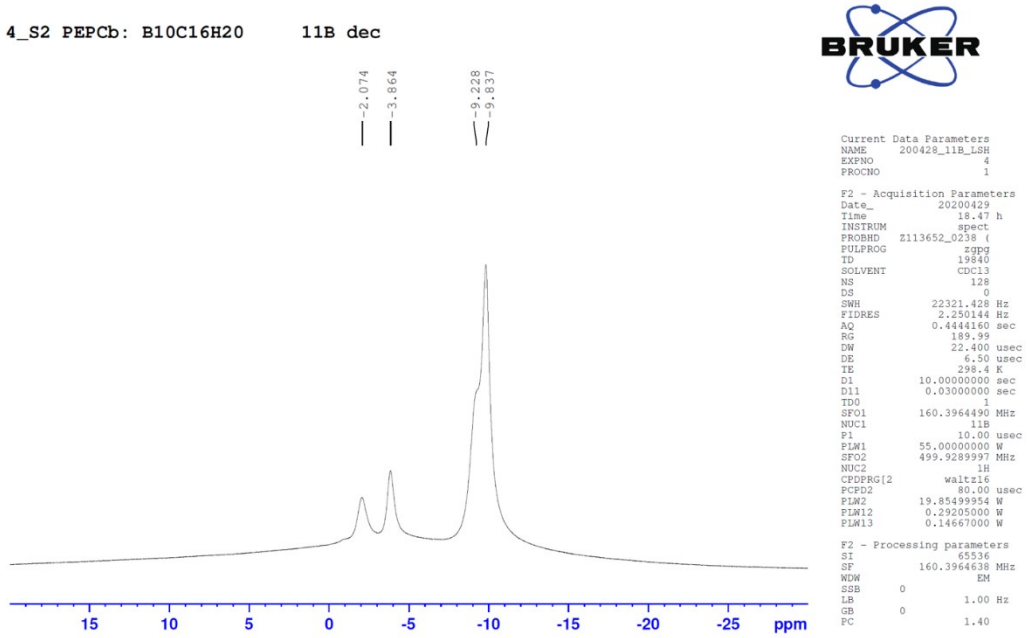


Figure S2. ^{13}C NMR spectra for (a) **II** and (b) **III** in $CDCl_3$.

(a)



(b)

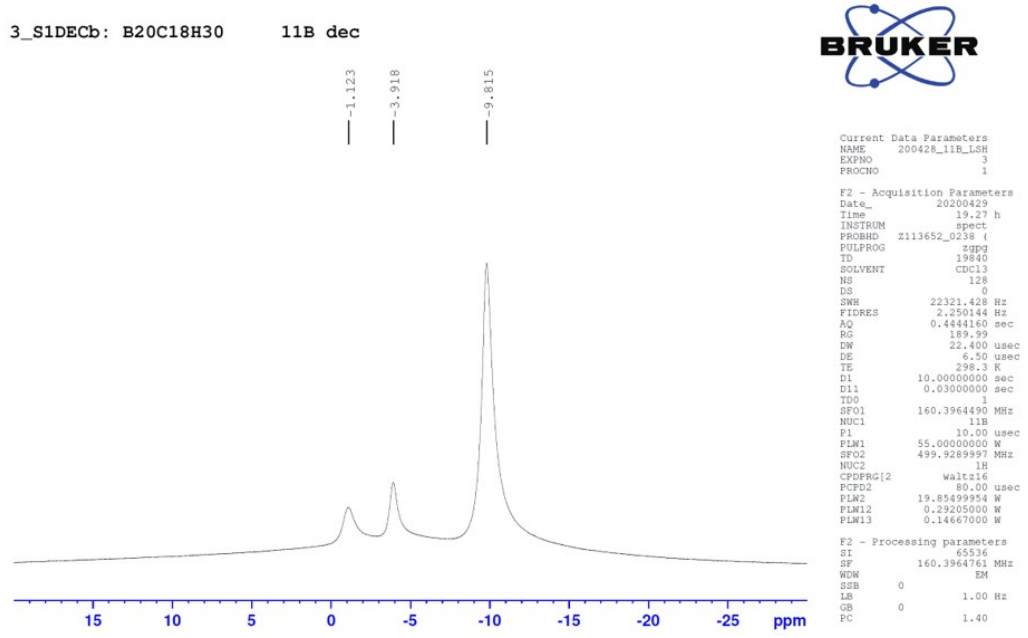
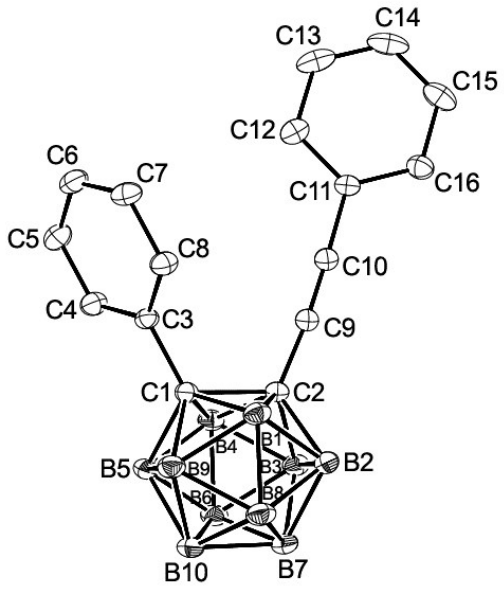


Figure S3. ^{11}B NMR spectra for (a) **II** and (b) **III** in $CDCl_3$.

(a)



(b)

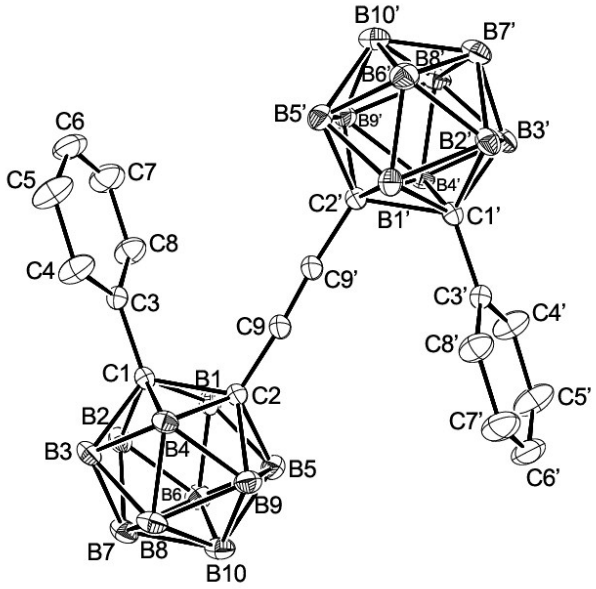


Figure S4. ORTEP(III)[11] drawings of (a) **II** and (b) **III** showing the thermal anisotropic displacement parameters at 30% probability. Hydrogen atoms are omitted for clarity.

Table S1. Crystal data and structure refinement for compounds **II** and **III**.

Identification code	**II**	**III**
Empirical formula	$C_{16}H_{10}B_{10}$	$C_{18}H_{10}B_{10}$
Formula weight	310.34	334.36
Temperature	223(2) K	223(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/n$
Unit cell dimensions	a = 7.2684(6) Å, α = 74.227(3)°	a = 10.796(1) Å
	b = 10.407(1) Å, β = 81.330(3)°	b = 9.7951(9) Å, β = 112.281(3)°
	c = 12.774 (1) Å, γ = 86.111(3)°	c = 13.782(1) Å
Volume	918.89(15) Å^3	1348.5(2) Å^3
Z, Calculated density	2, 1.122 Mg/m^3	4, 1.647 Mg/m^3
Absorption coefficient, μ	0.056 mm^{-1}	0.083 mm^{-1}
F(000)	312	672
Crystal size	0.22 × 0.16 × 0.09 mm	0.21 × 0.14 × 0.10 mm
θ range for data collection	2.265 to 28.426°	2.622 to 28.515°
Limiting indices	$-9 \le h \le 9$, $-13 \le k \le 13$, $-17 \le l \le 17$	$-14 \le h \le 14$, $-13 \le k \le 13$, $-18 \le l \le 18$
Reflections collected /unique	29616 / 4611 [R_{int} = 0.0798]	43152 / 3392 [R_{int} = 0.1113]
Completeness to θ = 28.40	99.9 %	100.0 %
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	4611 / 0 / 235	3392 / 0 / 173
Goodness-of-fit on F^2	1.035	1.025
Final R indices [$I>2\sigma(I)$]	$R_1{}^a$ = 0.0597, $wR_2{}^b$ = 0.1319	$R_1{}^a$ = 0.0624, $wR_2{}^b$ = 0.1498
R indices (all data)	R_1 = 0.1110, wR_2 = 0.1559	R_1 = 0.1065, wR_2 = 0.1764
Largest diff. peak and hole	0.258 and -0.221 e. Å^{-3}	0.254 and -0.276 e. Å^{-3}

$^aR_1 = \sum||F_o|-|F_c||$ (based on reflections with $F_o^2>2\sigma F^2$), $^bwR_2 = [\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2)+(0.095P)^2]$;, $P = [\max(F_o^2, 0) + 2F_c^2]/3$(also with $F_o^2>2\sigma F^2$)

Table S2. Bond lengths [Å] for **II**.

Compound **II**			
Bond	Length [Å]	Bond	Length [Å]
C(1)-C(9)	1.440(2)	C(14)-C(15)	1.372(3)
C(1)-B(2)	1.702(3)	C(15)-C(16)	1.374(3)
C(1)-B(3)	1.703(3)	B(1)-B(8)	1.760(3)
C(1)-C(2)	1.708(3)	B(1)-B(9)	1.771(3)
C(1)-B(4)	1.723(3)	B(1)-B(2)	1.781(3)
C(1)-B(1)	1.727(3)	B(2)-B(8)	1.771(3)
C(2)-C(3)	1.506(2)	B(2)-B(7)	1.772(3)
C(2)-B(5)	1.703(3)	B(2)-B(3)	1.778(3)
C(2)-B(9)	1.708(3)	B(3)-B(7)	1.770(3)
C(2)-B(1)	1.738(3)	B(3)-B(6)	1.777(3)
C(2)-B(4)	1.742(3)	B(3)-B(4)	1.779(3)
C(3)-C(4)	1.388(3)	B(4)-B(6)	1.761(3)
C(3)-C(8)	1.390(3)	B(4)-B(5)	1.769(3)
C(4)-C(5)	1.384(3)	B(5)-B(10)	1.773(3)
C(5)-C(6)	1.378(3)	B(5)-B(6)	1.777(3)
C(6)-C(7)	1.368(3)	B(5)-B(9)	1.783(3)
C(7)-C(8)	1.390(3)	B(6)-B(7)	1.777(3)
C(9)-C(10)	1.187(2)	B(6)-B(10)	1.783(3)
C(10)-C(11)	1.435(2)	B(7)-B(10)	1.772(3)
C(11)-C(16)	1.392(3)	B(7)-B(8)	1.783(3)
C(11)-C(12)	1.392(3)	B(8)-B(9)	1.777(3)
C(12)-C(13)	1.386(3)	B(8)-B(10)	1.781(3)
C(13)-C(14)	1.378(4)	B(9)-B(10)	1.781(3)

Symmetry transformations used to generate equivalent atoms:

Table S3. Bond lengths [Å] for **III**.

Compound **III**			
Bond	Length [Å]	Bond	Length [Å]
C(1)-C(3)	1.502(2)	B(1)-B(5)	1.780(3)
C(1)-C(2)	1.697(2)	B(2)-B(3)	1.777(3)
C(1)-B(3)	1.698(2)	B(2)-B(7)	1.780(3)
C(1)-B(2)	1.706(3)	B(2)-B(6)	1.781(3)
C(1)-B(4)	1.745(3)	B(3)-B(7)	1.777(3)
C(1)-B(1)	1.746(2)	B(3)-B(4)	1.780(3)
C(2)-C(9)	1.436(2)	B(3)-B(8)	1.780(3)
C(2)-B(5)	1.708(3)	B(4)-B(8)	1.756(3)
C(2)-B(9)	1.710(3)	B(4)-B(9)	1.778(3)
C(2)-B(4)	1.722(3)	B(5)-B(10)	1.769(3)
C(2)-B(1)	1.722(3)	B(5)-B(6)	1.775(3)
C(3)-C(4)	1.372(3)	B(5)-B(9)	1.778(3)
C(3)-C(8)	1.379(3)	B(6)-B(10)	1.777(3)
C(4)-C(5)	1.381(3)	B(6)-B(7)	1.782(3)
C(5)-C(6)	1.368(3)	B(7)-B(10)	1.777(4)
C(6)-C(7)	1.361(3)	B(7)-B(8)	1.785(3)
C(7)-C(8)	1.380(3)	B(8)-B(9)	1.776(3)
C(9)-C(9)#1	1.182(3)	B(8)-B(10)	1.780(3)
B(1)-B(6)	1.757(3)	B(9)-B(10)	1.770(3)
B(1)-B(2)	1.765(3)		

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z

Table S4. Bond angles [°] for **II**.

Compound **II**			
Bond	Angles [°]	Bond	Angles [°]
C(9)-C(1)-B(2)	123.29(16)	C(1)-B(3)-B(4)	59.27(11)
C(9)-C(1)-B(3)	123.12(16)	B(7)-B(3)-B(4)	107.37(16)
B(2)-C(1)-B(3)	62.96(13)	B(6)-B(3)-B(4)	59.36(12)
C(9)-C(1)-C(2)	114.96(14)	B(2)-B(3)-B(4)	107.86(16)
B(2)-C(1)-C(2)	111.07(14)	C(1)-B(4)-C(2)	59.07(11)
B(3)-C(1)-C(2)	111.33(14)	C(1)-B(4)-B(6)	104.93(15)
C(9)-C(1)-B(4)	116.19(15)	C(2)-B(4)-B(6)	105.60(15)
B(2)-C(1)-B(4)	114.14(14)	C(1)-B(4)-B(5)	105.26(15)
B(3)-C(1)-B(4)	62.58(12)	C(2)-B(4)-B(5)	58.05(11)
C(2)-C(1)-B(4)	61.02(11)	B(6)-B(4)-B(5)	60.48(12)
C(9)-C(1)-B(1)	116.15(16)	C(1)-B(4)-B(3)	58.15(12)
B(2)-C(1)-B(1)	62.57(13)	C(2)-B(4)-B(3)	106.23(15)
B(3)-C(1)-B(1)	114.34(14)	B(6)-B(4)-B(3)	60.26(13)
C(2)-C(1)-B(1)	60.78(11)	B(5)-B(4)-B(3)	108.45(15)
B(4)-C(1)-B(1)	113.06(14)	C(2)-B(5)-B(4)	60.18(11)
C(3)-C(2)-B(5)	122.00(15)	C(2)-B(5)-B(10)	105.72(15)
C(3)-C(2)-C(1)	117.66(14)	B(4)-B(5)-B(10)	107.78(16)
B(5)-C(2)-C(1)	108.87(14)	C(2)-B(5)-B(6)	106.51(15)
C(3)-C(2)-B(9)	124.21(15)	B(4)-B(5)-B(6)	59.53(12)
B(5)-C(2)-B(9)	63.00(12)	B(10)-B(5)-B(6)	60.27(13)
C(1)-C(2)-B(9)	109.17(14)	C(2)-B(5)-B(9)	58.63(11)
C(3)-C(2)-B(1)	119.20(15)	B(4)-B(5)-B(9)	108.34(15)
B(5)-C(2)-B(1)	112.98(14)	B(10)-B(5)-B(9)	60.11(13)
C(1)-C(2)-B(1)	60.17(11)	B(6)-B(5)-B(9)	108.50(16)
B(9)-C(2)-B(1)	61.82(12)	B(4)-B(6)-B(3)	60.39(12)
C(3)-C(2)-B(4)	115.62(14)	B(4)-B(6)-B(7)	107.87(15)
B(5)-C(2)-B(4)	61.77(12)	B(3)-B(6)-B(7)	59.74(13)
C(1)-C(2)-B(4)	59.92(11)	B(4)-B(6)-B(5)	59.99(12)
B(9)-C(2)-B(4)	113.14(14)	B(3)-B(6)-B(5)	108.17(15)
B(1)-C(2)-B(4)	111.61(14)	B(7)-B(6)-B(5)	107.54(16)
C(4)-C(3)-C(8)	118.93(17)	B(4)-B(6)-B(10)	107.73(16)
C(4)-C(3)-C(2)	119.27(16)	B(3)-B(6)-B(10)	107.66(16)
C(8)-C(3)-C(2)	121.80(16)	B(7)-B(6)-B(10)	59.70(13)
C(5)-C(4)-C(3)	120.54(19)	B(5)-B(6)-B(10)	59.75(13)
C(6)-C(5)-C(4)	120.16(19)	B(3)-B(7)-B(10)	108.45(16)
C(7)-C(6)-C(5)	119.77(18)	B(3)-B(7)-B(2)	60.27(13)
C(6)-C(7)-C(8)	120.77(19)	B(10)-B(7)-B(2)	108.15(16)
C(7)-C(8)-C(3)	119.82(18)	B(3)-B(7)-B(6)	60.12(13)
C(10)-C(9)-C(1)	174.9(2)	B(10)-B(7)-B(6)	60.31(13)
C(9)-C(10)-C(11)	177.8(2)	B(2)-B(7)-B(6)	108.35(15)
C(16)-C(11)-C(12)	119.83(17)	B(3)-B(7)-B(8)	108.14(15)
C(16)-C(11)-C(10)	120.37(17)	B(10)-B(7)-B(8)	60.14(14)
C(12)-C(11)-C(10)	119.79(18)	B(2)-B(7)-B(8)	59.75(13)

C(13)-C(12)-C(11)	119.1(2)	B(6)-B(7)-B(8)	108.33(16)
C(14)-C(13)-C(12)	120.4(2)	B(1)-B(8)-B(2)	60.61(12)
C(15)-C(14)-C(13)	120.3(2)	B(1)-B(8)-B(9)	60.09(12)
C(14)-C(15)-C(16)	120.2(2)	B(2)-B(8)-B(9)	108.63(15)
C(15)-C(16)-C(11)	120.1(2)	B(1)-B(8)-B(10)	108.02(15)
C(1)-B(1)-C(2)	59.05(11)	B(2)-B(8)-B(10)	107.79(17)
C(1)-B(1)-B(8)	104.57(15)	B(9)-B(8)-B(10)	60.09(13)
C(2)-B(1)-B(8)	105.39(15)	B(1)-B(8)-B(7)	108.17(16)
C(1)-B(1)-B(9)	105.47(15)	B(2)-B(8)-B(7)	59.82(13)
C(2)-B(1)-B(9)	58.26(11)	B(9)-B(8)-B(7)	107.96(16)
B(8)-B(1)-B(9)	60.43(13)	B(10)-B(8)-B(7)	59.63(13)
C(1)-B(1)-B(2)	58.03(12)	C(2)-B(9)-B(1)	59.92(11)
C(2)-B(1)-B(2)	106.05(15)	C(2)-B(9)-B(8)	105.94(16)
B(8)-B(1)-B(2)	60.00(13)	B(1)-B(9)-B(8)	59.48(12)
B(9)-B(1)-B(2)	108.41(16)	C(2)-B(9)-B(10)	105.18(16)
C(1)-B(2)-B(8)	105.16(15)	B(1)-B(9)-B(10)	107.52(16)
C(1)-B(2)-B(7)	104.65(15)	B(8)-B(9)-B(10)	60.08(13)
B(8)-B(2)-B(7)	60.43(13)	C(2)-B(9)-B(5)	58.37(11)
C(1)-B(2)-B(3)	58.52(12)	B(1)-B(9)-B(5)	107.72(15)
B(8)-B(2)-B(3)	108.31(16)	B(8)-B(9)-B(5)	107.67(17)
B(7)-B(2)-B(3)	59.81(13)	B(10)-B(9)-B(5)	59.69(12)
C(1)-B(2)-B(1)	59.40(11)	B(7)-B(10)-B(5)	107.95(15)
B(8)-B(2)-B(1)	59.39(13)	B(7)-B(10)-B(8)	60.23(13)
B(7)-B(2)-B(1)	107.68(16)	B(5)-B(10)-B(8)	107.88(15)
B(3)-B(2)-B(1)	108.14(15)	B(7)-B(10)-B(9)	108.24(16)
C(1)-B(3)-B(7)	104.72(16)	B(5)-B(10)-B(9)	60.20(12)
C(1)-B(3)-B(6)	105.10(16)	B(8)-B(10)-B(9)	59.83(13)
B(7)-B(3)-B(6)	60.14(13)	B(7)-B(10)-B(6)	59.99(13)
C(1)-B(3)-B(2)	58.52(12)	B(5)-B(10)-B(6)	59.98(13)
B(7)-B(3)-B(2)	59.92(13)	B(8)-B(10)-B(6)	108.15(16)
B(6)-B(3)-B(2)	108.08(17)	B(9)-B(10)-B(6)	108.34(14)

Symmetry transformations used to generate equivalent atoms:

Table S5. Bond angles [˚] for **III**.

Compound **III**			
Bond	Angles [˚]	Bond	Angles [˚]
C(3)-C(1)-C(2)	117.43(13)	C(2)-B(4)-B(8)	104.84(14)
C(3)-C(1)-B(3)	122.40(14)	C(1)-B(4)-B(8)	105.13(14)
C(2)-C(1)-B(3)	109.35(13)	C(2)-B(4)-B(9)	58.47(11)
C(3)-C(1)-B(2)	123.95(15)	C(1)-B(4)-B(9)	106.13(14)
C(2)-C(1)-B(2)	108.99(13)	B(8)-B(4)-B(9)	60.34(12)
B(3)-C(1)-B(2)	62.96(11)	C(2)-B(4)-B(3)	104.52(14)
C(3)-C(1)-B(4)	116.14(14)	C(1)-B(4)-B(3)	57.57(11)
C(2)-C(1)-B(4)	60.01(11)	B(8)-B(4)-B(3)	60.45(13)
B(3)-C(1)-B(4)	62.24(11)	B(9)-B(4)-B(3)	108.44(15)
B(2)-C(1)-B(4)	113.32(14)	C(2)-B(5)-B(10)	104.49(14)
C(3)-C(1)-B(1)	118.67(14)	C(2)-B(5)-B(6)	104.73(15)
C(2)-C(1)-B(1)	60.01(10)	B(10)-B(5)-B(6)	60.19(13)
B(3)-C(1)-B(1)	112.80(14)	C(2)-B(5)-B(9)	58.71(11)
B(2)-C(1)-B(1)	61.51(11)	B(10)-B(5)-B(9)	59.85(12)
B(4)-C(1)-B(1)	111.47(14)	B(6)-B(5)-B(9)	108.18(15)
C(9)-C(2)-C(1)	114.39(14)	C(2)-B(5)-B(1)	59.13(11)
C(9)-C(2)-B(5)	123.01(15)	B(10)-B(5)-B(1)	107.35(15)
C(1)-C(2)-B(5)	111.67(14)	B(6)-B(5)-B(1)	59.25(13)
C(9)-C(2)-B(9)	123.69(15)	B(9)-B(5)-B(1)	108.13(14)
C(1)-C(2)-B(9)	111.51(13)	B(1)-B(6)-B(5)	60.53(12)
B(5)-C(2)-B(9)	62.71(12)	B(1)-B(6)-B(10)	108.01(16)
C(9)-C(2)-B(4)	116.35(15)	B(5)-B(6)-B(10)	59.75(13)
C(1)-C(2)-B(4)	61.39(10)	B(1)-B(6)-B(2)	59.86(12)
B(5)-C(2)-B(4)	114.19(13)	B(5)-B(6)-B(2)	108.32(15)
B(9)-C(2)-B(4)	62.40(11)	B(10)-B(6)-B(2)	107.87(15)
C(9)-C(2)-B(1)	115.47(15)	B(1)-B(6)-B(7)	107.90(15)
C(1)-C(2)-B(1)	61.42(10)	B(5)-B(6)-B(7)	107.96(16)
B(5)-C(2)-B(1)	62.53(12)	B(10)-B(6)-B(7)	59.93(14)
B(9)-C(2)-B(1)	114.17(14)	B(2)-B(6)-B(7)	59.97(13)
B(4)-C(2)-B(1)	113.82(13)	B(3)-B(7)-B(10)	107.91(16)
C(4)-C(3)-C(8)	118.19(18)	B(3)-B(7)-B(2)	59.94(12)
C(4)-C(3)-C(1)	119.96(16)	B(10)-B(7)-B(2)	107.87(15)
C(8)-C(3)-C(1)	121.85(17)	B(3)-B(7)-B(6)	107.93(14)
C(3)-C(4)-C(5)	120.8(2)	B(10)-B(7)-B(6)	59.91(13)
C(6)-C(5)-C(4)	120.6(2)	B(2)-B(7)-B(6)	59.99(12)
C(7)-C(6)-C(5)	118.9(2)	B(3)-B(7)-B(8)	59.98(13)
C(6)-C(7)-C(8)	120.9(2)	B(10)-B(7)-B(8)	59.96(13)
C(3)-C(8)-C(7)	120.5(2)	B(2)-B(7)-B(8)	107.89(15)
C(9)#1-C(9)-C(2)	175.7(3)	B(6)-B(7)-B(8)	107.88(16)
C(2)-B(1)-C(1)	58.58(10)	B(4)-B(8)-B(9)	60.43(12)
C(2)-B(1)-B(6)	104.87(15)	B(4)-B(8)-B(10)	108.03(15)
C(1)-B(1)-B(6)	105.53(14)	B(9)-B(8)-B(10)	59.69(13)

C(2)-B(1)-B(2)	105.15(13)	B(4)-B(8)-B(3)	60.43(12)
C(1)-B(1)-B(2)	58.11(10)	B(9)-B(8)-B(3)	108.50(14)
B(6)-B(1)-B(2)	60.73(13)	B(10)-B(8)-B(3)	107.67(16)
C(2)-B(1)-B(5)	58.34(11)	B(4)-B(8)-B(7)	108.30(15)
C(1)-B(1)-B(5)	106.03(14)	B(9)-B(8)-B(7)	107.91(15)
B(6)-B(1)-B(5)	60.22(13)	B(10)-B(8)-B(7)	59.82(13)
B(2)-B(1)-B(5)	108.77(15)	B(3)-B(8)-B(7)	59.81(13)
C(1)-B(2)-B(1)	60.38(11)	C(2)-B(9)-B(10)	104.37(15)
C(1)-B(2)-B(3)	58.31(11)	C(2)-B(9)-B(8)	104.48(15)
B(1)-B(2)-B(3)	108.15(15)	B(10)-B(9)-B(8)	60.26(13)
C(1)-B(2)-B(7)	105.36(15)	C(2)-B(9)-B(4)	59.12(11)
B(1)-B(2)-B(7)	107.60(16)	B(10)-B(9)-B(4)	107.53(16)
B(3)-B(2)-B(7)	59.95(12)	B(8)-B(9)-B(4)	59.23(12)
C(1)-B(2)-B(6)	106.25(15)	C(2)-B(9)-B(5)	58.58(11)
B(1)-B(2)-B(6)	59.41(12)	B(10)-B(9)-B(5)	59.81(13)
B(3)-B(2)-B(6)	107.97(16)	B(8)-B(9)-B(5)	108.05(16)
B(7)-B(2)-B(6)	60.04(13)	B(4)-B(9)-B(5)	108.13(15)
C(1)-B(3)-B(2)	58.73(11)	B(5)-B(10)-B(9)	60.34(13)
C(1)-B(3)-B(7)	105.82(14)	B(5)-B(10)-B(6)	60.07(13)
B(2)-B(3)-B(7)	60.11(12)	B(9)-B(10)-B(6)	108.48(15)
C(1)-B(3)-B(4)	60.19(10)	B(5)-B(10)-B(7)	108.41(16)
B(2)-B(3)-B(4)	108.28(14)	B(9)-B(10)-B(7)	108.53(16)
B(7)-B(3)-B(4)	107.58(16)	B(6)-B(10)-B(7)	60.16(13)
C(1)-B(3)-B(8)	106.13(14)	B(5)-B(10)-B(8)	108.31(15)
B(2)-B(3)-B(8)	108.21(15)	B(9)-B(10)-B(8)	60.06(13)
B(7)-B(3)-B(8)	60.21(13)	B(6)-B(10)-B(8)	108.29(16)
B(4)-B(3)-B(8)	59.12(12)	B(7)-B(10)-B(8)	60.22(13)
C(2)-B(4)-C(1)	58.60(10)		

Symmetry transformations used to generate equivalent atoms: #1 -*x*+1, -*y*+1, -*z*

Computational method. The calculations were performed with the *Gaussian16* package, using the density functional theory (DFT) and time-dependent density functional theory (TD-DFT) method with the B3LYP hybrid functional. All structures were optimized using DFT or TD-DFT method with a 6-31G(d,p) basis set. The starting coordinates were obtained from the X-ray structures. The calculations of the anion species were performed in the spin unrestricted regime. All calculations were performed in the gas phase.

Table S6. Optimized geometry coordinates for **I**.

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
C	2.372990	2.753790	-1.193885	B	-1.176926	-0.009037	1.411491
C	1.182791	2.028967	-1.196289	B	-2.941994	-0.009428	1.443365
C	2.988240	3.093017	0.010814	H	3.915482	-3.657923	-0.011601
C	2.397339	-2.709640	-1.214272	H	-4.499255	1.536850	0.009834
C	1.206961	-1.984955	-1.214415	H	-4.499368	-1.536647	-0.009950
C	0.587488	1.624821	0.008264	H	2.858286	2.978434	2.159887
C	-0.723015	0.879370	0.005960	H	-1.918626	2.434048	1.515338
C	2.988194	-3.093048	-0.010657	H	0.753743	1.711023	2.158849
C	2.397035	2.710070	1.214400	H	2.814606	-3.057348	2.138184
C	0.587421	-1.624864	-0.008254	H	-1.919369	-2.453295	1.482715
C	-0.723072	-0.879389	-0.006042	H	-0.452677	-0.016521	2.338830
C	1.206670	1.985368	1.214469	H	0.710105	-1.789583	2.140695
C	2.372585	-2.754291	1.193993	H	-3.515458	-0.016614	2.480754
C	1.182375	-2.029483	1.196316	H	2.815294	3.056483	-2.138060
B	-1.176898	0.008999	-1.411577	H	0.710788	1.788702	-2.140708
B	-2.941987	0.009560	-1.443474	H	-0.452650	0.016494	-2.338903
B	-2.068979	1.448514	-0.877465	H	2.858874	-2.977636	-2.159725
B	-2.069381	-1.437226	-0.897125	H	-3.515431	0.016836	-2.480885
B	-3.506714	0.888566	0.005855	H	0.754304	-1.710253	-2.158823
B	-3.506767	-0.888454	-0.005965	H	3.915521	3.657906	0.011816
B	-2.069279	1.437254	0.897033	H	-1.919245	2.453319	-1.482780
B	-2.069110	-1.448474	0.877366	H	-1.918743	-2.434044	-1.515416

Table S7. Optimized geometry coordinates for **II**.

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
C	-0.992789	-1.108877	0.014698	H	5.822366	-2.898748	-0.487707
C	-1.822206	0.413703	0.023664	C	3.844080	-2.090722	-0.277712
C	-1.019726	1.690408	-0.006459	H	3.344895	-3.031035	-0.486559
C	-0.837240	2.377647	-1.216335	B	-1.786544	-0.574448	1.453904
H	-1.258457	1.981554	-2.132043	H	-1.105885	-0.251524	2.358281
C	-0.125733	3.574960	-1.254422	B	-1.871382	-2.269720	0.913356
H	0.001794	4.090064	-2.201504	H	-1.239284	-3.066982	1.514777
C	0.415807	4.109085	-0.085214	B	-1.887620	-2.270599	-0.867787
H	0.970035	5.042343	-0.115357	H	-1.266523	-3.068990	-1.479296
C	0.230314	3.440297	1.124688	B	-1.811563	-0.575010	-1.409797
H	0.634648	3.851434	2.044655	H	-1.141495	-0.234123	-2.316440
C	-0.483977	2.243544	1.165893	B	-3.278059	0.258252	-0.851713
H	-0.628775	1.746539	2.116367	H	-3.645229	1.209386	-1.450560
C	0.435510	-1.067321	0.003929	B	-3.354677	-1.426639	-1.409290
C	1.646707	-1.016109	-0.001912	H	-3.872327	-1.705921	-2.438210
C	3.072068	-0.945719	-0.005006	B	-3.401164	-2.477549	0.037391
C	3.718907	0.275382	0.265792	H	-3.958414	-3.523685	0.043062
H	3.121454	1.156774	0.474562	B	-3.329156	-1.426706	1.482644
C	5.109144	0.343374	0.262140	H	-3.825236	-1.707732	2.521604
H	5.601051	1.288532	0.471189	B	-3.261902	0.260439	0.927965
C	5.869508	-0.796763	-0.008167	H	-3.611113	1.213748	1.534338
H	6.953782	-0.739192	-0.009329	B	-4.261671	-0.920036	0.045777
C	5.233826	-2.010990	-0.277158	H	-5.443797	-0.833743	0.055406

Table S8. Optimized geometry coordinates for **III**.

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
C	-2.976471	3.788453	-0.888616	H	-5.938849	-2.592139	-0.087309
C	-2.783084	4.378561	0.360179	H	-2.828867	1.585947	2.287331
C	-3.103793	2.405483	-1.000607	H	-5.096983	-0.110081	1.601601
C	-2.730135	3.575201	1.498960	H	3.027906	-4.403245	-1.781915
C	-3.035120	1.586765	0.137085	H	3.992435	2.916187	2.272078
C	-2.858421	2.191723	1.390607	H	5.097149	0.109780	1.601237
C	-3.210688	0.094218	0.015850	H	-3.447871	-4.365027	-0.386619
C	1.816000	0.918975	-0.156092	H	-2.164772	-0.416676	2.261443
C	0.538763	0.273182	-0.161643	H	2.165047	0.416441	2.261168
C	-0.538792	-0.272854	-0.161607	H	-1.118384	-2.922558	1.124418
C	-1.816013	-0.918708	-0.155986	H	-3.991925	-2.916577	2.272139
C	3.210875	-0.094334	0.015524	H	2.680472	-5.455966	0.446011
C	3.102176	-2.405535	-1.001003	H	2.831382	-1.585969	2.287271
C	2.974603	-3.788472	-0.888879	H	2.594194	-4.022858	2.478365
C	3.035054	-1.586820	0.136784	B	3.868025	2.082826	-1.607124
C	2.782537	-4.378549	0.360135	B	2.158769	2.262830	-1.158464
C	2.859697	-2.191756	1.390511	B	3.394065	3.185965	-0.280374
C	2.731178	-3.575198	1.498999	B	2.839831	0.653597	-1.516359
H	-3.031004	4.403223	-1.781580	B	-2.839903	-0.653447	-1.516297
H	-2.681213	5.456005	0.445957	B	-4.494728	-0.589549	-0.873593
H	4.261804	2.456838	-2.660144	B	4.836249	2.158886	-0.106615
H	-3.265664	1.965884	-1.976840	B	4.494777	0.589483	-0.873959
H	1.281371	2.647983	-1.850178	B	-3.867933	-2.082757	-1.606994
H	3.448365	4.365042	-0.386476	B	2.061953	2.426327	0.613730
H	-2.417028	0.021538	-2.383207	B	-2.158622	-2.262590	-1.158496
H	-5.258257	0.164933	-1.368676	B	3.712032	2.350227	1.269587
H	2.416873	-0.021118	-2.383436	B	-4.836007	-2.159046	-0.106399
H	-4.261790	-2.456712	-2.660007	B	-4.399970	-0.754428	0.897017
H	5.939144	2.591847	-0.087559	B	4.400167	0.754191	0.896677
H	-2.592090	4.022878	2.478170	B	2.687104	0.917924	1.332979
H	5.258138	-0.164996	-1.369311	B	-3.393711	-3.185954	-0.280391
H	3.263035	-1.965971	-1.977416	B	-2.686898	-0.918103	1.333270
H	1.118867	2.922689	1.124707	B	-2.061631	-2.426267	0.613671
H	-1.281162	-2.647592	-1.850215	B	-3.711672	-2.350467	1.269691

Table S9. Optimized geometry coordinates for $\mathbf{I}^{\bullet-}$.

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
C	3.254688	2.274956	1.203184	B	0.000052	-0.956246	-1.221065
C	2.454801	1.135422	1.204531	B	-0.000213	-2.775812	-1.434435
C	3.659916	2.858041	-0.000341	H	-4.282370	3.749101	0.000253
C	-3.252057	2.277010	1.203971	H	1.490137	-4.438778	-0.000072
C	-2.452136	1.137497	1.205507	H	-1.490133	-4.438779	0.000072
C	2.032261	0.536444	-0.000545	H	3.559687	2.714820	-2.150894
C	1.195049	-0.675110	-0.000637	H	2.466004	-1.988255	-1.587412
C	-3.659918	2.858038	0.000339	H	2.144107	0.695677	-2.146858
C	3.252059	2.277008	-1.203972	H	-3.564396	2.711152	-2.150175
C	-2.032261	0.536443	0.000545	H	-2.466036	-1.987671	-1.586528
C	-1.195049	-0.675111	0.000639	H	-0.000702	-0.236651	-2.168242
C	2.452138	1.137495	-1.205507	H	-2.148860	0.691962	-2.145793
C	-3.254693	2.274949	-1.203186	H	-0.000730	-3.343151	-2.482869
C	-2.454806	1.135416	-1.204531	H	3.564387	2.711163	2.150173
B	-0.000052	-0.956245	1.221065	H	2.148853	0.691971	2.145793
B	0.000216	-2.775813	1.434435	H	0.000702	-0.236653	2.168243
B	1.495554	-2.009817	0.897673	H	-3.559682	2.714826	2.150892
B	-1.495586	-2.010315	0.898463	H	0.000733	-3.343151	2.482870
B	0.879707	-3.414554	-0.000119	H	-2.144101	0.695683	2.146859
B	-0.879704	-3.414555	0.000120	H	4.282368	3.749105	-0.000257
B	1.495588	-2.010313	-0.898462	H	2.466038	-1.987670	1.586529
B	-1.495551	-2.009817	-0.897672	H	-2.466003	-1.988258	1.587413

Table S10. Optimized geometry coordinates for **II**$^{\bullet-}$.

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
C	-0.431780	-1.462745	0.000095	H	6.087619	0.077960	-2.151003
C	-2.085260	0.254424	-0.000206	C	4.210520	-0.368415	-1.212187
C	-1.790453	1.699859	-0.000105	H	3.677777	-0.494254	-2.149267
C	-1.650267	2.417678	-1.205124	B	-1.471368	-0.790712	1.232537
H	-1.754713	1.889416	-2.146405	H	-0.932465	-0.297679	2.169554
C	-1.384311	3.784483	-1.203782	B	-1.181387	-2.605269	0.903275
H	-1.282567	4.309959	-2.150431	H	-0.492480	-3.286159	1.592000
C	-1.247421	4.480205	-0.000032	B	-1.181677	-2.604706	-0.903572
H	-1.036759	5.546480	0.000003	H	-0.492821	-3.285422	-1.592539
C	-1.384391	3.784427	1.203680	B	-1.471439	-0.790297	-1.232376
H	-1.282690	4.309872	2.150352	H	-0.932617	-0.297649	-2.169643
C	-1.650367	2.417630	1.204962	B	-3.262621	-0.449360	-0.896770
H	-1.754893	1.889315	2.146200	H	-3.920262	0.266468	-1.582874
C	0.938410	-1.172096	0.000103	B	-2.772524	-2.057370	-1.434522
C	2.123173	-0.867420	0.000050	H	-3.177666	-2.454076	-2.482501
C	3.500832	-0.537157	0.000018	B	-2.617593	-3.132468	-0.000004
C	4.210341	-0.367574	1.212207	H	-2.929386	-4.282864	-0.000069
H	3.677478	-0.492764	2.149305	B	-2.772196	-2.057618	1.434660
C	5.563609	-0.046074	1.206471	H	-3.177423	-2.454279	2.482616
H	6.087315	0.079448	2.150974	B	-3.261913	-0.449459	0.897025
C	6.251510	0.116573	-0.000014	H	-3.919066	0.266342	1.583639
H	7.308548	0.367952	-0.000023	B	-3.842882	-1.869622	0.000146
C	5.563778	-0.046911	-1.206490	H	-5.002470	-2.144983	0.000237

Table S11. Optimized geometry coordinates for **III**$^{\bullet-}$.

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
C	4.109775	-3.283769	-1.203361	H	5.568208	3.534931	-0.000242
C	4.207453	-3.981614	0.001676	H	3.840749	-1.372454	2.148425
C	3.913482	-1.905168	-1.205191	H	5.385270	0.867494	1.572342
C	4.111084	-3.282613	1.206157	H	-4.182827	3.814995	-2.148465
C	3.812485	-1.187279	0.000550	H	-3.754107	-3.203899	2.477589
C	3.914790	-1.904020	1.206874	H	-5.385130	-0.868118	1.572031
C	3.632030	0.284958	0.000005	H	2.830963	4.785840	-0.001090
C	-1.576930	-1.231383	-0.000737	H	2.442564	0.392211	2.221161
C	-0.461317	-0.405568	-0.000629	H	-2.442366	-0.392049	2.220694
C	0.462070	0.405625	-0.000551	H	0.940320	2.931656	1.589514
C	1.577725	1.231421	-0.000531	H	3.754760	3.203768	2.478068
C	-3.632101	-0.284892	-0.000265	H	-4.354578	5.058049	0.002156
C	-3.914232	1.905214	-1.205330	H	-3.841503	1.372288	2.148246
C	-4.110980	3.283750	-1.203421	H	-4.185412	3.812646	2.151632
C	-3.813068	1.187266	0.000366	B	-3.521540	-2.681516	-1.436814
C	-4.208959	3.981488	0.001657	B	-1.839299	-2.572970	-0.907607
C	-3.915674	1.903903	1.206730	B	-2.977810	-3.605675	-0.001256
C	-4.112422	3.282433	1.206095	B	-2.770599	-1.042914	-1.289711
H	4.181492	-3.814975	-2.148436	B	2.771104	1.043251	-1.289705
H	4.352704	-5.058224	0.002112	B	4.528928	1.332668	-0.895348
H	-3.754678	-3.202438	-2.479683	B	-4.578419	-2.874728	-0.000834
H	3.838423	-1.374512	-2.147171	B	-4.528531	-1.332809	-0.895766
H	-0.940272	-2.930621	-1.592064	B	3.522322	2.681683	-1.436403
H	-2.830020	-4.785754	-0.001621	B	-1.839054	-2.573527	0.905429
H	2.443406	0.391423	-2.221626	B	1.840044	2.573219	-0.907251
H	5.385932	0.866821	-1.571875	B	-3.521147	-2.682351	1.434993
H	-2.442929	-0.390952	-2.221566	B	4.579120	2.874520	-0.000324
H	3.755645	3.202653	-2.479200	B	4.528492	1.333022	0.895304
H	-5.567367	-3.535356	-0.000862	B	-4.528205	-1.333287	0.894923
H	4.183839	-3.812914	2.151660	B	-2.770216	-1.043736	1.288714
H	-5.385597	-0.867220	-1.572403	B	2.978613	3.605750	-0.000797
H	-3.838940	1.374634	-2.147338	B	2.770562	1.043894	1.289247
H	-0.939808	-2.931607	1.589372	B	1.839687	2.573646	0.905707
H	0.940978	2.930894	-1.591631	B	3.521749	2.682316	1.435442

Table S12. TD-DFT calculated transitions for **I**.

Excited state	Energy (eV)	Wavelength (nm)	*f*	Transitions			
1	5.0816	243.99	0.0077	57→80	-0.01040	76→78	0.60281
				68→81	-0.01272	76→80	-0.02467
				69→81	0.01505	76→83	0.02037
				71→80	-0.02194	77→78	0.06966
				74→79	-0.12328	77→80	0.28214
				74→84	0.01252	77→85	0.02129
				75→81	-0.18339	75→81	-0.01324
				75→82	-0.01145	77→80	0.01227
2	5.2103	237.96	0.1286	57→78	-0.01147	75→84	-0.01462
				58→78	-0.01011	76→78	-0.07390
				65→78	-0.01719	76→80	-0.08184
				67→82	-0.02410	77→78	0.68796
				69→84	-0.01134	77→80	-0.01736
				71→78	0.01756	77→83	-0.03032
				73→82	0.01612	77→87	0.01545
				74→81	0.02943	75→79	0.01453
				75→79	0.09473	77→78	-0.01892
3	5.3273	232.73	0.0901	60→78	0.01362	75→87	0.01473
				65→79	-0.01173	76→79	-0.02084
				68→78	-0.01453	76→81	0.04402
				69→78	0.02317	77→79	0.23404
				74→80	-0.06896	75→78	-0.01439
				75→78	0.65914	77→79	0.01583
				75→83	-0.03255		
4	5.6116	220.94	0.0018	71→80	0.01067	76→80	0.02050
				72→78	-0.01365	76→83	-0.05879
				74→79	0.52991	76→87	0.01624
				74→84	-0.02241	77→78	0.02482
				75→81	0.11217	77→80	-0.33197
				76→78	0.30014		
5	5.8437	212.17	0.0098	65→78	0.01228	76→80	0.38105
				68→79	-0.01028	77→78	-0.03153
				71→78	-0.02602	77→80	0.01881
				74→81	-0.01272	77→83	0.02688
				75→79	0.59086	75→79	-0.01636
				75→84	0.01635	77→78	0.01165

Table S13. TD-DFT calculated transitions for **II**.

Excited state	Energy (eV)	Wavelength (nm)	*f*	Transitions			
1	4.5593	271.93	0.0519	73→85	-0.01021	79→86	0.01167
				74→84	-0.02900	79→87	0.02587
				74→85	0.03196	79→88	0.02336
				74→87	0.01798	79→92	-0.01562
				74→88	0.01598	81→88	0.01275
				74→89	0.01012	82→85	-0.01115
				77→84	-0.02568	83→84	-0.44503
				77→85	0.02527	83→85	0.50745
				77→87	0.01336	83→86	0.05868
				77→88	0.01175	83→87	0.11546
				78→84	0.02212	83→88	0.10473
				78→85	-0.02444	83→89	0.05732
				78→87	-0.01083	83→92	-0.04401
				79→84	-0.03548	83→97	0.01312
				79→85	0.02134	83→84	0.01209
2	4.8151	257.49	0.4665	57→101	-0.01005	79→97	-0.02681
				72→87	0.01282	79→98	-0.01027
				72→88	0.01169	80→84	-0.02263
				73→85	-0.01683	80→85	0.02079
				73→87	-0.01315	80→87	0.01497
				73→88	-0.01197	81→87	0.04321
				74→84	0.03579	81→88	-0.04757
				74→85	0.02517	82→84	-0.02950
				76→85	-0.01128	82→85	0.03619
				77→84	0.03966	83→84	0.50279
				77→85	0.02340	83→85	0.43018
				77→89	-0.01163	83→86	0.04949
				78→84	-0.03082	83→87	0.07802
				78→85	-0.02569	83→88	0.07259
				78→87	-0.01147	83→89	-0.05613
				78→88	-0.01051	83→91	-0.01180
				79→84	0.07194	83→92	-0.01674
				79→85	-0.07317	83→94	0.02416
				79→86	-0.03594	79→92	0.01029
				79→87	-0.07672	83→84	-0.03639
				79→88	-0.06939	83→85	-0.01697
				79→89	-0.03069	83→89	-0.01314
				79→92	0.05048		
3	4.9722	249.36	0.0015	74→87	0.02090	81→85	0.16858
				74→88	-0.02374	81→86	-0.01547
				77→87	0.02562	81→87	-0.02049
				77→88	-0.02858	81→88	-0.01913
				78→87	-0.02542	81→89	0.07093
				78→88	0.02817	81→94	-0.01636
				80→84	0.04461	82→84	-0.01304
				80→85	0.01557	83→87	-0.31296
				81→84	0.50549	83→88	0.32349
4	5.1594	240.31	0.0101	72→84	0.01691	80→88	0.02192
				72→86	0.01172	80→90	-0.02303
				73→84	-0.01656	81→84	-0.04414
				75→84	-0.01078	81→85	0.04531
				75→86	-0.01066	82→84	-0.15719

				76→84	-0.01522	82→85	0.12650
				76→86	0.02254	82→86	0.29684
				79→84	-0.22522	82→87	-0.06271
				79→85	-0.08542	82→88	-0.06429
				79→94	-0.02638	82→91	0.02440
				80→84	0.40446	83→84	0.03168
				80→85	-0.34450	83→87	0.02544
				80→86	0.09814	83→88	0.03039
				80→87	0.02097	82→86	0.01553
5	5.2932	234.23	0.0239	67→84	-0.01508	80→86	-0.04424
				70→84	-0.01031	81→85	-0.01527
				72→84	0.01689	81→87	0.01074
				72→85	0.01218	81→88	-0.01175
				73→84	-0.02409	82→84	0.53221
				73→85	-0.01127	82→85	0.07690
				74→87	-0.01037	82→86	-0.04468
				76→84	-0.02786	82→89	-0.04301
				77→87	-0.01114	83→84	0.02124
				78→84	-0.01615	83→85	0.08624
				79→84	-0.29991	83→86	-0.13508
				79→85	-0.10737	83→87	-0.13804
				79→87	-0.01147	83→88	-0.13100
				79→88	-0.01061	83→89	-0.04597
				79→94	-0.03127	83→92	0.02067
				80→84	0.14428	83→97	-0.01188
				80→85	0.10304		
6	5.5219	224.53	0.1392	71→85	0.01239	80→85	0.19103
				71→89	-0.01304	80→86	0.13281
				72→85	-0.01773	81→84	-0.01099
				74→84	-0.01532	81→86	-0.01521
				75→85	0.01599	82→84	-0.08504
				76→84	0.01308	82→85	0.62016
				76→85	-0.01974	82→86	-0.02990
				78→84	0.02232	82→87	0.11310
				78→85	0.01383	82→88	0.10674
				78→89	-0.01360	82→90	-0.03762
				79→84	-0.02757	82→97	-0.01328
				79→85	0.12236	83→85	-0.01063
				79→86	0.01738	83→88	0.02307
				79→87	0.02451	83→89	0.04823
				79→88	0.02192	82→84	0.01151
				80→84	-0.03172	82→85	-0.02543
7	5.7733	214.76	0.1868	62→84	-0.01119	79→97	-0.02262
				72→84	-0.01588	80→84	0.03409
				73→84	0.03344	80→85	-0.06874
				74→84	-0.04049	80→86	-0.07819
				74→85	-0.01409	80→87	-0.01946
				74→94	-0.01278	80→88	-0.02144
				76→84	0.01257	81→87	0.03235
				76→85	0.01927	81→88	-0.03278
				77→84	-0.03716	82→84	0.01871
				77→85	-0.01524	82→85	-0.08242
				77→94	-0.01111	82→86	-0.04821
				78→84	0.06843	82→87	-0.05602
				78→85	0.01519	82→88	-0.04896
				78→89	-0.01680	83→84	0.10890
				79→84	-0.19091	83→85	0.04402
				79→85	0.62561	83→86	-0.01502
				79→86	-0.01263	83→89	0.11005
				79→87	-0.01423	83→94	-0.03106
				79→88	-0.01262	83→108	0.01236
				79→92	0.01118	83→84	-0.01747

Table S14. TD-DFT calculated transitions for **III**.

Excited state	Energy (eV)	Wavelength (nm)	*f*	Transitions			
1	4.9420	250.88	0.0043	92→120	0.03582	115→139	0.01584
				92→123	-0.01791	115→142	-0.01259
				92→132	0.01323	116→121	-0.08933
				99→127	-0.01077	116→122	-0.05449
				107→120	0.02015	116→124	0.01459
				108→120	0.04062	117→120	0.43875
				108→123	-0.01531	117→125	-0.02984
				112→120	0.03242	118→120	0.20229
				112→123	-0.01168	118→123	-0.01262
				114→121	-0.01164	118→125	0.08993
				114→122	0.01318	118→131	-0.01085
				115→120	0.46339	119→121	0.02146
				115→123	-0.11235	119→124	0.09432
				115→132	0.03359	119→130	-0.01212
2	4.9640	249.77	0.0101	109→125	-0.01007	118→124	-0.13373
				114→120	-0.01577	118→130	0.01556
				116→120	0.61100	119→120	-0.23566
				116→123	0.02782	119→123	0.02487
				116→125	-0.02370	119→125	-0.13967
				117→121	-0.13051	119→131	0.01453
				117→122	-0.08562	118→124	-0.01012
				117→124	0.04524	119→125	-0.01053
				118→121	-0.05899		
3	4.9807	248.93	0.0019	92→120	0.03471	115→139	0.01497
				92→123	-0.01716	115→142	-0.01204
				92→132	0.01366	116→121	0.10984
				99→127	-0.01045	116→122	0.06476
				107→120	0.01715	116→124	-0.01359
				108→120	0.03804	117→120	-0.42553
				108→123	-0.01248	117→123	-0.02959
				112→120	0.02921	117→125	0.03021
				112→123	-0.01033	118→120	-0.12525
				113→127	-0.01006	118→125	-0.10468
				114→121	-0.01049	119→120	0.02286
				114→122	0.01477	119→121	-0.02693
				115→120	0.48946	119→122	0.01483
				115→123	-0.11277	119→124	-0.10818
				115→132	0.03206	119→130	0.01123
4	4.9847	248.73	0.1071	93→120	0.01259	117→124	-0.01785
				102→120	-0.01118	118→120	0.01048
				114→120	0.05830	118→122	0.01392
				114→123	-0.01687	118→124	-0.03908
				115→120	-0.01402	118→127	-0.02049
				115→121	-0.01052	118→129	0.01387
				115→122	0.01664	119→120	0.65215
				116→120	0.23196	119→123	-0.08518
				116→125	0.02325	119→125	-0.04072
				117→120	0.01567	119→128	-0.01392
				117→121	-0.04149	119→132	0.01111
				117→122	-0.01425		

5	5.0034	247.80	0.0017	96→120	-0.01204	118→123	-0.08676
				115→120	-0.04682	118→125	-0.02213
				115→126	0.01333	118→128	-0.01489
				116→121	0.01514	118→132	0.01014
				116→124	0.02948	119→121	0.01316
				117→120	-0.24299	119→122	0.01032
				117→123	0.02815	119→124	-0.01317
				117→125	-0.02580	119→127	-0.02257
				118→120	0.65153	119→129	0.01570
6	5.3500	231.75	0.0005	109→125	0.01317	117→127	0.02440
				111→124	0.01080	117→129	-0.02806
				114→120	-0.07976	118→120	0.01328
				114→123	0.01331	118→121	0.20479
				115→121	0.04205	118→122	-0.06537
				115→122	-0.04884	118→123	-0.01159
				116→120	0.23760	118→124	0.21051
				116→121	0.07145	118→125	-0.04088
				116→122	0.03563	118→130	-0.01936
				116→123	-0.25461	119→120	-0.02194
				116→125	0.02134	119→121	-0.03143
				116→128	-0.03000	119→122	0.02006
				117→120	0.04424	119→123	0.01544
				117→121	0.39694	119→124	-0.04019
				117→122	0.20593	119→125	0.22580
				117→123	-0.04871	119→126	-0.01684
				117→124	-0.06485	119→131	-0.01824
				117→125	0.01153		
7	5.3518	231.67	0.0021	109→124	-0.01329	117→124	0.01178
				111→125	-0.01093	117→125	0.05620
				114→120	0.01483	117→128	-0.02920
				114→122	0.01005	118→120	0.06908
				114→124	0.01024	118→121	-0.03756
				115→120	-0.03403	118→122	0.01342
				116→120	-0.04603	118→123	-0.06096
				116→121	0.41537	118→124	-0.04182
				116→122	0.20333	118→125	-0.21977
				116→123	0.04965	118→126	0.01870
				116→124	-0.03048	118→131	0.01822
				116→127	0.02604	119→121	-0.16142
				116→129	-0.02914	119→122	0.11098
				117→120	0.22712	119→124	-0.22290
				117→121	-0.06892	119→125	-0.03821
				117→122	-0.03514	119→130	0.02035
				117→123	-0.25152		
8	5.3844	230.27	0.0112	86→120	0.01144	112→121	-0.01692
				88→120	-0.01201	112→122	0.02603
				92→121	-0.01748	112→133	0.01028
				92→122	0.02685	114→120	0.53123
				92→133	0.02064	114→123	-0.09097
				93→120	-0.01652	114→132	0.02460
				99→126	0.01338	115→121	-0.24696
				102→120	-0.03997	115→122	0.32531
				102→123	0.01543	115→124	0.01523
				103→121	-0.01117	115→130	-0.02665
				104→120	-0.02951	115→133	0.05721
				105→121	-0.01209	116→120	0.03575
				106→120	-0.01041	116→123	-0.03886
				107→121	-0.01571	117→122	0.08651
				108→121	-0.01434	118→121	0.07657
				108→122	0.02727	118→122	0.02861
				108→133	0.01065	118→124	0.03602
				109→120	0.04162	119→120	-0.06741

				111→121 111→127	-0.01268 0.01071	119→123 119→125	0.02879 0.03810
9	5.4349	228.13	0.0001	93→121 93→122 96→126 102→121 102→122 111→126 114→121 114→122 116→121	-0.01006 0.01407 -0.01584 0.01075 -0.01334 -0.01524 -0.04727 0.06466 -0.16291	117→120 117→123 117→126 118→125 118→126 119→121 119→122 119→124	-0.03914 0.05717 -0.02256 0.07053 0.08051 -0.41521 0.51708 0.09029
10	5.4504	227.48	0.0039	93→126 96→121 96→122 109→126 111→122 115→122 116→120 116→123	0.01288 0.01299 -0.01863 -0.01144 -0.01275 0.02016 0.03252 -0.04733	117→121 117→122 117→124 118→121 118→122 118→124 119→125 119→126	0.21487 -0.09635 -0.01160 -0.39255 0.51589 0.08132 0.06423 0.08619

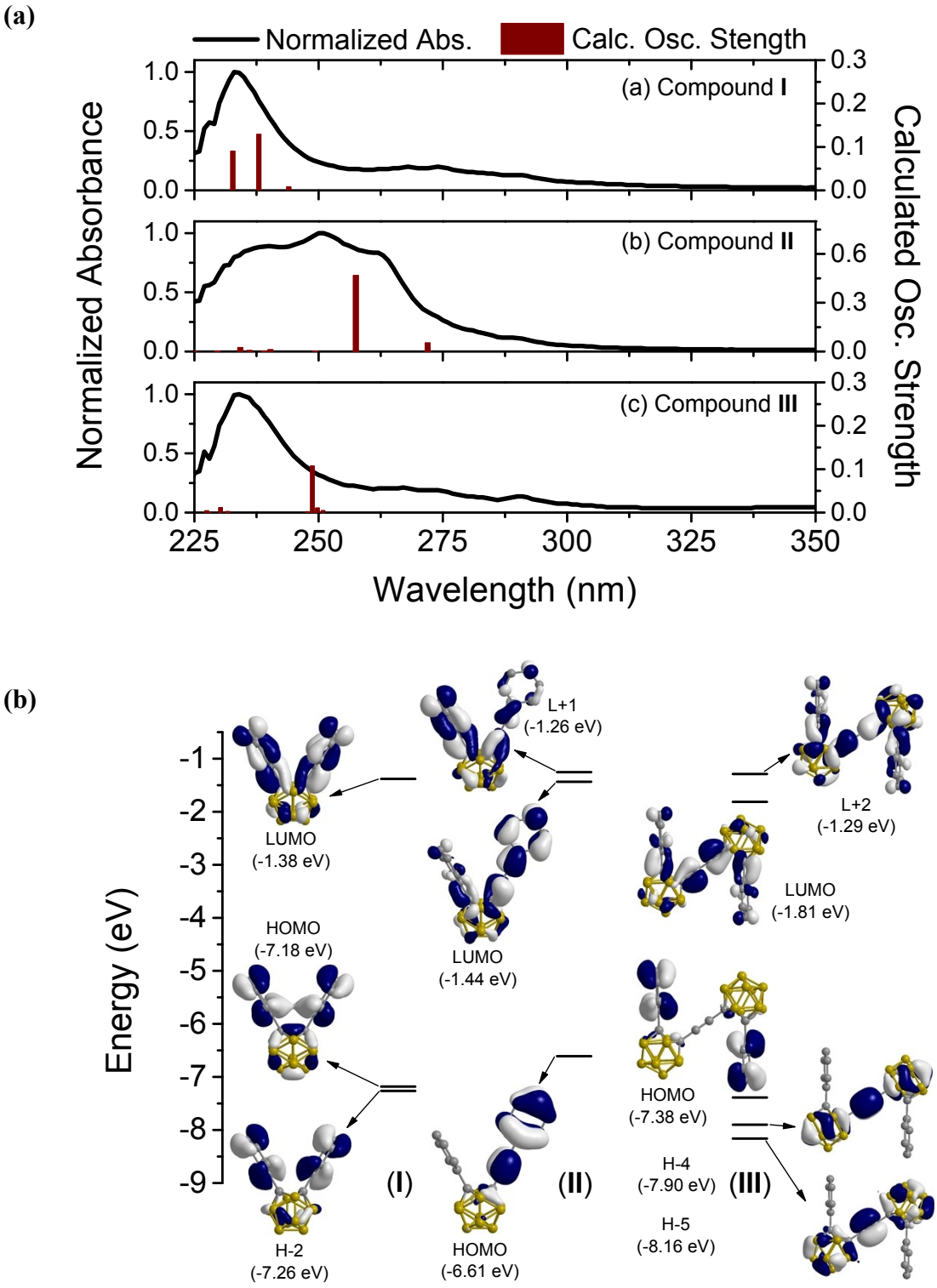


Figure S5. (a) TD-DFT calculated oscillation strengths with measured absorption spectra and (b) isodensity plots for the orbitals included in the major transitions of **I**–**III**, and their energy levels.

Table S15. Selected TD-DFT calculated transitions for **I**–**III** and their major contributions.

Compound	Wavelength (nm)	Osc. Strength	Major Contributions
I	237.96	0.1286	HOMO → LUMO (95%)
	232.73	0.0901	H–2 → LUMO (87%)
II	271.94	0.0519	HOMO → LUMO (40%), HOMO → L+1 (52%)
	257.49	0.4665	HOMO → LUMO (51%), HOMO → L+1 (37%)
III	248.73	0.1071	HOMO → LUMO (85%)
	230.27	0.0112	H–5 → LUMO (56%), H–4 → L+2 (21%)

Geometrical changes between neutral and anionic species. The optimised structures of the anionic species, $\mathbf{I}^{\bullet-}$–$\mathbf{III}^{\bullet-}$, are depicted in Figure S6 along with the neutral species for comparison. Note that the atom labels are differed from Figure 2 for comparison. The most notable structural differences between the neutral and the anionic geometries of **I**–**III** are the lengthening of the carboranyl C–C bonds (C1–C2) upon reduction. Along with this structural change, $\mathbf{II}^{\bullet-}$ and $\mathbf{III}^{\bullet-}$ exhibit important geometrical changes. The bond lengths between the carboranyl atom and the phenyl substituent (C1–C3) and between the carboranyl carbon and ethynyl group (C2–C4) in $\mathbf{II}^{\bullet-}$ and $\mathbf{III}^{\bullet-}$ are slightly shorter than those of their corresponding neutral species, while the ethynyl C–C bonds (C4–C5) are longer than that of the neutral species (Table S6). Moreover, the bond distance between the phenyl-substituted carbon and neighbouring boron in the carborane cage of $\mathbf{II}^{\bullet-}$ contracted upon reduction, while the distance between the ethynyl-substituted carbon and the neighbouring boron was extended. This trend is even more pronounced in $\mathbf{III}^{\bullet-}$. Therefore, we confirmed that the added electron is stabilized through the σ^* orbital of the carborane cage and the π^* orbital of the ethynyl group, rather than the π^* orbital of the phenyl group.

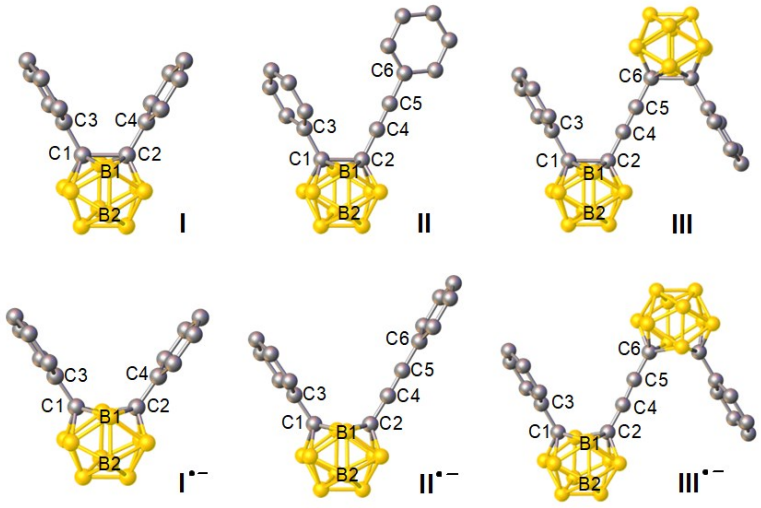


Figure S6. Optimized structures of **I**–**III** and **I**$^{\bullet-}$–**III**$^{\bullet-}$, with selected atoms labelled (note: the atom labels are differed from Figure 2 for comparison).

Table S16. Selected bond lengths (Å) in the DFT-optimised geometries of the neutral and radical-anionic states of **I**–**III**. Atom labels are provided in Figure 4a.

	I	**I**$^{\bullet-}$	**II**	**II**$^{\bullet-}$	**III**	**III**$^{\bullet-}$
C1–C2	1.759	2.390	1.734	2.384	1.733	2.262
C1–C3	1.508	1.473	1.508	1.475	1.508	1.483
C2–C4	1.508	1.473	1.429	1.401	1.431	1.388
C4–C5	–	–	1.212	1.223	1.208	1.229
C5–C6	–	–	1.427	1.417	1.431	1.388
C1–B1	1.724	1.731	1.739	1.729	1.742	1.726
C2–B1	1.725	1.732	1.728	1.747	1.725	1.767
B1–B2	1.765	1.832	1.763	1.827	1.762	1.808

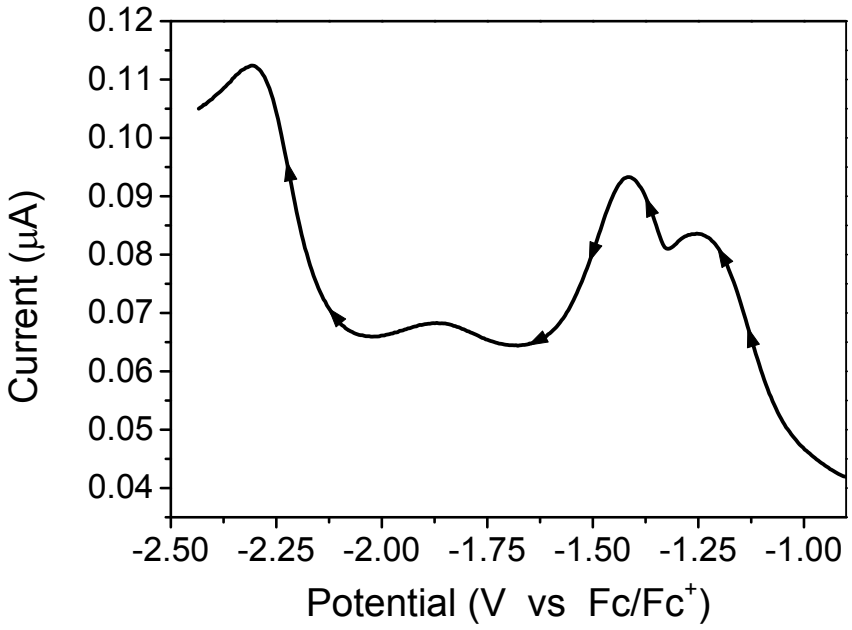


Figure S7. Square wave voltammetry scan for **III** from positive to negative potentials.

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