Supporting Information

Three-Dimensional π-Electron Acceptor, Tri-Phenyl-o-Carborane, Bearing a Rigid Conformation with End-On Phenyl Units

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General Procedures. All manipulations were performed under a dry nitrogen or argon atmosphere using standard Schlenk techniques. Tetrahydrofuran (THF) was distilled under nitrogen from sodium/benzophenone. The elemental analyses were performed using a Carlo Erba Instruments CHNS-O EA 1108 analyzer. High Resolution Tandem Mass Spectrometry (Jeol LTD JMS-HX 110/110A) was performed at the Korean Basic Science Institute. The ^{1}H, ^{11}B, and ^{13}C NMR spectra were recorded on a Bruker600 spectrometer operating at 600.1, 150.9, and 192.6 MHz, respectively. All ^{11}B chemical shifts were referenced to $BF_3{\cdot}O(C_2H_5)_2$ (0.0 ppm) with a negative sign indicating an up-field shift. All proton and carbon chemical shifts were measured relative to the internal residual $CHCl_3$ from the lock solvent (99.9% $CDCl_3$). The absorption and photoluminescence spectra were recorded on a SHIMADZU UV-3101PC UV-VIS-NIR scanning spectrophotometer and a VARIAN Cary Eclipse fluorescence spectrophotometer, respectively. Decaborane, o-carborane, and 1-phenyl-o-carborane were purchased from Katchem and *N*,*N*-dimethylaniline, dichlorophenylborane, n-BuLi (2.5 M in hexane), chromium hexacarbonyl [$Cr(CO)_6$], and benzene-chromium(0) tricarbonyl[(η^6-Bz)$Cr(CO)_3$] were purchased from Aldrich Chemicals.

Crystal Structure Determination. Crystals of **1**, **2**, **3**, and **4** were obtained from toluene, sealed in glass capillaries under argon, and mounted on the diffractometer. Preliminary examination and data collection were performed using a Bruker SMART CCD detector system single-crystal X-ray diffractometer equipped with a sealed-tube X-ray source (40 kV × 50 mA) using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Preliminary unit cell constants were determined with a set of 45 narrow-frame (0.3° inϖ) scans. The double-pass method of scanning was used to exclude any noise. The collected frames were integrated using an orientation matrix determined from the narrow-frame scans. The SMART software package was used for data collection, and SAINT was used for frame integration.[1] Final cell

constants were determined by a global refinement of *xyz* centroids of reflections harvested from the entire data set. Structure solution and refinement were carried out using the SHELXTL-PLUS software package.[2]

Cyclic voltammetry. The cyclic voltammetry experiments were performed using a BAS 100 electrochemical analyzer. A three-electrode cell system containing a platinum disk, a platinum wire, and $Ag/AgNO_3$ as the working, counter, and reference electrodes, respectively, was used. All data were obtained for Ar-purged CH_2Cl_2 solution containing 0.1M tetrabutylammonium perchlorate (TBAP) at a scan rate of 0.1 V s^{-1}.

Raman spectroscopy. Raman spectra were obtained using a micro-Raman system (JY-Horiba, LabRam 300) with a collimated 50 x objective lens (Olympus, NA 0.75). This system is equipped with a thermoelectrically cooled charged-coupled device (CCD) detector and the signal was obtained by 180°backscattering geometry. The 647 nm line of CW Kr ion laser (Coherent, Innova 300C) was used as a Raman excitation source.

Density Functional Calculations. Full geometry optimizations of the complexes in their singlet ground state were performed with DFT using the B3LYP functional,[3] with the relativistic effective core potential and basis set LanL2DZ[4] for the chromium and the 6-31G[5]basis set for the remaining atoms. No symmetry constraints were applied during the geometry optimizations, which were carried out with the Gaussian 09 package.[6] The nature of the stationary points located was further checked by computations of harmonic vibrational frequencies at the same level of theory. All Isodensity plots (isodensity contour = 0.03 a.u.) of the frontier orbitals were visualized by Chem3D Ultraprogram.[7] The various properties of all compounds, such as HOMOs, LUMOs, and energy gaps were obtained from the computed results and were compared to the available experimental data. The excitation energies and oscillator strengths for the lowest 30 singlet–singlet transitions at the optimized geometry in the ground state were obtained in TDDFT calculations using the same basis set and functional

as for the ground state. Frequency calculations of all carboranes including Raman data were calculated by the same functional basis set using an optimized structure. Simulated absorption spectra and Raman spectra of all carborane compounds were obtained by GaussSum 2.2 program.[8]

Synthesis of 1,2,3-triphenyl-o-carborane (1). 1-Phenyl-o-carborane (1.10 g, 5.0 mmol) was added to a solution of KOH (0.84 g, 15 mmol) in 50 mL of ethanol and the clear reaction mixture was heated to reflux. TLC of the reaction mixture sample showed no starting material spot after that time. The reaction mixture was evaporated to dryness and re-dissolved in 50 mL of distilled water. An excess of Me_4NCl was added to the reaction mixture and the precipitate of the tetramethylammonium nido-carborane salt formed was filtered off and dried using air suction (1.42 g, 100%). A 2.5 M solution of n-BuLi in hexane (1.0 mL, 2.2 mmol) was slowly added dropwise to a stirred solution of tetramethylammonium nido-carborane salt (0.57 g, 2.0 mmol) in 40 mL of THF at −78 °C, and then dichlorophenylborane (0.35 g, 2.2 mmol) was added *via* cannula. After this addition the reaction mixture was left to warm to room temperature and was then heated to reflux 6 h. The white precipitate of lithium chloride was removed by filtration in air and washed with THF. After evaporation the crude reaction mixture was purified by column chromatography (Hexane eluent) to give 1,2,3-triphenyl-o-carborane**1**and was then recrystallized from hexane to obtain a white powder.Yield: 86% (0.64 g, 1.72 mmol). m.p.: 193-194 °C. HRMS: Calcd for $[^{12}C_{20}{}^{11}B_{10}{}^{1}H_{24}]^+$ 374.2809. Found: 374.2802. IR spectrum (KBr pellet, cm^{-1}): ν(B−H) 2581, 2601; ν(C−H) 3237. ^{1}H NMR ($CDCl_3$, 600.1 MHz) δ 7.410 (m, 4H, Ph-*H*), 7.310 (m, 3H, Ph-*H*), 7.150 (m, 8H, Ph-*H*). ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 135.6, 131.3, 131.0, 129.9, 128.9, 128.0, 127.36 (*Ph*), 83.6 (Ph-*C*cab). ^{11}B NMR ($CDCl_3$, 192.6 MHz) δ −1.62 (1B), −2.99 (2B), −8.02 (3B), −8.57 (2B), −10.15 (2B).

Synthesis of 1,3,6-triphenyl-o-carborane (2). A procedure analogous to the preparation of

1was used and obtained a white powder. Yield: 58% (0.43 g, 1.2 mmol). m.p.: 178-179 °C. HRMS: Calcd for $[^{12}C_{20}{}^{11}B_{10}{}^{1}H_{24}]^{+}$ 374.2809. Found: 374.2819. IR spectrum (KBr pellet, cm^{-1}): ν(B−H) 2581, 2601; ν(C−H) 3237. ^{1}H NMR ($CDCl_3$, 600.1 MHz) δ 7.334 (d, 4H, *J* = 7.8 Hz), 7.218 (d, 1H, *J* = 7.2 Hz), 7.206 (d, 1H, *J* = 7.8 Hz), 7.129 (d, 2H, *J* = 7.2 Hz), 7.117 (d, 2H, *J* = 7.8 Hz), 7.001 (t, 1H, *J* = 7.2 Hz), 6.900 (d, 1H, *J* = 8.4 Hz), 6.887 (d, 1H, *J* = 7.2 Hz), 6.791 (d, 2H, *J* = 7.8 Hz), 4.433 (s, 1H). ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 133.7, 130.5, 129.2, 128.6, 127.7, 127.6, 127.1 (*Ph*), 78.3 (Ph-*C*cab), 57.8 (H-*C*cab). ^{11}B NMR ($CDCl_3$, 192.6 MHz) δ −0.88 (2B), −2.77 (1B), −4.82 (1B), −9.75 (2B), −11.04 (2B), −14.05 (2B).

Synthesis of 1,2,3,6-tetraphenyl-o-carborane (3). A procedure analogous to the preparation of **1** was used and obtained a white powder. Yield: 37% (0.33 g, 0.74 mmol). m.p.: 252-253 °C. HRMS: Calcd for $[^{12}C_{26}{}^{11}B_{10}{}^{1}H_{28}]^{+}$ 450.3122. Found: 450.3108. IR spectrum (KBr pellet, cm^{-1}): ν(B−H) 2581, 2601; ν(C−H) 3237. ^{1}H NMR ($CDCl_3$, 600.1 MHz) δ 7.294 (d, 4H, *J* = 7.8 Hz, Ph-*H*), 7.242 (d, 4H, *J* = 8.4 Hz, Ph-*H*), 7.229 (d, 4H, *J* = 7.8 Hz, Ph-*H*), 7.138 (d, 2H, *J* = 7.2 Hz, Ph-*H*), 7.126 (d, 2H, *J* = 7.8 Hz, Ph-*H*), 6.991 (t, 4H, *J* = 7.8 Hz, Ph-*H*). ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 134.6, 132.0, 130.2, 129.5, 128.9, 127.6, 127.1 (*Ph*), 80.3 (Ph-*C*cab). ^{11}B NMR ($CDCl_3$, 192.6 MHz) δ 1.44 (2B), −2.75 (2B), −8.50 (2B), −9.45 (4B).

Synthesis of 1,2-bis(phenyl-η^6-chromium(0)tricarbonyl)-3-phenyl-o-carborane (4). Compound **1** (0.37 g, 1.0 mmol) and $[Cr(CO)_6]$ (0.44 g, 2.0 mmol) were dissolved in a mixture of THF (5 mL) and di-*n*-butyl ether (50 mL). The mixture was refluxed for 72 h and the resulting dark reddish solution was cooled to room temperature and filtered over Celite. The solvents were evaporated under reduced pressure. After evaporation the crude reaction mixture was purified using column chromatography (CH_2Cl_2:Hexane eluent) to give chromium complex **4**, and then recrystallized from hexane to obtain red crystals. Yield: 87%

(0.59 g, 0.87 mmol). HRMS: Calcd for $[C_{28}H_{30}B_{10}Cr_2O_6]^+$ 676.1783. Found: 676.1768. IR spectrum (KBr pellet, cm^{-1}): ν(B−H) 2583, 2589; ν(CO) 1960, 1892. ^{1}H NMR ($CDCl_3$, 300.1 MHz) δ 7.62 (m, 4H, Ph-*H*), 7.47 (m, 3H, Ph-*H*), 7.30 (m, 8H, Ph-*H*). ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 231.4 (Cr-*C*O), 141.5, 137.9, 134.8, 132.7, 131.3, 130.8, 128.7 (*Ph*), 85.6 (Ph-*C*cab). ^{11}B NMR ($CDCl_3$, 96.3 MHz) δ −1.84 (1B), −3.11 (3B), −8.54 (3B), −8.71 (2B), −10.37 (1B).

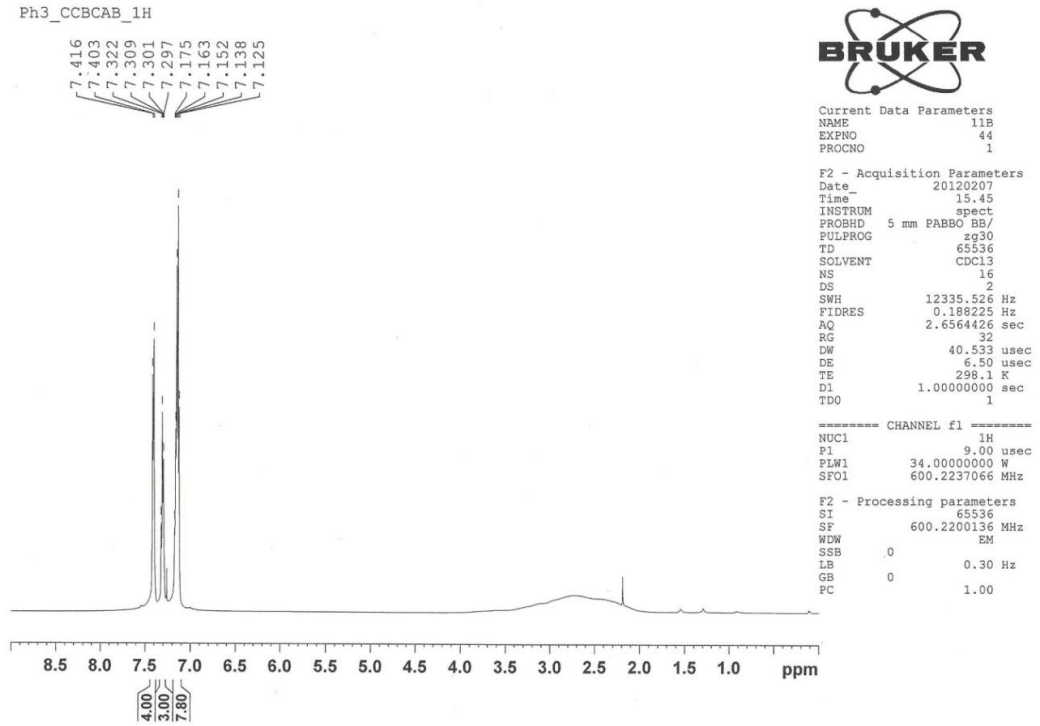

Figure S1. ^{1}H-NMR spectrum of **1**.

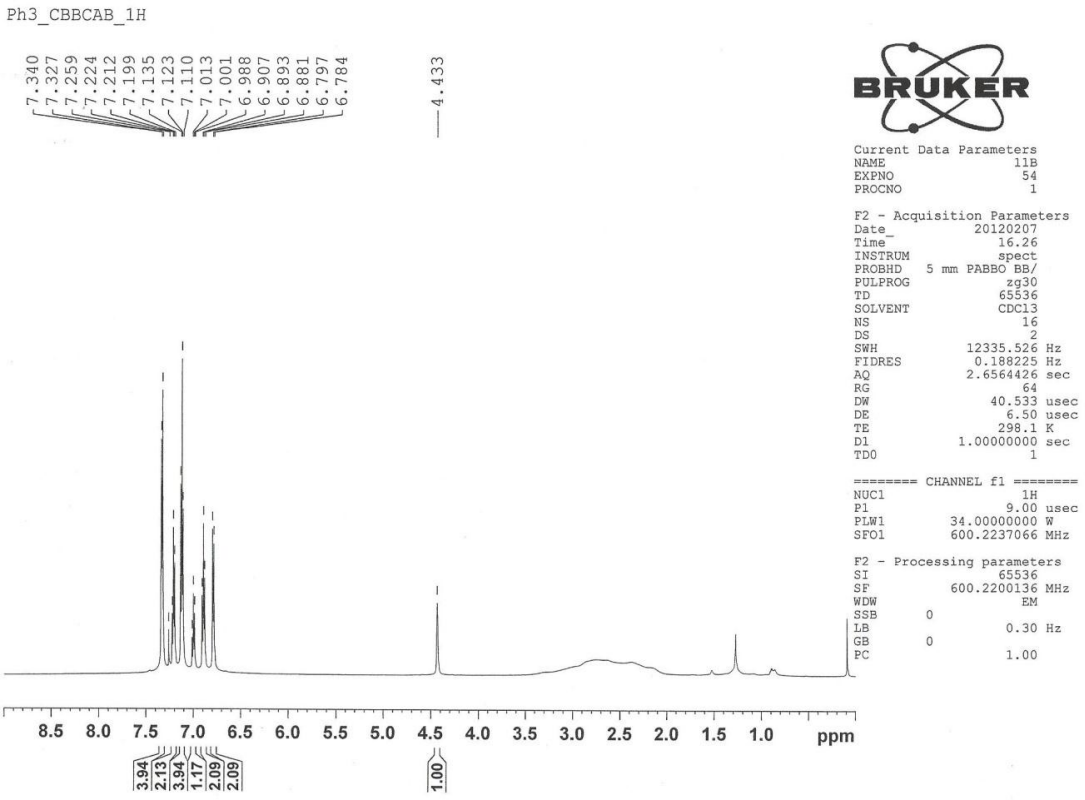

Figure S2. ^{1}H-NMR spectrum of **2**.

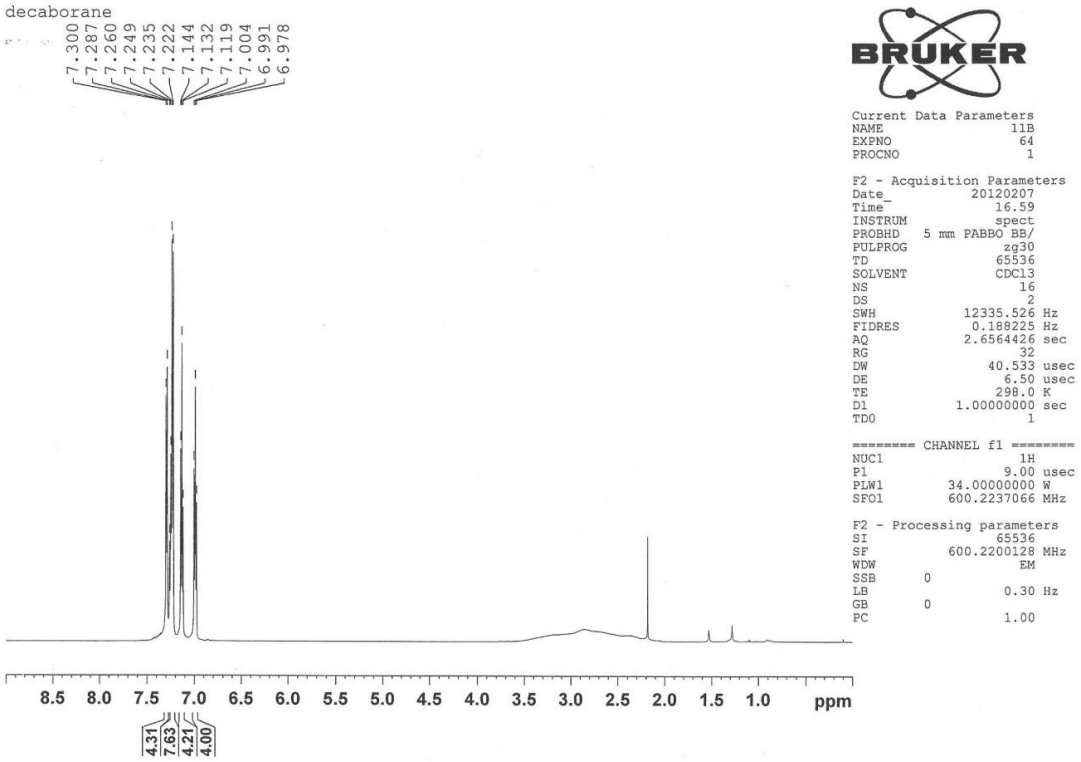

Figure S3. ^{1}H-NMR spectrum of **3**.

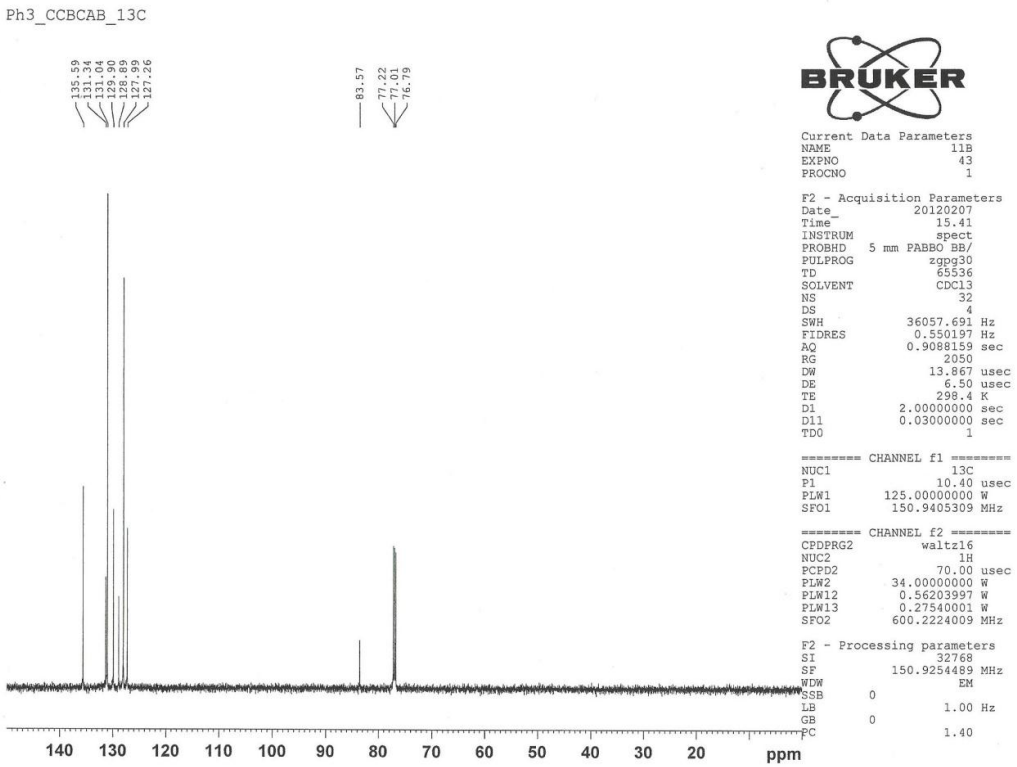

Figure S4. ^{13}C-NMR spectrum of **1**.

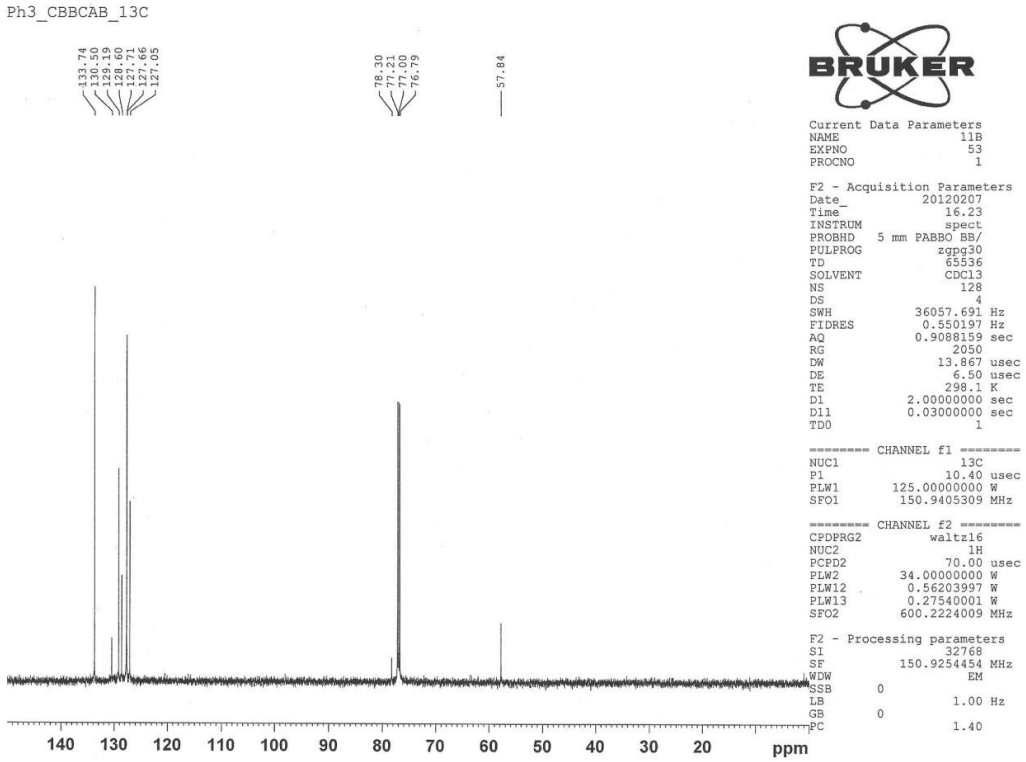

Figure S5. ^{13}C-NMR spectrum of **2**.

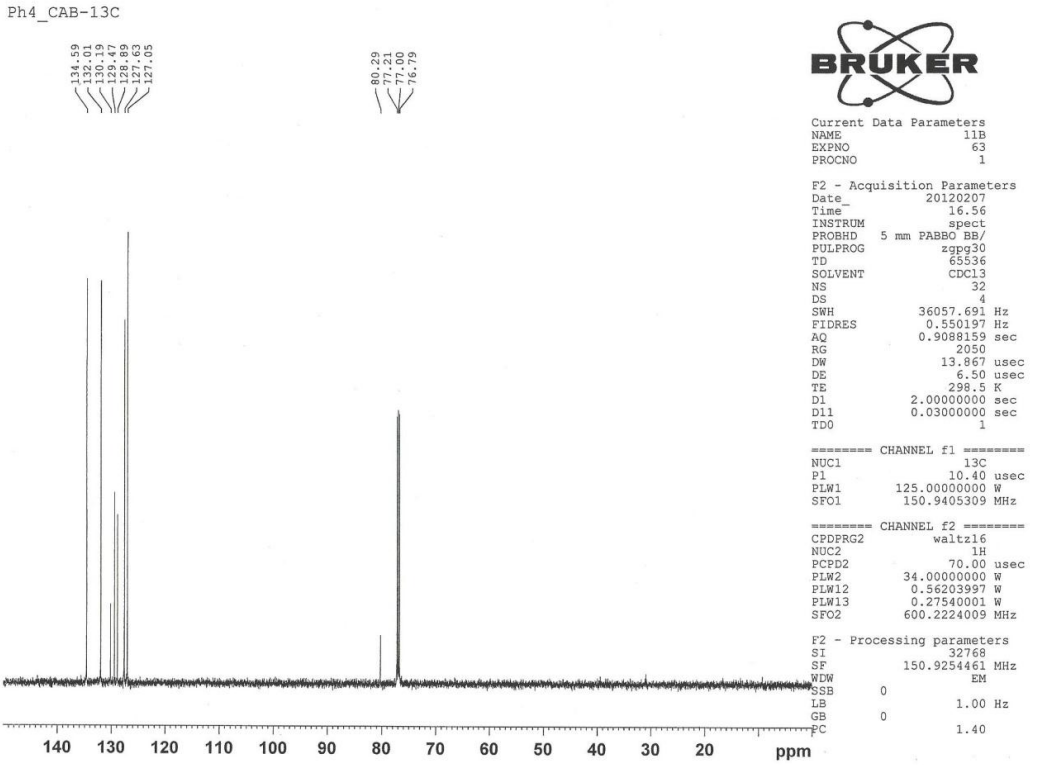

Figure S6. ^{13}C-NMR spectrum of **3**.

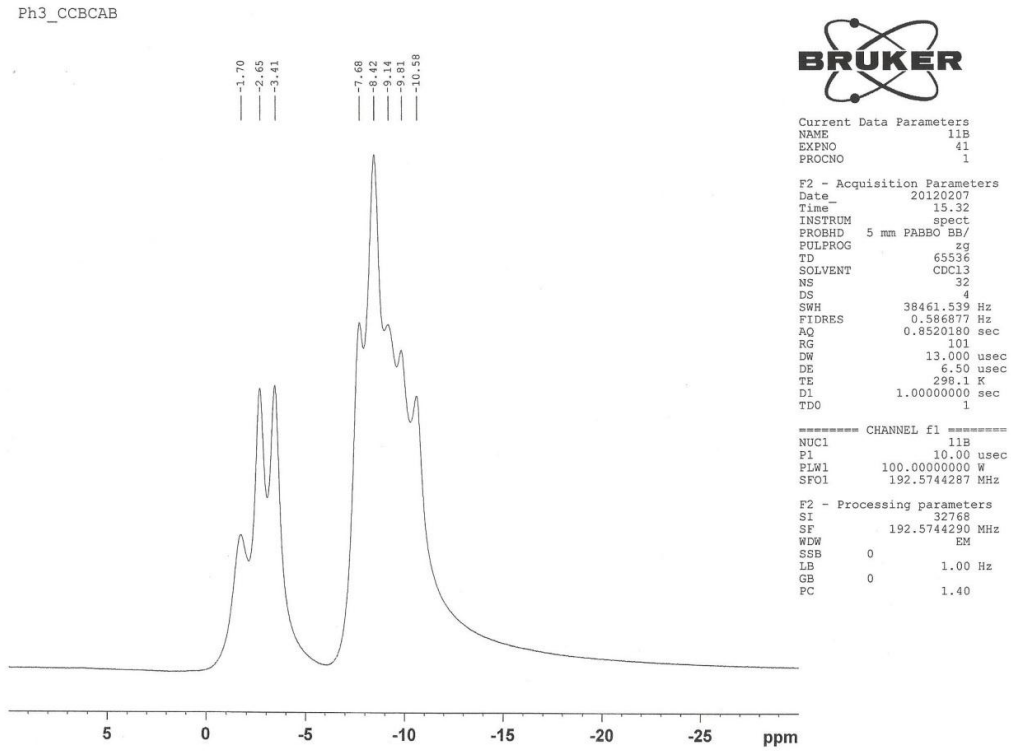

Figure S7. ^{11}B-NMR spectrum of **1**.

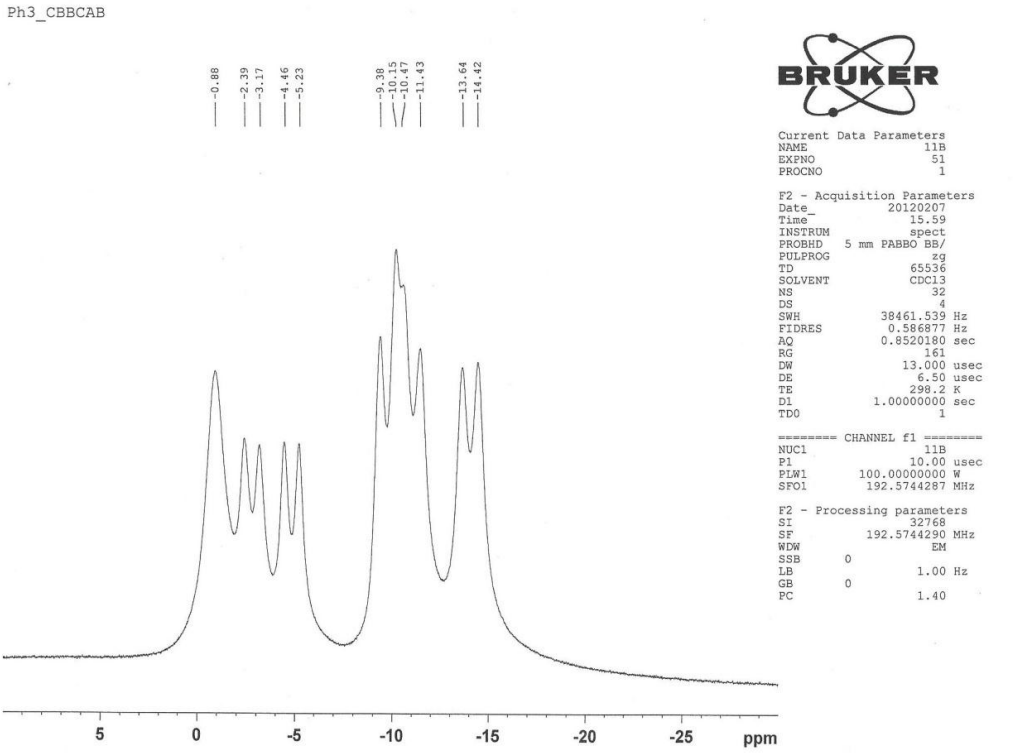

Figure S8. ^{11}B-NMR spectrum of **2**.

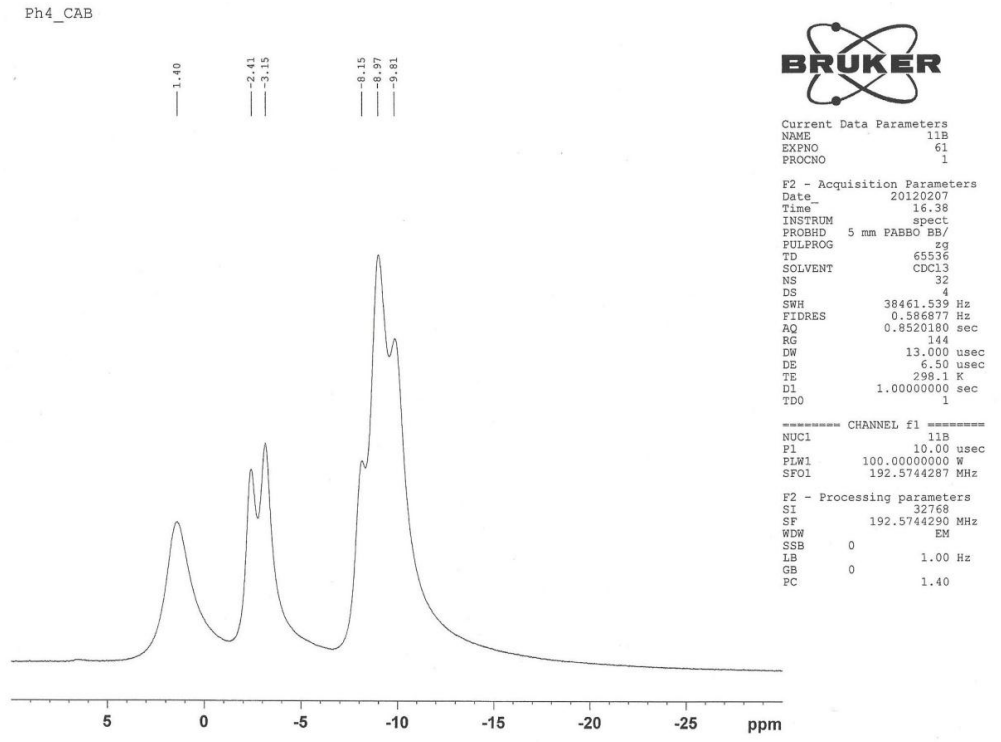

Figure S9. ^{11}B-NMR spectrum of **3**.

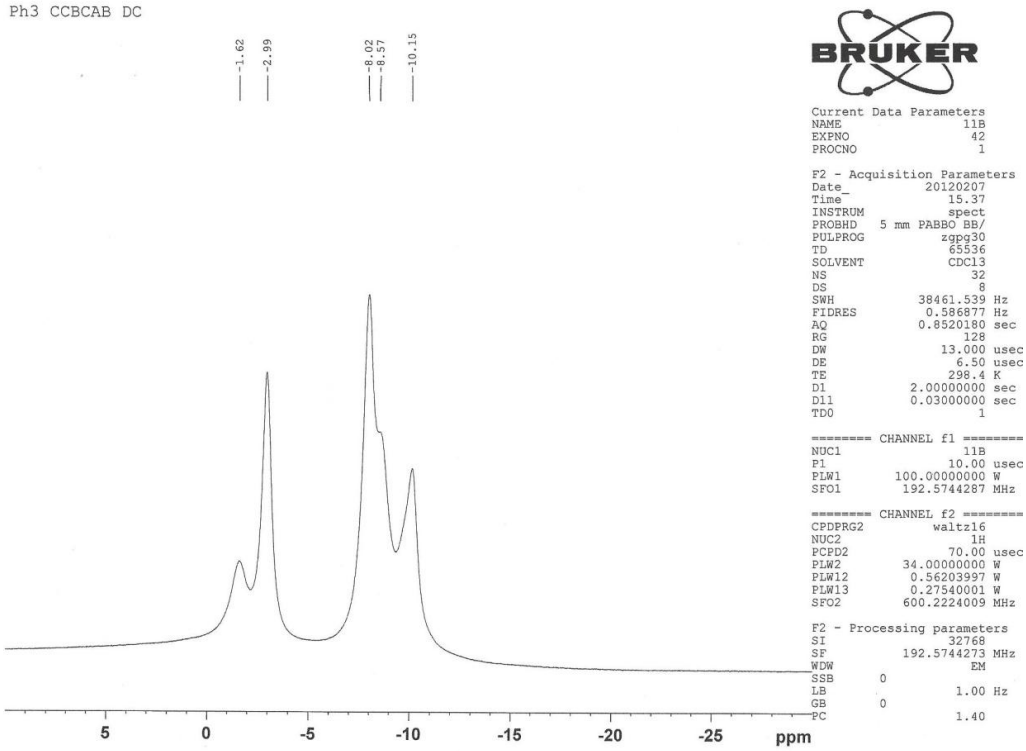

Figure S10. ^{11}B{^{1}H}-NMR spectrum of **1**.

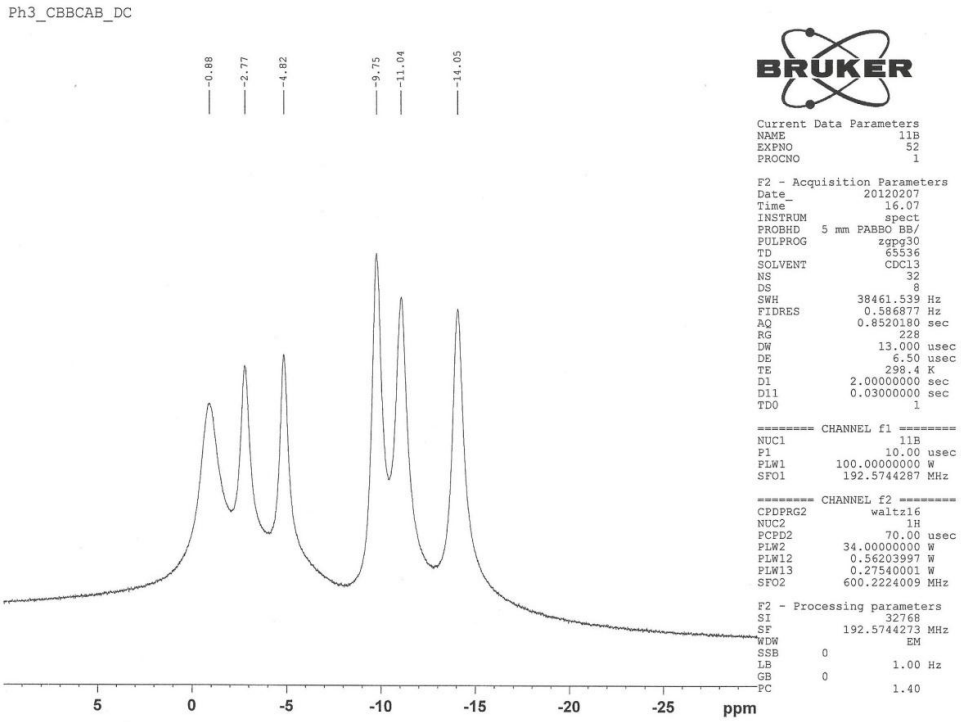

Figure S11. $^{11}B\{^{1}H\}$-NMR spectrum of **2**.

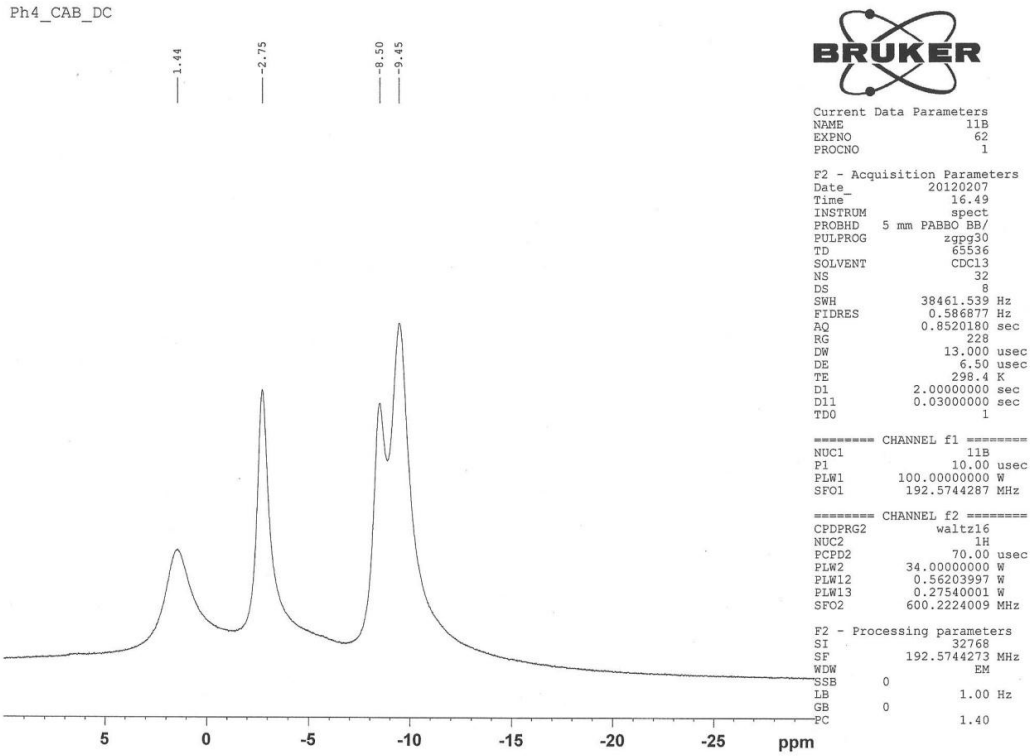

Figure S12. $^{11}B\{^{1}H\}$-NMR spectrum of **3**.

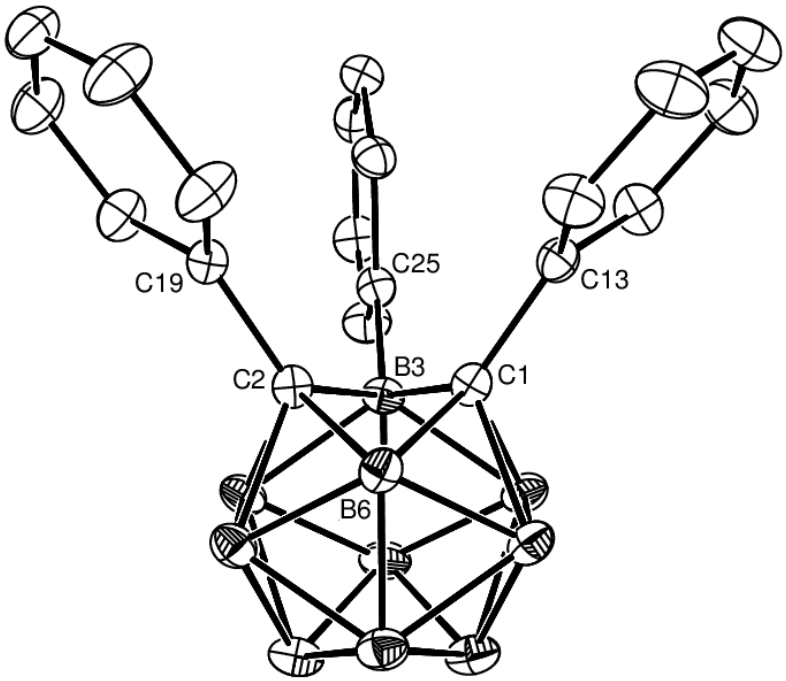

Figure S13. ORTEP drawing (30% probability for thermal ellipsoids) of **1** (the hydrogen atoms are omitted for clarity).

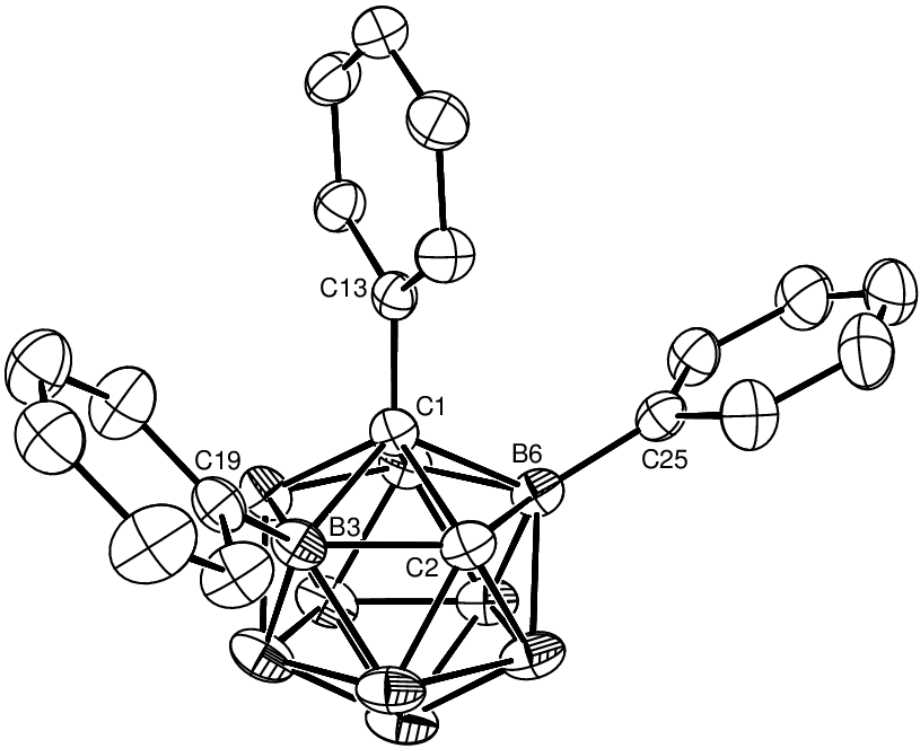

Figure S14. ORTEP drawing (30% probability for thermal ellipsoids) of **2** (the hydrogen atoms are omitted for clarity).

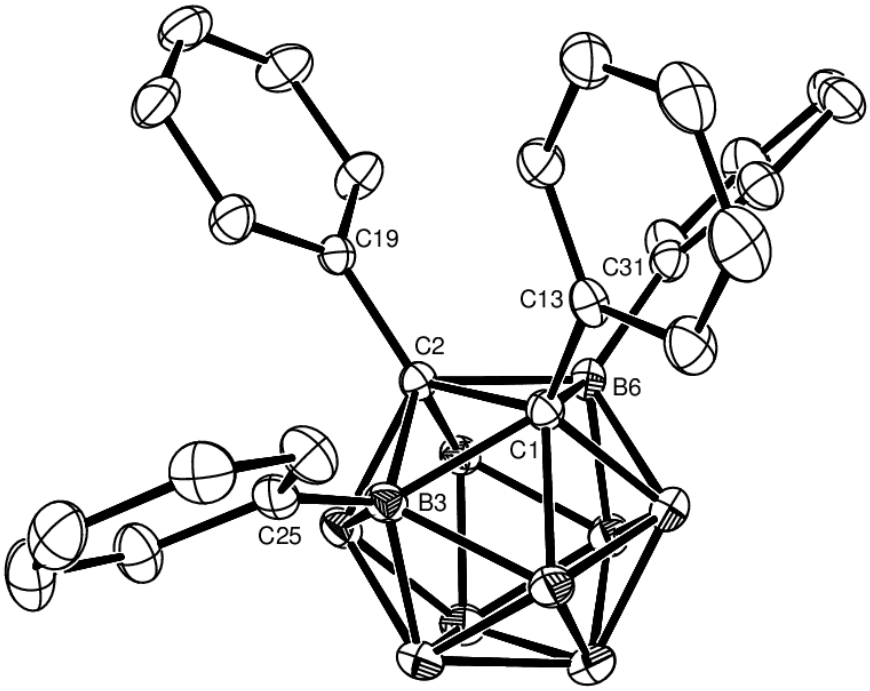

Figure S15. ORTEP drawing (30% probability for thermal ellipsoids) of **3** (the hydrogen atoms are omitted for clarity).

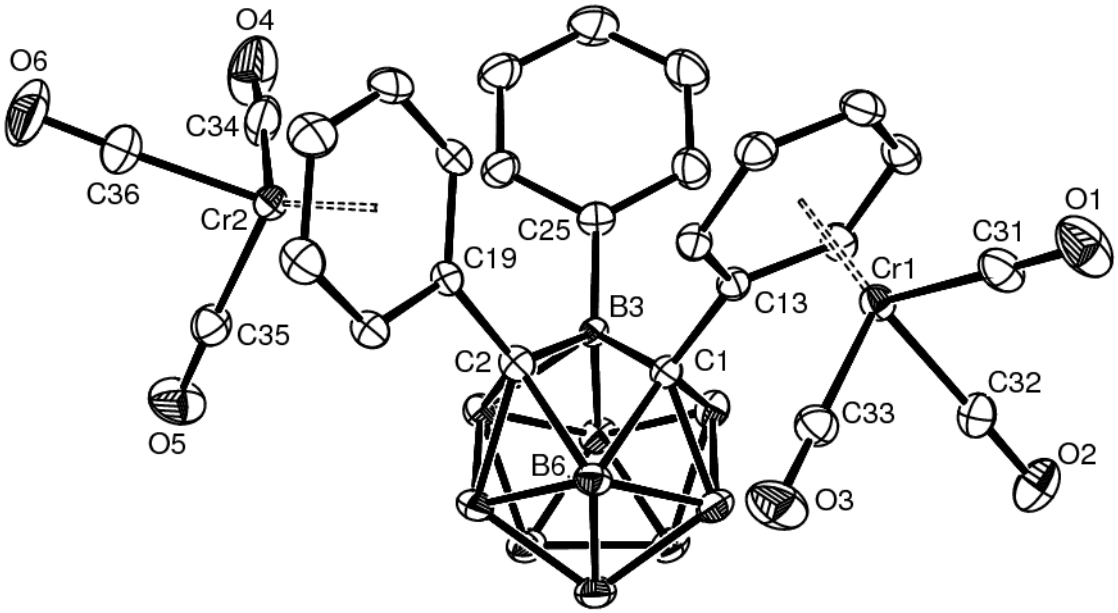

Figure S16. ORTEP drawing (30% probability for thermal ellipsoids) of **4** (the hydrogen atoms are omitted for clarity).

Table S1. Crystal data and structure refinement

	1	**2**	**3**	**4**
Identification code	k110211	k111101	k120303	k120304
Empirical formula	C_{20} H_{24} B_{10}	C_{20} H_{24} B_{10}	C_{26} H_{28} B_{10}	C26 H24 B10 Cr2 O6
Formula weight	372.49	372.49	448.58	644.55
Temperature	293(2) K	293(2) K	293(2) K	293(2) K
Wavelength	0.71073 A	0.71073 Å	0.71073 Å	0.71073 A
Crystal system, space group	Monoclinic, $P2_12_12_1$	Monoclinic, $P2_1$/n	Monoclinic, $P2_1$/c	Monoclinic, P 21/c
Unit cell dimensions	a = 8.2745(7) Å b = 15.5626(13) Å c = 16.2094(14) Å	a = 12.5359(8) Å b = 12.9150(8) Å c = 13.3882(8) Å	a = 18.545(3) Å b = 10.3481(15) Å c = 13.6761(19) Å	a = 16.531(3) Å b = 11.276(2) Å c = 15.770(3) Å
Volume	2087.3(3) $Å^3$	2137.1(2) $Å^3$	2484.3(6) $Å^3$	2929.1(9) $Å^3$
Z, D_{calc}	4, 1.185 g/cm^3	4, 1.158 g/cm^3	4, 1.199 g/cm^3	4, 1.462 g/cm^3
F(000)	776	776	936	1304
Crystal size	0.10 × 0.08 × 0.05 mm	0.40 × 0.20 × 0.20 mm	0.2 × 0.15 × 0.1 mm	0.3 × 0.2 × 0.15 mm
θ range for data collection	1.81 to 28.34º	2.06 to 28.36º	1.16 to 28.43º	1.24 to 28.31º
Limiting indices	−11≤h≤10, −20≤k≤20, −21≤l≤21	−16≤h≤16, −17≤k≤17, −17≤l≤17	−24≤h≤24, −13≤k≤13, −18≤l≤18	−22≤h≤22, −15≤k≤14, −20≤l≤21
Reflections collected / unique	21438 / 5180 [R(int) = 0.0326]	28537 / 5335 [R(int) = 0.0335]	24319 / 6192 [R(int) = 0.0750]	29354 / 7259 [R(int) = 0.0281]
Completeness to θ = 25.96	99.9 %	99.8 %	99.0 %	99.6 %
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5180 / 0 / 271	5335 / 0 / 280	6192 / 0 / 333	7259 / 0 / 406
Goodness-of-fit on F^2	1.019	1.054	1.055	1.060
Final R indices [I>2θ(I)]	[a]R_1 = 0.0427, [b]wR_2 = 0.1155	[a]R_1 = 0.0592, [b]wR_2 = 0.1565	[a]R_1 = 0.0758, [b]wR_2 = 0.1846	R_1 = 0.0422, wR_2 = 0.1228
R indices (all data)	[a]R_1 = 0.0458, [b]wR_2 = 0.1190	[a]R_1 = 0.0770, [b]wR_2 = 0.1759	[a]R_1 = 0.1346, [b]wR_2 = 0.2137	R_1 = 0.0558, wR_2 = 0.1359
Largest diff. peak and hole	0.263 and −0.191 e.$Å^{-3}$	0.270 and −0.305 e.$Å^{-3}$	0.292 and −0.269 e.$Å^{-3}$	0.782 and −0.574 e.$Å^{-3}$

[a]$R_1 = \sum||F_o|-|F_c|| / \sum|F_o|$ (based on reflections with $F_o^2 > 2\sigma F^2$), [b]$wR_2 = [\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2)+(0.095P)^2]$; , $P = [\max(F_o^2, 0)+2F_c^2]/3$(also with $F_o^2 > 2\sigma F^2$)

Table S2. Selected bond lengths [Å] and torsion angles[º] for **1**, **2**, **3**, and **4**

	Bond lengths [Å]		Torsion angles[º]	
1	C(1)-C(13)	1.519	C13-C18 vs C19-C24	88.73(6)
	C(1)-C(2)	1.763	C19-C24 vs C25-C30	41.27(5)
	C(2)-C(19)	1.515	C25-C30 vs C13-C18	50.05(6)
2	C(1)-C(13)	1.501	C13-C18 vs C19-C24	49.12(7)
	C(1)-C(2)	1.632	C19-C24 vs C25-C30	71.27(6)
			C25-C30 vs C13-C18	68.07(5)
3	C(1)-C(13)	1.520	C13-C18 vs C19-C24	67.06(1)
	C(1)-C(2)	1.704	C25-C30 vs C31-C36	26.43(1)
	C(2)-C(19)	1.513	C25-C30 vs C13-C18	85.20(8)
4	C(1)-C(13)	1.512	C13-C18 vs C19-C24	42.86(8)
	C(1)-C(2)	1.777	C25-C30 vs C13-C18	82.24(9)
	C(2)-C(19)	1.581	C19-C24 vs C25-C30	57.43(9)

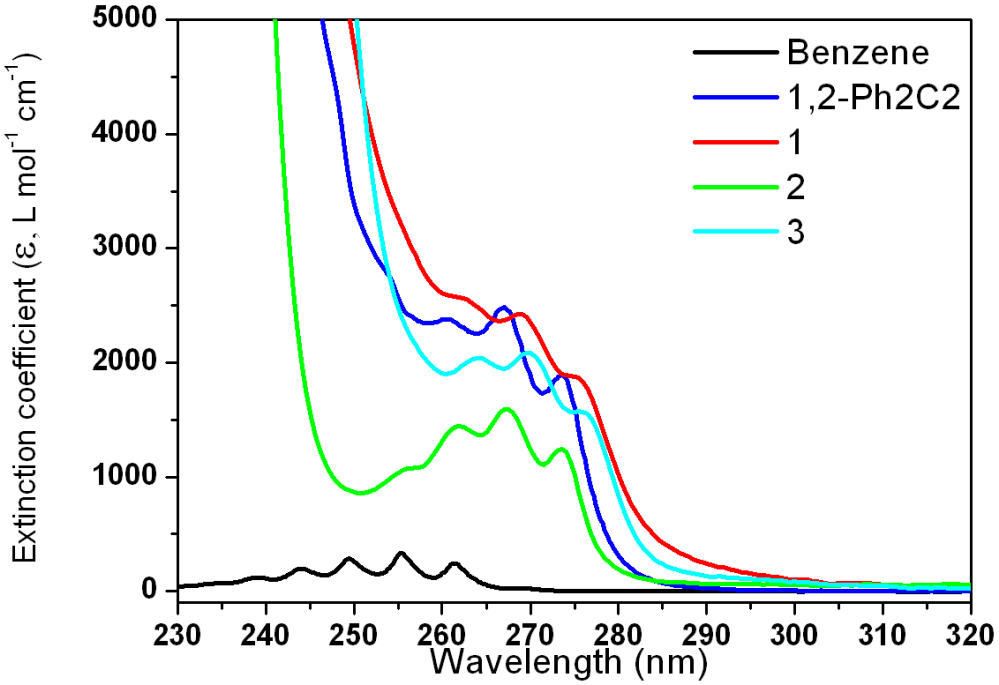

Figure S17. UV-vis absorption spectra of benzene, Ph2C2, **1**, **2**, and **3** in hexane solution at room temperature.

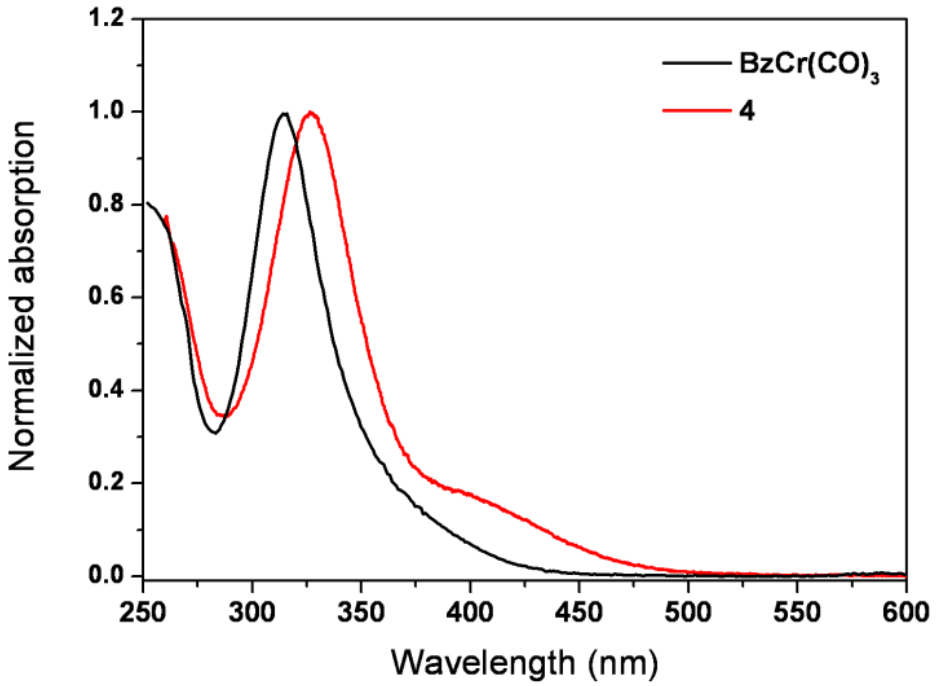

Figure S18. UV-vis absorption spectra of **4** and [(η^6-Bz)Cr(CO)$_3$](forcomparison) in hexane solution at room temperature.

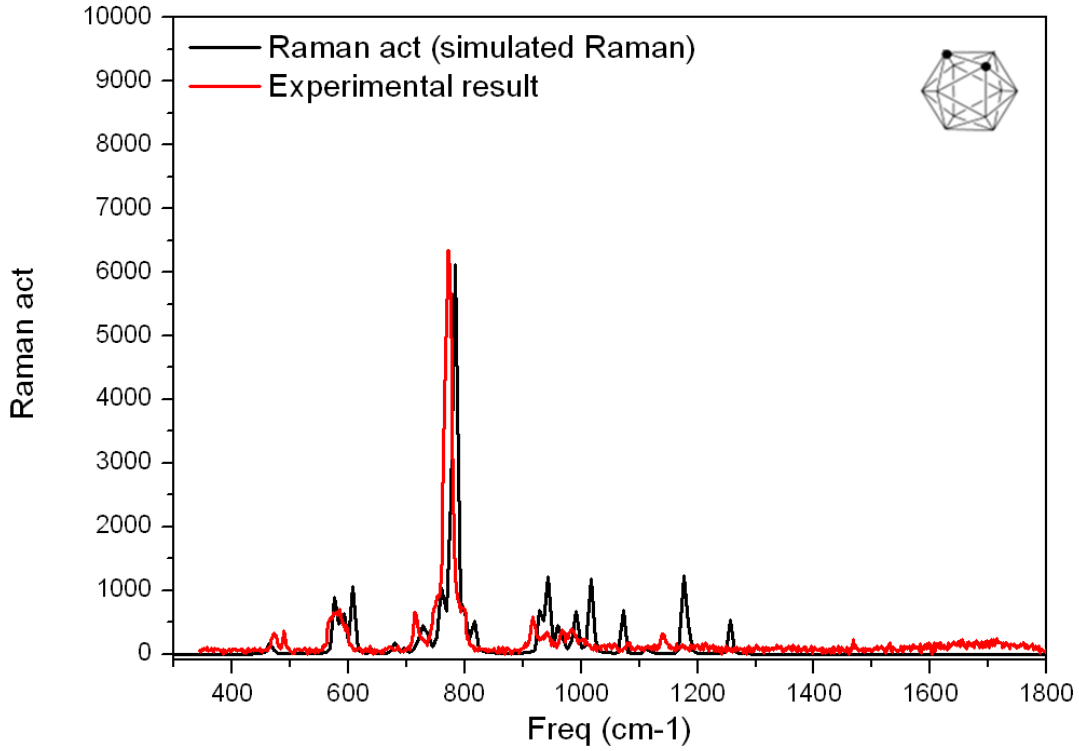

Figure S19. Simulated and experimental Raman spectra of o-carborane at room temperature.

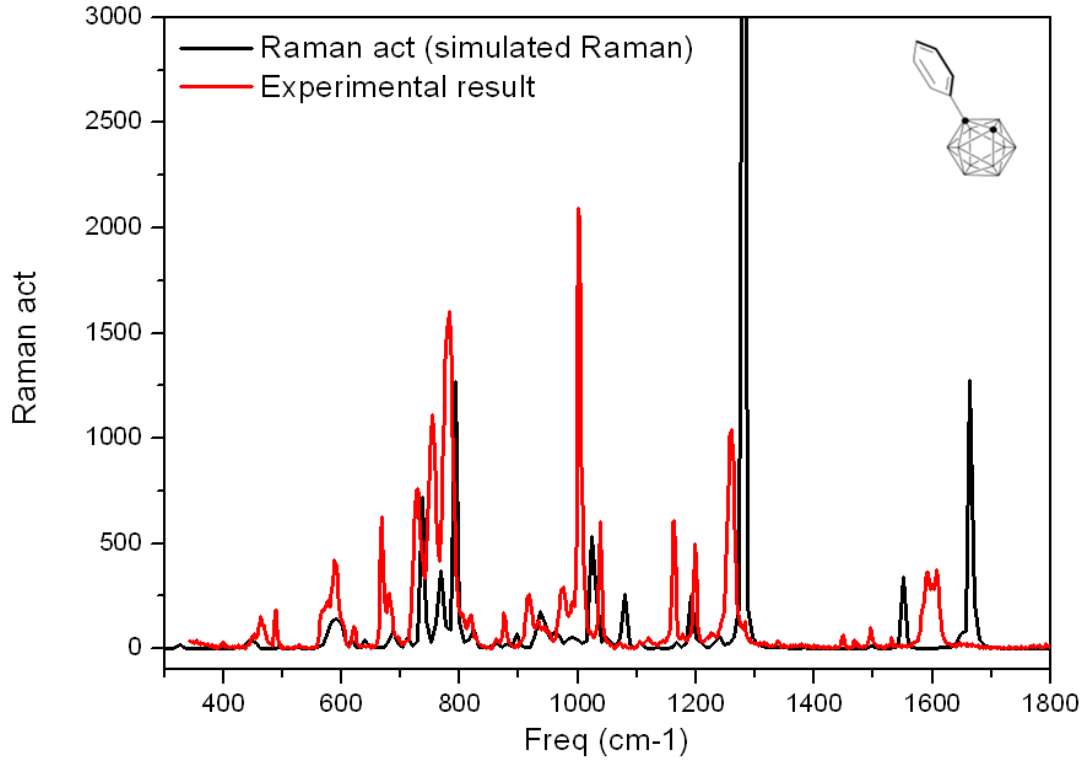

Figure S20. Simulated and experimental Raman spectra of PhC at room temperature.

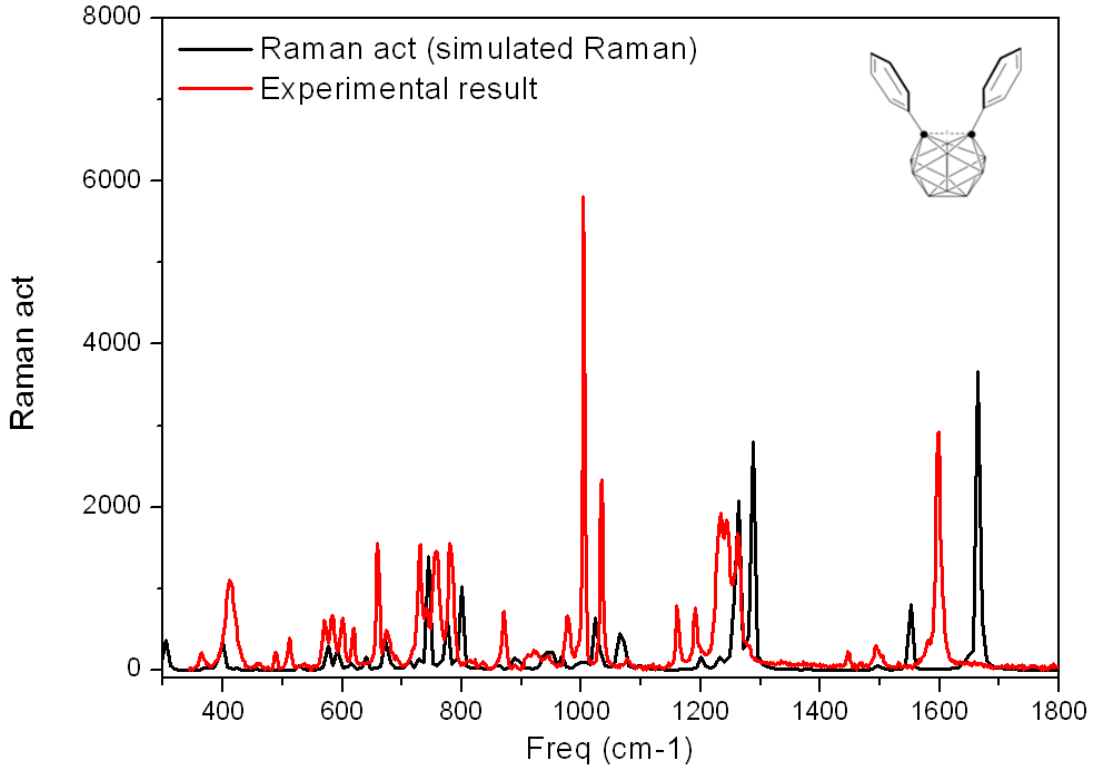

Figure S21. Simulated and experimental Raman spectra of Ph2C2 at room temperature.

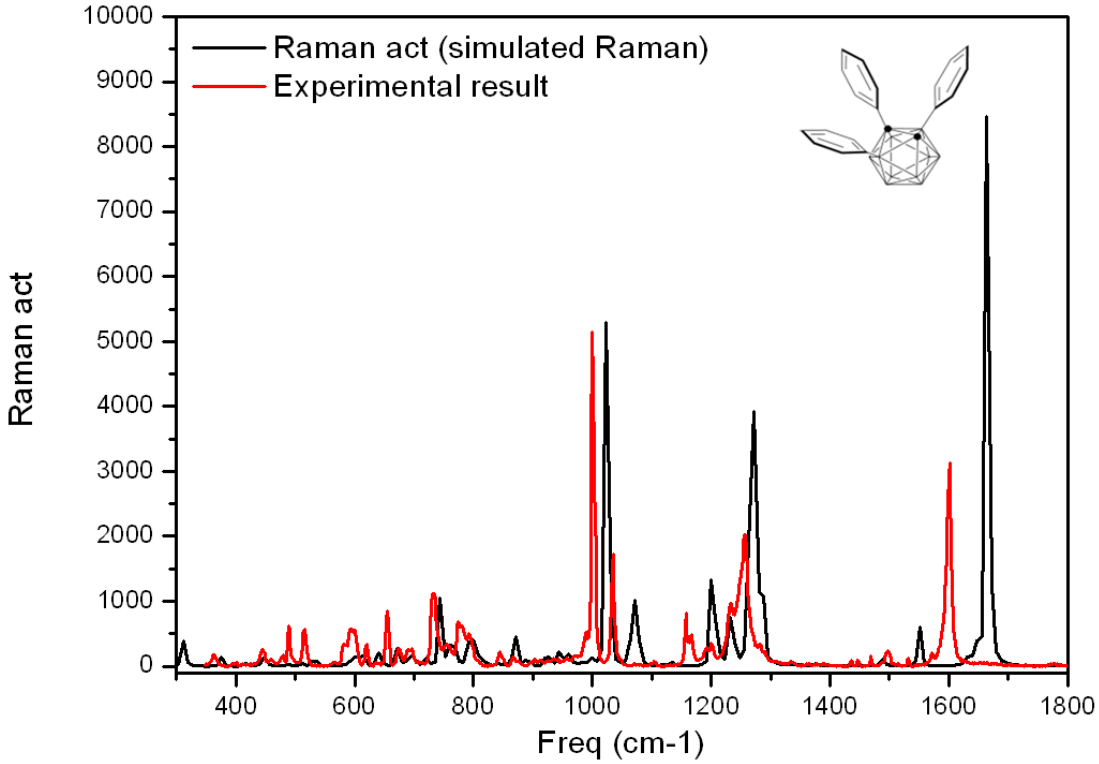

Figure S22. Simulated and experimental Raman spectra of **2** at room temperature.

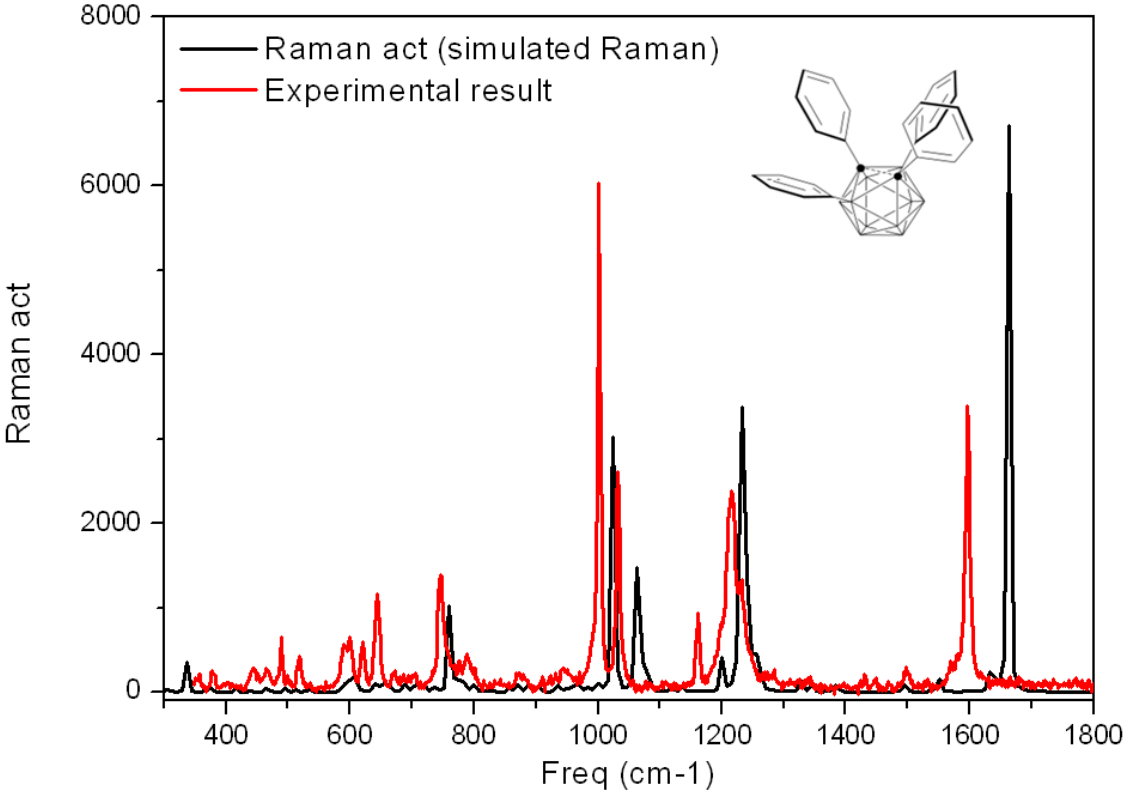

Figure S23. Simulated and experimental Raman spectra of **3** at room temperature.

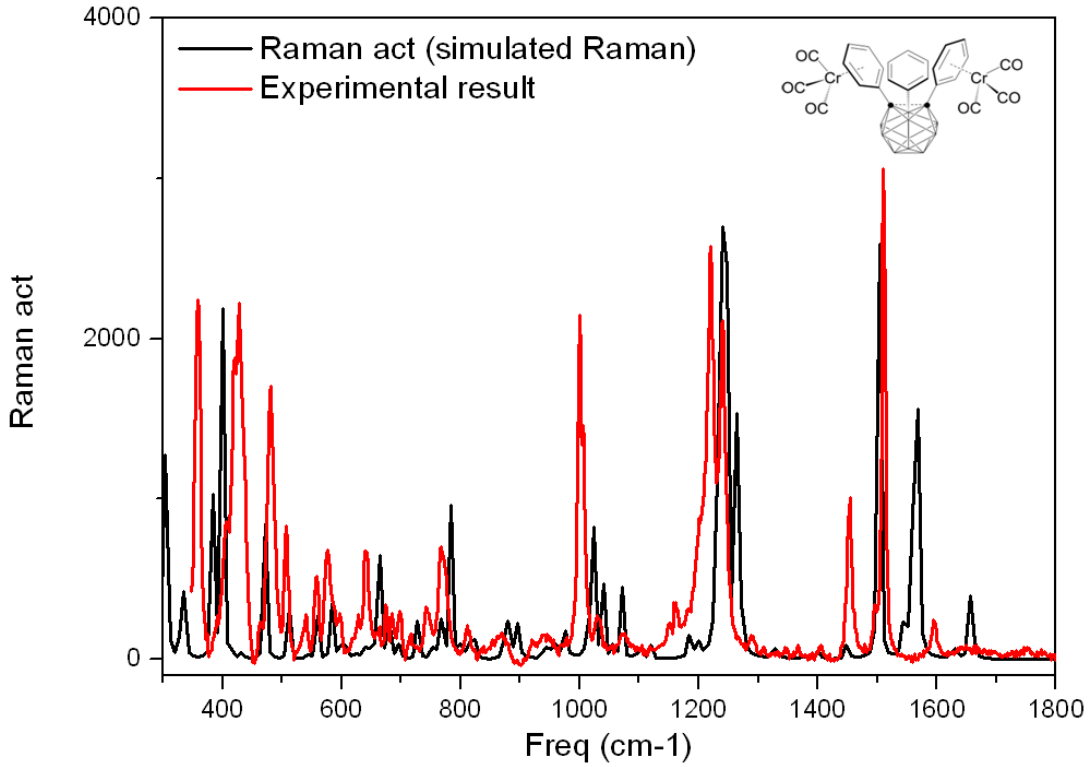

Figure S24. Simulated and experimental Raman spectra of **4** at room temperature.

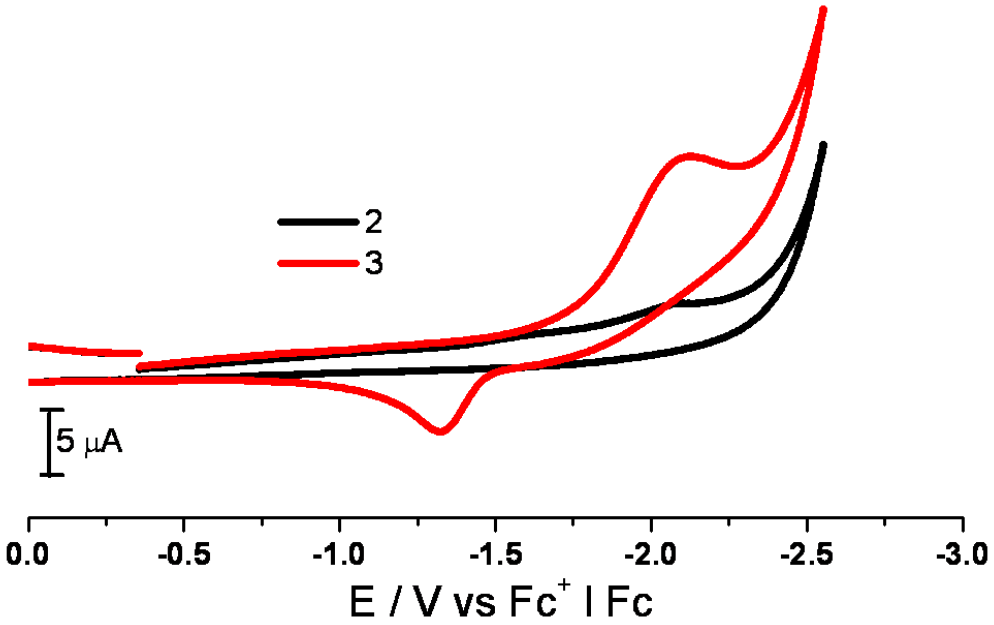

Figure S25. Cyclic Voltammetry for **2**(black)and**3**(red) (TBAP (0.1 M)/sample (1 mM), Scan rate: 100 mV/s, Solvent: CH_2Cl_2).

Table S3. Ground state optimized geometry of **1** obtained by DFT calculation[a]

No	Atom	X	Y	Z
1	C	1.127132	-0.003382	0.892335
2	C	0.282717	0.947058	-1.711569
3	C	-1.222469	2.643295	3.388872
4	C	1.127947	-0.001597	-0.891210
5	C	-1.218663	2.650355	-3.384910
6	C	0.511149	2.327595	1.731370
7	C	-1.448877	1.267271	3.395581
8	C	0.281006	0.943551	1.713779
9	C	0.514617	2.330841	-1.727829
10	C	-0.232803	3.173134	-2.549796
11	C	-0.237309	3.168123	2.554231
12	C	-1.446730	1.274615	-3.393051
13	C	-0.706447	0.432385	-2.566520
14	C	-0.707594	0.426823	2.568151
15	B	1.410908	-1.593651	1.434038
16	B	2.466108	0.625400	0.001749
17	B	0.356885	-1.316083	-0.000926
18	B	3.707108	-0.632939	0.001026
19	B	2.705497	-0.378087	-1.439474
20	B	2.704254	-0.380818	1.441209
21	B	3.043420	-2.029996	0.885438
22	B	1.607574	-2.600913	-0.001666
23	B	1.411995	-1.590858	-1.435609
24	B	3.044115	-2.028336	-0.886600
25	H	1.292265	2.757600	1.120715
26	H	-2.205011	0.839478	4.046550
27	H	1.296431	2.759189	-1.116897
28	H	-0.031069	4.239927	-2.541742
29	H	-0.036927	4.235178	2.547212
30	H	-2.203354	0.848418	-4.044497
31	H	-0.900495	-0.631247	-2.588786
32	H	-0.900476	-0.637044	2.589213
33	H	0.893167	-1.933508	2.439731
34	C	-1.204199	-1.593500	-0.001926
35	H	0.895109	-1.928731	-2.442434
36	H	1.277571	-3.738946	-0.002934
37	H	3.714611	-2.756189	-1.539467
38	H	3.713397	-2.759109	1.537435
39	H	3.044124	0.151676	2.440647
40	H	2.677620	1.781870	0.003112
41	H	3.046149	0.156250	-2.437664
42	H	4.852880	-0.329751	0.001790
43	H	-1.800961	3.298084	4.033534
44	H	-1.796367	3.306508	-4.028892
45	C	-1.643722	-2.931843	-0.004574
46	C	-2.999963	-3.259312	-0.005696
47	C	-3.963854	-2.251661	-0.004216
48	C	-3.556939	-0.917173	-0.001637
49	C	-2.199760	-0.596316	-0.000520
50	H	-0.913032	-3.733324	-0.005817
51	H	-3.300564	-4.303193	-0.007741
52	H	-5.020805	-2.502742	-0.005093
53	H	-4.295782	-0.120739	-0.000517
54	H	-1.919229	0.450164	0.001420

[a]Cartesian coordinates

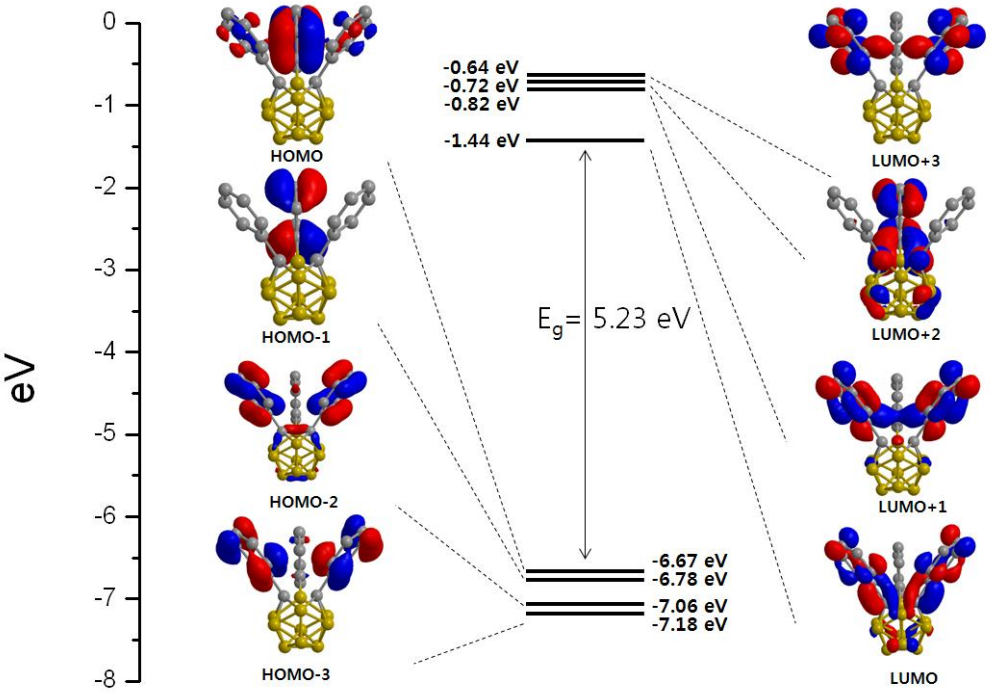

Figure S26. Energy levels and isodensity plots (isodensity contour = 0.03 a.u.) for selected occupied and unoccupied molecular orbitals of **1** obtained by DFT calculations.

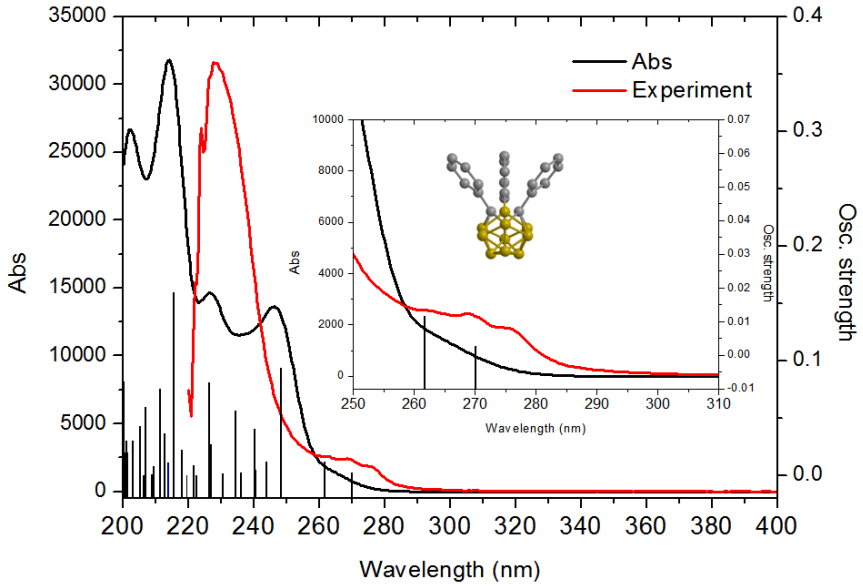

Figure S27. Simulated absorption spectra and oscillator strengths of **1** obtained by TDDFT calculations.

Table S4. Calculated electronic transitions and oscillator strengths of **1**

No.	Wavelength (nm)	Osc. Strength	Major contribs
1	270.022	0.0026	HOMO->LUMO (97%)
2	261.623	0.0116	H-1->LUMO (98%)
3	248.165	0.0935	H-2->LUMO (79%)
4	243.754	0.0115	H-5->LUMO (13%), H-3->LUMO (66%)
5	240.398	0.0044	H-1->L+2 (35%), HOMO->L+2 (25%), HOMO->L+4 (15%)
6	240.096	0.0403	H-4->LUMO (37%), H-2->LUMO (15%), HOMO->L+1 (29%)
7	236.046	0.0021	H-4->LUMO (32%), HOMO->L+1 (63%)
8	234.448	0.0564	H-5->LUMO (68%), H-3->LUMO (17%)
9	230.422	0.0013	H-1->L+1 (98%)
10	226.955	0.0266	HOMO->L+3 (85%)
11	226.213	0.0805	H-1->L+2 (20%), HOMO->L+2 (51%), HOMO->L+4 (12%)
12	222.379	0.0	H-1->L+3 (87%)
13	221.529	0.0088	H-4->L+1 (30%), H-2->L+1 (25%), H-2->L+3 (19%)
14	219.486	0.0	H-3->L+1 (15%), H-2->L+2 (58%)
15	217.877	0.0223	H-5->L+1 (13%), H-3->L+1 (23%), H-2->L+2 (38%)
16	215.503	0.1597	H-1->L+2 (20%), HOMO->L+4 (49%)
17	213.635	0.0111	H-1->L+4 (54%)
18	212.788	0.0364	H-3->L+2 (46%), H-2->L+1 (17%)
19	211.236	0.0753	H-5->L+2 (10%), H-3->L+2 (34%), H-2->L+1 (23%)
20	209.286	0.0076	H-6->LUMO (12%), H-5->L+1 (33%), H-3->L+1 (24%)
21	208.754	0.0007	H-6->LUMO (85%)
22	206.835	0.059	H-5->L+2 (60%), H-1->L+4 (13%)
23	206.411	0.0	H-4->L+2 (87%)
24	205.066	0.0427	H-5->L+3 (15%), H-3->L+3 (16%), H-2->L+4 (53%)
25	202.955	0.0301	H-4->L+3 (26%), H-3->L+4 (41%), H-2->L+3 (17%)
26	201.435	0.0198	H-7->LUMO (54%), H-5->L+3 (15%), H-4->L+4 (11%)
27	200.864	0.0304	H-7->LUMO (41%), H-4->L+4 (23%), H-3->L+3 (14%)
28	200.454	0.0198	H-5->L+4 (27%), H-3->L+4 (11%), HOMO->L+5 (27%)
29	200.315	0.0812	H-5->L+4 (10%), H-4->L+3 (12%), H-1->L+6 (17%)
30	198.850	0.0235	H-8->LUMO (90%)

Table S5. Ground state optimized geometry of **2** obtained by DFT calculation[a]

No	Atom	X	Y	Z
1	C	-0.000041	-1.138154	0.824994
2	C	-0.000053	1.080676	-0.746108
3	C	-0.000045	-0.423678	-0.630365
4	C	-0.000040	3.877113	-1.053473
5	H	-0.000301	-0.479383	1.681918
6	C	-0.000256	1.923204	0.372627
7	C	-0.000242	3.308603	0.219312
8	C	0.000140	3.046421	-2.173654
9	C	0.000136	1.661060	-2.022853
10	B	-0.886876	-2.587785	0.870542
11	B	1.501671	-1.195406	-0.056411
12	B	-1.501715	-1.195595	-0.056673
13	B	1.451202	-2.804806	-0.797995
14	B	0.891020	-1.394516	-1.720647
15	B	0.886914	-2.587718	0.870728
16	B	0.000139	-3.674054	-0.217441
17	B	-1.450928	-2.805022	-0.798249
18	B	-0.890790	-1.394659	-1.720843
19	B	0.000235	-2.926857	-1.833144
20	H	-0.000450	1.516548	1.376387
21	H	-0.000400	3.941410	1.101362
22	H	0.000291	3.473673	-3.171768
23	H	0.000282	1.028810	-2.902544
24	H	-1.462890	-2.857999	1.868067
25	C	-2.717801	-0.311422	0.399908
26	H	-1.469146	-0.849812	-2.596550
27	H	-2.477479	-3.340457	-1.050397
28	H	0.000404	-3.551085	-2.841100
29	H	0.000255	-4.845730	-0.037682
30	H	1.462806	-2.857766	1.868366
31	C	2.717714	-0.311224	0.400232
32	H	1.469384	-0.849630	-2.596323
33	H	2.477819	-3.340140	-1.050091
34	H	-0.000029	4.956407	-1.170930
35	C	-3.578774	0.281707	-0.540114
36	C	-4.673835	1.046002	-0.138507
37	C	-4.935612	1.236224	1.219004
38	C	-4.098190	0.652709	2.170507
39	C	-3.006082	-0.112294	1.761957
40	H	-3.391798	0.142081	-1.600341
41	H	-5.323419	1.491978	-0.886222
42	H	-5.788777	1.830577	1.533272
43	H	-4.298241	0.787554	3.229708
44	H	-2.378930	-0.575107	2.519932
45	C	3.579695	0.280455	-0.539783
46	C	4.674777	1.044717	-0.138180
47	C	4.935570	1.236359	1.219323
48	C	4.097148	0.654281	2.170824
49	C	3.005015	-0.110690	1.762276
50	H	3.393505	0.139671	-1.599996
51	H	5.325154	1.489558	-0.885883
52	H	5.788744	1.830698	1.533590
53	H	4.296427	0.790224	3.230030
54	H	2.377086	-0.572391	2.520290

[a]Cartesian coordinates

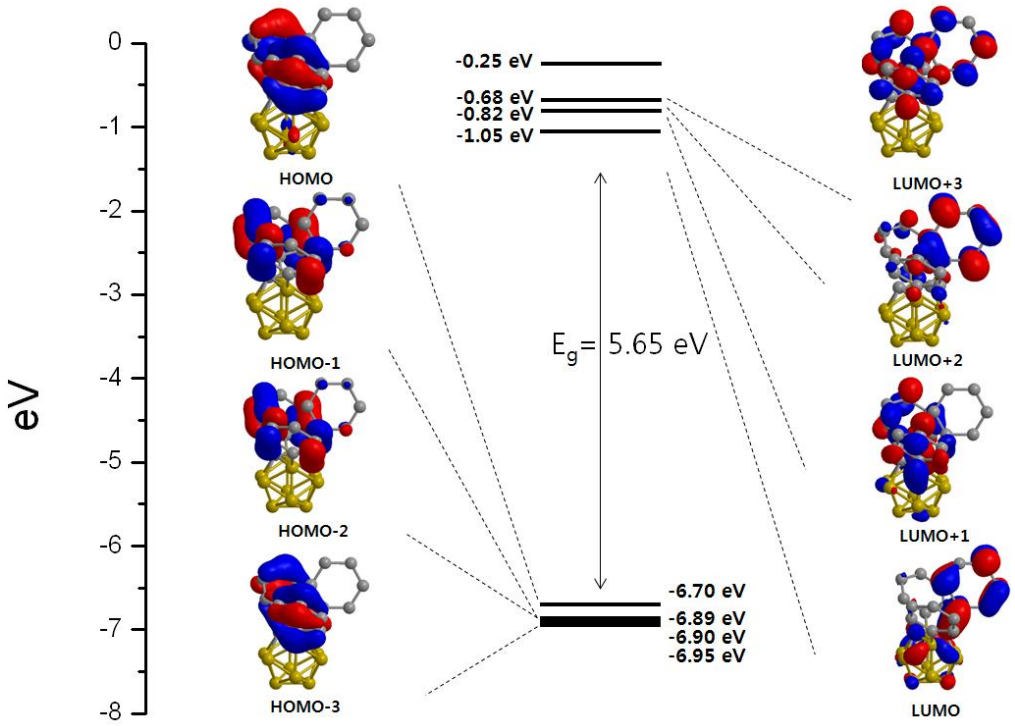

Figure S28. Energy levels and isodensity plots (isodensity contour = 0.03 a.u.) for selected occupied and unoccupied molecular orbitals of **2** obtained by DFT calculations.

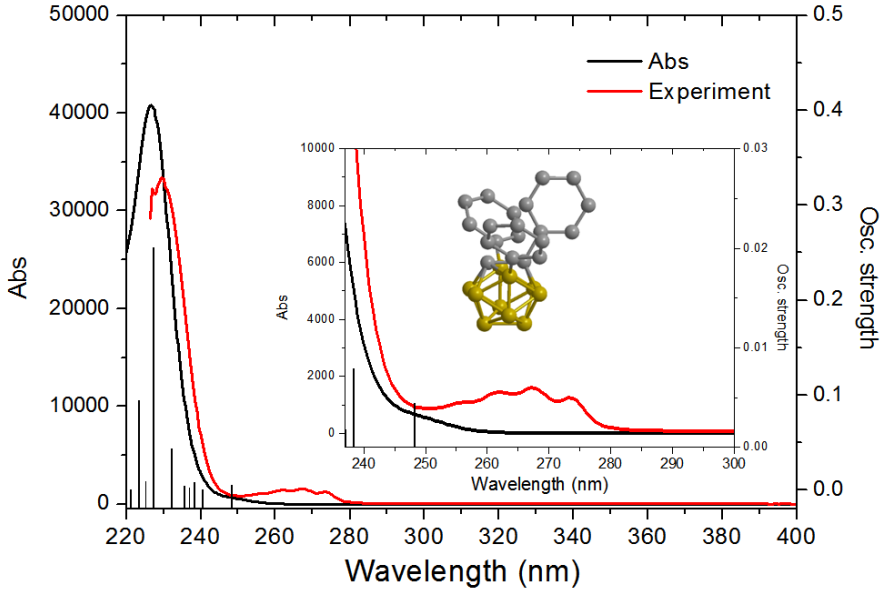

Figure S29. Simulated absorption spectra and oscillator strengths of **2** obtained by TDDFT calculations.

Table S6. Calculated electronic transitions and oscillator strengths of **2**

No.	Wavelength (nm)	Osc. Strength	Major contribs
1	248.269	0.0044	HOMO->LUMO (89%)
2	240.389	0.0	H-3->LUMO (24%), H-2->LUMO (24%), H-1->L+1 (21%)
3	238.379	0.0079	H-5->LUMO (13%), H-4->L+2 (10%), H-1->LUMO (62%)
4	236.948	0.0018	H-5->LUMO (20%), H-4->L+2 (12%), H-2->L+1 (23%)
5	235.642	0.0041	H-3->LUMO (44%), H-2->LUMO (52%)
6	232.204	0.0437	H-3->LUMO (30%), H-2->LUMO (20%), H-1->L+1 (21%)
7	232.122	0.0002	H-5->LUMO (18%), H-2->L+1 (16%), H-1->LUMO (30%)
8	227.333	0.2555	H-1->L+1 (11%), HOMO->L+1 (80%)
9	225.235	0.0088	HOMO->L+2 (79%)
10	223.421	0.0942	H-4->LUMO (67%)
11	221.161	0.0002	H-4->L+1 (87%)
12	218.376	0.0288	H-3->L+1 (14%), H-2->L+1 (21%), H-1->L+2 (51%)
13	217.904	0.0136	H-2->L+2 (69%), H-1->L+1 (10%)
14	215.998	0.0875	H-3->L+2 (83%)
15	215.844	0.0368	H-3->L+1 (64%), H-1->L+2 (19%)
16	213.055	0.0056	H-5->L+1 (95%)
17	207.743	0.029	H-4->L+2 (11%), HOMO->L+3 (49%)
18	206.966	0.0	H-5->L+2 (11%), H-2->L+1 (13%), H-1->L+3 (49%)
19	206.856	0.001	H-2->L+3 (56%), H-1->L+1 (18%), HOMO->L+4 (11%)
20	206.181	0.0115	H-5->L+2 (10%), H-4->L+2 (40%), H-4->L+3 (28%)
21	202.497	0.1261	H-5->L+2 (32%), H-5->L+3 (10%), HOMO->L+3 (11%)
22	200.047	0.0079	H-3->L+3 (73%), H-1->L+4 (13%)
23	197.936	0.0083	H-3->L+4 (32%), HOMO->L+5 (49%)
24	197.542	0.0015	H-3->L+5 (36%), HOMO->L+4 (46%)
25	196.350	0.017	H-4->L+4 (68%), H-1->L+4 (21%)
26	195.940	0.005	H-4->L+3 (36%), H-4->L+5 (32%), H-1->L+5 (13%)
27	195.252	0.0	HOMO->L+6 (93%)
28	194.367	0.0045	H-2->L+4 (39%), H-1->L+5 (36%)
29	194.027	0.0014	H-4->L+4 (27%), H-2->L+5 (36%), H-1->L+4 (25%)
30	191.891	0.0022	H-5->L+3 (37%), H-5->L+5 (17%), H-4->L+5 (16%)

Table S7. Ground state optimized geometry of **3** obtained by DFT calculation[a]

No	Atom	X	Y	Z
1	C	0.000014	0.303492	-1.049524
2	C	0.000014	-1.232773	1.383818
3	C	0.000000	4.305554	0.627617
4	C	-0.000057	-1.140632	-0.137125
5	C	0.000080	-1.560475	4.189391
6	C	0.000036	1.906158	0.965747
7	C	-0.000059	4.097139	-0.751664
8	C	-0.000024	1.684226	-0.418630
9	C	-1.203244	-1.333276	2.100826
10	C	-1.201269	-1.488191	3.486321
11	C	0.000043	3.203154	1.479813
12	C	1.201386	-1.488738	3.486194
13	C	1.203296	-1.333822	2.100698
14	C	-0.000070	2.803443	-1.269987
15	B	0.880385	0.067023	-2.518347
16	B	-1.494663	-0.652196	-1.011390
17	B	1.494620	-0.652131	-1.011349
18	B	-1.436695	-1.613293	-2.504625
19	B	-0.887212	-2.332989	-0.985859
20	B	-0.880392	0.067008	-2.518363
21	B	0.000020	-1.160699	-3.445816
22	B	1.436728	-1.613273	-2.504621
23	B	0.887204	-2.332948	-0.985820
24	B	0.000039	-2.656273	-2.491554
25	H	0.000069	1.076421	1.654960
26	H	-0.000093	4.941838	-1.433830
27	H	-2.150633	-1.289058	1.585397
28	H	-2.149127	-1.558761	4.011276
29	H	0.000092	3.343519	2.556426
30	H	2.149264	-1.559736	4.011054
31	H	2.150661	-1.290035	1.585185
32	H	-0.000109	2.666903	-2.343532
33	H	1.489530	0.990433	-2.934209
34	C	2.880610	-0.186718	-0.399844
35	H	1.464501	-3.124851	-0.324062
36	H	2.472649	-1.918963	-2.992258
37	H	0.000024	-3.742416	-2.967385
38	H	-0.000010	-1.129146	-4.631103
39	H	-1.489491	0.990443	-2.934234
40	C	-2.880657	-0.186782	-0.399888
41	H	-1.464452	-3.124900	-0.324060
42	H	-2.472585	-1.918963	-2.992341
43	H	0.000018	5.313551	1.031053
44	H	0.000115	-1.682137	5.268469
45	C	3.890593	-1.156158	-0.226629
46	C	5.167328	-0.814586	0.216475
47	C	5.479363	0.517611	0.490651
48	C	4.505341	1.497749	0.306173
49	C	3.227653	1.150370	-0.135768
50	H	3.674774	-2.197112	-0.446627
51	H	5.919366	-1.588928	0.338839
52	H	6.473469	0.788971	0.834282
53	H	4.738381	2.540798	0.501181
54	H	2.502480	1.940250	-0.283939
55	C	-3.890591	-1.156252	-0.226582
56	C	-5.167323	-0.814710	0.216565
57	C	-5.479394	0.517482	0.490711
58	C	-4.505410	1.497649	0.306165
59	C	-3.227734	1.150305	-0.135829
60	H	-3.674743	-2.197209	-0.446534
61	H	-5.919320	-1.589080	0.338998
62	H	-6.473491	0.788821	0.834382
63	H	-4.738481	2.540693	0.501160
64	H	-2.502585	1.940202	-0.284026

[a]Cartesian coordinates

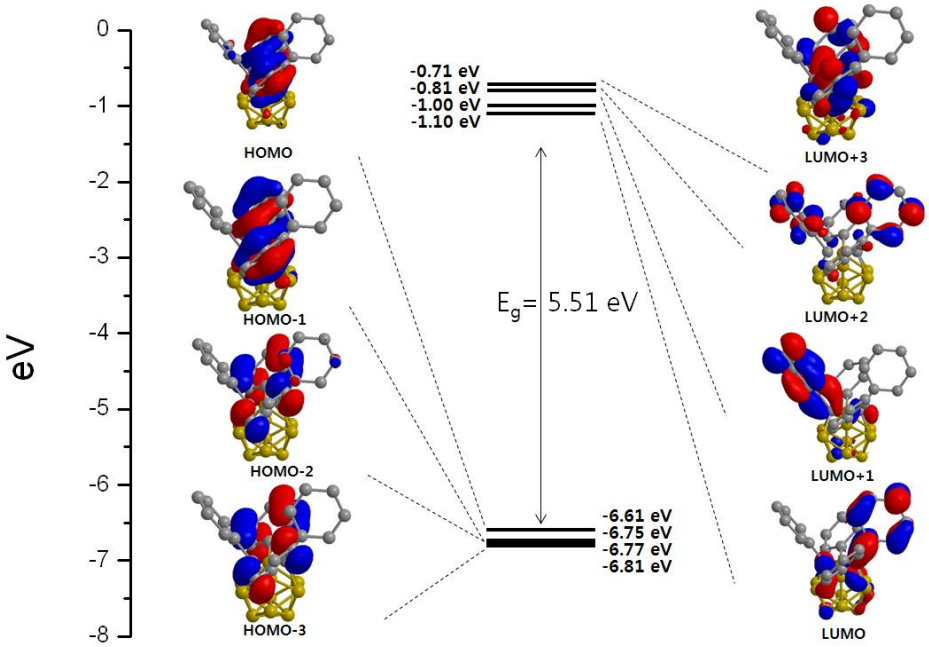

Figure S30. Energy levels and isodensity plots (isodensity contour = 0.03 a.u.) for selected occupied and unoccupied molecular orbitals of **3** obtained by DFT calculations.

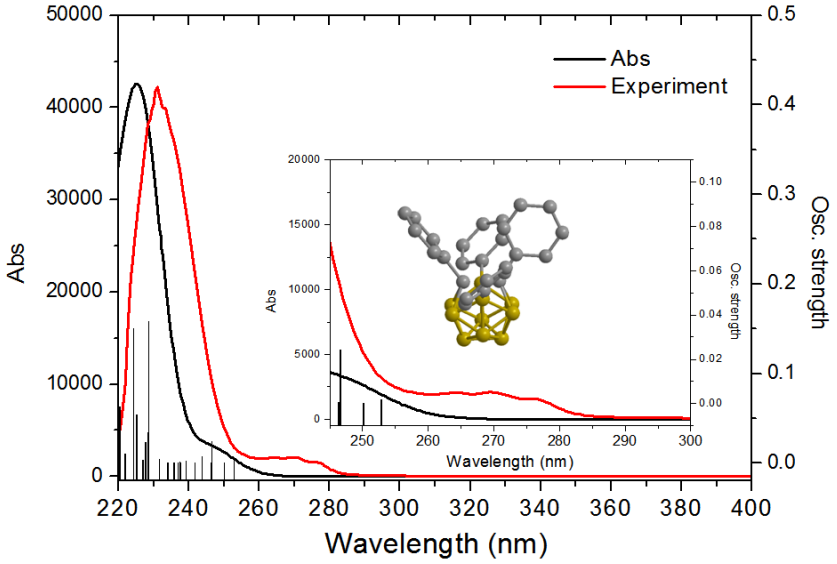

Figure S31. Simulated absorption spectra and oscillator strengths of **3** obtained by TDDFT calculations.

Table S8. Calculated electronic transitions and oscillator strengths of **3**

No.	Wavelength (nm)	Osc. Strength	Major contribs
1	252.913	0.0019	HOMO->LUMO (96%)
2	250.163	0.0001	HOMO->L+1 (96%)
3	246.625	0.0243	H-1->LUMO (88%)
4	246.306	0.0007	H-2->LUMO (67%)
5	243.754	0.0076	H-3->LUMO (60%)
6	241.730	0.0002	H-1->L+1 (80%)
7	239.280	0.0018	H-6->L+1 (25%), H-5->L+2 (15%), H-2->L+1 (39%)
8	239.202	0.0009	H-3->L+3 (13%), H-1->L+1 (16%), HOMO->L+2 (30%)
9	237.716	0.0007	H-6->L+1 (10%), H-2->L+1 (51%)
10	237.379	0.0014	H-7->LUMO (20%), H-6->LUMO (20%), H-4->L+2 (14%)
11	236.966	0.0003	H-3->LUMO (21%), H-2->L+3 (18%), H-1->L+2 (11%)
12	235.862	0.0	H-3->L+1 (98%)
13	234.010	0.0005	H-5->LUMO (98%)
14	231.614	0.0041	H-3->L+3 (14%), H-2->L+2 (22%), HOMO->L+2 (42%)
15	228.658	0.1581	H-3->L+2 (18%), H-1->L+2 (19%), HOMO->L+3 (50%)
16	228.368	0.0337	H-6->LUMO (10%), H-4->LUMO (66%)
17	227.688	0.0231	H-6->L+1 (14%), H-4->L+1 (73%)
18	226.984	0.0029	H-2->L+3 (18%), H-1->L+2 (51%), HOMO->L+3 (16%)
19	225.301	0.0154	H-3->L+3 (13%), H-2->L+2 (40%)
20	225.154	0.054	H-7->LUMO (15%), H-6->LUMO (51%), H-4->LUMO (13%)
21	224.351	0.1499	H-3->L+2 (67%), HOMO->L+3 (19%)
22	221.898	0.0102	H-5->L+1 (17%), H-1->L+3 (39%), HOMO->L+4 (33%)
23	220.371	0.0631	H-6->L+2 (12%), H-5->L+1 (42%), HOMO->L+4 (32%)
24	218.326	0.001	H-4->L+3 (78%)
25	218.311	0.0582	H-1->L+3 (40%), HOMO->L+4 (23%)
26	217.175	0.0016	H-7->L+1 (74%), H-6->L+1 (17%)
27	215.765	0.0024	H-5->L+3 (95%)
28	215.103	0.0746	H-1->L+4 (88%)
29	214.790	0.0104	H-3->L+3 (19%), H-2->L+4 (67%)
30	213.993	0.0	H-4->L+3 (15%), H-3->L+4 (60%), H-2->L+3 (19%)

Table S9. Ground state optimized geometry of **4** obtained by DFT calculation[a]

No	Atom	X	Y	Z
1	C	0.918925	0.239069	1.056342
2	C	-1.692016	-0.123845	-0.186992
3	C	3.108601	-0.722960	-2.597541
4	C	-0.918654	0.238660	1.056320
5	C	-3.107755	-0.724888	-2.597478
6	C	1.657084	-1.420744	-0.764472
7	C	3.202930	0.568001	-2.025895
8	C	1.692501	-0.122987	-0.186995
9	C	-1.657104	-1.421939	-0.763438
10	C	-2.315519	-1.714371	-1.982642
11	C	2.315416	-1.712531	-1.983798
12	C	-3.201595	0.566605	-2.026718
13	C	-2.533797	0.843212	-0.818162
14	C	2.534844	0.844000	-0.817248
15	B	1.440763	1.467252	2.094705
16	B	0.000571	-0.972183	1.873702
17	B	0.000106	1.752828	1.045275
18	B	0.000282	-0.517643	3.590179
19	B	-1.442666	-0.233722	2.609299
20	B	1.443133	-0.232944	2.609639
21	B	0.884558	1.024810	3.725172
22	B	-0.000420	2.237776	2.767457
23	B	-1.441014	1.466563	2.094437
24	B	-0.884845	1.024302	3.725070
25	H	1.118734	-2.212771	-0.264847
26	H	3.833602	1.324483	-2.475923
27	H	-1.119518	-2.213957	-0.262959
28	H	-2.266655	-2.715063	-2.393943
29	H	2.265875	-2.712771	-2.396103
30	H	-3.831649	1.323109	-2.477584
31	H	-2.649543	1.819197	-0.368689
32	H	2.651012	1.819590	-0.367007
33	H	2.439435	2.032521	1.815481
34	C	0.000082	2.782979	-0.160889
35	H	-2.439832	2.031386	1.814841
36	H	-0.000747	3.386803	3.054462
37	H	-1.535691	1.315184	4.671227
38	H	1.535137	1.316135	4.671380
39	H	2.432458	-0.872782	2.650693
40	H	0.000890	-2.077130	1.465959
41	H	-2.431625	-0.874156	2.650268
42	H	0.000488	-1.358742	4.423985
43	H	3.663460	-0.957262	-3.499009
44	H	-3.662421	-0.959504	-3.498980
45	C	-0.000160	4.159098	0.145089
46	C	-0.000013	5.135212	-0.851856
47	C	0.000358	4.764738	-2.196674
48	C	0.000535	3.409947	-2.530848
49	C	0.000395	2.439103	-1.528127
50	H	-0.000465	4.474193	1.182656
51	H	-0.000203	6.185363	-0.574261
52	H	0.000506	5.522091	-2.975340
53	H	0.000780	3.104863	-3.573700
54	H	0.000522	1.397563	-1.828473
55	Cr	3.817277	-0.955504	-0.478991
56	C	5.444334	-1.436728	-1.216901
57	C	4.725562	0.027881	0.804710
58	C	3.913372	-2.444240	0.619980
59	Cr	-3.817403	-0.955121	-0.478701
60	C	-4.723466	0.026950	0.807585
61	C	-3.916112	-2.446178	0.616920
62	C	-5.445613	-1.431257	-1.217357
63	O	-5.277327	0.658979	1.603383
64	O	-6.452545	-1.723818	-1.710358
65	O	-3.951819	-3.387523	1.290352
66	O	5.280784	0.660780	1.598869
67	O	6.450599	-1.732523	-1.709335
68	O	3.947475	-3.384051	1.295629

[a]Cartesian coordinates

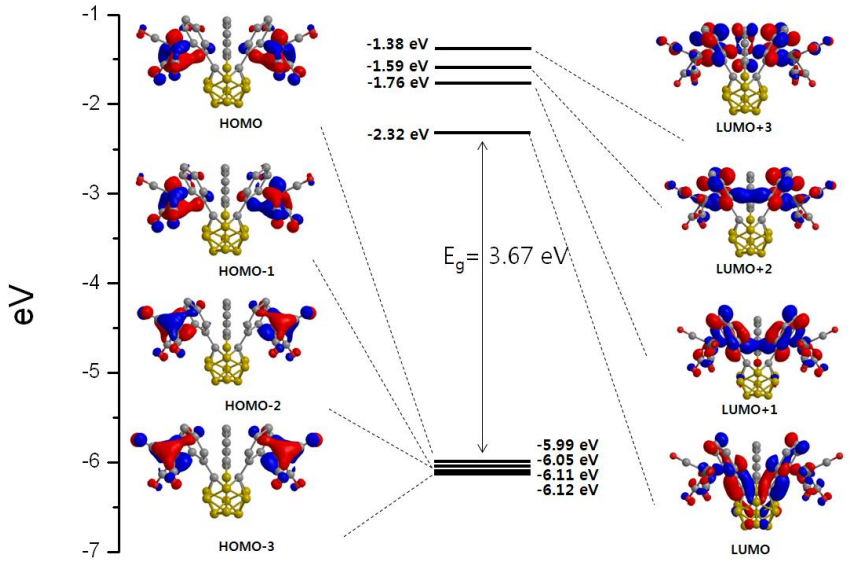

Figure S32. Energy levels and isodensity plots (isodensity contour = 0.03 a.u.) for selected occupied and unoccupied molecular orbitals of **4** obtained by DFT calculations.

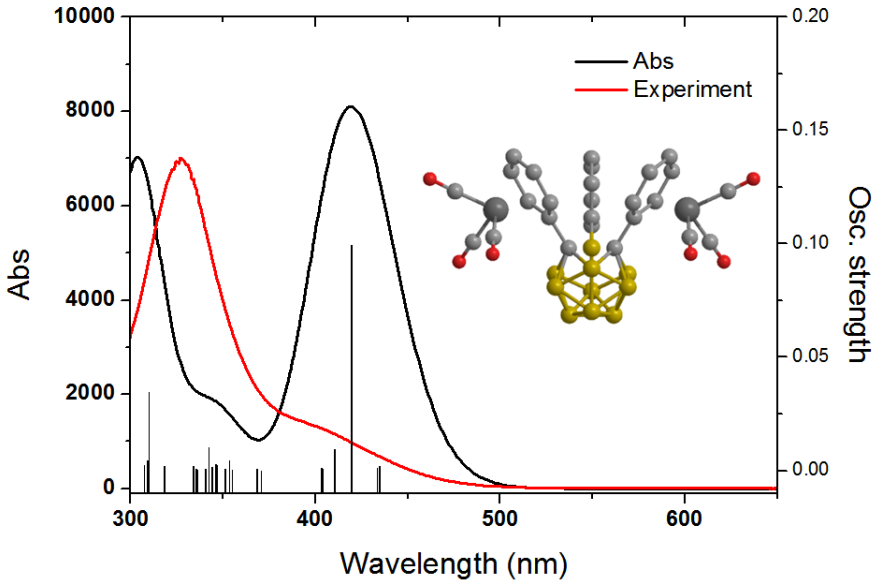

Figure S33. Simulated absorption spectra and oscillator strengths of **1** obtained by TDDFT calculations.

Table S10. Calculated electronic transitions and oscillator strengths of **4**

No.	Wavelength (nm)	Osc. Strength	Major contribs
1	434.861	0.0018	H-3->L+1 (16%), H-2->LUMO (73%)
2	433.538	0.0012	H-3->LUMO (76%), H-2->L+1 (16%)
3	419.670	0.0993	HOMO->LUMO (76%)
4	410.568	0.0094	H-1->LUMO (66%)
5	403.933	0.0006	H-5->L+1 (16%), H-4->LUMO (72%)
6	403.565	0.0012	H-5->LUMO (75%), H-4->L+1 (17%)
7	370.619	0.0	H-1->L+3 (20%), HOMO->L+2 (62%)
8	368.416	0.0006	H-1->L+2 (53%), HOMO->L+3 (28%)
9	354.948	0.0001	H-5->L+7 (11%), HOMO->L+1 (29%)
10	353.520	0.0044	H-5->L+8 (10%), H-4->L+7 (16%), H-1->L+1 (17%)
11	351.217	0.0003	H-4->L+2 (10%), H-3->L+8 (10%), H-2->L+7 (16%)
12	351.108	0.0005	H-5->L+2 (10%), H-3->L+7 (16%), H-2->L+8 (11%)
13	346.758	0.0024	H-5->L+7 (12%), H-4->L+8 (11%), HOMO->L+1 (13%)
14	346.138	0.0027	H-4->L+2 (12%), HOMO->L+5 (10%)
15	344.073	0.0014	H-5->L+2 (13%), HOMO->L+1 (24%)
16	342.476	0.0101	H-1->L+1 (37%)
17	340.641	0.0005	H-3->L+6 (10%), HOMO->L+7 (13%)
18	340.520	0.0001	H-2->L+1 (12%)
19	336.335	0.0001	H-3->LUMO (12%), H-2->L+1 (49%)
20	335.652	0.0005	H-5->L+2 (10%), H-3->L+1 (48%), H-2->LUMO (10%)
21	333.979	0.0001	H-5->L+3 (14%), H-4->L+2 (23%), H-2->L+1 (10%)
22	333.916	0.002	H-5->L+2 (21%), H-4->L+3 (13%), H-3->L+1 (16%)
23	318.649	0.0	H-5->LUMO (18%), H-4->L+1 (67%)
24	318.387	0.002	H-5->L+1 (67%), H-4->LUMO (17%)
25	309.942	0.0345	H-2->L+2 (18%), H-2->L+6 (10%)
26	309.169	0.0046	H-3->L+2 (19%), H-3->L+6 (10%)
27	307.384	0.0009	HOMO->L+6 (11%)
28	307.246	0.0024	H-2->L+7 (10%), H-1->L+6 (10%)
29	299.505	0.0419	H-1->L+2 (15%), HOMO->L+3 (25%), HOMO->L+4 (22%)
30	298.532	0.0209	HOMO->L+3 (16%), HOMO->L+4 (44%)

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