Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Modulation of Luminescent Chromic Behaviors and Environment-Responsive Intensity Changes by Substituents in Bis-*o*-carborane-Substituted Conjugated Molecules

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Experimental

General. ^{1}H (400 MHz), ^{11}B (128 MHz) and ^{13}C (100 MHz) NMR measurements were recorded on a JEOL JNM-EX400 instrument. The ^{1}H and ^{13}C NMR spectra used 0.05% Me_4Si as an internal standard. The ^{11}B chemical shift values were expressed relative to $BF_3 \cdot Et_2O$ as an external standard. High-resolution mass spectra (HRMS) were obtained on a Thermo Fisher Scientific EXACTIVE spectrometer for atmospheric pressure chemical ionization (APCI). Analytical thin-layer chromatography (TLC) was performed with silica gel 60 Merck F_{254} plates. Column chromatography was performed with Wakogel C-300 silica gel. In X-ray crystallography, intensity data were collected on a Rigaku R-AXIS RAPID imaging plate area detector with graphite monochromated Mo $K\alpha$ radiation (λ = 0.71069 Å) at –180 °C. The structures were solved by direct method (SIR97)[1] and refined by full-matrix least-squares procedures based on F^2 (SHELX-97).[2] UV–vis absorption spectra were obtained on a SHIMADZU UV3600 spectrophotometer. Photoluminescence (PL) spectra were obtained on a Horiba FluoroMax-4 luminescence spectrometer. Absolute PL quantum efficiencies (Φ_{PL}) were determined using a Horiba FL-3018 Integrating Sphere. Fluorescence lifetime measurement was performed on a Horiba FluoroCube spectrofluorometer system; excitation was carried out using a UV diode laser (NanoLED 375 nm). All computations were carried out with the Gaussian 09 suit program.[3] The molecular geometries were investigated by time-dependent DFT (TDDFT) calculations with the B3LYP/6-31+G(d) level of theory. Cyclic voltammetry (CV) was carried out on a BAS CV-50W electrochemical analyzer in CH_2Cl_2 containing 0.1 M of sample and 0.1 M of Bu_4NPF_6 with a glassy carbon working electrode, a Pt counter electrode, a Ag/AgCl (Ag/Ag+) reference electrode, and a ferrocene/ferrocenium external reference. X-Ray diffraction (XRD) data were obtained on a Rigaku MiniFlex diffractometer using CuKα radiation in a range of $2 \leq 2\theta \leq 50°$ at intervals of 0.01° at a scanning rate of 0.25° min^{-1}.

Materials. All synthetic procedures were performed under Ar atmosphere. Trimethylsilylacetylene, $Pd(PPh_3)_4$, CuI, K_2CO_3, decaborane, *N*,*N*-dimethylaniline, propyne, $PdCl_2(PPh_3)_2$, CH_3CN, $AgNO_3$, THF, ^{i}Pr$_2$NH, NEt_3, MeOH and toluene were obtained commercially and used without purification. 1,4-dibromo-2,5-bis(2'-trimethylsilylethyn-1'-yl)benzene (**2a**) and 1,4-dibromo-2,5-bis(2'-methylethyn-1'-yl)benzene (**2b**) were characterized according to the literatures.[4]

Synthetic procedures

1,4-Dibromo-2,5-bis(2'-trimethylsilylethyn-1'-yl)benzene (2a). The mixture of **1** (4.88 g, 10.0 mmol), $Pd(PPh_3)_4$ (578 mg, 0.50 mmol), and CuI (305 mg, 1.60 mmol) was dissolved in dry THF (100 mL) and ^{i}Pr$_2$NH (20 mL) at room temperature under Ar atmosphere. Trimethylsilylacetylene (2.9 mL, 21.0 mmol) was added, and the mixture was stirred at room temperature for 36 h, then the reaction was quenched by the saturated aqueous NH_4Cl solution. To the mixture $CHCl_3$ was added, and the organic layer was washed with H_2O and brine. The organic layer was dried over $MgSO_4$. After $MgSO_4$ was removed by filtration, the solvent was evaporated. The residue was purified to silica gel column chromatography with hexane ($R_f = 0.48$) as an eluent to give **2a** as a colorless solid (3.56 g, 8.31 mmol, 83%). The identification was performed according to the lieterature.[4a]

1,4-Bis(2'-phenylethyn-1'-yl)-2,5-bis(2"-trimethylsilylethyn-1"-yl)benzene (3a). The mixture of **2a** (3.21 g, 7.50 mmol), $Pd(PPh_3)_4$ (433 mg, 0.37 mmol), and CuI (143 mg, 0.75 mmol) was dissolved in dry THF (75 mL) and NEt_3 (75 mL) at room temperature under Ar atmosphere. Ethynylbenzene (1.9 mL, 17.3 mmol) was added, and the mixture was refluxed at 65 °C for 22 h. After cooling to room temperature, the reaction was quenched by the addition of saturated aqueous NH_4Cl solution. To the mixture $CHCl_3$ was added, and the organic layer was washed with H_2O and brine. The organic layer was dried over $MgSO_4$. After $MgSO_4$ was removed, the solvent was evaporated. The residue was purified to silica gel column chromatography with hexane/$CHCl_3$ (v/v = 9/1, R_f = 0.23) as an eluent to give **3a** as a pale yellow solid (3.11 g, 6.61 mmol, 88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.67 (2H, s, Ar-*H*), 7.62–7.49 (4H, m, Ar-*H*), 7.46–7.30 (6H, m, Ar-*H*), 0.27 (18H, s, Si-C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 135.5, 131.9, 128.9, 128.5, 125.6, 125.5, 123.1, 102.5, 101.1, 95.5, 87.5, 0.1. HRMS (APCI): Calcd. for $C_{32}H_{30}Si_2$ $[M+H]^+$ m/z 471.1959, found m/z 471.1951.

1,4-Diethynyl-2,5-bis(2'-phenylethyn-1'-yl)benzene (3a'). To a solution of **3a** (3.11 g, 6.61 mmol) in 50 mL of THF was added K_2CO_3 (3.65 g, 26.4 mmol) and MeOH (50 mL). The mixture was stirred at room temperature for 4 h, then saturated aqueous NH_4Cl solution was added to quench the reaction. To the mixture $CHCl_3$ was added, and the organic layer was washed with excess H_2O and brine. The organic layer was dried over $MgSO_4$. After $MgSO_4$ was removed, the solvent was evaporated. Recrystallization from $CHCl_3$ and MeOH (good and poor solvent, respectively) to give **3a'** as a pale yellow solid (1.85 g, 5.67 mmol, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.70 (2H, s, Ar-*H*), 7.59–7.52 (4H, m, Ar-*H*), 7.39–7.33 (6H, m, Ar-*H*), 3.45 (2H, s, C≡C−*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 135.8, 132.0, 129.0, 128.6, 125.9, 125.0, 122.9, 95.9, 87.1, 83.2, 81.2.

HRMS (APCI): Calcd. for $C_{26}H_{14}$ $[M+CH_3OH+H]^+$ m/z 359.1430, found m/z 359.1421.

1,4-Di-*o*-carboran-1'-yl-2,5-bis(2"-phenylethyn-1"-yl)benzene (CBH). Decaborane (960 mg, 7.84 mmol) was dissolved in *N,N*-dimethylaniline (1.62 mL, 12.8 mmol) at room temperature under Ar atmosphere. The mixture was stirred for 2 h at room temperature, and then, dry toluene (70 mL) and **3a'** (1.16 g, 3.55 mmol) were added. The mixture was refluxed for 7 d. After cooling to room temperature, solvent was evaporated, and the residue was subjected to silica gel column chromatography with hexane/toluene (v/v = 2/1, $R_f = 0.80$) as an eluent. Recrystallization from THF and EtOH (good and poor solvent, respectively) to give **CBH** (400 mg, 0.71 mmol, 20%) as a colorless solid. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.87 (2H, s, Ar-*H*), 7.57–7.51 (4H, m, Ar-*H*), 7.49–7.40 (6H, m, Ar-*H*), 5.72 (2H, s, carborane_C-*H*), 3.19–1.66 (20H, br, B-*H*). ^1H NMR (400 MHz, THF-d_8): δ (ppm) 7.99 (2H, s, Ar-*H*), 7.62–7.56 (4H, m, Ar-*H*), 7.48–7.42 (6H, m, Ar-*H*), 5.86 (2H, s, carborane_C-*H*), 3.58–1.73 (20H, br, B-*H*). ^{13}C NMR (100 MHz, THF-d_8): δ (ppm) 137.9, 134.0, 132.1, 130.7, 129.5, 122.3, 121.7, 99.5, 87.0, 75.2, 60.4. ^{11}B NMR (128 MHz, THF-d_8): δ (ppm) –3.0, –4.0, –8.9, –10.0. HRMS (APCI): Calcd. for $C_{26}H_{34}B_{20}$ $[M-H]^-$ m/z 565.4563, found m/z 565.4564. Elemental analysis: Calcd. for $C_{26}H_{34}B_{20}$ C 55.49, H 6.09, found C 54.59, H 6.10.

1,4-Dibromo-2,5-bis(2'-methylethyn-1'-yl)benzene (2b). The mixture of **1** (4.88 g, 10.0 mmol), $PdCl_2(PPh_3)_2$ (702 mg, 1.00 mmol), and CuI (609 mg, 3.20 mmol) was dissolved in dry THF (100 mL) and $^iPr_2NH$ (50 mL) at room temperature under Ar atmosphere. Propyne (1M in THF, 23 mL, 23 mmol) was added, and the mixture was stirred at room temperature for 36 h, then the reaction was quenched by the saturated aqueous NH_4Cl

solution. To the mixture $CHCl_3$ was added, and the organic layer was washed with H_2O and brine. The organic layer was dried over $MgSO_4$. After $MgSO_4$ was removed by filtration, the solvent was evaporated. The residue was purified to silica gel column chromatography with hexane/$CHCl_3$ (v/v = 10/1, $R_f = 0.55$) as an eluent to give **2b** as a colorless solid (2.40 g, 7.70 mmol, 77%). The identification was performed according to the lieterature.[4b]

1,4-Bis(2'-mrthylethyn-1'-yl)-2,5-bis(2"-phenylethyn-1"-yl)benzene (3b). The mixture of **2b** (2.03 g, 6.50 mmol), $Pd(PPh_3)_4$ (381 mg, 0.33 mmol), and CuI (124 mg, 0.65 mmol) was dissolved in dry THF (60 mL) and NEt_3 (60 mL) at room temperature under Ar atmosphere. Ethynylbenzene (1.64 mL, 15.0 mmol) was added, and the mixture was refluxed at 65 °C for 48 h. After cooling to room temperature, the reaction was quenched by the addition of saturated aqueous NH_4Cl solution. To the mixture $CHCl_3$ was added, and the organic layer was washed with H_2O and brine. The organic layer was dried over $MgSO_4$. After $MgSO_4$ was removed, the solvent was evaporated. The residue was purified to silica gel column chromatography with hexane/$CHCl_3$ (v/v = 3/1, R_f = 0.55) as an eluent to give **3b** as a pale orange solid (1.61 g, 4.54 mmol, 70%). ^1H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.56 (2H, s, Ar-*H*), 7.55–7.51 (4H, m, Ar-*H*), 7.39–7.32 (6H, m, Ar-*H*), 2.16 (6H, s, C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 135.0, 131.9, 128.7, 128.5, 125.7, 125.3, 123.3, 94.8, 92.1, 87.9, 77.9. HRMS (APCI): Calcd. for $C_{28}H_{18}$ $[M+H]^+$ m/z 355.1481, found m/z 355.1472.

1,4-Bis(2'-methyl-*o*-carboran-1'-yl)-2,5-bis(2"-phenylethyn-1"-yl)benzene (CBMe). Decaborane (1.71 g, 14.0 mmol) was dissolved in CH_3CN (6.15 mL, 117 mmol) at room temperature under Ar atmosphere. The mixture was stirred for 2 h at 50 °C, and then, dry toluene (60 mL) and **3b** (2.07 g, 5.83 mmol) were added. The mixture was refluxed for 5 d. After cooling to room temperature, solvent was evaporated, and the residue was subjected to silica gel column chromatography with hexane/CH_2Cl_2 (v/v = 6/1, $R_f = 0.35$) as an eluent. Recrystallization from THF and EtOH (good and poor solvent, respectively) to give **CBMe** (45.5 mg, 0.077 mmol, 2%) as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 8.11 (2H, s, Ar-*H*), 7.70–7.63 (4H, m, Ar-*H*), 7.49–7.41 (6H, m, Ar-*H*), 3.90–1.91 (20H, br, B-*H*), 1.80 (6H, s, C*H*$_3$). ^{1}H NMR (400 MHz, THF-d_8): δ(ppm) 8.24 (2H, s, Ar-*H*), 7.70–7.64 (4H, m, Ar-*H*), 7.49–7.44 (6H, m, Ar-*H*), 3.60–1.70 (20H, br, B-*H*), 1.84 (6H, s, C*H*$_3$). ^{13}C NMR (100 MHz, THF-d_8): δ(ppm) 141.7, 132.1, 131.7, 130.6, 129.6, 126.5, 123.2, 100.7, 89.0, 81.3, 80.8, 23.6. ^{11}B NMR (128 MHz, THF-d_8): δ(ppm) 8.1, 7.0, 4.6, 3.6, 0.0. HRMS (APCI): Calcd. for $C_{28}H_{38}B_{20}$ $[M+Cl]^-$ m/z 629.4572, found m/z 629.4574. Elemental analysis: Calcd. for $C_{28}H_{38}B_{20}$ C 56.92, H 6.48, found C 55.75, H 6.58.

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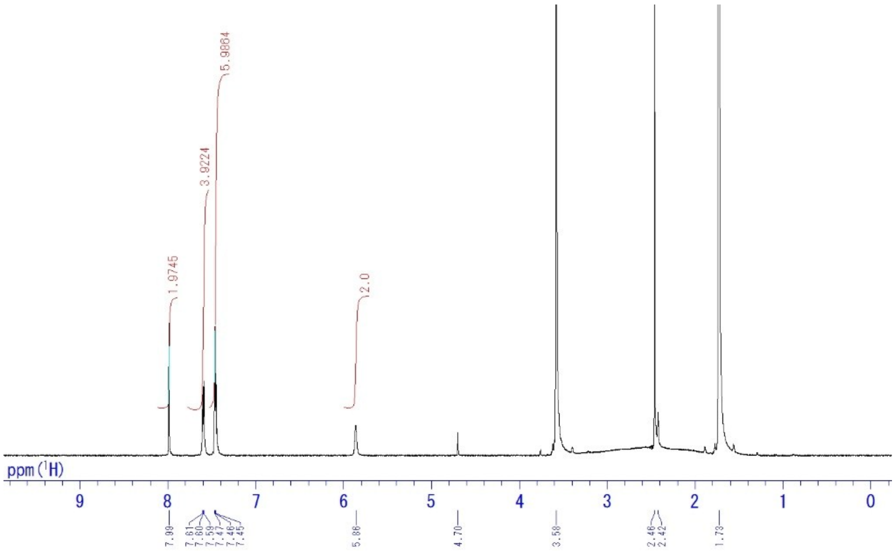


Chart S1. ^{1}H NMR spectrum of **CBH** in THF-d_8.

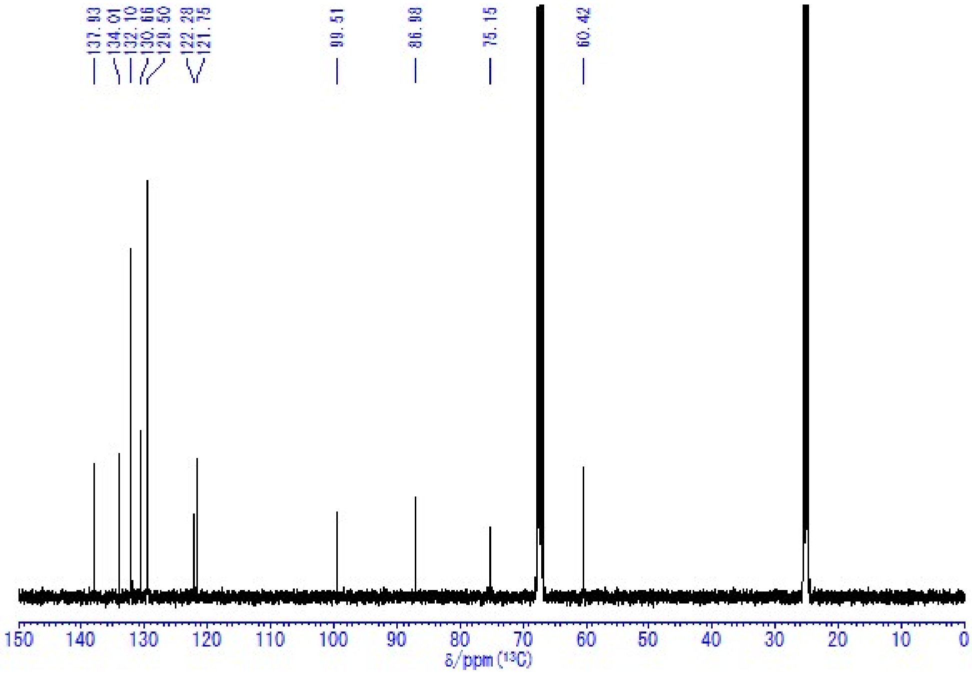


Chart S2. ^{13}C NMR spectrum of **CBH** in THF-d_8.

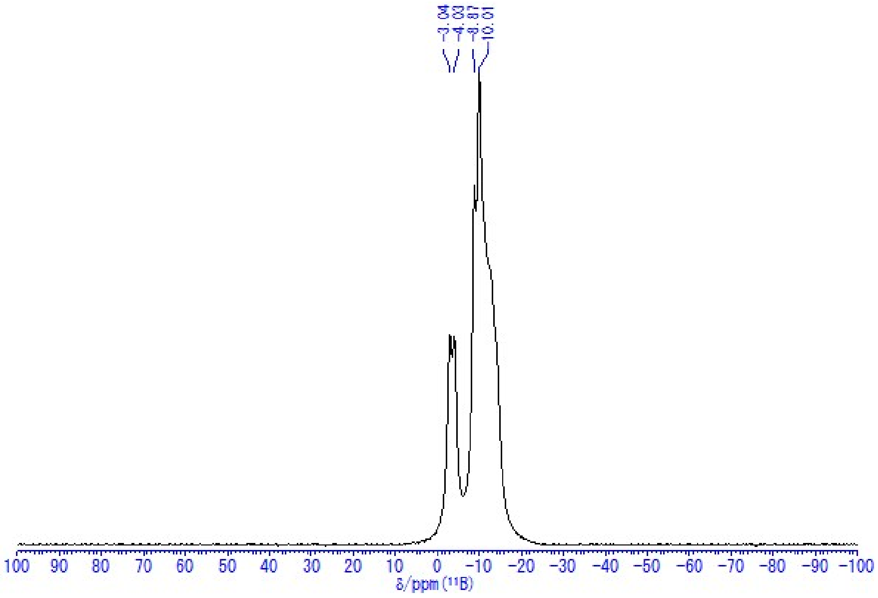


Chart S3. ^{11}B NMR spectrum of **CBH** in THF-d_8.

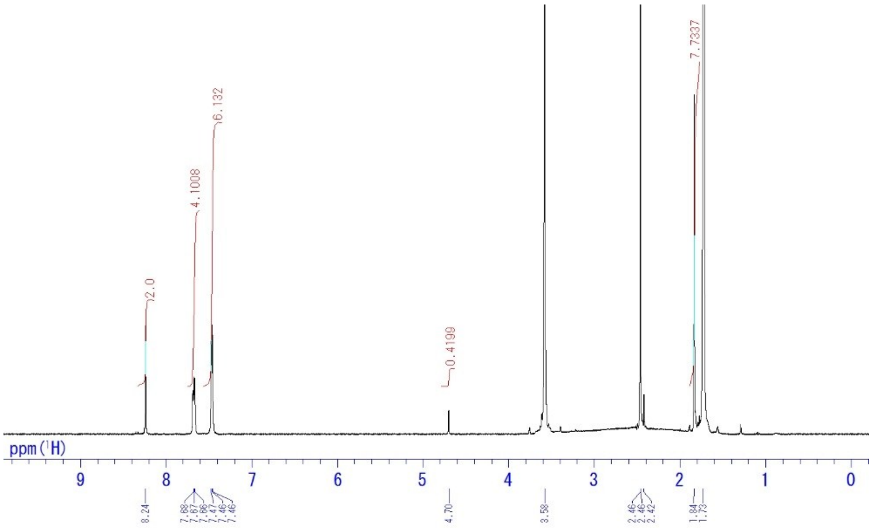


Chart S4. ^{1}H NMR spectrum of **CBMe** in THF-d_8.

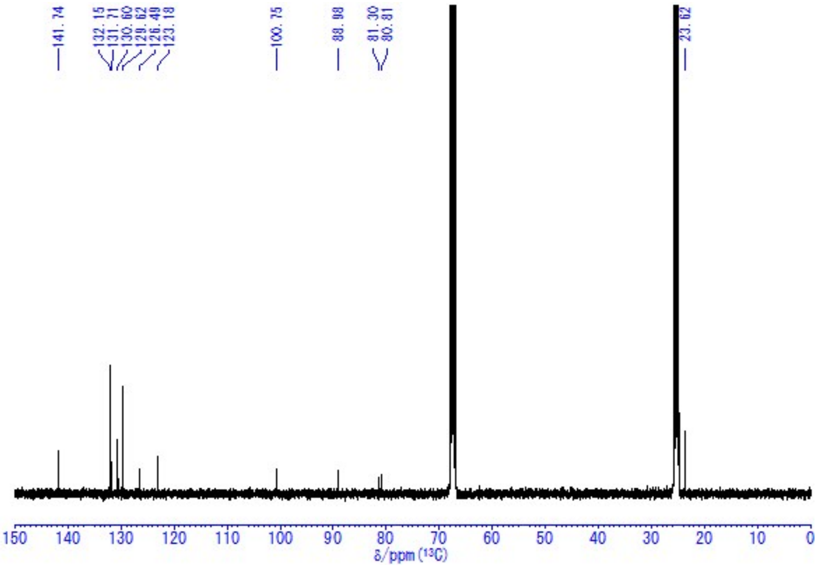


Chart S5. ^{13}C NMR spectrum of **CBMe** in THF-d_8.

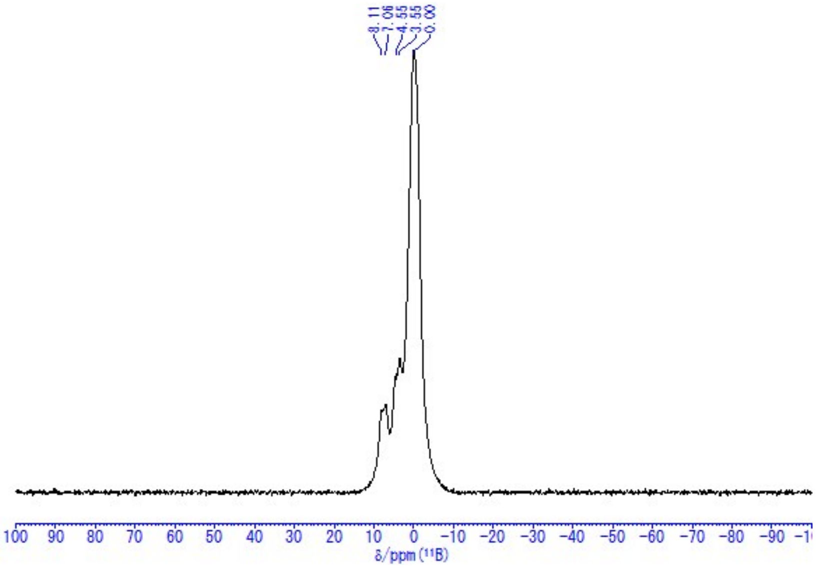
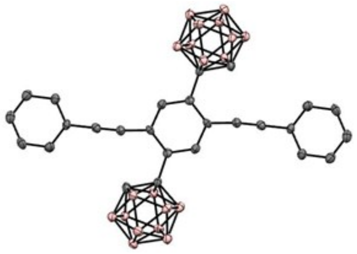


Chart S6. ^{11}B NMR spectrum of **CBMe** in THF-d_8.

Table S1. Crystallographic data of **CBH**[a]

Empirical formula	$C_{26}H_{34}B_{20}$
Formula weight	562.76
Temperature (K)	93(2)
Wavelength (Å)	0.71075
Crystal system, space group	Triclinic, *P -1*
Unit cell dimensions	$a = 7.1876(12)$
	$b = 10.5590(2)$
	$c = 10.8410(2)$
	$\alpha = 77.421$
	$\beta = 88.462$
	$\gamma = 76.313$
V (Å^3)	780.0(2)
Z, calculated density (Mg m^{-3})	1, 1.198
Absorption coefficient	0.058
$F(000)$	290.0
Crystal size (mm)	0.60 × 0.20 × 0.10
θ range for data collection	3.09 –27.48
Limiting indices	$-8 \leq h \leq 9$, $-13 \leq k \leq 13$, $-14 \leq l \leq 13$
Reflections collected (unique)	7361/3566 [R(int) = 0.1582]
Completeness to theta = 27.480	0.995
Max. and min. transmission	0.994 and 0.986
Goodness-of-fit on F^2	1.005
Final R indices [$I > 2\sigma(I)$][b]	$R_1 = 0.1011$, $wR_2 = 0.2833$



[a] The structures were solved by direct method (SIR97)[1] and refined by full-matrix least-squares procedures based on F^2 (SHELX-97).[2] [b] $R_1 = \Sigma(|F_0|-|F_c|)/\Sigma|F_0|$. $wR_2 = [\Sigma w(F^2_0-F^2_c)^2/ \Sigma w(F^2_0)^2]^{1/2}$. $w = 1/[\sigma^2(F^2_0)+[(ap)^2+bp]]$, where $p = [\max(F^2_0,0)+2F^2_c]/3$.

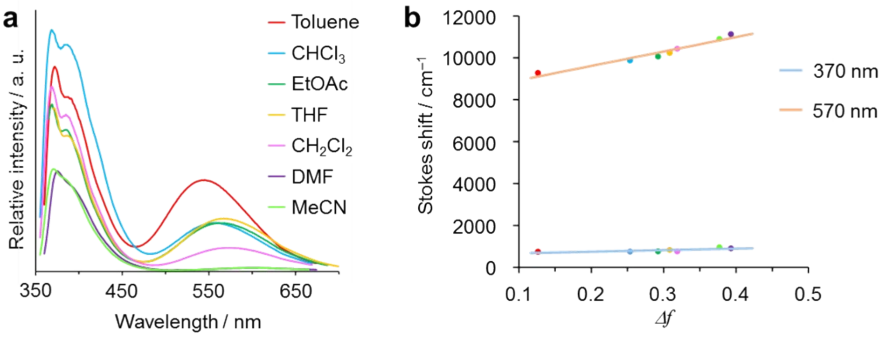


Figure S1. (a) PL spectra of **CBH** in various solvents (1.0×10^{-6} M) and (b) Lippert−Mataga plots for each emission peak.

Table S2. Optical properties of **CBH** in various solvents (1.0×10^{-6}M)

solvent	$\lambda_{abs, max}$ / nm	λ_{PL370} / nm	λ_{PL570} / nm	Δf
Toluene	362	372	545	0.1264
$CHCl_3$	359	369	556	0.2535
EtOAc	359	369	562	0.2923
THF	360	371	570	0.3084
CH_2Cl_2	359	369	574	0.3188
DMF	362	375	598	0.3771
MeCN	359	371	598	0.3928

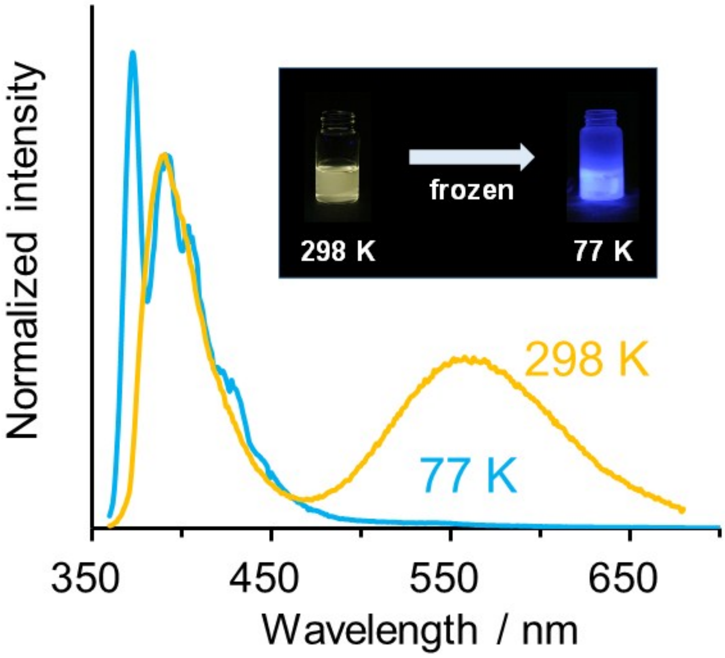


Figure S2. PL spectra of **CBH** at 77 K in 2-MeTHF (1.0×10^{-5} M).

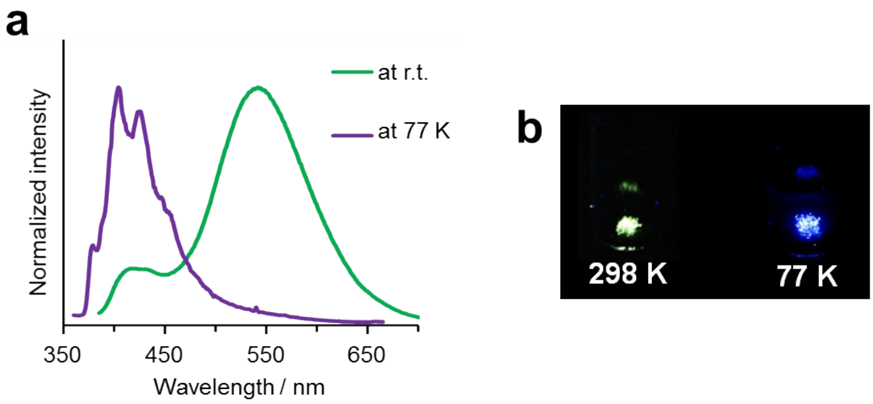


Figure S3. (a) PL spectra and (b) photoluminescence of **CBH** in the crystalline state at room temperature and at 77 K.

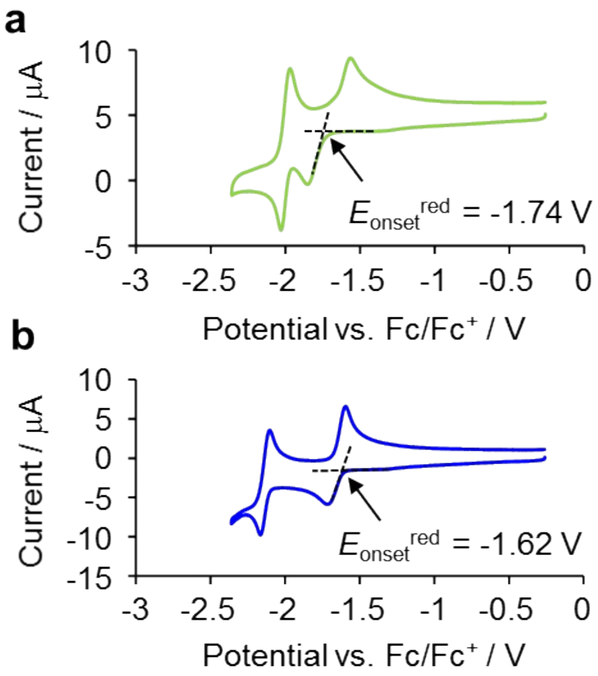


Figure S4. Cyclic voltammograms of (a) **CBH** and (b) **CBMe** in CH_2Cl_2 including 0.1 M of Bu_4NPF_6 using a glassy carbon working electrode at a scan rate of 100 mVs^{-1}.

Table S3. Optical and electrochemical properties of **CBH** and **CBMe**

Compound	UV–vis[a]			CV[d]		
	λ_{abs} / nm (ε /10^4 M^{-1} cm^{-1})[b]	$\lambda_{abs,\ edge}$ / nm	E_g / eV[c]	E_{onset}^{red} / V[e]	HOMO / eV[f]	LUMO / eV[g]
CBH	258(2.99), 344(3.63)	372	3.33	–1.74	–6.39	–3.06
CBMe	257(2.81), 368(3.92)	384	3.23	–1.62	–6.41	–3.18

[a] Measured in THF solution (1.0×10^{-5} M) at room temperature. [b] Molar absorption coefficient. [c] Band gap energy: $E_g = 1240 / \lambda_{abs,\ edge}$. [d] CV was carried out in CH_2Cl_2 with 0.1 M Bu_4NPF_6 as supporting electrolyte. [e] Onset potential of first reduction wave. [f] HOMO = LUMO – E_g (eV). [g] Calculated from the empirical formula, LUMO = $- E^{red} - 4.80$ (eV).

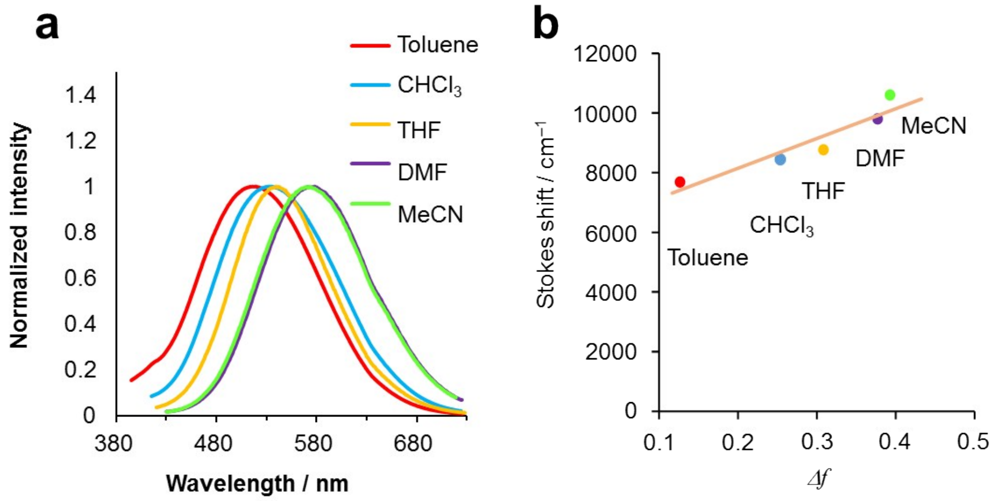


Figure S5. (a) PL spectra of **CBMe** in various solvents and (b) Lippert-Mataga plot of **CBMe**.

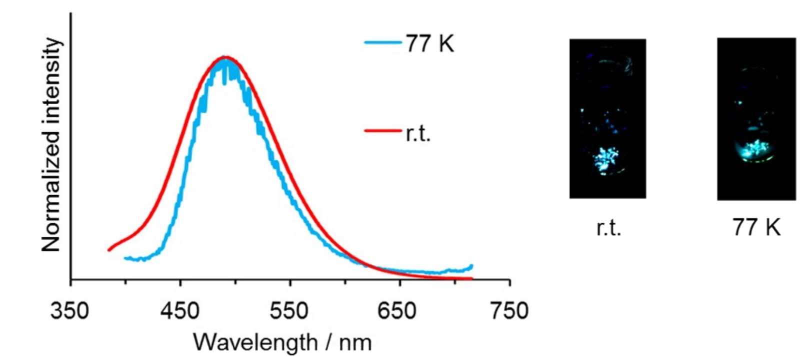


Figure S6. PL spectra of **CBMe** in the crystalline state at 77 K and at room temperature.

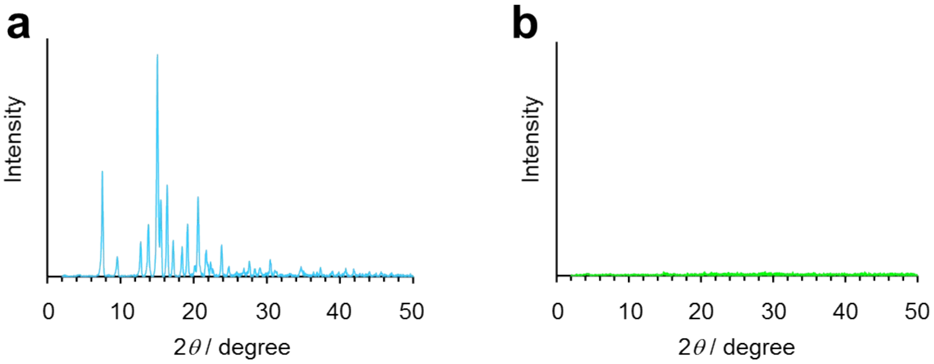


Figure S7. XRD patterns of (a) crystal and (b) ground solid of **CBMe**.

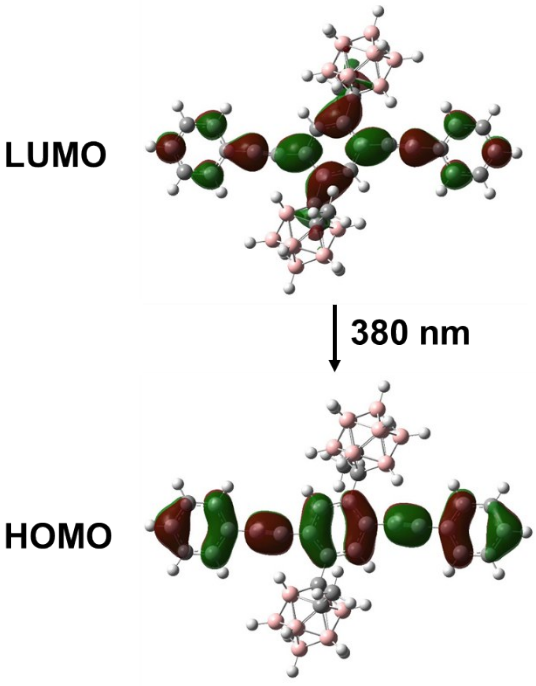


Figure S8. Optimized structures of frontier orbitals of **CBMe** calculated with the DFT calculation at the B3LYP/6-31+G(d) level of the theory (φ = 97°).

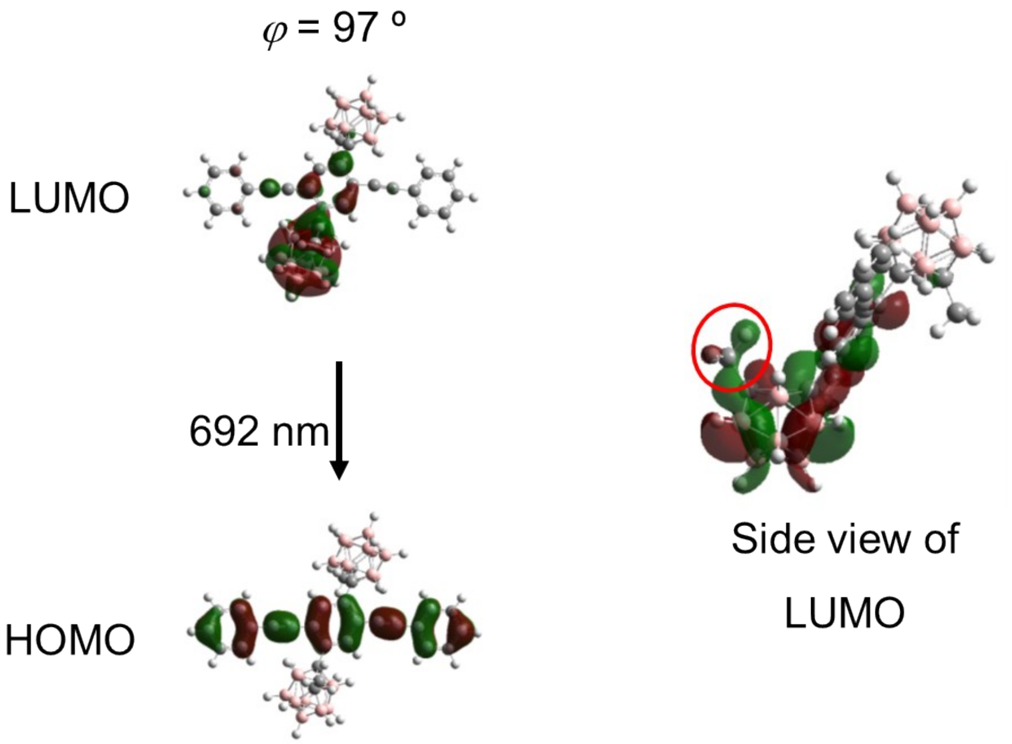


Figure S9. Frontier orbitals involved in the S_1−S_0 transition for **CBMe**.

Table S4. Calculated emission data for **CBH** and **CBMe**

compound	λ_{max} / nm	ΔE /eV	f^{a}	Transition^{b}
CBH	395.0	3.14	2.0972	L→H (95%)
	733.5	1.69	0.0759	L→H (98%)
CBMe	692.2	1.79	0.0861	L→H (98%)

^{a} Oscillator strength. ^{b} H = HOMO and L = LUMO.