

Supporting Information

**Dual Emission via Remote Control of Molecular
Rotation of *o*-Carborane in the Excited State by the
Distant Substituents in Tolane-Modified Dyads**

Kenta Nishino, Kyoya Uemura, Kazuo Tanaka*, and Yoshiki Chujo*

*Department of Polymer Chemistry, Graduate School of Engineering, Kyoto
University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan*

E-mail: tanaka@poly.synchem.kyoto-u.ac.jp; chujo@poly.synchem.kyoto-u.ac.jp

Experimental Section

General

All reagents were obtained from commercial sources and used without further purification. THF was purified using a two-column solid-state purification system (Glass Contour Solvent System, Joerg Meyer, Irvine, CA). ^1H , ^{13}C , and ^{11}B NMR spectra were recorded on a JEOL JNM-EX400 instrument at 400, 100, and 128 MHz, respectively. The ^1H chemical shift values were expressed relative to Me_4Si in CDCl_3 as an internal standard. The ^{13}C shift values were expressed relative to CHCl_3 in CDCl_3 as an internal standard. The ^{11}B chemical shift values were expressed relative to $\text{BF}_3 \cdot \text{Et}_2\text{O}$ as an external standard. High-resolution mass spectra (HRMS) were obtained on a Thermo Fisher Scientific EXACTIVE spectrometer for atmospheric pressure chemical ionization (APCI). The samples were diluted with $\text{CHCl}_3/\text{MeOH}$ (50/50 vol%) before measurements. Analytical thin-layer chromatography (TLC) was performed with silica gel 60 Merck F254 plates. Column chromatography was performed with Wakogel C-300 silica gel. 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.

Synthesis

General synthesis of *p*-(*o*-carboran-1-yl)tolane derivatives

The mixture of *p*-(*o*-carboranyl)-bromobenzene¹ (1.00 mmol), $\text{Pd}_2(\text{dba})_3$ (0.025 mmol), XPhos (0.12 mmol) and CuI (0.091 mmol) was placed in 20 mL eggplant flask. This flask was purged with Ar, followed by introducing THF (3 mL) and triethylamine

(3 mL). Then, ethynylbenzene derivative (1.09 mmol) was added to the solution. The reaction was carried out at 40 °C. After stirring the mixture for 12 h, saturated NH₄Cl solution was added to the reaction mixture. The organic layer was extracted three times with CHCl₃ and dried over MgSO₄. Then, MgSO₄ was removed, and the solvent was evaporated. The crude residue was purified by silica gel column chromatography with hexane as an eluent. Recrystallization from CHCl₃ and MeOH gave the product as a colorless crystal.

TCB-H¹: 28% as a white powder. ¹H NMR (CDCl₃, 400 MHz) δ (ppm) 7.53–7.50 (m, 2H, Ar-*H*), 7.47–7.42 (m, 4H, Ar-*H*), 7.36–7.33 (m, 3H, Ar-*H*), 3.91 (s, 1H, carborane-*C-H*), 3.50–1.50 (br, 10H, B-*H*). ¹³C NMR (CDCl₃, 100 MHz) δ (ppm) 133.0, 131.8, 131.7, 128.8, 128.4, 127.6, 125.3, 122.6, 92.0, 87.7, 76.0, 60.1. ¹¹B NMR (CDCl₃, 128 MHz) δ (ppm) -1.4, -2.5, -3.6, -4.6, -8.2, -9.5, -10.2, -11.4, -11.9, -13.3. HRMS (APCI) calcd. For C₁₆H₂₀B₁₀ [M]⁻: 322.2501, found 322.2503.

TCB-OMe¹: 84% as a white powder. ¹H NMR (CDCl₃, 400 MHz) δ (ppm) 7.47–7.43 (m, 6H, Ar-*H*), 6.88 (td, 2H, *J* = 8.8, 2.4, Ar-*H*), 3.93 (s, 1H, carborane-*C-H*), 3.83 (s, 3H, CH₃), 3.24–1.54 (br, 10H, B-*H*). ¹³C NMR (CDCl₃, 100 MHz) δ (ppm) 160.1, 133.2, 132.7, 131.6, 127.6, 125.8, 114.7, 114.1, 92.1, 86.6, 76.2, 60.2, 55.3. ¹¹B NMR (CDCl₃, 128 MHz) δ (ppm) -1.4, -2.5, -3.6, -4.7, -8.3, -9.5, -10.2, -11.4, -12.0, -13.3. HRMS (APCI) calcd. For C₁₇H₂₂B₁₀O [M]⁻: 352.2607, found 352.2610.

TCB-(CF₃)₂¹: 37% as a white powder. ¹H NMR (CDCl₃, 400 MHz) δ (ppm) 7.95 (s, 2H, Ar-*H*), 7.84 (s, 1H, Ar-*H*), 7.51 (s, 4H, Ar-*H*), 3.96 (s, 1H, C(carborane)-*H*), 3.47–1.58

(br, 10H, B-H). ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 134.3, 132.1, 132.1, 131.6, 127.8, 125.0, 123.9, 122.1 (q, $J = 3$ Hz, CF_3), 121.6, 90.9, 88.5, 77.2, 60.1. ^{11}B NMR (CDCl_3 , 128 MHz) δ (ppm) -1.4, -2.5, -3.6, -4.7, -8.2, -9.4, -10.2, -11.5, -13.2. HRMS (APCI) calcd. For $\text{C}_{18}\text{H}_{18}\text{B}_{10}\text{F}_6$ $[\text{M}]^-$: 458.2249, found 458.2255.

TCB-CF₃: 26% as a white solid. ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 7.65–7.63 (m, 4H, Ar-H), 7.52–7.47 (m, 4H, Ar-H), 3.97 (s, 1H, C(carborane)-H), 3.50–1.60 (br, 10H, B-H). ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 133.7, 132.0, 131.9, 127.7, 126.4, 125.41, 125.38, 125.3, 124.6, 90.3, 89.9, 77.2, 60.1. ^{11}B NMR (CDCl_3 , 128 MHz) δ (ppm) -1.4, -2.6, -3.6, -4.5, -8.2, -9.4, -10.2, -11.5, -12.0, -13.2. HRMS (APCI) calcd. For $\text{C}_{17}\text{H}_{19}\text{B}_{10}\text{F}_3$ $[\text{M}]^-$: 388.2448, found 388.2449.

TCB-Me: 1% as a white solid. ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 7.52–7.41 (m, 6H, Ar-H), 7.22 (dt, 2H, $J = 8.8, 2.4$, Ar-H), 3.96 (s, 1H, C(carborane)-H), 2.38 (s, 3H, CH_3), 3.24–1.60 (br, 10H, B-H). ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 139.1, 132.9, 131.7, 131.6, 129.2, 127.6, 125.6, 119.6, 92.2, 87.1, 77.2, 60.2, 21.5. ^{11}B NMR (CDCl_3 , 128 MHz) δ (ppm) -1.5, -2.6, -3.6, -4.6, -8.3, -9.5, -10.2, -11.5, -12.1, -13.3. HRMS (APCI) calcd. For $\text{C}_{17}\text{H}_{22}\text{B}_{10}\text{Cl}$ $[\text{M}+\text{Cl}]^-$: 371.2341, found 371.2355.

TCB-(OMe)₃: 5% as a white powder. ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 7.46 (m, 4H, Ar-H), 6.76 (s, 2H, Ar-H), 3.95 (s, 1H, C(carborane)-H), 3.884 (s, 3H, OMe), 3.877 (s, 6H, OMe), 3.47–1.58 (br, 10H, B-H). ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 153.2, 139.4, 133.0, 131.7, 127.6, 125.3, 117.5, 109.0, 92.0, 86.9, 77.2, 61.0, 60.1, 56.2. ^{11}B NMR

(CDCl₃, 128 MHz) δ (ppm) -1.4, -2.6, -3.8, -4.6, -8.3, -9.5, -10.2, -11.5, -12.0, -13.2.

HRMS (APCI) calcd. For C₁₉H₂₆B₁₀O₃Cl [M+Cl]⁻: 445.2501, found 445.2589.

TCB-NMe₂: 32% as a yellow powder. ¹H NMR (CDCl₃, 400 MHz) δ (ppm) 7.42–7.38 (m, 6H, Ar–H), 6.65 (d, 2H, *J* = 4 Hz, Ar–H), 3.94 (s, 1H, C(carborane)–H), 2.99 (s, 6H, NMe₂), 3.47–1.58 (br, 10H, B–H). ¹³C NMR (CDCl₃, 100 MHz) δ (ppm) 150.5, 133.0, 132.1, 131.4, 127.5, 126.4, 111.8, 109.3, 93.6, 86.0, 77.3, 60.3, 40.1. ¹¹B NMR (CDCl₃, 128 MHz) δ (ppm) -1.5, -2.6, -3.9, -4.6, -8.4, -9.6, -10.1, -11.5, -12.0, -13.3. HRMS (APCI) calcd. For C₁₈H₂₆B₁₀N₁ [M+H]⁺: 364.3063, found 364.3054.

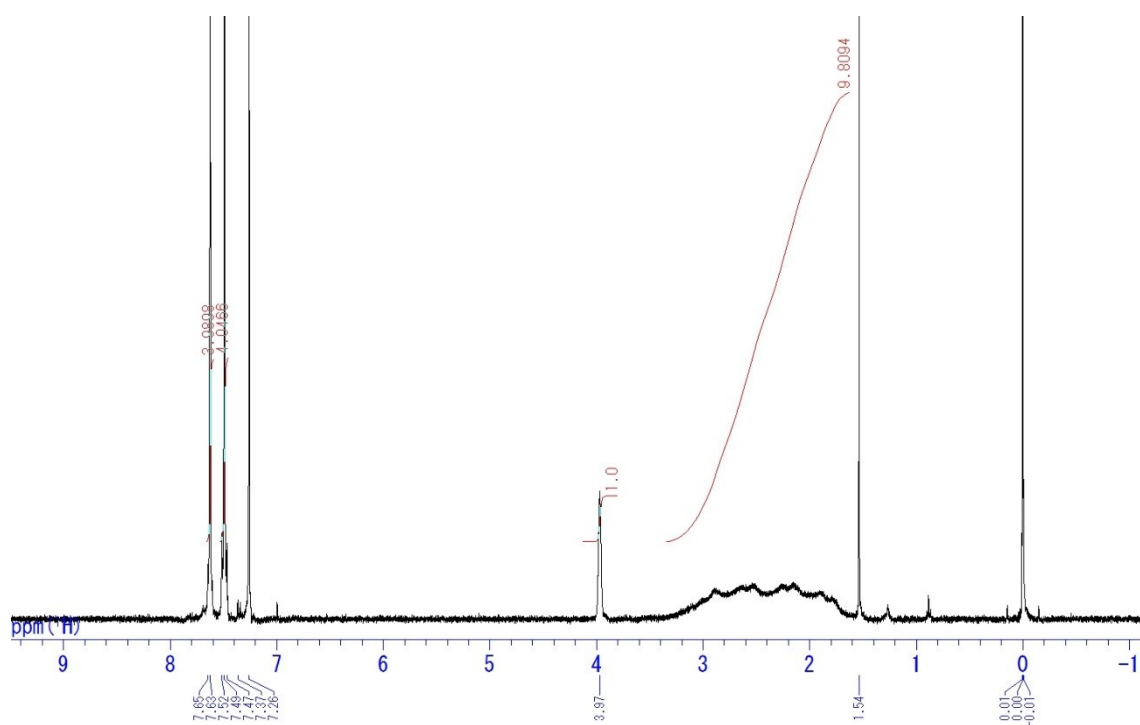


Chart S1. ¹H NMR spectrum of TCB-CF₃ in CDCl₃.

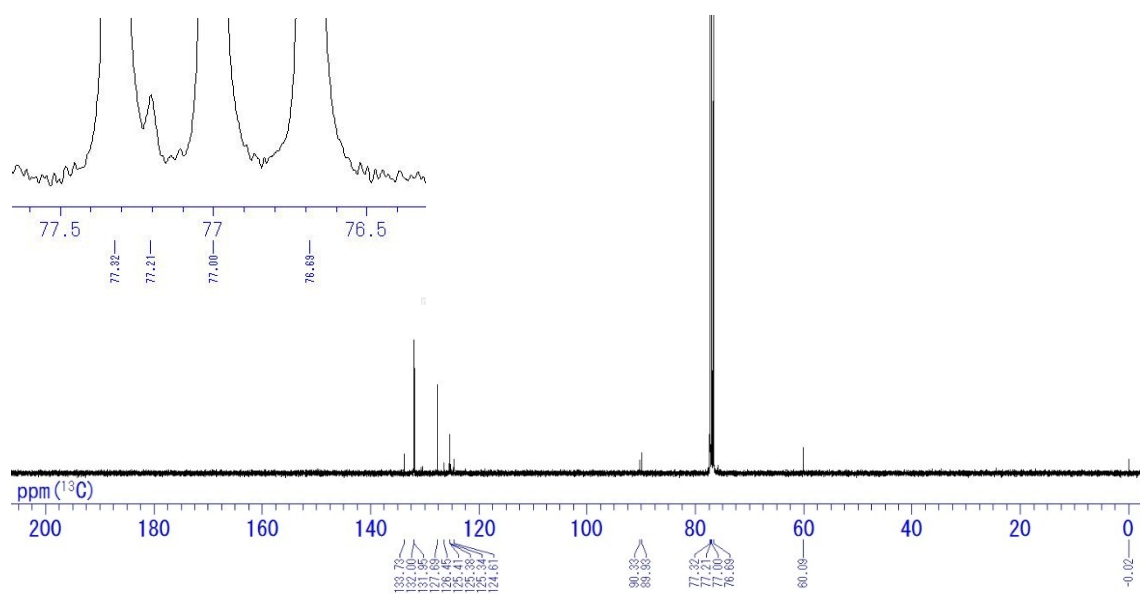


Chart S2. ¹³C NMR spectrum of TCB-CF₃ in CDCl₃.

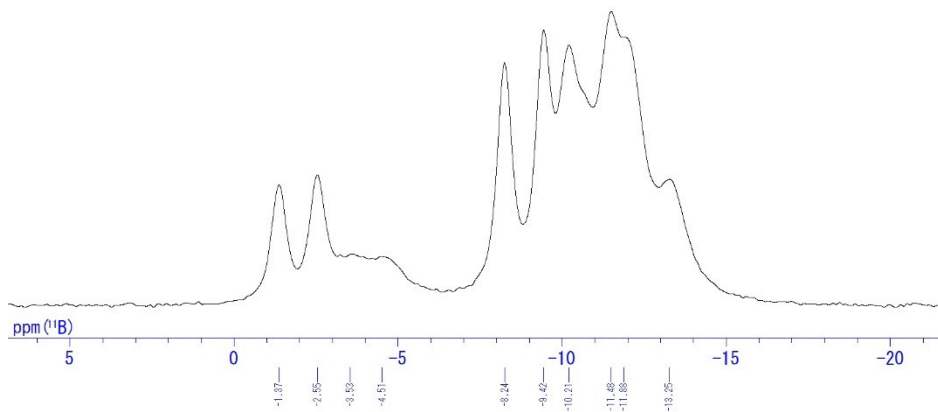


Chart S3. ^{11}B NMR spectrum of **TCB-CF₃** in CDCl_3 .

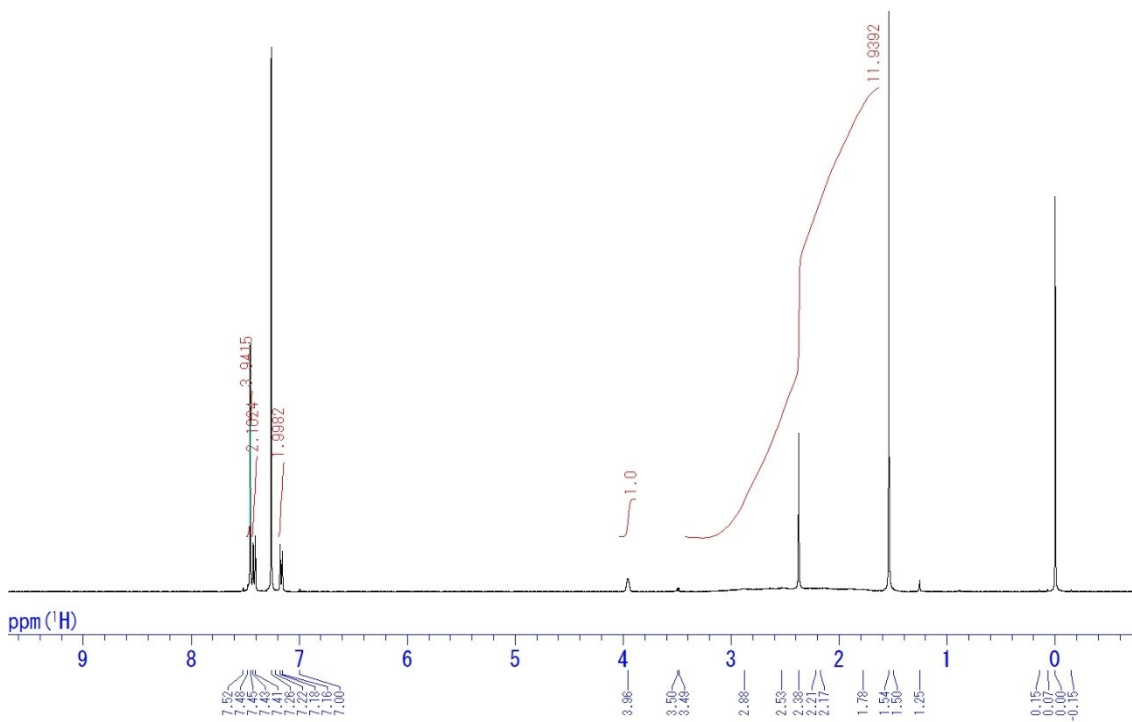


Chart S4. ^1H NMR spectrum of **TCB-Me** in CDCl_3 .

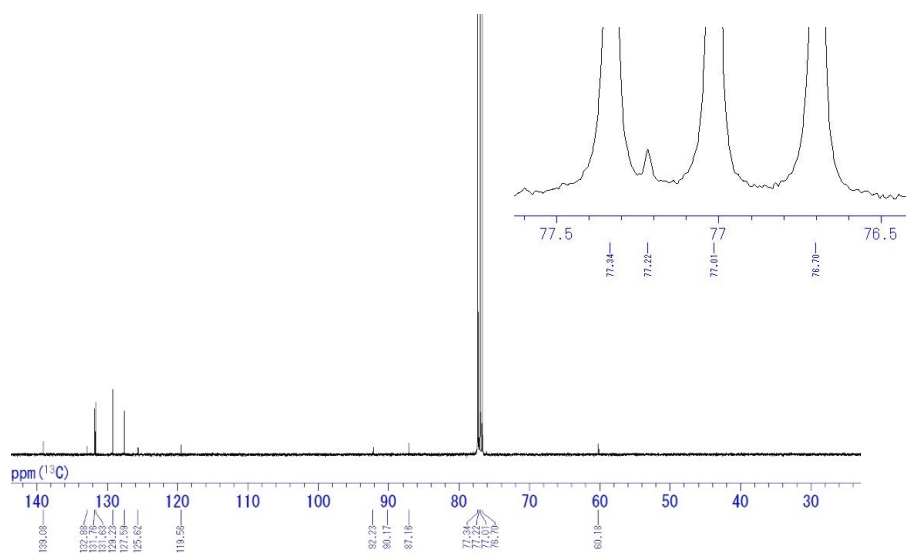


Chart S5. ^{13}C NMR spectrum of TCB-Me in CDCl_3 .

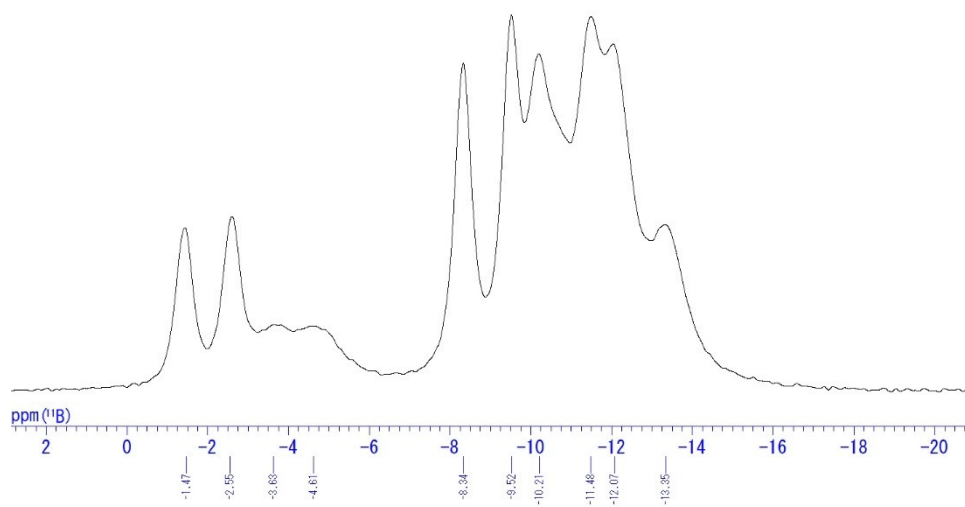


Chart S6. ^{11}B NMR spectrum of TCB-Me in CDCl_3 .

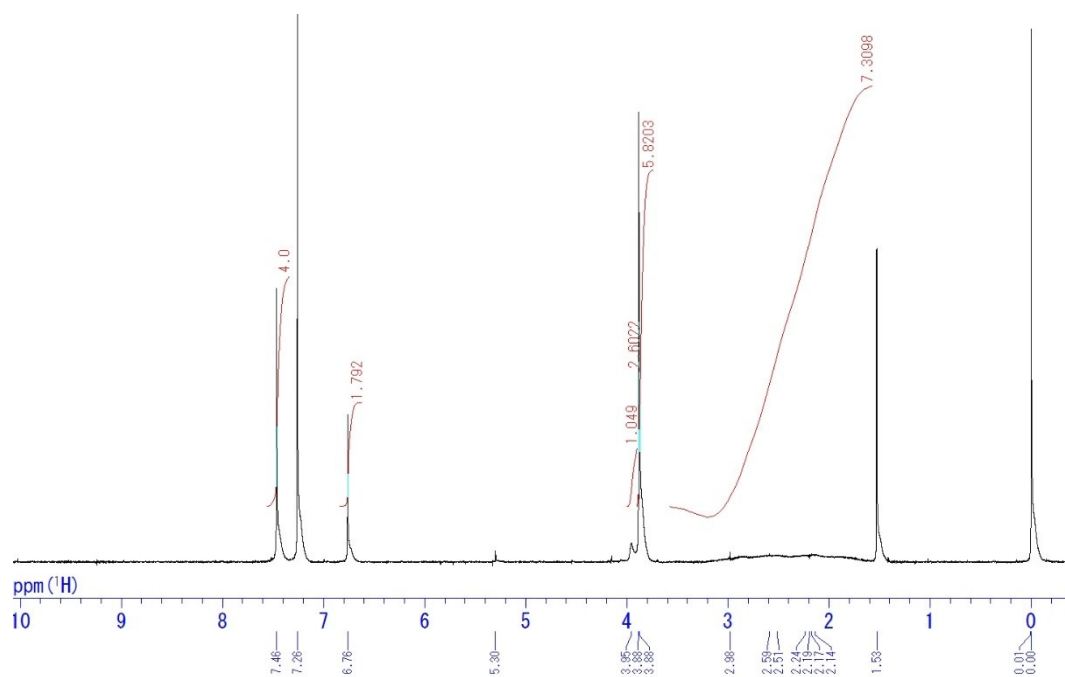


Chart S7. ¹H NMR spectrum of TCB-(OMe)₃ in CDCl₃.

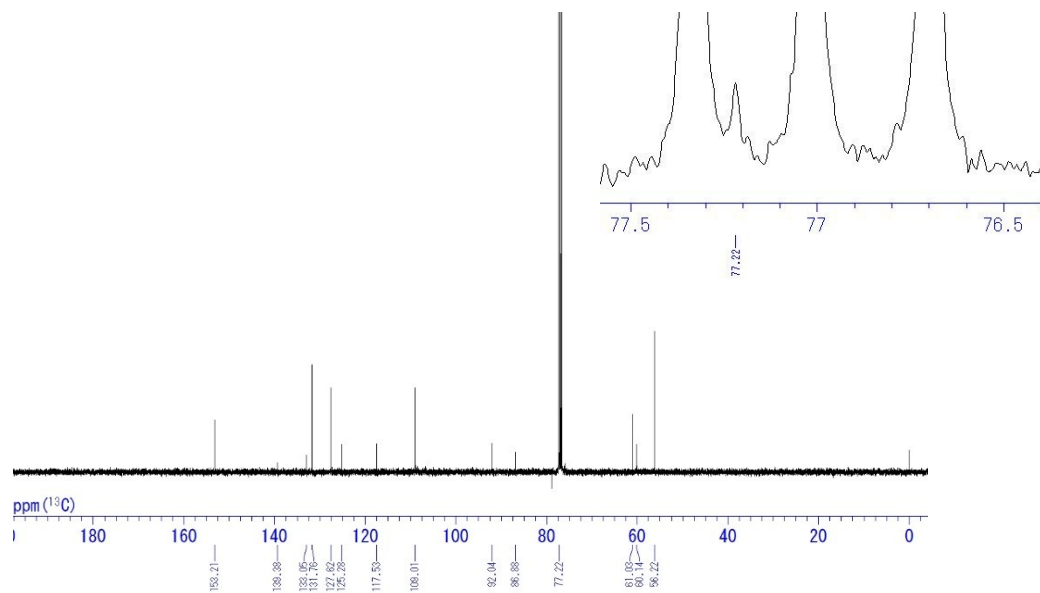


Chart S8. ¹³C NMR spectrum of TCB-(OMe)₃ in CDCl₃.

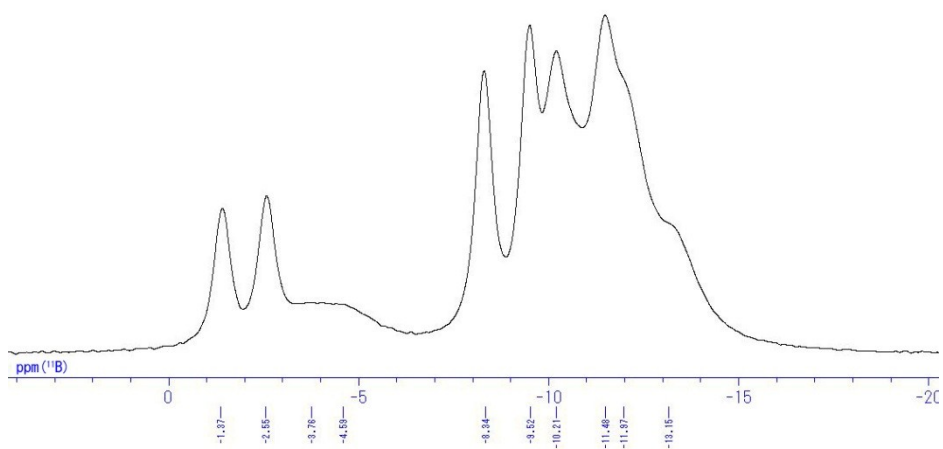


Chart S9. ¹¹B NMR spectrum of TCB-(OMe)₃ in CDCl₃.

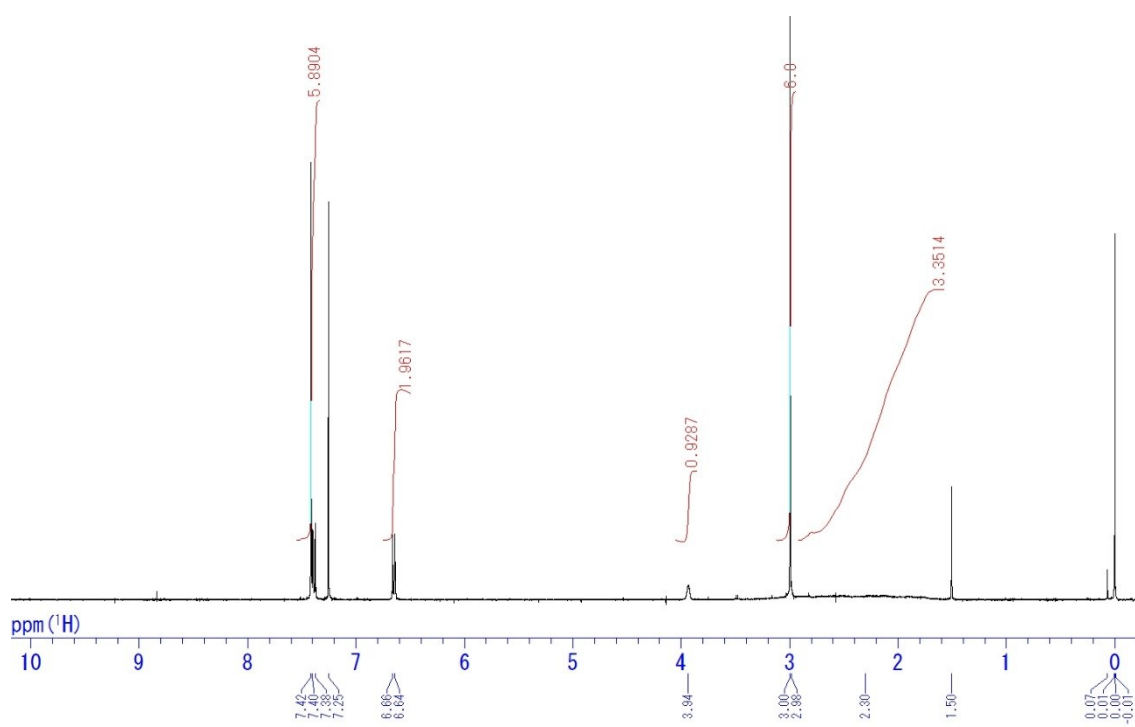


Chart S10. ¹H NMR spectrum of TCB-NMe₂ in CDCl₃.

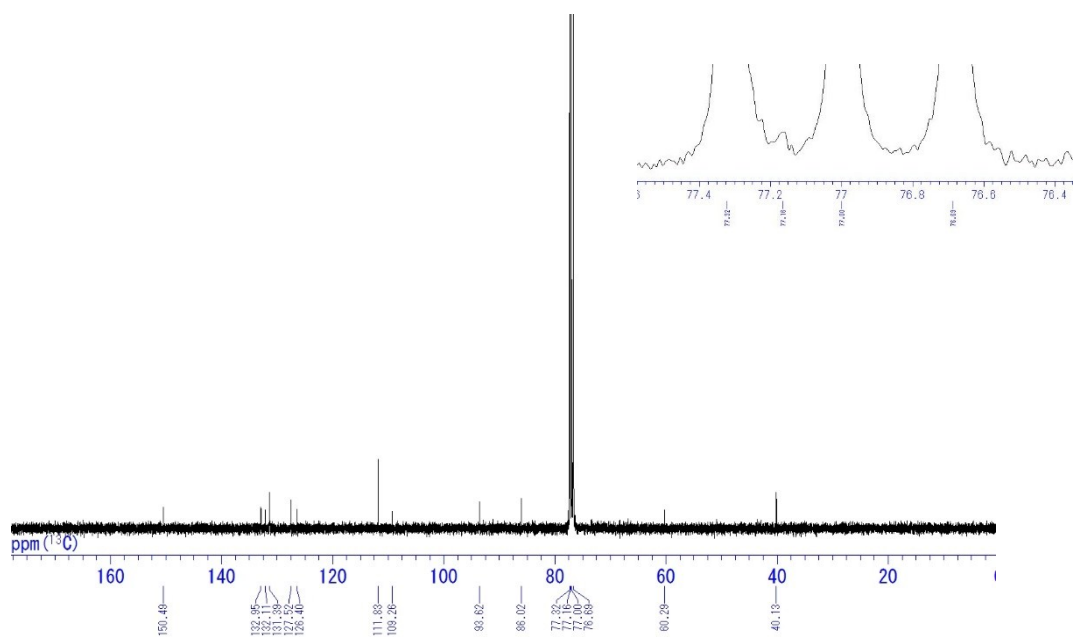


Chart S11. ¹³C NMR spectrum of TCB-NMe₂ in CDCl₃.

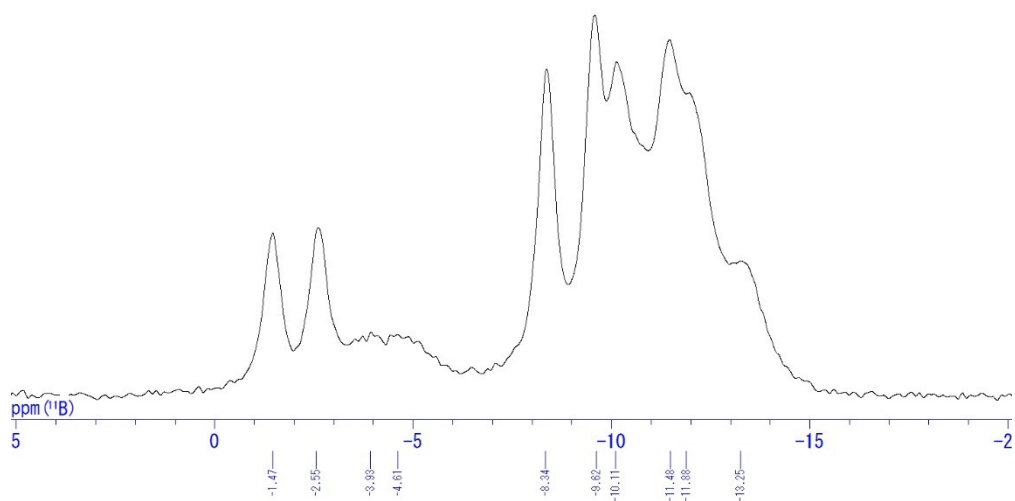


Chart S12. ¹¹B NMR spectrum of TCB-NMe₂ in CDCl₃.

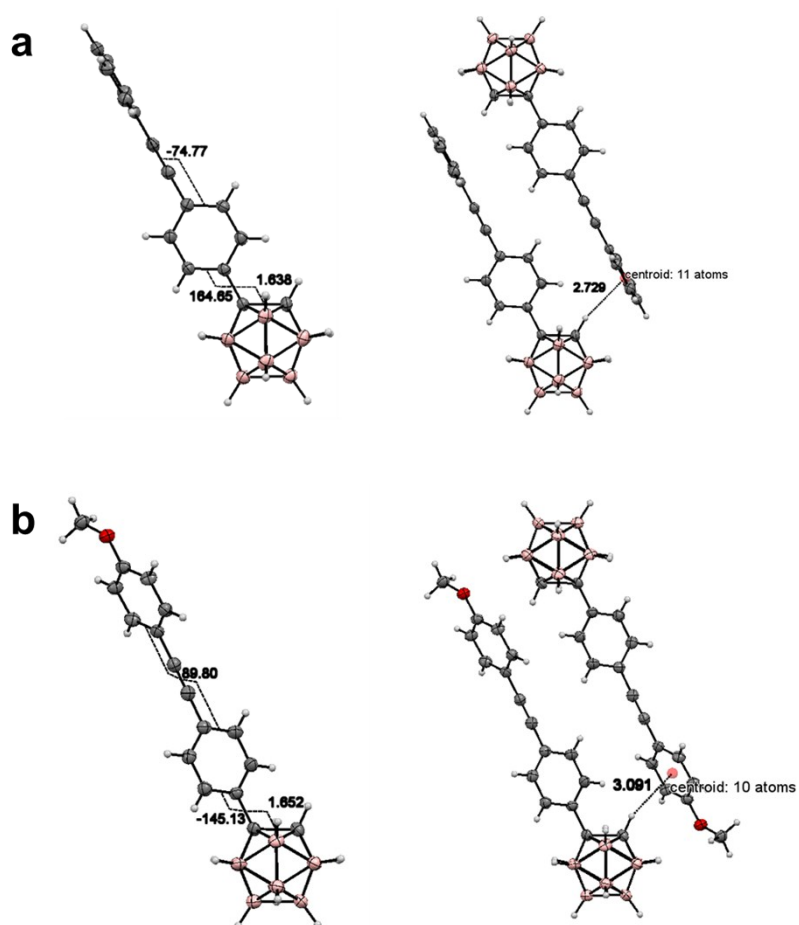
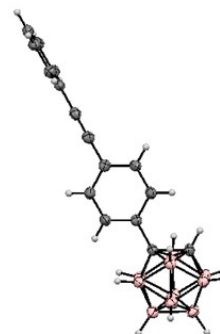


Figure S1. Molecular structures and packing diagrams of (a) **TCB-H** and (b) **TCB-OMe** (hydrogen atoms are omitted for clarity, and thermal ellipsoids are displayed at 30% probability).

Table S1. Crystallographic data of TCB-H^a

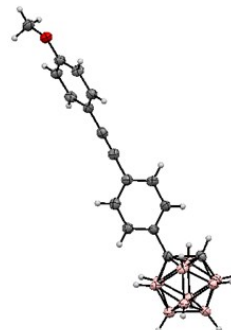
Empirical formula	C ₁₆ H ₂₀ B ₁₀
Formula weight	320.42
Temperature (K)	93(2)
Wavelength (Å)	0.71075
Crystal system, space group	Triclinic, <i>P</i> -1
Unit cell dimensions	<i>a</i> = 7.3558(5) <i>b</i> = 9.8281(7) <i>c</i> = 13.8221(12) α = 72.201(5) β = 78.852(6) γ = 74.947(5)
<i>V</i> (Å ³)	911.69(13)
<i>Z</i> , calculated density (Mg m ⁻³)	2, 1.167
Absorption coefficient	0.058
<i>F</i> (000)	332
Crystal size (mm)	1.00 × 0.60 × 0.60
θ range for data collection	3.05 –27.58
Limiting indices	-9 ≤ <i>h</i> ≤ 9, -12 ≤ <i>k</i> ≤ 12, -17 ≤ <i>l</i> ≤ 17
Reflections collected (unique)	8554/4123 [<i>R</i> (int) = 0.0487]
Completeness to theta = 27.575	0.986
Max. and min. transmission	0.945 and 0.966
Goodness-of-fit on <i>F</i> ²	1.221
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] ^b	<i>R</i> ₁ = 0.0674, w <i>R</i> ₂ = 0.1945
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0813, w <i>R</i> ₂ = 0.2427



^aThe structures were solved by direct method (SHELXT)² and refined by full-matrix least-squares procedures based on *F*² (SHELX-2014/7).³ ^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 $p = [\max(F^2_0, 0) + 2F^2_c] / 3$.

Table S2. Crystallographic data of TCB-OMe^a

Empirical formula	C ₁₇ H ₂₂ B ₁₀ O
Formula weight	350.44
Temperature (K)	103(2)
Wavelength (Å)	0.71075
Crystal system, space group	Triclinic, <i>P</i> -1
Unit cell dimensions	<i>a</i> = 7.0713(12) <i>b</i> = 10.2615(16) <i>c</i> = 14.668(3) α = 109.044(8) β = 93.259(7) γ = 104.545(7)
<i>V</i> (Å ³)	962.6(3)
<i>Z</i> , calculated density (Mg m ⁻³)	2, 1.209
Absorption coefficient	0.064
<i>F</i> (000)	364
Crystal size (mm)	0.30 × 0.10 × 0.10
θ range for data collection	3.01 –27.37
Limiting indices	-9 ≤ <i>h</i> ≤ 9, -13 ≤ <i>k</i> ≤ 12, -19 ≤ <i>l</i> ≤ 18
Reflections collected (unique)	9234/4288 [<i>R</i> (int) = 0.1364]
Completeness to theta = 27.37	0.975
Max. and min. transmission	0.981 and 0.994
Goodness-of-fit on <i>F</i> ²	1.027
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] ^b	<i>R</i> ₁ = 0.0939, w <i>R</i> ₂ = 0.1952
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1923, w <i>R</i> ₂ = 0.2415



^aThe structures were solved by direct method (SHELXT)² and refined by full-matrix least-squares procedures based on *F*² (SHELX-2014/7).³ ^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 $p = [\max(F^2_0, 0) + 2F^2_c] / 3$.

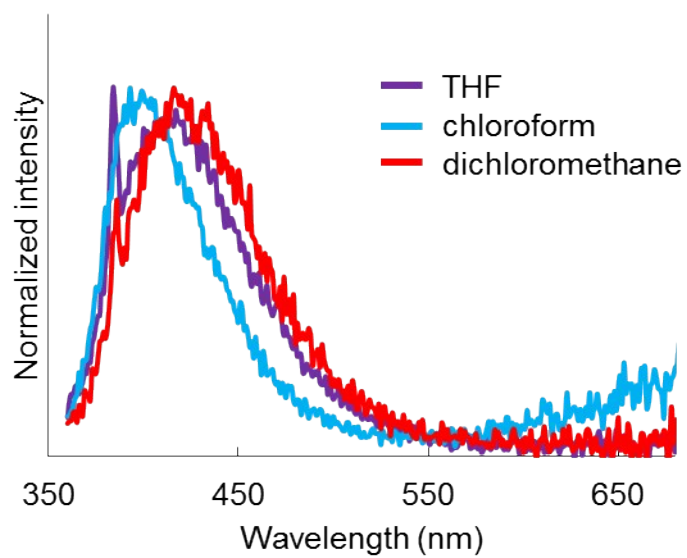


Figure S2. PL spectra of TCB-NMe₂ (1.0×10^{-5} M) in various solvents.

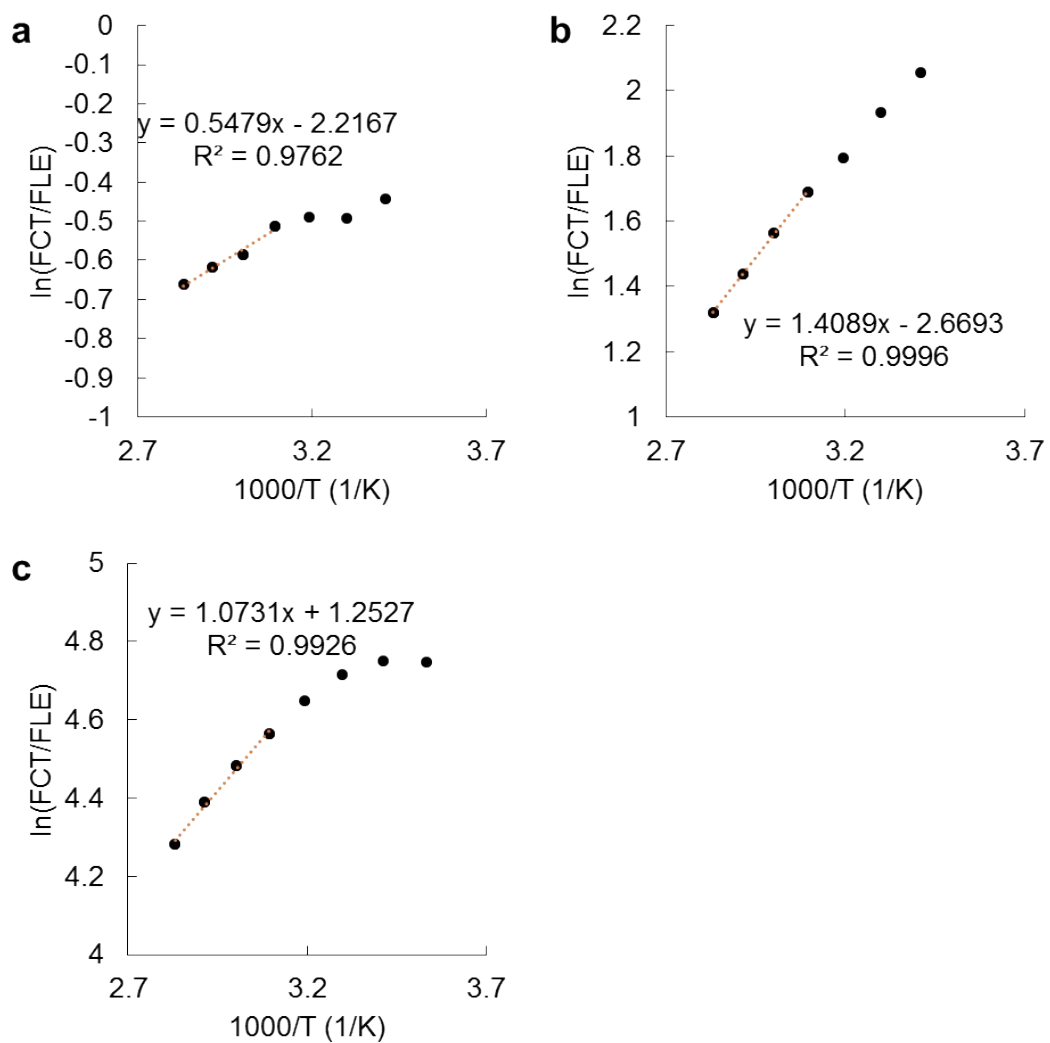


Figure S3. Stenens-Ban plots from the PL spectra of (a) TCB-MeO, (b) TCB-(MeO)₃ and (c) TCB-NMe₂.

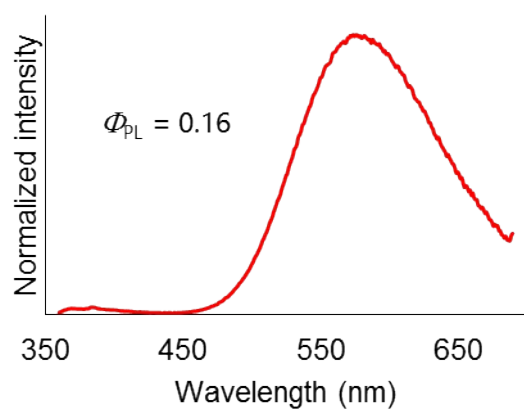


Figure S4. Emission spectrum of TCB-NMe₂ in the solid state.

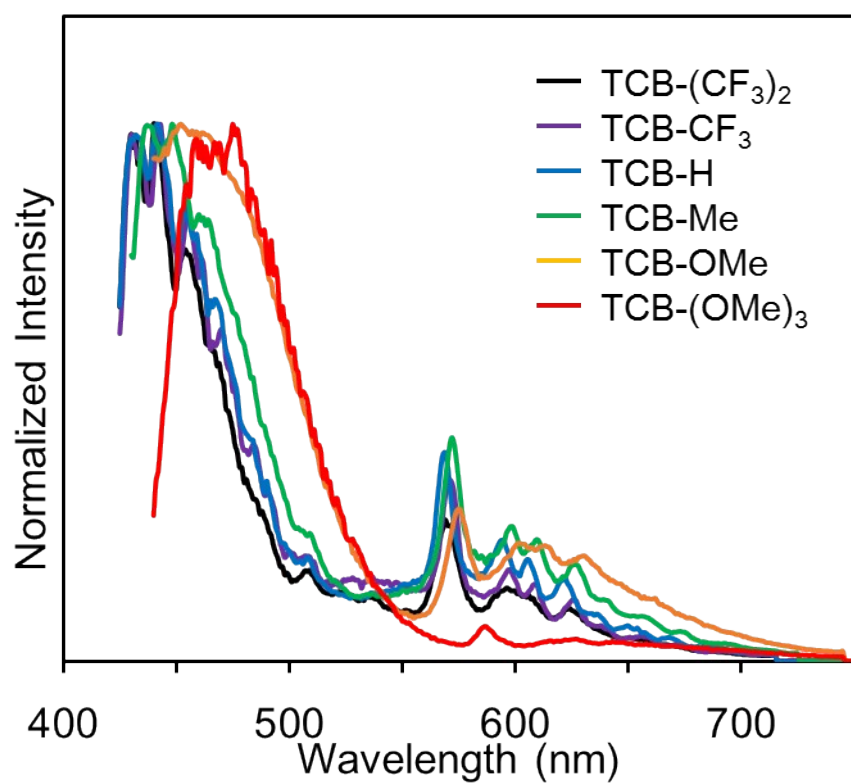


Figure S5. Emission spectra in 2-methyltetrahydrofuran at 77 K.

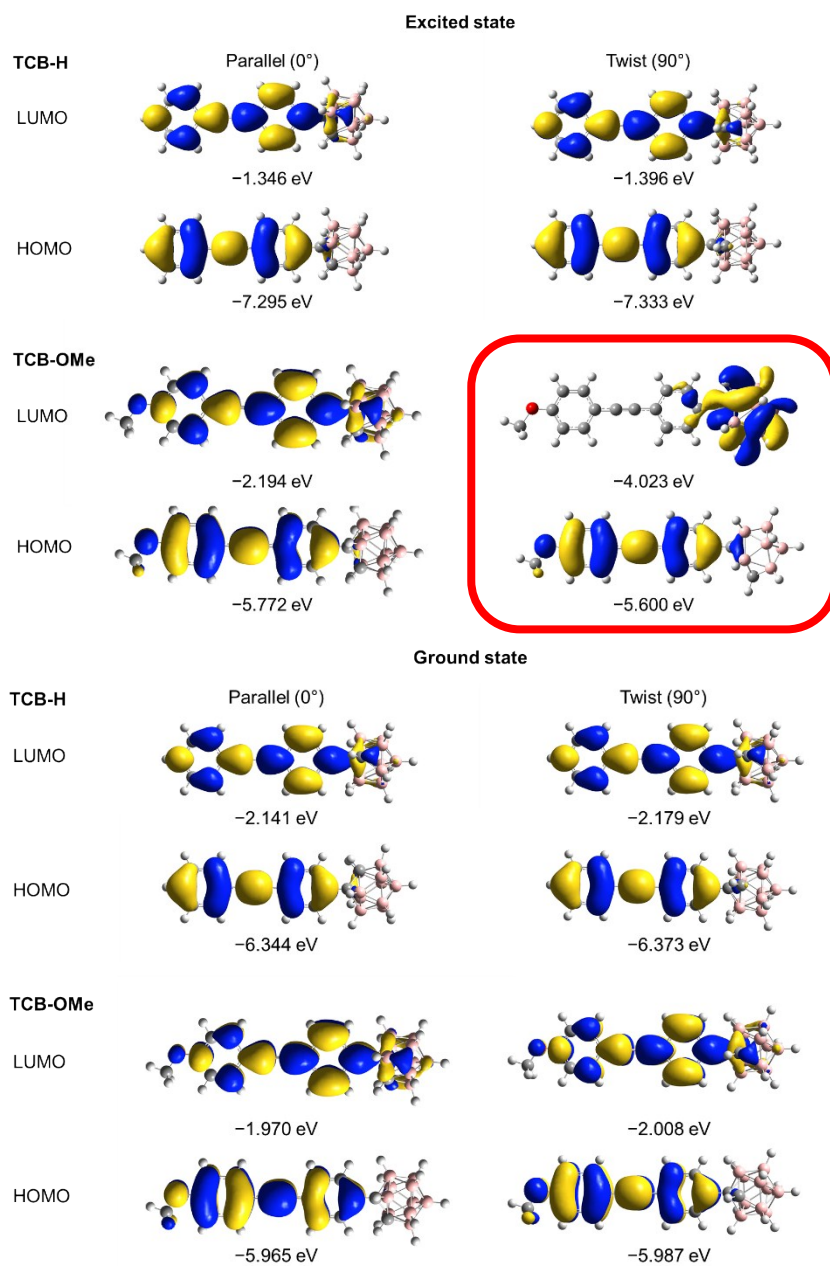


Figure S6. Molecular orbitals and energy levels of the parallel and twisted conformations of **TCB-H** and **TCB-OMe** in the ground and excited states. Calculations for the ground and excited states were performed with DFT and TD-DFT at the CAM-B3LYP/6-31+G(d,p)//B3LYP/6-31G(d,p) level, respectively.

References

1. Nishino, K.; Morisaki, Y.; Tanaka, K.; Chujo, Y. *New J. Chem.* **2017**, *15*, 10550–10554.
2. Sheldrick, G. M. A short history of SHELX, *Acta Cryst.* (2008). A64, 112–122.
3. Sheldrick, G. M. SHELXTL Version 2014/7. <http://shelx.uni-ac.gwdg.de/SHELX/index.php>.