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Supporting Information

Electron-Donating Abilities and Luminescent Properties of Tolane-Substituted

nido-Carboranes

Kenta Nishino¹, Yasuhiro Morisaki^{1,2}, Kazuo Tanaka¹, and Yoshiki Chujo^{1*}

¹Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University,

Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

²Present address: Department of Applied Chemistry for Environment, School of Science and Technology, Kwansei Gakuin University, 2-1 Gakuen, Sanda, Hyogo 669-1337, Japan

E-mail: chujo@chujo.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, ¹³C, and ¹¹B 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 Me₄Si in CDCl₃ or CH₂Cl₂ in CD₂Cl₂ as an internal standard. The ¹³C shift values were expressed relative to CHCl₃ in CDCl₃ or CH₂Cl₂ in CD₂Cl₂ as an internal standard. The ¹¹B chemical shift values were expressed relative to BF₃·Et₂O 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 F254 plates. Column chromatography was performed with Wakogel C-300 silica gel. UV-vis absorption SHIMADZU spectra were obtained on а 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

p-(*o*-Carboran-1-yl)-bromobenzene (1)

Decaborane (1.40 g, 11.4 mmol) and *N*,*N*-dimethylaniline (2.3 mL, 18.2 mmol) were dissolved in dry toluene (100 mL) at room temperature under Ar atmosphere. *p*-Bromoethynylbenzene (1.82 g, 10.0 mmol) was added, and the mixture was refluxed for

12 h. After cooling to room temperature, the mixture was decanted from the solid residue and evaporated. The crude reside was purified by silica gel column chromatography with hexane as an eluent. Recrystallization from CHCl₃ and MeOH to provide compound **1** as a colorless crystal (2.10 g, 7.01 mmol, 70 %). ¹H NMR (CDCl₃, 400 MHz) δ (ppm) 7.47 (dt, 2H, J = 8.8, 2.3 Hz), 7.35 (dt, 2H, J = 8.8, 2.3 Hz, Ar–*H*), 6.95 (d, 1H, J = 6.1 Hz, Ar–*H*), 3.90 (s, 1H, carborane_C–*H*), 3.59–1.52 (br, 10H, B–*H*). ¹³C NMR (CDCl₃, 100 MHz) δ (ppm) 132.6, 132.1, 129.2, 124.6, 75.5, 60.2. ¹¹B NMR (CDCl₃, 100 MHz) δ (ppm) –1.3, –2.4, –3.6, –4.8, –6.2, –9.5, –10.2, –10.8, –11.4, –12.0, –13.3. HRMS (APCI) calcd. For C₈H₁₅B₁₀Br [M+Cl]⁻: 335.1034, found 335.1024.

General synthesis of p-(o-carboran-1-yl)tolane derivatives 1a, 1c and 1d

The mixture of *p*-(*o*-carboranyl)-bromobenzene (1.00 mmol), $Pd_2(dba)_3$ (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 Mg₂SO₄. Then, Mg₂SO₄ was removed, and solvent was evaporated. The crude reside was purified by silica gel column chromatography with hexane as an eluent. Recrystallization from CHCl₃ and MeOH to give the product as colorless crystal.

1a: 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, 125 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.

1c: 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, C*H*₃), 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, 100 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.

1d: 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*). ¹³C NMR (CDCl₃, 100 MHz) δ (ppm) 134.3, 132.1, 132.1, 131.6, 127.8, 125.0, 123.9, 122.1 (q, *J* = 3 Hz, CF₃), 121.6, 90.9, 88.5, 77.2, 60.1. ¹¹B NMR (CDCl₃, 100 MHz) δ (ppm) –1.4, –2.5, –8.2, –9.4, –10.2, –11.5, –13.2. HRMS (APCI) calcd. For C₁₈H₁₈B₁₀F₆ [M]⁻: 458.2249, found 458.2255.

Synthesis of *p*-(1-methyl-*o*-carboran-2-yl)tolane (1b)

1a (0.160 mg, 0.5 mmol) was dissolved in Et_2O (4 mL) under Ar atmosphere. Then *n*-BuLi (1.6 M hexane solution, 0.32 mL, 0.5 mmol) was added at 0 °C and stirred. After 1 h, MeI (0.06 mL, 1.0 mmol) was added to the solution and stirred for 1 d at room temperature. The reaction was quenched by adding water, and the organic layer was extracted with CHCl₃ and dried over Mg₂SO₄. Then, Mg₂SO₄ was removed, and solvent was evaporated. The crude residue was purified by silica gel column chromatography with hexane as an eluent. Recrystallization from CHCl₃ and MeOH to give **1b** (0.0682 mg, 41%) as colorless crystal. ¹H NMR (CDCl₃, 400 MHz) δ (ppm) 7.63 (d, 2H, *J* = 8.3, Ar–*H*), 7.55–7.52 (m, 4H, Ar–*H*), 7.39–7.35 (m, 3H, Ar–*H*), 3.73–1.55 (br, 13H, B–*H*, *CH*₃). ¹³C NMR (CDCl₃, 100 MHz) δ (ppm) 134.3, 132.1, 132.1, 131.6, 127.8, 125.0, 123.9, 122.1, 121.6, 90.9, 88.5, 77.2, 60.1. ¹¹B NMR (CDCl₃, 100 MHz) δ (ppm) –1.4, –2.5, –8.2, –9.4, –10.2, –11.5, –13.2. HRMS (APCI) calcd. For C₁₆H₂₀B₉ [M]⁻: 311.2408, found 311.2411.

General synthesis of nido-carboranyltolane derivatives 2a-d

Tetrabutylammonium fluoride (1 M THF solution, 1.1 mmol) was added to a THF (1 mL) and distilled water (0.1 mL) solution of 1a-d (0.11 mmol). The mixture was stirred at room temperature for 24 h, and then the product was extracted with CH₂Cl₂. The CH₂Cl₂ solution was dried over MgSO₄. MgSO₄ was removed, and the solvent was evaporated. Recrystallization from CH₂Cl₂ and MeOH to give the *nido* derivatives as a colorless crystal.

2a: 82% as a white powder. ¹H NMR (CD₂Cl₂, 400 MHz) δ (ppm) 7.50 (dd, 2H, *J* = 7.3, 1.96 Hz, Ar–*H*), 7.36–7.29 (m, 5H), 7.24 (d, 2H, *J* = 8.3 Hz), 3.09 (t, 8H, *J* = 8.4, NC*H*₂), 2.76–0.27 (m, 38H C*H*₂C*H*₃, B–*H*), –2.30 (s, 1H, B–*H*–B). ¹³C NMR (CDCl₃, 100 MHz) δ (ppm) 147.2, 131.9, 131.1, 128.8, 128.4, 127.1, 124.1, 119.5, 90.3, 89.0,

59.6, 24.4, 20.2, 13.8. ¹¹B NMR (CDCl₃, 100 MHz) δ (ppm) –9.4, –13.5, –18.0, –22.6, –32.1, –35.8. HRMS (APCI) calcd. For C₁₆H₂₀B₉ [M]^{-:} 311.2408, found 311.2411.

2b: 47% as a white powder. ¹H NMR (CDCl₃, 400 MHz) δ (ppm) 7.50–7.47 (m, 2H, Ar–*H*), 7.34–7.26 (m, 7H), 3.14 (t, 8H, *J* = 8.5 Hz, C*H*₂C*H*₃), 2.66–0.92 (m, 29H, C*H*₂C*H*₃, B–*H*), 1.11 (s, 3H, C*H*₃), 1.00 (t, 8H, *J* = 7.3 Hz, NC*H*₂) –1.98 (s, 1H, B–*H*–B). ¹³C NMR (CDCl₃, 100 MHz) δ (ppm) 144.3, 132.0, 131.8, 130.9, 128.8, 128.4, 124.2, 120.6, 90.5, 89.2, 59.6, 24.6, 23.7, 20.2, 14.1. ¹¹B NMR (CDCl₃, 100 MHz) δ (ppm) –9.0, –13.0, –18.8, –21.0, –33.5, –36.4. HRMS (APCI) calcd. For C₁₇H₂₂B₉ [M]⁻: 325.2564, found 325.2567.

2c: 56% as a white powder. ¹H NMR (CDCl₃, 400 MHz) δ (ppm) 7.42 (d, 2H, J = 8.80 Hz, Ar–H), 7.26 (s, 4H), 6.85 (d, 2H, J = 8.76 Hz), 3.81 (s, 3H, OCH₃), 3.12 (t, 8H, J = 8.54 Hz, NCH₂), 1.64–0.85 (m, 38H, CH₂CH₃, B–H), –2.30 (s, 1H, B–H–B). ¹³C NMR (CDCl₃, 100 MHz) δ (ppm) 159.4, 132.9, 130.5, 126.7, 113.9, 59.1, 55.3, 24.1, 19.7, 13.6 (due to low solubility, C₄ were not detected). ¹¹B NMR (CDCl₃, 100 MHz) δ (ppm) –10.9, –13.0, –18.8, –22.5, –33.0, –35.8. HRMS (APCI) calcd. For C₁₇H₂₂B₉O [M]⁻: 341.2514, found 341.2514.

2d: 67% as a white powder. ¹H NMR (CDCl₃, 400 MHz) δ (ppm) 7.90 (s, 2H, Ar–*H*), 7.76 (s, 1H, Ar-*H*), 7.33–7.26 (m, 4H, Ar-*H*), 3.14 (t, 8H, *J* = 8.42 Hz, NC*H*₂), 2.39– 0.71 (m, 38H, C*H*₂C*H*₃, B–*H*), –2.40 (s, 1H, B–*H*–B). ¹³C NMR (CDCl₃, 100 MHz) δ (ppm) 147.7, 132.1, 131.7, 131.3, 131.0, 126.8, 126.2, 121.7 (q, *J* = 3 Hz, CF₃), 117.7, 93.7, 85.8, 59.1, 24.0, 19.7, 13.6. ¹¹B NMR (CDCl₃, 100 MHz) δ (ppm) –9.7, –14.0, -18.7, -22.8, -32.8, -35.6. HRMS (EI) calcd. For $C_{18}H_{18}B_9F_6$ [M]⁻: 447.2156, found 447.2163.





Chart S1. (a) 1 H, (b) 13 C and (c) 11 B NMR spectra of 1a in CDCl₃.





Chart S2. (a) 1 H, (b) 13 C and (c) 11 B NMR spectra of 1b in CDCl₃.





Chart S3. (a) 1 H, (b) 13 C and (c) 11 B NMR spectra of 1c in CDCl₃.





Chart S4. (a) 1 H, (b) 13 C and (c) 11 B NMR spectra of 1d in CDCl₃.





Chart S5. (a) 1 H, (b) 13 C and (c) 11 B NMR spectra of 2a in CD₂Cl₂.



c



Chart S6. (a) 1 H, (b) 13 C and (c) 11 B NMR spectra of 2b in CDCl₃.





Chart S7. (a) 1 H, (b) 13 C and (c) 11 B NMR spectra of 2c in CDCl₃.





Chart S8. (a) 1 H, (b) 13 C and (c) 11 B NMR spectra of 2d in CDCl₃.



Figure S1. Lippert–Mataga plots of **2a** (dot) and **2b** (square). The solvent from left to right are EtOAc, THF, DMF, DMSO and MeCN, respectively. Solvent polarizabilities Δf were calculated according to the equation 4.

Solvent	$\lambda_{\rm abs}/{ m nm}$	$\lambda_{ m PL}$ / nm	Stokes-shift / cm ⁻¹
THF	310	446	983
DMF	308	457	1058
DMSO	308	465	1096
EtOAc	308	459	1068
MeCN	305	470	1151

 Table S1. Photophysical properties of 2a in different solvents^a

^{*a*} Measured in 1.0×10^{-5} M solutions of each solvent.

Solvent	λ_{abs}/nm	$\lambda_{\rm PL}$ / nm	Stokes-shift /
	405	T L	cm^{-1}
THF	289	474	1350
DMF	289	501	1432
DMSO	291	499	1464
AcOEt	288	504	1488
MeCN	287	518	1553

 Table S2. Photophysical properties of 2b in different solvents^a

^{*a*} Measured in 1.0×10^{-5} M solutions of each solvent.

Compound	Slope / cm ⁻¹	a / Å a	$\mu_{ m G}$ / Debye ^b	$\mu_{\rm G}$ – $\mu_{\rm E}$ / Debye	$\mu_{\rm E}$ / Debye
2a	10111	5.28	19.22	3.85	23.07
2b	9890	5.20	19.51	3.72	23.23

Table S3. Results of Lippert–Mataga plots and estimated electric dipole moments

 a Effective radii of the Onsager cavity were estimated from the molecular dimensions of each model compound obtained from the DFT calculations at B3LYP/6-31G(d,p) level of theory and from the assumption of a spherical shape of this cavity with Gaussian09 keyword "volume". b Electric dipole moments in a ground state were estimated from the optimized structure of each model compound obtained from the DFT calculations at B3LYP/6-31G(d,p) level of theory.

Excited state	Transitions	λ_{calc} (nm)	Oscillator strength
$S_0 \to S_1$	$H-1 \to L (21\%)$ $H \to L (65\%)$	328.21	0.9612
$S_0 \to S_2$	$H-1 \rightarrow L (62\%)$ $H \rightarrow L (20\%)$	290.38	0.4123
$S_0 \to S_3$	$H-1 \rightarrow L+1 (14\%)$ $H \rightarrow L+1 (49\%)$ $H \rightarrow L+4 (17\%)$	265.22	0.0010

 Table S4. Calculation results of 2a in the ground state

Excited state	Transitions	λ_{calc} (nm)	Oscillator strength
$S_0 \rightarrow S_1$	$\mathrm{H} \rightarrow \mathrm{L} \; (80\%)$	331.56	0.2049
$S_0 \to S_2$	H−1 → L (80%)	298.34	1.0853
$S_0 \rightarrow S_3$	$H-1 \rightarrow L+2 (21\%)$ $H \rightarrow L+2 (32\%)$	259.03	0.0046

 Table S5. Calculation results of 2b in the ground state

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