Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Design of Bond-Cleavage-Induced Intramolecular Charge Transfer Emission with Dibenzoboroles and Their Application to Ratiometric Sensors for Discriminating Chain Lengths of Alkanes

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Page Contents

Experimental Section

Measurements ^{1}H (400 MHz), ^{13}C (100 MHz) and ^{11}B (128 MHz) NMR spectra were recorded on a JEOL JNM-EX400 and JNM-AL400 spectrometers. ^{1}H, ^{13}C and ^{11}B NMR spectra were obtained with CD_2Cl_2. ^{11}B NMR spectra were measured with $BF_3 \cdot Et_2O$ as an external reference. High-resolution mass spectra (HRMS) were obtained on a Thermo Fisher Scientific EXACTIVE for atomic pressure chemical ionization (APCI) and electrospray ionization (ESI). UV–vis absorption spectra were recorded on a Shimadzu UV-3600 spectrophotometer. Fluorescence emission spectra were recorded on a HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer, and the absolute quantum yield was calculated by the integrating sphere method on the HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer. Photoluminescence lifetime measurement was performed on a Horiba FluoreCube spectrofluorometer system; excitation was carried out using a UV diode laser (NanoLED 290 or 375 nm). Viscosity measurement wascarried out with a KYOTO ELECTRONICS MANIFACTURING CO., LTD. EMS−1000 viscometer. X-ray crystallographic analysis was carried out by a Rigaku R-AXIS RAPID-F graphite-monochromated Mo Kα radiation diffractometer with an imaging plate. A symmetry related absorption correction was carried out by using the program ABSCOR[1]. The analysis was carried out with direct methods (SHELX-97[2] or SIR97[3]) using Yadokari-XG[4]. All reactions were performed under argon atmosphere

Materials. All reagents were obtained from commercial sources and used without further purification. Tetrahydrofuran (THF), diethyl ether (Et_2O), and triethylamine (NEt_3) were purified using a two-column solid-state purification system (Glass Contour Solvent System, Joerg Meyer, Irvine, CA). Dibenzoborole (**1**) was prepared according to the literature[5].

Synthesis of 3,7-dibromodibenzoborole (2). The mixture of **1** (0.81 g, 2.0 mmol) and *N*-bromosuccinimide (0.93 g, 5.2 mmol) in *N*,*N*–dimethylformamide (12 mL) was stirred overnight at room temperature. The mixture was washed with $NaHSO_3$ (10 mL) and brine (30 mL) and dried over $MgSO_4$. Then, the solution was filtered and evaporated to remove the solvent. The crude product was purified by silica gel column chromatography (hexane/ ethyl acetate = 10 : 1) to give the **2** as a white solid (0.95 g, 84%). ^{1}H NMR ($CDCl_3$, δ, ppm): 7.53 (d, J = 8.1 Hz, 2H), 7.39−7.37 (m, 3H), 7.33 (d, J = 2.0 Hz, 2H), 7.14 (d, J = 1.4 Hz, 1H), 4.20 (s, 2H), 2.41 (s, 6H), 1.37 (s, 9H), 0.92 (s, 9H). ^{13}C NMR (CD_2Cl_2, δ, ppm): 154.9, 149.5, 147.8, 141.0, 135.6, 130.6, 123.0, 121.7, 121.4, 117.8, 68.9, 48.4, 37.4, 35.0, 31.9, 31.7. ^{11}B NMR (CD_2Cl_2, δ, ppm): 5.57. HRMS (APCI): m/z calcd. for $C_{29}H_{34}BBr_2N$ $[M+H]^+$: 566.1224; found: 566.1217.

General procedure. 2 (113 mg, 0.20 mmol), aryldiboronic acid (0.44 mmol), $Pd_2(dba)_3$ (4.6 mg, 5.0 μmol), X-Phos (9.5 mg, 20 μmol), and Cs_2CO_3 (390 mg, 1.2 mmol) were dissolved in tetrahydrofuran (1.5 mL) and H_2O (1.5 mL) under an inert atmosphere. After stirring at 60 °C for 10 h, the mixture was diluted with chloroform, washed with brine, and dried over Na_2SO_4, and then the solvent was removed under reduced pressure. The crude products were purified by silica gel column chromatography (hexane/ ethyl acetate = 10 : 1) to give a white solid.

3a

A white solid, 83% yield. ^{1}H NMR (CD_2Cl_2, δ, ppm): 7.83 (d, J = 7.8 Hz, 2H), 7.68 (ddd, J = 10.5 Hz, 8H), 7.59 (d, J = 2.0 Hz, 1H), 7.57 (d, J = 2.0 Hz, 1H), 7.54 (d, J = 1.5 Hz, 2H), 7.40 (d, J = 1.7 Hz, 1H), 7.19 (d, J = 1.7 Hz, 1H), 4.30 (s, 2H), 2.48 (s, 6H), 1.38 (s, 9H), 0.99 (s, 9H). ^{13}C NMR (CD_2Cl_2, δ, ppm): 155.0, 149.9, 149.2, 146.42, 146.40, 141.3, 137.6, 131.8, 129.3, 129.1, 129.0, 128.7, 128.3, 127.7, 127.1, 126.4, 126.0 (q, J = 4.1 Hz), 123.7, 122.9, 121.0, 120.6, 117.8, 68.9, 48.5, 37.6, 35.0, 32.0, 31.8. ^{11}B NMR (CD_2Cl_2, δ, ppm): 6.25.; HRMS (ESI): m/z calcd. for $C_{43}H_{42}BF_6NCl$ $[M+Cl]^-$: 732.3009; found: 732.3023.

3b

A white solid, 95% yield. ^{1}H NMR (CD_2Cl_2, δ, ppm): 7.80 (d, J = 7.8 Hz, 2H), 7.60−7.52 (m, 8H), 7.41−7.37 (m, 5H), 7.32−7.28 (m, 2H), 7.18 (d, J = 1.2 Hz, 1H), 4.29 (s, 2H), 2.48 (s, 6H), 1.39 (s, 9H), 1.01 (s, 9H). ^{13}C NMR (CD_2Cl_2, δ, ppm): 155.0, 149.2, 149.0, 142.8, 161.3, 138.9, 131.6, 129.0, 127.3, 127.0, 126.8, 126.00, 12122.7, 120.2, 117.7, 68.8, 48.4, 37.5, 35.0, 32.0, 31.8. ^{11}B NMR (CD_2Cl_2, δ, ppm): 6.35.; HRMS (ESI): m/z calcd. for $C_{41}H_{44}BNNa$ $[M+Na]^+$: 584.3459; found: 584.3462.

3c

A white solid, 85% yield. ^{1}H NMR (CD_2Cl_2, δ, ppm): 7.73 (d, J = 7.8 Hz, 2H), 7.51−7.45 (m, 8H), 7.38 (d, J = 1.9 Hz, 1H), 7.16 (d, J = 1.9 Hz, 1H), 6.92 (m, 4H), 4.27 (s, 2H), 3.81 (s, 6H), 2.46 (s, 6H), 1.37 (s, 9H), 0.98 (s, 9H). ^{13}C NMR (CD_2Cl_2, δ, ppm): 159.3, 154.9, 148.9, 148.7, 141.3, 138.4, 135.3, 131.2, 128.3, 126.2, 122.7, 120.1, 117.7, 114.4, 68.8, 55.7, 48.4, 37.5, 35.0, 32.0, 31.8. ^{11}B NMR (CD_2Cl_2, δ, ppm): 6.16.; HRMS (ESI): m/z calcd. for $C_{43}H_{48}BNO_2Na$ $[M+Na]^+$: 644.3670; found: 644.3680.

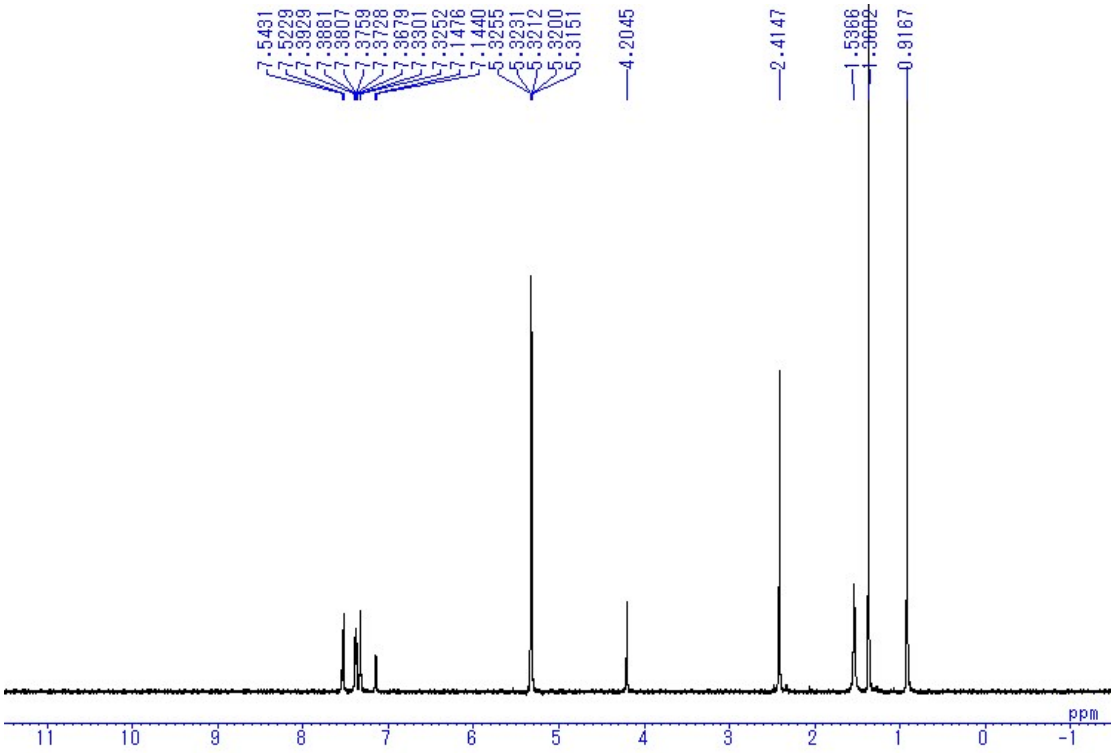


Figure S1. ^{1}H NMR spectrum of **2** in CD_2Cl_2.

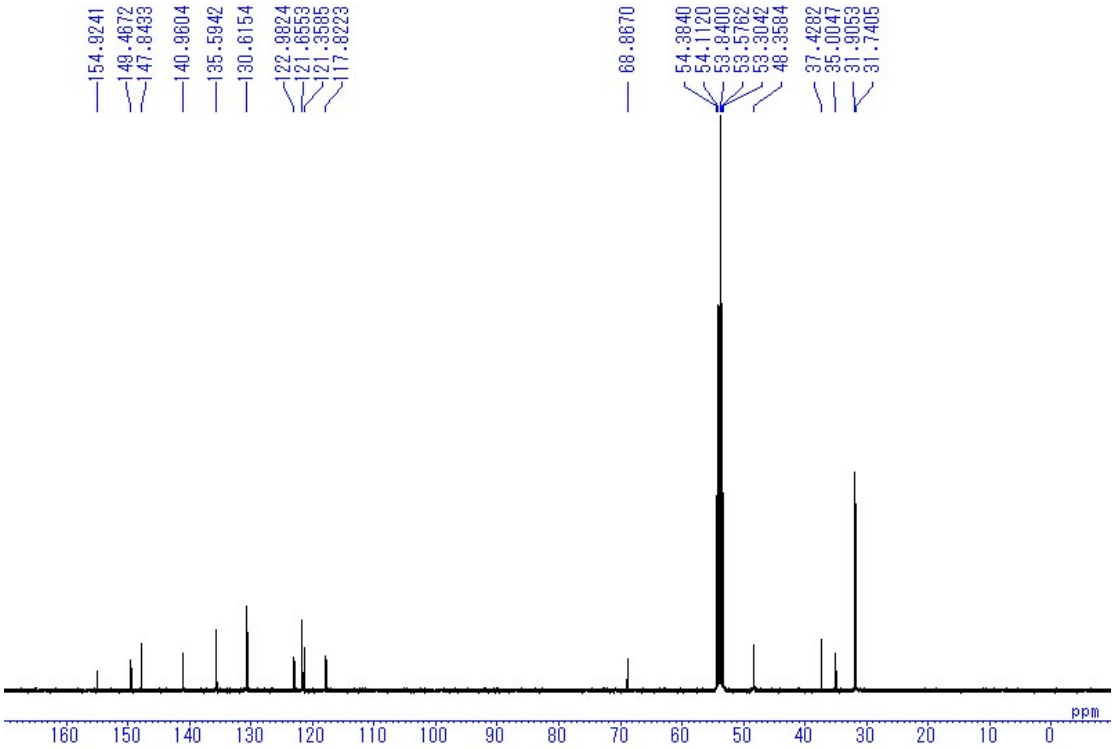


Figure S2. ^{13}C NMR spectrum of **2** in CD_2Cl_2.

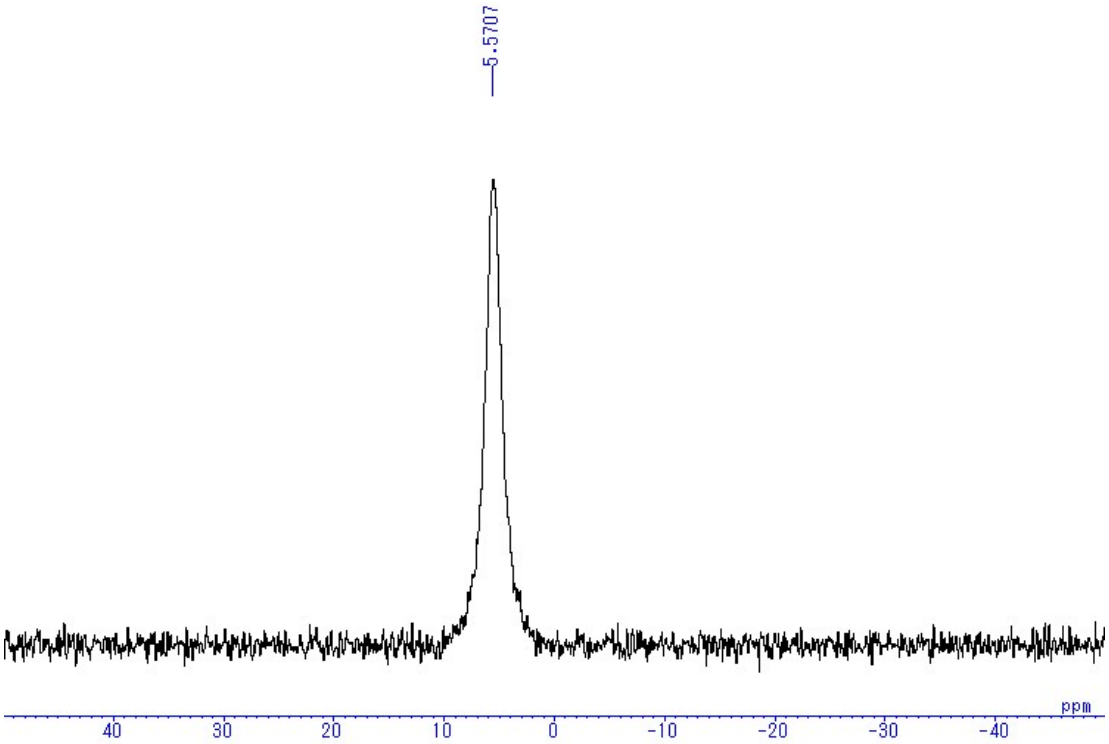


Figure S3. ^{11}B NMR spectrum of **2** in CD_2Cl_2.

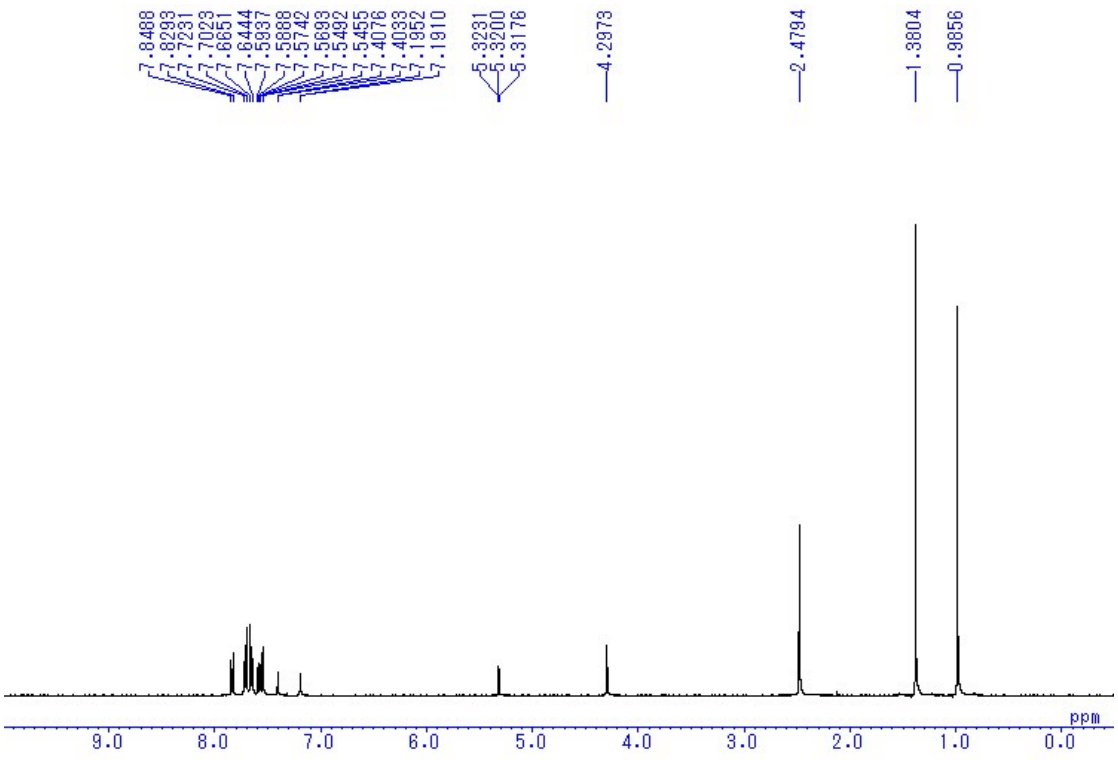


Figure S4. ^{1}H NMR spectrum of **3a** in CD_2Cl_2.

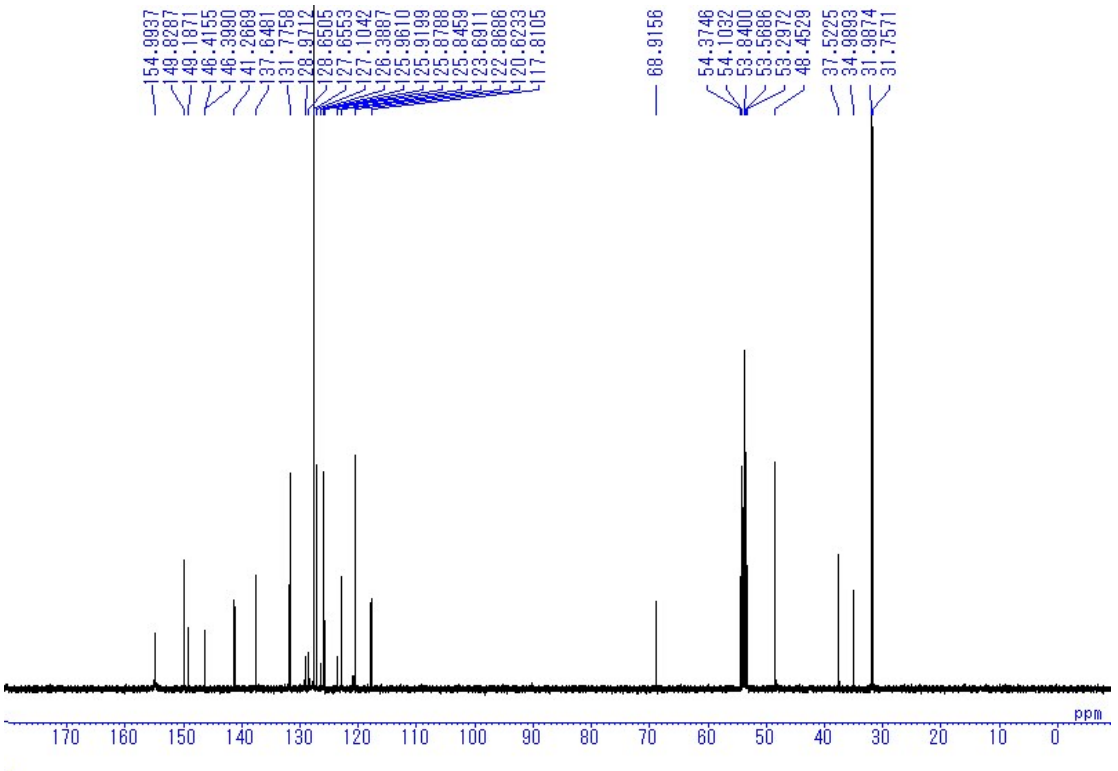


Figure S5. ^{13}C NMR spectrum of **3a** in CD_2Cl_2.

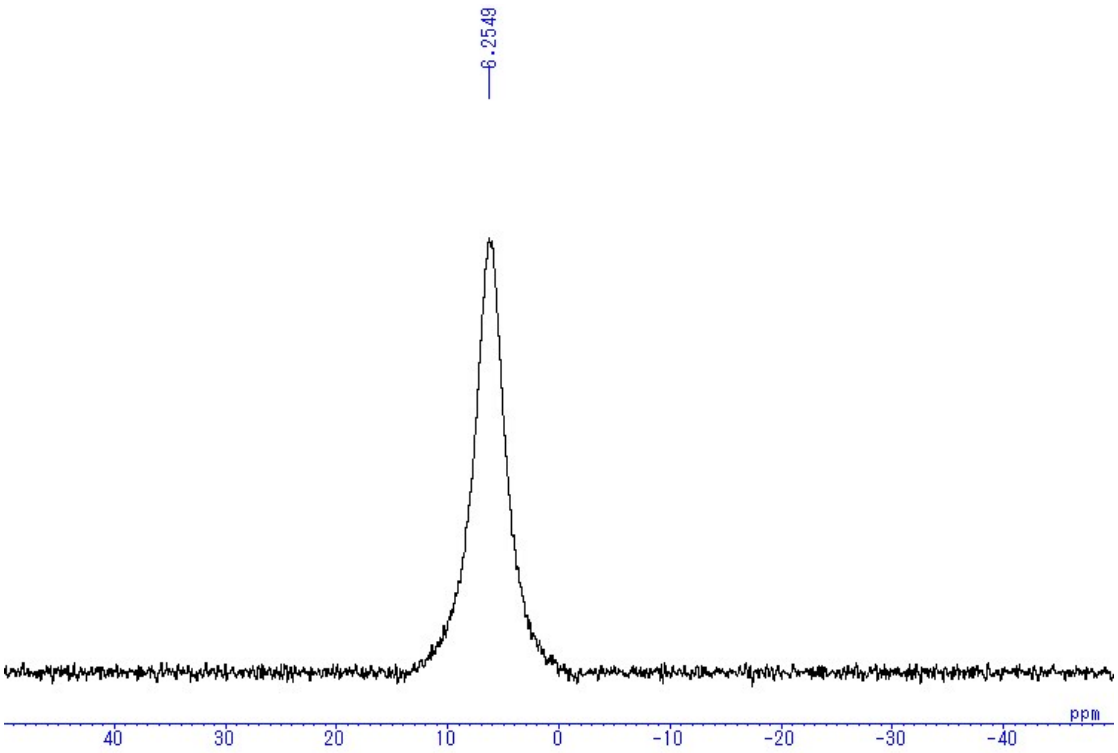


Figure S6. ^{11}B NMR spectrum of **3a** in CD_2Cl_2.

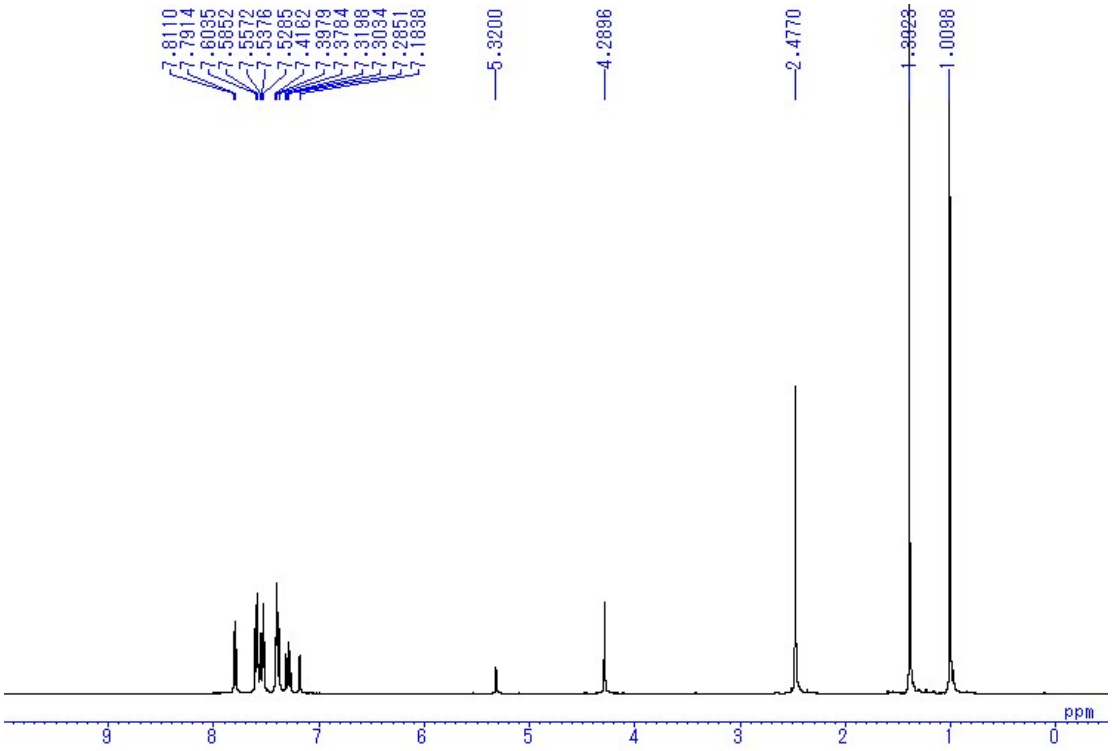


Figure S7. ^{1}H NMR spectrum of **3b** in CD_2Cl_2.

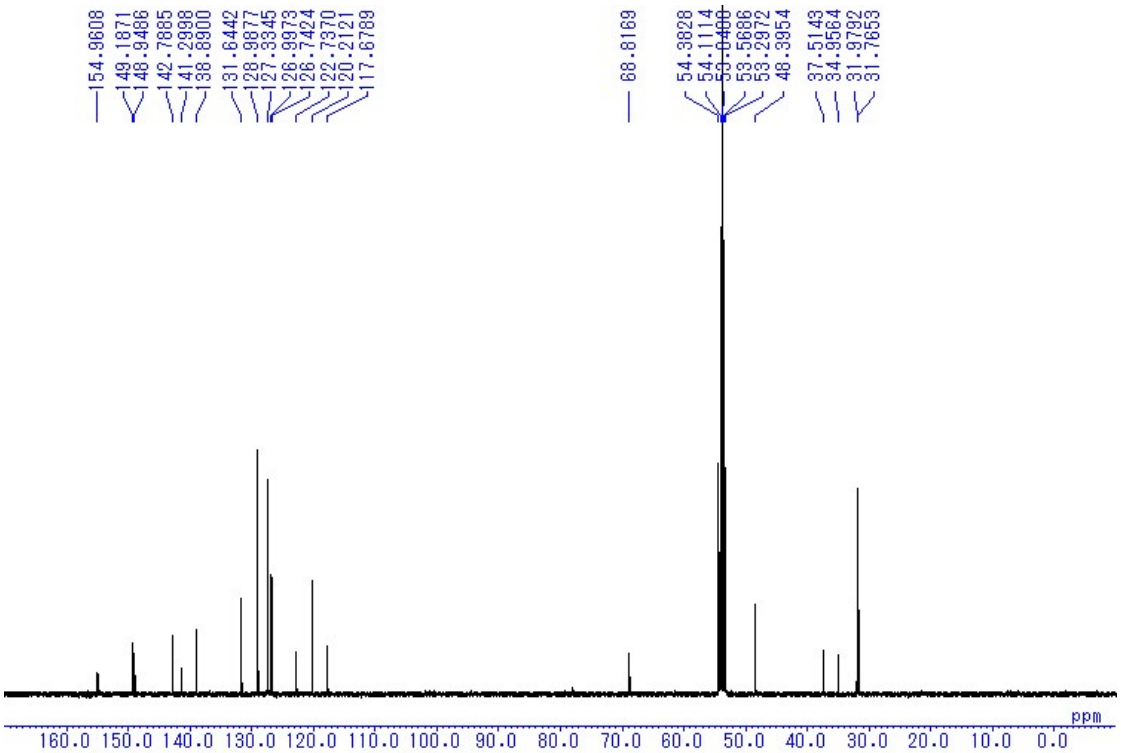


Figure S8. ^{13}C NMR spectrum of **3b** in CD_2Cl_2.

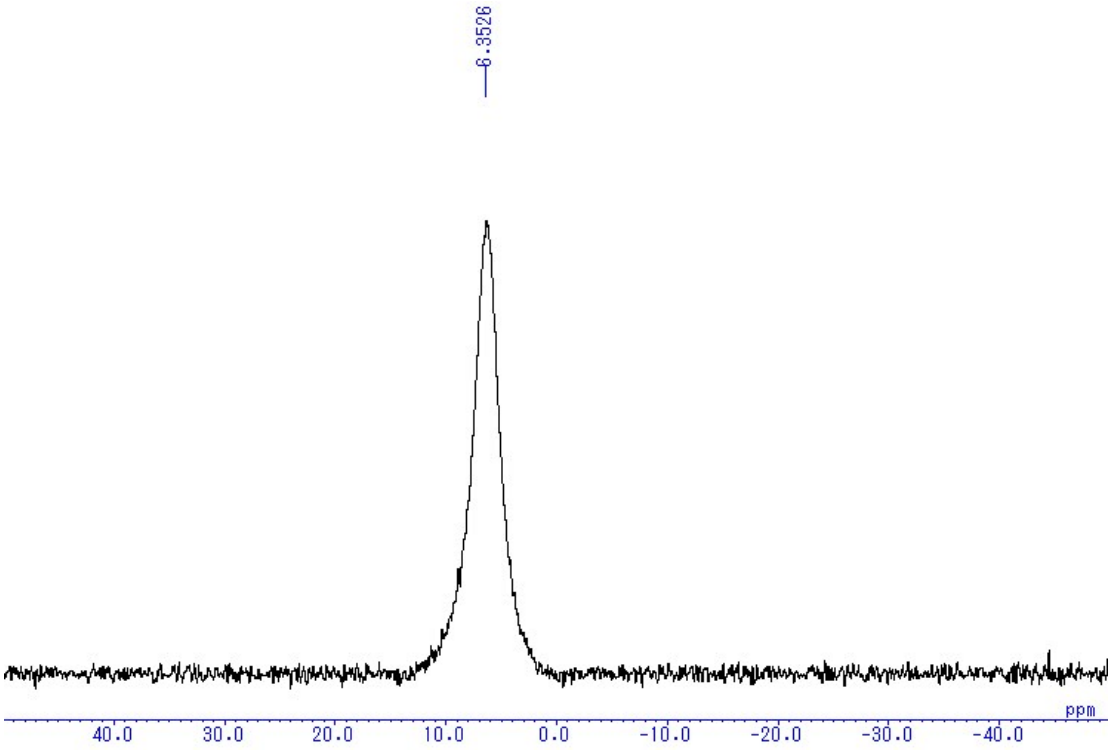


Figure S9. ^{11}B NMR spectrum of **3b** in CD_2Cl_2.

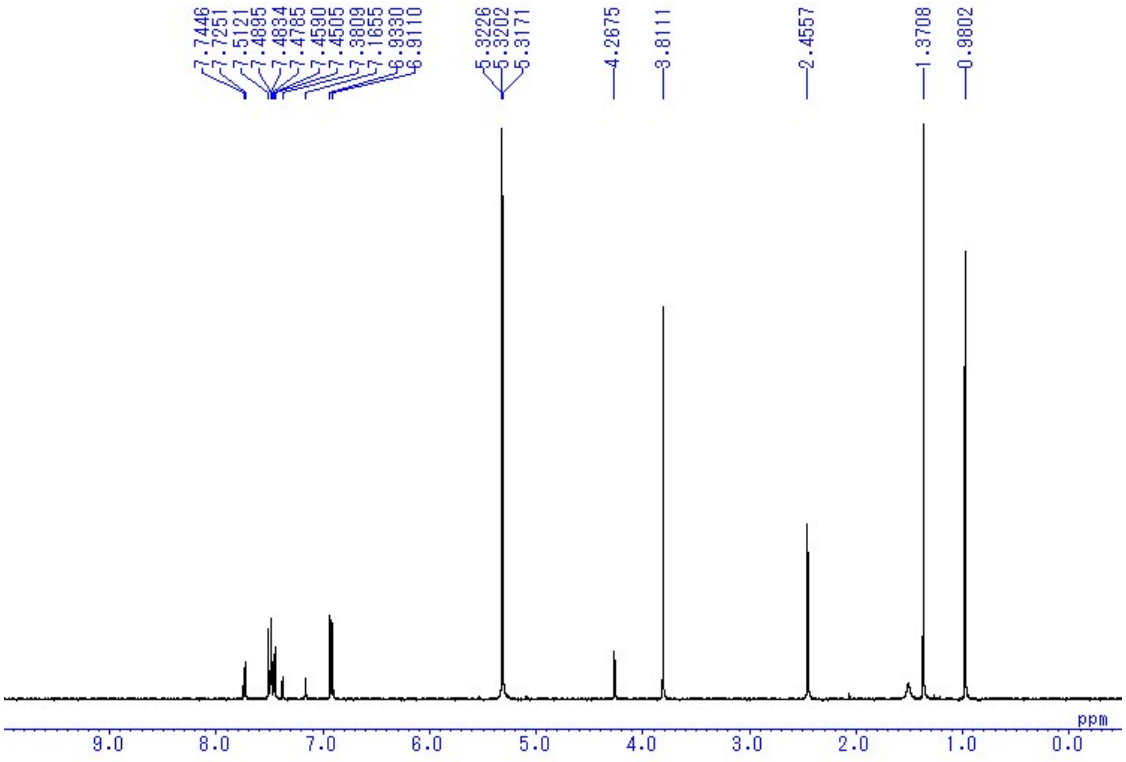


Figure S10. ^{1}H NMR spectrum of **3c** in CD_2Cl_2.

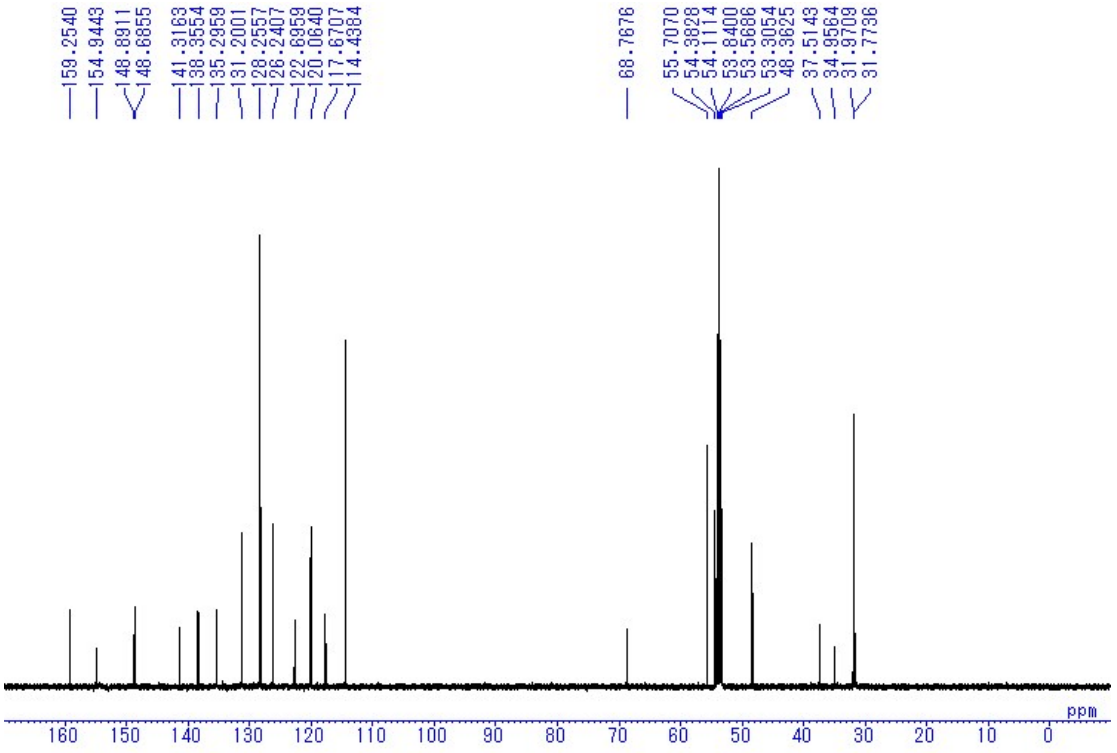


Figure S11. ^{13}C NMR spectrum of **3c** in CD_2Cl_2.

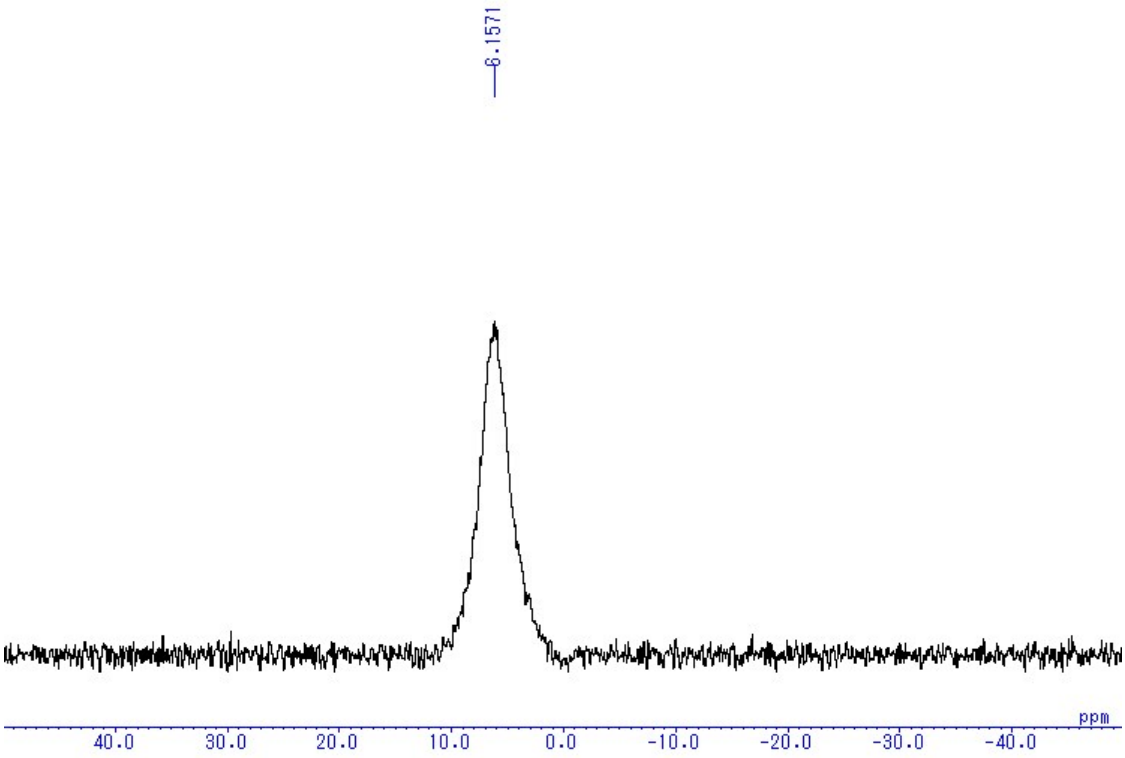
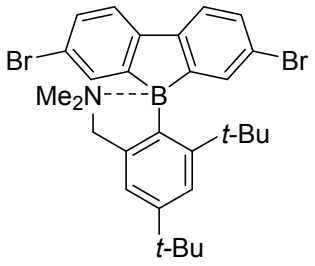


Figure S12. ^{11}B NMR spectrum of **3c** in CD_2Cl_2.

Preparation of Single Crystal. The single crystal of **2** was prepared by recrystallization from chloroform and methanol solution in the two-layer method.

X-ray Crystal Structure Analyses. Intensity data were collected on a Rigaku R-AXIS RAPID imaging plate area detector with graphite monochromated Mo *K*α radiation at –180 °C. The structures were solved by direct method (SIR97)[9] and refined by full-matrix least-squares procedures based on F^2 (SHELX-97)[10].

Table S1. Crystallographic data of **2**



2

Empirical formula	$C_{29}H_{34}BBr_2N$
Formula weight	567.20
Temperature (K)	93(2)
Wavelength (Å)	0.71075
Crystal system, space group	triclinic, *P-1*
Unit cell dimensions	a = 7.9955(14)
	b = 11.139(2)
	c = 14.735(3)
	α = 87.095(6)
	β = 78.445(6)
	γ = 81.208(6)
V (Å^3)	1270.4(4)
Z, calculated density (Mg m^{-3})	2, 1.483
Absorption coefficient	3.209
F(000)	580
Crystal size (mm)	0.30 × 0.10 × 0.10
θ range for data collection	3.06–27.48
Limiting indices	$-10 \le h \le 10$, $-14 \le k \le 14$, $-19 \le l \le 19$
Reflections collected (unique)	12232 / 5793 [R(int) = 0.1390]
Completeness to theta = 27.49	0.992
Max. and min. transmission	0.7397 and 0.4461
Goodness-of-fit on F^2	0.960
Final R indices [$I > 2\sigma(I)$][a]	R_1 = 0.0840 wR_2 = 0.1671
R indices (all data)	R_1 = 0.1758, wR_2 = 0.2049

[a] $R_1 = \Sigma(|F_0|-|F_c|)/\Sigma|F_0|$. w$R_2 = [\Sigma w(F^2_0-F^2_c)^2/ \Sigma w(F^2_0)^2]^{1/2}$. $w = 1/[\sigma^2(F^2_0)+[(ap)^2+bp]]$, where $p = [\max(F^2_0,0)+2F^2_c]/3$.

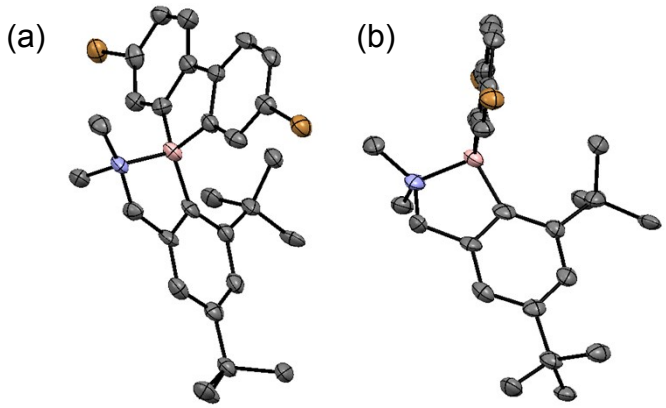


Figure S13. ORTEP drawings of (a) **2** and (b) side view (50% probability for thermal ellipsoids). Hydrogen atoms are omitted for clarity.

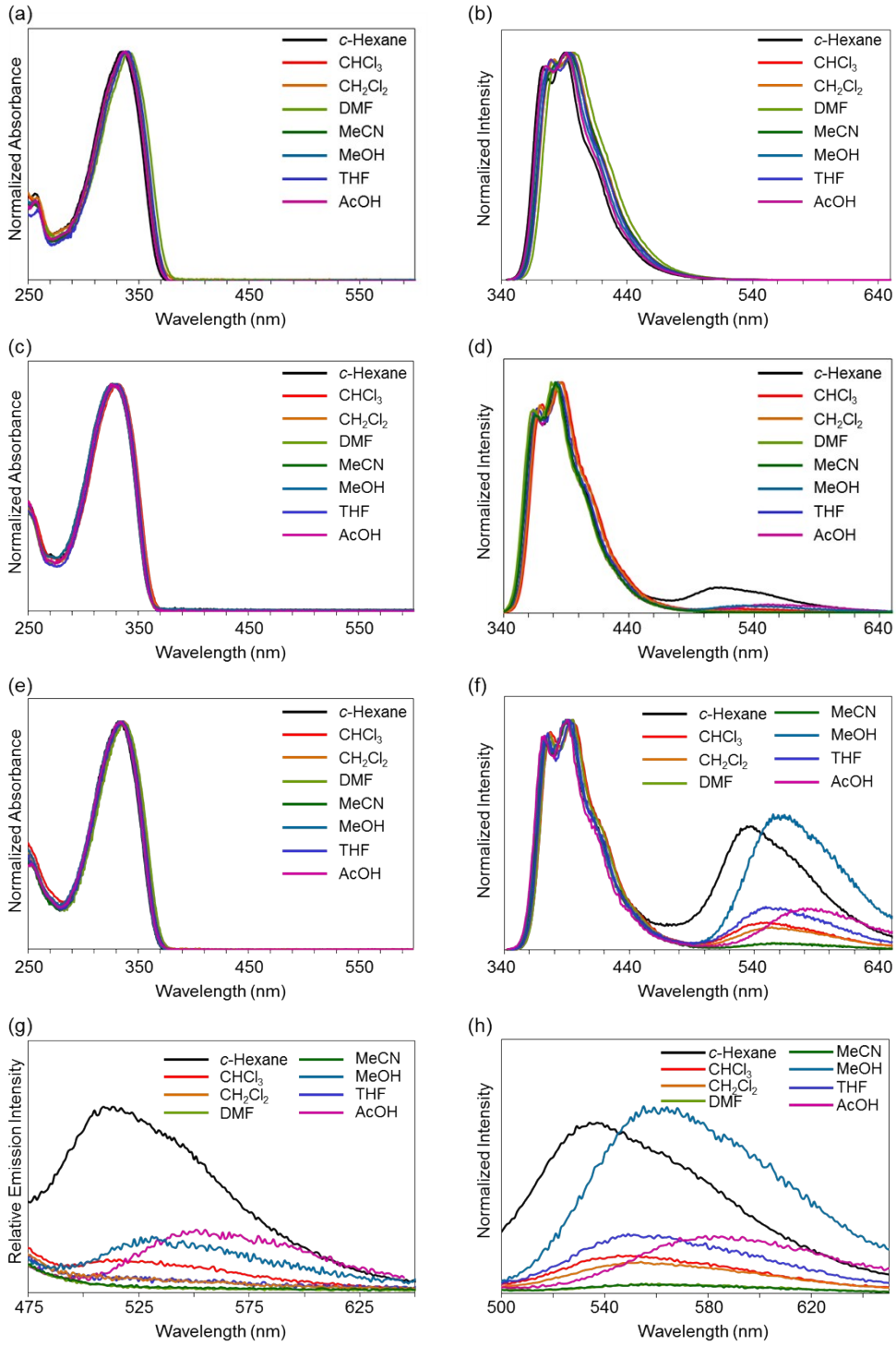


Figure S14. Absorption and emission spectra of dibenzoborole derivative **3a–c** (1.0×10^{-5} M) excited at $\lambda_{max,abs}$. (a) : Absorption spectra of **3a**. (b) : Emission spectra of **3a** excited at $\lambda_{max,abs}$. (c) : Absorption spectra of **3b**. (d) : Emission spectra of **3b** excited at $\lambda_{max,abs}$. (e) : Absorption spectra of **3c**. (f) : Emission spectra of **3c** excited at $\lambda_{max,abs}$. (g) : Expanded emission spectra of **3b**. (h) : E Expanded emission spectra of **3c**.

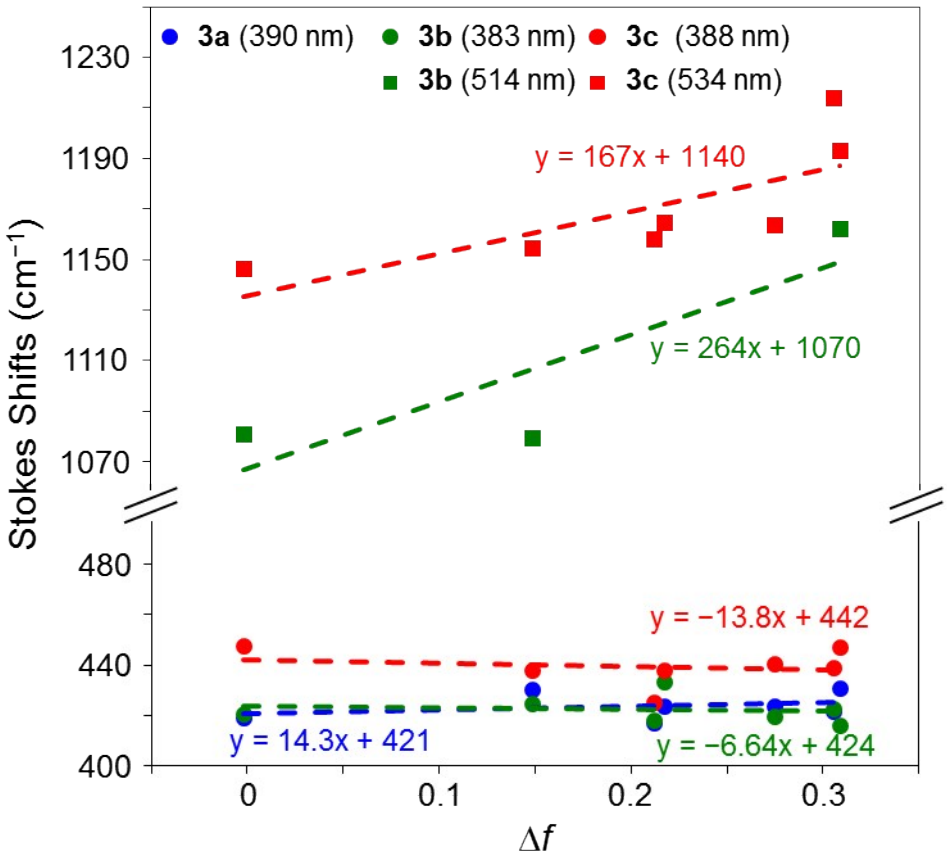


Figure S15. Lippert-Mataga plots of emission bands of **3a**–**c**.

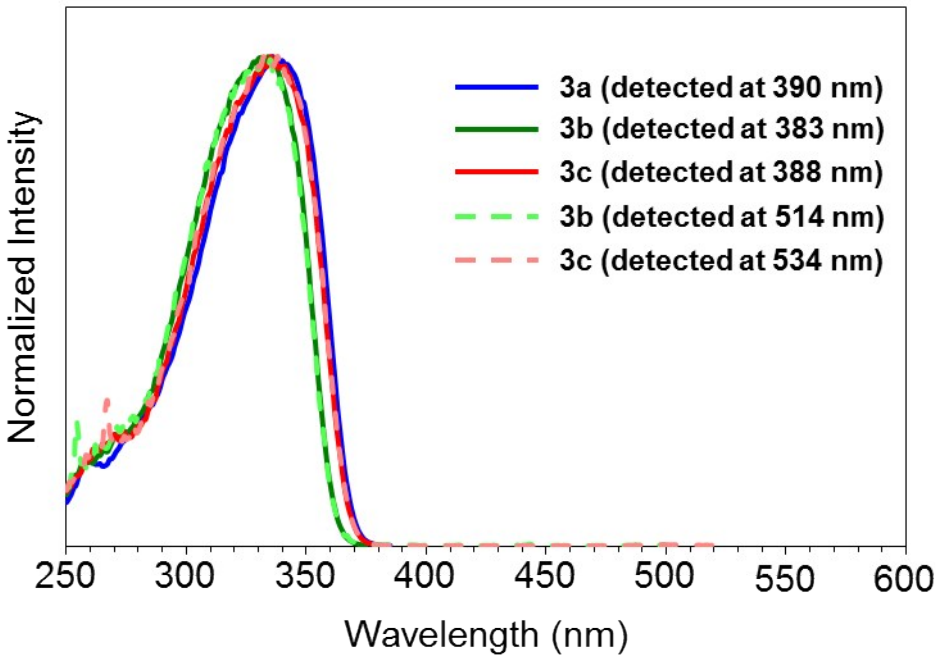


Figure S16. Excitation spectra of dibenzoboroles in cyclohexane solutions collected at $\lambda_{max,FL}$ (1.0×10^{-5} M).

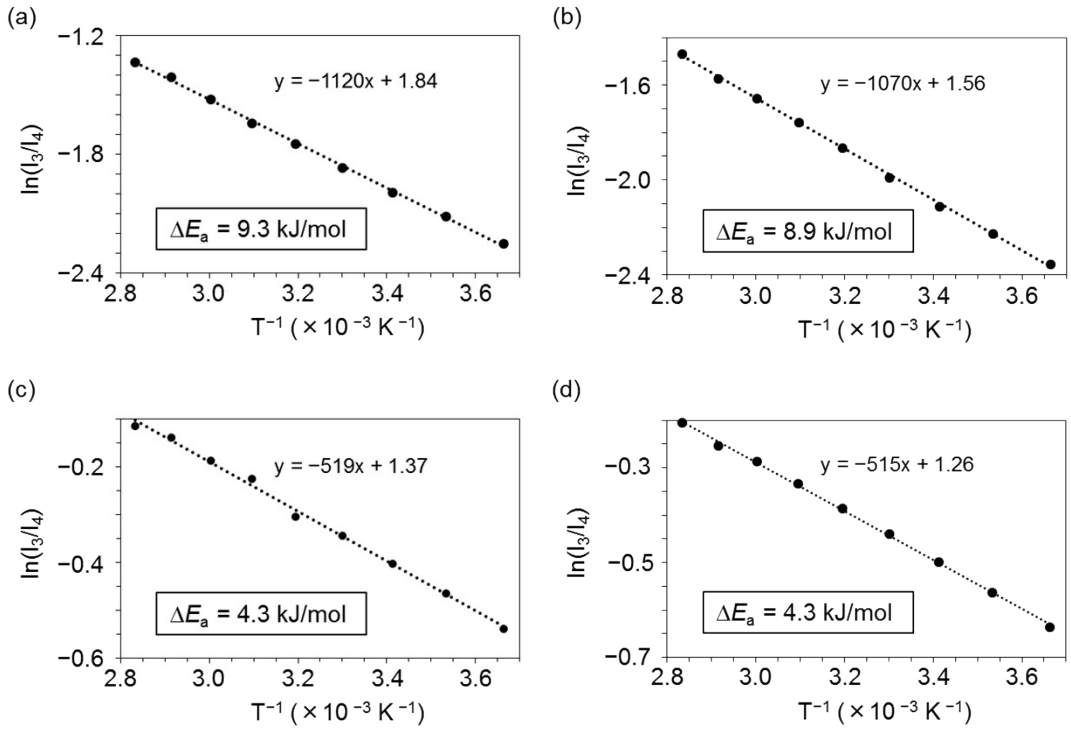


Figure S17. Stevens–Ban plots of the ratio of dual emission bands (I_3 and I_4) of **3b** in *n*-octane (a) and in *n*-decane (b) and **3c** in *n*-octane (c) and in *n*-decane (d).

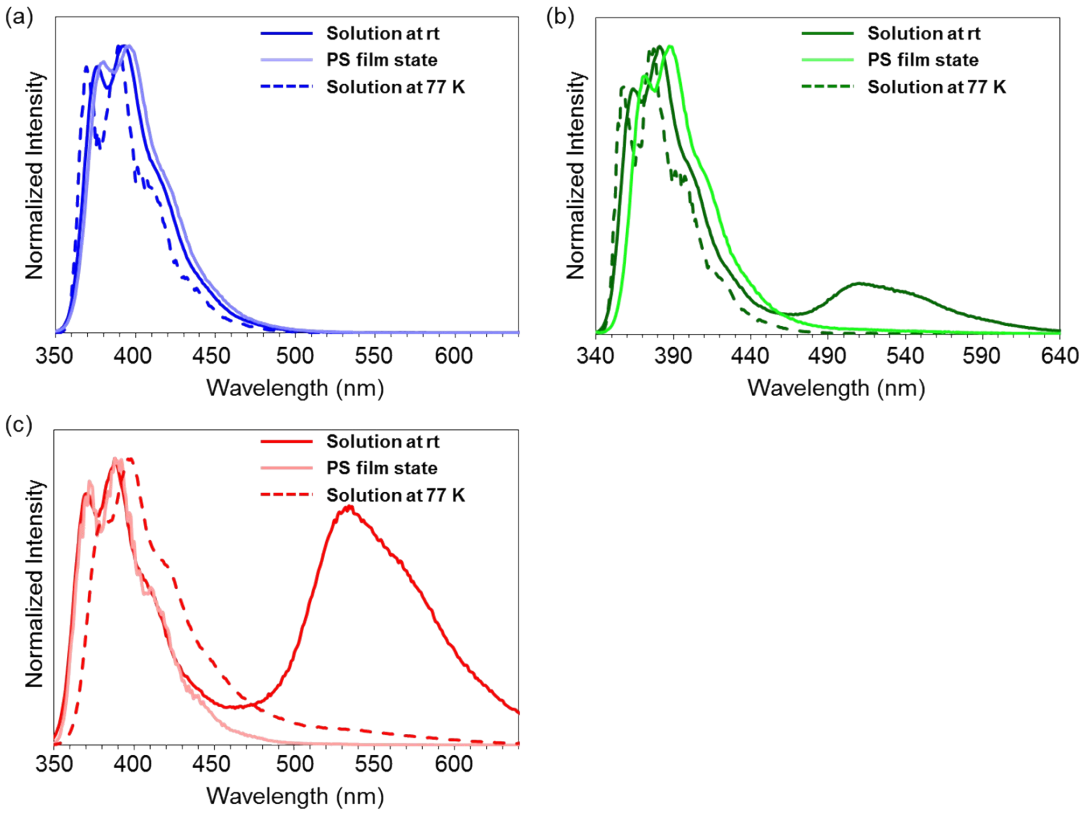


Figure S18. Emission spectra of dibenzoborole derivatives **3a**–**c** excited at $\lambda_{max,abs}$. (a) : **3a**, (b) : **3b**, and (c) : **3c**. (solid line : in the 2-methylbutane/3-methylpentane (1 : 1, 1.0×10^{-5} M) at room temperature ; diluted line : in the 2-methylbutane/3-methylpentane (1 : 1, 1.0×10^{-5} M) at 77 K; dashed line : in polystyrene film at room temperature).

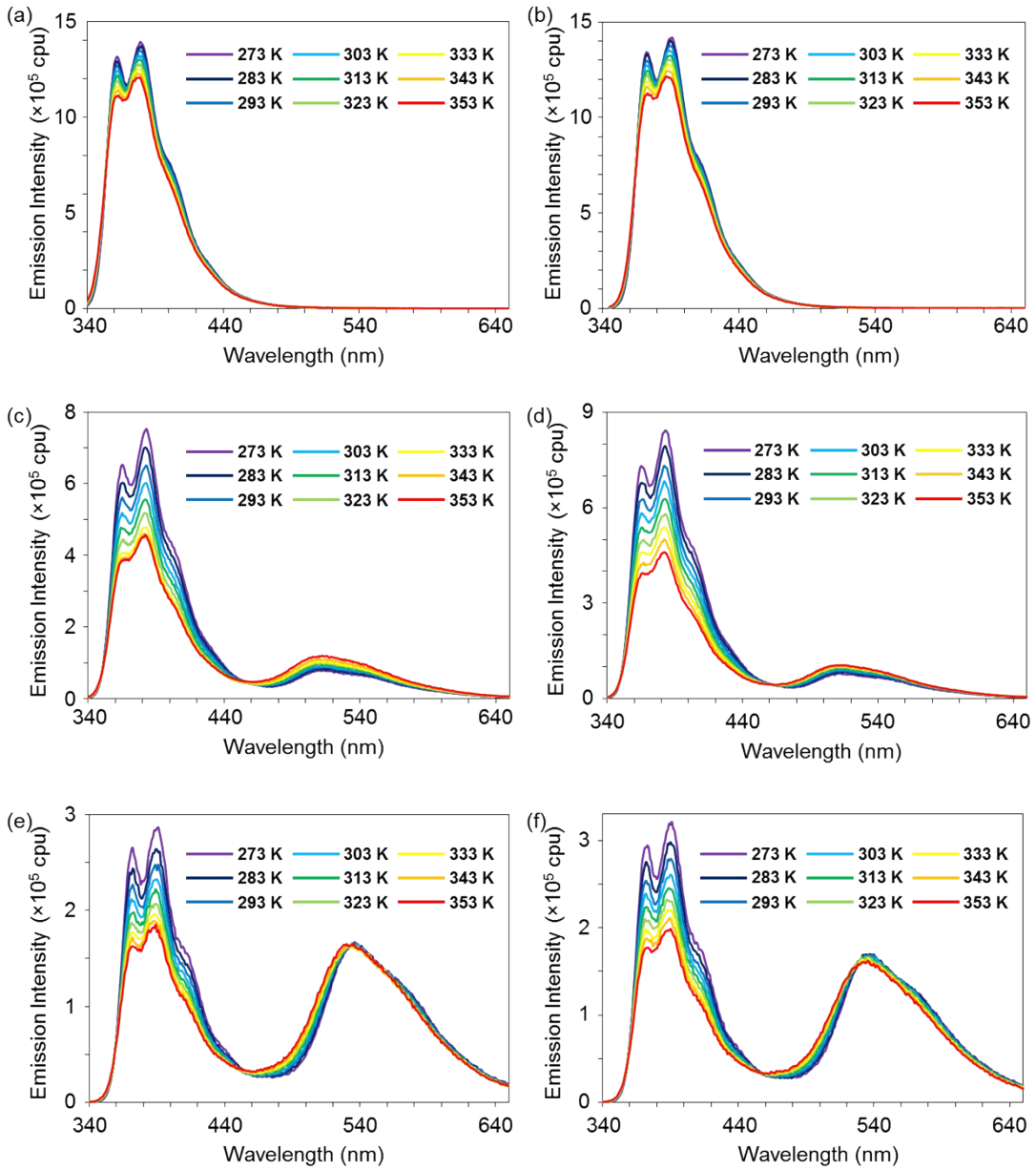


Figure S19. Emission spectra of dibenzoborole derivatives **3a**–**c**. (a) : **3a** in *n*-octane (1.0×10^{-5} M) excited at $\lambda_{max,abs}$. (b) : **3a** in *n*-decane (1.0×10^{-5} M) excited at $\lambda_{max,abs}$. (c) : **3b** in *n*-octane (1.0×10^{-5} M) excited at $\lambda_{max,abs}$. (d) : **3b** in *n*-decane (1.0×10^{-5} M) excited at $\lambda_{max,abs}$. (e) : **3c** in *n*-octane (1.0×10^{-5} M) excited at $\lambda_{max,abs}$. (f) : **3a** in *n*-decane (1.0×10^{-5} M) excited at $\lambda_{max,abs}$.

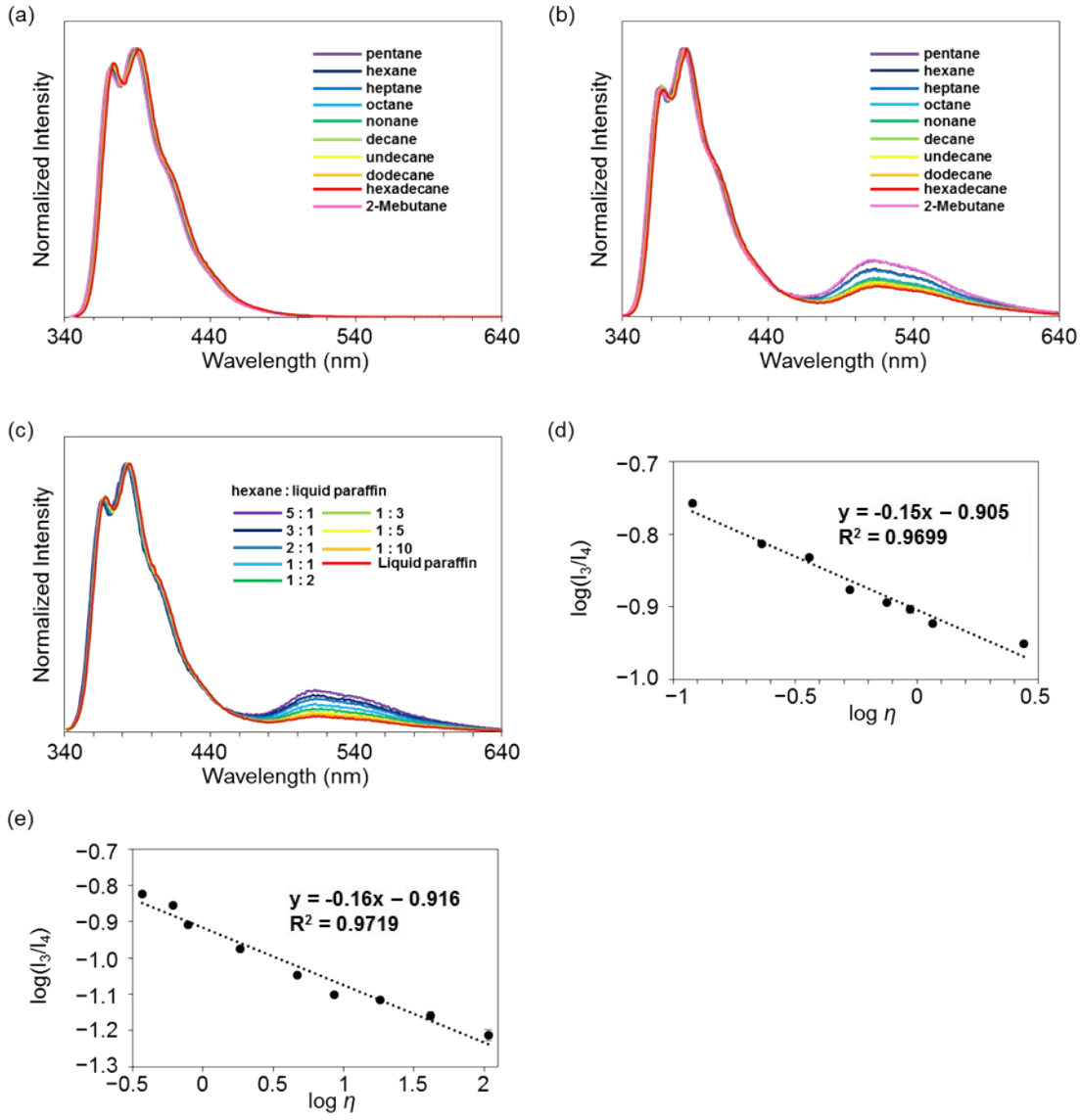


Figure S20. Emission spectra of dibenzoborole derivatives **3a** (a) and **3b** (b) in *n*-alkane solvents (1.0×10^{-5} M) and **3b** in the mixed solvents of hexane and liquid paraffin (1.0×10^{-5} M) (c). (a) : the number of carbon atoms of *n*-alkane solvents was from 5 to 16. Förster-Hoffmann plots of the ratio of dual emission bands (I_3 and I_4) of **3c** in *n*-alkane solvents (d) and in the mixed solvents of hexane and liquid paraffin (e). (d) and (e) : Emission spectra were collected at $\lambda_{max,abs}$.

DFT Calculation by Gaussian 09 Program[6]

The optimized structures of **3a–c** were obtained by DFT calculation at the B3LYP/6-31G(d,p) level in the ground states and at the TD-B3LYP/6-31G(d,p) level in the excited states. TD-DFT calculation was carried out at the TD-B3LYP/6-31G(d,p) level in the ground states and the TD-CAM-B3LYP/6-31G(d,p) level in the excited states.

Table S2. Cartesian coordinates of optimized structure of **3a** in the ground state calculated at the B3LYP/6-31G(d,p) level

Center Symbol	Coordinates (Angstroms)		
	X	Y	Z
C	1.0326284	−2.335271	−0.1212723
C	−0.4389243	−2.4236046	−0.1337621
C	1.4683263	−1.0335088	0.2477378
C	1.9483974	−3.339275	−0.4458182
C	3.3136538	−3.064631	−0.4135078
C	2.8430497	−0.7935089	0.2735652
C	3.785692	−1.7901036	−0.0584249
C	−1.0173544	−1.1885322	0.2437616
C	−1.2392131	−3.51032	−0.4940915
C	−2.6265234	−3.3716508	−0.4880579
C	−2.4041047	−1.0676116	0.2164809
C	−3.2334307	−2.151605	−0.1419661
B	0.1631507	−0.1267503	0.6195056
H	1.608109	−4.3345386	−0.7193424
H	4.0238918	−3.8532205	−0.6438064
H	3.2163188	0.1985662	0.5148595
C	5.2404031	−1.4997795	−0.0407419
H	−0.7967532	−4.4553149	−0.7986806
H	−3.247122	−4.2074324	−0.7973822
H	−2.8685507	−0.1201165	0.4812107
C	−4.7095963	−2.006641	−0.1607129
C	−0.1778777	1.4287032	0.2440309
C	−0.7966137	2.0149584	1.3675628
C	−0.1038058	2.2378341	−0.9270516
C	−0.6006816	3.5496797	−0.8540442
C	−1.2851004	3.318731	1.4149862
C	−1.1870599	4.125811	0.2833231
C	0.5144985	1.7729821	−2.272399
H	−0.5323389	4.1703303	−1.7368782
C	−0.9195026	1.0805756	2.5434421
H	−1.7341548	3.6868949	2.3319209
C	−1.6895589	5.5805856	0.2379436
C	2.0565859	1.7834057	−2.1588008
C	0.0267608	0.3606186	−2.6566932

C	0.1375765	2.6993679	−3.452387
H	2.4212513	2.7863132	−1.9111902
H	2.4078474	1.0924367	−1.3928289
H	2.5109706	1.4846064	−3.1108703
H	0.3451013	−0.3970604	−1.9442604
H	−1.0652646	0.3254704	−2.7247542
H	0.4356299	0.081282	−3.6341882
H	−0.9471186	2.8018657	−3.5629616
H	0.5708615	3.7002371	−3.3614448
H	0.5268755	2.2689437	−4.3804531
C	−0.5154529	6.5264046	−0.1083774
C	−2.7891933	5.7143399	−0.8423929
C	−2.2854325	6.0316601	1.5849825
H	−3.1487814	5.4230221	1.8736164
H	−1.5475785	5.9839416	2.3927975
H	−2.625501	7.0696194	1.5104342
H	0.2745325	6.4621386	0.6470976
H	−0.0698906	6.2849557	−1.0776582
H	−0.8613325	7.5654891	−0.1502815
H	−2.4182604	5.446374	−1.8357898
H	−3.6400119	5.0629408	−0.6171426
H	−3.1546056	6.7464741	−0.8898484
H	−0.8164404	1.5715007	3.5187072
H	−1.8757349	0.5469676	2.5363236
N	0.1587191	0.0602711	2.3533821
C	1.4468639	0.6306589	2.8428773
C	−0.1207317	−1.1840756	3.1165368
H	1.6748024	1.5357837	2.2806525
H	1.3587044	0.8727391	3.9070979
H	2.2398984	−0.1002464	2.6977786
H	−0.1273055	−0.96975	4.1903459
H	−1.0848755	−1.5873666	2.8126244
H	0.6571067	−1.9162316	2.894988
C	6.1026377	−2.0584666	−1.0007157
C	5.8040189	−0.6604543	0.9370951
C	7.1678218	−0.3887253	0.9561141
C	7.4683201	−1.7925535	−0.9859471
C	8.0074435	−0.9557748	−0.0062179
H	5.1684118	−0.2367779	1.7080347
H	7.5861457	0.2484328	1.7281035
H	5.6927914	−2.6904307	−1.7819673
H	8.117023	−2.2320959	−1.7357659
C	−5.5489535	−3.0626854	0.2369085
C	−5.3148184	−0.8075107	−0.5779722
C	−6.6986373	−0.6664108	−0.5924599
C	−6.9335619	−2.9287354	0.2209412

C	−7.5149278	−1.727657	−0.1929139
H	−4.6929519	0.0123878	−0.9222951
H	−7.1481244	0.2605926	−0.9318569
H	−5.1088926	−3.9926137	0.582767
H	−7.5648781	−3.7545475	0.5309619
C	−9.0069185	−1.5569063	−0.1507317
F	−9.4256154	−1.0786199	1.0468783
F	−9.4426241	−0.6862814	−1.0894818
F	−9.6564392	−2.7265787	−0.3491776
C	9.4713055	−0.6172616	−0.0166642
F	9.7189946	0.5299102	−0.6940346
F	9.9551732	−0.4392501	1.2345641
F	10.2111061	−1.5846295	−0.603734

Table S3. Cartesian coordinates of optimized structure of **3b** in the ground state calculated at the B3LYP/6-31G(d,p) level

Center Symbol	Coordinates (Angstroms)		
	X	Y	Z
C	−1.4481131	−2.3583282	−0.1578762
C	−0.0067046	−2.6698707	−0.1730473
C	−2.5104802	−3.2126427	−0.4636007
C	−1.6778108	−1.0027744	0.2011411
C	−2.9990682	−0.554302	0.2335761
C	−3.8180214	−2.7322329	−0.4195049
C	−4.0878582	−1.3975835	−0.0745332
H	−3.217311	0.4726679	0.5157909
H	−2.3280535	−4.2458488	−0.748042
H	−4.6396616	−3.3906638	−0.6857922
C	−5.4822411	−0.8893086	−0.0342701
C	0.6182663	−3.86355	−0.5406701
C	0.7555483	−1.5405428	0.2109199
C	2.1451791	−1.6347945	0.1851952
C	2.0106248	−3.9395262	−0.5341583
C	2.7994816	−2.8308199	−0.1807558
B	−0.2502877	−0.3109305	0.5803421
H	2.7505866	−0.7579251	0.405658
H	0.0351599	−4.733515	−0.8324277
H	2.4955598	−4.8759279	−0.7941516
C	4.2814031	−2.916681	−0.2022975
C	−5.7931068	0.4112754	−0.4686712
C	−6.5331959	−1.6939418	0.4403309
C	−7.8427238	−1.2182466	0.4781148
C	−7.1021835	0.8884323	−0.4284018
C	−8.1341491	0.0762143	0.0446729
H	−6.3148262	−2.6934346	0.8046542
H	−8.6359927	−1.8576438	0.8553545
H	−5.0045406	1.0424291	−0.8670773
H	−7.3179157	1.8941635	−0.7781461
H	−9.1543049	0.4475566	0.0744489
C	5.0604134	−2.2644898	0.7693773
C	4.9512278	−3.6525145	−1.1958726
C	6.3422398	−3.7360559	−1.214493
C	6.4517157	−2.3446177	0.7500423
C	7.1002891	−3.082362	−0.2416036
H	4.3740991	−4.140511	−1.9754627
H	6.8356829	−4.3048625	−1.9976375
H	4.5662047	−1.7083425	1.5602963
H	7.0302878	−1.8369151	1.5168324
H	8.1843556	−3.1460618	−0.2567785

C	0.3173633	1.1805213	0.2190881
C	0.3680245	1.9997338	−0.94625
C	1.0012948	1.6680982	1.3515389
C	1.6648353	2.891188	1.4139042
C	1.0413224	3.2294354	−0.8592015
C	1.6901615	3.7117151	0.2878924
C	0.9862216	0.7160453	2.518897
H	2.151306	3.1867424	2.3381171
C	−0.2958526	1.6330696	−2.3000861
H	1.0696143	3.8591041	−1.7379951
C	2.3880333	5.0837676	0.2591473
C	0.228514	2.4945573	−3.4729537
C	−0.0212974	0.1640547	−2.6820223
C	−1.8202397	1.8741409	−2.2008807
C	3.0294725	5.4374488	1.6142029
C	3.5029728	5.0758512	−0.8133625
C	1.3563385	6.1843144	−0.0843152
H	0.8938179	6.018155	−1.0613616
H	0.5558397	6.2167327	0.6621509
H	1.8395909	7.1678218	−0.1075589
H	4.2534353	4.3101759	−0.5913584
H	3.1051355	4.8718492	−1.8115458
H	4.0082944	6.047945	−0.8476708
H	2.2853507	5.4857698	2.4162428
H	3.7969136	4.7118009	1.9032652
H	3.5108715	6.4187492	1.5512906
H	−2.2725222	1.2455944	−1.4337154
H	−2.0317352	2.9217481	−1.9592623
H	−2.3066978	1.6411778	−3.1555537
H	−0.0570718	3.5477341	−3.3873964
H	1.3181603	2.4392225	−3.5664205
H	−0.2046499	2.1239881	−4.4074906
H	1.0536586	−0.0346149	−2.73653
H	−0.4594249	−0.5372364	−1.9754535
H	−0.4557295	−0.0500729	−3.6651257
N	−0.2272895	−0.135801	2.3215677
H	1.8555148	0.0500004	2.5032095
H	0.9572229	1.2080138	3.4988775
C	−0.1321665	−1.4124711	3.0752279
C	−1.4213622	0.6102257	2.8123965
H	−1.2995508	0.8358284	3.8771136
H	−1.5185121	1.5393306	2.2516443
H	−2.3109353	0.0011431	2.6656515
H	0.765526	−1.9477472	2.7714117
H	−0.1010613	−1.2096055	4.1510617
H	−1.0054371	−2.023852	2.8431732

Table S4. Cartesian coordinates of optimized structure of **3c** in the ground state calculated at the B3LYP/6-31G(d,p) level

Center Symbol	Coordinates (Angstroms)		
	X	Y	Z
C	−2.8837685	−0.8766197	0.2342589
C	−3.8308125	−1.8776393	−0.0723073
C	−3.3575116	−3.1618779	−0.3897092
C	−1.9922334	−3.4414322	−0.4074921
C	−1.0736874	−2.4330358	−0.1056851
C	−1.5096541	−1.1211829	0.225195
C	0.3977292	−2.5266237	−0.0955232
C	0.9764394	−1.2911356	0.2807092
B	−0.2074973	−0.2205492	0.6164936
C	1.2016245	−3.6172512	−0.4347786
C	2.5894525	−3.4829769	−0.4059223
C	3.1985585	−2.2630356	−0.0620594
C	2.3645031	−1.1746361	0.2741824
C	0.152275	1.3319156	0.2461896
C	0.7507477	1.9181374	1.3803741
C	1.248549	3.218193	1.4326489
C	1.1824883	4.0209131	0.2955624
C	0.6152702	3.4452268	−0.8517585
C	0.1092689	2.1372122	−0.9287289
C	−0.4848181	1.6675785	−2.2828509
C	0.0127923	0.2546354	−2.6528292
C	−0.0909342	2.5910867	−3.4591944
C	−2.0287337	1.6745456	−2.1938305
C	1.7005714	5.4703426	0.2542639
C	0.5435784	6.4271202	−0.1184882
C	2.8225589	5.5883415	−0.804706
C	2.2750006	5.9210723	1.6107227
C	0.8415007	0.9863813	2.5613615
N	−0.2416722	−0.02347	2.3545853
C	0.0099645	−1.2668148	3.1279145
C	−1.5347111	0.5601711	2.8140843
H	−3.2583071	0.1101575	0.495502
C	−5.2847877	−1.5837951	−0.056097
H	−4.0666481	−3.941106	−0.6539282
H	−1.6530926	−4.4406816	−0.6688619
H	0.7610972	−4.5692947	−0.7207486
H	3.2129878	−4.3407811	−0.6410472
C	4.6752676	−2.1230499	−0.0623854
H	2.825709	−0.2123775	0.4875803
H	1.6808667	3.5864566	2.3576461
H	0.5716673	4.0623037	−1.7388273

H	1.1059127	0.2226613	−2.7002263
H	−0.3157929	−0.5009008	−1.9426252
H	−0.3779059	−0.0297544	−3.6364941
H	0.995352	2.6914751	−3.5548415
H	−0.4679299	2.1591912	−4.3917851
H	−0.5236805	3.593045	−3.3756352
H	−2.3865752	0.9859186	−1.4285679
H	−2.3991358	2.6783221	−1.9571877
H	−2.4671144	1.368686	−3.1513523
H	0.1135087	6.1847769	−1.0945499
H	−0.261043	6.3748862	0.622427
H	0.9011106	7.4624466	−0.1593614
H	2.4675945	5.322333	−1.8044149
H	3.2018117	6.6158549	−0.8473961
H	3.6601036	4.9262936	−0.5618948
H	1.5212751	5.8842118	2.4043536
H	3.1258731	5.304178	1.9181392
H	2.627533	6.9551757	1.5386952
H	0.7263493	1.4819069	3.5332178
H	1.7925964	0.4435266	2.5710943
H	−0.0002422	−1.0476325	4.2009661
H	−0.7721971	−1.9907587	2.8951662
H	0.9741761	−1.6825315	2.8414549
H	−1.4668042	0.8055221	3.8793221
H	−2.332483	−0.1621586	2.6536124
H	−1.7422937	1.4655819	2.2444868
C	−5.7880199	−0.3529303	−0.5003665
C	−6.2178202	−2.5310953	0.409854
C	−7.578443	−2.2612557	0.4311451
C	−7.153929	−0.0639276	−0.4838877
C	−8.0593258	−1.0220249	−0.0154592
H	−5.8643389	−3.4870993	0.784494
H	−8.291565	−2.9911514	0.8003259
H	−5.1032331	0.39156	−0.8951541
H	−7.4961106	0.8974477	−0.8482543
O	−9.4137541	−0.8514067	0.0478188
C	5.4728628	−2.7732205	−1.0146728
C	5.3365398	−1.3284771	0.8946984
C	6.7171663	−1.1927588	0.8996698
C	6.8634709	−2.6501706	−1.0234973
C	7.4946597	−1.8550236	−0.0609052
H	4.7556924	−0.826352	1.6624876
H	7.2210102	−0.5866704	1.6455844
H	4.9981096	−3.3708571	−1.7869262
H	7.4358806	−3.1643002	−1.7864824
O	8.8444997	−1.6609139	0.0287484

C	9.6784606	−2.3170099	−0.9120759
H	9.5776361	−3.4084426	−0.8522259
H	9.4644491	−1.9949453	−1.9394349
H	10.7013697	−2.0371766	−0.6556207
C	−9.9531861	0.3868059	−0.3844786
H	−9.568832	1.2266059	0.2088611
H	−9.7423341	0.573854	−1.4453707
H	−11.0323342	0.3121247	−0.242177

Table S5. Cartesian coordinates of optimized structure of **3a** in the excited state calculated at the TD-B3LYP/6-31G(d,p) level

Center Symbol	Coordinates (Angstroms)		
	X	Y	Z
C	1.000493	−2.39064	0.003163
C	−0.41669	−2.47453	−0.00638
C	1.45268	−1.03861	0.307267
C	1.948649	−3.41211	−0.27923
C	3.290389	−3.11791	−0.28912
C	2.812633	−0.78797	0.279095
C	3.777822	−1.79473	−0.01318
C	−1.01444	−1.18641	0.297393
C	−1.25053	−3.58613	−0.30864
C	−2.61524	−3.42292	−0.34072
C	−2.38529	−1.05023	0.205607
C	−3.23678	−2.14963	−0.09718
B	0.158253	−0.12475	0.662409
H	1.616228	−4.42536	−0.48805
H	4.001767	−3.91445	−0.47598
H	3.168531	0.221685	0.459014
C	5.205165	−1.50373	−0.02559
H	−0.81621	−4.55303	−0.54749
H	−3.23805	−4.26761	−0.61413
H	−2.83254	−0.08112	0.407912
C	−4.68565	−1.99974	−0.14938
C	−0.1781	1.42437	0.274529
C	−0.79205	2.030067	1.391891
C	−0.10297	2.215671	−0.90983
C	−0.58795	3.532795	−0.85164
C	−1.27135	3.336775	1.42171
C	−1.16735	4.128617	0.27888
C	0.50995	1.73816	−2.25421
H	−0.51586	4.141402	−1.7424
C	−0.92136	1.113015	2.58132
H	−1.71748	3.720731	2.333464
C	−1.65682	5.5869	0.21572
C	2.051594	1.835928	−2.17279
C	0.097386	0.290877	−2.59407
C	0.056293	2.608692	−3.45112
H	2.365675	2.864007	−1.96253
H	2.453551	1.18939	−1.39216
H	2.504496	1.531754	−3.12373
H	0.488332	−0.43168	−1.88101
H	−0.99181	0.185406	−2.6236
H	0.49035	0.018338	−3.57979

H	−1.03485	2.664879	−3.52494
H	0.451787	3.628041	−3.41089
H	0.430528	2.16247	−4.37772
C	−0.47282	6.517162	−0.13957
C	−2.75315	5.718049	−0.8684
C	−2.25108	6.059099	1.556321
H	−3.11988	5.461111	1.850771
H	−1.51509	6.015821	2.366083
H	−2.58273	7.098649	1.46827
H	0.315372	6.454216	0.617857
H	−0.02834	6.260423	−1.10538
H	−0.80894	7.558777	−0.19382
H	−2.38322	5.435485	−1.85807
H	−3.61078	5.077722	−0.63733
H	−3.10841	6.75299	−0.92804
H	−0.82381	1.619438	3.549189
H	−1.87995	0.582864	2.575588
N	0.15321	0.08792	2.413884
C	1.444593	0.657636	2.892019
C	−0.13452	−1.14504	3.189364
H	1.663705	1.567025	2.332789
H	1.369934	0.892815	3.95888
H	2.238473	−0.06973	2.730588
H	−0.17132	−0.91623	4.259651
H	−1.08856	−1.56034	2.86728
H	0.654363	−1.87455	3.000031
C	6.127578	−2.33344	−0.72
C	5.74713	−0.37895	0.654607
C	7.103654	−0.1041	0.639378
C	7.48409	−2.05368	−0.74111
C	7.990628	−0.93833	−0.05898
H	5.095089	0.263884	1.235613
H	7.489309	0.750304	1.185843
H	5.766166	−3.18649	−1.28334
H	8.161622	−2.70062	−1.28808
C	−5.55764	−3.10771	0.023776
C	−5.29225	−0.73633	−0.38236
C	−6.66846	−0.59188	−0.43498
C	−6.93474	−2.96141	−0.02286
C	−7.50629	−1.70257	−0.25434
H	−4.66935	0.131983	−0.56648
H	−7.10427	0.380867	−0.63671
H	−5.1459	−4.08884	0.233124
H	−7.57678	−3.82416	0.120002
C	−8.99479	−1.53329	−0.24678
F	−9.47161	−1.26082	0.995688

F	−9.39305	−0.51295	−1.04202
F	−9.63462	−2.6497	−0.66629
C	9.447945	−0.60275	−0.12235
F	9.733493	0.264053	−1.12874
F	9.882134	−0.01538	1.018927
F	10.21399	−1.699	−0.33121

Table S6. Cartesian coordinates of optimized structure of **3b** in the excited state calculated at the TD-B3LYP/6-31G(d,p) level

Center Symbol	Coordinates (Angstroms)		
	X	Y	Z
C	−1.43436	−2.4247	−0.03949
C	−0.05159	−2.73223	−0.03559
C	−2.53816	−3.28492	−0.29606
C	−1.66187	−1.0036	0.227392
C	−2.9654	−0.53949	0.182464
C	−3.81589	−2.78073	−0.3025
C	−4.07937	−1.38539	−0.07041
H	−3.16016	0.507702	0.394589
H	−2.37207	−4.33783	−0.50899
H	−4.64318	−3.44094	−0.53922
C	−5.44363	−0.86828	−0.07862
C	0.602215	−3.96381	−0.31761
C	0.741549	−1.54402	0.255105
C	2.118267	−1.62872	0.167135
C	1.974502	−4.01122	−0.36668
C	2.788259	−2.84414	−0.13945
B	−0.24758	−0.3102	0.581863
H	2.707216	−0.72444	0.297844
H	0.023303	−4.86434	−0.50571
H	2.460506	−4.96211	−0.55569
C	4.24292	−2.92046	−0.21893
C	−5.71888	0.500742	−0.33555
C	−6.55914	−1.71244	0.164118
C	−7.85708	−1.21781	0.155566
C	−7.01853	0.987984	−0.34656
C	−8.10198	0.13559	−0.10023
H	−6.39685	−2.75894	0.399577
H	−8.68636	−1.89038	0.357491
H	−4.90242	1.175862	−0.56915
H	−7.19315	2.038709	−0.56151
H	−9.11772	0.519051	−0.11092
C	5.076309	−1.95999	0.412779
C	4.894306	−3.95876	−0.93655
C	6.2791	−4.02405	−1.02005
C	6.459693	−2.03308	0.329372
C	7.077425	−3.0651	−0.3878
H	4.302548	−4.69554	−1.46888
H	6.7421	−4.82488	−1.5902
H	4.627086	−1.16765	1.001809
H	7.065534	−1.28591	0.834803
H	8.159895	−3.12043	−0.45123

C	0.322975	1.178525	0.233488
C	0.388378	1.979513	−0.94549
C	0.990167	1.686822	1.368077
C	1.644062	2.915254	1.419309
C	1.050061	3.21628	−0.86654
C	1.677777	3.720732	0.282353
C	0.973971	0.757179	2.555371
H	2.116092	3.227922	2.345494
C	−0.24929	1.594071	−2.30848
H	1.086079	3.833731	−1.75362
C	2.362265	5.099154	0.244448
C	0.332221	2.413081	−3.48599
C	−0.01217	0.10947	−2.65559
C	−1.76827	1.880454	−2.25752
C	2.98537	5.475943	1.601884
C	3.488933	5.09077	−0.81573
C	1.322619	6.184337	−0.12332
H	0.871293	6.000434	−1.10249
H	0.514596	6.217916	0.614943
H	1.795728	7.172555	−0.15477
H	4.244541	4.335194	−0.57704
H	3.104518	4.872129	−1.81604
H	3.984898	6.067473	−0.85493
H	2.232355	5.526445	2.395394
H	3.75696	4.76182	1.908154
H	3.45736	6.461334	1.531886
H	−2.25925	1.276164	−1.49444
H	−1.95679	2.936984	−2.03718
H	−2.23458	1.646064	−3.22183
H	0.066058	3.473658	−3.43945
H	1.423036	2.333628	−3.53994
H	−0.07695	2.026458	−4.42472
H	1.056022	−0.12901	−2.66795
H	−0.5003	−0.56344	−1.95374
H	−0.41892	−0.10512	−3.65035
N	−0.23397	−0.09745	2.387096
H	1.845413	0.092974	2.548099
H	0.955432	1.274019	3.523482
C	−0.13198	−1.36133	3.152826
C	−1.43411	0.648313	2.84773
H	−1.3466	0.870053	3.917442
H	−1.51275	1.580967	2.289051
H	−2.32256	0.044484	2.66942
H	0.750674	−1.91094	2.82706
H	−0.06428	−1.15194	4.226572
H	−1.01852	−1.96644	2.955875

Table S7. Cartesian coordinates of optimized structure of **3c** in the excited state calculated at the TD-B3LYP/6-31G(d,p) level

Center Symbol	Coordinates (Angstroms)		
	X	Y	Z
C	−2.49244	−1.1739	−0.16134
C	−3.35048	−2.28529	−0.10697
C	−2.78109	−3.60187	−0.04497
C	−1.41686	−3.78928	−0.04044
C	−0.55943	−2.667	−0.09237
C	−1.10218	−1.30991	−0.16694
C	0.859728	−2.62131	−0.06544
C	1.312988	−1.23104	−0.11067
B	0.075408	−0.297	−0.2031
C	1.7889	−3.68233	−0.00023
C	3.139363	−3.4051	0.022711
C	3.621896	−2.05463	−0.00697
C	2.691127	−1.00107	−0.07162
C	0.060547	1.291431	−0.1322
C	0.146463	1.856214	1.167
C	0.164198	3.241203	1.37222
C	0.091893	4.137069	0.308832
C	0.012612	3.581441	−0.97425
C	0.000654	2.203128	−1.23108
C	−0.06868	1.731512	−2.71135
C	1.149936	0.844381	−3.05445
C	−0.05804	2.903283	−3.71794
C	−1.37301	0.940516	−2.96365
C	0.097033	5.666581	0.490225
C	−1.20908	6.260758	−0.08829
C	1.307414	6.276798	−0.25551
C	0.19287	6.078271	1.971484
C	0.236054	0.975055	2.404589
N	−1.02492	0.314116	2.759097
C	−0.82349	−0.71514	3.76538
C	−2.06616	1.249564	3.152884
H	−2.91907	−0.17579	−0.15956
C	−4.80999	−2.12057	−0.1173
H	−3.43967	−4.46378	−0.04295
H	−1.00764	−4.79546	−0.00245
H	1.447681	−4.7135	0.044431
H	3.849685	−4.21964	0.113542
C	5.066567	−1.7926	0.02845
H	3.05181	0.021593	−0.1361
H	0.235648	3.602826	2.392789
H	−0.03658	4.26606	−1.81031
H	2.085249	1.39561	−2.90697

H	1.187576	−0.05342	−2.43552
H	1.105042	0.529341	−4.10386
H	0.848303	3.511956	−3.63496
H	−0.08958	2.499663	−4.73527
H	−0.92622	3.56039	−3.60175
H	−1.42548	0.038557	−2.35358
H	−2.24946	1.558802	−2.73774
H	−1.43583	0.638832	−4.01623
H	−1.32184	6.033511	−1.15235
H	−2.08431	5.8586	0.432719
H	−1.21804	7.351328	0.023581
H	1.275863	6.060449	−1.32729
H	1.322597	7.366531	−0.13544
H	2.248902	5.878574	0.136968
H	−0.65381	5.700661	2.553938
H	1.114743	5.713378	2.435978
H	0.190753	7.170352	2.053985
H	0.612795	1.584073	3.251535
H	0.972152	0.18191	2.236519
H	−0.45515	−0.31822	4.73301
H	−1.76812	−1.23503	3.95619
H	−0.09819	−1.45035	3.403349
H	−1.82359	1.804786	4.082088
H	−3.00243	0.707115	3.320808
H	−2.23059	1.981372	2.358653
C	−5.4183	−1.01693	−0.7481
C	−5.66877	−3.05761	0.504445
C	−7.0426	−2.89389	0.506235
C	−6.79803	−0.84276	−0.76242
C	−7.62366	−1.78349	−0.12924
H	−5.24422	−3.90817	1.027075
H	−7.69462	−3.60657	1.000124
H	−4.79791	−0.29432	−1.26707
H	−7.21906	0.014288	−1.27404
O	−8.97981	−1.71484	−0.07726
C	5.997765	−2.72004	−0.47956
C	5.586749	−0.5926	0.569597
C	6.94559	−0.33906	0.598346
C	7.367832	−2.476	−0.46552
C	7.853147	−1.27833	0.077654
H	4.908121	0.134926	1.001015
H	7.338724	0.576265	1.027885
H	5.642717	−3.6394	−0.9329
H	8.042643	−3.21296	−0.88388
O	9.165923	−0.93488	0.149801
C	10.13435	−1.84333	−0.35786

H	10.1069	−2.80084	0.176581
H	9.992585	−2.02417	−1.43039
H	11.10295	−1.36878	−0.1975
C	−9.62806	−0.60731	−0.68965
H	−9.31218	0.342028	−0.24047
H	−9.43843	−0.57676	−1.76954
H	−10.6948	−0.75149	−0.5155

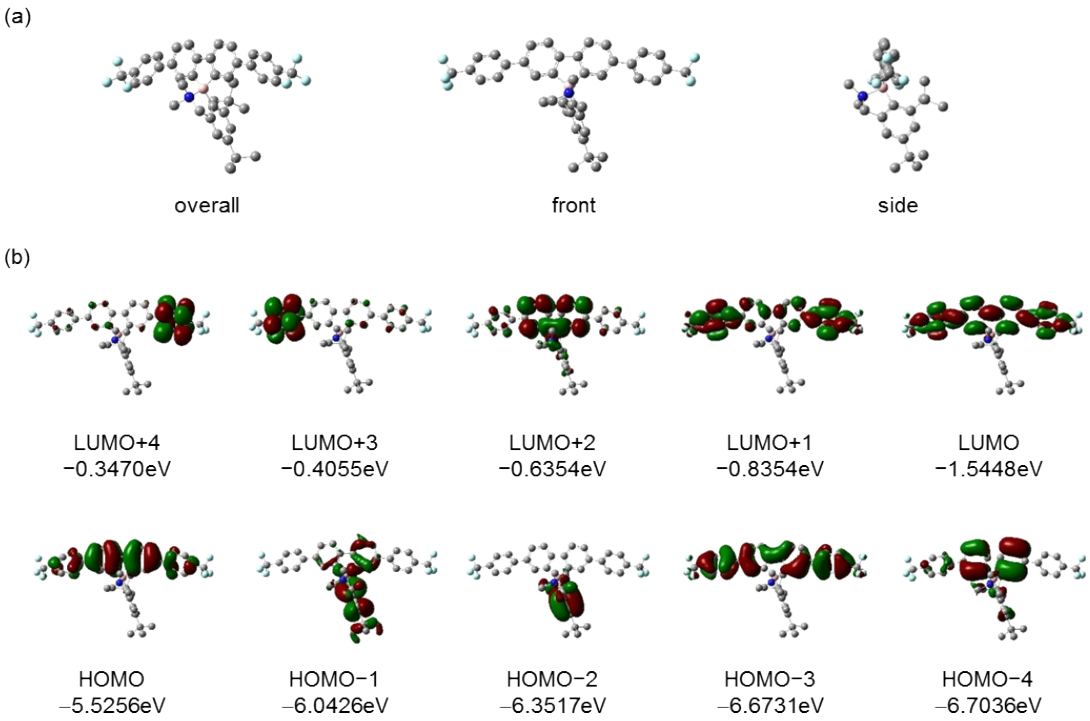


Figure S21. (a) Overall, front and side views of the optimized structure and (b) selected molecular orbitals and energy levels of **3a** in the ground state calculated at the B3LYP/6-31G(d,p) level. Hydrogen atoms are omitted for clarity.

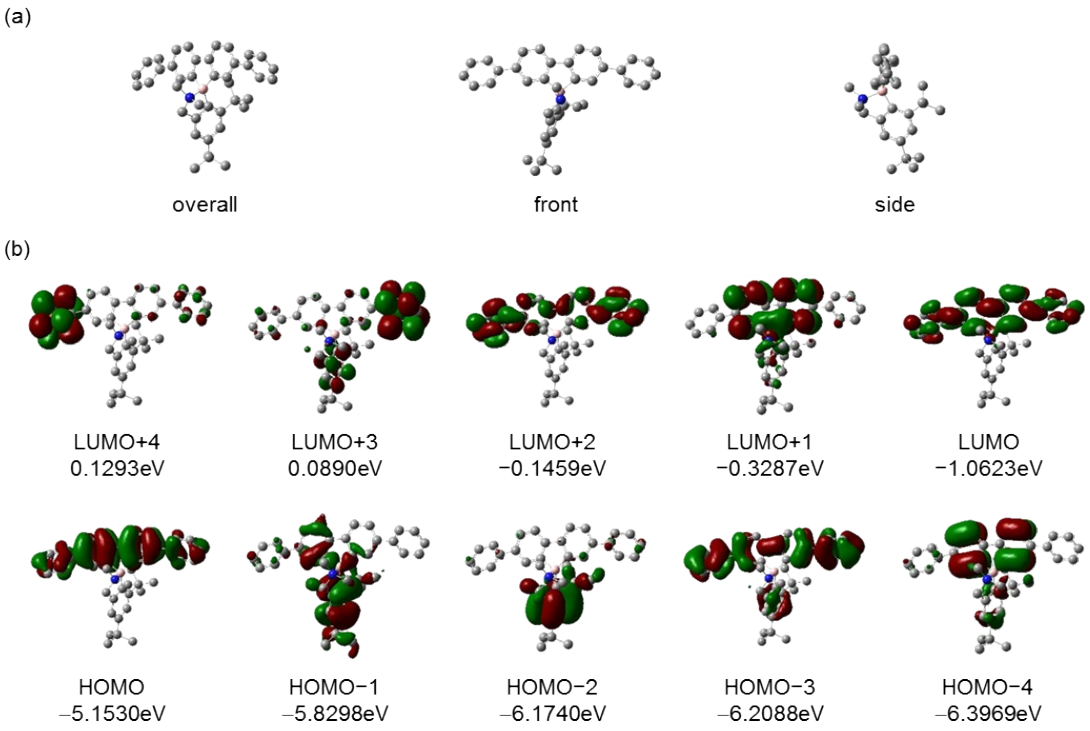


Figure S22. (a) Overall, front and side views of the optimized structure and (b) selected molecular orbitals and energy levels of **3b** in the ground state calculated at the B3LYP/6-31G(d,p) level. Hydrogen atoms are omitted for clarity.

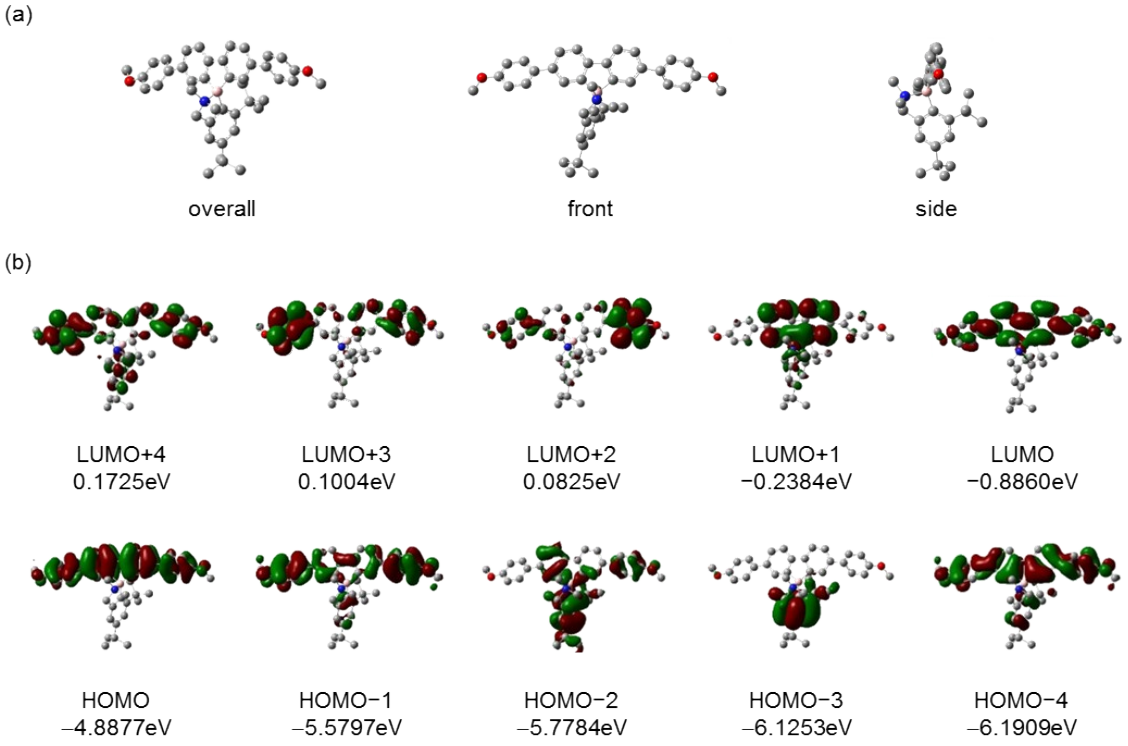


Figure S23. (a) Overall, front and side views of the optimized structure and (b) selected molecular orbitals and energy levels of **3c** in the ground state calculated at the B3LYP/6-31G(d,p) level. Hydrogen atoms are omitted for clarity.

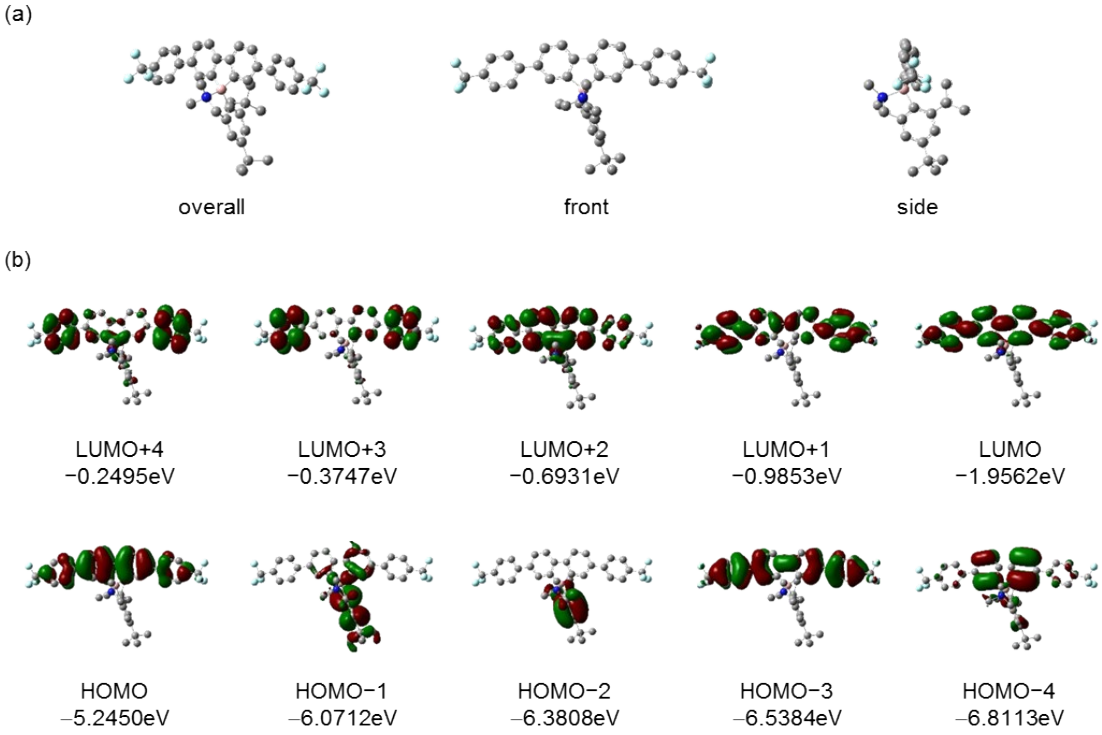


Figure S24. (a) Overall, front and side views of the optimized structure of **3a** in the excited state and (b) selected molecular orbitals and energy levels of **3a** with the optimized structure in the excited state calculated at the TD-B3LYP/6-31G(d,p) level. Hydrogen atoms are omitted for clarity.

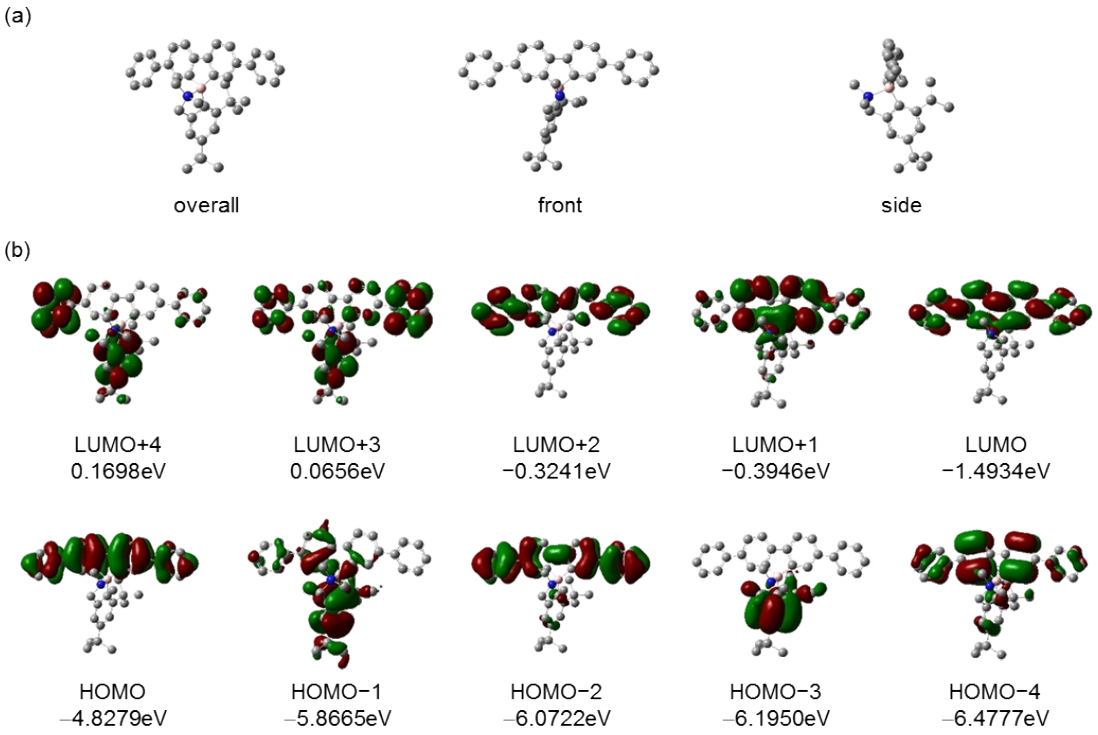


Figure S25. (a) Overall, front and side views of the optimized structure of **3b** in the excited state and (b) selected molecular orbitals and energy levels of **3b** with the optimized structure in the excited state calculated at the TD-B3LYP/6-31G(d,p) level. Hydrogen atoms are omitted for clarity.

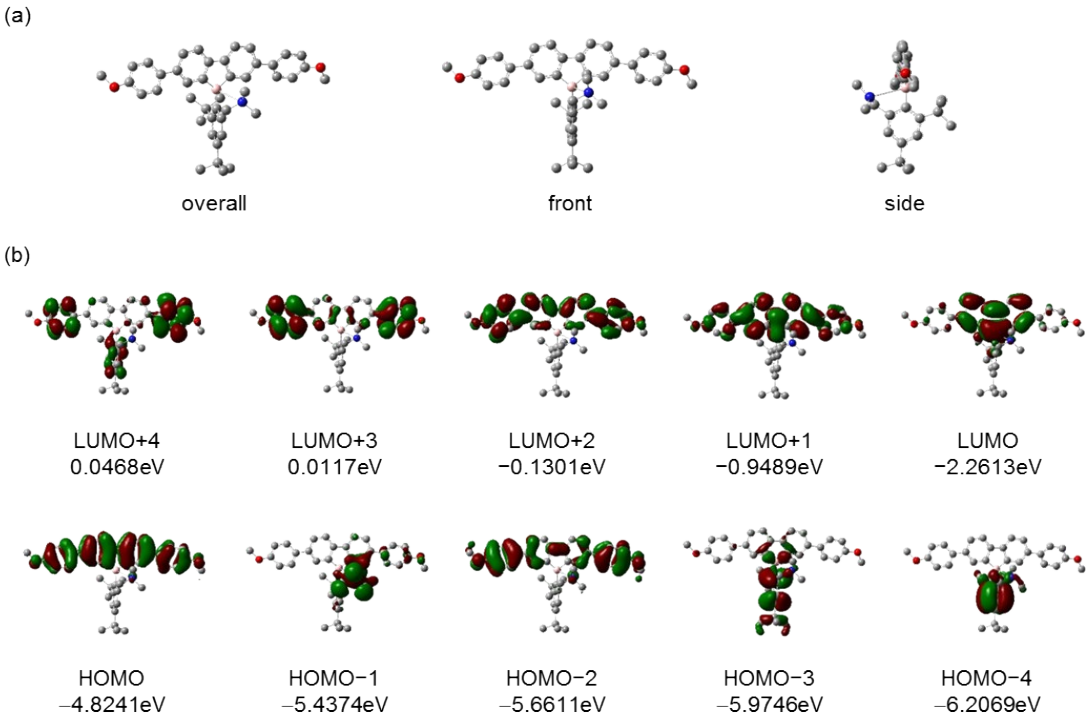


Figure S26. (a) Overall, front and side views of the optimized structure of **3c** in the excited state and (b) selected molecular orbitals and energy levels of **3c** with the optimized structure in the excited state calculated at the TD-B3LYP/6-31G(d,p) level. Hydrogen atoms are omitted for clarity.

Table S8. TD-DFT calculation result of **3a** with optimized structure in the ground state calculated at the TD-B3LYP/6-31G(d,p) level

Transition Energy (Wave Length)	Assignment with Contribution	Oscillator Strength *f*
3.5822 eV (346.11 nm)	HOMO→LUMO (100%)	1.0350
3.9560 eV (313.41 nm)	HOMO−1→LUMO (94.76%) HOMO→LUMO+2 (5.24%)	0.0632
4.1478 eV (298.92 nm)	HOMO−4→LUMO (19.20%) HOMO−1→LUMO (6.01%) HOMO→LUMO+2 (74.78%)	0.0494
4.2712 eV (290.28 nm)	HOMO−3→LUMO (3.28%) HOMO→LUMO+1 (96.72%)	0.0001
4.3522 eV (284.88 nm)	HOMO−2→LUMO (100%)	0.0009
4.5013 eV (275.44 nm)	HOMO−5→LUMO (59.32%) HOMO−4→LUMO (5.61%) HOMO−3→LUMO (4.93%) HOMO−3→LUMO+2 (2.69%) HOMO→LUMO+3 (6.15%) HOMO→LUMO+4 (3.89%) HOMO→LUMO+5 (7.62%) HOMO→LUMO+8 (9.79%)	0.0146

Table S9. TD-DFT calculation result of **3b** with optimized structure in the ground state calculated at the TD-B3LYP/6-31G(d,p) level

Transition Energy (Wave Length)	Assignment with Contribution	Oscillator Strength *f*
3.6867 eV (336.30 nm)	HOMO→LUMO (100%)	0.9302
4.0824 eV (303.70 nm)	HOMO−4→LUMO (10.20%) HOMO−1→LUMO (21.57%) HOMO→LUMO+1 (68.23%)	0.0169
4.2271 eV (293.31 nm)	HOMO−4→LUMO (3.85%) HOMO−1→LUMO (79.01%) HOMO→LUMO+1 (17.14%)	0.1102
4.5342 eV (273.44 nm)	HOMO−5→LUMO (10.34%) HOMO−3→LUMO (14.96%) HOMO→LUMO+2 (74.70%)	0.0004
4.5769 eV (270.89 nm)	HOMO−5→LUMO (42.84%) HOMO−3→LUMO (7.41%) HOMO−3→LUMO+1 (2.71%) HOMO→LUMO+2 (7.02%) HOMO→LUMO+3 (17.35%) HOMO→LUMO+4 (4.00%) HOMO→LUMO+5 (8.32%) HOMO→LUMO+7 (10.34%)	0.0051
4.6265 eV (267.99 nm)	HOMO−3→LUMO (6.18%) HOMO−2→LUMO (93.8%)	0.0009

Table S10. TD-DFT calculation result of **3c** with optimized structure in the ground state calculated at the TD-B3LYP/6-31G(d,p) level

Transition Energy (Wave Length)	Assignment with Contribution	Oscillator Strength *f*
3.5975 eV (344.64 nm)	HOMO→LUMO (100%)	1.1195
399.45 eV (310.39 nm)	HOMO−6→LUMO (6.13%) HOMO−2→LUMO (4.45%) HOMO→LUMO+1 (89.42%)	0.0830
4.2374 eV (292.59 nm)	HOMO−2→LUMO (25.22%) HOMO−1→LUMO (72.04%) HOMO→LUMO+1 (2.74%)	0.0412
4.3650 eV (284.04 nm)	HOMO−2→LUMO (67.29%) HOMO−1→LUMO (23.93%) HOMO→LUMO+3 (5.05%) HOMO→LUMO+4 (3.73%)	0.0368
4.4519 eV (278.50 nm)	HOMO−5→LUMO (6.21%) HOMO−2→LUMO (2.30%) HOMO−1→LUMO+1 (2.45%) HOMO→LUMO+2 (35.53%) HOMO→LUMO+3 (50.86%) HOMO→LUMO+5 (2.65%)	0.0071
4.4827 eV (276.59 nm)	HOMO−7→LUMO (34.59%) HOMO−1→LUMO+3 (2.96%) HOMO→LUMO+2 (5.12%) HOMO→LUMO+3 (3.51%) HOMO→LUMO+4 (13.99%) HOMO→LUMO+5 (5.13%)	0.0088

Table S11. TD-DFT calculation result of **3a** with optimized structure in the excited state calculated at the TD-CAM-B3LYP/6-31G(d,p) level

Transition Energy (Wave Length)	Assignment with Contribution	Oscillator Strength *f*
3.3350 eV (371.77 nm)	HOMO−3→LUMO+1 (2.56%) HOMO→LUMO (97.44%)	1.2475
4.2652 eV (290.69 nm)	HOMO−5→LUMO (2.80%) HOMO−4→LUMO (17.93%) HOMO−1→LUMO (6.24%) HOMO→LUMO+2 (70.29%) HOMO→LUMO+4 (2.74%)	0.0201
4.5506 eV (272.46 nm)	HOMO−10→LUMO (2.89%) HOMO−5→LUMO (16.86%) HOMO−4→LUMO (3.71%) HOMO−3→LUMO (4.24%) HOMO−1→LUMO (44.97%) HOMO→LUMO+1 (18.56%) HOMO→LUMO+2 (6.19%) HOMO→LUMO+3 (2.58%) HOMO→LUMO+8 (5.62%)	0.0882
4.6038 eV (269.31 nm)	HOMO−3→LUMO (16.92%) HOMO−1→LUMO (20.43%) HOMO→LUMO+1 (62.65%)	0.0530
4.7164 eV (262.88 nm)	HOMO−5→LUMO (39.17%) HOMO−4→LUMO+1 (2.54%) HOMO−3→LUMO+2 (5.26%) HOMO−1→LUMO (20.58%) HOMO→LUMO+1 (4.37%) HOMO→LUMO+2 (3.25%) HOMO→LUMO+3 (12.48%) HOMO→LUMO+8 (12.34%)	0.0677
4.9651 eV (249.71 nm)	HOMO−8→LUMO+3 (5.14%) HOMO−7→LUMO (34.01%) HOMO−7→LUMO+1 (17.76%) HOMO−5→LUMO (5.07%) HOMO−4→LUMO (10.39%) HOMO−3→LUMO+3 (12.18%) HOMO−3→LUMO+4 (11.39%) HOMO→LUMO+2 (4.06%) HOMO→LUMO+3 (10.08%)	0.0259

HOMO→LUMO+4 (5.42%)
HOMO→LUMO+5 (48.14%)

Table S12. TD-DFT calculation result of **3b** with optimized structure in the excited state calculated at the TD-CAM-B3LYP/6-31G(d,p) level

Transition Energy (Wave Length)	Assignment with Contribution	Oscillator Strength *f*
3.3445 eV (370.71 nm)	HOMO→LUMO (100%)	1.0160
4.1904 eV (295.88 nm)	HOMO−4→LUMO (13.54%) HOMO−1→LUMO (2.57%) HOMO→LUMO+1 (78.71%) HOMO→LUMO+2 (5.18%)	0.0907
4.6115 eV (268.86 nm)	HOMO−5→LUMO (33.55%) HOMO−4→LUMO (3.03%) HOMO−4→LUMO+2 (2.74%) HOMO−2→LUMO (2.95%) HOMO−2→LUMO+1 (3.12%) HOMO−1→LUMO (38.94%) HOMO−1→LUMO+1 (2.79%) HOMO→LUMO+2 (12.89%) HOMO→LUMO+3 (8.37%) HOMO→LUMO+8 (13.72%)	0.0621
4.7790 eV (259.44 nm)	HOMO−5→LUMO (17.55%) HOMO−2→LUMO (19.20%) HOMO−2→LUMO+1 (3.80%) HOMO−1→LUMO (10.32%) HOMO→LUMO+2 (34.13%) HOMO→LUMO+3 (8.13%) HOMO→LUMO+8 (6.87%)	0.0143
4.7865 eV (259.03 nm)	HOMO−10→LUMO (2.72%) HOMO−9→LUMO (3.06%) HOMO−5→LUMO (6.62%) HOMO−4→LUMO (4.66%) HOMO−2→LUMO (16.39%) HOMO−1→LUMO (37.40%) HOMO→LUMO+1 (11.90%) HOMO→LUMO+2 (17.25%)	0.1926
5.0194 eV (247.01 nm)	HOMO−8→LUMO+6 (5.14%) HOMO−7→LUMO (34.01%) HOMO−7→LUMO+2 (17.76%) HOMO−7→LUMO+7 (5.07%) HOMO−6→LUMO (10.39%)	0.0024

HOMO−2→LUMO+3 (12.18%)
HOMO−2→LUMO+4 (11.39%)
HOMO−2→LUMO+6 (4.06%)
HOMO→LUMO+3 (10.08%)
HOMO→LUMO+5 (5.42%)
HOMO→LUMO+6 (48.14%)

Table S13. TD-DFT calculation result of **3c** with optimized structure in the excited state calculated at the TD-CAM-B3LYP/6-31G(d,p) level

Transition Energy (Wave Length)	Assignment with Contribution	Oscillator Strength *f*
2.2736 eV (545.33 nm)	HOMO−5→LUMO (7.62%) HOMO→LUMO (92.38%)	0.0821
3.5365 eV (350.58 nm)	HOMO−6→LUMO (3.34%) HOMO−2→LUMO (57.85%) HOMO−1→LUMO (34.55%) HOMO→LUMO+1 (4.26%)	0.0180
3.6494 eV (339.74 nm)	HOMO−12→LUMO (4.69%) HOMO−3→LUMO (86.53%) HOMO−3→LUMO+1 (2.58%) HOMO−2→LUMO (4.07%) HOMO−1→LUMO (2.12%)	0.0034
3.8288 eV (323.82 nm)	HOMO−6→LUMO (17.93%) HOMO−5→LUMO (8.00%) HOMO−2→LUMO (2.57%) HOMO−1→LUMO (6.06%) HOMO→LUMO+1 (65.45%)	0.4399
4.0016 eV (309.84 nm)	HOMO−10→LUMO (3.86%) HOMO−9→LUMO (4.46%) HOMO−3→LUMO (6.21%) HOMO−2→LUMO (34.75%) HOMO−1→LUMO (50.73%)	0.0281
4.2232 eV (293.58 nm)	HOMO−6→LUMO (19.28%) HOMO−5→LUMO (48.15%) HOMO−1→LUMO+2 (3.74%) HOMO→LUMO (5.35%) HOMO→LUMO+1 (23.48%)	1.1657

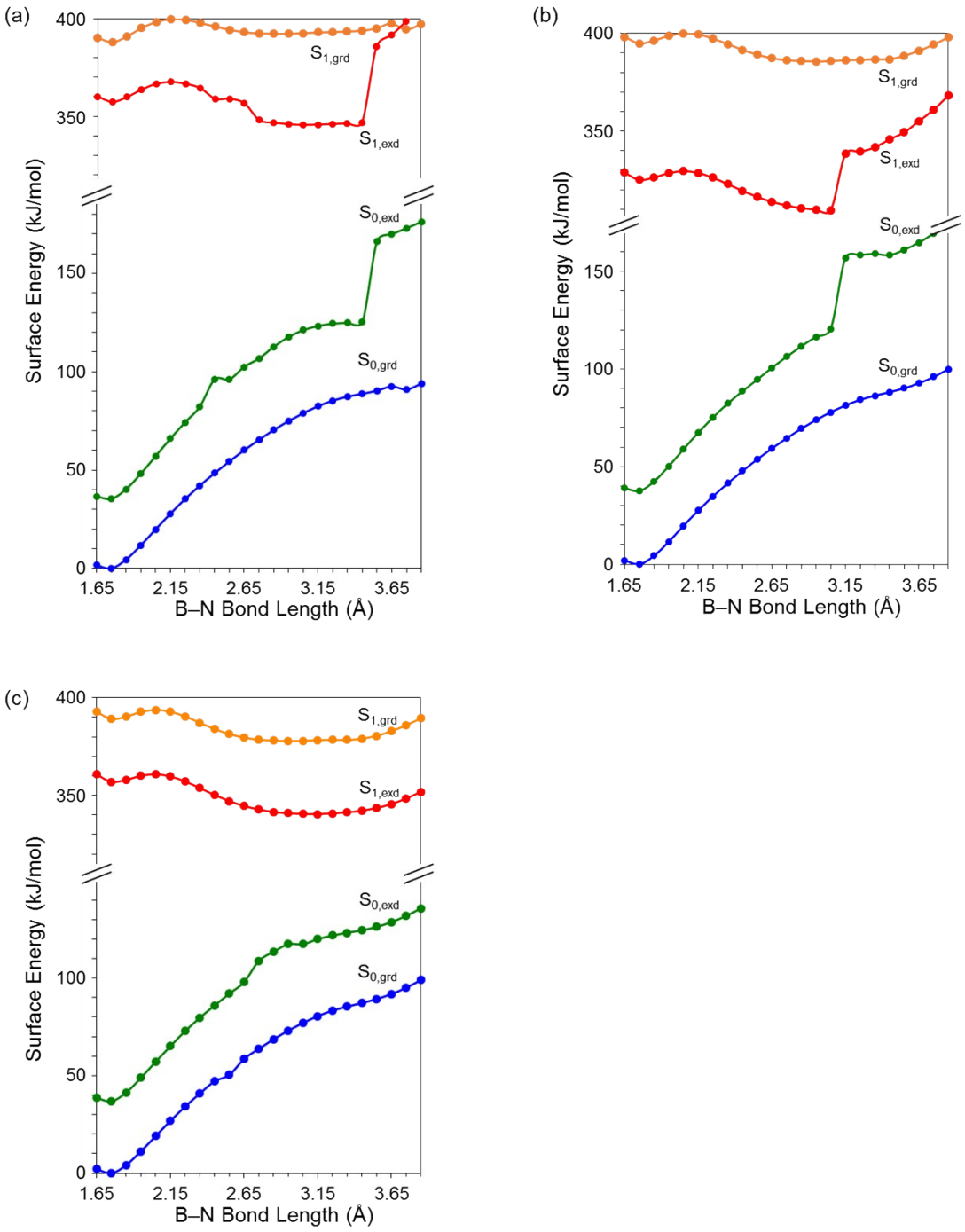


Figure S27. Potential energy surfaces of S_0 and S_1 of (a) **3a**, (b) **3b**, (c) **3c** in the ground and excited states calculated at the CAM-B3LYP/6-31G(d,p) and TD-CAM-B3LYP/6-31G(d,p) levels.

Table S14. Photophysical data of **3a–c** in cyclohexane (1.0×10^{-5} M)

	$\lambda_{max,abs}$ (nm)[a]	$\varepsilon_{max,abs}$ ($\times10^4$ $M^{-1}cm^{-1}$)[a]	$\lambda_{max,FL}$ (nm)[b]	Φ_F (%)[c]	$\tau_{1/2}$ (ns)[d]	$\tau_{1/2}$ (ns)[e]	ratio (I_3/I_4)[f]
3a	335	4.25	373, 390	81	1.14 (100%) $\chi^2 = 1.01$	—	0
3b	327	5.31	365, 382, 511	56	12.6 (87%) 1.09 (13%) $\chi^2 = 1.03$	13.1 (95%) 0.03 (5%) $\chi^2 = 1.26$	0.11
3c	334	4.42	374, 390, 535	55	22.2 (86%) 0.91 (13%) $\chi^2 = 1.10$	22.1 (100%) $\chi^2 = 1.07$	0.54

[a]Absorption maxima.

[b]Fluorescence maxima excited at $\lambda_{max,abs}$.

[c]Absolute quantum yields calculated by an integrating sphere method.

[d]Emission life times excited at 292 nm and detected around 390 nm.

[e]Emission life times excited at 375 nm and detected at 511 nm and 535 nm.

[f]Relative emission intensity. I_3 and I_4 were the intensities at $\lambda_{max,FL}$ and at 511 nm for **3b** and 535 nm for **3c**, respectively.

References

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