Supporting Information

The Most Intensely Fluorescent Azobenzene by Utilizing the B–N Interaction

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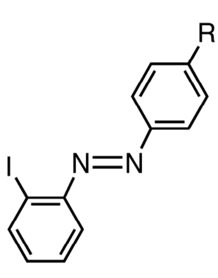
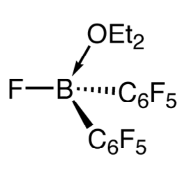
Synthetic Procedures and spectral data.

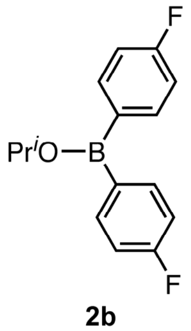
General Procedures. Solvents were purified before use by reported methods. All reactions were carried out under argon atmosphere unless otherwise noted. The ^{1}H NMR (400 MHz), ^{11}B NMR (128 MHz), ^{13}C NMR (100 MHz), and ^{19}F NMR (376 MHz) spectra were measured with a JEOL AL400 spectrometer. The ^{13}C NMR (126 MHz) spectra were measured with a Bruker DRX-500 spectrometer. Tetramethylsilane was used as an external standard for the ^{1}H and ^{13}C{^{1}H} NMR spectra. $BF_3{\cdot}OEt_2$ and CCl_3F were used as an external standard for the ^{11}B and ^{19}F NMR spectra, respectively. Absorption spectra were measured with a JASCO V-530 UV-vis spectrometer and a Hitachi U-3500 UV-vis spectrometer. Fluorescence spectra were measured with a Hitachi F-4500 fluorescence spectrophotometer and a JASCO FP-6500 fluorescence spectrophotometer. Preparative gel permeation liquid chromatography was performed by LC-908 with JAIGEL H1 + H2 columns (Japan Analytical Industry) with toluene as the solvent. All melting points are uncorrected. Elemental analyses were performed by the Microanalytical Laboratory of Department of Chemistry, Faculty of Science, The University of Tokyo. 2-Iodoazobenzene ((*E*)-**1**) and bis(4-fluorophenyl)isopropoxyborane (**2b**) were prepared according to the literatures.[1,2] The absolute values of the fluorescence quantum yields were calculated by assuming a quantum yield of 0.85 for fluorescein (0.1 M aq. NaOH solution)[3] and 1.00 for 9,10-diphenylanthracene (cyclohexane solution).[4]



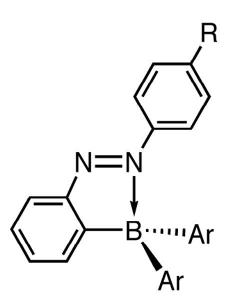
(*E*)-**1** (R = H)
(*E*)-**4** (R = OMe)



2a



2b



(*E*)-**3a** (R = H, Ar = C_6F_5)
(*E*)-**3b** (R = H, Ar = *p*-FC_6H_4)
(*E*)-**3c** (R = OMe, Ar = C_6F_5)

Preparation of Fluorobis(pentafluorophenyl)borane Diethyl Etherate (2a).

This compound was synthesized by a modification of a literature procedure.[5] An Et_2O solution (15 mL) of C_6F_5MgBr, prepared from bromopentafluorobenzene (1.05 mL, 8.29 mmol) and magnesium (196 mg, 8.07 mmol), was added to an Et_2O solution (10 mL) of $BF_3{\cdot}OEt_2$ (0.510 mL, 4.02 mmol) at 0 °C at once. After the reaction solution was stirred further at 0 °C for 30 min, evaporation of the solvents at 0 °C gave **2a** as a gray solid. This crude solid was used for the next reaction without purification.

Synthesis of (*E*)-Bis(pentafluorophenyl)[2-(phenylazo)phenyl]borane ((*E*)-3a).

n-BuLi (1.66 M in hexane, 2.42 mL, 4.02 mmol) was added to an Et_2O solution (30 mL) of 2-iodoazobenzene ((*E*)-**1**) (1.13 g, 3.65 mmol) at –112 °C. The reaction solution was stirred for 30 minutes, added to an Et_2O solution (20 mL) of fluoroborane **2a** (4.02 mmol) at –112 °C, and was allowed to warm gradually to room temperature. After the solvent was removed in vacuo, the residue was dissolved in toluene and insoluble materials were removed by filtration through a glass filter. Concentration of the filtrate followed by separation with gel permeation chromatography (eluent: toluene) afforded (*E*)-**3a** (539 mg, 28%) as brown solid; mp 178.7-179.1 °C (from benzene/hexane); (Found: C, 54.93; H, 1.99; N, 5.10. Calc. for $C_{24}H_9BF_{10}N_2$: C, 54.79; H, 1.72; N, 5.32%); λ_{max}(hexane)/nm 243 (ε/dm^3 mol^{-1} cm^{-1} 1.3×10^4) and 386 (1.9×10^4); δ_H(400 MHz, $CDCl_3$) 7.45-7.55 (4 H, m), 7.58 (1 H, dt, *J* 7.2 and 1.2 Hz), 7.65 (1 H, d, *J* 6.8 Hz), 8.04 (2 H, d, *J* 7.6 Hz) and 8.35 (1 H, d, *J* 7.5 Hz); δ_B(128 MHz, $CDCl_3$) –0.8 (line width $h_{1/2}$ 152 Hz); δ_C(100 MHz, $CDCl_3$) 114.25 (br s, *C*B), 122.61 (s, *C*H), 128.39 (s, *C*H), 128.57 (s, *C*H), 128.74 (s, *C*H), 129.67 (s, *C*H), 132.68 (s, *C*H), 135.96 (s, *C*H), 135.65-138.59 (m, *C*F), 138.62-141.59 (m, *C*F), 143.76 (s, *C*N), 146.21-149.06 (m, *C*F), 155.43 (br s, *C*B) and 156.29 (s, *C*N); δ_F(376 MHz, $CDCl_3$) –163.90 ~ –163.70 (4 F, m), –157.39 (2 F, t, *J* 19 Hz) and –132.75 ~ –132.60 (4 F, m); *m/z* (EI, 70 eV) 526 (M^+, 15%), 507 (3) and 77 (100).

Synthesis of (*E*)-Bis(4-fluorophenyl)[2-(phenylazo)phenyl]borane ((*E*)-3b).

Successive reactions of an Et_2O solution (40 mL) of (*E*)-**1** (1.82 g, 5.90 mmol) with *n*-BuLi (1.63 M in hexane, 4.30 mL, 6.57 mmol) and an Et_2O solution (10 mL) of isopropoxyborane **2b** (1.67 g, 6.44 mmol) gave yellow precipitates. After the supernatant was separated from the precipitates, the solvent of the supernatant was removed in vacuo and the residue was washed with cold hexane (10 mL) to give yellow solid, which was combined with the first precipitates. Combined solid was dissolved in toluene and the solution was refluxed for 2 hours to decompose intermediate isopropoxyborate. Evaporation of the solvent afforded (*E*)-**3b** (782 mg, containing 0.72 molar amount of lithium isopropoxide, 31%) as yellow solid; mp 130.3-132.3 °C (dec.); δ_H(400 MHz, $CDCl_3$) 6.83-6.90 (4 H, m), 7.10-7.19 (4 H, m), 7.35-7.42 (2 H, m), 7.42-7.50 (2 H, m), 7.50-7.55(1 H, m), 7.56-7.61 (1 H, m), 7.98-8.03 (2 H, m) and 8.32 (1 H, d, *J* 7.8 Hz); δ_B(128 MHz, $CDCl_3$) 7.0 (line width $h_{1/2}$ 223 Hz); δ_C(126 MHz, C_6D_6) 115.52 (d, $J_{C,F}$ 20 Hz, *C*H), 124.34 (s, *C*H), 127.95 (s, *C*H), 128.68 (s, *C*H), 129.63 (s, *C*H), 130.23 (s, *C*H), 132.50 (s, *C*H), 134.96 (s, *C*H), 135.58 (d, $J_{C,F}$ 6.9 Hz, *C*H), 141.77 (br s, *C*B), 145.12 (s, *C*N), 156.71 (s, *C*N), 163.05 (d, $J_{C,F}$ 245 Hz, *C*F) and 163.39 (br s, *C*B); δ_F(376 MHz, $CDCl_3$) –118.47 ~ –118.37 (2 F, m); *m/z* (FAB^+) 382.1432 (M^+. $C_{24}H_{17}BF_2N_2$ requires 382.1453).

Synthesis of (*E*)-2-iodo-4'-methoxyazobenzene ((*E*)-4).[6]

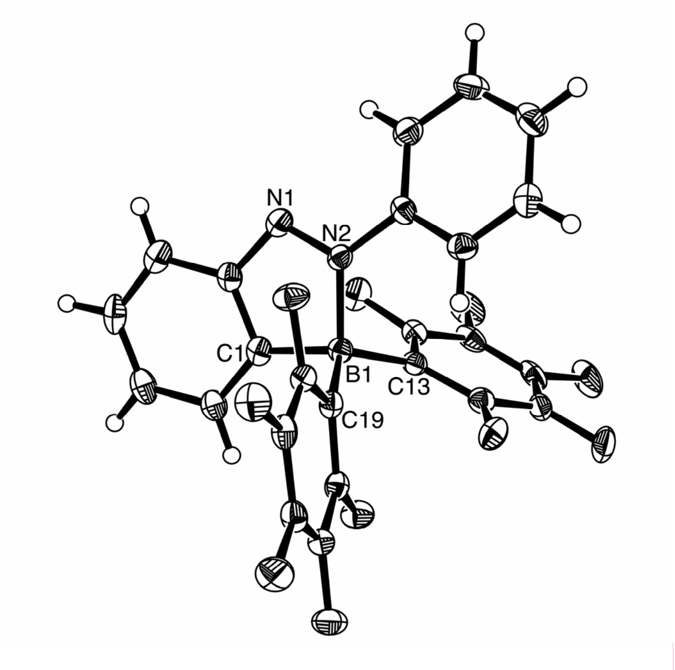
To a hydrochloric acid (0.24 M, 100 mL, 24 mmol) solution of 2-iodoaniline (2.19 g, 10.0 mmol), an aqueous solution (10 mL) of sodium nitrite (690 mg, 10.0 mmol) was added dropwise at 0 °C and the reaction mixture was stirred for 10 minutes. An aqueous sodium hydroxide (0.25 M, 40 mL, 10 mmol) solution of phenol (942 mg, 10.0 mmol) was added to the reaction mixture at 0 °C and the reaction mixture was allowed to warm gradually to room temperature. After further stirring for 16 hours, an aqueous sodium hydroxide solution was added to the reaction mixture until it became basic. After washing with chloroform, the aqueous layer was acidified by addition of hydrochloric acid. The organic layer was extracted with chloroform, dried with anhydrous magnesium sulfate and evaporated to give deep red oil. After purification with a silica gel column chromatography (eluent: chloroform), recrystallization from benzene-hexane afforded 4-(2-iodophenylazo)phenol[7] (1.59 g, 48%) containing 0.096 molar amount of phenol. This 4-(2-iodophenylazo)phenol (1.55g, 4.64 mmol) was added to a mixture of dimethyl sulfoxide (10 mL) and powdered potassium hydroxide (1.22 g, 21.7 mmol) at room temperature. After methyl iodide (0.7 mL, 11 mmol) was added to the mixture, the reaction mixture was stirred for 5 hours at room temperature, and then poured into water. The organic layer was extracted with chloroform, washed with water, dried with anhydrous magnesium sulfate, and then evaporated. The residue was recrystallized from ethanol to afford (*E*)-**4** (1.39 g, 88%) as red plates; δ_H(400 MHz, $CDCl_3$) 3.90 (3 H, s), 7.00-7.04 (2 H, m), 7.12 (1 H, ddd, *J* 7.6, 7.6 and 1.5 Hz), 7.40 (1 H, ddd, *J* 7.9, 7.4 and 1.2 Hz), 7.60 (1 H, dd, *J* 7.9 and 1.5 Hz) and 7.96-8.01 (3 H, m).

Synthesis of (*E*)-[2-(4-Methoxyphenylazo)phenyl]bis(pentafluorophenyl)borane ((*E*)-3c).

An Et_2O solution (80 mL) of 2-iodo-4'-methoxyazobenzene ((*E*)-**4**) (1.02 g, 3.02 mmol) was treated with *n*-BuLi (1.6 M in hexane, 2.00 mL, 3.20 mmol) and an Et_2O solution (15 mL) of fluoroborane **2a** (5.05 mmol) successively. After the solvent was removed in vacuo, the residue was dissolved in toluene and insoluble materials were removed by filtration through a glass filter. Concentration of the filtrate followed by separation with gel permeation chromatography (eluent: toluene) afforded (*E*)-**3c** (448 mg, 27%) as orange solid; mp 204.3-205.3 °C (from Et_2O/hexane); (Found: C, 54.17; H, 2.26; N, 4.86. Calc. for $C_{25}H_{11}BF_{10}N_2O$: C, 53.99; H, 1.99; N, 5.04%); λ_{max}(hexane)/nm 250 (ε/dm^3 mol^{-1} cm^{-1} 7.5×10^3), 306 (1.2×10^3) and 439 (1.2×10^4); δ_H(400 MHz, $CDCl_3$) 3.87 (3 H, s), 6.91-6.96 (2 H, m), 7.45-7.54 (2 H, m), 7.61 (1 H, d, *J* 6.1 Hz), 7.99-8.04 (2 H, m) and 8.23 (1 H, d, *J* 6.3 Hz); δ_B(128 MHz, $CDCl_3$) –0.6 (line width $h_{1/2}$ 201 Hz); δ_C(126 MHz, $CDCl_3$) 55.82 (s, CH_3), 114.99 (s, *C*H), 124.71 (s, *C*H), 127.71 (s, *C*H), 128.26 (s, *C*H), 128.44 (s, *C*H), 134.92 (s, *C*H), 135.91-138.37 (m, *C*F), 137.79 (s, *C*O), 138.79-141.23 (m, *C*F), 146.40-148.75 (m, *C*F), 151.89 (br s, *C*B), 156.22 (s, *C*N), 159.56 (br s, *C*B) and 163.22 (br s, *C*B); δ_F(376 MHz, $CDCl_3$) –162.34 ~ –162.15 (4 F, m), –155.93 (2 F, t, *J* 22 Hz) and –131.18 (4 F, dd, *J* 22 and 7.4 Hz); *m/z* (EI, 70 eV) 556 (M$^+$, 100%), 541 (24), 121 (16), 107 (52), 92 (36) and 77 (61).

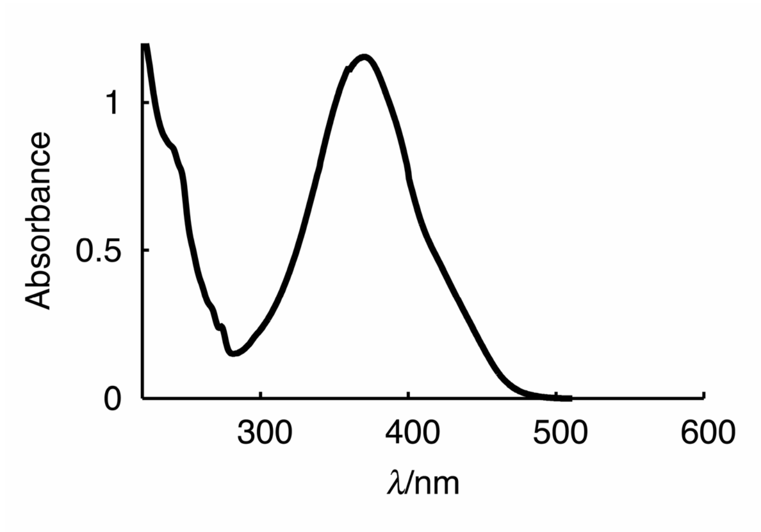
X-ray Crystallographic Analysis of (*E*)-3a.

Crystallographic data for (*E*)-3a. $C_{24}H_9BF_{10}N_2$, $M = 526.14$, triclinic, $a = 9.861(7)$, $b = 10.732(6)$, $c = 10.822(7)$ Å, $\alpha = 99.976(7)$, $\beta = 113.714(8)$, $\gamma = 91.109(7)°$, $U = 1027.7(11)$ Å^3, $T = 120$ K, space group $P\overline{1}$, $Z = 2$, μ(Mo-Kα) = 0.164 mm^{-1}, 6375 reflections measured, 3488 unique ($R_{\mathrm{int}} = 0.0191$) which were used in all calculations. The final $R1$ ($I > 2\sigma(I)$) and $wR2$ (all data) were 0.0371 and 0.1068, respectively. GOF = 1.089. Crystallographic data (excluding structure factors) for the structures of (*E*)-**3a** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 607217. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

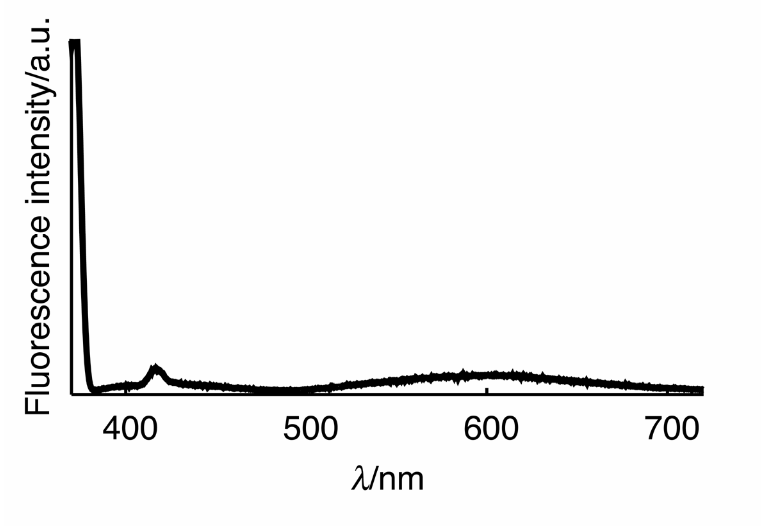


ORTEP drawing of (*E*)-3a with thermal ellipsoid plot (50% probability). Selected bond lengths (Å) and bond angles (deg): N1–N2, 1.2704(18); B1–N2, 1.625(2); B1–C1, 1.599(2); B1–C13, 1.629(2); B1–C19, 1.627(2); C1–B1–C13, 117.74(13); C1–B1–C19, 106.04(13); C13–B1–C19, 117.93(13); C1–B1–N2, 95.53(12); C13–B1–N2, 105.07(12); C19–B1–N2, 112.35(13).

Absorption and Fluorescence Spectra of (*E*)-3b.



Absorption spectra of (*E*)-**3b** (ca. 61 μM, containing lithium isopropoxide) in hexane.



Fluorescence spectra of (*E*)-**3b** (ca. 6 μM, containing lithium isopropoxide) in hexane. The far left signal (370 nm) is a Rayleigh scattering light. A signal at 417 nm would be a Raman scattering light by hexane. The broad peak lying near 600 nm cannot be determined whether it is a fluorescence of (*E*)-**3b** or not. (If it is, $\Phi_F < 8 \times 10^{-3}$.)

Theoretical Calculations.

All calculations were carried out at DFT level using the B3PW91[8,9] exchange-correlation functional implemented in the Gaussian 03 (Revision B.01)[10] suite of programs. All calculations for the optimized structures calculated with the 6-31G(d) basis set were performed with the 6-31+G(d) basis se. The transition energies were obtained by a time-dependent DFT (TD-DFT) method. Zero point energies corrections are not included in all the calculations.

Geometry (Cartesian Coordinates) of (*E*)-3a.

6	–0.629381	2.421237	4.331002
6	–0.732166	1.022874	4.383766
6	–0.554968	0.228411	3.246359
6	–0.253338	0.831082	2.030755
6	–0.158377	2.236432	2.006346
6	–0.339797	3.051876	3.129582
5	–0.051959	0.328991	0.517865
7	0.154228	2.751657	0.762346
7	0.225905	1.813841	–0.095720
6	0.619597	2.155459	–1.412883
6	0.489233	1.202089	–2.427717
6	0.872528	1.526502	–3.724840
6	1.386719	2.789208	–4.013312
6	1.517428	3.735313	–2.994152
6	1.138962	3.426036	–1.695177
6	–1.488665	–0.277031	0.029148
6	1.276526	–0.574672	0.235310
6	2.465718	–0.302519	0.917192
6	3.635250	–1.038751	0.757140

6	3.651719	−2.104858	−0.134174
6	2.501939	−2.404821	−0.854229
6	1.354116	−1.641311	−0.661785
6	−1.855997	−1.555612	0.453551
6	−3.085778	−2.138593	0.177860
6	−4.033128	−1.416892	−0.541818
6	−3.727484	−0.130059	−0.963480
6	−2.479934	0.415096	−0.664059
9	2.530074	0.729620	1.773987
9	4.736412	−0.726639	1.443584
9	4.760248	−2.821977	−0.306329
9	2.507184	−3.414712	−1.726858
9	0.298345	−1.977448	−1.425671
9	−0.990027	−2.288274	1.178183
9	−2.276947	1.677566	−1.080293
9	−4.630254	0.581240	−1.642517
9	−5.221441	−1.952821	−0.816024
9	−3.368517	−3.371872	0.602156
1	−0.777448	3.007686	5.233157
1	−0.953580	0.546284	5.335810
1	−0.646649	−0.851339	3.321112
1	−0.255719	4.131455	3.047604
1	0.083210	0.221184	−2.211670
1	0.766204	0.785922	−4.512273
1	1.688157	3.036212	−5.027535
1	1.923311	4.719216	−3.212265

1	1.241340	4.148805	−0.893928

Geometry (Cartesian Coordinates) of (*E*)-3b.

6	1.627110	4.019348	2.166308
6	1.832766	4.042375	0.776903
6	1.430496	2.984061	−0.041381
6	0.800238	1.876195	0.519383
6	0.606781	1.884271	1.914628
6	1.006770	2.929718	2.757973
5	0.238944	0.479290	−0.037201
7	−0.030080	0.752487	2.393150
7	−0.259776	−0.054681	1.432874
6	−0.961442	−1.245212	1.744752
6	−1.024543	−2.264377	0.788678
6	−1.707152	−3.440686	1.083116
6	−2.329464	−3.604302	2.318674
6	−2.266566	−2.581661	3.268704
6	−1.588068	−1.404003	2.989618
6	1.478800	−0.416584	−0.585344
6	−1.066342	0.602018	−0.997980
6	−2.036998	1.589588	−0.755181
6	−3.183054	1.717040	−1.536204
6	−3.364463	0.838355	−2.595570
6	−2.437772	−0.151938	−2.884412
6	−1.303388	−0.259478	−2.080100
6	1.944251	−0.208299	−1.896063
6	3.061119	−0.869444	−2.403253

6	3.738460	−1.758065	−1.580052
6	3.329922	−1.992655	−0.275842
6	2.209623	−1.316422	0.206678
9	−4.465250	0.953673	−3.363133
9	4.817180	−2.407251	−2.059431
1	1.955956	4.857372	2.774354
1	2.317431	4.907798	0.330661
1	1.611101	3.034512	−1.112424
1	0.832581	2.873817	3.828680
1	−0.530899	−2.139038	−0.166443
1	−1.750799	−4.231318	0.339505
1	−2.865528	−4.522726	2.542070
1	−2.755965	−2.701375	4.231436
1	−1.538476	−0.599940	3.714891
1	1.907068	−1.505315	1.234413
1	3.884309	−2.691038	0.344064
1	3.408519	−0.705501	−3.419101
1	1.417784	0.487704	−2.545583
1	−0.578011	−1.034486	−2.317417
1	−2.608396	−0.819912	−3.723582
1	−1.895437	2.287718	0.067503
1	−3.926841	2.483784	−1.340332

Geometry (Cartesian Coordinates) of (*E*)-3c.

6	2.093436	1.234742	4.600467
6	2.747606	1.866061	3.532923
6	2.338958	1.678635	2.208173

6	1.248658	0.860982	1.936251
6	0.613099	0.236375	3.026521
6	1.008781	0.402643	4.358091
5	0.516245	0.329255	0.608768
7	−0.464418	−0.554819	2.667362
7	−0.590586	−0.571909	1.399049
6	−1.691776	−1.260651	0.852516
6	−1.746691	−1.487537	−0.531168
6	−2.819498	−2.163688	−1.079794
6	−3.863265	−2.624260	−0.262701
6	−3.811549	−2.395348	1.120634
6	−2.732580	−1.717987	1.669027
6	1.601220	−0.589854	−0.195273
6	−0.296861	1.450979	−0.254288
6	−0.969562	2.486026	0.401153
6	−1.661164	3.498127	−0.256839
6	−1.710525	3.497349	−1.645646
6	−1.077227	2.478289	−2.346085
6	−0.397069	1.485752	−1.646187
6	2.599029	0.047508	−0.935836
6	3.628922	−0.621526	−1.583714
6	3.705477	−2.007413	−1.485545
6	2.752849	−2.687054	−0.738958
6	1.736297	−1.973944	−0.105315
9	−0.987191	2.534745	1.743027
9	−2.279994	4.459944	0.431645

9	–2.369335	4.454039	–2.297119
9	–1.130922	2.453754	–3.679669
9	0.154335	0.517273	–2.401237
9	2.591266	1.389676	–1.041874
9	0.874177	–2.705700	0.622590
9	2.820023	–4.015553	–0.623097
9	4.685972	–2.672295	–2.095364
9	4.544474	0.048494	–2.286917
1	2.438211	1.397980	5.617566
1	3.592041	2.518457	3.742348
1	2.870461	2.176956	1.402494
1	0.480110	–0.106123	5.158779
1	–0.946550	–1.145239	–1.176500
1	–2.873865	–2.351450	–2.147269
1	–4.608670	–2.733497	1.773190
1	–2.688786	–1.532593	2.736314
8	–4.866362	–3.266210	–0.897063
6	–5.951403	–3.755085	–0.128333
1	–6.476605	–2.940436	0.385998
1	–6.629180	–4.228744	–0.839874
1	–5.618704	–4.498948	0.606441

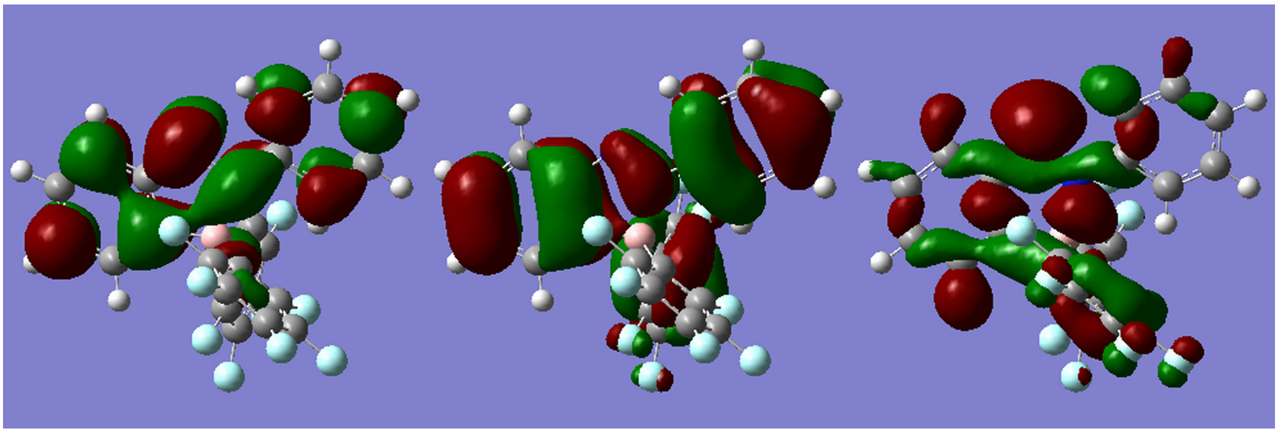
Geometry (Cartesian Coordinates) of (*E*)-Azobenzene ((*E*)-5).

6	–1.292865	3.664090	0.000000
6	–0.189597	4.524502	0.000000
6	1.102635	4.001833	0.000000
6	0.189597	1.760916	0.000000

6	−1.111112	2.288370	0.000000
7	0.499785	0.381291	0.000000
7	−0.499785	−0.381291	0.000000
6	−0.189597	−1.760916	0.000000
6	−1.291702	−2.622885	0.000000
6	−1.102635	−4.001833	0.000000
6	0.189597	−4.524502	0.000000
6	1.292865	−3.664090	0.000000
6	1.111112	−2.288370	0.000000
1	−2.299210	4.075664	0.000000
1	−0.341989	5.600807	0.000000
1	1.961779	4.667439	0.000000
1	−1.952187	1.602808	0.000000
1	−2.286212	−2.185692	0.000000
1	−1.961779	−4.667439	0.000000
1	0.341989	−5.600807	0.000000
1	2.299210	−4.075664	0.000000
1	1.952187	−1.602808	0.000000
6	1.291702	2.622885	0.000000
1	2.286212	2.185692	0.000000

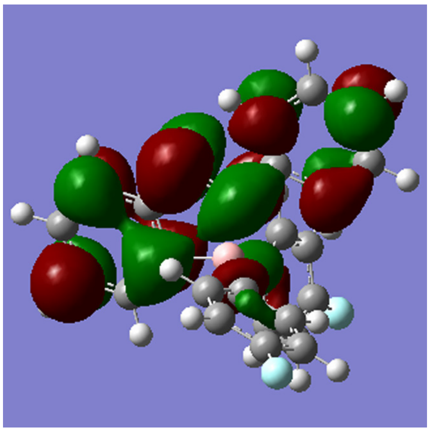
Molecular Orbital Diagrams for the HOMOs and LUMO of (*E*)-3a.

LUMO (left), HOMO (center), and HOMO–8 (right)

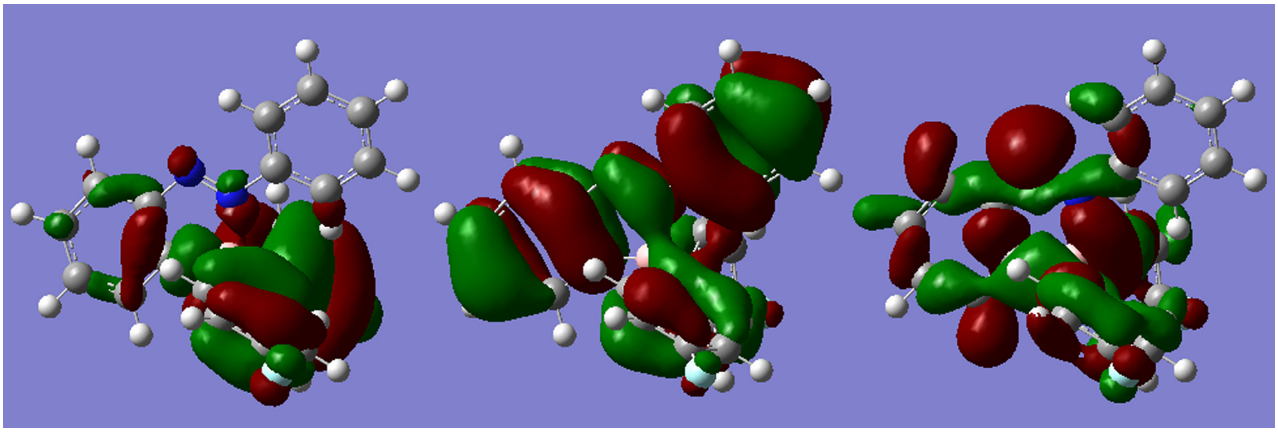


Molecular Orbital Diagrams for the HOMOs and LUMO of (*E*)-3b.

LUMO

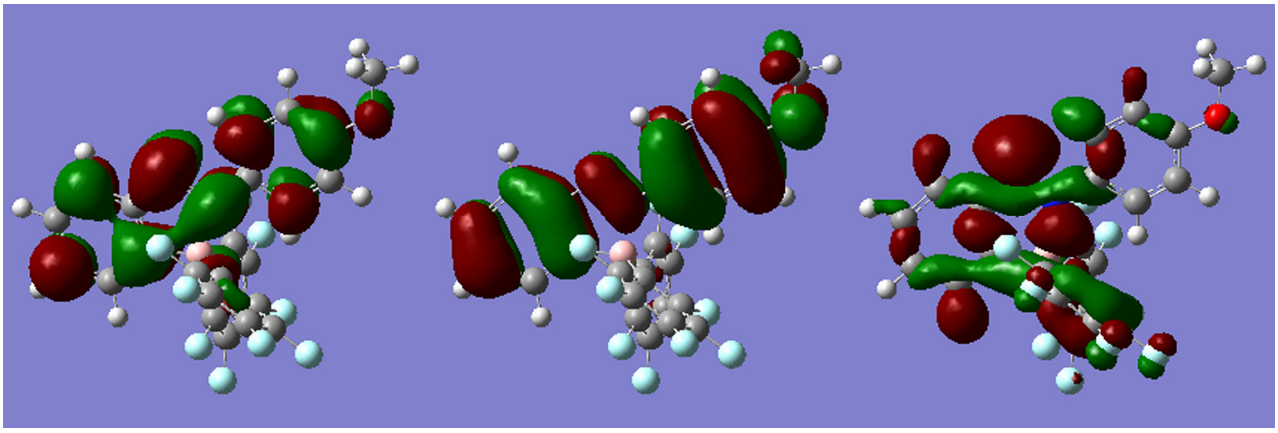


HOMO (left), HOMO–2 (center), and HOMO–9 (right)



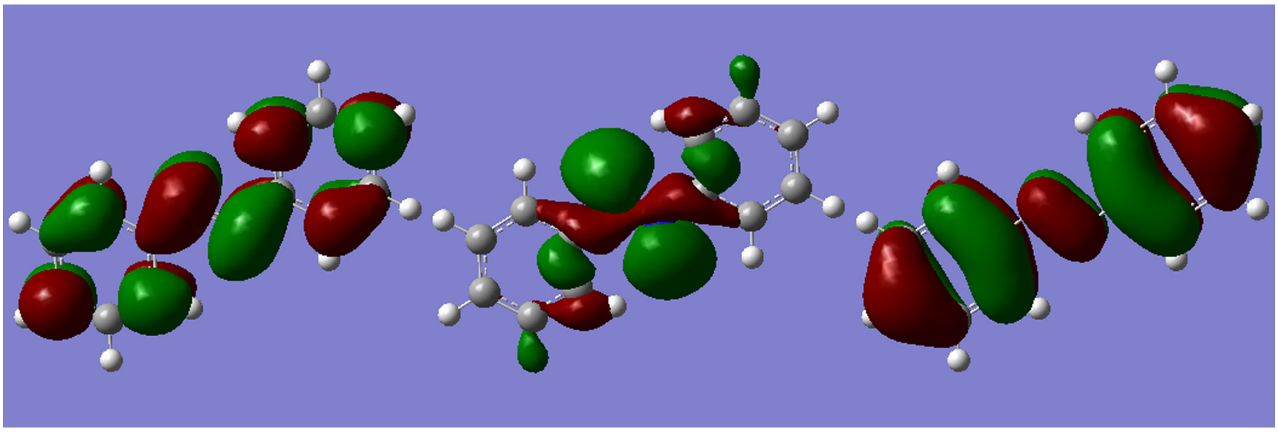
Molecular Orbital Diagrams for the HOMOs and LUMO of (*E*)-3c.

LUMO (left), HOMO (center), and HOMO–8 (right)



Molecular Orbital Diagrams for the HOMOs and LUMO of (*E*)-Azobenzene ((*E*)-5).

LUMO (left), HOMO (center), and HOMO–1 (right)



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Color Version of Fig. 2:

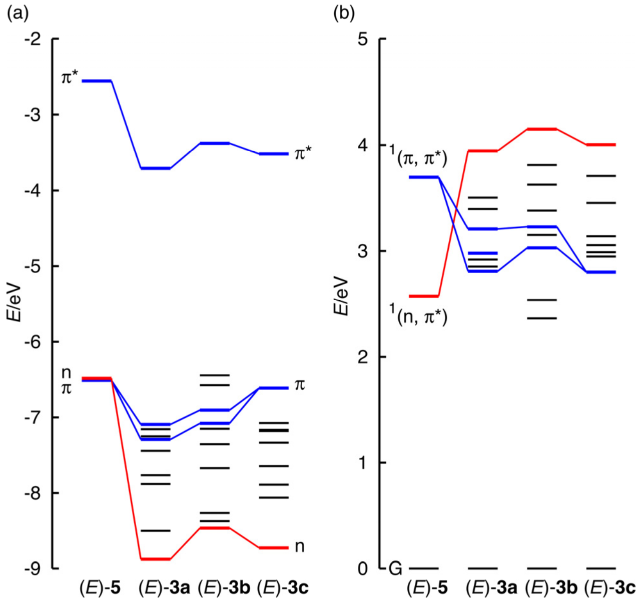

Fig. 2 Calculated (a) energy levels of frontier molecular orbitals and (b) singlet excitation energies of (*E*)-azobenzene ((*E*)-**5**) and (*E*)-**3a–c** at the B3PW91/6-31+G(d)//B3PW91/6-31G(d) level of theory. In (a), the orbitals indicated by blue-colored and red-colored levels originate from the π (π*) and n orbitals of the azo group, respectively. In (b), blue-colored and red-colored excited states have the character of ^{1}(π, π*) and ^{1}(n, π*) states, respectively.

Complete Ref. 15:

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