

Supporting Information

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1,2-Azaborine Cations**

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Supporting Information

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General

All oxygen- and moisture-sensitive manipulations were carried out under an inert atmosphere using either standard Schlenk techniques or a glove box.

THF, Et₂O, CH₂Cl₂, and pentane were purified by passing through a neutral alumina column under argon. Cyclohexene was dried over CaH₂ and distilled under N₂ prior to use.

All chemicals and solvents were purchased (Aldrich or Strem) and used as received.

¹¹B NMR spectra were recorded on a Varian Unity/Inova 600 spectrometer at ambient temperature. ¹H NMR spectra were recorded on a Varian Unity/Inova 300 or Varian Unity/Inova 600 spectrometer. ¹³C NMR spectra were recorded on a Varian Unity/Inova 300 spectrometer or Varian Unity/Inova 500 spectrometer. ¹¹B NMR spectra were externally referenced to BF₃•Et₂O (δ 0).

IR spectra were recorded on a Nicolet Magna 550 FT-IR instrument with OMNIC software. UV-Vis spectra were recorded on an Agilent 8453 spectrometer with ChemStation software. Fluorescence spectra were recorded on a Horiba Jobin-Yvon Fluoromax 4 fluorometer equipped with an integrating sphere. Quantum yields are reported as the average of 3 runs.

High-resolution mass spectroscopy data were obtained at the Mass Spectroscopy Facilities and Services Core of the Environmental Health Sciences Center at Oregon State University. Financial support for this facility has been furnished in part by the National Institute of Environmental Health Sciences, NIH (P30 ES00210).

Synthesis

Scheme 2

Compound 2. In a glovebox, a solution of **1**¹ (0.600 g, 4.24 mmol in 25.0 mL benzene) was added dropwise to a stirring suspension of AgOTf (1.31 g, 5.09 mmol in 25.0 mL benzene). The reaction was stirred at rt for 8 h, whereupon the solvent was removed under reduced pressure. Compound **2** was purified by vacuum distillation (bp 35 °C, 100 mTorr) from the resulting crude material as a clear, colorless liquid (0.639 g, 59%).

¹H NMR (600 MHz, CD₂Cl₂): δ 7.76 (br m, 1H), 7.21 (d, ³J_{HH} = 6.3 Hz, 1H), 6.65 (d, ³J_{HH} = 11.4 Hz, 1H), 6.39 (ddd, ³J_{HH} = 11.4, 6.3, 3.2 Hz, 1H), 3.78 (q, ³J_{HH} = 7.3 Hz, 2H), 1.34 (t, ³J_{HH} = 7.3 Hz, 3H). ¹³C NMR (75 MHz, CD₂Cl₂): δ 148.6, 138.9, 119 (br), 119 (q, ¹J_{CF} = 318 Hz), 111.5, 46.5, 17.7. ¹¹B NMR (192.5 MHz, CD₂Cl₂): δ 28.0. FTIR (thin film) 3139, 3080, 2986, 2939, 2908, 2880, 1870, 1764, 1611, 1528, 1481, 1456, 1444, 1413, 1351, 1209, 1153, 1112, 1060, 1006, 944, 830, 785, 768, 747, 684, 618, 572, 518, 448 cm⁻¹.

Scheme 3

Compound 3a. In a glove box, a solution of 4-methylpyridine (0.047 g, 0.51 mmol in 1.0 mL CH₂Cl₂) was added to a stirring solution of **2** (0.100 g, 0.392 mmol in 1.0 mL CH₂Cl₂). The reaction was stirred for 1 h at rt. Subsequently, the solvents and all volatiles were removed under reduced pressure. The resulting material was washed with pentane (3 x 5 mL) to give **3a** as a light-yellow crystalline solid (0.130 g, 95%).

¹H NMR (600 MHz, CD₂Cl₂): δ 8.64 (d, ³J_{HH} = 6.2 Hz, 2H), 8.01 (d, ³J_{HH} = 6.2 Hz, 2H), 7.96 (dd, ³J_{HH} = 10.5, 7.1 Hz, 1H), 7.54 (d, ³J_{HH} = 7.6, 1H), 6.80 (app t, ³J_{HH} = 6.8 Hz, 1H), 6.75 (d, ³J_{HH} = 10.5 Hz, 1H), 3.72 (q, ³J_{HH} = 7.3 Hz, 2H), 2.72 (s, 3H), 1.30 (t, ³J_{HH} = 7.3 Hz, 3H). ¹³C NMR (75 MHz, CD₂Cl₂): δ 161.2, 149.2, 144.8, 139.5, 129.4, 124 (br), 121 (q, ¹J_{CF} = 320 Hz), 115.5, 47.4, 22.7, 17.9. ¹¹B NMR (192.5 MHz, CD₂Cl₂): δ 30.9. FTIR (thin film) 3112, 3087, 3042, 2976, 2939, 2883, 2309, 1972, 1820, 1707, 1639, 1607, 1528, 1452, 1412, 1388, 1368, 1334, 1267, 1145, 1086, 1028, 989, 858, 832, 806, 767, 754, 738, 720, 700, 661, 636 cm⁻¹.

Compound 3b. In a glove box, a solution of 4-phenylpyridine (0.073 g, 0.47 mmol in 1.0 mL CH₂Cl₂) was added to a stirring solution of **2** (0.100 g, 0.392 mmol in 1.0 mL CH₂Cl₂). The reaction was stirred for 1 h at rt, whereupon the product was crystallized by cooling the reaction to -20 °C for 24 h. The supernatant was decanted and the crystallized product was washed with pentane (3 x 5 mL). Residual solvents were removed under reduced pressure to provide **3b** as clear, colorless crystals (0.155 g, 97%).

(1) A. J. V. Marwitz, E. R. Abbey, J. T. Jenkins, L. N. Zakharov, S.-Y. Liu *Org. Lett.* **2007**, *9*, 4905-4908.

^1H NMR (600 MHz, CD_2Cl_2): δ 8.82 (d, $^3J_{\text{HH}} = 6.9$ Hz, 2H), 8.44 (d, $^3J_{\text{HH}} = 6.9$ Hz, 2H), 8.02 (dd, $^3J_{\text{HH}} = 9.8, 6.6$ Hz, 1H), 7.97 (dd, $^3J_{\text{HH}} = 8.1$ Hz, $^4J_{\text{HH}} = 1.7$ Hz, 2H), 7.68 (m, 3H), 7.55 (d, $^3J_{\text{HH}} = 6.6$, 1H), 6.85 (app t, $^3J_{\text{HH}} = 7.5$ Hz, 2H), 3.83 (q, $^3J_{\text{HH}} = 7.3$ Hz, 2H), 1.38 (t, $^3J_{\text{HH}} = 7.3$ Hz, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 158.1, 149.5, 145.8, 139.6, 134.3, 133.2, 130.5, 128.7, 125.7, 124 (br), 115.7, 47.7, 18.2. ^{11}B NMR (192.5 MHz, CD_2Cl_2): δ 31.0. FTIR (thin film) 3220, 3138, 3078, 2915, 1638, 1612, 1513, 1488, 1474, 1442, 1412, 1377, 1349, 1292, 1233, 1218, 1174, 1151, 1029, 833, 765, 736, 693 cm^{-1} . HRMS (EI) calcd for $\text{C}_7\text{H}_9\text{BNO}_3\text{SF}_3$ (M⁺) 255.03484, found 255.03528.

Compound 3c. In a glove box, a solution of pyridine (0.040 g, 0.51 mmol in 1.0 mL CH_2Cl_2) was added to a stirring solution of **2** (0.100 g, 0.392 mmol in 1.0 mL CH_2Cl_2). The reaction was stirred for 1 h at rt. Subsequently, the solvents and all volatiles were removed under reduced pressure. The resulting material was washed with pentane (3 x 5 mL) to provide **3c** as a light-yellow crystalline solid (0.125 g, 95%).

^1H NMR (600 MHz, CD_2Cl_2): δ 8.85 (dd, $^3J_{\text{HH}} = 6.1$ Hz, $^4J_{\text{HH}} = 0.9$ Hz, 2H), 8.65 (tt, $^3J_{\text{HH}} = 7.2$ Hz, $^4J_{\text{HH}} = 0.9$ Hz, 1H), 8.25 (dd, $^3J_{\text{HH}} = 7.2, 6.1$ Hz, 2H), 7.98 (dd, $^3J_{\text{HH}} = 11.4, 7.0$ Hz, 1H), 7.55 (d, $^3J_{\text{HH}} = 6.4$ Hz, 1H), 6.83 (dt, $^3J_{\text{HH}} = 7.0, 1.1$ Hz, 1H), 6.77 (dd, $^3J_{\text{HH}} = 11.4, 1.1$ Hz, 1H), 3.72 (q, $^3J_{\text{HH}} = 7.3$ Hz, 2H), 1.30 (t, $^3J_{\text{HH}} = 7.3$ Hz, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 149.4, 147.0, 146.0, 139.5, 129.0, 125 (br), 121 (q, $^1J_{\text{CF}} = 321$ Hz), 115.7, 47.5, 17.9. ^{11}B NMR (192.5 MHz, CD_2Cl_2): δ 30.9. FTIR (thin film) 3116, 3073, 3048, 2985, 1969, 1909, 1799, 1611, 1526, 1463, 1412, 1391, 1360, 1334, 1282, 1226, 1162, 1123, 1081, 1030, 988, 784, 758, 698, 685, 638, 599, 573 cm^{-1} .

Compound 3d. In a glove box, a solution of 4-trifluoromethylpyridine (0.075 g, 0.51 mmol in 1.0 mL CH_2Cl_2) was added to a stirring solution of **2** (0.100 g, 0.392 mmol in 1.0 mL CH_2Cl_2). The reaction was stirred for 4 h at rt. Subsequently, the solvents and all volatiles were removed under reduced pressure. The resulting material was washed with pentane (3 x 5 mL) to give **3d** as a bright-yellow crystalline solid (0.142 g, 90%).

^1H NMR (600 MHz, CD_2Cl_2): δ 9.10 (d, $^3J_{\text{HH}} = 5.0$ Hz, 2H), 8.27 (br m, 2H), 7.96 (dd, $^3J_{\text{HH}} = 10.6, 7.4$ Hz, 1H), 7.48 (d, $^3J_{\text{HH}} = 7.1$, 1H), 6.80 (d, $^3J_{\text{HH}} = 10.6$ Hz, 1H), 6.75 (br m, 1H), 3.77 (q, $^3J_{\text{HH}} = 7.3$ Hz, 2H), 1.33 (t, $^3J_{\text{HH}} = 7.3$ Hz, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 149.5, 148.9, 139.5, 124.3, 122 (br), 120.2, 115.1, 47.4, 18.0 (R-CF₃ carbons not observed). ^{11}B NMR (192.5 MHz, CD_2Cl_2): δ 30.0. FTIR (thin film) 3054, 2987, 2361, 2306, 1653, 1609, 1559, 1521, 1473, 1456, 1321, 1264, 1166, 1081, 1031, 896, 740, 639, 574, 518 cm^{-1} .

Compound 3e. In a glove box, a solution of 4-(N,N-dimethyl)pyridine (0.057 g, 0.47 mmol in 1.0 mL CH_2Cl_2) was added to a stirring solution of **2** (0.100 g, 0.392 mmol in 1.0 mL CH_2Cl_2). The reaction was stirred for 1 h at rt, whereupon the solvent was removed under reduced pressure. The product was washed with Et_2O (3 x 5 mL) providing **3e** as an oil. Crystallization of **3e** was initiated by adding a seed crystal of **3b**, which was later removed. The resultant tan solid of **3e** was washed with Et_2O (3 x 5 mL) and residual solvent was removed under reduced pressure to provide **3e** as an off-white crystalline solid (0.144 g, 98%).

^1H NMR (600 MHz, CD_2Cl_2): δ 7.98 (d, $^3J_{\text{HH}} = 6.9$ Hz, 2H), 7.71 (d, $^3J_{\text{HH}} = 6.6$ Hz, 1H), 7.28 (d, $^3J_{\text{HH}} = 6.6$ Hz, 1H), 6.90 (d, $^3J_{\text{HH}} = 6.9$ Hz, 2H), 6.48 (d, $^3J_{\text{HH}} = 13.0$ Hz, 1H), 6.41 (m, 1H), 3.67 (q, $^3J_{\text{HH}} = 7.3$ Hz, 2H), 3.23 (s, 6H), 1.22 (t, $^3J_{\text{HH}} = 7.3$ Hz, 3H). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 156.8, 145.0, 143.7, 138.9, 124 (br), 121 (q, $^1J_{\text{CF}} = 321$ Hz), 110.2, 108.4, 46.7, 40.4, 17.6. ^{11}B NMR (192.5 MHz, CD_2Cl_2): δ 26.7. FTIR (thin film) 3230, 3094, 2976, 2935, 2873, 2822, 2625, 2441, 2296, 1975, 1899, 1796, 1644, 1611, 1564, 1525, 1483, 1445, 1383, 1342, 1266, 1151, 1066, 1031, 948, 917, 822, 754, 735, 656, 637, 573, 517 cm^{-1} .

Scheme 4

Preparation of protonated pyridinium salts (4a-4e). In a glovebox, the corresponding pyridine (12.4 mmol) was dissolved in 15 mL CH_2Cl_2 . Triflic acid (1.7 g/mL; 1.1 mL, 12.4 mmol) was added dropwise to the pyridine-containing solution. The solutions were then stirred at rt for 1 h. The pyridinium salts precipitated out of the solution at the conclusion of the reaction. The supernatant solutions were decanted, and the resultant solids were washed with CH_2Cl_2 (3 x 10 mL). The pyridinium salts were then recrystallized from CH_2Cl_2 at -20 °C prior to photophysical measurements.

UV-Vis/Fluorescence Data

Compounds **3a-e** were recrystallized from a concentrated CH_2Cl_2 solution at $-20\text{ }^\circ\text{C}$ prior to making the photophysical measurements.

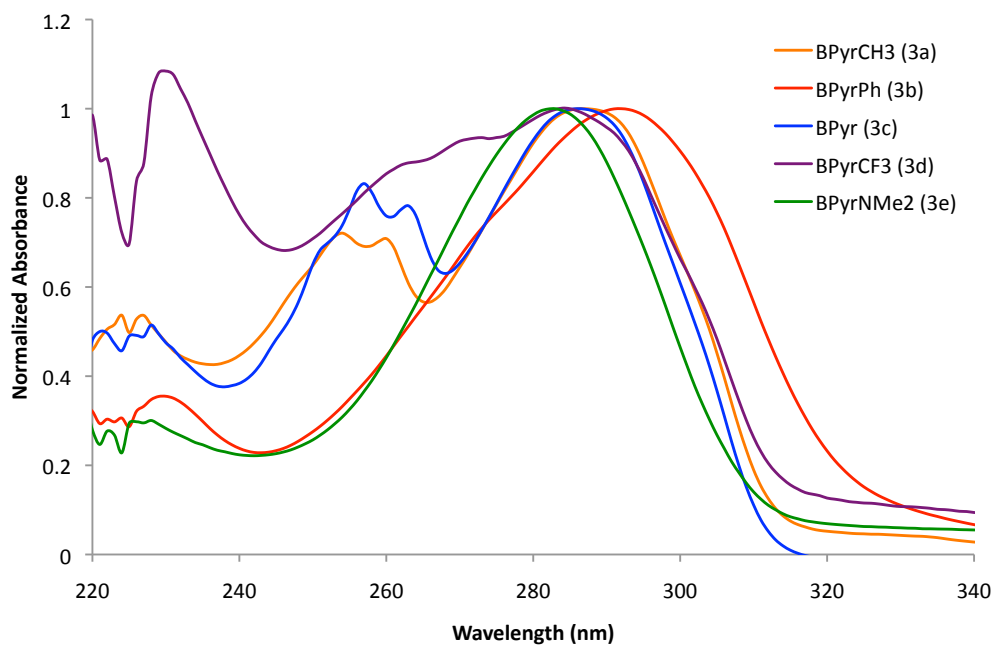


Figure S1. Normalized absorption spectra for **3a-e** in CH_2Cl_2 .

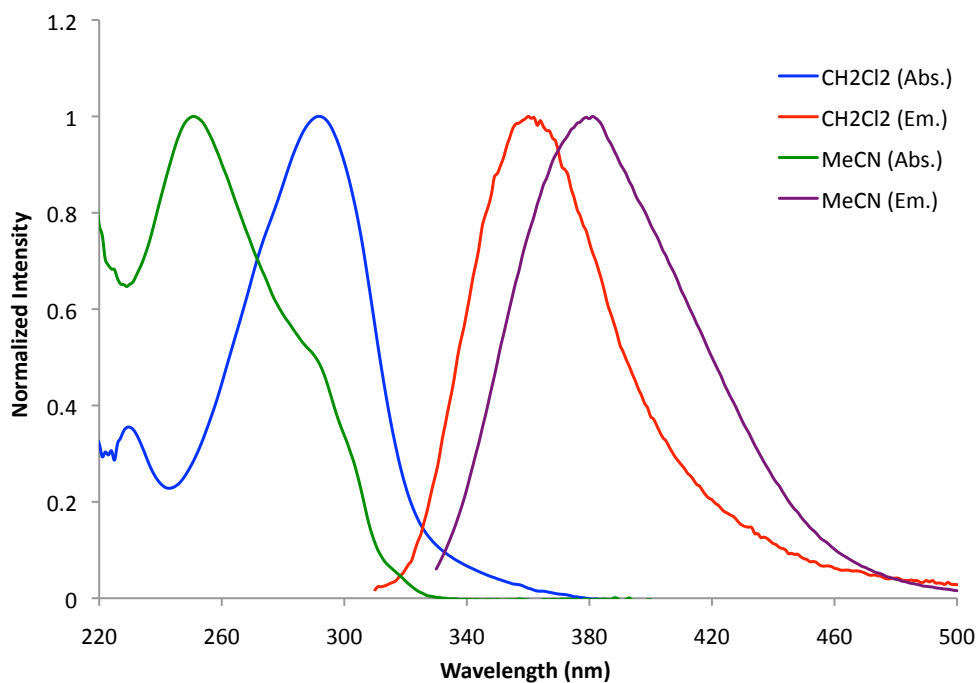


Figure S2. Normalized absorption and emission spectra for **3b** in CH_2Cl_2 and MeCN.

Solid-state fluorescence. Solid-state fluorescence data were recorded using an integrating sphere. Crystalline samples of substrates **3** or **4** were added to a 0.5 mL cylindrical cuvette in an inert atmosphere glovebox and sealed with a teflon plug. In all cases, the crystalline samples adhered to the side of the cuvette, ensuring that the excitation light was in line with the sample. In cases where no emission was observed, several attempts were made to align the crystalline samples at the appropriate level within the integrating sphere. Solid-state fluorescence data for **3a-e** are presented in the main text.

Solution-phase fluorescence quenching with iodide. To a solution of **3b** in MeCN (10^{-4} M, 4.0 mL) were added successive aliquots of solution of NaI in MeCN (20 mg NaI/mL, each aliquot 0.05–0.2 mL). The emission spectrum of **3b** was recorded immediately after each aliquot was added, the results of which are shown in Figure S3. A control experiment was performed wherein a sample of **3b** in MeCN (10^{-4} M, 4.0 mL) was diluted with MeCN only (each aliquot 0.2–1.0 mL); the fluorescence intensity did not precipitously drop off in this case, indicating that the addition of NaI resulted in fluorescence quenching.

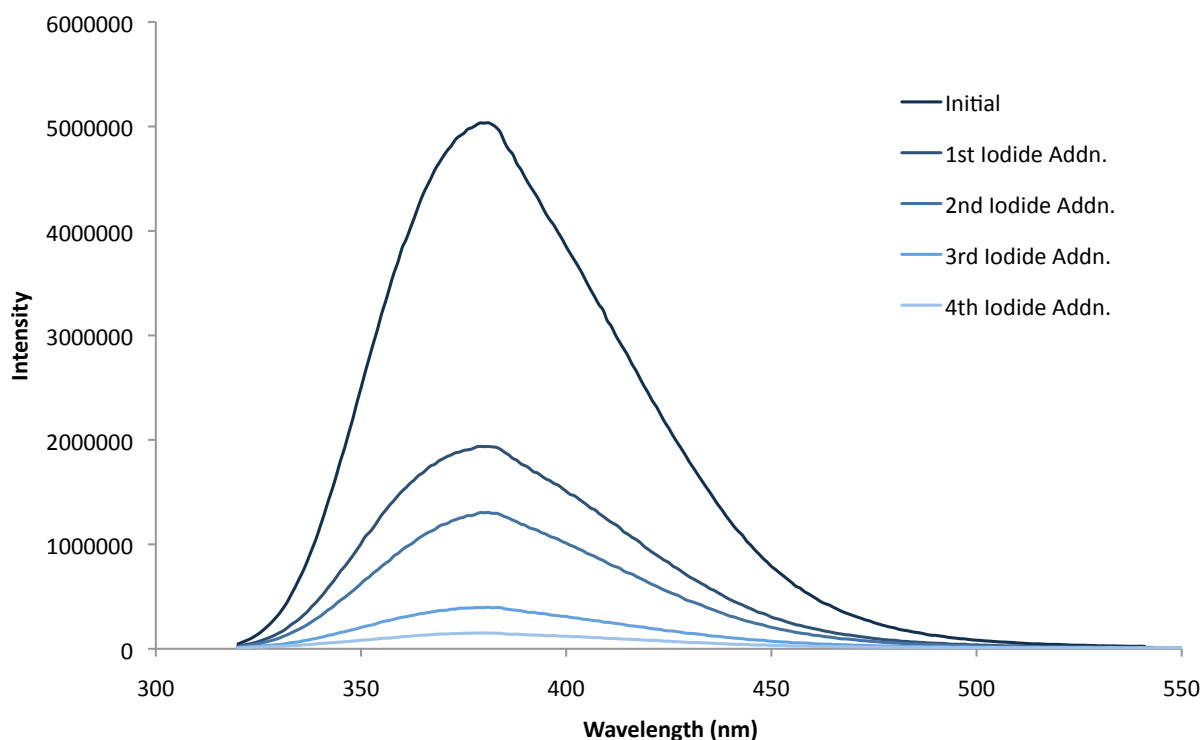


Figure S3. Emission spectra of **3b** in MeCN upon addition of NaI.