

**Supporting Information for:**

**Efficient Bimolecular Mechanism of Photochemical Hydrogen  
Production Using Halogenated Boron-Dipyrromethene (Bodipy) Dyes  
and a Bis(dimethylglyoxime) Cobalt(III) Complex**

Randy P. Sabatini, Brian Lindley, Theresa M. McCormick, Theodore Lazarides, William W. Brennessel,  
David W. McCamant\* and Richard Eisenberg\*

Department of Chemistry, University of Rochester, Rochester, NY 14627

\* Corresponding Authors: [mccamant@chem.rochester.edu](mailto:mccamant@chem.rochester.edu), [eisenberg@chem.rochester.edu](mailto:eisenberg@chem.rochester.edu)

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**Synthesis of 4,4-Difluoro-1,3,5,7-tetramethyl-8-phenyl-4-bora-3a,4a-diaza-s-indacene (2a).**

Benzaldehyde (0.63 mL, 6.17 mmol) and 2,4-dimethylpyrrole (1.28 mL, 12.4 mmol) were dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (200 mL). Trifluoroacetic acid (2 drops) was added and the reaction mixture was stirred at room temperature under a N<sub>2</sub> atmosphere overnight. When TLC monitoring showed complete disappearance of the benzaldehyde, a solution of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone ( $6.35 \times 10^{-2}$  M, 100 mL) in dry CH<sub>2</sub>Cl<sub>2</sub> was added to the reaction mixture and stirred for 40 min. The reaction mixture was washed with H<sub>2</sub>O (2 × 100 mL). The combined aqueous layers were then extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 100 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated to yield a dark purple solid. The product was purified by column chromatography over silica gel (5% MeOH in CH<sub>2</sub>Cl<sub>2</sub>) and then dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (150 mL). Triethylamine (2.0 mL, 14.4 mmol) was added to the reaction mixture and stirred for 10 min. Boron trifluoride-diethyl etherate (2.0 mL, 7.9 mmol) was added to the reaction mixture and stirred overnight. The reaction mixture was washed with H<sub>2</sub>O (2 × 150 mL) followed by 0.1 M KOH<sub>(aq)</sub> (2 × 150 mL). Each aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (100 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated. The product was purified by column chromatography over silica gel (CH<sub>2</sub>Cl<sub>2</sub>) to afford an orange solid (0.146 g, 7% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 1.36 (s, 6H); 2.55 (s, 6H); 5.97 (s, 2H); 7.25-7.27 (m, 2H); 7.4-7.5 (m, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz): δ 14.3, 14.6, 121.2, 127.9, 128.8, 129.2, 131.4, 135.0, 141.7, 143.2, 155.4. Anal. Calcd for C<sub>19</sub>H<sub>19</sub>BF<sub>2</sub>N<sub>2</sub>: C, 70.40; H, 5.91; N, 8.64. Found: C, 70.17; H, 5.93; N, 8.60.

**Synthesis of 4,4-Difluoro-1,3,5,7-tetramethyl-8-mesityl-4-bora-3a,4a-diaza-s-indacene (3a).**

Mesitaldehyde (0.80 mL, 5.37 mmol) and 2,4-dimethylpyrrole (1.15 mL, 13.1 mmol) were dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (200 mL). Trifluoroacetic acid (3 drops) was added and the reaction mixture was stirred at room temperature under a N<sub>2</sub> atmosphere overnight. When TLC monitoring showed complete disappearance of the mesitaldehyde, a solution of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone ( $5.52 \times 10^{-2}$  M, 100 mL) in dry CH<sub>2</sub>Cl<sub>2</sub> was added to the reaction mixture and stirred for 30 min. The reaction mixture was washed with H<sub>2</sub>O (2 × 100 mL). The combined aqueous layers were then extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 100 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated to yield a dark purple solid. The product was purified by column chromatography over silica gel (5% MeOH in CH<sub>2</sub>Cl<sub>2</sub>) and was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (150 mL). Triethylamine (4.0 mL, 28.8 mmol) was added to the reaction mixture and stirred for 10 min. Boron trifluoride-diethyl etherate (3.5 mL, 27.5 mmol) was added to the reaction mixture and stirred overnight. The reaction mixture was washed with H<sub>2</sub>O (2 × 150 mL) then with 0.1 M KOH<sub>(aq)</sub> (2 × 150 mL). Each aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (75 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated. The product was purified by column chromatography

over silica gel (CH<sub>2</sub>Cl<sub>2</sub>) to afford an orange solid (0.644 g, 23 % yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 1.37 (s, 6H); 2.08 (s, 6H); 2.32 (s, 3H); 2.55 (s, 6H); 5.95 (s, 2H); 6.93 (s, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz): δ 13.3, 13.5, 14.6, 19.5, 120.7, 128.9, 129.0, 130.6, 131.1, 134.9, 138.5, 141.7, 142.3, 155.1. Anal Calcd for C<sub>22</sub>H<sub>25</sub>BF<sub>2</sub>N<sub>2</sub>: C, 72.15; H, 6.88; N, 7.65. Found: C, 71.60; H, 7.15; N, 7.46.

**Synthesis of 4,4-Difluoro-2,6-dibromo-1,3,5,7-tetramethyl-8-phenyl-4-bora-3a,4a-diaza-s-indacene (2b).** Compound **2a** (0.047 g, 0.145 mmol), N-bromosuccinimide (0.149 g, 0.84 g), and azobisisobutyronitrile (0.137 g, 0.835 mmol) were dissolved in benzene (8 mL) and purged with N<sub>2</sub> while stirring for 30 min. The solution was heated to reflux for 40 min while stirring and then left to dry overnight. The product was purified by column chromatography over silica gel (5:1 CH<sub>2</sub>Cl<sub>2</sub>:hexanes) to afford a red solid (0.051 g, 73 % yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 1.36 (s, 6H); 2.60 (s, 6H); 7.24-7.26 (m, 2H); 7.50-7.52 (m, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz): δ 13.6, 13.8, 111.8, 127.7, 129.6, 130.4, 134.4, 140.7, 142.1, 153.9. Anal. Calcd for C<sub>19</sub>H<sub>17</sub>BF<sub>2</sub>Br<sub>2</sub>N<sub>2</sub>: C, 47.35; H, 3.56; N, 5.81. Found: C, 46.82; H, 3.29; N, 5.72.

**Synthesis of 4,4-Difluoro-2,6-diiodo-1,3,5,7-tetramethyl-8-phenyl-4-bora-3a,4a-diaza-s-indacene (2c).** Compound **2a** (0.08 g, 0.247 mmol) and iodine (0.156 g, 0.615 mmol) were dissolved in ethanol (10 mL). In a separate flask, iodic acid (0.086 g, 0.489 mmol) was dissolved in a minimal amount of H<sub>2</sub>O (1.5 mL). Both solutions were purged with N<sub>2</sub> while stirring for 30 min. The iodic acid solution was added dropwise to the reaction flask, which was heated at 60° C for 20 min. The solvent/I<sub>2</sub> mixture was evaporated on a vacuum line to yield a red solid. The solid was purified by column chromatography over silica gel (4:1 CH<sub>2</sub>Cl<sub>2</sub>:hexanes) to afford red crystals (0.075 g, 53 % yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 1.37 (s, 6H); 2.64 (s, 6H); 7.22-7.25 (m, 2H); 7.50-7.52 (m, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz): δ 16.1, 16.9, 85.7, 127.8, 129.4, 129.6, 131.3, 134.7, 141.37, 145.4, 156.8. Anal. Calcd for C<sub>19</sub>H<sub>17</sub>BF<sub>2</sub>I<sub>2</sub>N<sub>2</sub>: C, 39.62; H, 2.97; N, 4.86. Found: C, 39.19; H, 2.82; N, 4.77.

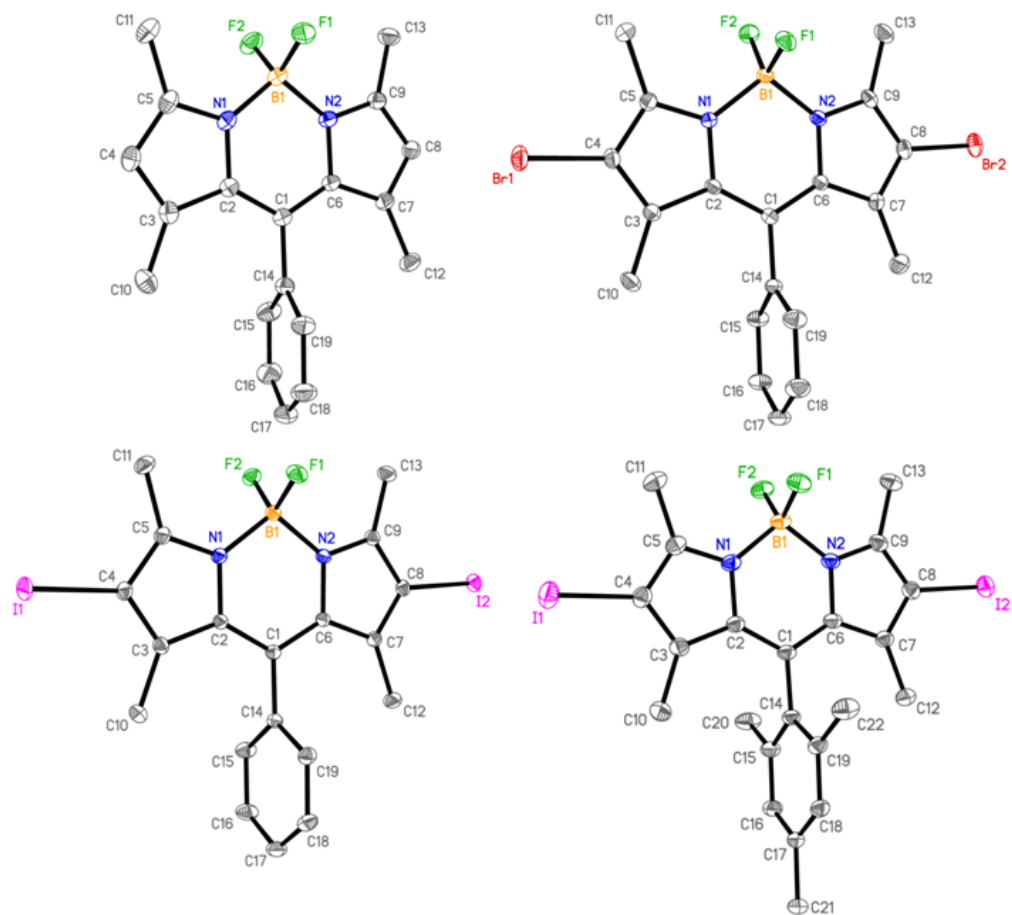
**Synthesis of 4,4-Difluoro-2,6-dibromo-1,3,5,7-tetramethyl-8-mesityl-4-bora-3a,4a-diaza-s-indacene (3b).** Compound **3a** (0.15 g, 0.41 mmol), N-bromosuccinimide (0.149 g, 0.84 g), and azobisisobutyronitrile (0.137 g, 0.835 mmol) were dissolved in benzene (8 mL) and purged with N<sub>2</sub> while stirring for 30 min. The solution was heated to reflux for 40 min while stirring and then left to dry overnight. The product was purified by column chromatography over silica gel (5:1 CH<sub>2</sub>Cl<sub>2</sub>:hexanes) to afford a red solid (0.140 g, 65 % yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 1.37 (s, 6H); 2.06 (s, 6H); 2.35 (s, 3H); 2.60 (s, 6H); 6.97 (s, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz): δ 12.5, 12.7, 13.7, 19.5, 111.4, 129.2, 129.6,

130.5, 134.8, 139.3, 139.8, 142.4, 153.6. Anal. Calcd for  $C_{22}H_{23}BF_2Br_2N_2$ : C, 50.42; H, 4.42; N, 5.35. Found: C, 50.19; H, 4.41; N, 5.22.

**Synthesis of 4,4-Difluoro-2,6-diiodo-1,3,5,7-tetramethyl-8-mesityl-4-bora-3a,4a-diaza-s-indacene (3c).**

Compound **3a** (0.15 g, 0.41 mmol) and iodine (0.26 g, 1.025 mmol) were dissolved in ethanol. In a separate flask, iodic acid (0.144 g, 0.82 mmol) was dissolved in a minimal amount of  $H_2O$  (1.5 mL). Both solutions were purged with  $N_2$  while stirring for 30 min. The iodic acid solution was added dropwise to the reaction flask, which was heated at  $60^\circ C$  for 20 min. The solvent/ $I_2$  mixture was evaporated on a vacuum line to yield a red solid. The solid was purified by column chromatography over silica gel (4:1  $CH_2Cl_2$ :hexanes) to afford red crystals (0.146 g, 58 % yield).  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  1.39 (s, 6H); 2.05 (s, 6H); 2.35 (s, 3H); 2.64 (s, 6H); 6.96 (s, 2H).  $^{13}C$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  15.7, 16.0, 19.5, 21.3, 85.3, 129.3, 130.5, 130.8, 134.8, 139.3, 141.7, 144.6, 156.4. Anal. Calcd for  $C_{22}H_{23}BF_2I_2N_2$ : C, 42.75; H, 3.75; N, 4.53. Found: C, 42.47; H, 3.63; N, 4.41.

**X-ray crystallography:** Technical details of the experiments are shown below along with atom-atom distances and angles. The angles between the pendant phenyl rings and the fused ring portions are 80.36(3), 89.14(5), 81.47(3), and 85.63(5) degrees, respectively, for structures **2a**, **2b**, **2c**, and **3c**. There are halogen-halogen close contacts in two of four structures. In **2b** the Br...F intermolecular distance of 2.951(1) Å is 0.37 Å shorter than the sum of the van der Waals radii and in **2c** the I...F distance of 3.2464(8) Å is 0.20 Å shorter than the sum of the van der Waals radii. Despite having both fluorine and iodine, there are no halogen-halogen close contacts in **3c**.



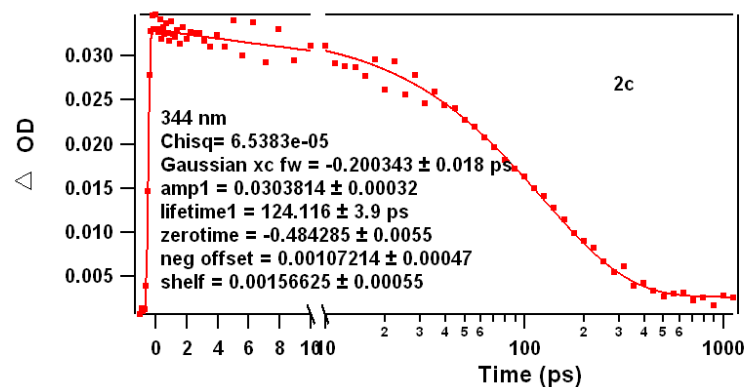
**Figure S1.** X-ray crystal structure of **2a-c** and **3c**. Thermal displacement ellipsoids are drawn at the 50% probability level. All hydrogens have been omitted for clarity.

**Table S1.** Summary of unit cell, space group, data collection and structure refinement parameters for 1a, 1b, 1c and 2c

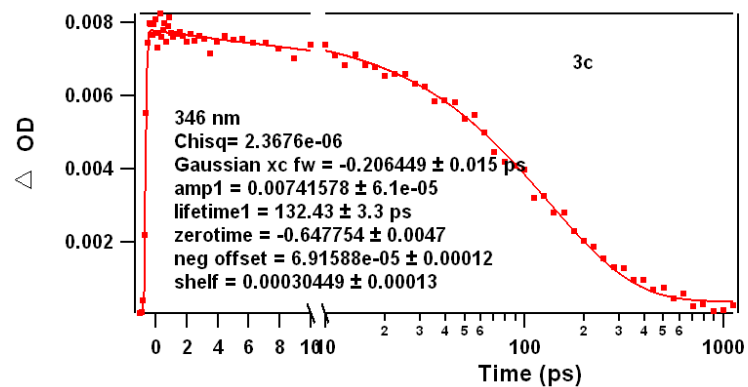
Compound	<b>2a</b>	<b>2b</b>	<b>2c</b>	<b>3c</b>
Empirical formula	C <sub>19</sub> H <sub>19</sub> BF <sub>2</sub> N <sub>2</sub>	C <sub>19</sub> H <sub>17</sub> BBr <sub>2</sub> F <sub>2</sub> N <sub>2</sub>	C <sub>19</sub> H <sub>17</sub> BF <sub>2</sub> I <sub>2</sub> N <sub>2</sub>	C <sub>22</sub> H <sub>23</sub> BF <sub>2</sub> I <sub>2</sub> N <sub>2</sub>
Formula weight	324.17	481.98	575.96	618.03
Temperature (K)	100.0(1)	100.0(1)	100.0(1)	100.0(1)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>Pbca</i>	<i>P2<sub>1</sub>/n</i>	<i>P2<sub>1</sub>/c</i>	<i>C2/c</i>
<i>a</i> (Å)	12.7692(16)	11.3510(15)	15.0745(13)	20.561(2)
<i>b</i> (Å)	12.5068(15)	12.7404(16)	7.5342(6)	10.4502(10)
<i>c</i> (Å)	20.213(3)	12.8357(16)	17.0536(15)	21.699(2)
$\alpha$ (°)	90	90	90	90
$\beta$ (°)	90	93.362(2)	91.451(2)	108.168(2)
$\gamma$ (°)	90	90	90	90
Unit cell volume (Å <sup>3</sup> )	3228.0(7)	1853.1(4)	1936.2(3)	4429.9(7)
Z	8	4	4	8
$\mu$ (mm <sup>-1</sup> )	0.094	4.399	3.272	2.867
Reflections collected	60046	66069	69217	79757
Independent reflections	8623 [ <i>R</i> (int) = 0.0591]	9817 [ <i>R</i> (int) = 0.0652]	10346 [ <i>R</i> (int) = 0.0318]	11850 [ <i>R</i> (int) = 0.0415]
Final R indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> 1 = 0.0510, <i>wR</i> 2 = 0.1286	<i>R</i> 1 = 0.0381, <i>wR</i> 2 = 0.0812	<i>R</i> 1 = 0.0206, <i>wR</i> 2 = 0.0485	<i>R</i> 1 = 0.0296, <i>wR</i> 2 = 0.0685
R indices (all data)	<i>R</i> 1 = 0.0831, <i>wR</i> 2 = 0.1487	<i>R</i> 1 = 0.0700, <i>wR</i> 2 = 0.0910	<i>R</i> 1 = 0.0244, <i>wR</i> 2 = 0.0500	<i>R</i> 1 = 0.0438, <i>wR</i> 2 = 0.0742

**Table S2.** Selected bond lengths (Å), angles (°) and torsions (°) for **2a-c** and **3c**. The labels are shown in Figure S1

<b>2a</b>		<b>2b</b>		<b>2c</b>		<b>3c</b>	
C4-H4	0.9500	Br2-C4	1.867(2)	I1-C4	2.072(1)	I1-C4	2.073(2)
C8-H8	0.9500	Br1-C8	1.870(2)	I2-C8	2.074(1)	I2-C8	2.072(2)
N1-C5	1.347(1)	N2-C5	1.339(2)	N1-C5	1.345(1)	N1-C5	1.337(2)
N2-C9	1.350(1)	N1-C9	1.344(2)	N2-C9	1.348(1)	N2-C9	1.342(2)
B1-N1	1.549(1)	B1-N1	1.547(2)	N1-B1	1.548(2)	B1-N1	1.550(2)
B1-N2	1.547(1)	B1-N2	1.542(2)	N2-B1	1.545(2)	B1-N2	1.547(2)
C1-C14	1.487(1)	C1-C14	1.490(2)	C1-C14	1.486(1)	C1-C14	1.495(2)
N2-B1-N1	106.67(7)	N2-B1-N1	107.0(1)	N2-B1-N1	106.88(9)	N2-B1-N1	106.57(1)
C2-C1-C6	121.02(8)	C2-C1-C6	121.5(1)	C6-C1-C2	121.41(9)	C2-C1-C6	120.8(1)
C6-C1-C14	119.53(7)	C6-C1-C14	118.7(1)	C6-C1-C14	119.44(9)	C6-C1-C14	119.6(1)
C2-C1-C14	119.45(8)	C2-C1-C14	119.8(1)	C2-C1-C14	119.13(9)	C2-C1-C14	119.6(1)
C5-C4-H4	125.8	C5-C4-Br2	124.4(1)	C5-C4-I1	124.44(8)	C5-C4-I1	123.4(1)
C9-C8-H8	125.7	C9-C8-Br1	123.6(1)	C9-C8-I2	123.46(8)	C9-C8-I2	124.7(1)
N2-B1-N1-C5	-176.31(8)	N1-B1-N2-C5	-171.9(1)	C5-N1-B1-N2	-179.6(1)	N2-B1-N1-C5	-174.4(1)
		Br1-C8-C9-N1	179.7(1)	I2-C8-C9-N2	178.00(8)	I2-C8-C9-N2	-179.7(1)
		Br2-C4-C5-N2	179.3(1)	I1-C4-C5-N1	-179.43(8)	I1-C4-C5-N1	-179.0(1)
C6-C1-C2-C3	176.32(9)	C6-C1-C2-C3	-174.6(2)	C6-C1-C2-C3	179.3(1)	C6-C1-C2-C3	175.5(2)
C2-C1-C6-C7	179.76(9)	C2-C1-C6-C7	177.5(2)	C2-C1-C6-C7	-174.0(1)	C2-C1-C6-C7	-177.5(2)
C2-C1-C14-C15	97.1(1)	C2-C1-C14-C15	90.3(2)	C2-C1-C14-C15	81.0(1)	C2-C1-C14-C15	85.9(2)
C2-C1-C14-C19	-82.2(1)	C2-C1-C14-C19	-90.0(2)	C2-C1-C14-C19	-97.9(1)	C2-C1-C14-C19	-93.3(2)



**Figure S2.** Transient absorption results of **2c**, showing the kinetic trace of the 344-nm excited state absorption of **2c** in acetonitrile following excitation by a 530-nm laser pulse.



**Figure S3.** Transient absorption results of **3c**, showing the kinetic trace of 344-nm excited state absorption of **3c** in acetonitrile following excitation by a 530-nm laser pulse.