A benzofuran[b]-fused BODIPY as an efficient sensitizer for photocatalytic hydrogen production

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Table of contents
Synthesis of 1 and 2 ............................................................... S2 – S4
Fig. S1. Cyclic voltammogram of ascorbic acid in several pH containing phosphate buffer solution .............. S5
Table S1. Theoretical data for compound 1. (Calculated by B3LYP/6-31G(d,p) level using Gaussian 16W)....... S5
Fig. S2. Normalized absorption (blue solid line) and fluorescence (dashed line) spectra of 1 and 2. ............... S5
Fig. S3. HAADF-STEM images of Pt/P25. ............................................................................................................. S6
Fig. S4. UV-vis absorption spectrum of electrolyte after 30 h photocatalysis using P25/Pt/ 1. ......................... S6
Fig. S5. Photographs of P25/Pt/1 before (left) and after (right) 30 h-photoirradiation. ............................. S6
Fig. S6. Photographs of P25/Pt/2 before (left) and after (right) 10 h-photoirradiation. ................................. S7
Fig. S7. Cycling test of H₂ evaluation for Pt/P25/1 in the presence of ascorbic acid in phosphate buffer (pH 7.0) under 100 mW cm⁻² light irradiation (λ > 400 nm) . ................................................................. S7
Fig. S8. Liner sweep voltammetry of FTO/P25/1 and FTO/P25/2 with and without photoirradiation. ........... S7
Table S2. Photoluminescence decay profiles of 1 in the presence and absence of ascorbic acid in MeOH. ...... S7
Fig. S9. ¹H NMR spectrum of 5 ....................................................................................................................... S8
Fig. S10. ¹H NMR spectrum of 6 .................................................................................................................... S9
Fig. S11. ¹H NMR spectrum of 7 ................................................................................................................... S10
Fig. S12. ¹H NMR spectrum of 9 .................................................................................................................. S11
Fig. S13. ¹H NMR spectrum of 11 ............................................................................................................... S12
Fig. S14. ¹H NMR spectrum of 1 .............................................................................................................. S13
Fig. S15. ¹H NMR spectrum of 2 .............................................................................................................. S14
Fig. S16. ¹³C NMR spectrum of 5 ................................................................................................................ S15
Fig. S17. ¹³C NMR spectrum of 6 ................................................................................................................ S16
Fig. S18. ¹³C NMR spectrum of 7 ............................................................................................................. S17
Fig. S19. ¹³C NMR spectrum of 9 ............................................................................................................. S18
Fig. S20. ¹³C NMR spectrum of 11 ......................................................................................................... S19
Fig. S21. ¹³C NMR spectrum of 1 .......................................................................................................... S20
Fig. S22. ¹³C NMR spectrum of 2 .......................................................................................................... S21
Fig. S23. High resolution of APCI mass spectrum of 5 ................................................................................. S22
Fig. S24. High resolution of APCI mass spectrum of 6 ........................................................................... S23
Fig. S25. High resolution of APCI mass spectrum of 7 ......................................................................... S24
Fig. S26. High resolution of APCI mass spectrum of 9 ......................................................................... S25
Fig. S27. High resolution of APCI mass spectrum of 11 ....................................................................... S26
Fig. S28. High resolution of APCI mass spectrum of 1 ....................................................................... S27
Fig. S29. High resolution of APCI mass spectrum of 2 ....................................................................... S28
Synthesis of 1 and 2

Ethyl 3-(4-bromophenyl)-5-phenyl-1H-pyrrole-2-carboxylate (5): To a solution of 3 (17.7 g, 61.6 mmol) in EtOH (300 mL) was added ethyl nitroacetate 4 (6.8 mL, 61.6 mmol) and Et3N (0.85 mL, 6.16 mmol). The resultant mixture was refluxed overnight. After the reaction, it was extracted EtOAc and water. The organic layer was dried with Na2SO4 and was evaporated. The residue was chromatographed on silica gel (Wakogel C-300) using benzene and hexane (3:1 v/v) to give 25.4 g of Michael adduct (FAB-MS: m/z = 420 [M+H]+, 422[M+2+H]+) quantitatively, being then dissolved in dry EtOH (180 mL). To the solution was added formamidine sulfinic acid (22.9 g, 212 mmol). The resultant mixture was refluxed overnight. Atter the reaction, resultant solid was filtered off and washed with water. In this way, 5.2 g of 5 was obtained in 23% yield.

1H NMR (500 MHz, CDCl3): δ (ppm), 1.28 (3H, t, J = 7.08 Hz), 4.29 (2H, q, J = 7.11 Hz), 6.59 (1H, d, J = 3.10 Hz), 7.34 (1H, tt, J = 7.42, 1.38 Hz), 7.44 (2H, tt, J = 7.72, 1.60 Hz), 7.48 (2H, dt, J = 8.70, 2.04 Hz), 7.51 (2H, dt, J = 8.65, 2.02 Hz), 7.57–7.60 (2H, m), 9.30 (1H, s); 13C NMR (126 MHz, CDCl3) δ (ppm) ; 160.9, 135.5, 134.0, 132.2, 131.2, 130.9, 130.8, 129.2, 129.2, 128.8, 121.2, 118.6, 109.7, 60.5, 14.3. HRMS (APCI): calcd for C19H16BrNO2, 370.0437, 344.0418, found 370.0431 [M + H]+, 372.0412 [M+H+2]+.

3-(4-Bromophenyl)-5-phenyl-1H-pyrrole-2-carboxylic acid (6): To a solution of 5 (5.18 g, 14.0 mmol) in EtOH (370 mL) was added 2M NaOH aqueous solution (95 mL). The resultant solution was refluxed for 2 h. After the reaction, adding 35% HCl aqueous solution caused solidification that was filtered off and washed with water. 3.2 g of 6 was obtained in 68% yield.

1H NMR (500 MHz, DMSO-d6): δ (ppm), 6.76 (1H, d, J = 2.70 Hz), 7.28 (1H, tt, J = 7.40, 1.34 Hz), 7.39 (2H, tt, J = 7.72, 1.53 Hz), 7.52 (2H, dt, J = 8.85, 2.00 Hz), 7.55 (2H, dt, J = 8.75, 1.98 Hz), 7.80–7.90 (2H, m), 11.9 (1H, s), 12.5 (1H, s). 13C NMR (126 MHz, DMSO-d6) δ (ppm), 161.8, 135.3, 134.7, 131.4, 131.0, 130.6, 130.4, 128.6, 127.3, 125.3, 119.8, 119.3, 109.6. HRMS (APCI): calcd. for C17H12BrNO2, 342.0124, 344.0104. found 342.0117 [M + H]+, 344.0095 [M+H+2]+.

3-(4-Bromophenyl)-5-phenyl-1H-pyrrole-2-carbaldehyde (7): Compound 6 (7.5 g, 21.9 mmol) was dissolved in CF3COOH (180 mL) under N2 atmosphere and resultant solution was stirred at 50 °C for 30 min. After adding trimethyl orthoformate (40 mL, 766 mmol) into the solution, the mixture was stirred at 50 °C over night. And then the reaction solution was neutralized with NaHCO3 aqueous solution and extracted with dichloromethane. The organic phase was dried with Na2SO4 and evaporated. The residue was chromatographed on silica gel (Wakogel C-300) using dichloromethane as eluent to give 4.17 g of 7 in 57% yield.

1H NMR (500 MHz, CDCl3): δ (ppm) 6.70 (1H, d, J = 2.80 Hz), 7.38–7.43 (3H, m), 7.47 (2H, tt, J = 7.58, 1.62 Hz), 7.60 (2H, dt, J = 8.40, 2.19Hz), 7.62–7.64 (2H, m), 9.50 (1H, br), 9.61 (1H, s). 13C NMR (126 MHz, CDCl3) δ (ppm) 178.9, 139.0, 136.8, 132.4, 132.0, 130.6, 130.6, 130.2, 129.3, 129.1, 129.0, 125.3, 122.3, 108.9. HRMS (APCI): calcd. for C17H12BrNO, 326.0175, 328.0155. found 326.0169 [M + H]+, 328.0152 [M+H+2]+.

Difluoroboron chlated 2-(Z)-(3-(4-bromophenyl)-5-phenyl-1H-pyrrole-2-yl)methylele)-1H-benzofuro[3,2-b]pyrrole (9): After a solution of 1H-benzofuro[3,2-b]pyrrole-2-carboxylic acid 8 (1.10 g, 5.47 mmol) was stirred at 50 °C for 40 min, 7 (1.80 g, 5.52 mmol) and POCl3 (30 mL, 329 mmol) was added to the solution and resultant
mixture was stirred for 3 h. After quenching the reaction by adding saturated NaHCO₃ aqueous solution, the resultant solution was partitioned between water and dichloromethane. The organic phase was dried with Na₂SO₄ aqueous solution and was evaporated to give solid that was then dissolved in dry dichloromethane (240 mL). To the solution were added Et₃N (8.2 mL, 59 mmol) and BF₃·Et₂O (11 mL, 88 mmol) under N₂ atmosphere. The mixture was stirred for 6 h. After quenching the reaction by adding saturated NaHCO₃ aqueous solution, the resultant solution was extracted with dichloromethane and water. The organic phase was dried with Na₂SO₄ aqueous solution and then evaporated. The residue was washed with water and chromatographed on silica gel (Wakogel C-300) using dichloromethane and hexane (2:3 v/v) as eluent to give 1.20 g of 9 in 42% yield.

$$\text{1H NMR (500 MHz, CDCl}_3\): } \delta (\text{ppm}) 6.62 (1H, s), 6.73 (1H, s), 7.29–7.32 (2H, m), 7.41–7.44 (3H, m), 7.47 (1H, ddd, J = 7.75, 7.12, 1.32 Hz), 7.50–7.55 (3H, m), 7.65 (2H, dt, J = 9.05, 2.18 Hz), 8.01–8.04 (2H, m), 8.08 (1H, d, J = 7.55 Hz, Ha).$$

$$\text{13C NMR (126 MHz, CDCl}_3\): } \delta (\text{ppm}) 164.8, 158.3, 132.3, 132.2, 132.1, 130.7, 130.4, 130.4, 130.0, 129.5, 128.4, 128.2, 124.3, 124.2, 123.3, 116.8, 112.8, 103.6. \text{HRMS (APCI): calcd for C}_{27}\text{H}_{16}\text{BBrF}_2\text{N}_2\text{O}, 512.0506, 514.0484. \text{found 512.0531 [M]+, 514.0525 [M+2]+.}$$

Difluoroboron chlated 2-(Z)-(3-(4-formylphenyl)-5-phenyl-1H-pyrrol-2-yl)methylene)-1H-benzofuro[3,2-b]pyrrole (11): To a solution of 9 (1.2 g, 2.3 mmol) and 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-hexylthiophene-5-carbaldehyde 10 (1.9 g, 5.8 mmol) in dry THF (80 mL) were added 2.0 M K₂CO₃ aqueous solution (23 mL). The resultant solution was degassed by three freeze–pump–thaw cycles, then Pd(PPh₃)₄ (0.78 g, 0.67 mmol) was added to it. The mixture was refluxed overnight and then cooled to room temperature. After removing Pd, it was extracted with CH₂Cl₂ and water. The organic phase was dried with Na₂SO₄ and then evaporated. The residue was washed with CH₂Cl₂ and water. The organic phase was dried with Na₂SO₄ and then evaporated. The residue was chromatographed on silica gel (Wakogel C-300) using benzene and hexane (4:1 v/v) as eluent to give 0.68 g of 11 in 47% yield.

$$\text{1H NMR (500 MHz, CDCl}_3\): } \delta (\text{ppm}) 0.88 (3H, t, J = 6.92 Hz), 1.24–1.31 (3H, m), 1.68 (2H, quint, J = 7.66 Hz), 2.75 (2H, t, J = 7.85 Hz), 6.64 (1H, s), 6.79 (1H, s), 7.31 (1H, ddd, J = 7.42, 6.95, 1.05 Hz), 7.42 (1H, s), 7.43 (1H, d, J = 8.00 Hz), 7.47 (1H, ddd, J = 7.75, 7.12, 1.30 Hz), 7.52–7.57 (3H, m), 7.61 (2H, dd, J = 6.38, 2.10 Hz), 7.65 (2H, dd, J = 8.35 Hz), 7.70 (1H, s), 8.04–8.06 (2H, m), 8.09 (1H, d, J = 7.65 Hz), 9.90 (1H, s). \text{13C NMR (126 MHz, CDCl}_3\): } \delta (\text{ppm}) 182.9, 165.1, 147.5, 144.5, 143.5, 141.7, 140.8, 138.6, 137.5, 137.4, 134.1, 133.7, 132.2, 130.7, 130.0, 129.8, 129.5, 129.5, 129.3, 128.5, 124.3, 124.2, 118.6, 116.8, 112.8, 103.6, 30.8, 30.5, 29.1, 28.9, 28.9, 28.7, 22.6, 22.5, 14.1, 14.0. \text{HRMS (APCI): calcd for C}_{38}\text{H}_{31}\text{BF}_2\text{N}_2\text{O}_2\text{S, 629.2247, found 629.2285 [M+H]+.}$$

Difluoroboron chlated 2-(Z)-(3-(1-(3-hexyl-5-(2-carboxy-2-cyanovinyl)thiophen))-2-yl)-phenyl-4-yl)-5-phenyl-1H-pyrrol-2-yl)methylene)-1H-benzofuro[3,2-b]pyrrole (1): Under N₂ condition, a solution of 10 (1.09 g, 1.74 mmol), 2-cyanoacetic acid (0.355 g, 4.17 mmol) and ammonium acetate (0.383 g, 4.97 mmol) in acetic acid (100 mL) was refluxed for 2 h. After quenching with water, the solution was extracted with CH₂Cl₂. The organic layer was washed with water, dried with Na₂SO₄ and evaporated. The residue was chromatographed on silica gel (Wakogel C-300) using a gradient of AcOH (0–0.5% v/v) in CH₂Cl₂ as an eluent. Obtained solid was reprecipitated with THF/MeOH. In this way, 0.467 g of 1 was obtained with 39% yield.

$$\text{1H NMR (500 MHz, DMSO-}d_6\): } \delta (\text{ppm}) 0.84 (3H, t, J = 6.80 Hz), 1.23–1.33 (6H, m), 1.63 (2H, quint, J = 7.54 Hz), 2.76 (2H, t, J = 7.70 Hz), 7.19 (1H, s), 7.23 (1H, s), 7.45 (1H, t, J = 7.78 Hz), 7.55–7.63 (4H, m), 7.70 (1H, d,
$J = 8.35$ Hz), 7.73 (2H, dd, $J = 6.45$, 1.80 Hz), 7.87–7.89 (2H, m), 8.02 (2H, s), 8.08 (2H, dt, $J = 6.55$, 1.72 Hz), 8.49 (1H, s), 13.8 (1H, s). $^{13}$C NMR (126 MHz, THF-$d_8$) $\delta$ (ppm) 166.0, 163.9, 159.6, 155.4, 147.9, 146.6, 141.6, 141.2, 135.7, 134.9, 134.8, 133.4, 131.3, 130.6, 130.6, 130.6, 130.5, 130.4, 130.4, 130.3, 129.0, 124.9, 124.7, 119.6, 117.9, 116.4, 113.5, 104.6, 100.4, 93.6, 32.6, 31.5, 30.0, 29.3, 23.5, 14.4. HRMS (ESI-MS) : calcld for C$_{41}$H$_{32}$BF$_2$N$_3$O$_3$S, 695.2238, found 695.2244 [M]$^+$; Elemental analysis: Calc. For C$_{41}$H$_{32}$BF$_2$N$_3$O$_3$S · 1.2 H$_2$O: C, 68.66; H, 4.83; N, 5.86, Found: C, 68.64; H, 4.50; N, 5.91

**Difluoroboronic chlatted (E)-2-cyano-3-(Z)-2-(3,5-dimethyl-1H-pyrrol-2-yl)ethylidene)-3,5-dimethyl-2H-pyrrol-4-yl)acrylic acid 2**; Under N$_2$ condition, a solution of 12 (0.931 g, 3.37 mmol), 2-cyanoacetic acid (0.714 g, 8.40 mmol) and ammonium acetate (0.843 g, 10.9 mmol) in acetic acid (180 mL) was refluxed for 2 h. After quenching with water, the solution was separated between CH$_2$Cl$_2$ and 1M HCl aqueous solution. The organic layer was dried with Na$_2$SO$_4$ and evaporated. The residue was washed with CH$_2$Cl$_2$, solved in THF and chromatographed on silica gel (Wakogel C-300) using a gradient of AcOH (0–0.8% v/v) in CH$_2$Cl$_2$ as an eluent. 0.351 g of 2 was obtained with 34% yield after washing with THF.

$^1$H NMR (500 MHz, THF-$d_8$): $\delta$ (ppm) 2.32 (1H, s), 2.42 (1H, s), 2.53 (1H, s), 2.57 (1H, s), 6.27 (1H, s), 7.59 (1H, s), 8.21 (1H, s), 11.9 (1H, s). $^{13}$C NMR (126 MHz, DMSO-$d_6$) $\delta$ (ppm) 163.2, 161.9, 153.2, 148.1, 146.0, 138.7, 135.5, 131.7, 123.3, 122.0, 121.6, 116.4, 104.9, 14.6, 13.9, 11.5, 11.1. HRMS (APCI) : calcld. For C$_{17}$H$_{16}$BF$_2$N$_3$O$_2$, 343.1301, found 343.1298 [M]$^+$. Elemental analysis: calcld. For C$_{17}$H$_{16}$BF$_2$N$_3$O$_2$: C, 59.51; H, 4.70; N, 12.25, Found: C, 59.46; H, 4.83; N, 12.22
**Fig. S1.** Cyclic voltammogram of ascorbic acid in several pH containing phosphate buffer solution as an electrolyte.

**Table S1.** Theoretical data for compound 1. (Calculated by B3LYP/6-31G(d,p) level using Gaussian 16W).

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<th>(\lambda_{\text{calcd.}}/\text{nm} )</th>
<th>Calculated assignment (^a)</th>
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<td>HOMO−5 → LUMO (3.1%)</td>
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\(^a\) Data given in parentheses are \(2 \times (\text{CI coefficient})^2 \times 100\%

**Fig. S2.** Normalized absorption (blue solid line) and fluorescence (dashed line) spectra of 1 (a) and 2 (b) in THF.
**Fig. S3.** High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images of P25/Pt.

**Fig. S4.** UV-vis absorption spectrum of electrolyte (blue solid line) after 30 h photocatalysis using P25/Pt/I and ascorbic acid in phosphate buffer solution (orange dashed line).

**Fig. S5.** Photographs of P25/Pt/I before (left) and after (right) 30 h of photoirradiation.
Fig. S6. Photographs of P25/Pt/2 before (left) and after (right) 10 h of photoirradiation.

Fig. S7. Cycling test of H₂ evaluation for P25/Pt/1 (6.0 mg) in the presence of ascorbic acid in phosphate buffer (pH 7.0) under 100 mW cm⁻² light irradiation (λ > 400 nm).

Fig. S8. Liner sweep voltammetry of FTO/P25/1 and FTO/P25/2 with photoirradiation (a) and under dark conditions (b). Scan rate = 0.05 V s⁻¹.

Table S2. Photoluminescence decay profiles of I in the presence and absence of ascorbic acid in MeOH.

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<th>A₁ / %</th>
<th>τ₂ / ns</th>
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<th>&lt; τ &gt;^a</th>
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^aThe < τ > values of were determined with < τ > = (A₁τ₁^2 + A₂τ₂^2) / (A₁τ₁ + A₂τ₂).
Fig. S9. $^1$H NMR spectrum of 5 (500 MHz) in CDCl$_3$. 
Fig. S10. $^1$H NMR spectrum of 6 (500 MHz) in DMSO-$d_6$. 
Fig. S11. $^1$H NMR spectrum of 7 (500 MHz) in CDCl$_3$. 
Fig. S12. $^1$H NMR spectrum of 9 (500 MHz) in CDCl$_3$. 
Fig. S13. $^1$H NMR spectrum of 11 (500 MHz) in CDCl$_3$. 
Fig. S14. $^1$H NMR spectrum of 1 (500 MHz) in DMSO-$d_6$. 
Fig. S15. $^1$H NMR spectrum of 2 (500 MHz) in THF-$d_8$. 
Fig. S16. $^{13}$C NMR spectrum of 5 (500 MHz) in CDCl$_3$. 
Fig. S17. $^{13}$C NMR spectrum of 6 (500 MHz) in DMSO-$d_6$. 
Fig. S18. $^{13}$C NMR spectrum of 7 (500 MHz) in CDCl$_3$. 
Fig. S19. $^{13}$C NMR spectrum of 9 (500 MHz) in CDCl$_3$. 

$9$
Fig. S20. $^{13}$C NMR spectrum of 11 (500 MHz) in CDCl$_3$. 
Fig. S21. $^{13}$C NMR spectrum of 1 (500 MHz) in THF-$d_8$. 
Fig. S22. $^{13}$C NMR spectrum of 2 (500 MHz) in DMSO-$d_6$. 
Fig. S23. High resolution of APCI mass spectrum (positive mode) of 5.
Fig. S24. High resolution of APCI mass spectrum (positive mode) of 6.
Fig. S25. High resolution of APCI mass spectrum (positive mode) of 7.
Fig. S26. High resolution of APCI mass spectrum (positive mode) of 9.
Fig. S27. High resolution of APCI mass spectrum (positive mode) of 11.
Fig. S28. High resolution of APCI mass spectrum (negative mode) of 1.
Fig. S29. High resolution of APCI mass spectrum (positive mode) of 2.