## Supporting information

# Synthesis and Fluorescence Properties of Novel Squarylium Boron Complexes

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### **Experimental Section**

#### **General information**

NMR spectra were recorded on ECX400P or ECA–600 spectrometers. Chemical shifts are referred to TMS (<sup>1</sup>H and <sup>13</sup>C) as internal standards and CFCl<sub>3</sub> (<sup>19</sup>F) as an external standard. Infrared (IR) spectra were determined on a Simazu IR–Affinity spectrometer. UV–vis spectra were taken on a Hitachi U4100 spectrophotometer. Fluorescence spectra were measured on a FP–8600 spectrofluorometer. Fluorescence quantum yields were recorded on a Quantaurus–QY. Fluorescence lifetimes were measured using a Quantaurus– $\tau$ . Mass spectra were recorded on a JEOL JMS–700 spectrometer. Melting points were measured on a Yanagimoto MP–S2 micro–melting–point apparatus. Analytical Thin-layer chromatography (TLC) was performed on precoated plates (Merck, silica gel 60 F254). Silica gel (Wakogel C–200) was used for column chromatography. X–ray data were taken on a Rigaku XtaLABmini. Cyclic voltammograms (CV) were measured by using a three-electrode system with platinum wire as the working and counter electrodes and AgQRE as the reference electrode. Fc/Fc<sup>+</sup> was used as external reference.

### X-ray crystallography

Single-crystal X-ray diffraction measurements were carried out on a Rigaku Mercury 375R/M CCD (XtaLAB-mini) diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71075$  Å). The crystal structure was solved using direct method with SHELXL-2014/7 and refined by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on  $F^2$  using SHELXL-2014/7. The Cambridge Crystallographic Data Center (CCDC) numbers for **3** is 1536662.

Crystallographic details for **3**: C<sub>20</sub>H<sub>23</sub>BF<sub>2</sub>N<sub>2</sub>O<sub>2</sub>, *M*= 372.21 gmol<sup>-1</sup>; *T*=293(2) K; triclinic space group *P*-1; *a*=9.003(10), *b*=10.762(12), *c*=11.631(12) Å, *α*=73.19(6), *β*=69.99(5), *γ*=72.45(4)°; *V*= 987.6(19) Å<sup>3</sup>; *Z*=2; 4.94<2*θ*<54.74°;  $\rho_{calcd}$ =1.252 gcm<sup>-3</sup>;  $\mu$ =0.093 mm<sup>-1</sup>; *R*<sub>int</sub>=0.0341; *R*<sub>1</sub>=0.0596, *wR*<sub>2</sub>=0.1833 for 4385 reflections with *I*>2*σ*(*I*) and 248 parameters; *S*=1.048.



**1** (500 mg, 1.54 mmol) was dissolved in dry dichloromethane (200 mL). Triethylamine (2.15 mL, 15.4 mmol) and the boron trifluoride diethyl ether complex (1.93 mL, 15.4 mmol) were added to the solution and stirred at room temperature for two days. Saturated brine was then added to the solution. The solution was extracted with dichloromethane and washed with water. The organic layer was dried over MgSO<sub>4</sub>. After concentration of the solvent, the residue was purified *via* chromatography with silica gel (CH<sub>2</sub>Cl<sub>2</sub>,  $R_f$  = 0.5) to afford **3** (304 mg, 53%) as a violet-blue solid. **3**: mp 227.0–228.0°C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 1.08 (t, *J* = 7.6 Hz, 3H), 1.10 (t, *J* = 7.6 Hz, 3H), 2.34 (s, 3H), 2.35 (s, 3H), 2.43 (q, *J* = 7.6 Hz, 2H), 2.47 (q, *J* = 7.6 Hz, 2H), 2.45 (s, 3H), 2.51 (s, 3H), 9.36 (brs, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 10.6, 10.8, 12.4, 13.0, 14.2, 14.7, 17.3, 17.7, 121.1, 127.0, 129.1, 132.7, 134.6, 136.3, 140.6, 148.9, 154.7, 157.0, 173.9, 174.6; <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>) *δ*-137.5 (q, *J* = 30.0 Hz, 2F); IR (KBr) 3367, 2932, 1775, 1682, 1566, 1501, 1439, 1358, 1304, 1157, 1115, 957 cm<sup>-1</sup>; EIMS (*m*/*z*) (rel intensity) 372 (M<sup>+</sup>; 100), 357 (51); Anal. calcd for C<sub>20</sub>H<sub>23</sub>BF<sub>2</sub>N<sub>2</sub>O<sub>2</sub>: C, 64.54; H, 6.23; N, 7.53, found: C, 64.37; H, 6.19; N, 7.21.



**2** (400 mg, 1.49 mmol) was dissolved in dry dichloromethane (200 mL). Triethylamine (2.08 mL, 14.9 mmol) and boron trifluoride diethyl ether complex (1.87 mL, 14.9 mmol) was added to the solution and stirred at room temperature for 2 days. Then water was added to the solution. The solution was extracted with dichloromethane and washed with water. The organic layer was dried over MgSO<sub>4</sub>. After concentration of solvent, the residue was purified *via* chromatography with

silica gel (CH<sub>2</sub>Cl<sub>2</sub>,  $R_f = 0.4$ ) to afford 4 (201 mg, 43%) as a violet-blue solid.

4: mp 161.0–163.0°C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 2.40 (s, 3H), 2.43 (s, 3H), 2.52 (s, 3H), 2.55 (s, 3H), 6.10 (s, 1H), 6.34 (s, 1H), 9.45 (brs, 1H); <sup>13</sup>C NMR (100 MHz, pyridine-*d*<sub>5</sub>) δ 12.2, 13.3, 13.8, 14.8, 117.0, 117.3, 119.7, 122.5, 138.6, 138.9, 147.1, 154.3, 156.8, 158.4, 171.4, 175.9; IR (KBr) 3360, 2939, 1775, 1682, 1562, 1508, 1454, 1354, 1296, 1169, 1141, 1119, 964 cm<sup>-1</sup>; EIMS (*m/z*) (rel intensity) 316 (M<sup>+</sup>; 100), 315 (30); Anal. calcd for C<sub>16</sub>H<sub>15</sub>BF<sub>2</sub>N<sub>2</sub>O<sub>2</sub>: C, 60.79; H, 4.78; N, 8.86. found: C, 60.55; H, 4.79; N, 8.89.



Scheme S1. Synthesis of bis(pyrrol-2-yl)squaraine dyes.



Scheme S2. Reaction of 3 with LiHMDS.



Figure S1. Comparison of resonance structure of squarylium boron complex 3 with those of squarylium dye 1.



Figure S2. Molecular orbital energy diagram and isodensity surface plots of 1–4.

**Figure S4**. UV-vis absorption spectra of **3** in various solvents  $(2.0 \times 10^{-6} \text{ M})$ .

Figure S5. Normalized fluorescence spectra of 1 in various solvents ( $2.0 \times 10^{-6}$  M).

Figure S6. Normalized fluorescence spectra of **3** in various solvents  $(2.0 \times 10^{-6} \text{ M})$ .

$\begin{array}{c} Me \\ H \\ Et \\ He \\ Me \\ \end{array} \begin{array}{c} Me \\ He \\ He \\ He \\ \end{array} \begin{array}{c} Me \\ He \\$			
solvent	$\lambda_{\max}\left(\varepsilon\right)/\operatorname{nm}$	F <sub>max</sub> / nm	$\phi_{\mathrm{f}}{}^b$
Hexane	563 (205,000)	574	0.49
Toluene	564 (200,000)	583	0.06
CHCl <sub>3</sub>	564 (191,000)	578	0.07
THF	569 (196,000)	582	0.02
CH <sub>2</sub> Cl <sub>2</sub>	565 (198,000)	578	0.03
МеОН	559 (205,000)	574	< 0.01
MeCN	562 (205,000)	576	< 0.01

Table S1. Absorption and fluorescence properties of 1 in various solvents<sup>a</sup>

<sup>a</sup>Measured at a concentration of 2.0 x 10<sup>-6</sup> mol dm<sup>-3</sup>. <sup>b</sup> Measured using an integrating sphere method.

Et Мe Ňе 3  $F_{\rm max}$  / nm  $\phi_{\rm f}{}^b$ solvent  $\lambda_{\max}\left(\varepsilon\right)/\operatorname{nm}$ Hexane 0.92 542 (208,000) 551 Toluene 567 0.11 554 (194,000) CHCl<sub>3</sub> 552 (195,000) 0.12 564 554 (206,000) THF 0.02 567  $CH_2Cl_2$ 551 (197,000) 0.05 564 MeOH 551 (202,000) < 0.01 574 MeCN < 0.01 548 (193,000) 562

Table S2. Absorption and fluorescence properties of 3 in various solvents<sup>*a*</sup>

Me

Et

<sup>a</sup>Measured at a concentration of 2.0 x 10<sup>-6</sup> mol dm<sup>-3</sup>. <sup>b</sup> Measured using an integrating sphere method.



Figure S7. <sup>1</sup>H NMR spectra of 3.



Figure S8. <sup>13</sup>C NMR spectra of 3.



Figure S9. <sup>1</sup>H NMR spectra of 4.



Figure S10. <sup>13</sup>C NMR spectrum of 4 in pyridine- $d_5$  at 100°C.