

Supplementary Information

A Straightforward Substitution Strategy to Tune BODIPY Dyes Spanning the Near-Infrared Region via Suzuki–Miyaura Cross-Coupling

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1. Synthetic Procedures of dyes 1–6

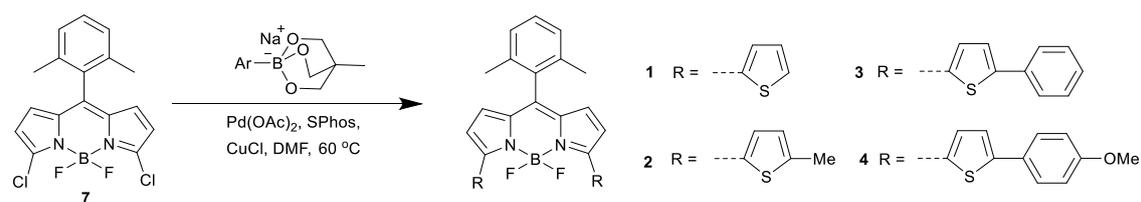


Figure S1. Synthesis scheme of dyes 1–4

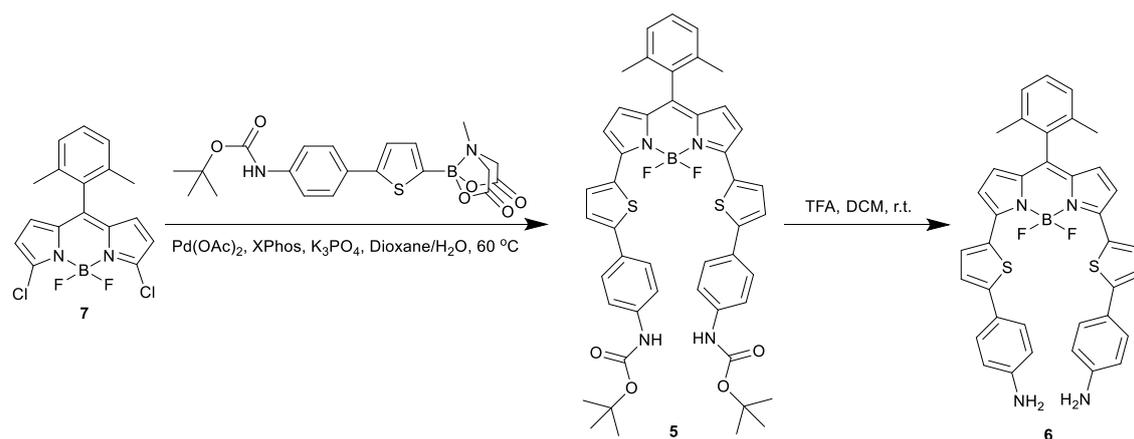


Figure S2. Synthesis scheme of dyes 5 and 6

2. Synthetic Procedures and characterization of cyclotriol boronates (S2 and S6) and MIDA boronate (S10)

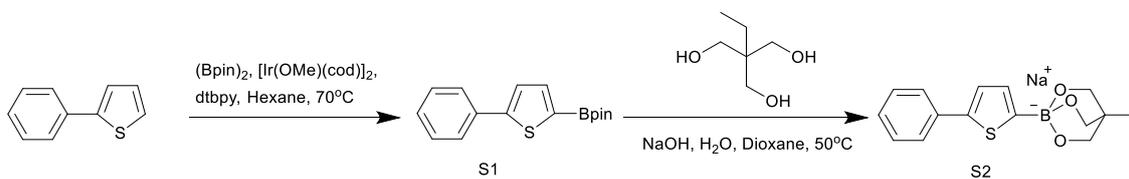


Figure S3. Synthesis scheme of S2

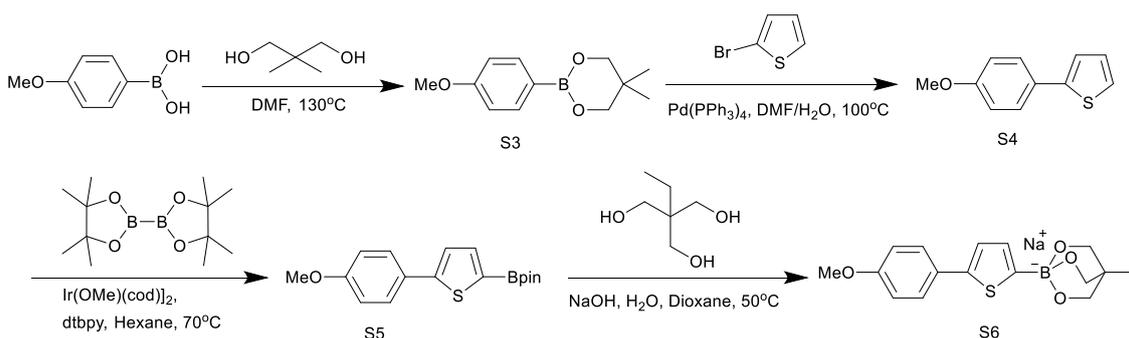


Figure S4. Synthesis scheme of S6

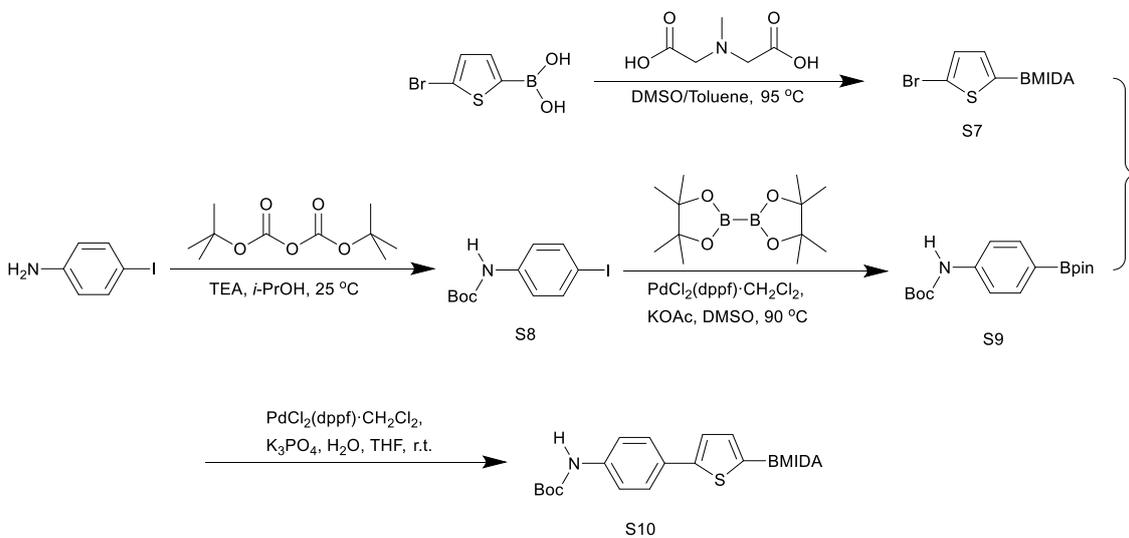
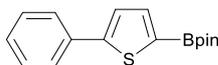


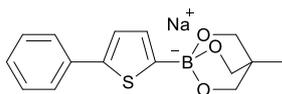
Figure S5. Synthesis scheme of S10



4,4,5,5-Tetramethyl-2-(5-phenylthiophen-2-yl)-1,3,2-dioxaborolane (S1)

2-Phenylthiophene (400 mg, 2.5 mmol, 1 equiv), Bis(pinacolato)diboron (1.268 g, 5.0 mmol, 2 equiv), [Ir(OMe)(cod)]₂ (33 mg, 0.05 mmol, 2 mol%) and dtbpy (33.5 mg, 0.12 mmol, 5 mol%) were dissolved in hexane (150 mL), flushed with nitrogen gas three times in an oven-dried two-neck flask. The reaction mixture was stirred at 70 °C for 1 h. After cooling to room temperature, the mixture was extracted with EtOAc, washed with H₂O and brine successively. The organic layer was collected, dried over Na₂SO₄, filtered, and then concentrated. The crude sample was purified by silica gel column chromatography (EtOAc: hexane 1: 40) to give target compound **S1** as grey solid (421 mg, 59%).

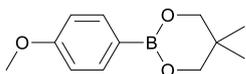
¹H-NMR (400 MHz, CDCl₃): δ = 7.65 (d, *J* = 7.4 Hz, 2H), δ = 7.61 (d, *J* = 3.4 Hz, 1H), δ = 7.40~7.37 (m, 3H), δ = 7.30 (t, *J* = 7.1 Hz, 1H), δ = 1.37 (s, 12H). APCI-FTMS (*m/z*) calcd for C₁₆H₁₉BO₂S: 286.12; Found [M+H]⁺: 287.16.



2-(5-phenylthiophene) Cyclic-triolborate Sodium salt (S2)

S1 (100 mg, 0.35 mmol, 1 equiv), 1,1,1-tris(hydroxymethyl)ether (42 mg, 0.35 mmol, 1 equiv), crushed NaOH (14 mg, 0.35 mmol, 1 equiv) were placed in a two-necked round bottom flask. The flask was then purged with nitrogen gas three times before addition of dioxane (5 mL) and H₂O (19 μL, 10.5 mmol, 3 equiv). The mixture was stirred at 50 °C for 24 h. After the reaction was complete, the mixture was allowed to cool to room temperature, and the white precipitate was collected by filtration, washed with diethyl ether (3 × 10 mL) to give target compound **S2** as grey solid (73 mg, 68%).

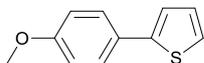
¹H-NMR (400 MHz, DMSO): δ = 7.53 (d, *J* = 7.3 Hz, 2H), δ = 7.32 (t, *J* = 7.7 Hz, 2H), δ = 7.18 (d, *J* = 3.3 Hz, 1H), δ = 7.14 (t, *J* = 7.4 Hz, 1H), δ = 6.69 (d, *J* = 3.2 Hz, 1H), δ = 3.56 (s, 6H), δ = 0.48 (s, 3H). ESI-FTMS (*m/z*) calcd for C₁₅H₁₆BO₃SNa: 310.08; Found [M-Na]⁺: 287.09.



5,5-Dimethyl-2-(4-methoxyphenyl)-1,3,2-dioxaborinane (S3)

p-methoxyphenyl boronic acid (1.00 g, 6.6 mmol, 1 equiv), 2,2-Dimethyl-1,3-propanediol (0.822 g, 7.9 mmol, 1.2 equiv) were dissolved in DMF (20 mL), flushed with nitrogen gas three times in an oven-dried two-neck flask. The mixture was stirred at 130 °C for 2 h. After cooling to room temperature, the mixture was extracted with EtOAc, washed with H₂O and brine successively. The organic layer was collected, dried over Na₂SO₄, filtered, and then

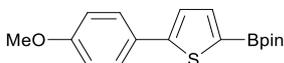
concentrated. The crude sample was purified by silica gel column chromatography (EtOAc: Hexane 1: 40) to give target compound **S3** as white solid (1.50 g, 100%). APCI-FTMS (m/z) calcd for $C_{12}H_{17}BO_3$: 220.13; Found $[M+H]^+$: 221.14.



2-(4-methoxyphenyl)-thiophene (**S4**)

S3 (1.50 g, 6.82 mmol, 1 equiv), bromothiophene (1.334 g, 8.18 mmol, 1.2 equiv), CS_2CO_3 (4.442 g, 18.36 mmol, 2 equiv), $Pd(PPh_3)_4$ (394 mg, 0.34 mmol, 5 mol%) were placed in a two-necked round bottom flask. The flask was then purged with nitrogen gas three times before addition of DMF (20 mL) and H_2O (2 mL). The mixture was stirred at 100 °C for 3 h. After the reaction was complete, the mixture was allowed to cool to room temperature, extracted with EtOAc, washed with H_2O and brine successively. The organic layer was collected, dried over Na_2SO_4 , filtered, and then concentrated. The crude sample was purified by silica gel column chromatography (DCM: hexane 1: 5) to give target compound **S4** as yellowish solid (1.185 g, 91%).

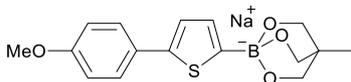
1H -NMR (400 MHz, $CDCl_3$): δ = 7.72 (dt, J = 8.5 Hz, J = 2.3 Hz, 2H), δ = 6.87 (dt, J = 8.7 Hz, J = 2.4 Hz, 2H), δ = 3.80 (s, 3H), δ = 3.73 (s, 4H), δ = 1.00 (s, 6H). APCI-FTMS (m/z) calcd for $C_{11}H_{10}OS$: 190.05; Found $[M+H]^+$: 191.05.



4,4,5,5-Tetramethyl-2-[5-(4-methoxyphenyl)-2-thienyl]-1,3,2-dioxaborolane (**S5**)

The synthesis of **S5** (light green solid, 660 mg, yield 66%) is the same as the synthesis of **S1**, using **S4** (600 mg, 3.15 mmol, 1 equiv), Bis(pinacolato)diboron (916 mg, 3.78 mmol, 1.2 equiv), $[Ir(OMe)(cod)]_2$ (42 mg, 0.06 mmol, 2 mol%) and dtbpy (42 mg, 0.16 mmol, 5 mol%) and hexane (150 mL).

1H -NMR (400 MHz, $CDCl_3$): δ = 7.59-7.56 (m, 3H), δ = 7.27 (d, J = 3.7 Hz, 1H), δ = 6.91 (d, J = 8.9 Hz, 2H), δ = 3.83 (s, 3H), δ = 1.36 (s, 12H). ESI-FTMS (m/z) calcd for $C_{17}H_{21}BO_3S$: 316.13; Found $[M+H]^+$: 317.14.

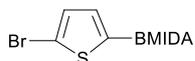


2-[5-(4-methoxyphenyl) thiophene] Cyclic-triolborate Sodium salt (**S6**)

The synthesis of **S6** (gray solid, 584 mg, yield 82%) is the same as the synthesis of **S2**, using **S5** (660 mg, 2.09 mmol), 1,1,1-tris(hydroxymethyl)ether (251 mg, 2.09 mmol, 1 equiv), crushed NaOH (84 mg, 2.09 mmol, 1 equiv) dioxane (20 mL) and H_2O (113 μ L, 6.3 mmol, 3 equiv).

1H -NMR (400 MHz, DMSO): δ = 7.44 (d, J = 8.7 Hz, 2H), δ = 7.03 (d, J = 2.9 Hz, 1H), δ = 6.90

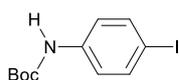
(d, $J = 8.8$ Hz, 2H), $\delta = 6.64$ (m, $J = 2.9$ Hz, 1H), $\delta = 0.47$ (s, 3H). ESI-FTMS (m/z) calcd for $C_{16}H_{18}BO_4SNa$: 340.09; Found $[M-H]^+$: 339.20.



4-bromothiophene-2-boronic acid MIDA ester (S7)

The 4-bromothiophene-2-boronic acid (1.0 g, 4.83 mmol, 1 equiv), *N*-methyliminodiacetic acid (MIDA, 0.78 g, 5.31 mmol, 1.1 equiv) were dissolved in DMSO (3 mL) and Toluene (30 mL), flushed with nitrogen gas three times in an oven-dried two-neck flask. The flask was fitted with a Dean–Stark trap, and the mixture was stirred at 95 °C for 20 h, toluene was removed under reduced pressure. H_2O was added and the resulting precipitate was collected by filtration. The precipitate was washed with H_2O (3×30 mL) and diethyl ether (3×30 mL) to give the target compound as white crystalline solid (1.45 g, 94%).

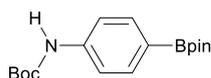
1H -NMR (400 MHz, ACETONE- d_6): $\delta = 7.19$ (d, $J = 3.5$ Hz, 1H), 7.13 (d, $J = 3.5$ Hz, 1H), $\delta = 4.39$ (d, $J = 17$ Hz, 2H), $\delta = 4.20$ (d, $J = 17$ Hz, 2H), $\delta = 2.92$ (s, 3H). ESI-FTMS (m/z) calcd for $C_{20}H_{23}BN_2O_6S$: 316.95; Found $[M+H]^+$: 317.94.



tert-butyl (4-iodophenyl) carbamate (*N*-Boc-4-Iodoaniline) (S8)

The 4-Iodoaniline (2.0 g, 9.13 mmol, 1 equiv), di-*tert*-butyl dicarbonate ((Boc) $_2O$, 2.39 g, 10.96 mmol, 1.2 equiv), Triethylamine (1.08 g, 18.26 mmol, 2 equiv) were placed in a two-necked round bottom flask. The flask was then purged with nitrogen gas three times before addition of *i*-PrOH (50 mL). The mixture was stirred at 25 °C for 20 h. After the reaction was complete, the mixture was extracted with EtOAc, washed with H_2O and brine successively. The organic layer was collected, dried over Na_2SO_4 , filtered, and then concentrated. The crude sample was purified by silica gel column chromatography (EtOAc: hexane 1: 9) to yield the target compound as white solid (2.83 g, 99%).

1H -NMR (400 MHz, $CDCl_3$): $\delta = 7.58$ (d, $J = 8.9$ Hz, 2H), $\delta = 7.14$ (d, $J = 8.7$ Hz, 2H), $\delta = 6.44$ (bs, 1H), $\delta = 1.51$ (s, 9H). ESI-FTMS (m/z) calcd for $C_{11}H_{14}INO_2$: 319.01; Found $[M-H]^+$: 318.00.

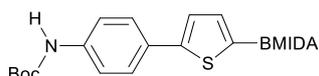


tert-Butyl (4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-phenyl) carbamate (S9)

S8 (1.5 g, 4.70 mmol, 1 equiv), Bis(pinacolato)diboron (1.43 g, 5.64 mmol, 1.2 equiv), KOAc (2.31 g, 23.5 mmol, 5 equiv) and $PdCl_2(dppf) \cdot CH_2Cl_2$ (115 mg, 0.14 mmol, 3 mol%) were placed in a two-necked round bottom flask. The flask was then purged with nitrogen gas three times before addition of DMSO (45 mL). The mixture was stirred at 90 °C for 20 h.

After the reaction was complete, the mixture was extracted with EtOAc, washed with H₂O and brine successively. The organic layer was collected and dried over Na₂SO₄ and evaporated to dryness under reduced pressure. The crude sample was purified by silica gel column chromatography (EtOAc: hexane 1: 9) to yield target compound as white solid (1.43 g, 95%).

¹H-NMR (400 MHz, CDCl₃): δ = 7.73 (d, *J* = 8.6 Hz, 2H), δ = 7.36 (d, *J* = 8.8 Hz, 2H), δ = 6.52 (bs, 1H), δ = 1.52 (s, 9H), δ = 1.33 (s, 12H). ESI-FTMS (*m/z*) calcd for C₁₇H₂₆BNO₄: 319.20; Found [M+Na]⁺: 342.19.



4-(Boc-amino) phenylthiophene-2-boronic MIDA ester (S10)

S7 (1.0 g, 3.15 mmol, 1 equiv), **S9** (1.21 g, 3.80 mmol, 1.2 equiv), K₃PO₄ (1.0 g, 9.42 mmol, 3 equiv), PdCl₂(dppf)·CH₂Cl₂ (103 mg, 0.13 mmol, 4 mol%) were placed in a two-necked round bottom flask. The flask was then purged with nitrogen gas three times before addition of THF (5 mL) and H₂O (0.28 mL, 15.75 mmol, 5 equiv). The mixture was stirred at r.t. for 24 h. The reaction mixture was diluted with acetone (5mL), dried over Na₂SO₄, filtrated through a pad Celite, washed with acetone, and then concentrated. The crude sample was purified by silica gel column chromatography (Acetone: Hexane 1:2) to yield the target compound as yellow solid (0.94 g, 75%).

¹H-NMR (400 MHz, ACETON-6d): δ = 8.52 (bs, 1H), δ = 7.61 (s, 4H), δ = 7.42 (d, *J* = 3.8 Hz, 1H), δ = 7.26 (d, *J* = 3.6 Hz, 1H), δ = 4.29 (d, *J* = 17 Hz, 2H), δ = 4.19 (d, *J* = 17 Hz, 2H), δ = 3.21 (s, 3H), δ = 1.50 (s, 9H). ESI-FTMS (*m/z*) calcd for C₂₀H₂₃BN₂O₆S: 430.14; Found [M-H]⁺: 429.13.



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