

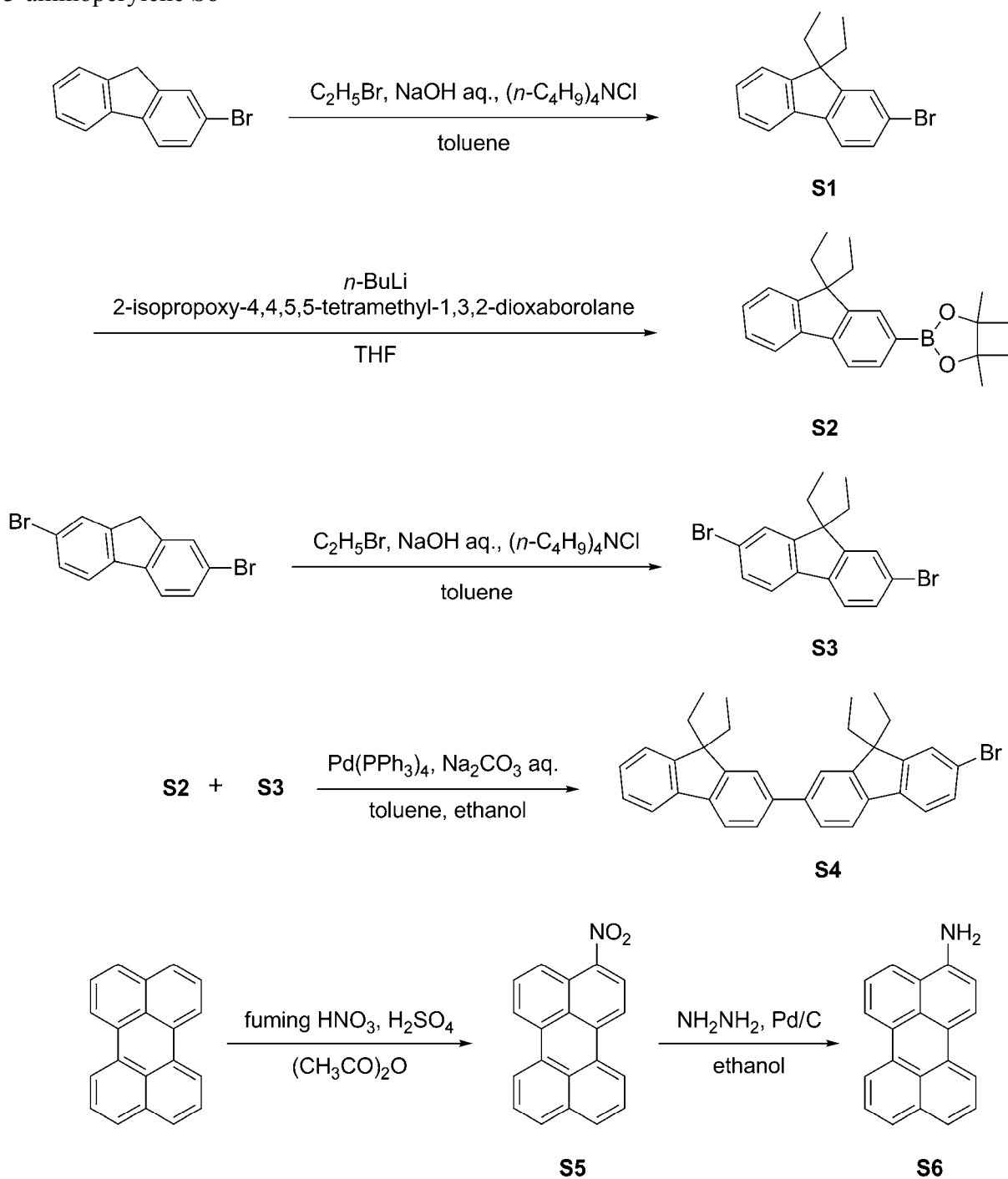
Supplementary Data for

Solution-processable organic fluorescent dyes for multicolor emission in organic light emitting diodes

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Scheme S1. Synthetic route for 2-(2'-bromo-9', 9'-diethylfluorene-7'-yl)-9, 9-diethylfluorene **S4** and 3-aminoperylene **S6**



S1: A mixture of 2-bromofluorene (10.0 g, 40.8 mmol), 1-bromoethane (15.0 cm³, 201 mmol), tetra-*n*-butylammonium chloride (0.567 g, 2.04 mmol), aqueous sodium hydroxide (50wt%, 70 cm³), and toluene (120 cm³) was heated at 60 °C under nitrogen for 8 h. The mixture was allowed to cool to room temperature and then chloroform was added. The organic layer was washed with water, dried over magnesium sulfate, and filtered. The solvent was removed and the residue was purified by column chromatography over silica using a *n*-hexane as eluent to give **S1** as colorless oil (9.46 g, 77%). ¹H-NMR (400 MHz, CDCl₃, TMS, ppm) 7.67-7.65 (1H, m), 7.56-7.54 (1H, m), 7.46-7.43 (2H, m), 7.33-7.30 (3H, m), 2.04-1.95 (4H, m), 0.31 (6H, t, *J* = 7.5 Hz). EI-MS (*m/z*) calcd. 301.2. found 300, 302.

S2: *n*-Butyllithium (1.6 M in hexane, 24 cm³, 38.4 mmol) was added dropwise to a THF (120 cm³) solution of **S1** (9.70 g, 32.2 mmol) at -78 °C under nitrogen, and the solution was stirred for 2 h. Then, 2-isopropoxy-4, 4, 5, 5-tetramethyl-1, 3, 2-dioxaborolane (9.8 cm³, 48.0 mmol) was slowly added to the solution at -78 °C. After 2 h, the solution was allowed to cool to room temperature, and then stirred for 2 h. Chloroform was added to the solution, and then the organic layer was washed with water, dried over magnesium sulfate, and filtered. The solvent was removed and the residue was purified by column chromatography over silica using a *n*-hexane: toluene mixture (3: 1) as eluent to give **S2** as white solid (6.84 g, 61%). ¹H-NMR (400 MHz, CDCl₃, TMS, ppm) 7.83-7.79 (1H, m), 7.75-7.69 (3H, m), 7.33-7.32 (3H, m), 2.13-1.98 (4H, m), 1.31 (12H, s), 0.28 (6H, t, *J* = 7.0 Hz). EI-MS (*m/z*) calcd. 348.3. found 349.

S3: A mixture of 2, 7-dibromofluorene (10.0 g, 30.9 mmol), 1-bromoethane (11.5 cm³, 154 mmol), tetra-*n*-butylammonium chloride (0.431 g, 1.55 mmol), aqueous sodium hydroxide (50wt%, 100 cm³) was heated at 60 °C under nitrogen for 10 h. The mixture was allowed to cool to room temperature and then chloroform was added. The organic layer was washed with water, dried over magnesium sulfate, and filtered. The solvent was removed and the residue was purified by column chromatography over silica using a *n*-hexane: toluene mixture (3: 1) as eluent to give **S3** as white solid (8.34 g, 71%). ¹H-NMR (400 MHz, CDCl₃, TMS, ppm) 7.54-7.52 (2H, m), 7.47-7.46 (1H, m), 7.45-7.44 (3H, m), 1.99 (4H, q, *J* = 7.5 Hz), 0.32 (6H, t, *J* = 7.3 Hz). EI-MS (*m/z*) calcd. 380.1. found 378, 380, 382.

S4: A mixture of **S2** (3.50 g, 10.0 mmol), **S3** (7.64 g, 20.1 mmol), aqueous sodium carbonate (2 M, 100 cm³), tetrakis(triphenylphosphine)palladium(0) (0.578 g, 0.50 mmol), and toluene (100 cm³) was degassed and placed under nitrogen, and then heated at 90 °C for 24 h. The mixture was allowed to cool to room temperature and then toluene was added. The organic layer was washed with water, dried over magnesium sulfate, and filtered. The solvent was removed and the residue was purified by column chromatography over silica using a *n*-hexane: chloroform mixture (5: 1) as eluent to give **S4** as white solid (2.97 g, 57%). ¹H-NMR (400 MHz, CDCl₃, TMS, ppm) 7.79-7.55 (7H, m), 7.48-7.32 (6H, m), 2.15-2.03 (8H, m), 0.41-0.36 (12H, m). EI-MS (*m/z*) calcd. 521.5. found 520.2, 522.2.

S5: A mixture (20 cm³, 1/200 v/v) of fuming nitric acid and acetic anhydride was added dropwise to a solution of perylene (0.500 g, 1.98 mmol) in acetic anhydride (550 cm³) at 10 °C, and then a mixture (20 cm³, 1/4000 v/v) of sulfuric acid (98%) and acetic anhydride was added dropwise to the solution. After 5 min, the reaction mixture was poured into ice water (ca. 3000 cm³), and stirred overnight. Red precipitate was filtered, and dissolved in chloroform. The chloroform solution was washed with water, dried over magnesium sulfate, and filtered. The solvent was removed and the residue was purified by column chromatography over silica using a *n*-hexane: toluene mixture (1: 2) as eluent to give **S5** as red solid (0.42 g, 71%). ¹H-NMR (400 MHz, CDCl₃, TMS, ppm) 8.46 (1H, d, *J* = 8.6 Hz), 8.26-8.17 (4H, m), 8.09 (1H, d, *J* = 8.8 Hz), 7.81 (1H, d, *J* = 8.2 Hz), 7.75 (1H, d, *J* = 7.8 Hz), 7.68-7.64 (1H, m), 7.55-7.51 (2H, m). EI-MS (*m/z*) calcd. 297.3. found 297.

S6: Palladium carbon (5%) (0.35 g) and hydrazine monohydrate (10.4 g, 206 mmol) was added to a solution of **S5** (0.499 g, 1.68 mmol) in ethanol (500 cm³) at 80 °C. After the mixture was stirred for 20 min. The catalyst was filtered off, and the solvent was removed to give **S6** as orange solid (0.35 g, 78%). ¹H-NMR (400 MHz, CDCl₃, TMS, ppm) 8.20 (1H, d, *J* = 7.3 Hz), 8.13 (1H, d, *J* = 7.7 Hz), 8.05-8.00 (2H, m), 7.64 (1H, s), 7.62 (1H, s), 7.55 (1H, d, *J* = 8.2 Hz), 7.48-7.39 (3H, m), 6.81 (1H, d, *J* = 8.2 Hz), 4.21 (2H, s). EI-MS (*m/z*) calcd. 267.3. found 267.