Supporting Information

Novel Fluorophores: Efficient Synthesis and Photophysical Study

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Fluorophore 10

A mixture of 675.3mg (1.51mmol) of **8**, 1.3mL (9.20mmol) of (trimethylsilyl)acetylene, 213mg (0.303mmol) of $(PPh_3)_2PdCl_2$, 39.8mg (0.152mmol) of CuI in Et_3N (30mL) was stirred at 45-50°C. After being stirred for 2h, the mixture was evaporated. Column chromatography [SiO_2, hexane] yielded 714mg (91%) of **10** as a solid.
m.p. 118 – 120 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86(s, 4H; ArH), 7.04(s, 2H; CCH), 0.27 and 0.24 (2s, 36H; $SiCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.1, 136.2, 128.9, 104.2, 103.8, 102.2, 101.7, 94.2, -0.2, -0.3; MS (FAB, m/z) 514.3 (M^+); UV ($CHCl_3$): λ_{max} ($\varepsilon \times 10^{-5}$) = 412 (4.7); Elemental anal. Calcd. for $C_{30}H_{42}Si_4 \cdot H_2O$: C, 67.60; H, 8.32. Found: C, 67.30; H, 8.19.

Fluorophore 11

A mixture of 198mg (0.442mmol) of **9**, 749μL (5.30mmol) of (trimethylsilyl)acetylene, 62.0mg (0.088mmol) of $(PPh_3)_2PdCl_2$, 17.0mg (0.088mmol) of CuI in Et_3N (8.8mL) was stirred at 45-50°C. After being stirred for 3h, the mixture was evaporated. Column chromatography [SiO_2, hexane] yielded 210mg (91%) of **11** as a solid.
m.p. 146 – 148 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62(s, 4H; ArH), 7.07(s, 2H; CCH), 0.26 and 0.19 (2s, 36H; $SiCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.4, 136.8, 130.0, 104.9, 103.7, 102.0, 101.9, 95.4, -0.2, -0.4; MS (FAB, m/z) 520.2 (M^+); UV ($CHCl_3$): λ_{max} ($\varepsilon \times 10^{-5}$) = 458 (4.8); Elemental anal. Calcd. for $C_{28}H_{40}S_1Si_4$: C, 64.55; H, 7.74. Found: C, 64.20; H, 7.99.

Fluorophore 12a

To a solution of **8** (322mg, 0.722mmol) and phenyl acetylene (1.2mL, 11.6mmol) in Et_3N/MeOH (2mL/8mL) were added $(PPh_3)_2PdCl_2$ (76mg, 0.108mmol) and CuI (21mg, 0.108mmol). The mixture was stirred at 45-50°C for 3h. After evaporation solvent *in Vacuo*, the residue was subject to chromatography on silica gel column with hexane as eluent to give **12a** (299mg, 60%).
m.p. 182 – 185 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98(s, 4H; ArH), 7.55-7.52(m, 8H; ArH), 7.38(m, 12H; ArH), 7.15(s, 2H; CCH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.2, 131.7, 131.6, 129.0, 128.8, 128.5, 128.3, 125.9; MS (FAB, m/z) 530.2 (M^+); UV ($CHCl_3$): λ_{max} ($\varepsilon \times 10^{-5}$) = 416 (5.5); Elemental anal. Calcd. for $C_{42}H_{26} \cdot 0.5H_2O$: C, 93.48; H, 5.04. Found: C, 93.44; H, 4.87.

Fluorophore 12b

A mixture of 111mg (0.216mmol) of **10**, 0.3mL (3.10mmol) of 2-bromothiophene, 141mg (2.51mmol) of KF, 44mg (0.0627mmol) of $(PPh_3)_2PdCl_2$ and 12mg (0.063mmol) of CuI in Et_2NH/MeOH (25mL/6.3mL) was stirred at 45-50°C. After being stirred for 4h, the mixture was evaporated. Column chromatography [SiO_2, hexane : ethyl acetate, 20:1] yielded 54.5mg (45%) of **12b** as a solid.
m.p. 190 – 191 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92(s, 4H; ArH), 7.33(m, 8H; ThH), 7.11(s,

2H; C=CH), 7.03-6.99(m, 4H; ThH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.1, 136.4, 132.7, 132.5, 129.1, 128.4, 127.8, 127.3, 127.2, 122.7, 103.4, 92.5, 90.7, 89.2, 82.7; MS (FAB, m/z) 553.9 (M^+); UV ($CHCl_3$): λ_{max} ($\varepsilon \times 10^{-5}$) = 438 (6.0); Elemental anal. Calcd. for $C_{34}H_{18}S_4$: C, 73.61; H, 3.27. Found: C, 73.95; H, 3.13.

Fluorophore 12c

A mixture of 98.1mg (0.191mmol) of **10**, 88mg (1.52mmol) of 5-bromo-2-furaldehyde, 267mg (1.53mmol) of KF, 27mg (0.0385mmol) of $(PPh_3)_2PdCl_2$ and 2mg (0.020mmol) of CuCl in Et_3N/MeOH (14.3mL/4.8mL) was stirred at 45-50°C. After being stirred for 5h, the mixture was evaporated. Column chromatography [SiO_2, hexane : ethyl acetate, 1:1] yielded 43mg (38%) of **12c** as a solid.

m.p. > 131 °C dec.; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.66(s, 4H; CHO), 7.96(s, 4H; ArH), 7.31-7.25 (m, 10H; FuH and C=CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.2, 153.0, 152.8, 145.6, 141.1, 136.4, 129.7, 125.9, 121.3, 118.7, 118.0, 101.4, 94.6, 92.2, 87.2, 85.3; UV ($CHCl_3$): λ_{max} ($\varepsilon \times 10^{-5}$) = 450 (4.5); Elemental anal. Calcd. for $C_{38}H_{18}O_8$: C, 75.75; H, 3.01. Found: C, 75.52; H, 3.00.

Fluorophore 12d

To a solution of **10** (144mg, 0.28mmol) and 5-bromo-2-thiophenecarboxaldehyde (0.33mL, 2.78mmol) in Et_3N/MeOH (21mL/7mL) were added $(PPh_3)_2PdCl_2$ (39mg, 0.0556mmol) and CuI (5mg, 0.0263mmol). The mixture was stirred at 45-50°C for 5h. After evaporation solvent *in Vacuo*, the residue was subject to chromatography on silica gel column with hexane : ethyl acetate (1:1) as eluent to give **12d** (98.2mg, 53%).

m.p. > 146 °C dec.; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.88(s, 4H; CHO), 7.93(s, 4H; ArH), 7.70(br d, 4H; ThH), 7.38(br d, 4H; ThH), 7.24(s, 2H; C=CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 182.4, 182.3, 145.1, 144.7, 144.5, 136.5, 136.2, 135.9, 133.5, 133.2, 131.1, 129.5, 128.2, 102.6, 96.2, 94.0, 88.7, 82.7; MS (FAB, m/z) 669.9 (M^++H); UV ($CHCl_3$): λ_{max} ($\varepsilon \times 10^{-5}$) = 456 (2.8); Elemental anal. Calcd. for $C_{38}H_{18}O_4S_4 \cdot H_2O$: C, 66.45; H, 2.93. Found: C, 66.10; H, 2.64.

Fluorophore 12e

To a solution of **10** (102mg, 0.195mmol) and 4-bromopyridine hydrochloride (384mg, 1.97mmol) in Et_3N/MeOH (14.6mL/4.9mL) were added $(PPh_3)_2PdCl_2$ (27mg, 0.0385mmol) and CuI (4mg, 0.021mmol). The mixture was heated at 45-50°C for 8h. After evaporation solvent *in Vacuo*, the residue was subject to chromatography on silica gel column with ethyl acetate : methyl alcohol (10:1) as eluent to give **12e** (58.1mg, 56%).

m.p. > 380 °C dec.; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.60(br d, 8H; J = 4.7 Hz; PyH), 7.94(s, 4H; ArH), 7.39-7.30(m, 8H; PyH), 7.27(s, 2H; C=CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.9, 149.8, 145.1, 136.4, 130.6, 130.4, 129.4, 125.5, 125.3, 120.9, 95.3, 92.6, 92.3, 90.3; MS (FAB, m/z) 535.0 (M^++H); UV ($CHCl_3$): λ_{max} ($\varepsilon \times 10^{-5}$) = 420 (0.94); Elemental anal. Calcd. for $C_{38}H_{22}N_4 \cdot 0.5H_2O$: C, 83.96; H, 4.26; N, 10.30. Found: C, 84.08; H, 4.09; N, 10.23.

Fluorophore 13a

To a solution of **9** (232mg, 0.518mmol) and phenyl acetylene (0.85mL, 7.77mmol) in Et_3N/MeOH (2mL/8mL) were added $(PPh_3)_2PdCl_2$ (55mg, 0.0784mmol) and CuI (15mg, 0.0788mmol). The mixture was stirred at 45-50°C for 3h. After evaporation solvent *in Vacuo*, the residue was subject to chromatography on silica gel column with hexane as eluent to give **13a** (228mg, 78%).

m.p. 134 – 136 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62-7.56(m, 8H; ArH), 7.48(s, 2H; ArH), 7.43-7.39(m, 6H;ArH), 7.37(s, 2H; C=CH), 7.28-7.26(m, 6H; ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.0, 135.6, 131.6, 131.5, 130.6, 128.6, 128.4, 128.3, 128.2, 122.8, 122.4, 101.7, 98.1, 90.0, 89.2, 87.5; MS (FAB, m/z) 536.1 (M^+); UV ($CHCl_3$): λ_{max} ($\varepsilon \times 10^{-5}$) = 468 (3.9); Elemental anal. Calcd. for $C_{40}H_{24}S_1$: C, 89.52; H, 4.51. Found: C, 89.23; H, 4.64.

Fluorophore 13b

A mixture of 107mg (0.201mmol) of **11**, 0.19mL (1.96mmol) of 2-bromothiophene, 90mg

(1.6mmol) of KF, 28mg (0.0399mmol) of $(PPh_3)_2PdCl_2$ and 7.6mg (0.0399mmol) of CuI in Et_2NH/MeOH (16mL/4mL) was stirred at 45-50°C. After being stirred for 5h, the mixture was evaporated. Column chromatography [SiO_2, hexane : ethyl acetate, 10:1] yielded 55.2mg (49%) of **13b** as a solid.
m.p. > 126 °C dec.; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35(s, 2H; ArH), 7.25-7.20(m, 10H; ArH and C=CH), 6.96(t, 2H, *J* = 4.3 Hz; ArH), 6.84(t, 2H, *J* = 4.3 Hz; ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.1, 135.3, 132.6, 132.4, 130.7, 128.5, 127.8, 127.2, 122.8, 122.3, 101.2, 92.3, 92.0, 91.0, 83.7; MS (FAB, m/z) 559.8 (M^+); UV ($CHCl_3$): λ_{max} ($\varepsilon \times 10^{-5}$) = 486 (5.1); Elemental anal. Calcd. for $C_{32}H_{16}S_5$: C, 68.54; H, 2.88. Found: C, 68.54; H, 3.03.

Fluorophore 13c
A mixture of 69.2mg (0.13mmol) of **11**, 182mg (1.04mmol) of 5-bromo-2-furaldehyde, 75mg (1.29mmol) of KF, 18mg (0.0256mmol) of $(PPh_3)_2PdCl_2$ and 2.6mg (0.0263mmol) of CuCl in Et_3N/MeOH (9.7mL/3.2mL) was stirred at 45-50°C. After being stirred for 5h, the mixture was evaporated. Column chromatography [SiO_2, hexane : ethyl acetate, 3:2] yielded 30mg (38%) of **13c** as a solid.
m.p. > 133 °C dec.; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.63(s, 2H; CHO), 9.58 (s, 2H; CHO), 7.55-7.51(2d, 8H, *J* = 3.9 Hz; FuH), 7.45(s, 2H; ThH), 7.27(s, 2H; C=CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.2(d), 152.8, 138.7, 134.9, 132.9, 130.9, 130.4, 128.8, 128.0, 121.2, 118.4, 118.0, 101.2, 96.3, 93.1, 87.5, 85.8; MS (FAB, m/z) 608.9 (M^++H); UV ($CHCl_3$): λ_{max} ($\varepsilon \times 10^{-5}$) = 516 (1.4); Elemental anal. Calcd. for $C_{36}H_{16}O_8S_1$: C, 71.05; H, 2.65. Found: C, 71.28; H, 2.68.

Fluorophore 13d
To a solution of **11** (80.2mg, 0.151mmol) and 5-bromo-2-thiophenecarboxaldehyde (0.18mL, 1.51mmol) in Et_3N/MeOH (11.3mL/3.8mL) were added $(PPh_3)_2PdCl_2$ (21mg, 0.0299mmol) and CuI (3mg, 0.0157mmol). The mixture was stirred at 45-50°C for 4h. After evaporation solvent *in Vacuo*, the residue was subject to chromatography on silica gel column with hexane : ethyl acetate (1:1) as eluent to give **13d** (59.8mg, 59%).
m.p. > 88 °C dec.; ^{1}H NMR (300MHz, $CDCl_3$) δ 9.87(s, 2H; CHO), 9.78(s, 2H; CHO), 7.67(d, 2H, *J* = 3.9 Hz; ThH), 7.47(d, 2H, *J* = 3.9 Hz; ThH), 7.40(br d, 4H; ThH), 7.34(d, 2H, *J*=3.9Hz; ThH), 7.25(s, 2H; C=CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 182.3, 182.2, 145.1, 144.5, 142.8, 138.0, 135.9, 135.7, 133.2, 132.5, 131.7, 131.1, 102.0, 100.4, 95.9, 94.6, 91.3; MS (FAB, m/z) 672.9 (M^++H); UV ($CHCl_3$): λ_{max} ($\varepsilon \times 10^{-5}$) = 524 (4.0); Elemental anal. Calcd. for $C_{36}H_{16}O_4S_5$: C, 64.26; H, 2.40. Found: C, 63.89; H, 2.27.

Fluorophore 13e
To a solution of **11** (62.4mg, 0.12mmol) and 4-bromopyridine hydrochloride (186mg, 0.956mmol) in Et_3N/MeOH (9mL/3mL) were added $(PPh_3)_2PdCl_2$ (17mg, 0.0242mmol) and CuI (2mg, 0.0105mmol). The mixture was heated at 45-50°C for 10h. After evaporation solvent *in Vacuo*, the residue was subject to chromatography on silica gel column with ethyl acetate : methyl alcohol (10:1) as eluent to give **13e** (38.3mg, 59%).
m.p. 246 – 249 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.49(d, 4H, *J* = 4.7 Hz; PyH), 8.32(d, 4H, *J* = 4.9 Hz; PyH), 7.35(s, 2H; ThH), 7.29(s, 2H; C=CH), 7.26(d, 2H, *J* = 5.7 Hz; PyH), 7.25(d, 2H, *J* = 5.6 Hz; PyH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.9(d), 142.3, 138.7, 132.3, 130.4, 129.7, 125.2, 124.7, 100.2, 95.0, 92.1, 91.8, 90.6; MS (FAB, m/z) 540.0 (M^+); UV ($CHCl_3$): λ_{max} ($\varepsilon \times 10^{-5}$) = 522 (1.1); Elemental anal. Calcd. for $C_{36}H_{20}N_4S_1$: C, 79.98; H, 3.73; N, 10.36. Found: C, 79.78; H, 3.85; N, 10.21.