Supporting Information

New Efficient Ruthenium Sensitizers with Unsymmetrical Indeno[1,2-*b*]thiophene or Fused Dithiophene Ligand for Dye-Sensitized Solar Cells

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Table of Contents

Synthesis of **JK-189**

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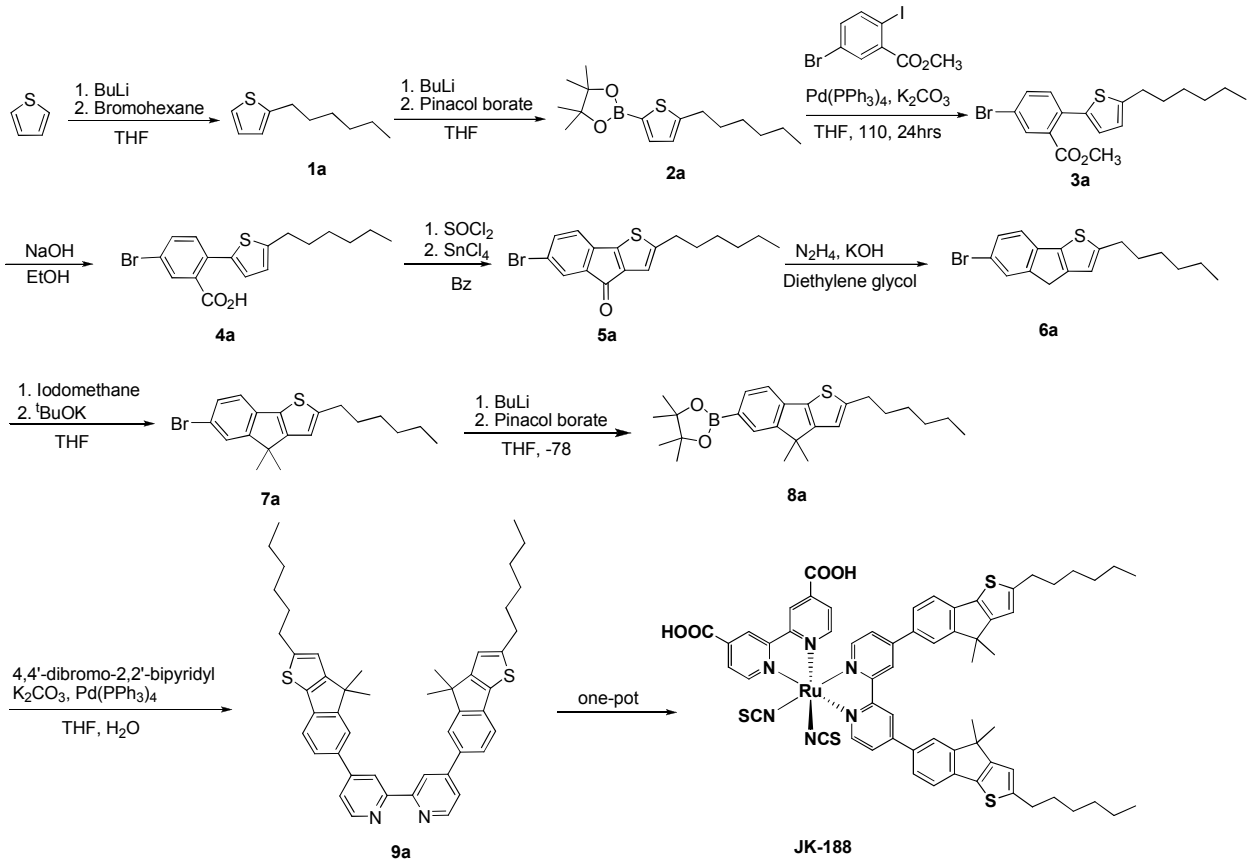
Experimental section



Methyl 5-bromo-2-(5-hexylthiophen-2-yl)benzoate (3a) : The compound of 2-(5-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **2a** (18 mmol), methyl 5-bromo-2-iodobenzoate (18 mmol), $Pd(PPh_3)_4$ (5 mol%), and K_2CO_3 (90 mmol) were dissolved in THF (100 ml) / H_2O (20 ml) and the mixture was refluxed for 15 h. After evaporating the solvent under reduced pressure, H_2O (10 ml) and dichloromethane (3X50 ml) were added. The organic layer was separated and dried in $MgSO_4$. The solvent was removed under reduced pressure. The pure product was obtained by column chromatography on silica gel (dichloromethane : hexane = 1 : 6). ^{1}H NMR ($CDCl_3$) : δ = 0.88 (t, 3H, J = 6.3Hz), 1.36 (m, 6H), 1.69 (t, 2H, J = 6.9Hz), 2.80 (t, 2H, J = 7.5Hz), 3.74 (s, 3H), 6.71 (d, 1H, J = 3.6Hz), 6.82 (d, 1H, J = 3.6Hz), 7.28 (d, 1H, J = 8.7Hz), 7.52 (d, 1H, J = 8.7Hz), 7.79 (s, 1H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 14.0, 24.7, 28.7, 30.1, 31.5, 31.6, 52.3, 120.9, 124.4, 126.2, 132.0, 132.1, 132.8, 133.2, 133.7, 137.8, 147.2, 167.8. Anal. Calcd for $C_{18}H_{21}BrO_2S$: C, 56.69; H, 5.55. Found: C, 56.78; H, 5.69.

5-Bromo-2-(5-hexylthiophen-2-yl)benzoic acid (4a) : A mixture of 6 (13.5 mmol) and sodium

hydroxide (40.5 mmol) in 50 mL of ethanol and 5 mL of water was refluxed overnight. The solvent was evaporated under vacuum to about half of its original volume. Water was added, and the resulting aqueous layer was treated with HCl to obtain a solid, which was filtered and dried to afford **4a**. ^{1}H NMR ($CDCl_3$) : δ = 0.86 (t, 3H, J = 6.9Hz), 1.30 (m, 6H), 1.68 (t, 2H, J = 6.6Hz), 2.80 (t, 2H, J = 7.5Hz), 6.71 (d, 1H, J = 3.6Hz), 6.88 (d, 1H, J = 3.6Hz), 7.32 (d, 1H, J = 8.1Hz), 7.60 (d, 1H, J = 8.7Hz), 7.91 (s, 1H), 10.44 (s, 1H) ^{13}C NMR (300 MHz, $CDCl_3$): δ 14.2, 22.6, 28.8, 30.3, 31.5, 31.6, 120.9, 124.4, 126.2, 130.3, 131.5, 132.8, 133.4, 133.9, 137.7, 147.3, 169.1. Anal. Calcd for $C_{17}H_{19}BrO_2S$: C, 55.59; H, 5.21. Found: C, 55.37; H, 5.07.

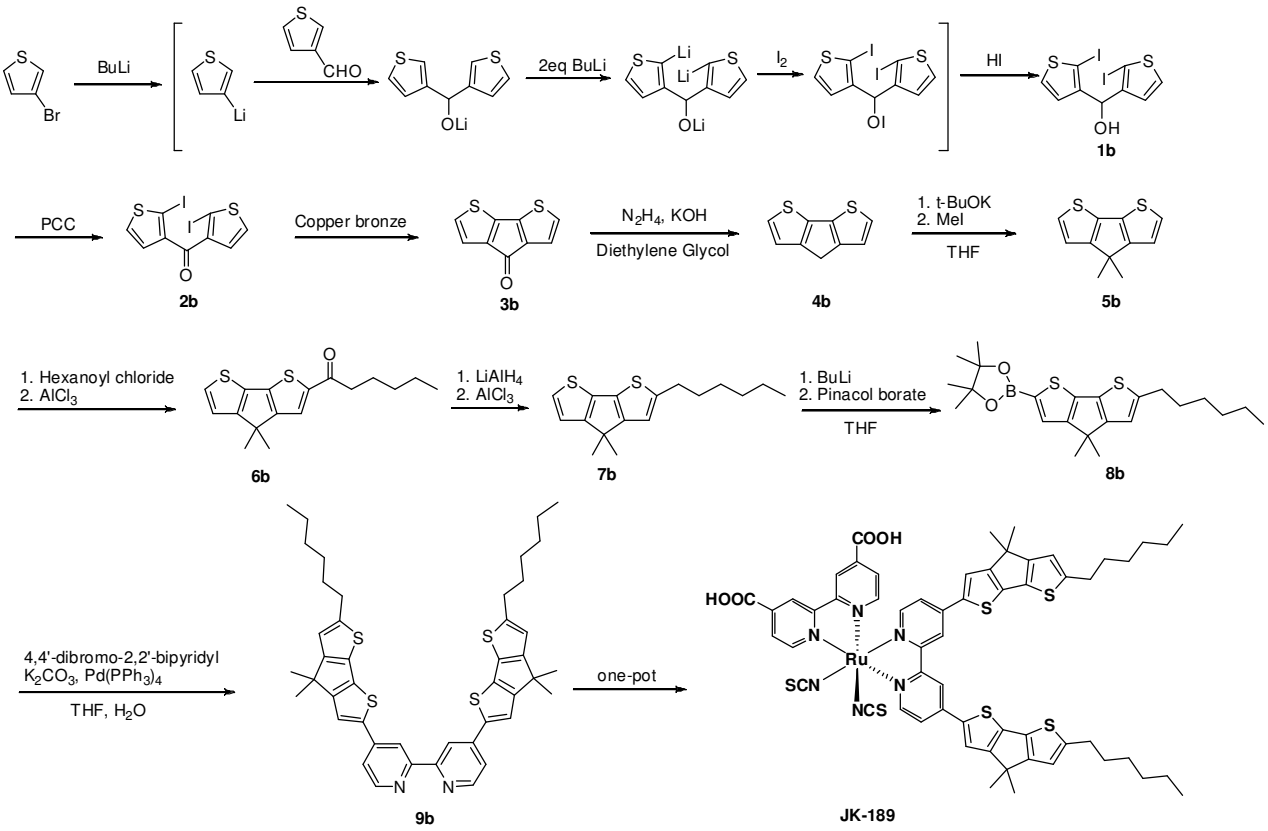
6-Bromo-2-hexyl-*4H*-indeno[1,2-*b*]thiophen-4-one (5a) : 5-Bromo-2-(5-hexylthiophen-2-yl)benzoic acid (12 mmol) dissolved in dry benzene (40 ml) and dry DMF (1.5 ml) was added thionyl chloride (3 ml). The solution was heated at reflux for 2 hr and cooled, and the benzene evaporated. The brown residue was kept under nitrogen and was freed from the last traces of thionyl chloride by treatment with four successive portions of dry benzene, followed by evaporation of each portion of benzene. Final evaporation of the benzene left the acid chloride as brown oil. A solution of the acid chloride obtained above in dry benzene (15 ml) was added to a three-necked, 250-ml flask protected by a calcium chloride drying tube and cooled to 0 ^{o}C. A solution of stannic chloride (1.5 ml) in dry benzene (6 ml) was added at such a rate as to keep the temperature at 4 ^{o}C. After addition was completed, the dark mixture was stirred for 10 min at 4 ^{o}C and for a further 10 min without external cooling. The dark mixture was poured onto a ice (60 ml) and 1 M HCl (30 ml), and were stirred well. The layers were separated and the aqueous layer was extracted with ether (150 ml) in three portions. The benzene solution was washed twice with water, three times with 1 M NaOH (15 ml), three times with water, dried ($MgSO_4$). Column chromatography (ethyl acetate) afforded of orange oil. ^{1}H NMR ($CDCl_3$): δ = 0.89 (t, 3H, J = 6.9Hz), 1.32 (m, 6H), 1.65 (t, 2H, J = 6.3Hz), 2.77 (t, 2H, J = 7.2Hz), 6.79 (s, 1H), 6.88 (d, 1H, J = 7.5Hz), 7.41 (d, 1H, J = 7.2Hz), 7.49 (s, 1H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 13.8, 22.5, 28.5, 30.5, 31.2, 31.4, 117.8, 119.9, 121.4, 126.4, 135.9, 137.4, 137.9, 141.4, 152.1, 156.1, 185.9. Anal. Calcd for : $C_{17}H_{17}BrOS$: C, 58.46; H, 4.91. Found: C, 58.21; H, 4.78.

6-Bromo-2-hexyl-*4H*-indeno[1,2-*b*]thiophene (6a): 6-Bromo-2-hexyl-*4H*-indeno[1,2-*b*]thiophen-4-one **5a** (9 mmol) was mixed with 95% hydrazine (3 ml), potassium hydroxide (45 mmol), and diethylene glycol (20 ml) at 45 ℃ in a three-necked, 150 ml flask fitted with a condenser arranged for downward distillation. The mixture was heated to 195 ℃ over a 1 hr period and maintained at this temperature for 0.5 hr. The reaction mixture was cooled, water (60 ml) was added, and the mixture was distilled. This procedure was repeated until 80 ml of distillate had collected. The distillate was extracted with three portions of ether. The combined ether solutions were washed twice with water and twice with brine, dried ($MgSO_4$), and concentrated to leave crude compound. Column chromatography (hexane : dichloromethane, 1 : 6) afforded **6a**. ^{1}H NMR ($CDCl_3$): δ = 0.88 (t, 3H, J = 6.9Hz), 1.31 (m, 6H), 1.66 (t, 2H, J = 6.6Hz), 2.75 (t, 2H, J = 7.2Hz), 3.69 (s, 2H), 6.94 (s, 1H), 7.01 (d, 1H, J = 7.8Hz), 7.48 (d, 1H, J = 8.1Hz), 7.69 (s, 1H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 13.6, 22.4, 28.5, 30.5, 30.9, 31.3, 31.4, 118.9, 120.2, 120.9, 126.2, 135.6, 137.3, 138.4, 142.5, 150.8, 156.1. Anal. Calcd for $C_{17}H_{19}BrS$: C, 60.89; H, 5.71. Found: 60.68; H, 5.58.

6-Bromo-2-hexyl-4,4-dimethyl-*4H*-indeno[1,2-*b*]thiophene (7a) : 6-Bromo-2-hexyl-*4H*-indeno[1,2-*b*]thiophene **6a** (6.4 mmol) was dissolved in THF and treated with potassium *tert*-butoxide (9.6 mmol), followed by methylation with iodomethane (19.2 mmol). This procedure was repeated once more to yield 6-bromo-2-hexyl-4,4-dimethyl-*4H*-indeno[1,2-*b*]thiophene. The compound was purified by silica gel column chromatography using dichloromethane and hexane as an eluent, followed by vacuum distillation. δ = 0.88 (t, 3H, J = 6.9Hz), 1.31 (m, 6H), 1.48 (s, 6H), 1.66 (t, 2H, J = 7.2Hz), 2.75 (t, 2H, J = 7.2Hz), 6.91 (s, 1H), 6.98 (d, 1H, J = 8.1Hz), 7.41 (d, 1H, J = 8.1Hz), 7.57 (s, 1H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 13.8, 22.3, 28.3, 30.4, 30.6 30.9, 31.2, 31.3, 118.9, 120.1, 119.6, 125.8, 135.1, 137.1, 137.7, 142.0, 150.8, 156.0. Anal. Calcd for $C_{19}H_{23}BrS$: C, 62.80; H, 6.38. Found: 62.60; H, 6.17.

2-(2-Hexyl-4,4-dimethyl-*4H*-indeno[1,2-*b*]thiophen-6-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8a) : *n*-BuLi solution in hexanes (7.2 mmol) was added via a syringe to a stirred solution of 6-bromo-2-hexyl-4,4-dimethyl-*4H*-indeno[1,2-*b*]thiophene **7a** (6 mmol) in THF (25 mL) at –30 ℃. Stirring was continued for 1 h and 2-isoproxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7.2 mmol) was added via

syringe at –30 ºC. The reaction mixture was stirred at r.t. for 8 h. The reaction mixture was added H_2O, and then the layers were separated, the organic layer was washed with H_2O, and dried over anhydride $MgSO_4$. The solvent was distilled off under reduced pressure. The pure product was obtained by column chromatography on silica gel (ethyl acetate : hexane = 1 : 5). ^{1}H NMR ($CDCl_3$) : δ = 0.88 (t, 3H, J = 6.9Hz), 1.36 (m, 18H), 1.47 (s, 6H), 1.66 (t, 2H, J = 6.9Hz), 2.76 (t, 2H, J = 7.2Hz), 6.93 (s, 1H), 7.31 (d, 1H, J = 8.4Hz), 7.52 (d, 1H, J = 8.1Hz), 7.64 (s, 1H).



7,7-Dimetyl-*4H*-cyclopenta-[2,1-*b*:3,4-*b*']dithiophene (**5b**): *4H*-Cyclopenta-[2,1-*b*:3,4-*b*']dithiophene **4b** (6 mmol) was dissolved in THF and treated with potassium *tert*-butoxide (9 mmol), followed by methylation with iodomethane (18 mmol). This procedure was repeated once more to yield 7,7-dimetyl-*4H*-cyclopenta-[2,1-*b*:3,4-*b*']dithiophene. The compound was purified by silica gel column chromatography using dichloromethane and hexane as an eluent, followed by vacuum distillation. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.46 (s, 6H), 6.99 (d, 2H, J = 4.5Hz), 7.15 (d, 2H, J = 4.8Hz). ^{13}C NMR (300 MHz, $CDCl_3$): δ = 31.7, 52.1, 120.3, 124.1, 130.2, 133.7. Anal. Calcd for $C_{11}H_{10}S_2$: C, 64.56; H, 4.88. Found: C, 64.26; H, 4.67.

1-(7,7-Dimetyl-*4H*-cyclopenta-[2,1-*b*:3,4-*b*']dithiophen-2-yl)haxan-1-one (**6b**): To a stirred solution of **5b** (5.7 mmol) in dry dichloromethane (50 ml) was added hexanoyl chloride (5.7 mmol). The mixture was stirred for 0.5 h at r.t, cooled to 0 °C, and $AlCl_3$ (6.0 mmol) was added portionwise. The mixture was then allowed to warm to 25 °C and stirred for 18 h. The reaction was quenched by the addition of water (30 ml) and acidified with 2M aqueous HCl (50 ml). The mixture was extracted with dichloromethane. The organic layers were combined, washed with water (30 ml), dried ($MgSO_4$) and

concentrated in vacuum. Column chromatography (*n*-hexane : dichloromethane, 1 : 1) afforded **6b**. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92 (t, 3H, *J* = 7.2Hz), 1.36 (m, 4H), 1.48 (s, 6H), 1.75 (t, 2H, *J* = 7.2Hz), 2.86 (t, 2H, *J* = 7.2Hz), 7.01 (d, 1H, *J* = 5.1Hz), 7.33 (d, 1H, *J* = 5.1Hz), 7.58 (s, 1H). ^{13}C NMR (300 MHz, $CDCl_3$): δ = 14.1, 22.6, 24.9, 25.2, 31.7, 39.1, 45.4, 121.1, 125.4, 128.9, 134.8, 144.1, 144.6, 160.6, 163.8, 193.6. Anal. Calcd for $C_{17}H_{20}OS_2$: C, 67.06; H, 6.62. Found: C, 68.82; H, 6.51.

2-Hexyl-7,7-dimetyl-*4H*-cyclopenta-[2,1-*b*:3,4-*b*']dithiophene (7b). Anhydrous ether (6 ml) at 0^{o}C was added to separate batches of $LiAlH_4$ (13 mmol) and $AlCl_3$ (13 mmol), and the resulting mixtures were combined. To this mixture was added 1-(7,7-dimetyl-*4H*-cyclopenta-[2,1-*b*:3,4-*b*']dithiophen-2-yl)haxan-1-one **6b** (5.3 mmol) in dry ether at 0 °C. The mixture was allowed to warm to r.t. and then stirred for 3 h. The reaction was quenched by the careful addition of ether (2 ml) and 2 M aqueous HCl (4 ml). The product was extracted by washing the gray precipitate with ether. The combined organic layers were dried ($MgSO_4$). Column chromatography (hexane) afforded **7b**. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, 3H, *J* = 6.9Hz), 1.27 (m, 6H), 1.42 (s, 6H), 1.68 (t, 2H, *J* =7.2Hz), 2.80 (t, 2H, *J* = 7.5Hz), 6.69 (s, 1H), 6.95 (d, 1H, *J* = 4.8Hz), 7.07 (d, 1H, *J* = 5.1Hz). ^{13}C NMR (300 MHz, $CDCl_3$): δ = 14.2, 22.7, 25.2, 28.9, 31.0, 31.7, 31.9, 45.0, 118.1, 120.8, 123.9, 132.4, 135.9, 146.8, 159.3, 160.2 Anal. Calcd for $C_{17}H_{22}S_2$: C, 70.29; H, 7.63. Found: C, 70.01; H, 7.41.

2-(6-Hexyl-4,4-dimetyl-*4H*-cyclopenta-[2,1-*b*:3,4-*b*']dithiophenyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8b) : *n*-BuLi solution in hexanes (6 mmol) was added via a syringe to a stirred solution of 2-hexyl-7,7-dimetyl-*4H*-cyclopenta-[2,1-*b*:3,4-*b*']dithiophene **7b** (5 mmol) in THF (10 mL) at –30 ºC. Stirring was continued for 1 h and 2-isoproxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6 mmol) was added via syringe at –30 ºC. The reaction mixture was stirred at r.t. for 4 h. The reaction mixture was added H_2O, and then the layers were separated, the organic layer was washed with H_2O, and dried over anhydride $MgSO_4$. The solvent was distilled off under reduced pressure. The pure product was obtained by column chromatography on silica gel (ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$) : δ = 0.87 (t, 3H, *J* = 6.9Hz), 1.35 (m, 18H), 1.42 (s, 6H), 1.68 (t, 2H, *J* = 7.2Hz), 2.80 (t, 2H, *J* = 7.5Hz), 6.69 (s, 1H), 7.48 (s, 1H).