Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics


*Supporting Information*

# Modulating the assembly of organic dye molecules on titania nanocrystals via alkyl chain elongation for efficient mesoscopic cobalt solar cells

**Yiming Cao,[a,b] Ning Cai,[a,b] Yinglin Wang,[a] Renzhi Li,*[a] Yi Yuan*[c] and Peng Wang*[a]**

[a] *State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China. E-mail: renzhi.li@ciac.jl.cn; peng.wang@ciac.jl.cn*

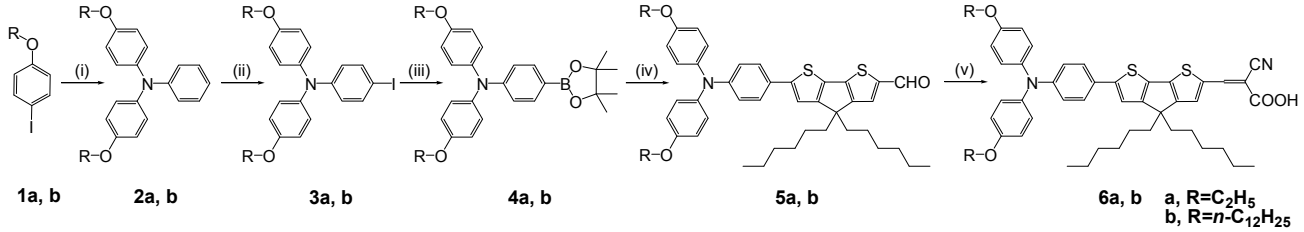
[b] *Graduate School, Chinese Academy of Sciences, Beijing, 100039, China*

[c] *College of Materials Science and Chemical Engineering, Harbin Engineering University, Harbin, 150001, China. E-mail: yi.yuan@hrbeu.edu.cn*

# 1. EXPERIMENTAL SECTION

## 1.1 Synthesis and characterization of C234 and C235 dye molecules

Scheme S1. Synthetic route of **C234** (6a) and **C235** (6b)[a]




[a]Reagents: (i) aniline, CuCl, 1,10-phenanthroline, KOH, toluene; (ii) $I_2$, $H_5IO_6$, EtOH; (iii) bis(pinacolato)diboron, Pd(dppf)$Cl_2$, KOAc, DMSO; (iv) 6-bromo-4,4-dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene-2-carbaldehyde, palladium diacetate, potassium phosphate, 1,4-dioxane/water (5/1, *v*/*v*); (v) cyanoacetic acid, piperidine, $CHCl_3$.

The synthetic route of C234 and C235 is shown in Scheme S1 and the experimental details are presented as follows. All solvents and reagents, unless otherwise stated, were of analytical quality and used as received. 1-ethoxyl-4-iodobenzene (**1a**),[S1] 1-(*n*-dodecyloxyl)-4-iodobenzene (**1b**)[S2] and 6-bromo-4,4-dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene-2-carbaldehyde[S3] were synthesized according to the literature methods.

***N*,*N*-bis(4-ethoxyphenyl)aniline (2a)**. To a stirred solution of **1a** (36.691 g, 147.90 mmol), aniline (5.510 g, 59.16 mmol), and 1,10-phenanthroline (2.132 g, 11.83 mmol) in toluene (115 mL) at 100 °C were added potassium hydroxide (26.556 g, 473.28 mmol) and cuprous chloride (1.168 g, 11.83 mmol) under argon. The reaction mixture was refluxed for 12 h and then water (80 mL) added. The crude product was extracted into dichloromethane, and the organic layer was washed with water and dried over anhydrous sodium sulfate. After removing solvent under reduced pressure, the residue was purified by column chromatography (ethyl acetate/petroleum ether 60–90 °C, 1/50, *v*/*v*) on silica gel to yield a yellow viscous liquid. Yield: 77 %. $^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$: 7.15 (t, *J*=7.8 Hz, 2H), 6.95 (d, *J*=9.0 Hz, 4H), 6.86 (d, *J*=9.0 Hz, 4H), 6.80 (t, *J*=7.2 Hz, 1H), 6.75 (d, *J*=8.4 Hz, 2H), 3.96 (m, 4H), 1.29 (t, *J*=6.9 Hz, 6H). $^{13}$C NMR (150 MHz, DMSO-$d_6$) $\delta$: 154.82, 148.41, 140.16, 129.02, 126.37, 120.16, 119.70, 115.36, 63.14, 14.68. MS (ESI) *m*/*z* calcd. for ($C_{22}H_{23}NO_2$): 333.2. Found: 334.5 ([M+H]$^+$). Anal. Calcd. for $C_{22}H_{23}NO_2$: C, 79.25, H, 6.95, N, 4.20. Found: C, 79.16, H, 6.87, N, 4.11.

***N*,*N*-bis(4-dodecyloxyphenyl)aniline (2b)**. The same procedure as above (**2a**). White solid. Yield: 70 %. $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$: 7.16 (t, *J*=7.8 Hz, 2H), 6.96 (d, *J*=9.0 Hz, 4H), 6.87 (d, *J*=9.0 Hz, 4H), 6.82 (t, *J*=6.6 Hz, 1H), 6.77 (d, *J*=7.8 Hz, 2H), 3.92 (m, 4H), 1.68 (m, 4H), 1.39 (m, 4H), 1.29 (m, 32H), 0.85 (t, *J*=6.9 Hz, 6H). $^{13}$C NMR (150 MHz, DMSO-$d_6$) $\delta$: 155.29, 148.85, 140.97, 128.86, 126.39, 120.81, 120.39, 115.21, 68.27, 31.91, 29.66, 29.63, 29.59, 29.41, 29.37, 29.34, 26.08, 22.68, 14.10. MS (ESI) *m*/*z* calcd. for ($C_{42}H_{63}NO_2$): 613.5. Found: 614.7. ([M+H]$^+$). Anal. Calcd. for $C_{42}H_{63}NO_2$: C, 82.16, H, 10.34, N, 2.28. Found: C, 82.04, H, 10.23, N, 2.17.

***N*,*N*-bis(4-ethoxyphenyl)-4-iodoaniline (3a)**. A suspended solution of **2a** (3.500 g, 10.50 mmol), iodine (1.372 g, 5.40 mmol), and periodic acid (0.410 g, 1.80 mmol) in anhydrous ethanol (40 mL) was under argon for overnight reaction at 55 $^{o}$C. The reaction mixture was cooled to room temperature and then saturated sodium subsulfite aqueous solution (30 mL) added. The crude product was extracted into chloroform, washed with water, and dried over anhydrous sodium sulfate. After removing solvent under reduced pressure, the residue was purified by column chromatography (ethyl acetate/petroleum ether 60–90 $^{o}$C, 1/50, *v*/*v*) on silica gel to yield a colourless viscous liquid. Yield: 94 %. $^{1}$H NMR (300 MHz, DMSO-$d_6$) $\delta$: 7.42 (d, *J*=8.4 Hz, 2H), 6.99 (d, *J*=8.7 Hz, 4H), 6.87 (d, *J*=8.7 Hz, 4H), 6.52 (d, *J*=8.7 Hz, 2H), 3.97 (m, 4H), 1.29 (t, *J*=6.9 Hz, 6H). $^{13}$C NMR (150 MHz, DMSO-$d_6$) $\delta$: 155.34, 148.35, 139.33, 137.40, 126.94, 120.94, 115.49, 81.60, 63.18, 39.92, 39.78, 39.64, 39.50, 39.36, 39.22, 39.08, 14.67. MS (ESI) *m*/*z* calcd. for ($C_{22}H_{22}INO_2$): 459.1. Found: 460.1 ([M+H]$^{+}$). Anal. Calcd. for $C_{22}H_{22}INO_2$: C, 57.53, H, 4.83, N, 3.05. Found: C, 57.40, H, 4.75, N, 2.96.

***N*,*N*-bis(4-dodecyloxyphenyl)-4-iodoaniline (3b)**. The same procedure as above (**3a**). Colorless viscous liquid. Yield: 93 %. $^{1}$H NMR (300 MHz, DMSO-$d_6$) $\delta$: 7.42 (d, *J*=8.4 Hz, 2H), 6.99 (d, *J*=8.7 Hz, 4H), 6.87 (d, *J*=8.7 Hz, 4H), 6.52 (d, *J*=8.7 Hz, 2H), 3.97 (m, 4H), 1.29 (t, *J*=6.9 Hz, 6H). $^{13}$C NMR (150 MHz, DMSO-$d_6$) $\delta$: 155.74, 148.68, 140.16, 137.60, 126.70, 122.13, 115.34, 81,72, 68.27, 31.91, 29.66, 29.63, 29.59, 29.58, 29.40, 29.34, 26.06, 22.68, 14.10. MS (ESI) *m*/*z* calcd. for ($C_{42}H_{62}INO_2$): 739.4. Found: 740.5 ([M+H]$^{+}$). Anal. Calcd. for $C_{42}H_{62}INO_2$: C, 68.18, H, 8.45, N, 1.89. Found: C, 68.07, H, 8.32, N, 1.78.

**4,4,5,5-tetramethyl-2-{4-[*N*,*N*-bis(4-ethoxyphenyl)amino]phenyl}-1,3,2-dioxaborolane (4a)**. A mixture of **3a** (2.300 g, 5.01 mmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (1.335 g, 5.26 mmol), potassium acetate (1.474 g, 15.02 mmol), and Pd(dppf)$Cl_2$ (0.110 g, 0.15 mmol) in anhydrous dimethyl sulfoxide (20 mL) was stirred at 45 $^{o}$C under argon for 12 h and then water (20 mL) added. The crude product was extracted into ethyl acetate, washed with water, and dried over anhydrous sodium sulfate. After removing solvent under reduced pressure, the residue was purified by column chromatography (ethyl acetate/petroleum ether 60–90 $^{o}$C, 1/30, *v*/*v*) on silica gel to yield a white powder. Yield: 71 %. $^{1}$H NMR (300 MHz, DMSO-$d_6$) $\delta$: 7.42 (d, *J*=8.7 Hz, 2H), 7.02 (d, *J*=8.7 Hz, 4H), 6.89 (d, *J*=9.0 Hz, 4H), 6.64 (d, *J*=8.4 Hz, 2H), 3.98 (m, 4H), 1.30 (t, *J*=6.9 Hz, 6H), 1.23 (s, 12H). $^{13}$C NMR (150 MHz, DMSO-$d_6$) $\delta$: 155.52, 151.14, 139.18, 135.59, 127.44, 116.83, 115.45, 83.07, 63.15, 24.60, 14.65. MS (ESI) *m*/*z* calcd. for ($C_{28}H_{34}BNO_4$): 459.3. Found: 460.5 ([M+H]$^{+}$). Anal. Calcd. for $C_{28}H_{34}BNO_4$: C, 73.21, H, 7.46, N, 3.05. Found: C, 73.15, H, 7.38, N, 2.95.

**4,4,5,5-tetramethyl-2-{4-[*N*,*N*-bis(4-dodecyloxyphenyl)amino]phenyl}-1,3,2-dioxaborolane (4b)**. The same procedure as above (**4a**). White powder. Yield: 71 %. $^{1}$H NMR (300 MHz, DMSO-$d_6$) $\delta$: 7.44 (d, *J*=8.4 Hz, 2H), 7.03 (d, *J*=9.0 Hz, 4H), 6.91 (d, *J*=9.0 Hz, 4H), 6.66 (d, *J*=9.0 Hz, 2H), 3.93 (t, *J*=6.6 Hz, 4H), 1.69 (m, 4H), 1.39(m, 4H), 1.25(m, 44H), 0.85 (t, *J*=6.8 Hz, 6H). $^{13}$C NMR (150 MHz, DMSO-$d_6$) $\delta$: 155.73, 151.38, 140.12, 135.65, 127.04, 118.44, 115.19, 83.29, 68.17, 31.85, 29.59, 29.56, 29.52, 29.34, 29.28, 26.01, 24.76, 22.61, 14.05. MS (ESI) *m*/*z* calcd. for ($C_{48}H_{74}BNO_4$): 739.6. Found: 740.8. ([M+H]$^{+}$). Anal. Calcd. for $C_{48}H_{74}BNO_4$: C,

77.92, H, 10.08, N, 1.89. Found: C, 77.83, H, 9.97, N, 1.77.

**6-{4-[*N*,*N*-bis(4-ethoxyphenyl)amino]phenyl}-4,4-dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene-2-carbaldehyde (5a)**. To a suspended solution of 6-bromo-4,4-dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene-2-carbaldehyde (0.270 g, 0.60 mmol), **4a** (0.301 g, 0.66 mmol), potassium phosphate (1.900 g, 8.95 mmol), Sphos (0.007 g, 0.02 mmol) and 1,4-dioxane/water (5/1, *v*/*v*, 6 mL) was added palladium diacetate (0.003 g, 0.01 mmol). The reaction mixture was heated up to 40 °C and react for 2 h. After cooled to room temperature, 10 mL water was added. The crude compound was extracted into ethyl acetate, washed with brine and water, and dried over anhydrous sodium sulfate. After removing solvent under reduced pressure, the residue was purified by column chromatography (ethyl acetate/petroleum ether 60–90 °C, 1/40, *v*/*v*) on silica gel to yield an orange solid. Yield: 96 %. $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$: 9.80 (s, 1H), 7.95 (s, 1H), 7.50 (d, *J*=8.4 Hz, 2H), 7.44 (s, 1H), 7.03 (d, *J*=9.0 Hz, 4H), 6.91 (d, *J*=9.0 Hz, 4H), 6.77 (d, *J*=8.4 Hz, 2H), 4.00 (m, 4H), 1.90 (m, 4H), 1.32 (t, *J*=7.2 Hz, 6H), 1.12 (m, 12H), 0.87 (m, 4H), 0.76 (t, *J*=6.9 Hz, 6H). $^{13}$C NMR (150 MHz, DMSO-$d_6$) $\delta$: 183.13, 163.65, 157.16, 155.28, 149.08, 148.33, 146.67, 142.48, 139.39, 132.28, 126.82, 126.06, 125.35, 119.08, 116.79, 115.43, 63.16, 53.55, 36.75, 30.90, 28.88, 23.96, 21.93, 14.65, 13.76. MS (ESI) *m*/*z* calcd. for ($C_{44}H_{51}NO_3S_2$): 705.3. Found: 706.4 ([M+H]$^+$). Anal. Calcd. for $C_{44}H_{51}NO_3S_2$: C, 74.85, H, 7.28, N, 1.98. Found: C, 74.73, H, 7.16, N, 1.87.

**6-{4-[*N*,*N*-bis(4-ethoxyphenyl)amino]phenyl}-4,4-dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene-2-carbaldehyde (5b)**. The same procedure as above (**5a**). Orange solid. Yield: 95 %. $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$: 9.81 (s, 1H), 7.97 (s, 1H), 7.51 (d, *J*=9.0 Hz, 2H), 7.44 (s, 1H), 7.03 (d, *J*=9.0 Hz, 4H), 6.92 (d, *J*=9.0 Hz, 4H), 6.78 (d, *J*=9.0 Hz, 2H), 3.94 (t, *J*=6.6 Hz, 4H), 1.91 (m, 4H), 1.69 (m, 4H), 1.40 (m, 4H), 1.27 (m, 30H), 1.11 (m, 14H), 0.86 (m, 10H), 0.77 (t, *J*=6.9 Hz, 6H). $^{13}$C NMR (150 MHz, DMSO-$d_6$) $\delta$: 182.28, 163.64, 157.15, 155.80, 150.07, 148.86, 148.43, 142.59, 140.15, 133.25, 126.79, 126.22, 126.13, 120.15, 116.09, 115.34, 68.28, 54.02, 37.77, 31.91, 31.96, 31.56, 29.65, 29.62, 29.59, 29.40, 29.34, 29.29, 26.07, 24.53, 22.68, 22.58, 14.10, 13.99. MS (ESI) *m*/*z* calcd. for ($C_{64}H_{91}NO_3S_2$): 985.6. Found: 986.7 ([M+H]$^+$). Anal. Calcd. for $C_{64}H_{91}NO_3S_2$: C, 77.92, H, 9.30, N, 1.42. Found: C, 77.80, H, 9.21, N, 1.32.

**2-cyano-3-{6-{4-[*N*,*N*-bis(4-ethoxyphenyl)amino]phenyl}-4,4-dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene-2-yl}acrylic acid (6a, C234)**. To a stirred solution of **5a** (0.305 g, 0.50 mmol) and cyanoacetic acid (0.126 g, 1.49 mmol) dissolved in chloroform (30 mL) was added piperidine (0.295 g, 3.47 mmol). The reaction mixture was refluxed under argon for 18 h and then acidified with 2 M hydrochloric acid aqueous solution. The crude product was extracted into chloroform, washed with water, and dried over anhydrous sodium sulfate. After solvent was removed under reduced pressure, the residue was purified by flash chromatography with chloroform and methanol/chloroform (1:10, *v*/*v*) in turn as the eluent to yield a purple powder. Yield: 89%. $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$: 13.35 (s, 1H), 8.41 (s, 1H), 7.93 (s, 1H), 7.53 (d, *J*=9.0 Hz, 2H), 7.48 (s, 1H), 7.05 (d, *J*=9.0 Hz, 4H), 6.92 (d, *J*=9.0 Hz, 4H), 6.78 (d, *J*=8.4 Hz, 2H), 4.01 (m, 4H), 1.88 (m, 4H), 1.33 (t, *J*=6.9 Hz, 6H), 1.13 (m, 12H), 0.89 (m, 4H), 0.77 (t, *J*=6.9 Hz, 6H). $^{13}$C NMR(150 MHz, DMSO-$d_6$) $\delta$: 164.43, 164.22, 157.15, 155.36, 150.28, 148.94, 148.52, 147.08, 139.33, 135.45, 133.14, 132.52, 126.95, 126.20,

125.21, 118.93, 117.38, 116.87, 115.47, 93.29, 63.18, 53.34, 36.76, 30.89, 28.85, 23.97, 21.92, 14.66, 13.78. HR-MS (ESI) *m*/*z* calcd. for ($C_{47}H_{52}N_2O_4S_2$): 772.33685. Found: 771.32578 ([M–H]$^-$). Anal. Calcd. for $C_{47}H_{52}N_2O_4S_2$: C, 73.02, H, 6.78, N, 3.62. Found: C, 72.91, H, 6.64, N, 3.54.

**2-cyano-3-{6-{4-[*N*,*N*-bis(4-dodecyloxyphenyl)amino]phenyl}-4,4-dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b′*]dithiophene-2-yl}acrylic acid (6b, C235)**. The same procedure as above (**6a**). Purple powder. Yield: 91 %. $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$: 13.35 (s, 1H), 8.41 (s, 1H), 7.93 (s, 1H), 7.52 (d, *J*=7.8 Hz, 2H), 7.48 (s, 1H), 7.03 (d, *J*=8.4 Hz, 4H), 6.92 (d, *J*=8.4 Hz, 4H), 6.78 (d, *J*=9.0 Hz, 2H), 3.94 (t, *J*=6.0 Hz, 4H), 1.88 (m, 4H), 1.70 (m, 4H), 1.40 (m, 4H), 1.28 (m, 30H), 1.13 (m, 14H), 0.85 (m, 10H), 0.77 (t, *J*=6.9 Hz, 6H). $^{13}$C NMR (150 MHz, DMSO-$d_6$) $\delta$: 168.78, 165.21, 158.20, 155.92, 152.31, 152.04, 149.22, 148.01, 139.99, 135.53, 133.28, 126.91, 126.40, 125.72, 119.92, 117.06, 116.08, 115.38, 91.34, 68.30, 54.15, 37.82, 31.91, 31.54, 29.66, 29.63, 29.59, 29.41, 29.34, 26.08, 24.53, 22.68, 22.57, 14.11, 13.99. HR-MS (ESI) *m*/*z* calcd. for ($C_{67}H_{92}N_2O_4S_2$): 1052.64985. Found: 1051.65864 ([M–H]$^-$). Anal. Calcd. for $C_{67}H_{92}N_2O_4S_2$: C, 76.38, H, 8.80, N, 2.66. Found: C, 76.25, H, 8.69, N, 2.54.

**1.2 References**

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## 2. ADDITIONAL DATA

**Table S1** The intensities (*I*) of $Ti2p_{3/2}$ signal originating from samples of $TiO_2$, C224/$TiO_2$, C220/$TiO_2$, C234/$TiO_2$ and C235/$TiO_2$

| sample | *I*/a.u. | $d^a$/Å |
|---|---|---|
| $TiO_2$ | 27999 | |
| C224/$TiO_2$ | 18054 | 14 |
| C220/$TiO_2$ | 13828 | 22 |
| C234/$TiO_2$ | 19158 | 12 |
| C235/$TiO_2$ | 13676 | 23 |

[a] The mean thickness of organic coatings on titania surface.