

## ***Electronic Supplementary Information***

### **Electrical and photophysical analyses on the impacts of arylamine electron donors in cyclopentadithiophene dye-sensitized solar cells†**

Mingfei Xu,<sup>ab</sup> Difei Zhou,<sup>ab</sup> Ning Cai,<sup>ab</sup> Jignyuan Liu,<sup>a</sup> Renzhi Li\*<sup>a</sup> and Peng Wang\*<sup>a</sup>

<sup>a</sup> State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

<sup>b</sup> Graduate School, Chinese Academy of Sciences, Beijing 100039, China

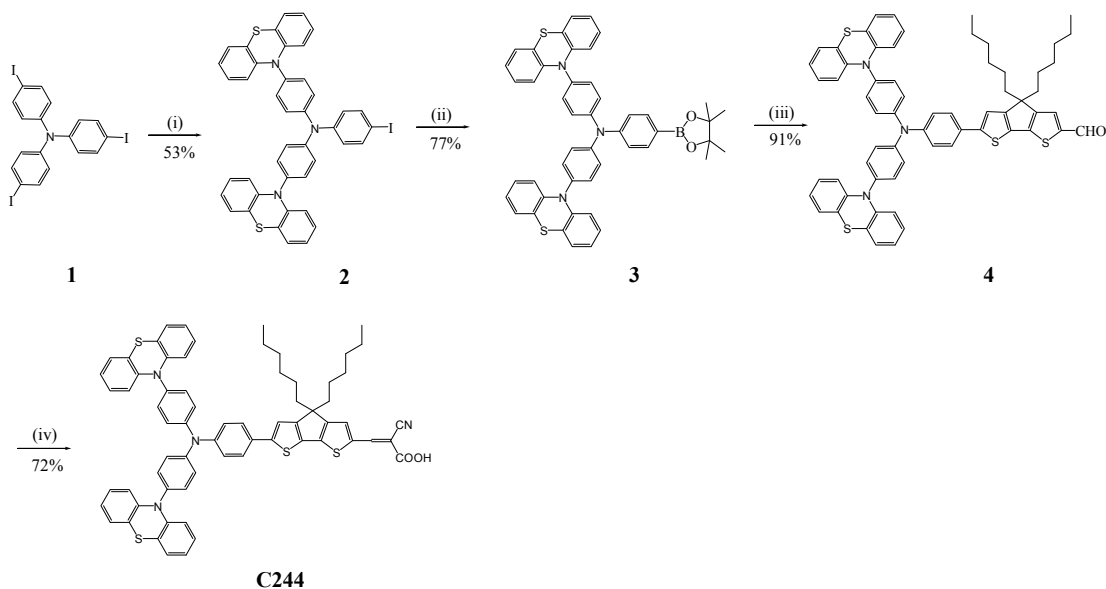
E-mail: renzhi.li@ciac.jl.cn; peng.wang@ciac.jl.cn

## Table of contents

1. Synthesis of intermediates of C244–C246.....	S3
2. Synthesis of cobalt(II) and cobalt(III) redox mediators.....	S10
3. Analysis of chemical capacitance ( $C_{\mu}$ ) and interfacial charge transfer resistance ( $R_{ct}$ ).....	S11
4. Additional experimental data .....	S12
5. References.....	S15

## 1. Synthesis of intermediates of C244–C246

Scheme 1. Synthetic Route of C244<sup>a</sup>



<sup>a</sup> Reagents: (i) phenothiazine,  $P(t\text{-Bu})_3$ ,  $\text{Pd}(\text{dba})_2$ ,  $\text{NaO}(t\text{-Bu})$ , toluene; (ii) bis(pinacolato)diboron,  $\text{Pd}(\text{dppf})\text{Cl}_2$ ,  $\text{KOAc}$ , DMSO; (iii) 6-bromo-4,4-dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-2-carbaldehyde,  $\text{Pd}(\text{OAc})_2$ , Sphos,  $\text{K}_3\text{PO}_4$ , THF,  $\text{H}_2\text{O}$ ; (iv) cyanoacetic acid, piperidine,  $\text{CHCl}_3$ .

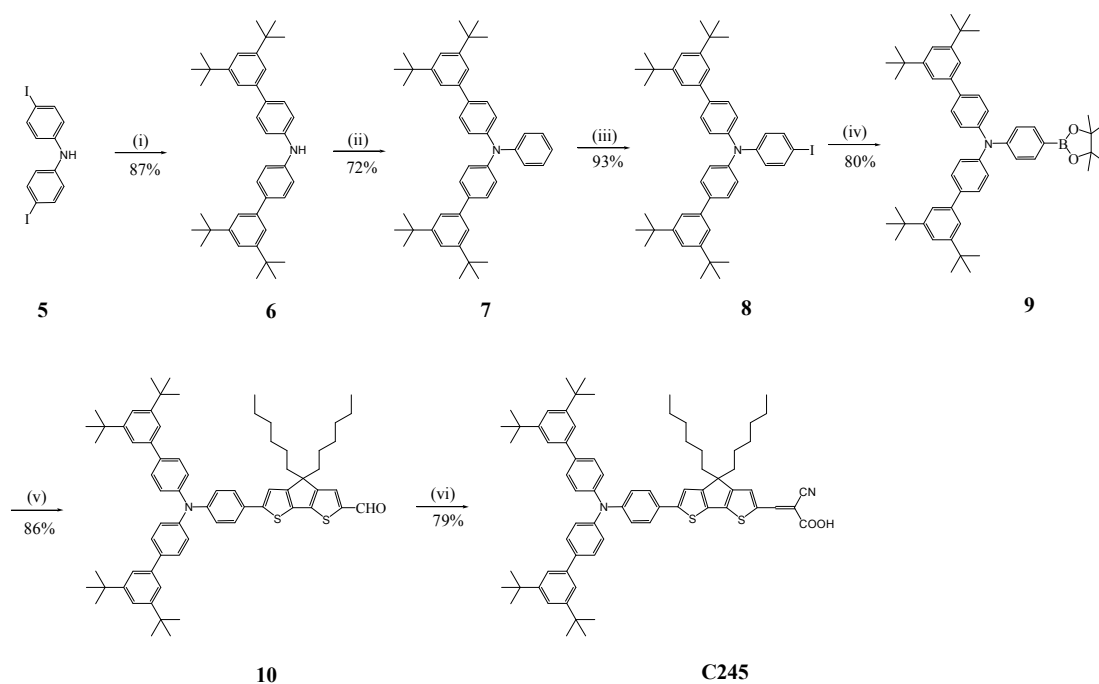
***N*-(4-(10*H*-phenothiazin-10-yl)phenyl)-*N*-(4-iodophenyl)-4-(10*H*-phenothiazin-10-yl)benzenamine (2).** A mixture of tris(4-iodophenyl)amine (0.200 g, 0.322 mmol), phenothiazine (0.128 g, 0.643 mmol) and  $\text{NaO}(t\text{-Bu})$  (0.093 g, 0.965 mmol) in toluene (10 mL) was added  $P(t\text{-Bu})_3$  (0.033 g, 0.016 mmol) and  $\text{Pd}(\text{dba})_2$  (0.009 g, 0.016 mmol) under nitrogen. The solution was heated to reflux for 30 hours under argon and then cooled to room temperature. The mixture was extracted with chloroform 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 (toluene/petroleum ether 60–90 °C, 1/5, *v/v*) on silica gel to get a white powder (0.131 g, 53% yield). <sup>1</sup>H NMR (600 MHz,  $\text{DMSO}-d_6$ )  $\delta$ : 7.72 (d,  $J=8.4$  Hz, 2H), 7.35 (s, 8H), 7.08 (d,  $J=8.4$  Hz, 2H), 7.06 (d,  $J=8.4$  Hz, 4H), 6.97 (m, 4H), 6.86 (m, 4H), 6.33 (d,  $J=8.4$  Hz, 4H). <sup>13</sup>C NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 146.44, 144.30, 138.69, 135.92, 131.65, 126.86, 125.59, 122.61, 120.63, 116.18. MS (ESI) *m/z* calcd. for  $(\text{C}_{42}\text{H}_{28}\text{IN}_3\text{S}_2)^+$ : 756.1. Found: 757.1. ( $[\text{M}+\text{H}]^+$ ). Anal. Calcd. for  $\text{C}_{42}\text{H}_{28}\text{IN}_3\text{S}_2$ : C, 65.88; H, 3.69; N, 5.49. Found: C, 65.42; H, 3.77; N, 5.34.

***N*-(4-(10*H*-phenothiazin-10-yl)phenyl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-4-(10*H*-**

**phenothiazin-10-yl)benzenamine (3).** A mixture of compound **2** (0.070 g, 0.091 mmol) and KOAc (0.027 g, 0.273 mmol) in DMSO (5 mL) was stirred under argon for 5 min, then bis(pinacolato)diboron (0.024 g, 0.096 mmol) and Pd(dppf)Cl<sub>2</sub> (0.002 g, 0.003 mmol) added. The solution was stirred at 45 °C for 6 hours and water (40 mL) was added to terminate the reaction. The mixture was extracted with ethyl acetate and the organic layer was dried over anhydrous sodium sulfate. After removing solvent under reduced pressure, the residue was purified by column chromatography (toluene/petroleum ether 60–90 °C, 1/3, v/v) on silica gel to get a white powder (0.054 g, 77% yield). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 7.71 (d, *J*=8.0 Hz, 2H), 7.36 (s, 8H), 7.23 (d, *J*=8.0 Hz, 2H), 7.04 (m, 4H), 6.97 (m, 4H), 6.86 (m, 4H), 6.36 (d, *J*=8.0 Hz, 4H), 1.24 (s, 12H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 144.31, 138.72, 135.97, 131.62, 126.86, 125.59, 122.62, 120.70, 116.22, 83.49, 25.02. MS (ESI) *m/z* calcd. for (C<sub>48</sub>H<sub>40</sub>BN<sub>3</sub>O<sub>2</sub>S<sub>2</sub>): 765.3. Found: 766.3. ([M+H]<sup>+</sup>). Anal. Calcd. for C<sub>48</sub>H<sub>40</sub>BN<sub>3</sub>O<sub>2</sub>S<sub>2</sub>: C, 75.28; H, 5.26; N, 5.49. Found: C, 75.17; H, 5.34; N, 5.33.

**6-{4-(Bis(4-(10*H*-phenothiazin-10-yl)phenyl)amino)phenyl}-4,4-dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-2-carbaldehyde (4).** A mixture of compound **3** (0.707 g, 0.923 mmol), 6-bromo-4,4-dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-2-carbaldehyde (0.381 g, 0.839 mmol) and K<sub>3</sub>PO<sub>4</sub> (0.980 g, 4.615 mmol) in THF/H<sub>2</sub>O (25 mL, 5/1, v/v) was added Pd(OAc)<sub>2</sub> (0.004 g, 0.018 mmol) and Sphos (0.008 g, 0.018 mmol) under argon. The solution was stirred for 12 hours at 40 °C and then extracted with chloroform. The organic layer was washed with water and dried over anhydrous sodium sulfate and removed under reduced pressure. The residue was purified by column chromatography (toluene/petroleum ether 60–90 °C, 1/1, v/v) on silica gel to get an orange powder (0.851 g, 91% yield). <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>) δ: 9.82 (s, 1H), 7.94 (s, 1H), 7.74 (d, *J*=8.4 Hz, 2H), 7.57 (s, 1H), 7.39 (d, *J*=8.4 Hz, 4H), 7.37 (d, *J*=8.4 Hz, 4H), 7.31 (d, *J*=8.4 Hz, 2H), 7.06 (m, 4H), 6.97 (m, 4H), 6.86 (m, 4H), 6.36 (d, *J*=8.4 Hz, 4H), 1.76 (m, 4H), 1.11 (m, 12H), 0.84 (m, 4H), 0.77 (t, *J*=6.4 Hz, 6H). <sup>13</sup>C NMR (150 MHz, THF-*d*<sub>8</sub>) δ: 182.94, 164.48, 158.97, 149.89, 148.37, 148.22, 147.85, 145.92, 145.63, 137.45, 135.93, 133.05, 131.78, 131.23, 128.13, 128.07, 127.92, 126.98, 126.80, 123.80, 122.10, 118.99, 117.61, 55.55, 39.15, 33.03, 31.12, 26.26, 23.96, 14.83. MS (ESI) *m/z* calcd. for (C<sub>64</sub>H<sub>57</sub>N<sub>3</sub>OS<sub>4</sub>): 1011.3. Found: 1012.3 ([M+H]<sup>+</sup>). Anal. Calcd. for C<sub>64</sub>H<sub>57</sub>N<sub>3</sub>OS<sub>4</sub>: C, 75.93; H, 5.67; N, 4.15. Found: C, 75.91; H, 6.74; N, 4.02.

**Scheme 2.** Synthetic Route of C245<sup>b</sup>



<sup>b</sup> Reagents: (i) 2-(3,5-di-*tert*-butylphenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane, Pd(PPh<sub>3</sub>)<sub>4</sub>, Aliquat 336, Na<sub>2</sub>CO<sub>3</sub>, toluene; (ii) iodobenzene, KOH, 1,10-phenanthroline, CuCl, toluene; (iii) I<sub>2</sub>, H<sub>5</sub>IO<sub>6</sub>, EtOH; (iv) bis(pinacolato)diboron, Pd(dppf)Cl<sub>2</sub>, KOAc, DMSO; (v) 6-bromo-4,4-dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-2-carbaldehyde, Pd(OAc)<sub>2</sub>, Sphos, K<sub>3</sub>PO<sub>4</sub>, THF, H<sub>2</sub>O; (vi) cyanoacetic acid, piperidine, CHCl<sub>3</sub>.

**Bis(3',5'-di-*tert*-butylbiphenyl-4-yl)aniline (6).** A mixture of bis(4-iodophenyl)amine (1.040 g, 2.470 mmol), 2-(3,5-di-*tert*-butylphenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (1.718 g, 5.434 mmol), Aliquat 336 (0.020 g, 0.049 mmol) and Na<sub>2</sub>CO<sub>3</sub> aqueous solution (2 M, 6.40 mL) in toluene (30 mL) was added Pd(PPh<sub>3</sub>)<sub>4</sub> (0.246 g, 0.198 mmol) under argon. The solution was refluxed overnight and cooled to room temperature and then extracted with chloroform. 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 get a white powder (1.173 g, 87% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ: 7.52 (d, *J*=8.4 Hz, 4H), 7.40 (m, 6H), 7.18 (d, *J*=8.4 Hz, 4H), 5.82 (s, 1H), 1.38 (s, 36H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 150.93, 145.06, 140.51, 133.26, 128.31, 121.07, 120.54, 115.54, 34.93, 31.53. MS (ESI) *m/z* calcd. for (C<sub>40</sub>H<sub>51</sub>N): 545.4. Found: 546.4 ([M+H]<sup>+</sup>). Anal. Calcd. for C<sub>40</sub>H<sub>51</sub>N: C, 88.02; H, 9.42; N, 2.57. Found: C, 87.91; H, 9.57; N, 2.52.

**Bis(3',5'-di-*tert*-butylbiphenyl-4-yl)aniline (7).** A mixture of compound 6 (0.090 g, 0.165 mmol), iodobenzene

(0.040 g, 0.198 mmol) and 1,10-phenothroline (0.006 g, 0.033 mmol) in toluene (10 mL) was heated to 100 °C under argon. Then KOH (0.074 g, 1.320 mmol) and CuCl (0.003 g, 0.033 mmol) were added to the solution, which was refluxed for another 12 hours. The mixture was extracted with chloroform 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 (toluene/petroleum ether 60–90 °C, 1/5, v/v) on silica gel to get a white solid (0.074 g, 72% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.70 (d, *J*=5.4 Hz, 2H), 7.40 (d, *J*=5.4 Hz, 4H), 7.32 (m, 7H), 7.09 (d, *J*=5.4 Hz, 2H), 6.76 (d, *J*=5.4 Hz, 4H), 1.37 (s, 36H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 150.91, 145.48, 140.54, 137.47, 132.98, 130.22, 128.28, 127.44, 121.05, 120.49, 115.34, 34.92, 31.53. MS (ESI) *m/z* calcd. for (C<sub>46</sub>H<sub>55</sub>N): 621.4. Found: 622.4 ([M+H]<sup>+</sup>). Anal. Calcd. for C<sub>46</sub>H<sub>55</sub>N: C, 88.83; H, 8.91; N, 2.25. Found: C, 88.72; H, 9.04; N, 2.24.

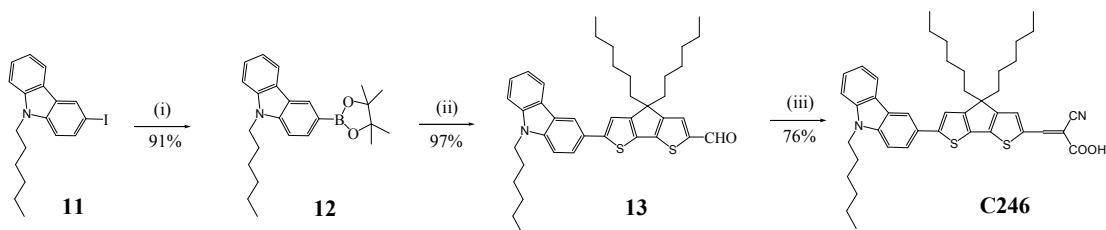
***N,N*-bis(3',5'-di-*tert*-butylbiphenyl-4-yl)-4-iodoaniline (8).** A mixture of compound **7** (0.873 g, 1.404 mmol), I<sub>2</sub> (0.306 g, 1.203 mmol) and H<sub>5</sub>IO<sub>6</sub> (45.730 mg, 0.201 mmol) in EtOH (50 mL) was stirred at 40 °C for 18 hours under argon. Then the mixture was extracted with chloroform, washed with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> aqueous solution 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, 1/30, v/v) on silica gel to get a white solid (0.976 g, 93% yield). <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>) δ: 7.50 (d, *J*=8.4 Hz, 2H), 7.46 (d, *J*=8.4 Hz, 4H), 7.32 (m, 6H), 7.11 (d, *J*=8.4 Hz, 4H), 6.87 (d, *J*=8.4 Hz, 2H), 1.32 (s, 36H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 150.91, 145.22, 143.12, 140.51, 133.12, 129.31, 128.27, 121.05, 120.98, 120.51, 117.80, 115.46, 34.91, 31.52. MS (ESI) *m/z* calcd. for (C<sub>46</sub>H<sub>54</sub>IN): 747.3. Found: 748.3 ([M+H]<sup>+</sup>). Anal. Calcd. for C<sub>46</sub>H<sub>54</sub>IN: C, 73.88; H, 7.28; N, 1.87. Found: C, 73.77; H, 7.36; N, 1.81.

**4,4,5,5-Tetramethyl-2-{4-[*N,N*-(bis(3',5'-di-*tert*-butylbiphenyl)-4-yl)-amino]phenyl}-1,3,2-dioxaborolane (9).** A mixture of compound **8** (0.450 g, 0.602 mmol) and KOAc (0.018 g, 0.181 mmol) in DMSO (40 mL) was stirred under argon for 5 minutes, then bis(pinacolato)diboron (0.168 g, 0.662 mmol) and Pd(dppf)Cl<sub>2</sub> (0.013 g, 0.018 mmol) added. The solution was stirred at 45 °C for 6 hours and water (40 mL) was added to terminate the reaction. The mixture was extracted with ethyl acetate and the organic layer was 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, 1/20, v/v) on silica gel to get a white powder (0.361 g, 80% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.62 (d, *J*=8.4 Hz, 2H), 7.38 (d, *J*=8.4 Hz, 4H), 7.36 (m, 6H), 6.75 (d, *J*=8.4 Hz, 4H), 6.65 (d, *J*=8.4 Hz, 2H), 1.37 (s, 36H), 1.32 (s, 12H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 150.90, 149.26, 145.53, 140.54, 136.39, 132.93, 128.27, 121.03, 120.48, 115.30, 114.05, 83.27, 34.91, 31.52, 24.82. MS (ESI) *m/z* calcd.

for (C<sub>52</sub>H<sub>66</sub>BNO<sub>2</sub>): 747.5. Found: 748.5. ([M+H]<sup>+</sup>). Anal. Calcd. for C<sub>52</sub>H<sub>66</sub>BNO<sub>2</sub>: C, 83.51; H, 8.89; N, 1.87. Found: C, 83.42; H, 8.96; N, 1.82.

**6-{4-[N,N-(bis(3',5'-di-*tert*-butylbiphenyl)-4-yl)-amino]phenyl}-4,4-dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-2-carbaldehyde (10).** A mixture of compound **9** (0.310 g, 0.414 mmol), 6-bromo-4,4-dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-2-carbaldehyde (0.171 g, 0.376 mmol) and K<sub>3</sub>PO<sub>4</sub> (0.400 g, 1.880 mmol) in THF/H<sub>2</sub>O (15 mL, 5/1, v/v) was added Pd(OAc)<sub>2</sub> (0.002 g, 0.008 mmol) and Sphos (0.003 g, 0.008 mmol) under argon. The solution was stirred for 12 hours at 40 °C and then extracted with chloroform. The organic layer was washed with water and dried over anhydrous sodium sulfate and removed under reduced pressure. The residue was purified by column chromatography (ethyl acetate/petroleum ether 60–90 °C, 1/20, v/v) on silica gel to get an orange powder (0.355 g, 86% yield). <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>) δ: 9.82 (s, 1H), 7.99 (s, 1H), 7.67 (d, *J*=8.4 Hz, 2H), 7.64 (d, *J*=8.4 Hz, 4H), 7.58 (s, 1H), 7.41 (m, 4H), 7.39 (m, 2H), 7.18 (d, *J*=8.4 Hz, 4H), 7.11 (d, *J*=8.4 Hz, 2H), 1.89 (m, 4H), 1.34 (s, 36H), 1.11 (m, 12H), 0.84 (m, 4H), 0.77 (t, *J*=6.4 Hz, 6H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 182.38, 163.56, 157.39, 151.14, 149.49, 148.21, 147.69, 146.16, 142.88, 139.99, 137.52, 133.90, 129.88, 128.42, 128.32, 126.45, 124.72, 123.64, 121.33, 121.24, 116.74, 54.11, 37.79, 34.99, 31.59, 31.54, 29.64, 24.57, 22.60, 14.01. MS (ESI) *m/z* calcd. for (C<sub>68</sub>H<sub>83</sub>NOS<sub>2</sub>): 993.6 Found: 994.6 ([M+H]<sup>+</sup>). Anal. Calcd. for C<sub>68</sub>H<sub>83</sub>NOS<sub>2</sub>: C, 82.12; H, 8.41; N, 1.41. Found: C, 82.01; H, 8.50; N, 1.37.

**Scheme 3.** Synthetic Route of C246<sup>c</sup>



<sup>c</sup> Reagents: (i) bis(pinacolato)diboron, Pd(dppf)Cl<sub>2</sub>, KOAc, DMSO; (ii) 6-bromo-4,4-dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-2-carbaldehyde, Pd(OAc)<sub>2</sub>, Sphos, K<sub>3</sub>PO<sub>4</sub>; (iii) cyanoacetic acid, piperidine, CHCl<sub>3</sub>.

**9-Hexyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-carbazole (12).** A mixture of **11** (1.360 g, 3.605 mmol) and KOAc (1.061 g, 10.815 mmol) in DMSO (25 mL) was stirred under argon for 5 minutes, then bis(pinacolato)diboron (1.098 g, 4.326 mmol) and Pd(dppf)Cl<sub>2</sub> (0.084 g, 0.115 mmol) added. The solution was stirred at 45 °C for 6 h and water (40 mL) was added to terminate the reaction. The mixture was extracted with ethyl acetate and the organic layer was 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, 1/30, v/v) on silica gel to get a yellow oil (1.237 g, 91% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.19 (d, *J*=2.0 Hz, 1H), 8.03 (d, *J*=7.6 Hz, 1H), 7.52 (dd, *J*=8.8, 2.0 Hz, 1H), 7.47 (m, 1H), 7.38 (d, *J*=8.0 Hz, 1H), 7.22 (m, 2H), 4.25 (t, *J*=7.2 Hz, 2H), 1.85 (m, 2H), 1.36 (m, 6H), 1.26 (s, 12H), 0.85 (t, *J*=7.2 Hz, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 140.69, 139.05, 128.18, 126.28, 124.53, 123.04, 121.79, 120.50, 119.14, 111.47, 110.08, 108.89, 83.47, 43.19, 31.51, 28.84, 26.90, 25.00, 22.49, 13.95. MS (ESI) *m/z* calcd. for (C<sub>24</sub>H<sub>32</sub>BNO<sub>2</sub>): 377.3. Found: 378.3 ([M+H]<sup>+</sup>). Anal. Calcd. for C<sub>24</sub>H<sub>32</sub>BNO<sub>2</sub>: C, 76.39; H, 8.55; N, 3.71. Found: C, 76.47; H, 8.44; N, 3.62.

**6-(9-Hexyl-9*H*-carbazole-2-yl)-4,4-dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-2-carbaldehyde (13).** A mixture of **12** (0.320 g, 0.847 mmol), 6-bromo-4,4-dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-2-carbaldehyde (0.320 g, 0.727 mmol) and K<sub>2</sub>CO<sub>3</sub> (2.401 mL, 2 M, 4.801 mmol) in THF (22 mL) was added Pd(PPh<sub>3</sub>)<sub>4</sub> (0.098 g, 0.085 mmol) under argon. The solution was refluxed for 12 hours and then extracted with ethyl acetate. The organic layer was dried over anhydrous sodium sulfate and removed under reduced pressure. The residue was purified by column chromatography (ethyl acetate/petroleum ether 60–90 °C, 1/30, v/v) on silica gel to get a red powder (0.430 g, 97% yield). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 9.83 (s, 1H), 8.55 (d, *J*=1.6 Hz, 1H), 8.24 (d, *J*=8.4 Hz, 1H), 7.98 (s, 1H), 7.79 (dd, *J*=8.4, 1.6 Hz, 1H), 7.65 (m, 3H), 7.48 (m, 1H), 7.24 (m, 1H), 4.41 (t, *J*=7.2 Hz, 2H), 1.97 (m, 4H), 1.77 (m, 2H), 1.27 (m, 6H), 1.15 (m, 12H), 0.94 (m, 4H), 0.80 (m, 9H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ:



183.20, 163.79, 157.14, 157.06, 150.40, 146.80, 142.48, 140.56, 139.88, 132.38, 131.60, 126.20, 123.49, 122.65, 121.96, 120.60, 119.10, 117.22, 117.11, 109.92, 109.57, 53.65, 42.34, 36.82, 30.93, 28.93, 28.45, 26.06, 24.02, 21.96, 13.77. MS (ESI)  $m/z$  calcd. for (C<sub>40</sub>H<sub>49</sub>NOS<sub>2</sub>): 623.3. Found: 624.3 ([M+H]<sup>+</sup>). Anal. Calcd. for C<sub>40</sub>H<sub>49</sub>NOS<sub>2</sub>: C, 77.00; H, 7.92; N, 2.24. Found: C, 77.11; H, 7.81; N, 2.14.

## 2. Synthesis of cobalt(II) and cobalt(III) redox mediators

**Tris(1,10-phenanthroline)cobalt(II) di[tetracyanoborate].** To a 5 mL aqueous solution of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.263 g, 1.106 mmol) was dropwise added 3 mL methanolic solution of 1,10-phenanthroline (0.698 g, 3.871 mmol). The mixture was stirred for 30 min and then added 3 mL methanol/water solution of 1-ethyl-3-methylimidazolium tetracyanoborate (2.000 g, 8.848 mmol). After stirring for 30 min, the precipitate was filtered, washed with water and dried under vacuum to yield a yellow powder (0.840 g, 92% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 9.08 (d,  $J=7.2$  Hz, 6H), 8.50 (d,  $J=7.2$  Hz, 6H), 8.00 (s, 6H), 7.77 (d,  $J=7.2$  Hz, 3H), 7.67 (d,  $J=7.2$  Hz, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 197.43, 196.39, 142.48, 131.37, 131.10, 130.86, 121.89, 121.42, 121.19, 120.95. MS (ESI)  $m/z$  calcd. for ( $\text{C}_{44}\text{H}_{24}\text{B}_2\text{CoN}_{14}$ ): 829.18. Found: 714.00. ( $[\text{M}-\text{B}(\text{CN})_4]^+$ ).

**Tris(1,10-phenanthroline)cobalt(III) tri[tetracyanoborate].** To a 5 mL aqueous solution of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.250 g, 1.051 mmol) was dropwise added 0.625 mL methanolic solution of 1,10-phenanthroline (0.625 g, 3.468 mmol). The mixture was stirred for 30 min and then added 2.5 mL bromine water. After refluxing for 30 min, the reaction system was added 1-ethyl-3-methylimidazolium tetracyanoborate (2.000 g, 8.848 mmol), and was refluxed for another 30 min. The suspension was cooled to ambient temperature and the precipitate was filtered, recrystallised from methanol and dried under vacuum to yield a yellow crystal (0.861 g, 87% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 9.16 (d,  $J=7.2$  Hz, 6H), 8.57 (s, 6H), 7.97 (d,  $J=7.2$  Hz, 3H), 7.96 (d,  $J=7.2$  Hz, 3H), 7.66 (d,  $J=7.2$  Hz, 6H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 153.59, 145.61, 141.92, 131.92, 129.15, 128.70, 122.39, 121.92, 121.45, 120.98. MS (ESI)  $m/z$  calcd. for ( $\text{C}_{48}\text{H}_{24}\text{B}_3\text{CoN}_{18}$ ): 944.20. Found: 829.38. ( $[\text{M}-\text{B}(\text{CN})_4]^+$ ).

### 3. Analysis of chemical capacitance ( $C_{\mu}$ ) and interfacial charge transfer resistance ( $R_{ct}$ )

We estimate the quantity of  $E_c - E_{F,redox}$  by analyzing the chemical capacitance ( $C_{\mu}$ ), which takes the following equation:<sup>S1</sup>

$$C_{\mu} = \frac{e^2 N_t d (1-p)}{k_B T_c} \exp\left(\frac{E_{F,redox} - E_c}{k_B T_c}\right) \exp\left(\frac{E_{F,n} - E_{F,redox}}{k_B T_c}\right) \quad (S1)$$

where  $e$  is the elementary charge,  $N_t$  is the total density of surface states (taken as a constant  $2 \times 10^{20} \text{ cm}^{-3}$  so as to facilitate a comparative study<sup>S2</sup>),  $d$  is the thickness of the titania film (2.3  $\mu\text{m}$ ),  $p$  is the film porosity (0.64),  $k_B$  is the Boltzmann constant,  $T_c$  is a parameter depicting the distribution profile of interband states, and  $V$  is the potential bias in impedance measurements. Fitting the  $C_{\mu}$  data in Fig. S2A to eqn (S1) directly affords the values of  $E_c - E_{F,redox}$  as collected in Table 2.

Consider the recently developed  $\beta$ -recombination model, the rate of charge recombination at the titania/electrolyte interface can be expressed as a function of free electron density in titania  $n_c$ , the effective reaction rate constant  $k_0$ , and the reaction order of titania electrons:<sup>S3</sup>

$$U_n = k_0 n_c^{\beta} \quad (S2)$$

Combining eqn (S2) and the function for  $n_c$

$$n_c = N_c \exp\left(\frac{E_{F,n} - E_c}{k_B T}\right), \quad (S3)$$

where  $N_c$  is taken as  $7 \times 10^{20} \text{ cm}^{-3}$ , and the definition of the charge recombination resistance  $R_{ct}$ <sup>S3</sup>

$$R_{ct} = \frac{1}{A} \left( \frac{\partial j_{rec}}{\partial (E_{F,n} - E_{F,redox}) / e} \right)^{-1}, \quad (S4)$$

where  $A$  is the projection area of titania film (0.2826  $\text{cm}^2$ ), and  $j_{rec}$  is the recombination current, we have<sup>S4</sup>

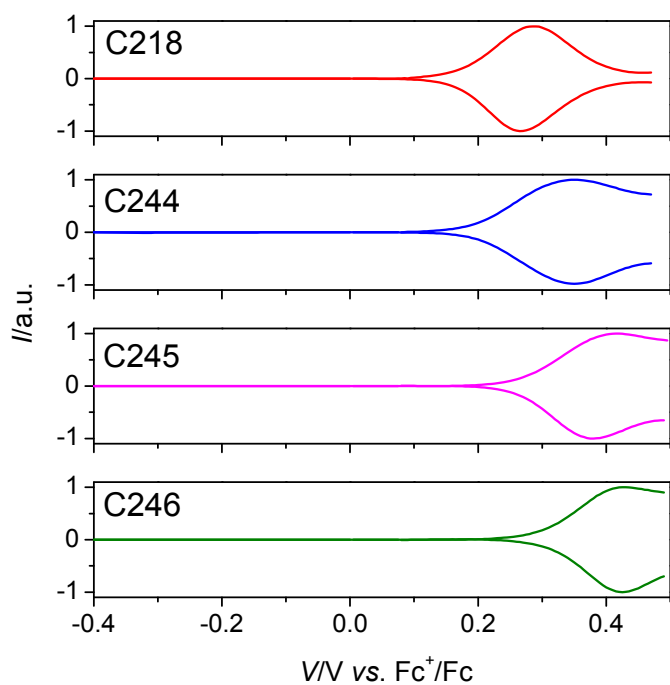
$$R_{ct} = \frac{k_B T}{k_0 \beta N_c^{\beta} e^2 d A} \exp\left[\frac{\beta(E_c - E_{F,redox})}{k_B T}\right] \exp\left(-\frac{\beta(E_{F,n} - E_{F,redox})}{k_B T}\right). \quad (S5)$$

Defining effective recombination constant  $U_{0k} = k_0 N_c^{\beta}$ , eqn (S5) becomes

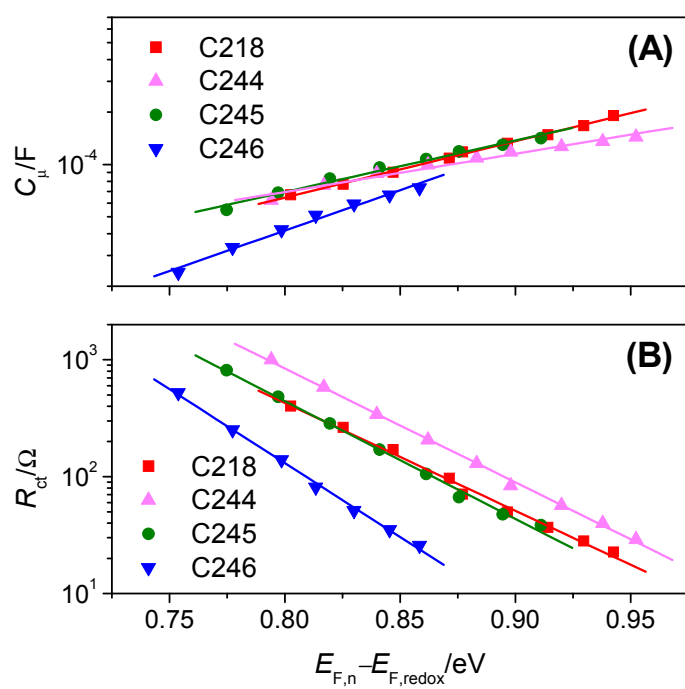
$$R_{ct} = \frac{k_B T}{U_{0k} \beta e^2 d A} \exp\left[\frac{\beta(E_c - E_{F,redox})}{k_B T}\right] \exp\left(-\frac{\beta(E_{F,n} - E_{F,redox})}{k_B T}\right) \quad (S6)$$

On the basis of the as-resolved  $E_c - E_{F,redox}$  values, fitting the  $R_{ct}$  data in Fig. S2B gives  $\beta$  and  $U_{0k}$ , as listed in Table 2.

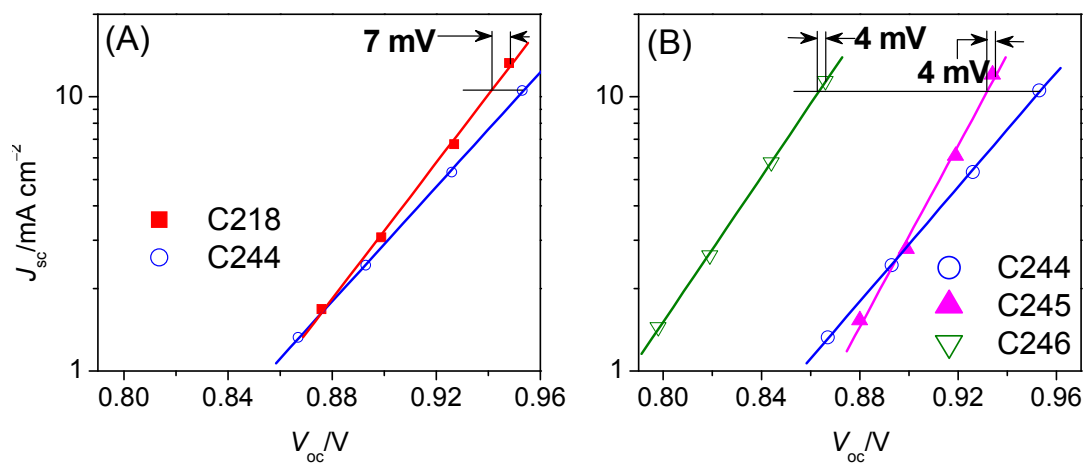
#### 4. Additional experimental data



**Fig. S1** Normalized square-wave voltammograms of dye-coated titania films. Supporting electrolyte: 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide. Scan rate: 5 mV s<sup>-1</sup>.



**Fig. S2** Plots of (A) chemical capacitance (B) interfacial charge recombination resistance as a function of the energy difference  $E_{F,n} - E_{F,redox}$ .



**Fig. S3** Short-circuit photocurrent density plotted against open-circuit photovoltage.

## 5. References

- (S1) J. Bisquert, *Phys. Chem. Chem. Phys.*, 2003, **5**, 5360.
- (S2) E. M. Barea, J. Ortiz, F. J. Payá, F. Fernández-Lazaro, F. Fabregat-Santiago, A. Sastre-Santos and J. Bisquert, *Energy Environ. Sci.*, 2010, **3**, 1985.
- (S3) J. Bisquert and I. Mora-Seró, *J. Phys. Chem. Lett.*, 2010, **1**, 450.
- (S4) Y. Bai, J. Zhang, Y. Wang, M. Zhang and P. Wang, *Langmuir*, 2011, **27**, 4749.