Electronic Supplementary Material (ESI) for Energy and Environmental Science

Electronic supplementary information

Mesoscopic titania solar cells with the tris(1,10-phenanthroline)cobalt redox shuttle: uniped *versus* biped organic dyes

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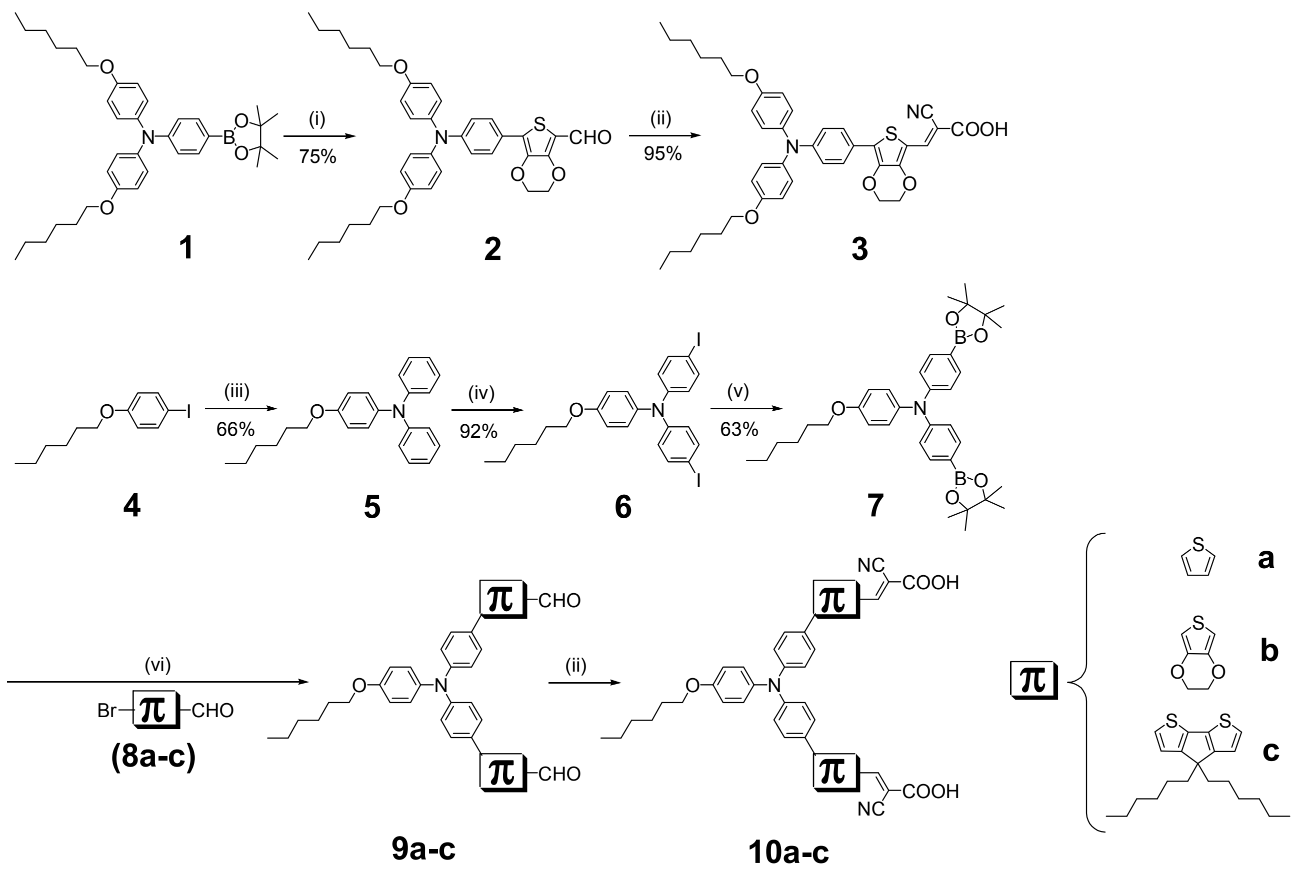
1. Synthesis of intermediates

1.1. Scheme S1: Synthetic route of uniped and biped dyes[a]



[a]Reagents: (i) 5-bromo-3,4-ethylenedioxy-2-formylthiophene (**8b**), $Pd(PPh_3)_4$, K_2CO_3, THF; (ii) cyanoacetic acid, piperidine, $CHCl_3$; (iii) diphenylamine, 1,10-phenathroline, CuCl, KOH, mesitylene; (iv) I_2, H_5IO_6, EtOH; (v) bis(pinacolato)diboron, Pd(dppf)Cl_2, KOAc, DMSO; (vi) $Pd(PPh_3)_4$, K_2CO_3, THF.

1.2. Materials

All solvents and reagents, unless otherwise stated, were of analytical quality and used as received. 4,4,5,5-Tetramethyl-2-{4-[*N*,*N*-bis(4-hexyloxyphenyl)amino]phenyl}-1,3,2-dioxaborolane (**1**),[S1] 1-(*n*-hexyloxy)-4-iodobenzene (**4**),[S2] 5-bromo-thiophene-2-carbaldehyde (**8a**),[S3] 5-bromo-3,4-ethylenedioxy-2-formylthiophene (**8b**)[S4] and 6-bromo-4,4-dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene-2-carbaldehyde (**8c**)[S1] were synthesized according to the literature methods.

1.3. Synthesis of the intermediates of uniped and biped dyes

5-{4-[*N*,*N*-Bis(4-hexyloxyphenyl)amino]phenyl}-3,4-ethylenedioxythienyl-2-carbaldehyde (2). To a suspended solution of **1** (0.62 g, 1.09 mmol), **8b** (0.35 g, 1.41 mmol) and tetrakis(triphenylphosphine)palladium

(0.13 g, 0.11 mmol) in tetrahydrofuran (50 mL) was added potassium carbonate aqueous solution (2 M, 8.20 mL) under argon. The reaction mixture was refluxed for 12 h and then water (50 mL) 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 ^{o}C, 1/3, *v*/*v*) on silica gel to yield a viscous orange oil (75% yield). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 9.81 (s, 2H), 7.59 (d, *J*=9 Hz, 2H), 7.06 (d, *J*=9Hz, 4H), 6.93 (d, *J*=9.0 Hz, 4H), 6.76 (d, *J*=8.4 Hz, 2H), 4.46 (s, 2H), 4.39 (s, 2H), 3.95 (t, *J*=6Hz, 4H), 1.71 (m, 4H), 1.41 (m, 4H), 1.31 (m, 8H), 0.88 (t, *J*=7.2 Hz, 6H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 178.60, 155.74, 149.72, 148.93, 139.01, 136.89, 127.82, 127.56, 127.25, 122.08, 117.99, 115.54, 113.12, 67.61, 65.26, 64.50, 30.95, 28.64, 25.16, 22.03, 13.86. MS (ESI) *m*/*z* calcd. for ($C_{37}H_{43}NO_5S$): 613.29. Found: 614.32 ($[M+H]^+$). Anal. Calcd. for $C_{37}H_{43}NO_5S$: C, 72.40; H, 7.06; N, 2.28. Found: C, 72.49; H, 7.12; N, 2.37.

4-(Hexyloxy)-*N*,*N*-diphenylaniline (5). To a stirred solution of diphenylamine (23.18 g, 136.98 mmol), **4** (50.00 g, 164.37 mmol) and 1,10-phenanthroline (4.94 g, 27.4 mmol) in mesitylene (100 mL) at 100 ^{o}C were added potassium hydroxide (61.45 g, 1.10 mol) and cuprous chloride (2.71 g, 27.40 mmol) under argon. The reaction mixture was refluxed for 12 h and then water (100 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 (toluene/hexane, 1/5, *v*/*v*) on silica gel to yield a yellowish oil (66% yield). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 7.23 (t, *J*=4.8 Hz, 4H), 6.99 (d, *J*=9.6 Hz, 2H), 6.95-6.89 (m, 8H), 3.92 (t, *J*=6.6 Hz, 2H), 1.71 (m, 2H), 1.41 (m, 2H), 1.31 (m, 4H), 0.87 (t, *J*=7.2 Hz, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 155.46, 147.61, 139.69, 129.22, 127.24, 122.18, 121.79, 115.49, 67.56, 30.94, 28.65, 25.15, 22.02, 13.84. MS (ESI) *m*/*z* calcd. for ($C_{24}H_{27}NO$): 345.21. Found: 346.22 ($[M+H]^+$). Anal. Calcd. for $C_{24}H_{27}NO$: C, 83.44; H, 7.88; N, 4.05. Found: C, 83.35; H, 7.81; N, 3.98.

4-(Hexyloxy)-*N*,*N*-bis(4-iodophenyl)aniline (6). A suspended solution of **5** (5.00 g, 14.73 mmol), iodine (3.46 g, 13.65 mmol) and periodic acid (1.04 g, 4.55 mmol) in 95% ethanol (45 mL) was stirred at 55 ^{o}C for 1 h. The reaction mixture was cooled to room temperature and then saturated sodium subsulfite aqueous solution (40 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 (petroleum ether) on silica gel to yield a yellow oil (92% yield). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 7.55 (d, *J*=8.4 Hz, 4H), 7.01 (d, *J*=9.6 Hz, 2H), 6.92 (d, *J*=9.6 Hz, 2H), 6.74 (d, *J*=8.4 Hz, 4H), 3.93 (t, *J*=6.6 Hz, 2H), 1.71 (m, 2H), 1.41 (m, 2H), 1.31 (m, 4H), 0.87 (t, *J*=7.2 Hz, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 156.07, 146.88, 138.52, 137.88, 127.68, 124.30, 115.70, 85.15, 67.61, 30.94, 28.63, 25.14, 22.02, 13.85. MS (ESI) *m/z* calcd. for ($C_{24}H_{25}I_2NO$): 597.00. Found: 597.98 ($[M+H]^+$). Anal. Calcd. for $C_{24}H_{25}I_2NO$: C, 48.26; H, 4.22; N, 2.35; Found: C, 48.20; H, 4.17; N, 2.26.

4-(Hexyloxy)-*N*,*N*-bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl) aniline (7). A mixture of **6** (3.00 g, 5.02 mmol), bis(pinacolato)diboron (3.83 g, 15.07 mmol), potassium acetate (2.96 g, 30.14 mmol) and Pd(dppf)Cl_2 (0.03 g, 0.4 mmol) in anhydrous dimethyl sulfoxide (55 mL) was stirred at 45 ^oC under argon for 12 h and then water (45 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 ^oC, 1/20, *v*/*v*) on silica gel to yield a white solid (63% yield). ^1H NMR (600 MHz, DMSO-d_6) δ: 7.55 (d, *J*=8.4 Hz, 4H), 7.01 (d, *J*=9.6 Hz, 2H), 6.93 (d, *J*=9.6 Hz, 2H), 6.92 (d, *J*=8.4 Hz, 4H), 3.95 (t, *J*=6.6 Hz, 2H), 1.71 (m, 2H), 1.41 (m, 2H), 1.31 (m, 4H), 1.27 (m, 24H), 0.87 (t, *J*=7.2 Hz, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 156.40, 150.33, 139.63, 135.79, 128.05, 121.72, 115.40, 83.54, 68.24, 31,60, 29.31, 25.75, 24.85, 22.59, 14.01. MS (ESI) *m/z* calcd. for ($C_{36}H_{49}B_2NO_5$): 597.38. Found: 598.50 ($[M+H]^+$). Anal. Calcd. for $C_{36}H_{49}B_2NO_5$: C, 72.38; H, 8.27; N, 2.34. Found: C, 72.43; H, 8.22; N, 2.41.

General synthesis procedure of 9. To a suspended solution of **4** (1.00 mmol), **8** (1.25 mmol for **6** and 2.50 mmol for **7**) and tetrakis(triphenylphosphine)palladium (0.05 mol for **6** and 0.10 mmol for **7**) in tetrahydrofuran (40 mL) was added potassium carbonate aqueous solution (2 M, 4 mL for **6** and 8 mL for **7**) under argon. The reaction mixture was refluxed for 24 h and then water (50 mL) 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 ^oC, 1/50, *v*/*v*) on silica gel to yield the product.

5-{4-[*N*,*N*-Bis(4-hexyloxyphenyl)amino]phenyl}-3,4-ethylenedioxythienyl-2-carbaldehyde (2). Yield: 75%. ^1H NMR (600 MHz, DMSO-d_6) δ: 9.81 (s, 2H), 7.59 (d, *J*=9 Hz, 2H), 7.06 (d, *J*=9Hz, 4H), 6.93 (d, *J*=9.0 Hz, 4H), 6.76 (d, *J*=8.4 Hz, 2H), 4.46 (s, 2H), 4.39 (s, 2H), 3.95 (t, *J*=6Hz, 4H), 1.71 (m, 4H), 1.41 (m, 4H), 1.31 (m, 8H), 0.88 (t, *J*=7.2 Hz, 6H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 178.60, 155.74, 149.72, 148.93, 139.01, 136.89, 127.82, 127.56, 127.25, 122.08, 117.99, 115.54, 113.12, 67.61, 65.26, 64.50, 30.95, 28.64, 25.16, 22.03, 13.86. MS (ESI) *m/z* calcd. for ($C_{37}H_{43}NO_5S$): 613.29. Found: 614.32 ($[M+H]^+$). Anal. Calcd. for $C_{37}H_{43}NO_5S$: C, 72.40; H, 7.06; N, 2.28. Found: C, 72.49; H, 7.12; N, 2.37.

4-(Hexyloxy)-*N*,*N*-bis[4-(5-formylthien-2-yl)phenyl]aniline (9a). Yield: 92%. ^1H NMR (600 MHz, DMSO-d_6) δ: 9.87 (s, 2H), 8.01 (d, *J*=4.0 Hz, 2H), 7.72 (d, *J*=8.8 Hz, 4H), 7.63 (d, *J*=4.0 Hz, 2H), 7.12 (d, *J*=8.8 Hz, 2H), 7.05

(d, *J*=8.8 Hz, 4H), 6.99 (d, *J*=8.8 Hz, 2H), 3.97 (t, *J*=6.4 Hz, 2H), 1.71 (m, 2H), 1.41 (m, 2H), 1.31 (m, 4H), 0.88 (t, *J*=7.2 Hz, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 183.65, 156.46, 152.68, 147.88, 140.99, 139.34, 138.18, 128.15, 127.40, 126.11, 124.12, 122.32, 115.82, 67.67, 30.94, 28.63, 25.14, 22.01, 13.84. MS (ESI) *m*/*z* calcd. for ($C_{34}H_{31}NO_3S_2$): 565.17. Found: 566.6 ($[M+H]^+$). Anal. Calcd. for $C_{34}H_{31}NO_3S_2$: C, 72.18; H, 5.52; N, 2.48. Found: C, 72.24; H, 5.45; N, 2.55.

4-(Hexyloxy)-*N*,*N*-bis[4-(5-formyl-3,4-ethylenedioxythien-2-yl)phenyl]aniline (9b). Yield: 73%. ^{1}H NMR (600 MHz, DMSO-d_6) δ: 9.85 (s, 2H), 7.69 (d, *J*=8.8 Hz, 4H), 7.09 (d, *J*=8.8 Hz, 2H), 7.04 (d, *J*=8.8 Hz, 4H), 7.12 (d, *J*=8.8 Hz, 2H), 6.97 (d, *J*=8.8 Hz, 2H), 4.48 (d, *J*=4.8 Hz, 4H), 4.42 (d, *J*=4.8 Hz, 4H), 3.97 (t, *J*=6.4 Hz, 2H), 1.71 (m, 2H), 1.41 (m, 2H), 1.31 (m, 4H), 0.88 (t, *J*=7.2 Hz, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 178.84, 156.32, 149.60, 147.17, 138.25, 137.49, 127.97, 127.71, 126.89, 124.87, 122.13, 115.78, 113.77, 67.64, 65.25, 64.56, 30.93, 28.62, 25.14, 22.01, 13.84. MS (ESI) *m*/*z* calcd. for ($C_{38}H_{35}NO_7S_2$): 681.19. Found: 682.4 ($[M+H]^+$). Anal. Calcd. for $C_{38}H_{35}NO_7S_2$: C, 66.94; H, 5.17; N, 2.05. Found: C, 66.85; H, 5.10; N, 2.13.

4-(Hexyloxy)-*N*,*N*-bis[4-(6-formyl-4,4-dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithien-2-yl)phenyl]aniline (9c). Yield: 90%. ^{1}H NMR (600 MHz, DMSO-d_6) δ: 9.82 (s, 2H), 7.98 (s, 2H), 7.62 (d, *J*=8.4 Hz, 4H), 7.56 (s, 2H), 7.08 (d, *J*=8.4 Hz, 2H), 7.02 (d, *J*=8.4 Hz, 4H), 6.97 (d, *J*=8.4 Hz, 2H), 3.97 (t, *J*=6.4 Hz, 2H), 1.92 (m, 8H), 1.72 (m, 2H), 1.41 (m, 2H), 1.32 (m, 4H), 1.11 (m, 24H), 0.88 (m, 11H), 0.77 (t, *J*=7.2 Hz, 12H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 182.98, 163.40, 157.30, 155.96, 148.25, 146.80, 146.27, 142.65, 138.62, 132.90, 131.17, 127.63, 127.40, 126.13, 122.46, 117.50, 115.66, 67.65, 53.55, 36.57, 30.73, 30.66, 28.64, 28.48, 24.93, 23.78, 21.76, 21.66, 13.56, 13.48. MS (ESI) *m*/*z* calcd. for ($C_{68}H_{83}NO_3S_4$): 1089.53. Found: 1090.80 ($[M+H]^+$). Anal. Calcd. for $C_{68}H_{83}NO_3S_4$: C, 74.88; H, 7.67; N, 1.28. Found: C, 74.80; H, 7.75; N, 1.20.

1.4. References

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S2. Y. Hiroko, T. Ikuyoshi, O. Kazuchika and E. Takeshi, *Mol. Cryst. Liq. Cryst. A*, 2001, **369**, 47.

S3. C. Videlot-Ackermann, J. Ackermann, H. Brisset, K. Kawamura, N. Yoshimoto, P. Raynal, A. El Kassmi and F. Fages, *J. Am. Chem. Soc.*, 2005, **127**, 16346.

S4. V. G. Albano, M. Bandini, G. Barbarella, M. Melucci, M. Monari, F. Piccinelli, S. Tommasi and A. Umani-Ronchi, *Chem. Eur. J.*, 2006, **12**, 667.

2. Additional experimental data

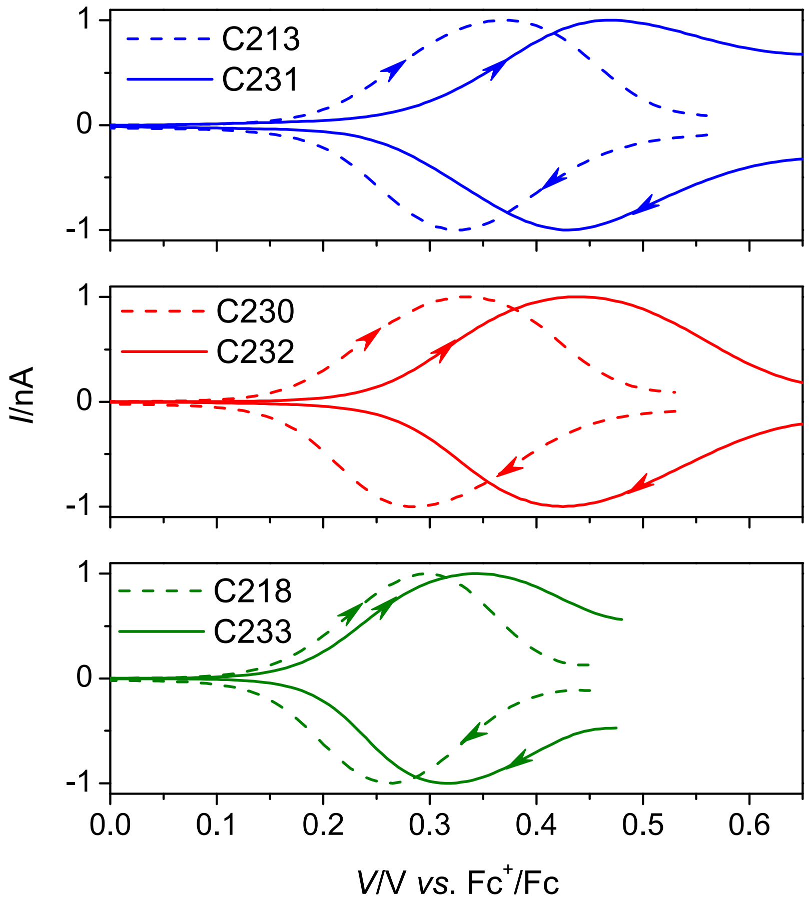

Fig. S1 Square-wave voltammograms of dye-coated titania films. The arrows indicate scan directions. Supporting electrolyte: 0.3 M 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide.

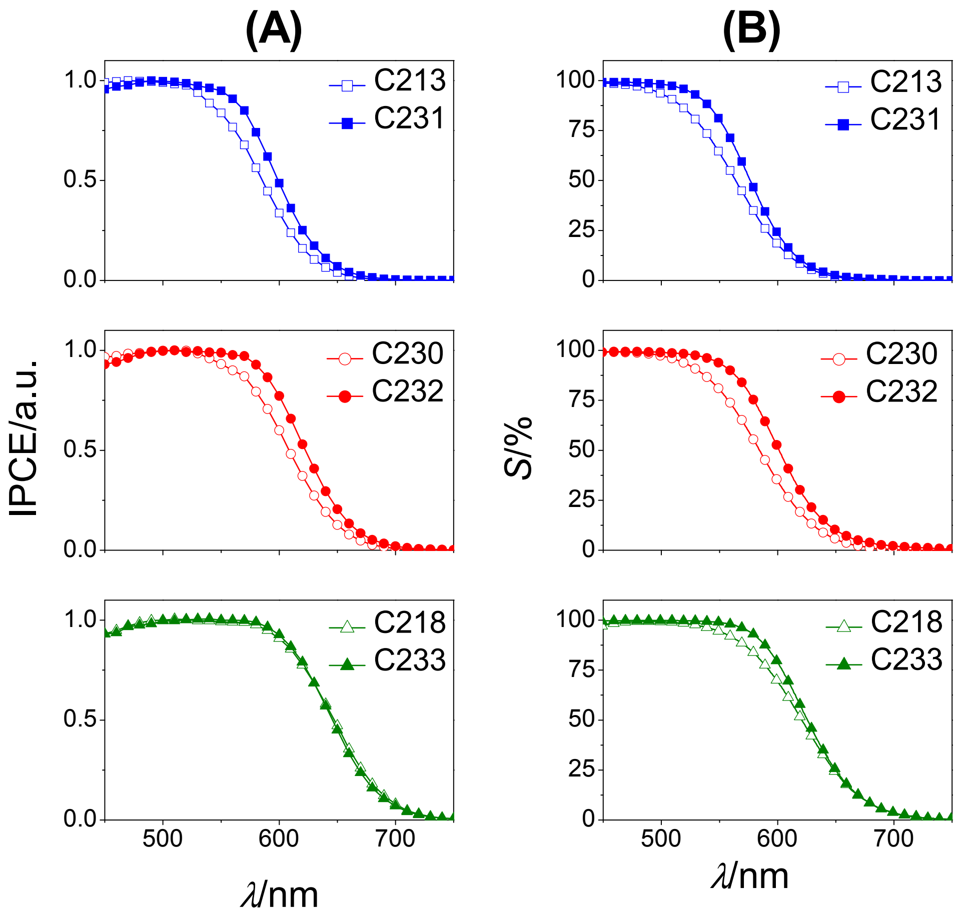

Fig. S2 (A) Normalized photocurrent action spectra. (B) Absorption percentages (*S*) of cells made from a transparent 2-µm-thick mesoporous titania film in contact with the Co-1 electrolyte.