Electronic supplementary information

Joint electrical, photophysical and computational studies on D-π-A dye sensitized solar cells: the impacts of dithiophene rigidification

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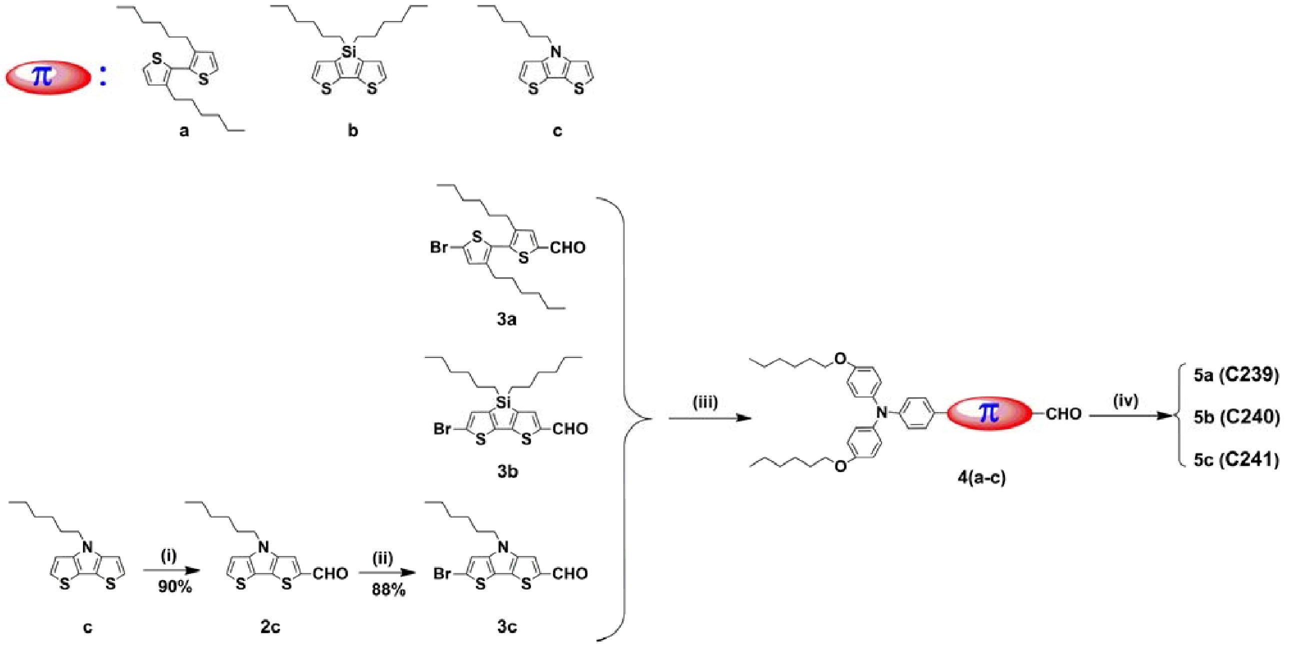
1. Synthesis of C239, C240 and C241 intermediates

Scheme S1. Synthetic route of C239, C240 and C241[a]



[a] Reagents: (i) 1.5 equiv. $POCl_3$, 2.0 equiv. DMF, 1,2-dichloroethane, 0–40 °C, 6 h; (ii) 1.1 equiv. NBS, THF, 0 °C–RT, 5 h; (iii) 1.2 equiv. 4,4,5,5-tetramethyl-2-{4-[*N*,*N*-bis(4-hexyloxyphenyl)amino]phenyl}-1,3,2-dioxaborolane, 2% $Pd(OAc)_2$, 2% SPhos, 5.0 equiv. K_3PO_4, dioxane/H_2O (*v*/*v*, 5:1), RT, overnight; (iv) 3.0 equiv. cyanoacetic acid, 7.0 equiv. piperidine, $CHCl_3$, reflux, 18 h.

Synthesis of intermediates

5-Bromo-5′-formyl-3,3′-dihexyl-2,2′-bithiophene (3a),[S1] 5-bromo-5′-formyl-3,3′-di-*n*-hexylsilylene-2,2′-bithiophene (3b),[S2] *N*-hexyldithieno[3,2-b:2′,3′-d]pyrrole (c)[S3] and 4,4,5,5-tetramethyl-2-{4-[*N*,*N*-bis(4-hexyloxyphenyl)amino]phenyl}-1,3,2-dioxaborolane[S4] were prepared according to the corresponding literature methods.

N-Hexyldithieno[*3,2-b:2′,3′-d*]*pyrrole-5-carbaldehyde* (***2c***). To a solution of **c** (1.87 g, 7.11 mmol) and *N*,*N*-dimethylformide (1.10 mL, 14.22 mmol) in 1,2-dichloroethane (100 mL) was added phosphorus chloride oxide (0.99 mL, 10.67 mmol) under argon at 0 °C. The reaction mixture was stirred at 0 °C for 2 h and then heated to 40 °C for another 4 h. Subsequently, saturated sodium acetate aqueous solution (50 mL) was added. The mixture was further stirred at room temperature for 2 h. The crude product was extracted into dichloromethane.

The organic layer was 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, 1/10, *v*/*v*) on silica gel to yield a yellowish powder (1.87 g, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 9.88 (s, 1H), 7.65 (s, 1H), 7.38 (d, *J*=5.6 Hz, 1H), 7.02 (d, *J*=5.6 Hz, 1H), 4.23 (t, *J*=6.8 Hz, 2H), 1.89 (m, 2H), 1.31 (m, 6H), 0.86 (t, *J*=6.8 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) *δ*: 182.90, 149.14, 144.22, 140.00, 128.43, 123.16, 119.35, 114.88, 110.85, 47.45, 31.29, 30.17, 26.59, 22.41, 13.91. MS (ESI) *m*/*z* calcd. for ($C_{15}H_{17}NOS_2$): 291.1. Found: 292.1 ($[M+H]^+$). Anal. Calcd. for $C_{15}H_{17}NOS_2$: C, 61.82; H, 5.88; N, 4.81. Found: C, 61.77; H, 5.92; N, 4.79.

5′-Bromo-N-hexyldithieno[*3,2-b:2′,3′-d*]*pyrrole-5-carbaldehyde* (***3c***). To a cold solution of **2c** (0.70 g, 2.40 mmol) in tetrahydrofuran (45 mL) was added *N*-bromosuccinimide (0.52 g, 2.92 mmol) at −10 °C under argon. The reaction mixture was warmed to room temperature and stirred for 4 h. Subsequently water (50 mL) was added to quench the reaction. The crude product was extracted into ethyl acetate. The organic layer was washed with saturated sodium bicarbonate aqueous solution, 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, 1/10, *v*/*v*) on silica gel to yield a yellow solid (0.78 g, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 9.88 (s, 1H), 7.63 (s, 1H), 7.08 (s, 1H), 4.17 (t, *J*=6.8 Hz, 2H), 1.86 (m, 2H), 1.29 (m, 6H), 0.87 (t, *J*=6.8 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) *δ*: 182.91, 149.15, 144.24, 140.04, 128.44, 123.20, 119.33, 114.92, 110.85, 47.48, 31.31, 30.19, 26.61, 22.43, 13.92. MS (ESI) *m*/*z* calcd. for ($C_{15}H_{16}BrNOS_2$): 369.0. Found: 370.1 ($[M+H]^+$). Anal. Calcd. for $C_{15}H_{16}BrNOS_2$: C, 48.65; H, 4.35; N, 3.78. Found: C, 48.57; H, 4.39; N, 3.73.

*General Synthesis of **4***. To a suspended solution of **3a**, **3b** or **3c** (1.0 equiv.), 4,4,5,5-tetramethyl-2-{4-[*N*,*N*-bis(4-hexyloxyphenyl)amino]phenyl}-1,3,2-dioxaborolane (1.2 equiv.), SPhos (2% equiv.) and K_3PO_4 (5.0 equiv.) in dioxane/H_2O (5/1, *v*/*v*) was added $Pd(OAc)_2$ (2% equiv.). The reaction mixture was stirred at room temperature overnight under argon and then added water. 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, 1/10, *v*/*v*) on silica gel.

5-{4-[N,N-Bis(4-hexyloxyphenyl)amino]phenyl}-(3,3′-dihexyl-2,2′-bithiophene)-5′-carbaldehyde (***4a***). Viscous orange oil. Yield: 90%. ^{1}H NMR (400 MHz, DMSO-d_6) *δ*: 9.88 (s, 1H), 7.99 (s, 1H), 7.46 (d, *J*=8.8 Hz, 2H), 7.32 (s, 1H), 7.03 (d, *J*=8.8 Hz, 4H), 6.91 (d, *J*=8.8 Hz, 4H), 6.76 (d, *J*=8.8 Hz, 2H), 3.94 (t, *J*=6.4 Hz, 4H), 2.58 (m, 4H), 1.70 (m, 4H), 1.55 (m, 4H), 1.42 (m, 4H), 1.32 (m, 8H), 1.21 (m, 12H), 0.88 (t, *J*=6.8 Hz, 6H), 0.81 (t, *J*=6.8

Hz, 6H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 184.01, 155.46, 148.36, 144.47, 143.89, 143.28, 141.95, 139.46, 139.33, 131.67, 126.90, 126.20, 124.42, 124.11, 124.06, 118.97, 115.50, 67.61, 30.97, 30.87, 29.83, 29.67, 28.68, 28.53, 28.31, 28.21, 25.18, 22.04, 21.92, 13.87, 13.84. MS (ESI) *m*/*z* calcd. for ($C_{51}H_{67}NO_3S_2$): 805.5. Found: 806.6 ([M+H]$^+$). Anal. Calcd. for $C_{51}H_{67}NO_3S_2$: C, 75.98; H, 8.38; N, 1.74. Found: C, 76.01; H, 8.41; N, 1.69.

5-{4-[N,N-Bis(4-(hexyloxy)phenyl)amino]phenyl}-3,3'-di-n-hexylsilylene-2,2'-bithiophene-5'-carbaldehyde (***4b***). Orange oil. Yield: 76%. ^{1}H NMR (600 MHz, DMSO-d_6) δ: 9.86 (s, 1H), 8.05 (s, 1H), 7.50 (d, *J*=9.0 Hz, 2H), 7.48 (s, 1H), 7.05 (d, *J*=8.4 Hz, 4H), 6.92 (d, *J*=8.4 Hz, 4H), 6.75 (d, *J*=9.0 Hz, 2H), 3.94 (t, *J*=6.4 Hz, 4H), 1.69 (m, 4H), 1.42 (m, 4H), 1.31 (m, 12H), 1.24 (m, 4H), 1.17 (m, 8H), 0.97 (m, 4H), 0.88 (t, *J*=6.9 Hz, 6H), 0.79 (t, *J*=6.6 Hz, 6H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 183.47, 157.17, 155.56, 148.77, 148.57, 148.47, 144.05, 143.74, 141.92, 141.16, 139.30, 127.07, 126.52, 125.15, 124.50, 118.72, 115.51, 67.60, 31.88, 30.95, 30.68, 28.65, 25.16, 23.42, 22.02, 21.85, 18.51, 13.86, 11.08. MS (ESI) *m*/*z* calcd. for ($C_{51}H_{67}NO_3S_2Si$): 833.43. Found: 834.44 ([M+H]$^+$). Anal. Calcd. for $C_{51}H_{67}NO_3S_2Si$: C, 73.42; H, 8.09; N, 1.68; Found: C, 73.50; H, 8.13; N, 1.63.

5'-{4-[N,N-Bis(4-hexyloxyphenyl)amino]phenyl}-N-hexyldithieno[3,2-b:2',3'-d]pyrrole-5-carbaldehyde (***4c***). Viscous orange oil. Yield: 94%. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.84 (s, 1H), 8.19 (s, 1H), 7.63 (s, 1H), 7.53 (d, *J*=8.8 Hz, 2H), 7.04 (d, *J*=8.8 Hz, 4H), 6.91 (d, *J*=8.8 Hz, 4H), 6.78 (d, *J*=8.8 Hz, 2H), 4.33 (t, *J*=6.8 Hz, 2H), 3.93 (t, *J*=6.4 Hz, 4H), 1.83 (m, 2H), 1.70 (m, 4H), 1.41 (m, 4H), 1.30 (m, 8H), 1.21 (m, 6H), 0.88 (t, *J*=6.8 Hz, 6H), 0.81 (t, *J*=6.8 Hz, 3H). ^{13}C NMR(150 MHz, DMSO-d_6) δ: 183.37, 155.44, 149.68, 148.39, 146.50, 143.49, 139.38, 139.08, 126.85, 126.12, 125.79, 121.95, 121.90, 118.97, 115.43, 111.98, 106.41, 67.58, 46.52, 30.95, 30.72, 29.61, 28.66, 25.81, 25.16, 22.02, 21.94, 13.84, 13.77. MS (ESI) *m*/*z* calcd. for ($C_{45}H_{54}N_2O_3S_2$): 734.4. Found: 735.5 ([M+H]$^+$). Anal. Calcd. for $C_{45}H_{54}N_2O_3S_2$: C, 73.53; H, 7.40; N, 3.81. Found: C, 73.47; H, 7.45; N, 3.76.

2. Analysis of chemical capacitance (C_μ) and interfacial charge transfer resistance (R_{ct})

We estimate the quantity of $E_c - E_{F,redox}$ by analyzing the chemical capacitance (C_μ), which takes the following equation:[S5]

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

where e is the elementary charge, N_t is the total density of surface states (taken as a constant 2×10^{20} cm^{-3} so as to facilitate a comparative study[S6]), d is the thickness of the titania film (2.1 μm), p is the film porosity (0.64), k_B is the Boltzmann constant, and T_c is a parameter depicting the distribution profile of interband states. Fitting the C_μ data in Fig. S4A to eqn S1 directly affords the values of $E_c - E_{F,redox}$ and T_c.

Consider the recently developed β–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:[S7]

$$U_n = k_0 n_c^{\ \beta} \qquad \text{S2}$$

Combining eqn S2 and the function for n_c

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

where N_c is taken as 7×10^{20} cm^{-3}, and the definition of the charge recombination resistance R_{ct}[S7]

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

where A is the projection area of titania film (0.158 cm^2), and j_{rec} is the recombination current, we have[S8]

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

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

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

On the basis of the as-resolved $E_c - E_{F,redox}$ values, fitting the R_{ct} data in Fig. S4C gives β, k_0 and U_{0k}.

3. Additional experimental data

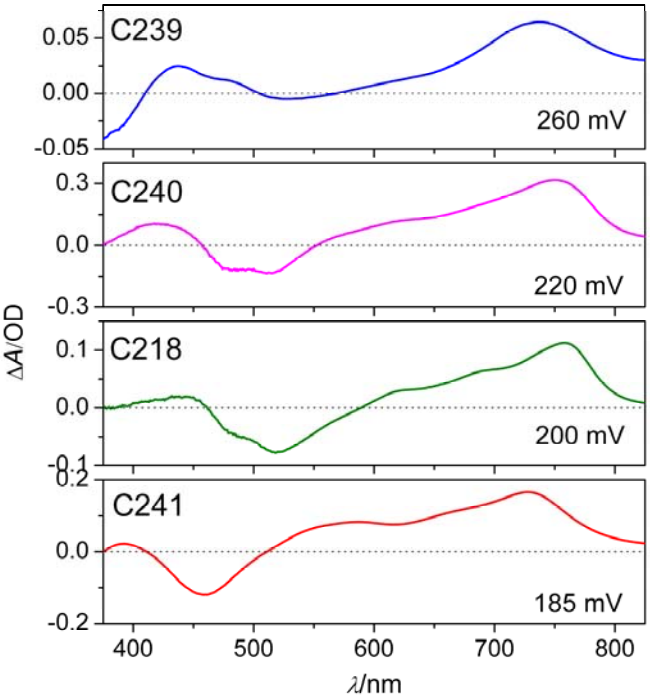


Fig. S1. Wavelength-dependent absorption change upon applying a positive potential bias to a 2.1-µm-thick, dye-coated titania film immersed in 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide. The applied potentials are reported versus the ferrocene/ferrocenium reference.

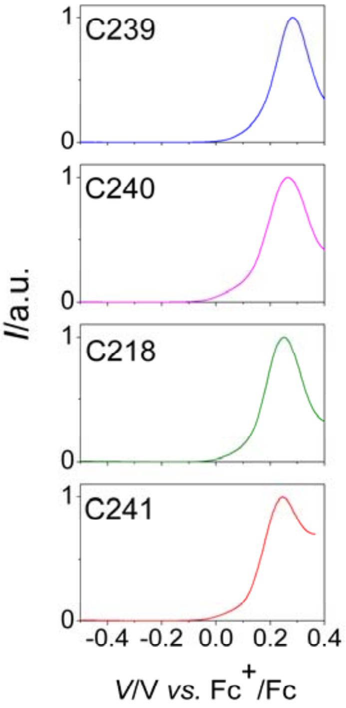


Fig. S2. Normalized square-wave voltammograms of dye-coated titania films in contact with an electrolyte composed of 0.1 M LiTFSI and 0.5 M TBP in acetonitrile.

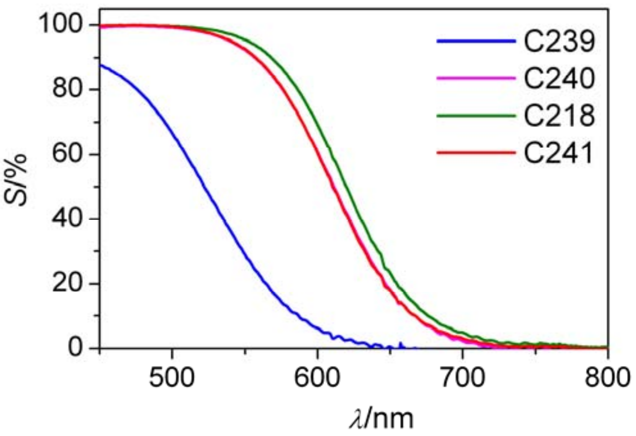


Fig. S3. Absorption percentages (*S*) of 2.1-μm-thick, dye-coated titania films immersed in the cobalt electrolyte for cell fabrication.

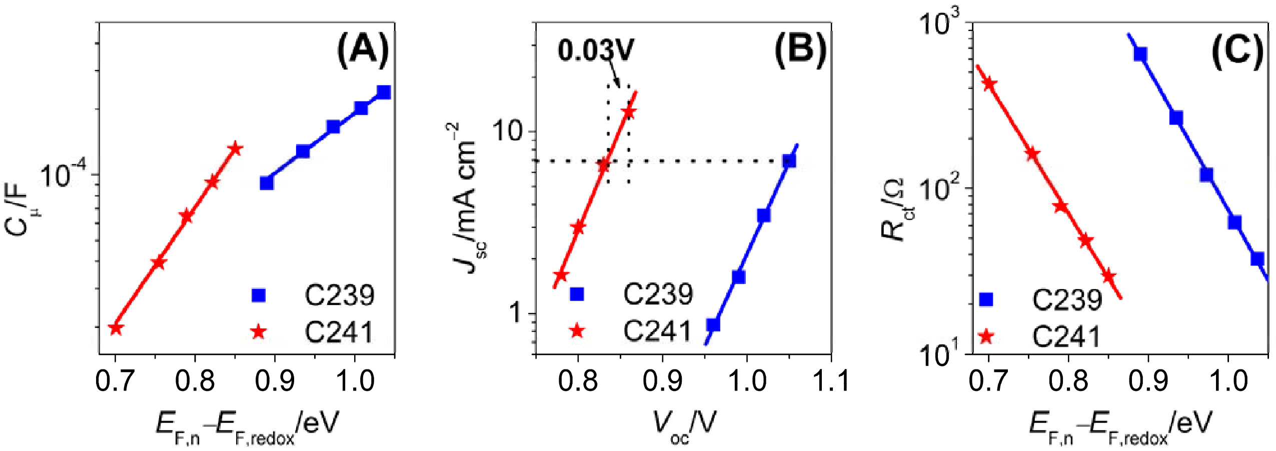


Fig. S4. (A) Chemical capacitance (C_μ) of a mesoporous titania film. (B) Plots of J_{sc} versus V_{oc}. (C) Charge transfer resistance (R_{ct}) at the titania/electrolyte interface. Solid lines are fittings to proper functions.

4. References

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