Supporting Information

Effective Suppression of Interfacial Charge Recombination by 12-Crown-4 Substituent on Double-Anchored Organic Sensitizer and Rotating Disk Electrochemical Evidence

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1. Materials

All the chemicals used in this work were of the purist quality available; and they were purchased from Acros, Aldrich, Alfa Aesar, J. T. Baker, Merck, Matrix scientific, Tokyo Chemical Industry Co., Ltd., or Ishihara Sangyo, Ltd. Solvents used were purified by standard procedures, or purged with nitrogen before use. A ruthenium dye, cis-diisothiocyanato bis(2,2’–bipyridyl–4,4’–dicarboxylato) ruthenium (II) bis(tetrabutylammonium) (N719 dye), was obtained from Luminescence Technology Corp., Taiwan. A commercial transparent TiO₂ paste (Ti-nanoxide HT/SP, with an average particle size of 20 nm) was purchased from Solaronix S. A., Switzerland. A home-made transparent TiO₂ paste and a home-made scattering TiO₂ paste was prepared according to the published procedures¹. A commercial light scattering TiO₂ particle (US3547, rutile, average size = 300 nm) was obtained from US Research Nanomaterials Inc., Houston, USA.

2. Synthetic procedure of the DCE dyes

Unless otherwise specified, all the reactions were performed under N₂ atmosphere, using...
standard Schlenk techniques. All the chemicals used in this work were of the purist quality available. All sensitizers were synthesized in high yields by using traditional Stille or Suzuki coupling reactions. Specific details of DCE dyes are listed below.

10-(2,3,5,6,8,9-Hexahydrobenzo[b][1,4,7,10]tetraoxacyclododecin-12-yl)-10H-phenothiazine

1. 10-H-Phenothiazine (1.20 g, 6.02 mmol), 12-bromo-2,3,5,6,8,9-hexahydrobenzo[b][1,4,7,10]-tetraoxacyclododecine (1.6 g, 5.28 mmol), sodium tert-butoxide (0.90 g, 9.03 mmol), and (Pd(dba)2) (0.13 g) were added to a 100 mL two-necked round-bottomed flask under nitrogen. Dry toluene (15 mL) and tri(tert-butyl)phosphine (0.494 M in toluene, 0.48 mL) were injected into the flask. The mixture was heated at 120 °C for 20 h. After the reaction was complete, the solution was extracted with dichloromethane and washed with brine. The organic extracts collected were dried over MgSO4 and filtered. The filtrate was dried under vacuum and the crude product was further purified by column chromatography with EA/dichloromethane (1:10 by vol.) as the eluent. The product was obtained as a white solid (1.28 g, 50%). 1H NMR (CDCl3, 400 MHz): δ 7.15 (d, 1H, J = 8.8 Hz), 6.96 (d, 4H, J = 6.8 Hz), 6.84-6.75 (m, 4H), 6.21 (d, 2H, J = 8.0 Hz), 4.26 (t, 2H, J = 4.0 Hz), 4.16 (t, 2H, J = 4.0 Hz), 3.89 (t, 2H, J = 4.0 Hz), 3.85 (t, 2H, J = 4.0 Hz), 3.82 (s, 4H).

10-(4-(Hexyloxy)phenyl)-10H-phenothiazine (2). 10-H-Phenothiazine (1.55 g, 7.78 mmol), 1-bromo-4-(hexyloxy)benzene (2.00 g, 7.78 mmol), sodium tert-butoxide (1.12 g, 11.7 mmol), and (Pd(dba)2) (0.13 g) were added to a 100 mL two-necked round-bottomed flask under nitrogen. Dry toluene (15 mL) and tri(tert-butyl)phosphine (0.494 M in toluene, 0.6 mL) were injected into the flask. The mixture was heated at 120 °C for 20 h. After the reaction was complete, the solution was extracted with dichloromethane and washed with brine. The organic extracts collected were dried over MgSO4 and filtered. The filtrate was dried under vacuum and the crude product was further purified by column chromatography with hexanes/dichloromethane (6:1 by vol.) as the eluent. The product was obtained as a colorless oil (2.5 g, 87%). 1H NMR (CDCl3, 500 MHz): δ 7.27 (d, 2H, J = 8.5 Hz), 7.07 (d, 2H, J = 8.5 Hz), 6.96 (d, 2H, J = 7.5 Hz), 6.82-6.74 (m, 4H), 6.18 (d, 2H, J =
1 8.0 Hz), 4.01 (t, 2H, J = 6.0 Hz), 1.84-1.79 (m, 2H), 1.49-1.47 (m, 2H), 1.36 (m, 4H), 0.91 (t, 3H, J = 5.0 Hz).

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4 **10-Phenyl-10H-phenothiazine (3).** 10-H-Phenothiazine (3.00 g, 15.05 mmol), iodobenzene (2.00 mL, 15.05 mmol), sodium tert-butoxide (4.00 g, 45.26 mmol), and (Pd(db)₂ (0.30 g) were added to a 100 mL two-necked round-bottomed flask under nitrogen. Dry toluene (15 mL) and tri(tert-butyl)phosphine (0.494 m in toluene, 1.2 mL) were injected into the flask. The mixture was heated at 120 °C for 20 h. After the reaction was complete, the solution was extracted with CH₂Cl₂ and washed with brine. The organic extracts collected were dried over MgSO₄ and filtered. The filtrate was dried under vacuum and the crude product was further purified by column chromatography with hexanes/dichloromethane (6:1 by vol.) as the eluent. The product was obtained as a colorless oil (3.1 g, 76%). ¹H NMR (acetone-d₆, 400 MHz) : δ 7.69 (t, 2H, J = 8.0 Hz), 7.55 (t, 1H, J = 8.0 Hz), 7.44 (s, 1H), 7.43 (d, 1H, J = 8.0 Hz), 7.05 (dd, 2H, J = 8.0; 2.0 Hz), 6.93-6.83 (m, 3H), 6.23 (dd, 2H, J = 8.0; 1.2 Hz).

10-(2,3,5,6,8,9-Hexahydrobenzo[b][1,4,7,10]tetracyclododecine-12-yl)-10H-phenothiazine-3-carbaldehyde (4). To a 100 mL round flask was added 1 (0.90 g, 2.14 mmol) and dry DMF (2.0 mL) as solvent under nitrogen at 0 °C. The solution was injected slowly POCl₃ (0.30 mL, 3.25 mmol) and stirred for 1 hr. The mixture was heated at 65 °C for 20 h. The mixture was extracted with dichloromethane, and the organic extracts were collected and dried over MgSO₄. After filtration, the filtrate was pumped dry. The crude product was further purified by chromatography using dichloromethane/EA (3:1 by vol.) as the eluent. The product was obtained as a yellow oil (0.20 g, 24%). ¹H NMR (acetone-d₆, 400 MHz) : δ 9.74 (s, 1H), 7.48 (d, 1H, J = 2.0 Hz), 7.44 (d, 1H, J = 1.6 Hz), 7.33 (d, 1H, J = 8.8 Hz), 7.13 (d, 1H, J = 2.4 Hz), 7.03 (dd, 1H, J = 2.4; 8.4 Hz), 7.01 (d, 1H, J = 8.8 Hz), 6.94-6.87 (m, 2H), 6.36 (d, 1H, J = 8.4 Hz), 6.28 (d, 1H, J = 8.0 Hz), 4.28 (t, 2H, J = 4.0 Hz), 4.24 (t, 2H, J = 4.0 Hz), 3.85 (t, 2H, J = 4.0 Hz), 3.82 (t, 2H, J = 4.0 Hz), 3.74 (s, 4H). HRMS (FAB, m/z): [M]⁺ Calcd for C₂₅H₂₃NO₅S: 449.5210; found: 449.1297.
7-Bromo-10-(2,3,5,6,8,9-hexahydrobenzo[b][1,4,7,10]tetraoxacyclododecin-12-yl)-10H-phenothiazine-3-carbaldehyde (5). Compound 4 was dissolved in DCM (2.0 mL) in a round flask and a solution of NBS (0.10 g, 0.56 mmol) in 2.0 mL of DCM was added to the reaction mixture. The mixture was stirred for 18 h at room temperature and then poured into ice water, and extracted with dichloromethane. The combined organic layers were dried over MgSO₄ and filtered. The filtrate was evaporated to dryness, and the crude product was further purified by silica chromatography using EA/dichloromethane (1:3 by vol.) as the eluent. The product was obtained as a yellow oil (0.3 g, 99%). ¹H NMR (acetone-d₆, 400 MHz): δ 9.77 (s, 1H), 7.49 (d, 1H, J = 2.0 Hz), 7.45 (d, 1H, J = 1.6 Hz), 7.33 (d, 1H, J = 8.8 Hz), 7.13 (d, 1H, J = 2.4 Hz), 7.03 (dd, 1H, J = 2.4; 8.4 Hz), 7.01 (d, 1H, J = 8.8 Hz), 6.94-6.87 (m, 1H), 6.36 (d, 1H, J = 8.4 Hz), 6.28 (d, 1H, J = 8.0 Hz), 4.28 (t, 2H, J = 4.0 Hz), 4.24 (t, 2H, J = 4.0 Hz), 3.85 (t, 2H, J = 4.0 Hz), 3.82 (t, 2H, J = 4.0 Hz), 3.74 (s, 4H).

HRMS (FAB, m/z): [M]⁺ Calcd for C25H22BrNO₅S: 527.0402; found: 527.0100.

10-(2,3,5,6,8,9-Hexahydrobenzo[b][1,4,7,10]tetraoxacyclododecin-12-yl)-3,7-bis(4-hexylthiophen-2-yl)-10H-phenothiazine (6). To a 100 mL two-neck round flask was added 3,7-dibromo-10-(2,3,5,6,8,9-hexahydrobenzo[b][1,4,7,10]tetraoxacyclododecin-12-yl)-10H-phenothiazine (1.5 g, 2.63 mmol), (4-hexylthiophen-2-yl)boronic acid (1.39 g, 6.60 mmol), potassium carbonate (2.18 g, 15.78 mmol) and Pd(PPh₃)₄ (0.15 g) under nitrogen. The mixture was injected dry toluene (3.0 mL) and water (3.0 mL). The mixture was heated at 120 °C for 20 h. The mixture was extracted with dichloromethane and washed with brine. The organic extracts collected were dried over MgSO₄. The crude product was further purified by chromatography using dichloromethane/EA (4:1 by vol.) as the eluent. The product was obtained as a yellow oil (0.78 g, 39%). ¹H NMR (acetone-d₆, 400 MHz): δ 7.32 (d, 1H, J = 8.4 Hz), 7.28 (d, 2H, J = 2.0 Hz), 7.21 (s, 2H), 7.16 (dd, 2H, J = 2.0; 8.4 Hz), 7.13 (d, 1H, J = 2.0 Hz), 7.03 (dd, 1H, J = 2.0; 8.4 Hz), 6.96 (s, 2H), 6.26 (d, 2H, J = 8.4 Hz), 4.28 (t, 2H, J = 4.0 Hz), 4.25 (t, 2H, J = 4.0 Hz), 3.85 (t, 2H, J = 4.0 Hz), 3.83 (t, 2H, J = 4.0 Hz), 3.74 (s, 4H).
To a 50 mL round flask was added 3,7-dibromo-10-(4-(hexyloxy)phenyl)-10H-phenothiazine (1.39 g, 2.60 mmol), tributyl(4-hexylthiophen-2-yl)stannane (2.97 g, 6.50 mmol), and PdCl$_2$(PPh$_3$)$_2$ (0.070 g, 4 mol%) as the catalyst under nitrogen. The mixture was injected dry DMF (3 mL), and heated at 100 oC for 18 h. After cooling, the mixture was quenched by aqueous potassium fluoride (KF) and the aqueous layer was extracted with dichloromethane. The combined organic layers were dried over MgSO$_4$ and filtered. The filtrate was evaporated to dryness, and the crude product was further purified by silica chromatography using hexanes/dichloromethane (4:1 by vol.) as the eluent. The product was obtained as a yellow oil (1.3 g, 71%). $^1$H NMR (acetone-$d_6$, 400 MHz) : $\delta$ 7.33 (d, 2H, $J = 8.4$ Hz), 7.27 (d, 2H, $J = 2.4$ Hz), 7.21 (d, 2H, $J = 8.8$ Hz), 7.18 (s, 2H), 7.13 (dd, 2H, $J = 2.0$; 8.8 Hz), 6.94 (s, 2H), 6.17 (s, 2H, $J = 8.4$ Hz), 2.58(t, 4H, $J = 7.6$ Hz), 1.86-1.79 (m, 2H), 1.71-1.49 (m, 6H), 1.39-1.27 (m, 18H), 0.94-0.87 (m, 9H).

To a 50 mL round flask was added 3,7-dibromo-10-phenyl-10H-phenothiazine (1.50 g, 3.46 mmol), tributyl(4-hexylthiophen-2-yl)stannane (3.95 g, 8.66 mmol), and PdCl$_2$(PPh$_3$)$_2$ (0.10 g, 4 mol%) as the catalyst under nitrogen. The mixture was injected dry DMF (3 mL), and heated at 100 oC for 18 h. After cooling, the mixture was quenched by aqueous potassium fluoride (KF) and the aqueous layer was extracted with dichloromethane. The combined organic layers were dried over MgSO$_4$ and filtered. The filtrate was evaporated to dryness, and the crude product was further purified by silica chromatography using hexanes/dichloromethane (4:1 by vol.) as the eluent. The product was obtained as a yellow oil (1.0 g, 48%). $^1$H NMR (acetone-$d_6$, 400 MHz) : $\delta$ 7.73 (t, 2H, $J = 8.0$ Hz), 7.60 (t, 1H, $J = 8.0$ Hz), 7.48 (d, 2H, $J = 8.4$ Hz), 7.31 (d, 2H, $J = 1.2$ Hz), 7.21 (s, 2H), 7.15 (d, 2H, 7.10 (t, 2H, $J = 8.4$ Hz), 7.06 (d, 2H, $J = 8.4$ Hz), 2.60 (t, 4H, $J = 7.6$ Hz), 1.91-1.84 (m, 2H), 1.81-1.50 (m, 6H), 1.39-1.29 (m, 18H), 0.94-0.87 (m, 9H).
J = 8.4 Hz), 6.96 (s, 2H), 6.17 (d, 2H, J = 8.8 Hz), 2.51 (t, 4H, J = 7.6 Hz), 1.71-1.61 (m, 4H), 1.39-1.31 (m, 12H), 0.86 (t, 6H, J = 6.8 Hz).

10-(2,3,5,6,8,9-Hexahydrobenzo[b][1,4,7,10]tetraoxacyclododecin-12-yl)-7-(4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)-10H-phenothiazine-3-carbaldehyde (DCE1al). To a 100 mL two-neck round flask was added 10-(2,3,5,6,8,9-hexahydrobenzo[b][1,4,7,10]-tetraoxacyclododecin-12-yl)-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10H-phenothiazine-3-carbaldehyde (0.29 g, 0.50 mmol), 1-bromo-4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzene (0.24 g, 0.50 mmol), potassium carbonate (0.40 g, 3.00 mmol) and Pd(PPh₃)₄ (0.030 g) under nitrogen. The mixture was injected dry toluene 1 mL and water 1 mL. The mixture was heated at 120 °C for 20 h. The mixture was extracted with dichloromethane and washed with brine. The organic extracts collected were dried over MgSO₄. The crude product was further purified by chromatography using dichloromethane/EA (1:1 by vol.) as the eluent. The product was obtained as a yellow oil (0.15 g, 44%). ¹H NMR (acetone-d₆, 400 MHz) : δ 9.74 (s, 1H), 7.51 (d, 2H, J = 8.8 Hz), 7.48 (s, 1H), 7.43 (d, 1H, J = 8.4 Hz), 7.34 (d, 1H, J = 8.4 Hz), 7.26 (s, 1H), 7.18 (dd, 1H, J = 2.4; 8.4 Hz), 7.17 (s, 1H), 7.03 (dd, 1H, J = 2.4; 8.4 Hz), 6.99 (d, 2H, J = 8.8 Hz), 6.36 (d, 1H, J = 8.8 Hz), 6.31 (d, 1H, J = 8.8Hz), 4.29 (t, 2H, J = 4.0 Hz), 4.25 (t, 2H, J = 4.0 Hz), 4.16 (t, 2H, J = 4.8 Hz), 3.86 (t, 2H, J = 4.0 Hz), 3.83 (t, 4 H, J = 4.8 Hz), 3.75 (s, 4H), 3.66 (t, 2H, J = 4.0 Hz), 3.61-3.56 (m, 4H), 3.46 (t, 2H, J = 4.0 Hz), 3.28 (s, 3H). HRMS (FAB, m/z): [M]⁺ Calcd for C₃₈H₄₁NO₉S: 687.2502; found: 687.2400.

(Z)-2-Cyano-3-(10-(2,3,5,6,8,9-hexahydrobenzo[b][1,4,7,10]tetraoxacyclododecin-12-yl)-7-(4-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)-10H-phenothiazin-3-yl)acrylic acid (DCE1). To a 100 mL round flask was added DCE1al (0.15 g, 0.21 mmol), cyanoacetic acid (0.10 g, 0.63 mmol), and NH₄OAc (2.97 mg). The mixture was added AcOH (2.0 mL) as the solvent, and heated at 110 °C for 20 h. After the solution was cooled to room temperature, the volatiles were removed in vacuo, and the residue was extracted with EA. The organic extracts were collected and dried over
MgSO₄. After filtration, the filtrate was pumped dry. The crude product was further purified by short silica chromatography using EA/AcOH (25:1 by vol.) as the eluent. The product was obtained as a red solid (60 mg, 40%). 

\[^1\]H NMR (acetone-\textit{d}_6, 400 MHz): \(\delta\) 8.06 (s, 1H), 7.80 (s, 1H), 7.63 (dd, 1H, \(J = 2.4; 8.4\) Hz), 7.52 (d, 2H, \(J = 8.8\) Hz), 7.35 (d, 1H, \(J = 8.4\) Hz), 7.28 (s, 1H) 7.19 (d, 1H, \(J = 8.0\) Hz), 7.18 (s, 1H), 7.05 (dd, 1H, \(J = 2.4; 8.4\) Hz), 7.00 (d, 2H, \(J = 8.4\) Hz), 6.35 (d, 1H, \(J = 8.8\) Hz), 6.31 (d, 1H, \(J = 8.8\) Hz), 4.29 (t, 2H, \(J = 4.0\) Hz), 4.26 (t, 2H, \(J = 4.0\) Hz), 4.16 (t, 2H, \(J = 4.4\) Hz), 3.85 (t, 2H, \(J = 4.0\) Hz), 3.83 (t, 4H, \(J = 4.4\) Hz), 3.74 (s, 4H), 3.66 (t, 2H, \(J = 4.0\) Hz), 3.61-3.56 (m, 4H), 3.46 (t, 2H, \(J = 4.0\) Hz), 3.28 (s, 3H).

\[^{13}\]C NMR (acetone-\textit{d}_6, 500 MHz): \(\delta\) 165.74, 164.34, 160.60, 153.15, 152.17, 151.51, 149.08, 142.54, 134.69, 132.89, 132.56, 129.29, 127.03, 126.33, 125.33, 121.11, 120.60, 120.11, 119.37, 117.89, 117.07, 116.36, 100.62, 73.08, 73.05, 71.88, 71.83, 71.70, 71.66, 71.52, 71.50, 70.74, 70.69, 69.24, 68.83, 59.23, 59.21. HRMS (FAB, m/z): [M]\(^+\) Calcd for C\(_{41}\)H\(_{40}\)N\(_2\)O\(_{10}\)S: 754.8510; found: 754.2555. Anal. Calcd for C\(_{41}\)H\(_{40}\)N\(_2\)O\(_{10}\)S: C, 65.24; H, 5.61; N, 3.71. Found: C, 65.10; H, 5.46; N, 3.78.

5,5’-(10-(2,3,5,6,8,9-Hexahydrobenzo[b][1,4,7,10]tetraoxacyclododecin-12-yl)-10\(^\text{H}\)-phenothiazine-3,7-diyl)bis(3-hexylthiophene-2-carbaldehyde) (DCE2al). To a 100 mL round flask was added 6 (0.78 g, 1.03 mmol) and injected dry DMF (2.0 mL) as solvent under nitrogen at 0 °C. The solution was injected slowly POCl\(_3\) (0.30 mL, 3.25 mmol) and stirred for 1 h. The mixture was heated at 65 °C for 20 h. The mixture was extracted with dichloromethane, and the organic extracts were collected and dried over MgSO\(_4\). After filtration, the filtrate was pumped dry. The crude product was further purified by chromatography using dichloromethane/EA (1:1 by vol.) as the eluent. The product was obtained as a red oil (0.25 g, 29%). 

\[^1\]H NMR (CDCl\(_3\), 500 MHz): \(\delta\) 9.95 (s, 2H), 7.22 (d, 3H, \(J = 1.5\) Hz), 7.18 (d, 1H, \(J = 8.5\) Hz), 7.10 (dd, 2H, \(J = 8.0; 1.5\) Hz), 7.04 (s, 2H), 6.94 (d, 2H, \(J = 8.5\) Hz), 6.17 (d, 2H, \(J = 8.5\) Hz), 4.27 (t, 2H, \(J = 3.5\) Hz), 4.18 (t, 2H, \(J = 3.5\) Hz), 3.91 (t, 2H, \(J = 3.5\) Hz), 3.87 (t, 2H, \(J = 3.5\) Hz), 3.82 (s, 4H), 2.90 (t, 4H, \(J = 7.5\) Hz), 1.69-1.63 (m, 4H), 1.30-1.48 (m, 12H), 0.86 (t, 6H, \(J = 6.0\) Hz). HRMS (FAB, m/z): [M]\(^+\) Calcd for C\(_{46}\)H\(_{51}\)NO\(_6\)S\(_3\): 809.2879; found: 809.2866.
**2E,2'E-3,3'-(10-(2,3,5,6,8,9-Hexahydrobenzo[b][1,4,7,10]tetraoxacyclododecin-12-yl)-10H-phenothiazine-3,7-divl)bis(3-hexylthiophene-5,2-divl))bis(2-cyanoacrylic acid) (DCE2).** To a 100 mL round flask was added **DCE2al** (0.25 g, 0.30 mmol), cyanoacetic acid (0.10 g, 0.63 mmol), and NH$_4$OAc (2.97 mg). The mixture was added AcOH (2.0 mL) as the solvent, and heated at 110 °C for 20 h. After the solution was cooled to room temperature, the volatiles were removed in vacuo, and the residue was extracted with EA. The organic extracts were collected and dried over MgSO$_4$. After filtration, the filtrate was pumped dry. The crude product was further purified by short silica chromatography using EA/AcOH (20:1 by vol.) as the eluent. The product was obtained as a red solid (0.20 g, 70%). $^1$H NMR (THF-$d_8$, 500 MHz): $\delta$ 8.37 (s, 2H), 7.39 (d, 4H, $J = 8.5$ Hz), 7.26 (t, 3H, $J = 8.5$ Hz), 7.10 (s, 1H), 6.99 (d, 1H, $J = 8.0$ Hz), 6.27 (d, 2H, $J = 8.5$ Hz), 4.24 (t, 2H, $J = 3.0$ Hz), 4.18 (t, 2H, $J = 3.0$ Hz), 3.84 (t, 2H, $J = 3.0$ Hz), 3.80 (t, 2H, $J = 3.0$ Hz), 3.73 (s, 4H), 2.82 (t, 4H, $J = 7.5$ Hz), 1.69-1.63 (m, 4H), 1.39-1.33 (m, 12H), 0.91 (t, 6H, $J = 6.5$ Hz). $^{13}$C NMR (THF-$d_8$, 500 MHz): $\delta$ 164.74, 164.69, 156.60, 152.66, 151.84, 145.39, 145.32, 145.26, 144.50, 143.24, 143.83, 134.83, 134.72, 130.21, 130.13, 130.10, 128.78, 128.77, 128.72, 128.70, 127.12, 127.07, 126.99, 126.95, 125.85, 125.79, 125.62, 125.34, 125.28, 124.33, 124.06, 124.00, 121.37, 121.22, 121.17, 120.78, 120.72, 120.10, 117.96, 117.00, 116.90, 116.67, 72.38, 71.18, 71.06, 70.87, 69.96, 68.35, 32.05, 31.99, 31.69, 29.60, 29.49, 29.42, 29.27, 24.74, 22.88, 14.05. HRMS (FAB, m/z): [M]$^+$ Calcd for C$_{52}$H$_{53}$N$_3$O$_8$S$_3$: 944.1890; found: 944.1875. Anal. Calcd for C$_{52}$H$_{53}$N$_3$O$_8$S$_3$: C, 66.15; H, 5.66; N, 4.45. Found: C, 66.47; H, 5.67; N, 4.58.

**5,5'-(10-(4-(Hexyloxy)Phenyl)-10H-phenothiazine-3,7-divl)bis(3-hexylthiophene-2-carbaldehyde) (DCE3al).** To a 100 mL round flask was added 7 (1.70 g, 2.40 mmol) and injected dry DMF (2 mL) as solvent under nitrogen at 0 °C. The solution was injected slowly POCl$_3$ (0.56 mL, 6.00 mmol) and stirred for 1 h. The mixture was heated at 65 °C for 20 h. The mixture was extracted with dichloromethane, and the organic extracts were collected and dried over MgSO$_4$. After filtration, the filtrate was pumped dry. The crude product was further purified by chromatography
using dichloromethane/hexanes (1:1 by vol.) as the eluent. The product was obtained as a red oil (1.2 g, 26%). \(^1\)H NMR (acetone-\(d_6\), 400 MHz) : \(\delta\) 10.05 (s, 2H), 7.44 (d, 4H, \(J = 2.4\) Hz), 7.39 (d, 2H, \(J = 6.8\) Hz), 7.30 (dd, 2H, \(J = 2.0; 8.4\) Hz), 7.27 (d, 2H, \(J = 8.8\) Hz), 6.22 (d, 2H, \(J = 8.8\) Hz), 4.13 (t, 2H, \(J = 6.4\) Hz), 3.01 (t, 4H, \(J = 7.6\) Hz), 1.89-1.81 (m, 2H), 1.76-1.69 (m, 4H), 1.56-1.50 (m, 2H), 1.42-1.38 (m, 8H), 1.35-1.30 (m, 8H), 0.93 (t, 3H, \(J = 6.8\) Hz), 0.86 (t, 6H, \(J = 6.8\) Hz).

HRMS (FAB, m/z): [M]+ Calcd for C_{46}H_{53}NO_3S_3: 763.3188; found: 763.3183.

\(\text{(2E,2'E)-3,3'-(10-(4-(Hexyloxy)phenyl)-10H-phenothiazine-3,7-diyl)bis(3-hexylthiophene-5,2-diyl))bis(2-cyanoacrylic acid) (DCE3).}\)

To a 100 mL round flask was added DCE3al (0.50 g, 0.65 mmol), cyanoacetic acid (0.30 g, 3.27 mmol), and NH_4OAc (2.97 mg). The mixture was added AcOH (2 mL) as the solvent, and heated at 110 °C for 20 h. After the solution was cooled to room temperature, the volatiles were removed in vacuo, and the residue was extracted with EA. The organic extracts were collected and dried over MgSO_4. After filtration, the filtrate was pumped dry. The crude product was further purified by short silica chromatography using EA/AcOH (25:1 by vol.) as the eluent. The product was obtained as a red solid (0.30 g, 51%). \(^1\)H NMR (THF-\(d_8\), 400 MHz) : \(\delta\) 8.39 (s, 2H), 7.43 (s, 2H), 7.39 (s, 2H), 7.36 (d, 2H, \(J = 8.8\) Hz), 7.24 (t, 4H, \(J = 8.8\) Hz), 6.22 (d, 2H, \(J = 8.4\) Hz), 4.10 (t, 2H, \(J = 6.4\) Hz), 2.84 (t, 4H, \(J = 8.0\) Hz), 1.90-1.84 (m, 2H), 1.68-1.64 (m, 4H), 1.58-1.56 (m, 2H), 1.42-1.41 (m, 8H), 1.39-1.34 (m, 8H), 0.96 (t, 3H, \(J = 6.8\) Hz), 0.91 (t, 6H, \(J = 6.8\) Hz). \(^{13}\)C NMR (THF-\(d_8\), 500 MHz): \(\delta\) 165.83, 164.73, 160.60, 156.40, 151.55, 145.45, 143.65, 133.12, 132.57, 130.06, 128.64, 126.23, 124.65, 120.84, 117.63, 117.14, 116.94, 114.90, 98.17, 69.12, 32.63, 32.57, 32.21, 30.25, 29.94, 29.74, 26.79, 24.40, 23.59, 23.48, 14.44.

HRMS (FAB, m/z): [M]+Calcd for C_{52}H_{55}N_3O_5S_3: 897.3304; found: 897.3204.

\(5,5'-(10-Phenyl-10H-phenothiazine-3,7-diyl)bis(3-hexylthiophene-2-carbaldehyde) \ (DCE4al).\)

To a 100 mL round flask was added 8 (1.00 g, 1.64 mmol) and injected dry THF (2.0 mL) as solvent under nitrogen. The solution was injected slowly \(n\)-BuLi (3.0 mL, 4.93 mmol) at -78 °C and stirred for 1 h. After 1 h, the solution was injected DMF (0.40 mL, 4.93 mmol), and the mixture was
stirred for 20 h. The mixture was extracted with ether, and the organic extracts were collected and dried over MgSO₄. After filtration, the filtrate was pumped dry. The crude product was further purified by chromatography using dichloromethane/EtOH (1:1 by vol.) as the eluent. The product was obtained as a red oil (0.12 g, 11%). ¹H NMR (acetone-­d₆, 400 MHz): δ 10.04 (s, 2H), 7.76 (t, 2H, J = 7.6 Hz), 7.65 (t, 1H, J = 7.6 Hz), 7.50 (d, 2H, J = 7.6 Hz), 7.44 (d, 2H, J = 1.6; 7.6 Hz), 7.42 (s, 2H), 7.28 (d, 2H, J = 1.6; 8.8 Hz), 6.17 (d, 2H, J = 8.8 Hz), 3.00 (t, 4H, J = 7.6 Hz), 1.74-1.68 (m, 4H), 1.40-1.30 (m, 12H), 0.87 (t, 6H, J = 6.8 Hz). HRMS (FAB, m/z): [M]^⁺ Calcld C₄₀H₄₁NO₂S₃; found: 663.2294.

(2E,2'E)-3,3'-(10-Phenyl-10H-phenothiazine-3,7-diyl)bis(3-hexylthiophene-5,2-diyl)bis(2-cyanoacrylic acid) (DCE4). To a 100 mL round flask was added DCE4al (0.50 g, 0.65 mmol), cyanoacetic acid (0.10 g, 3.27 mmol), and NH₄OAc (2.97 mg). The mixture was added AcOH (2.0 mL) as the solvent, and heated at 110 °C for 20 h. After the solution was cooled to room temperature, the volatiles were removed in vacuo, and the residue was extracted with EtOH. The organic extracts were collected and dried over MgSO₄. After filtration, the filtrate was pumped dry. The crude product was further purified by short silica chromatography using EtOH/AcOH (25:1 by vol.) as the eluent. The product was obtained as a red solid (0.50 g, 51%). ¹H NMR (THF-d₈, 400 MHz): δ 8.34 (s, 2H), 7.67 (t, 2H, J = 7.6 Hz), 7.54 (t, 1H, J = 7.6 Hz), 7.43 (d, 2H, J = 7.6 Hz), 7.40 (d, 2H, J = 2.0 Hz), 7.35 (s, 2H), 7.20 (d, 2H, J = 2.0; 8.4 Hz), 6.12 (d, 2H, J = 8.4 Hz), 2.79 (t, 4H, J = 7.6 Hz), 1.65-1.59 (m, 4H), 1.36-1.29 (m, 12H), 0.86 (t, 6H, J = 6.8 Hz). ¹³C NMR (THF-d₈, 500 MHz): δ 165.42, 156.03, 151.16, 144.69, 143.32, 140.78, 131.78, 131.35, 129.75, 129.61, 128.40, 125.92, 125.88, 124.32, 120.55, 116.78, 116.49, 114.42, 32.21, 31.84, 29.58, 29.38, 23.95, 23.11, 14.06. HRMS (FAB, m/z): [M]^⁺ Calcld for C₄₆H₄₃N₃O₄S₃: 797.2416; found: 797.2410.

3. Synthetic procedure of cobalt redox mediators

Unless otherwise specified, all the reactions were performed under N₂ atmosphere, using standard Schlenk techniques. All the chemicals used in this work were of the purist quality available.
The reduced-state cobalt mediator, tris(1,10-phenanthroline)cobalt bis(trifluoromethane-sulfonimide), was prepared via a three-step procedure as the following: (1) Cobalt(II) chloride hexahydrate (CoCl$_2$·6H$_2$O, 2.38 g, 10 mmol) was dissolved in 15 mL of EtOH, and 1,10-phenanthroline (5.95 g, 33 mmol) was dissolved in 10 mL of EtOH. (2) The 1,10-phenanthroline solution was dropwise added into the CoCl$_2$·6H$_2$O solution, and then the mixed solution was kept at 70 °C for at least 2 h. (3) A solution containing bis(trifluoromethane)sulfonimide lithium salt (LiTFSI, 6.32 g, 22 mmol) in EtOH was added into the previous solution to obtain the light yellow precipitate of Co$^{II}$(Phen)$_3$(TFSI)$_2$. The product was collected by filtration, washed by organic solvents (EtOH, deionized water, diethyl ether and acetonitrile) several times, and dried in vacuum. The oxidized-state cobalt mediator, tris(1,10-phenanthroline)cobalt tris(trifluoromethanesulfonimide), was prepared similarly as the following: (1) CoCl$_2$·6H$_2$O (0.50 g, 2.1 mmol) was dissolved in 5.0 mL of deionized water, and 1,10-phenanthroline (1.26 g, 7 mmol) was dissolved in 5.0 mL of MeOH; the latter solution was dropwise added into the former solution, and then the mixed solution was kept at 70 °C for at least 2 h. (2) A methanolic bromine solution (0.29 g, 1.8 mmol, 5 mL) was added in the previous mixture to obtain the chrome yellow precipitate immediately. This chrome yellow precipitate is collected by filtration, washed by organic solvents (EtOH, deionized water, diethyl ether and acetonitrile) several times, and dried in vacuum. (3) The chrome yellow precipitate was dissolved in deionized water, and then mixed with an aqueous solution of LiTFSI (2.01 g, 7 mmol); accordingly, the products of Co$^{III}$(Phen)$_3$(TFSI)$_3$ was collected by filtration, washed by organic solvents (EtOH and diethyl ether) several times, and dried in vacuum.

4. DSSCs’ assembly

The fluorine–doped tin oxide (FTO, TEC-7, 7 Ω square$^{-1}$, NSG America Inc., New Jersey, USA) conductive glasses were firstly cleaned via the ultra-sonication in the bathes of neutral cleaner, de-ionized water, acetone, and isopropanol, sequentially. For the iodide-based electrolyte, a 20 μm-thick TiO$_2$ film, containing a 15 μm-thick transparent layer (Solarnix transparent paste) and a
5 μm-thick scattering layer (home-made scattering paste), was casted on the cleaned FTO via the
doctor-blade technique with a controlled area of 0.20 cm² and was sintered at 450 °C for 30 min in
an air atmosphere. For the cobalt-based electrolyte, a 12 μm-thick TiO₂ film, containing an 8 μm-
4 thick transparent layer (home-made transparent paste) and a 4 μm-thick scattering layer (home-
5 made scattering paste), was prepared via the same procedure. Here, the home-made scattering paste
6 for cobalt-based electrolyte was prepared by adding 250 wt% of commercial TiO₂ particle (US3547,
w.r.t. the weight of TiO₂ nanoparticle) in previous home-made transparent paste. The film
8 thickness is measured by a profilometer (Dektak3, Veeco/Sloan Instruments Inc., USA). The
9 sintered TiO₂ film was immersed in 3×10⁻⁴ M dye solution at room temperature for at least 12 h
10 using a mixed solvent of acetonitrile/tert-butanol (ACN/TBA=1:1, in volume ratio). For the cases of
the dyes co-adsorbed with chenodeoxycholic acid (CDCA), 10 mM of CDCA is added into each
dye solution. After rinsing with acetonitrile, the dye-adsorbed TiO₂ photoanode was obtained.
13 Finally, a photoanode was assembled with a sputtered-platinum/FTO counter electrode using a 25
μm-thick Surlyn® (SX1170-25, Solaronix S. A., Switzerland) as the cell spacer. The iodide-based
15 electrolyte, containing 0.1 M lithium iodide (LiI), 1.0 M 1,2-dimethyl-3-propylimidazolium iodide
16 (DMPII), 0.04 M iodine (I₂), and 0.5 M 4–tert–butylpyridine (TBP) in acetonitrile/3–
17 methoxypropionitrile (ACN/MPN = 8:2, in volume ratio), was injected into the cell gap between
18 these two electrodes by capillarity. Similarly, the cobalt-based electrolyte, containing 0.35 M
19 tris(1,10-phenanthroline)cobalt bis(trifluoro-methanesulfonimide), 0.05 M tris(1,10-
20 phenanthroline)cobalt tris(trifluoromethanesulfonimide), 0.8 M TBP, and 0.1 M lithium perchlorate
21 (LiClO₄) in acetonitrile, was used.

5. Analytic techniques

¹H and ¹³C NMR spectra were recorded on Bruker 400 MHz and 500 MHz spectrometers,
respectively. Mass spectra (FAB) were recorded on a VG70-250S mass spectrometer. Elemental
analyses were carried out on a PerkinElmer 2400 CHN analyzer. Chromatographic separations were
conducted on silica gel (60M, 230–400 mesh). Absorption spectra were measured by Dynamica
DB-20 UV/Vis spectrophotometer. Fluorescence spectra were recorded on a Hitachi F-4500 spectrophotometer. The solution for both of absorption and fluorescence spectra was consisted of $10^{-4}$ M of dye in tetrahydrofuran (THF). Cyclic voltammetry (CV) was performed by a potentiostat (621A, CHI Instruments, Inc.) in a three-electrode system; a platinum electrode, a Pt wire, and a non-aqueous Ag/AgNO$_3$ (Ag/Ag$^+$) electrode were used as the working, counter, and reference electrodes, respectively. A scan rate was set at 50 mV s$^{-1}$. The electrolyte for CV analysis contained 10 mM of dye and 0.1 M of ferrocene/ferrocenium (an internal reference) in THF.

Photovoltaic performance of DSSCs was measured by a potentiostat/galvanostat (650B, CH Instruments, Inc.) at AM 1.5G sun light illumination by using a class A quality solar simulator (XES–40S2–CE, San–Ei Electric Co., Ltd., Osaka, Japan). The incident light intensity of 100 mW cm$^{-2}$ was calibrated with a standard Si cell (Oriel 91150, Newport Corp.). Incident photon–to–current conversion efficiencies (IPCE) of DSSCs were recorded by another potentiostat/galvanostat (PGSTAT 30, Autolab, Eco–Chemie, Utrecht, the Netherlands) under monochromatic light illumination in a wavelength range of 400-800 nm. To obtain the IPCE data, another class-A solar simulator (PEC–L11, AM1.5G, Peccell Technologies, Inc., Kanagawa, Japan) equipped with a monochromator (74100, Oriel Instrument, California, USA) was used. The incident radiation flux ($\phi$) was obtained by using an optical detector (818-SL, Newport, California, USA) and a power meter (1916-R, Newport, California, USA). Electrochemical impedance spectra (EIS) of DSSCs were recorded by the CHI potentiostat/galvanostat equipped with a FRA2 module in a frequency range of 10 mHz–65 kHz and AC amplitude of ±10 mV. Under dark condition, the EIS spectra were measured at an applied voltage of −0.70 V. Under 1 sun illumination (AM 1.5G, 100 mW cm$^{-2}$) the EIS spectra were measured at open-circuit condition. Charge extraction measurements were carried out on the electrochemical work-station (Zahner, Zennium) with a frequency response analyzer under an intensity modulated (10 to 300 W m$^{-2}$) white-light-emitting diode driven by a Zahner (0982wlr02) source supply. The frequency range was set from 100 kHz to 10 MHz.
6. Rotating disk electrode technique

Rotating disk electrode (RDE) was recorded by a potentiostat (900B, CHI Instrument) in a three-electrode system. A glassy carbon electrode (GCE, with a geometric area of 0.2 cm$^2$) coated with TiO$_2$/DCE$_2$ or TiO$_2$/DCE$_4$ films was individually used as the working electrode. A Pt wire and a non-aqueous Ag/AgNO$_3$ (Ag/Ag$^+$) electrode were used as the counter and reference electrodes, respectively. For measuring the diffusion coefficient of cobalt redox mediator, rotating disk electrode with Pt as the disk material (Pt–RDE, working area: 0.196 cm$^2$, Part #AFE2M050PT, PINE Instrument Company, Pennsylvania, USA) was used as the working electrode. The iodide-based electrolyte for RDE analysis contained 1.0 mM of tetrabutylammonium triiodide (I$_3^-$) and 0.1 M lithium perchlorate (LiClO$_4$) in acetonitrile. The cobalt-based electrolyte for RDE analysis included 1.0 mM of tris(1,10-phenanthroline)cobalt tris(trifluoromethanesulfonimide) (Co-phen$_{3+}$) and 0.1 M of lithium perchlorate in acetonitrile. A scan rate was set at 2 mV s$^{-1}$. Here, RDE analysis aims to obtain two key parameters for the reduction of I$_3^-$, i.e., the intrinsic heterogeneous rate constant ($k_0$) and the effective catalytic surface area ($A_c$), simultaneously. At a certain rotating speed (50, 100, 150, 200, 250, or 300 rpm), a linear sweep voltammetry (LSV) curve for the TiO$_2$/DCE$_2$ or TiO$_2$/DCE$_4$ film is scanned from 0 V to −0.3 V; in other word, more and more negative electrons accumulate at the TiO$_2$/DCE dye/electrolyte interface to trigger the reduction of the oxidized redox species (I$_3^-$ or Co-phen$_{3+}$). Thus, six LSV curves were obtained at different rotating speeds to get six values of the reciprocal currents ($i^{-1}$) at the standard potential ($E^0$) of I$^-$/I$_3^-$ or Co-phen$_{2+}$/Co-phen$_{3+}$. In accordance with the simplified Koutecký–Levich equation below, the values of $k_0$ and $A_c$ can be obtained via the plots of plots of $i^{-1}$ vs. $\omega^{-0.5}$.

$$i^{-1} = \frac{I}{nFAk_0C} + \frac{I}{0.62nFA_cD^{2/3} \nu^{1/6} \omega^{1/2} C}$$

where $i$ is the specific current obtained from the LSV curve at the standard potential of the redox mediator (I$^-$/I$_3^-$ or Co-phen$_{2+}$/Co-phen$_{3+}$), $n$ is the number of electrons transferred, $F$ is Faraday constant, $C$ is the concentration of the oxidized redox species (I$_3^-$ or Co-phen$_{3+}$), $D$ is the apparent diffusion coefficient of the oxidized redox species, $\nu$ is the kinetic viscosity of electrolyte, and $\omega$ is
Accordingly, the standard redox potential ($E^0'$) and the apparent diffusion coefficient ($D$) for cobalt redox mediator (Co-phen$^{2+}$/Co-phen$^{3+}$) need to be determined. First, the redox potential ($E^0'$) of Co-phen$^{2+}$/Co-phen$^{3+}$ was confirmed to be 0.62 V versus NHE by its CV curve in Figure S9; this value agrees well with the literatures.$^2,3$ A three-electrode system was used; a platinum electrode, a Pt wire, and a non-aqueous Ag/AgNO$_3$ (Ag/Ag$^+$) electrode were used as the working, counter, and reference electrodes, respectively. A cobalt-based electrolyte contains 10 mM tris(1,10-phenanthroline)cobalt bis(trifluoromethanesulfonimide), 1 mM tris(1,10-phenanthroline)cobalt tris(trifluoromethanesulfonimide) and 0.1 M of lithium perchlorate in acetonitrile. A scan rate was set at 100 mV s$^{-1}$. Second, the diffusion coefficient ($D$) of Co-phen$^{2+}$/Co-phen$^{3+}$ was measured using Pt–RDE as the working electrode, where Pt is the disk material. The pertinent cobalt-based electrolyte for RDE analysis contains 1.0 mM of tris(1,10-phenanthroline)cobalt tris(trifluoromethanesulfonimide) (Co-phen$^{3+}$) and 0.1 M of lithium perchlorate in acetonitrile. A scan rate was set at 2 mV s$^{-1}$. At different rotating speeds (100, 200, 300, 400, and 500 rpm), five LSV curves were scanned from 0.5 V to –0.5 V to obtain five values of $i_{lc}$ at the horizontal part of cathodic potential region (Figure S10a). In accordance with the Levich equation$^4$ below, the diffusion coefficient Co$^{III}$(phen)$_3$(TFSI)$_3$ was determined to be $21.89 \times 10^{-6}$ cm$^2$ s$^{-1}$ via the plot of cathodic limiting current ($i_{lc}$) vs. rotating rate root ($\omega^{0.5}$), as shown in Figure S10b.

$$i_{lc} = \frac{0.62nFAD^{2/3}v^{-1/6}\omega^{1/2}C}{\nu}$$

where $i_{lc}$ is the cathodic limiting current obtained from the LSV curve at the horizontal part of cathodic potential region, $n$ is the number of electrons transferred, $F$ is Faraday constant, $C$ is the concentration of Co$^{III}$(phen)$_3$(TFSI)$_3$, $D$ is the apparent diffusion coefficient of Co$^{III}$(phen)$_3$(TFSI)$_3$, $v$ is the kinetic viscosity of electrolyte, and $\omega$ is the angular velocity converted from the rotating speed.
Figure S1. Cyclic voltammograms of various DCE dyes dissolved in THF (10 mM). The ferrocene was added as an internal reference (ferrocene/ferrocenium) with a standard potential of 0.76V vs. NHE. The oxidation potential of the dye \((E_{OX})\) is obtained at the center position between the anodic peak and cathodic peak potentials of the dye. The value of HOMO level is obtained via turning the \(E_{OX}\) value into being versus to vacuum level. The value of LUMO level is calculated from the equation of LUMO=HOMO \(-E_{g\text{opt}}\) (vs. vacuum).
Figure S2. The detailed Frontier orbitals of various DCE dyes.
Figure S3. Schematic representation of the calculated electronic structure in the gas-phase for various DCE dyes.

Figure S4. Plot of Mulliken charge variation between the ground-state and the excited state for DCE dyes.
Table S1. Calculated lower-lying transitions of the dyes.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Dye</th>
<th>State</th>
<th>excitation\textsuperscript{b}</th>
<th>(\lambda_{\text{cal}}), eV</th>
<th>(f)</th>
<th>(\Delta(\text{Mulliken charge})),\textsuperscript{d} [e]</th>
<th>(f \times \Delta q)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>DCE1</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S\textsubscript{1}</td>
<td>S \rightarrow L (97%)</td>
<td>2.51</td>
<td>0.34</td>
<td>Ac:-0.50; Ptz(CE):0.41; EO:0.09</td>
<td>-0.17</td>
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<tr>
<td>S\textsubscript{2}</td>
<td>H\rightarrow L (91%)</td>
<td>3.30</td>
<td>0.05</td>
<td>Ac:-0.58; Ptz(CE):0.10; EO:0.47</td>
<td>-0.03</td>
<td></td>
</tr>
<tr>
<td></td>
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</tr>
<tr>
<td>S\textsubscript{3}</td>
<td>H1\rightarrow L (97%)</td>
<td>3.50</td>
<td>0.03</td>
<td>Ac:-0.56; Ptz(CE):0.55; EO:0.00</td>
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<tr>
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<tr>
<td>S\textsubscript{1}</td>
<td>H \rightarrow L (99%)</td>
<td>2.26</td>
<td>0.61</td>
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<td>-0.11</td>
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<tr>
<td>S\textsubscript{2}</td>
<td>H \rightarrow L\textsubscript{1} (97%)</td>
<td>2.48</td>
<td>0.18</td>
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<td>-0.04</td>
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<tr>
<td>S\textsubscript{3}</td>
<td>H2\rightarrow L (93%)</td>
<td>3.19</td>
<td>0.26</td>
<td>Ac:-0.15; T:-0.10; Ptz(CE):0.42; T':-0.05; Ac':-0.12</td>
<td>-0.03</td>
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</tr>
<tr>
<td><strong>DCE3</strong></td>
<td></td>
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<td></td>
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<tr>
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<td>2.27</td>
<td>0.62</td>
<td>Ac:-0.17; T:-0.13; Ptz(OR):0.60; T':-0.13; Ac':-0.17</td>
<td>-0.11</td>
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</tr>
<tr>
<td>S\textsubscript{2}</td>
<td>H \rightarrow L\textsubscript{1} (96%)</td>
<td>2.49</td>
<td>0.18</td>
<td>Ac:-0.20; T:-0.13; Ptz(OR):0.67; T':-0.13; Ac':-0.20</td>
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<tr>
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<td>0.61</td>
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<td></td>
</tr>
<tr>
<td>S\textsubscript{2}</td>
<td>H1\rightarrow L (96%)</td>
<td>2.51</td>
<td>0.17</td>
<td>Ac:-0.20; T:-0.13; Ptz(P):0.67; T':-0.13; Ac':-0.20</td>
<td>-0.03</td>
<td></td>
</tr>
<tr>
<td>S\textsubscript{3}</td>
<td>H2\rightarrow L (94%)</td>
<td>3.20</td>
<td>0.23</td>
<td>Ac:-0.13; T:-0.07; Ptz(P):0.42; T':-0.09; Ac':-0.14</td>
<td>-0.03</td>
<td></td>
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</table>

\textsuperscript{a}Results are based on gas-phase TD-DFT calculation. \textsuperscript{b}H = HOMO, L = LUMO, H1 = The next highest occupied molecular orbital, or HOMO\textendash;1, H2 = HOMO\textendash;2, L1 = LUMO+1, L2 = LUMO 2.

\textsuperscript{c}In parentheses is the population of a pair of molecular orbital (MO) excitations. \textsuperscript{d}Oscillator strength.

\textsuperscript{e}The difference of the Mulliken charge between the ground state and excited state.
Figure S5. Schematic divisions and dihedral angles of various DCE dyes.

Figure S6. (a) Incident photon-to-current conversion efficiency (IPCE) curves of the DSSCs with various DCE dyes (*the DSSC without chenodeoxycholic acid (CDCA) as the co-adsorbent) and (b) photocurrent density–voltage curve of the N719-based DSSCs, measured under simulated AM 1.5G illumination in an iodide-based electrolyte.
Figure S7. (a) Nyquist plots and (b) Bode plots of the DSSCs with various DCE dyes, measured under 1 sun (100 mW cm\(^{-2}\), AM1.5G). An iodide-based electrolyte was used for EIS measurement.

Table S2. Impedance parameters of the DSSCs with various DCE dyes, measured in an iodide-based electrolyte.

<table>
<thead>
<tr>
<th>Dye</th>
<th>(R_{\text{rec}}) (Ω)</th>
<th>(\tau_{\text{e, dark}}) (ms)</th>
<th>(R_{\text{ct2}}) (Ω)</th>
<th>(\tau_{\text{e, light}}) (ms)</th>
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<tbody>
<tr>
<td>DCE1</td>
<td>18.70</td>
<td>5.13</td>
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<td>DCE2</td>
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<td>11.65</td>
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<td>11.64</td>
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<td>DCE3</td>
<td>22.49</td>
<td>6.74</td>
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<td>DCE4</td>
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<td>5.13</td>
<td>14.56</td>
<td>2.26</td>
</tr>
</tbody>
</table>
Figure S8. Linear sweep voltammograms (LSV) for the films of (a) TiO$_2$/DCE2 and (b) TiO$_2$/DCE4, measured in the iodide-based electrolyte containing 1.0 mM of tetrabutylammonium triiodide (I$_3^-$) and 0.1 M lithium perchlorate (LiClO$_4$) in acetonitrile. And the linear sweep voltammograms for the films of (c) TiO$_2$/DCE2 and (b) TiO$_2$/DCE4, measured in the cobalt-based electrolyte, containing 1 mM of tris(1,10-phenanthroline)cobalt tris(trifluoromethanesulfonimide) and 0.1 M of lithium perchlorate in acetonitrile. A scan rate was set at 2 mV s$^{-1}$. 

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(Images of linear sweep voltammograms for TiO$_2$/DCE2 and TiO$_2$/DCE4 in iodide-based electrolyte, and for TiO$_2$/DCE2 and TiO$_2$/DCE4 in cobalt-based electrolyte, showing the voltage vs. current for different scan rates and with inset details at formal potential of I$_3^-$ and Cu$^{2+}$/Cu$^+$.)
**Figure S9.** Cyclic voltammogram of cobalt-based electrolyte, containing 10 mM of tris(1,10-phenanthroline)cobalt bis(trifluoromethanesulfonimide), 1 mM of tris(1,10-phenanthroline)cobalt tris(trifluoromethanesulfonimide) and 0.1 M of lithium perchlorate in acetonitrile, measured at a scan rate of 100 mV s\(^{-1}\).

**Figure S10.** (a) Linear sweep voltammograms (LSV) and (b) plot of \(i_{lc}\) vs. \(\omega^{1/2}\), measured in a cobalt-based electrolyte, containing 1 mM of tris(1,10-phenanthroline)cobalt tris(trifluoromethanesulfonimide) and 0.1 M of lithium perchlorate in acetonitrile, using a rotating disk electrode with Pt as the disk material (Pt–RDE), measured at a scan rate of 2 mV s\(^{-1}\).
References:


