

Supplementary Data

Dual-Channel Anchorable Organic Dyes with Well-Defined Structures for Highly Efficient Dye-sensitized Solar Cells

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Experimental

1. Materials

All reactions were carried out under a nitrogen atmosphere. Solvents were distilled from appropriate reagents. All reagents were purchased from Aldrich. (5'-(1,3-dioxolan-2-yl)-2,2'-bithiophen-5-yl)tributylstannane¹ was synthesised following the same procedures as described previously.

2. Measurements

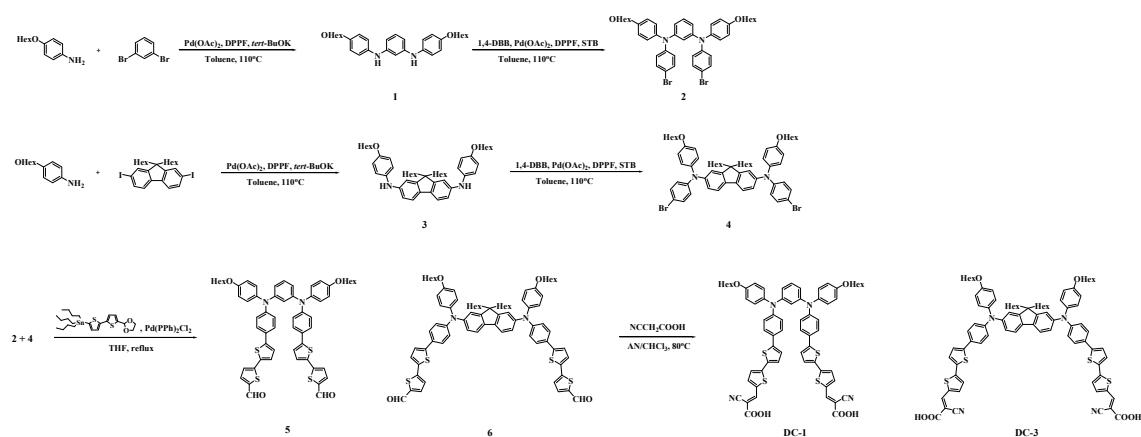
¹H-NMR and ¹³C-NMR spectra were recorded at room temperature with Varian Oxford 300 spectrometers and chemical shifts were reported in ppm units with tetramethylsilane as the internal standard. FTIR spectra were taken on a JASCO, 4200 + ATR Pro-450-S spectrophotometer. UV-visible absorption spectra were obtained in THF on a Shimadzu UV-2401PC spectrophotometer. Cyclic voltammetry was carried out with a Versa STAT3 (AMETEK). A three-electrode system was used and consisted of a reference electrode (Ag/AgCl), a working electrode, and a platinum wire electrode. The redox potential of dyes on TiO₂ was measured in CH₃CN with 0.1M TBAPF₆ with a scan rate between 50 mVs⁻¹.

3. Density functional theory (DFT)/time-dependent DFT (TDDFT) calculations

Structural optimization of DC dyes was done with a PBE exchange-correlation function using the Vienna ab initio simulation package (VASP).^{2,3} We used 400 eV as the cut-off energy, and the conjugate gradient method was employed to optimize the geometry until the force exerted on an atom was less than 0.03 eV/Å. In order to calculate the absorption spectra, we performed the TD-DFT calculations for more stable one between the two

configurations. Calculations were done in the gas phase using the 6-31G(d,p) basis set in GAUSSIAN03 program.⁴ We focused on transitions occurring in the range of 350~800 nm, specifically those whose oscillation strengths were greater than 0.1. In order to treat the low wavelength excitations correctly around 350 nm, we made extensive calculations up to 100 singlet→singlet transitions.

4. Synthesis



Scheme 1 Chemical structures and synthesis of DC dyes.

General procedure of benzenediamines

1,3-dibromobenzene or 1,4-dibromobenzene, 4-hexyloxyaniline, (3.00 equiv), Pd(OAc)₂ (0.05 equiv.), bis(diphenylphosphanyl)ferrocene (DPPF), (0.10 equiv) and sodium *tert*-butoxide (3.00 equiv) were heated in of dry Toluene at 110°C for 12 h under an inert N₂ atmosphere. The reaction was monitored by thin layer chromatography. After complete consumption of starting material, the reaction mixture was subjected to an aqueous work up, dried over magnesium sulfate (MgSO₄), and the solvent was evaporated under vacuum. The crude product was then purified by chromatography on silica gel.

N¹, N³-bis(4-(hexyloxy)phenyl)benzene-1,3-diamine (1)

The above general procedure was followed using 4-hexyloxy aniline (12.3 g, 63.6 mmol) and 1,3-dibromobenzene (5.00 g, 21.2 mmol) in 50 mL of toluene under an inert N₂ atmosphere. After 12 h, the crude reaction mixture was treated with a saturated ammonium chloride solution and extracted with toluene. The organic phase was washed with brine, dried over MgSO₄, and the solvent was evaporated under vacuum. The crude product was purified by column chromatography (silica gel, CH₂Cl₂–hexane 2 : 1) to give 7.05 g (72%) of compound 1. ¹H NMR (300 MHz, CDCl₃) δ 0.88 (s, 6H), 1.32-1.37 (m, 12H), 1.44-1.47 (m, 4H), 1.78 (m, 4H), 3.91 (t, 4H), 5.41 (s, 2H), 6.37 (d, 2H), 6.44 (t, 1H), 6.82 (d, 4H), 7.03 (s, 1H), 7.06 (d, 4H). ¹³C NMR (300 MHz, CDCl₃) δ 14.2, 22.8, 25.9, 29.5, 31.8, 68.6, 102.5, 107.2, 115.4, 122.6, 130.2, 135.5, 146.5, 154.9.

N¹, N³-bis(4-bromophenyl)-N¹, N³-bis(4-(hexyloxy)phenyl)benzene-1,3-diamine (2)

The above general procedure was followed using compound 1 (4.50 g, 9.77 mmol) and 1,4-dibromobenzene (23.0 mg, 97.5 mmol) in 50 mL of dry toluene under an inert N₂ atmosphere. After 12 h, the crude reaction mixture was treated with a saturated ammonium chloride solution and extracted with dichloromethane. The organic phase was washed with brine, dried over MgSO₄, and the solvent was evaporated under vacuum. The crude product was purified by column chromatography (silica gel, CH₂Cl₂–hexane 1 : 2) to give 5.09 g (68%) of compound 2. ¹H NMR (300 MHz, DMSO-d₆) δ 0.89 (s, 6H), 1.32-1.37 (m, 12H), 1.44-1.48 (m, 4H), 1.78 (m, 4H), 3.88 (t, 4H), 6.55 (d, 2H), 6.58 (s, 1H), 6.71-6.81 (m, 9H), 6.99 (d, 4H), 7.19 (d, 4H). ¹³C NMR (300 MHz, DMSO-d₆) δ 14.2, 22.8, 26.0, 29.5, 31.8, 68.5, 113.9, 115.5, 117.1, 123.9, 127.4, 131.9, 139.8, 147.1, 148.5, 156.1.

9,9-dihexyl-N², N⁷-bis(4-(hexyloxy)phenyl)-9H-fluorene-2,7-diamine (3)

The above general procedure was followed using 4-hexyloxy aniline (5.00 g, 25.9 mmol) and 9,9-dihexyl-2,7-diiodo-9*H*-fluorene (3.00 g, 8.61 mmol) in 50 mL of toluene under an inert N₂ atmosphere. After 12 h, the crude reaction mixture was treated with a saturated ammonium chloride solution and extracted with toluene. The organic phase was washed with brine, dried over MgSO₄, and the solvent was evaporated under vacuum. The crude product was purified by column chromatography (silica gel, CH₂Cl₂–hexane 2 : 1) to give 3.60 g (58%) of compound 3. ¹H NMR (300 MHz, DMSO-*d*₆) δ 0.72-0.74 (m, 6H), 0.83-0.89 (m, 6H), 1.08-1.10 (m, 6H), 1.29-1.42 (m, 8H), 1.65-1.70 (m, 2H), 1.78 (m, 2H), 3.86 (t, 4H), 6.80-6.86 (m, 6H), 6.71 (s, 2H), 6.98 (d, 2H), 7.82 (s, 2H). ¹³C NMR (300 MHz, DMSO-*d*₆) □ 14.0, 22.1, 23.5, 28.8, 29.0, 31.1, 54.1, 67.6, 110.0, 114.3, 115.1, 115.6, 119.1, 132.5, 136.8, 142.8, 151.0, 152.6.

***N*²,*N*⁷-bis(4-bromophenyl)-9,9-dihexyl-*N*²,*N*⁷-bis(4-(hexyloxy)phenyl)-9*H*-fluorene-2,7-diamine (4)**

The above general procedure was followed using compound 3 (3.00 g, 4.18 mmol) and 1,4-dibromobenzene (9.87 g, 41.8 mmol) in 50 mL of dry toluene under an inert N₂ atmosphere. After 12 h, the crude reaction mixture was treated with a saturated ammonium chloride solution and extracted with dichloromethane. The organic phase was washed with brine, dried over MgSO₄, and the solvent was evaporated under vacuum. The crude product was purified by column chromatography (silica gel, CH₂Cl₂–hexane 1 : 2) to give 3.30 g (77%) of compound 4. ¹H NMR (300 MHz, Acetone-*d*₆) δ 0.69-0.71 (m, 6H), 0.78-0.84 (m, 6H), 1.06-1.34 (m, 6H), 1.33-1.48 (m, 8H), 1.74-1.85 (m, 8H), 3.95 (t, 4H), 6.89 (d, 8H), 6.94 (dd, 2H), 7.05 (d, 4H), 7.14 (s, 2H), 7.30 (d, 4H), 7.57 (d, 2H). ¹³C NMR (300 MHz, Acetone-*d*₆) δ 14.4, 23.2, 24.6, 26.5, 30.6, 40.7, 55.8, 68.7, 113.4, 116.2, 119.6, 120.8, 123.8, 127.8, 132.6, 137.0, 140.8, 147.1, 148.6, 152.7, 156.9.

5',5''-(4,4'-(1,3-phenylenebis((4-(hexyloxy)phenyl)azanediyl))bis(4,1-phenylene))di-2,2'-bithiophene-5-carbaldehyde (5)

A mixture of compound 2 (0.90, 1.17 mmol), (5'-(1,3-dioxolan-2-yl)-2,2'-bithiophen-5-yl)tributylstannane (1.70 g, 3.52 mmol), Pd(PPh₃)₂Cl₂ (0.10 g, 0.14 mmol), in 50 mL dry THF was refluxed overnight under N₂ atmosphere. The reaction was monitored by thin layer chromatography. After complete consumption of starting material, concentrated hydrochloric acid (2 mL) was added, the mixture was stirred at room temperature for 10 min and extracted with dichloromethane. The organic phase was washed with brine, dried over MgSO₄, and the solvent was evaporated under vacuum. The crude product was purified by column chromatography (silica gel, CH₂Cl₂) to give 0.74 g (64%) of compound 5. ¹H NMR (300 MHz, CDCl₃) δ 1.25-1.35 (m, 12H), 11.59 (m, 4H), 1.75-1.80 (m, 4H), 3.92 (t, 4H), 6.64 (d, 2H), 6.83 (d, 4H), 6.97 (d, 4H), 7.06-7.13 (d, 8H), 7.19 (d, 2H), 7.26 (d, 2H), 7.38 (d, 4H), 7.63 (d, 2H), 7.84 (s, 2H). ¹³C NMR (300 MHz, CDCl₃) δ 14.4, 23.3, 29.1, 32.4, 68.7, 116.3, 121.1, 124.9, 126.2, 127.2, 128.1, 134.2, 138.9, 140.3, 142.2, 143.0, 146.9, 149.3, 157.1, 183.3.

5',5''-(4,4'-(9,9-dihexyl-9H-fluorene-2,7-diyl))bis((4-(hexyloxy)phenyl)azanediyl))bis(4,1-phenylene))di-2,2'-bithiophene-5-carbaldehyde (6)

A mixture of compound 4 (1.00 g, 0.97 mmol), (5'-(1,3-dioxolan-2-yl)-2,2'-bithiophen-5-yl)tributylstannane (1.54 g, 2.92 mmol), Pd(PPh₃)₂Cl₂ (0.10 g, 0.14 mmol), in 50 mL dry THF was refluxed overnight under N₂ atmosphere. The reaction was monitored by thin layer chromatography. After complete consumption of starting material, concentrated hydrochloric acid (2 mL) was added, the mixture was stirred at room temperature for 10 min and extracted with dichloromethane. The organic phase was washed with brine, dried

over MgSO₄, and the solvent was evaporated under vacuum. The crude product was purified by column chromatography (silica gel, CH₂Cl₂) to give 0.500 g (41%) of compound 6. ¹H NMR (300 MHz, CDCl₃) δ 0.70-0.74 (m, 6H), 0.82-0.91 (m, 6H), 1.17-1.21 (m, 6H), 1.35-1.48 (m, 8H), 1.75-1.80 (m, 8H), 3.94 (t, 4H), 6.85 (d, 4H), 6.99-7.15 (m, 14H), 7.23 (d, 2H), 7.31 (d, 2H), 7.42-7.50 (m, 6H), 7.66 (d, 2H), 9.85 (s, 2H). ¹³C NMR (300 MHz, CDCl₃) δ 13.8, 17.7, 24.0, 26.0, 27.0, 28.0, 29.5, 29.8, 31.8, 40.2, 55.2, 68.4, 115.4, 119.0, 119.9, 121.5, 122.9, 123.3, 126.0, 127.2, 127.4, 133.8, 136.3, 137.6, 140.1, 140.2, 146.1, 146.6, 147.6, 148.7, 152.1, 156.0, 182.4.

(2E,2'E)-3,3'-(5',5''-(4,4'-(1,3-phenylenebis((4-(hexyloxy)phenyl)azanediyl))bis(4,1-phenylene))bis(2,2'-bithiophene-5',5-diyl))bis(2-cyanoacrylic acid) (DC1)

Compound 5 (0.11 g, 0.11 mmol), dissolved in CHCl₃ (50 mL) and acetonitrile (50 mL), was condensed with 2-cyanoacetic acid (0.02 g, 0.24 mmol) in the presence of piperidine (0.03 mL, 0.35 mmol). The mixture was refluxed for 12 h. After cooling the solution, the organic layer was removed *in vacuo*. Dark red solid of **DC1** was obtained by silica gel chromatography (MC/MeOH=3:1) Yield was 75%. ¹H NMR (300 MHz, DMSO-*d*₆) δ 0.86 (s, 6H), 1.21-1.27 (m, 12H), 1.38(m, 4H), 1.66-1.68 (m, 4H), 3.91 (t, 4H), 6.39 (d, 2H), 6.68 (s, 1H), 6.90-6.92 (m, 10H), 7.03 (d, 4H), 7.29 (d, 6H), 7.51-7.55 (m, 5H), 8.06 (s, 2H). ¹³C NMR (300 MHz, DMSO-*d*₆) δ 14.2, 22.4, 25.5, 29.0, 31.3, 67.0, 115.8, 11.92, 122.6, 124.1, 126.5, 127.2, 127.8, 133.8, 135.5, 138.8, 141.9, 144.2, 147.3, 148.0, 156.0, 163.3. UV-vis (THF, nm): λ_{max} (log ε) 458 (41 600). PL (THF, nm): λ_{max} 640. MS (MALDI-TOF): Calcd. for C₆₆H₅₈N₄O₆S₄, 1131.45; found, 1131.5.

(2Z,2'Z)-3,3'-(5',5''-(4,4'-(9,9-dihexyl-9H-fluorene-2,7-diyl))bis((4-

(hexyloxy)phenyl)azanediy)bis(4,1-phenylene))bis(2,2'-bithiophene-5',5'-diyl))bis(2-cyanoacrylic acid) (DC3)

Compound 6 (0.45 g, 0.36 mmol), dissolved in CHCl_3 (50 mL) and acetonitrile (50 mL), was condensed with 2-cyanoacetic acid (0.04g, 3.00 mmol) in the presence of piperidine (0.02 g, 0.28 mmol). The mixture was refluxed for 12 h. After cooling the solution, the organic layer was removed *in vacuo*. Dark solid of **DC3** was obtained by silica gel chromatography (MC/MeOH=3:1) Yield was 40%. ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ 0.71-0.73 (m, 6H), 0.80-0.82 (m, 6H), 0.91-0.95 (m, 6H), 1.03-1.10 (m, 8H), 1.61-1.72 (m, 8H), 3.82 (t, 4H), 6.82-7.01 (m, 14H), 7.27 (d, 2H), 7.41-7.46 (m, 12H), 7.89 (d, 2H), 8.40 (s, 2H). ^{13}C NMR (300 MHz, $\text{DMSO}-d_6$) δ 13.9, 25.2, 30.4, 34.4, 97.6, 115.3, 116.5, 120.5, 123.6, 124.2, 125.1, 126.2, 126.7, 128.1, 132.7, 133.5, 135.7, 139.1, 141.3, 145.5, 145.8, 147.8, 151.3, 155.5, 163.5. UV-vis (THF, nm): λ_{max} (log ϵ) 494 (60 100). PL (THF, nm): λ_{max} 724. MS (MALDI-TOF): Calcd. for $\text{C}_{78}\text{H}_{73}\text{N}_5\text{O}_6\text{S}_5$, 1387.9; found, 1388.1.

5. Fabrication and testing of DSSC

FTO glass plates (Pilkington) were cleaned in a detergent solution using an ultrasonic bath for 1 hr, then rinsed with water and ethanol. The FTO glass plates were immersed in an aqueous solution of 40 mM TiCl_4 at 70°C for 30 min and then washed with water and ethanol. The first TiO_2 layer with a thickness of 12 μm was prepared by screen-printing TiO_2 paste (Solaronix, 13 nm anatase), and the second scattering layer containing 400 nm sized anatase particles was deposited by screen printing. The TiO_2 electrodes were immersed into the dye solution (0.3 mM) in THF/EtOH (2:1) with DCA (40 mM) or HC-A1 (1 mM) and kept at room temperature overnight. Counter-electrodes were prepared by coating with a drop of H_2PtCl_6 solution (2 mg of Pt in 1 mL of ethanol) on an FTO plate. The dye-adsorbed TiO_2 electrode and Pt counter electrode were assembled in a sealed

sandwich-type cell. One drop of electrolyte was then introduced into the cell, which was composed of 0.6 M 1,2-dimethyl-3-propyl imidazolium iodide, 0.05 M iodine, 0.1 M LiI, and 0.5 M *tert*-butylpyridine in acetonitrile. The electrolyte was introduced into the inter-electrode space from the counter electrode side through predrilled holes. The drilled holes were sealed with a microscope cover slide and Surlyn to avoid leakage of the electrolyte solution.

6. Photoelectrochemical measurements of DSSC

Photoelectrochemical data were measured using a 1000 W xenon light source (Oriel, 91193) that was focused to give 1000 W/m^2 , the equivalent of one sun at AM 1.5G, at the surface of the test cell. The light intensity was adjusted with a Si solar cell that was double-checked with an NREL-calibrated Si solar cell (PV Measurement Inc.). The applied potential and measured cell current were measured using a Keithley model 2400 digital source meter. The current–voltage characteristics of the cell under these conditions were determined by biasing the cell externally and measuring the generated photocurrent. This process was fully automated using Wavemetrics software.

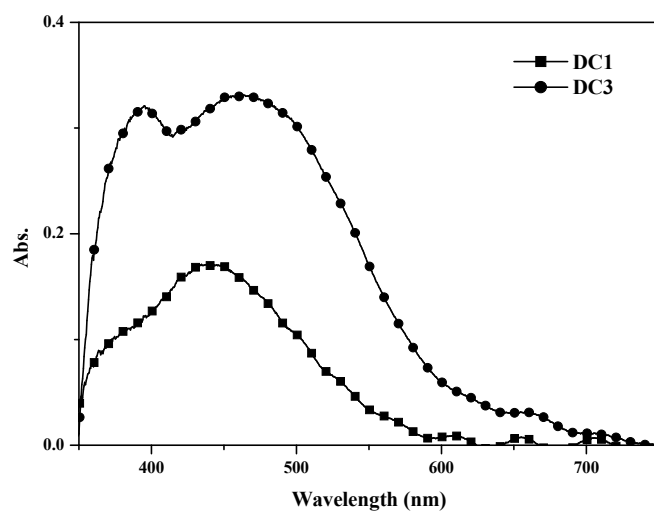


Fig. S1 Absorption spectra of DC dyes on 2 μm TiO_2 transparent films.

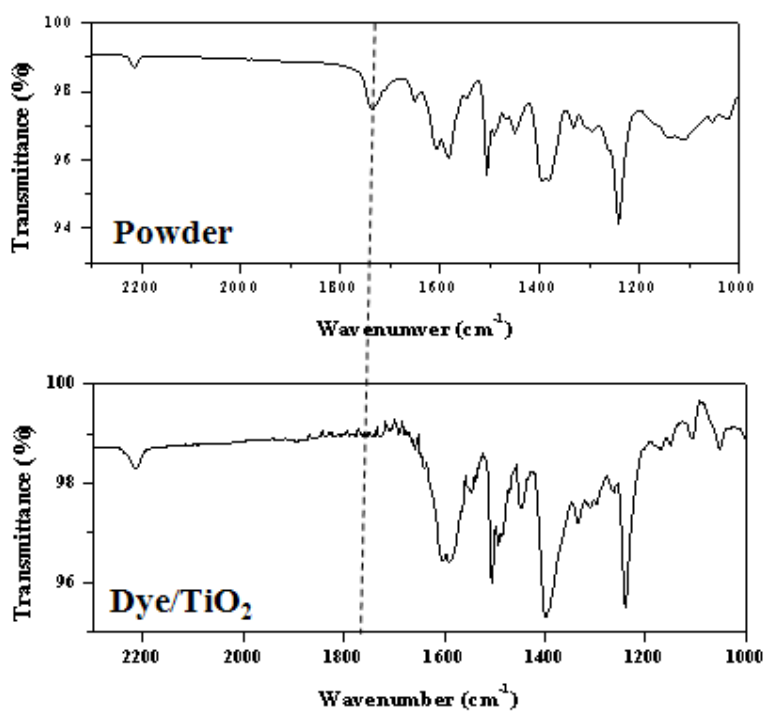


Fig. S2 ATR-FTIR spectra of DC1 dye.

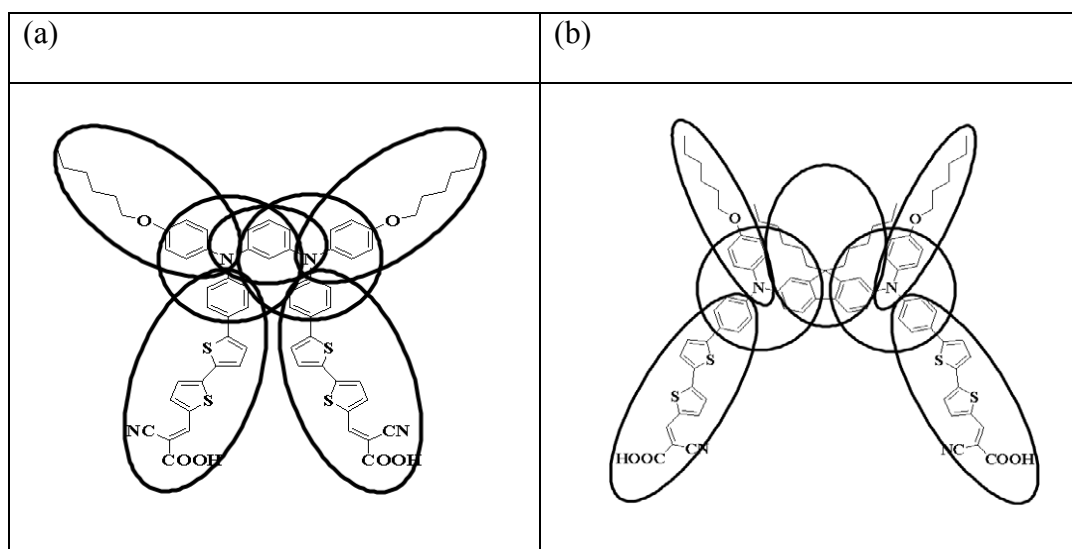


Fig. S3 Fragments of DC1 (a) and DC3 (b) dyes separately optimized before being combined into the final dye molecules and reoptimized.

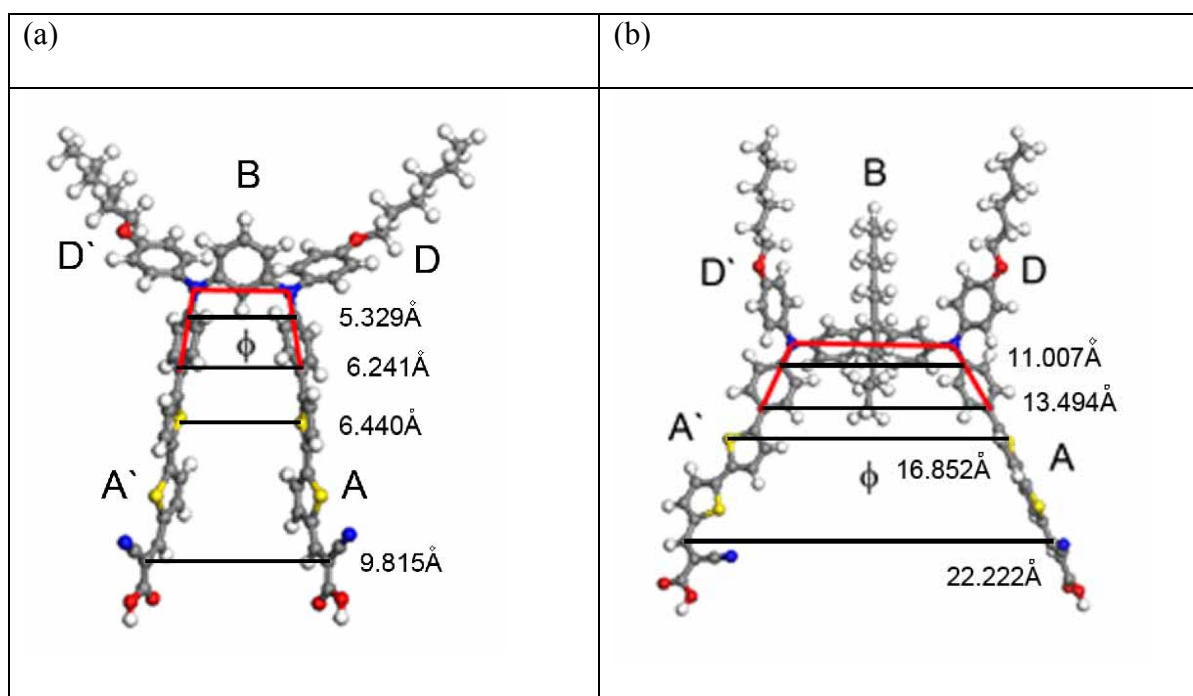


Fig. S4 Interatomic distances between the same kind of atoms in the two channels for DC1 (a) and DC3 (b).

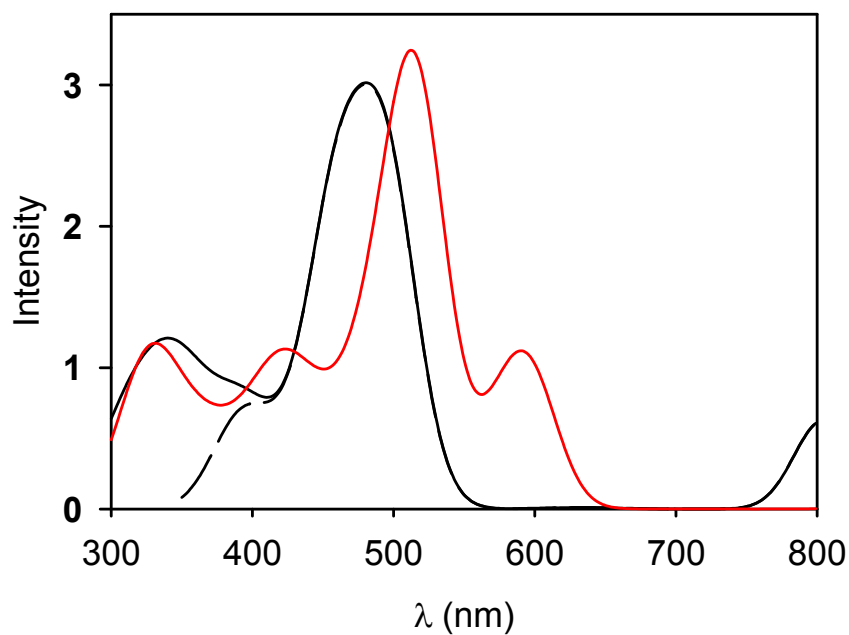


Fig S5 Absorption spectra of DC1 (black) and DC3 (red) dyes obtained from the TD-DFT calculations using the 6-31G(d,p) basis set. For the DC1 dye, the solid line corresponds to the calculation for 100 singlet \rightarrow single transitions, while the dashed line corresponds to 40 transitions. For the DC3 dye, the result shown in the figure corresponds to the calculation for 100 transitions.

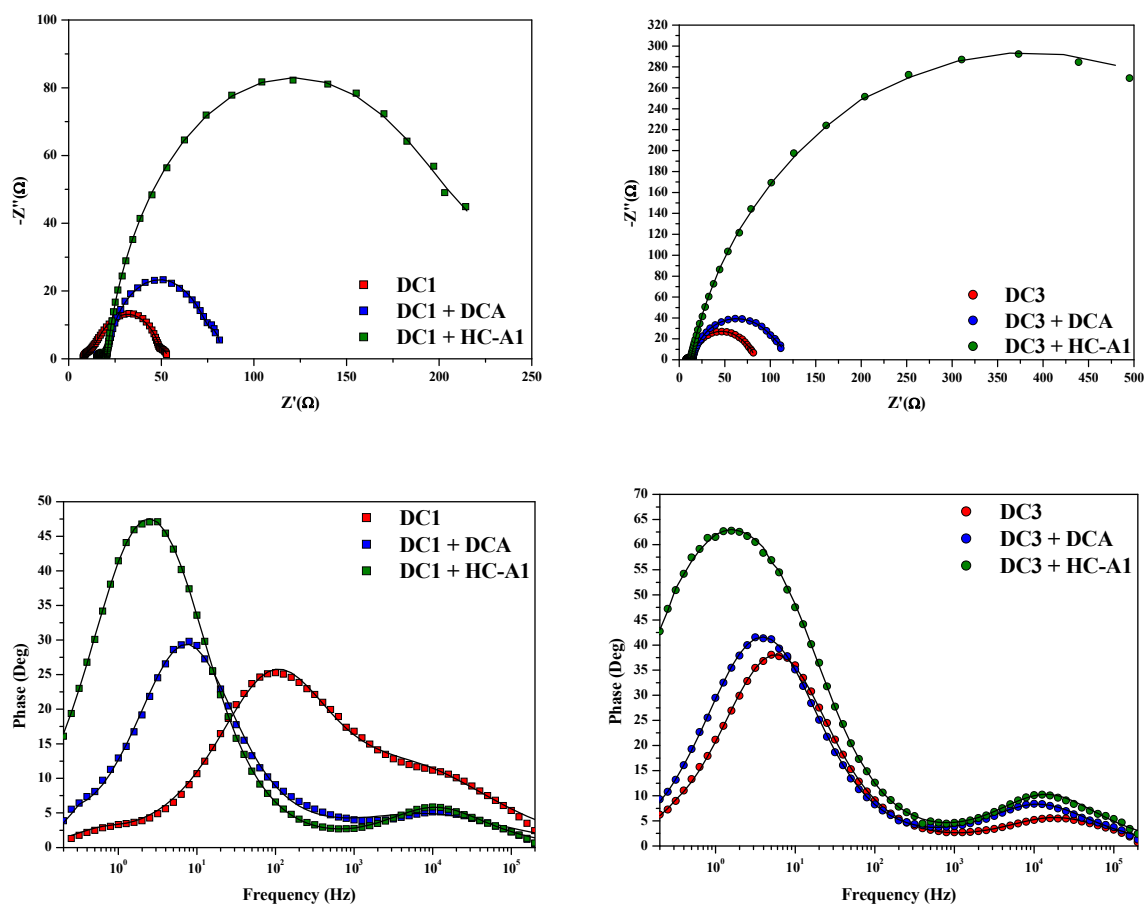


Fig. S6 Nyquist and Bode-phase plots of electrochemical impedance spectra for the DSSCs based DC dyes.

Table S1 Major contributions to those transitions with the oscillator strength greater than 0.1 obtained from the TD-DFT calculations: the absorption wavelength (λ), oscillation strength (f), the character of the transition, % contribution of a particular molecular transition, and nature of the transition. See labels in Fig. S3 for nature of transition.

dye	λ (nm)	f	Character	%	Nature
DC1	391	0.10	HOMO-2 \rightarrow LUMO +3	48	A, D \rightarrow A
			HOMO-1 \rightarrow LUMO +5	13	B \rightarrow B
	459	0.85	HOMO-4 \rightarrow LUMO +1	28	D \rightarrow A
			HOMO-1 \rightarrow LUMO +3	54	B \rightarrow A
	473	0.20	HOMO-5 \rightarrow LUMO	29	B, D' \rightarrow A'
			HOMO-1 \rightarrow LUMO +2	55	B \rightarrow A'
	494	0.96	HOMO-5 \rightarrow LUMO	23	B, D' \rightarrow A'
			HOMO-4 \rightarrow LUMO +1	22	D \rightarrow A
			HOMO-2 \rightarrow LUMO +1	21	A, D \rightarrow A
	514	0.12	HOMO \rightarrow LUMO +2	64	B \rightarrow A'
DC3	417	0.10	HOMO-6 \rightarrow LUMO +1	19	A, A' \rightarrow A'
			HOMO-2 \rightarrow LUMO +3	51	A' \rightarrow A, A'
	422	0.13	HOMO-7 \rightarrow LUMO	19	B \rightarrow A
			HOMO-7 \rightarrow LUMO +1	24	B \rightarrow A'
			HOMO-6 \rightarrow LUMO	22	A, A' \rightarrow A
	467	0.12	HOMO-5 \rightarrow LUMO	66	A' \rightarrow A
	478	0.10	HOMO \rightarrow LUMO +4	74	B \rightarrow B
	491	0.13	HOMO-1 \rightarrow LUMO +3	42	D, D' \rightarrow A, A'
			HOMO-3 \rightarrow LUMO	20	A \rightarrow A
	495	0.33	HOMO-2 \rightarrow LUMO +1	17	A' \rightarrow A'
			HOMO-1 \rightarrow LUMO +2	22	D, D' \rightarrow B, A, A'
	514	0.43	HOMO-1 \rightarrow LUMO +2	32	D, D' \rightarrow B, A, A'
			HOMO-1 \rightarrow LUMO +3	46	D, D' \rightarrow A, A'
	519	0.90	HOMO-2 \rightarrow LUMO +1	39	A' \rightarrow A'
			HOMO-1 \rightarrow LUMO +2	39	D, D' \rightarrow D, A, A'
	574	0.20	HOMO \rightarrow LUMO+2	90	B \rightarrow A, A'
597	0.43	HOMO \rightarrow LOUM+3	96	B \rightarrow B, A, A'	

Reference

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