Electronic Supplementary Information

for

Fluorene-bridged organic dyes with di-anchoring groups for efficient co-adsorbent-free dye-sensitized solar cells

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General synthetic procedure for 1a–1b

A mixture of 4-(*N*-phenyl-*N*-*p*-tolylamino)phenylboronic acid (3 g, 9.90 mmol), 2,7-dibromo-9,9-dialkyl-9H-fluorene (2.50 mmol), and 2 M K_2CO_3 (10 mL) in tetrahydrofuran (50 mL) were degassed with N_2 for 5 min. $Pd(PPh_3)_4$ (100 mg) was added and the resulting mixture was heated to reflux for two days. After being cooled to room temperature, water was added and the mixture was extracted with ethyl acetate. The combined organic fractions were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude compound was purified by silica gel column chromatography using hexane as eluent to afford the products as pale yellow oils.

1a: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 7.8 Hz, 2H, Ar), 7.55–7.53 (m, 8H, Ar), 7.27–7.23 (m, 4H, Ar), 7.15–7.11 (m, 8H, Ar), 7.09–7.05 (m, 8H, Ar), 7.03–7.00 (m, 2H, Ar), 2.33 (s, 6H, alkyl), 2.03–1.99 (m, 4H, alkyl), 1.30–1.04 (m, 20H, alkyl), 0.80–0.77 (m, 6H, alkyl), 0.72–0.71 (m, 4H, alkyl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.60, 147.88, 147.22, 145.11, 139.70, 139.38, 135.71, 135.56, 135.24, 132.97, 131.89, 131.67, 130.00, 129.20, 127.70, 125.47, 125.08, 123.83, 123.56, 123.52, 122.48, 121.76, 120.87, 119.86 (Ar), 55.21, 40.52, 31.80, 31.63, 30.07, 29.26, 23.83, 22.69, 20.88, 14.15 (alkyl) ppm. MALDI-TOF: *m/z* = 904.56 (M^+).

1b: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 7.8 Hz, 2H, Ar), 7.60 (s, 2H, Ar), 7.57–7.53 (m, 6H, Ar), 7.31–7.26 (m, 4H, Ar), 7.19–7.15 (m, 10H, Ar), 7.13–7.09 (m, 6H, Ar), 7.05–7.01 (m, 2H, Ar), 2.37 (s, 6H, alkyl), 2.10–2.08 (m, 4H, alkyl), 1.32–1.30 (m, 2H, alkyl), 0.91–0.78 (m, 16H, alkyl), 0.67–0.63 (m, 6H, alkyl), 0.60–0.55 (m, 6H, alkyl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.24, 147.94, 147.11, 145.17, 139.92, 138.96, 135.69, 135.58, 135.46, 132.95, 130.03, 129,22, 127.70, 125.62, 125.11, 123.91, 123.84, 123.65, 123.53, 123.43, 122.46, 122.27, 122.10, 119.82 (Ar), 55.01, 44.61, 34.72, 33.84, 31.69, 28.25, 27.17, 22.82, 20.94, 14.22 (alkyl) ppm. MALDI-TOF: *m/z* = 904.65 (M^+).

General synthetic procedure for 2a–2b

NBS (410 mg, 2.3 mmol) was added to the solution of **1a** or **1b** (2 g, 2.2 mmol) in chloroform (50 mL) at 0 °C. The mixture was allowed to warm to room temperature and stirring was continued for 12 h. Then, the reaction was quenched by addition of water (50 mL), and extracted with dichloromethane. The collected organic layer was evaporated under vacuum and the residue was purified by column chromatography on silica gel with hexane as eluent to give **2a** or **2b** as a pale yellow oil, respectively.

2a: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 7.7 Hz, 2H, Ar), 7.56–7.52 (m, 8H, Ar), 7.34–7.32 (m, 4H, Ar), 7.15–7.10 (m, 8H, Ar), 7.06–7.03 (m, 4H, Ar), 7.00–6.98 (m, 4H, Ar), 2.34 (s, 6H, alkyl), 2.03–2.00 (m, 4H, alkyl), 1.26–1.24 (m, 4H, alkyl), 1.07–1.04 (m, 16H, alkyl), 0.80–0.77 (m, 6H, alkyl), 0.70–0.68 (m, 4H, alkyl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.16, 147.04, 146.68, 144.66, 139.78, 139.26, 136.90, 135.87, 133.54, 132.11, 130.15, 127.85, 125.59, 125.53, 125.20, 125.09, 124.76, 124.52, 123.87, 123.08, 122.85, 120.90, 119.91, 114.47 (Ar), 55.22, 40.47, 31.79, 30.04, 29.23, 23.82, 22.67, 22.60, 20.89, 14.14 (alkyl) ppm. MALDI-TOF: *m/z* = 1060.53 (M^+).

2b: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 7.8 Hz, 2H, Ar), 7.58 (s, 2H, Ar), 7.54–7.51 (m, 6H, Ar), 7.35–7.33 (m, 4H, Ar), 7.15–7.11 (m, 8H, Ar), 7.08–7.04 (m, 4H, Ar), 7.02–6.98 (m, 4H, Ar), 2.35 (s, 6H, alkyl), 2.06–2.05 (m, 4H, alkyl), 1.26–1.28 (m, 2H, alkyl), 0.86–0.72 (m, 16H, alkyl), 0.65–0.61 (m, 6H, alkyl), 0.58–0.54 (m, 6H, alkyl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.26, 147.08, 146.56, 144.66, 139.98, 138.81, 136.29, 136.18, 136.08, 132.11, 130.15, 127.82, 125.28, 125.65, 125.28, 125.21, 125.13, 124.75, 123.97, 123.87, 123.79, 122.30, 119.84, 114.48 (Ar), 55.01, 44.57, 34.72, 33.83, 31.63, 28.23, 27.16, 22.78, 20.91, 14.17 (alkyl) ppm. MALDI-TOF: *m/z* = 1060.55 (M^+).

General synthetic procedure for 3a–3b

A mixture of thiophen-2-yl-2-boronic acid (0.51 g, 4.0 mmol), **2a** or **2b** (1.5 g, 1.41 mmol) and 2 M K_2CO_3 (10 mL) in tetrahydrofuran (50 mL) were degassed with N_2 for 5 min. $Pd(PPh_3)_4$ (100 mg) was added and the resulting mixture was heated to reflux for two days. After being cooled to room temperature, water was added and the mixture was extracted with ethyl acetate. The combined organic fractions were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude compound was purified by silica gel column chromatography using hexane as eluent to afford the target products as pale yellow solids.

3a: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 8.0 Hz, 2H, Ar), 7.50–7.47 (m, 8H, Ar), 7.43–7.39 (m, 4H, Ar), 7.17–7.09 (m, 8H, Ar), 7.06–7.00 (m, 12H, Ar), 7.00–6.97 (m, 2H, Ar), 2.27 (s, 6H, alkyl), 1.96–1.92 (m, 4H, alkyl), 1.09–1.03 (m, 20H, alkyl), 0.73–0.69 (m, 6H, alkyl), 0.65–0.63 (m, 4H, alkyl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.64, 147.25, 146.84, 144.77, 144.35, 139.77, 139.33, 135.66, 133.35, 130.10, 128.38, 127.99, 127.79, 126.74, 125.52, 125.25, 124.75, 124.42, 124.04, 123.96, 123.80, 123.46, 123.10, 122.19, 120.90, 119.91 (Ar), 54.17, 39.46, 30.75, 30.57, 29.02, 28.21, 22.79, 21.64, 19.86, 13.10 (alkyl) ppm. MALDI-TOF: *m/z* =

1068.55 (M^+).

3b: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 7.9 Hz, 2H, Ar), 7.76 (s, 2H, Ar), 7.70–7.63 (m, 10H, Ar), 7.37–7.32 (m, 8H, Ar), 7.28–7.24 (m, 12H, Ar), , 7.18–7.16 (m, 2H, Ar), 2.49 (s, 6H, alkyl), 2.24–2.22 (m, 4H, alkyl), 1.44–1.42 (m, 8H, alkyl), 1.07–1.03 (m, 10H, alkyl), 0.79–0.74 (m, 6H, alkyl), 0.72–0.69 (m, 6H, alkyl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.34, 147.36, 146.82, 144.91, 144.44, 140.06, 138.99, 136.05, 133.33, 130.21, 128.45, 128.07, 127.87, 126.83, 125.81, 125.76, 125.41, 125.34, 125.27, 124.01, 123.50, 123.55, 122.38, 122.26, 122.20, 119.99 (Ar), 55.12, 44.69, 34.82, 31.75, 28.34, 27.30, 22.92, 21.04, 14.31, 10.58 (alkyl) ppm. MALDI-TOF: *m/z* = 1068.52 (M^+).

General synthetic procedure for 4a–4b

NBS (178 mg, 1 mmol) was added to the solution of **3a** or **3b** (1.07 g, 1 mmol) in chloroform (50 mL) at 0 °C. The mixture was allowed to warm to room temperature and stirring was continued for 12 h. Then, the reaction was quenched by the addition of water (50 mL) and the mixture was extracted with dichloromethane. The collected organic layer was evaporated under vacuum and the residue was purified by column chromatography on silica gel with hexane as eluent to give **4a** or **4b** as a pale yellow oil.

4a: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 7.6 Hz, 2H, Ar), 7.71–7.65 (m, 8H, Ar), 7.57–7.46 (m, 4H, Ar), 7.33–7.23 (m, 4H, Ar), 7.23–7.19 (m, 12H, Ar), 7.08–7.03 (m, 4H, Ar), 2.46 (s, 6H, alkyl), 2.19–2.15 (m, 4H, alkyl), 1.33–1.18 (m, 20H, alkyl), 0.93–0.90 (m, 6H, alkyl), 0.86–0.85 (m, 4H, alkyl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.75, 148,31, 147.72, 146.74, 145.95, 144.71, 144.53, 140.18, 139.89, 135.98, 133.80, 133.59, 130.90, 130.27, 129.59, 127.95, 127.43, 126.50, 125.68, 125.47, 124.71, 124.23, 123.24, 122.29, 120.99, 120.12, 110.39, 105.90 (Ar), 54.14, 39.43, 30.73, 30.57, 29.01, 28.19, 22.80, 21.62, 19.88, 13.11 (alkyl) ppm. MALDI-TOF: *m/z* = 1224.55 (M^+).

4b: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 7.8 Hz, 2H, Ar), 7.67 (s, 2H, Ar), 7.54–7.48 (m, 6H, Ar), 7.43–7.32 (m, 4H, Ar), 7.20–7.14 (m, 4H, Ar), 7.09–7.05 (m, 12H, Ar), 6.93–6.88 (m, 4H, Ar), 2.31 (s, 6H, alkyl), 2.08–2.07 (m, 4H, alkyl), 1.29–1.26 (m, 8H, alkyl), 0.88–0.77 (m, 10H, alkyl), 0.61–0.59 (m, 6H, alkyl), 0.56–0.52 (m, 6H, alkyl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.41, 148.39, 147.80, 146.70, 146.02, 144.80, 144.62, 140.14, 138.99, 136.33, 133.85, 133.56, 130.93, 130.30, 129.63, 127.96, 127.43, 126.53, 125.90, 125.51, 124.77, 124.29, 123.27, 122.30, 121.97, 120.09, 110.43, 105.93 (Ar), 55.17, 44.73, 34.86, 31.78, 28.38, 27.35, 22.85,

21.09, 14.35, 10.62 (alkyl) ppm. MALDI-TOF: *m/z* = 1224.37 (M^+).

General synthetic procedure for TPS-1 and TPS-2

A mixture of aldehyde precursors and 3 equivalents of cyanoacetic acid in the presence of ammonium acetate was refluxed overnight under a nitrogen atmosphere. After that, water was added and the resulting mixture was extracted with chloroform. The solvent was removed under vacuum and the solid was washed with ethanol and hexane to give pure products of **TPS-1** and **TPS-2** as dark red solids.

TPS-1: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (s, 1H, C=CH), 7.97 (d, *J* = 4.3 Hz, 1H, Ar), 7.64–7.59 (m, 3H, Ar), 7.34–7.30 (m, 2H, Ar), 7.18 (d, *J* = 8.1 Hz, 2H, Ar), 7.11–7.05 (m, 3H, Ar), 7.01–6.99 (m, 2H, Ar), 6.93–6.90 (m, 2H, Ar), 2.28 (s, 3H, alkyl) ppm. MALDI-TOF: *m/z* = 502.09 (M^+).

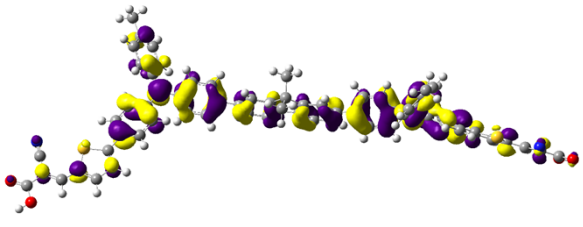
TPS-2: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.46 (s, 1H, C=CH), 7.96 (d, *J* = 4.2 Hz, 1H, Ar), 7.60–7.55 (m, 4H, Ar), 7.46 (d, *J* = 3.9 Hz, 1H, Ar), 7.32–7.29 (m, 2H, Ar), 7.16 (d, *J* = 8.2 Hz, 2H, Ar), 7.08–7.02 (m, 3H, Ar), 6.99–6.97 (m, 2H, Ar), 6.92–6.90 (m, 2H, Ar), 2.27 (s, 3H, alkyl) ppm. MALDI-TOF: *m/z* = 518.11 (M^+).

Table S1. Electronic excitation energies and the corresponding oscillator strengths (f), the main configurations and CI coefficients of the low-lying electronically excited states of **DA-1** calculated by CAM//B3LYP/6-31G(d) based on the optimized ground-state geometries. THF was used as the solvent in the calculations (PCM model).

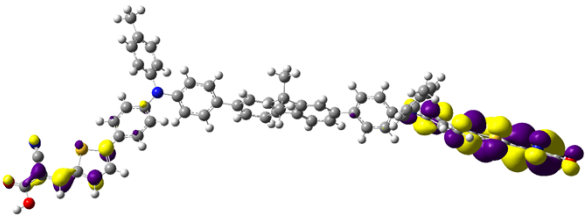
DA-1	Electronic transition	CAM//B3LYP/6-31G(d)			
		Energy [a]	f [b]	Composition [c]	CI [d]
	$S_0 \rightarrow S_1$	2.77 eV (447 nm)	2.7280	H-4→L	0.11087
				H-3→L+1	0.14752
				H-2→L	0.17422
				H-1→L	0.21701
				H-1→L+1	0.38401
				H→L	0.38887
				H→L+1	0.19365
	$S_0 \rightarrow S_2$	2.79 eV (444 nm)	0.4259	H-4→L+1	0.11185
				H-3→L	0.14883
				H-2→L+1	0.17624
				H-1→L	0.38129
				H-1→L+1	0.23614
				H→L	0.20462
				H→L+1	0.37786
	$S_0 \rightarrow S_3$	3.76 eV 330 nm	0.7476	H-4→L	0.16156
				H-3→L	0.12466
				H-3→L+1	0.19126
				H-2→L	0.18327
				H-2→L+2	0.24429
				H-1→L+3	0.15580
				H-1→L+5	0.11522
				H→L	0.12561
				H→L+2	0.46160
	$S_0 \rightarrow S_{14}$	4.58 eV (270 nm)	0.2920	H-17→L	0.17209
				H-16→L+1	0.21352
				H-15→L	0.12457
				H-14→L+1	0.15437
				H-12→L+1	0.12095
				H-11→L	0.11410
				H-11→L+4	0.33725

				H-11→L+9	0.14045
				H-10→L+3	0.24994
				H-10→L+5	0.19407
				H-10→L+7	0.15606
				H-10→L+6	0.10431

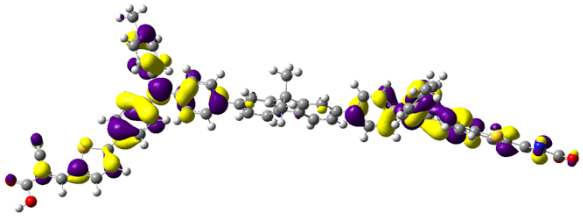
[a] Only the selected low-lying excited states are presented. [b] oscillator strength. [c] H stands for HOMO and L stands for LUMO. Only the main configurations are presented. [d] the coefficients of the wavefunction for each excitation are shown in absolute values.



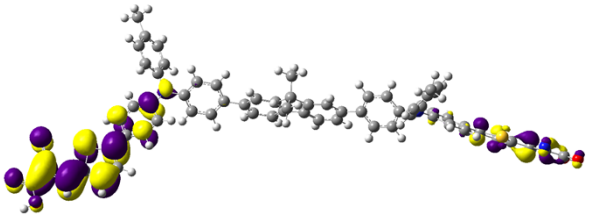
HOMO (–5.036 eV)



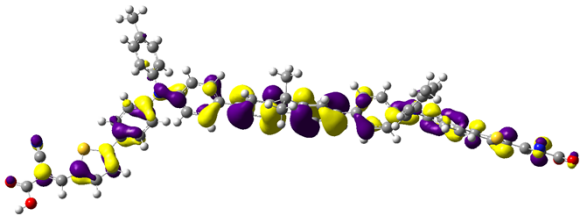
LUMO (–2.682 eV)



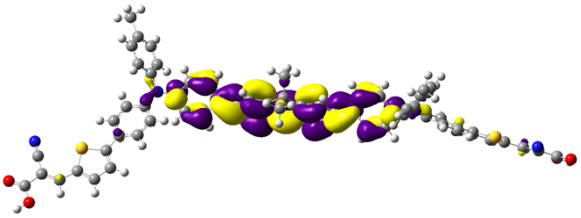
HOMO-1



LUMO+1



HOMO-2



LUMO+2

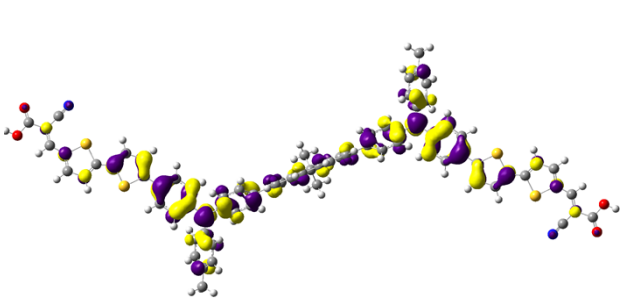
Figure S1. Molecular orbitals of **DA-1** calculated by CAM//B3LYP/6-31G(d) based on the optimized ground-state geometries. THF was used as the solvent in the calculations (PCM model).

Table S2. Electronic excitation energies and the corresponding oscillator strengths (f), the main configurations and CI coefficients of the low-lying electronically excited states of **DA-3** calculated by CAM//B3LYP/6-31G(d) based on the optimized ground-state geometries. THF was used as the solvent in the calculations (PCM model).

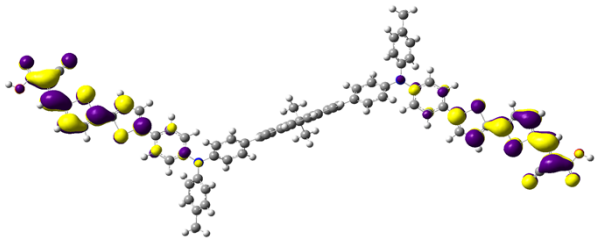
DA-3	Electronic transition	CAM//B3LYP/6-31G(d)			
		Energy [a]	f [b]	Composition [c]	CI [d]
	$S_0 \rightarrow S_1$	2.44 eV (507 nm)	3.7279	H-4→L	0.11894
				H-3→L+1	0.21862
				H-2→L	0.23537
				H-1→L+1	0.42343
				H-1→L+3	0.10411
				H→L	0.40526
				H→L+2	0.10194
	$S_0 \rightarrow S_3$	3.44 eV (360 nm)	0.1765	H-7→L	0.12116
				H-5→L+1	0.11584
				H-4→L	0.25746
				H-3→L+1	0.36721
				H-2→L	0.28813
				H-1→L+1	0.10113
				H-1→L+3	0.17333
				H→L	0.23939
				H→L+2	0.22045
	$S_0 \rightarrow S_5$	3.79 eV (326 nm)	1.5231	H-3→L+1	0.10683
				H-2→L+4	0.23443
				H-1→L+3	0.22918
				H-1→L+5	0.15140
				H→L	0.31186
				H→L+2	0.39966
				H→L+4	0.18506
	$S_0 \rightarrow S_{21}$	4.60 eV (269 nm)	0.4887	H-21→L+1	0.12399
				H-20→L	0.20900
				H-19→L+1	0.19729
				H-8→L+1	0.12214
				H-7→L	0.17681
				H-5→L+1	0.12462
				H-4→L+4	0.13362

				H-3→L+1	0.18771
				H-3→L+3	0.17040
				H-2→L	0.22533
				H-2→L+2	0.16667
				H-1→L+5	0.10218
				H-1→L+9	0.16293
				H→L+8	0.17808

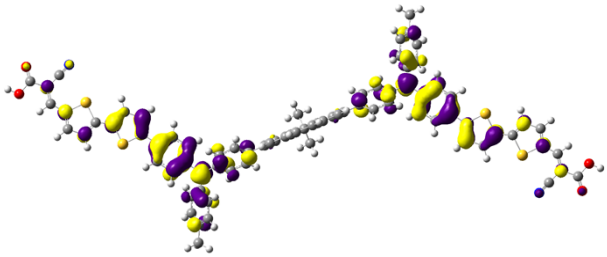
[a] Only the selected low-lying excited states are presented. [b] oscillator strength. [c] H stands for HOMO and L stands for LUMO. Only the main configurations are presented. [d] the coefficients of the wavefunction for each excitation are shown in absolute values.



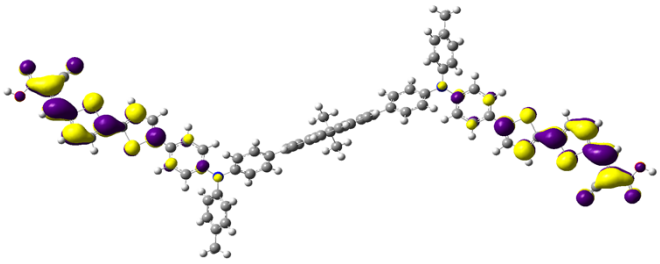
HOMO (−5.087 eV)



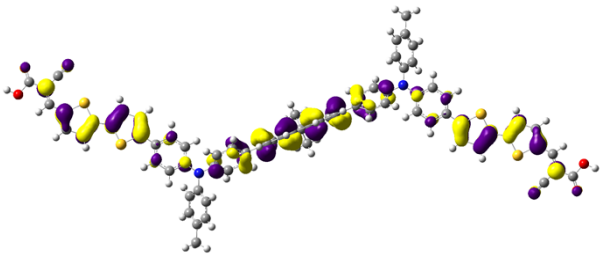
LUMO (−2.945 eV)



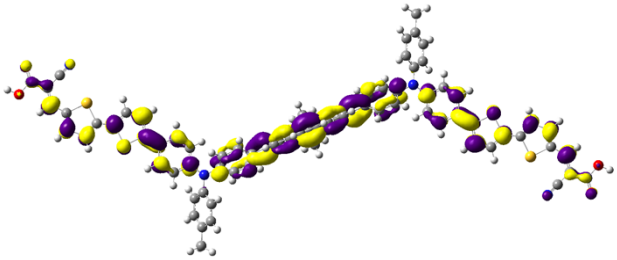
HOMO-1



LUMO+1



HOMO-2



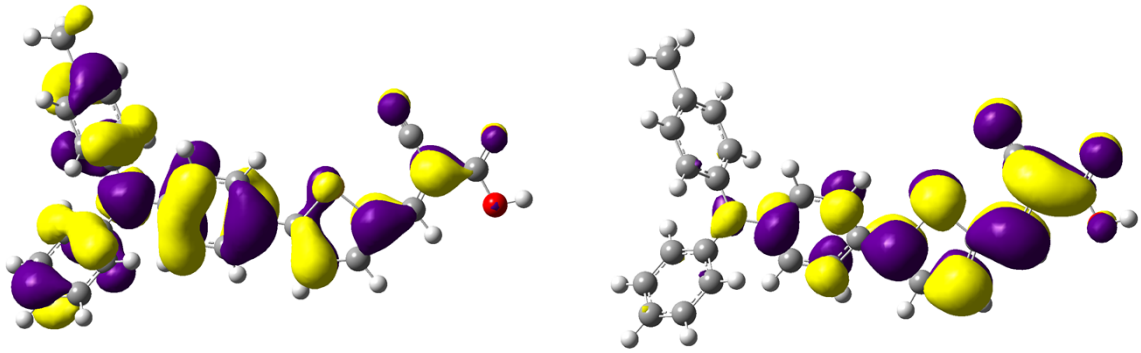
LUMO+2

Figure S2. Molecular orbitals of **DA-3** calculated by CAM//B3LYP/6-31G(d) based on the optimized ground-state geometries. THF was used as the solvent in the calculations (PCM model).

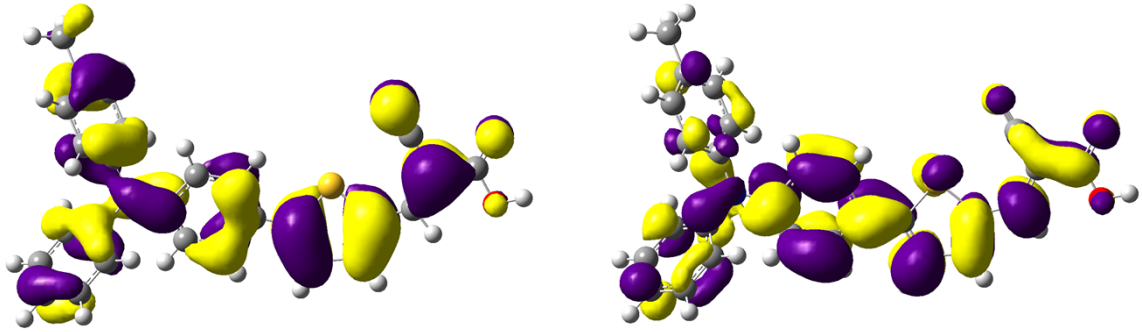
Table S3. Electronic excitation energies and the corresponding oscillator strengths (f), the main configurations and CI coefficients of the low-lying electronically excited states of complex **TPS-1** calculated by CAM//B3LYP/6-31G(d) based on the optimized ground-state geometries. THF was used as the solvent in the calculations (PCM model).

TPS-1	Electronic transition	CAM//B3LYP/6-31G(d)			
		Energy [a]	f [b]	Composition [c]	CI [d]
	$S_0 \rightarrow S_1$	2.80 eV (441 nm)	1.3143	H-1→L	0.24273
				H→L	0.64421
				H→L+1	0.12135
	$S_0 \rightarrow S_6$	4.65 eV (267 nm)	0.3483	H-5→L	0.10655
				H-1→L+3	0.16352
				H→L+1	0.14930
				H→L+2	0.12939
				H→L+3	0.60955

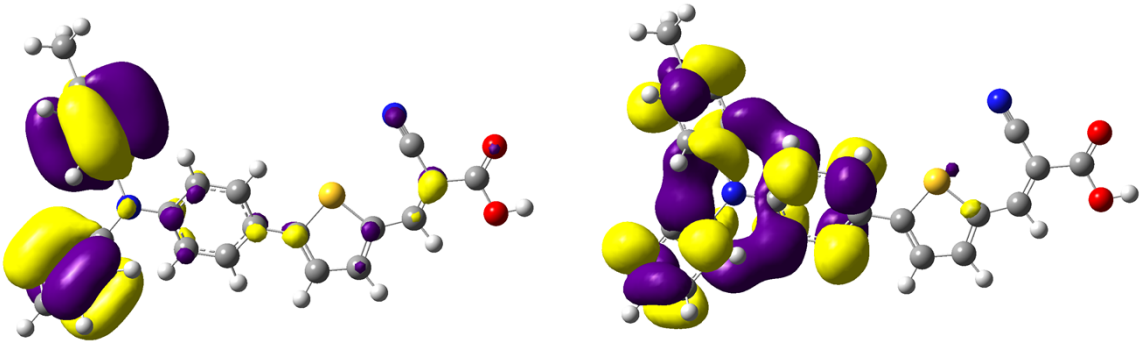
[a] Only the selected low-lying excited states are presented. [b] oscillator strength. [c] H stands for HOMO and L stands for LUMO. Only the main configurations are presented. [d] the coefficients of the wavefunction for each excitation are shown in absolute values.



HOMO (–5.151 eV) LUMO (–2.661 eV)



HOMO-1 LUMO+1



HOMO-2 LUMO+2

Figure S3. Molecular orbitals of **TPS-1** calculated by CAM//B3LYP/6-31G(d) based on the optimized ground-state geometries. THF was used as the solvent in the calculations (PCM model).

Table S4. Electronic excitation energies and the corresponding oscillator strengths (f), the main configurations and CI coefficients of the low-lying electronically excited states of **TPS-2** calculated by CAM//B3LYP/6-31G(d) based on the optimized ground-state geometries. THF was used as the solvent in the calculations (PCM model).

TPS-2	Electronic transition	CAM//B3LYP/6-31G(d)			
		Energy [a]	f [b]	Composition [c]	CI [d]
	$S_0 \rightarrow S_1$	2.61 eV (475 nm)	1.7012	H-1→L	0.34555
				H→L	0.58673
				H→L+1	0.14576
	$S_0 \rightarrow S_2$	3.59 eV (345 nm)	0.0055	H-4→L	0.10263
				H-2→L	0.18840
				H-1→L	0.53804
				H→L	0.26224
				H→L+1	0.26719
	$S_0 \rightarrow S_3$	4.05 eV (306 nm)	0.2578	H-1→L	0.18010
				H-1→L+1	0.17095
				H→L	0.25903
				H→L+1	0.56024
				H→L+4	0.13815
	$S_0 \rightarrow S_6$	4.58 eV (271 nm)	0.2551	H-1→L+3	0.21991
				H-1→L+4	0.12211
				H→L+3	0.56343
				H→L+4	0.23287

[a] Only the selected low-lying excited states are presented. [b] oscillator strength. [c] H stands for HOMO and L stands for LUMO. Only the main configurations are presented. [d] the coefficients of the wavefunction for each excitation are shown in absolute values.

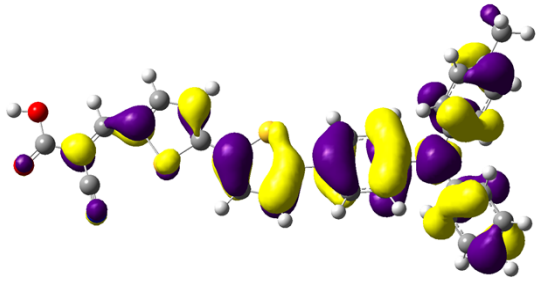
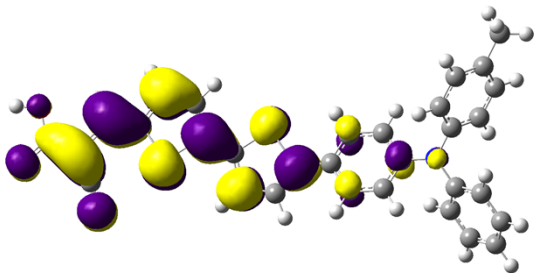
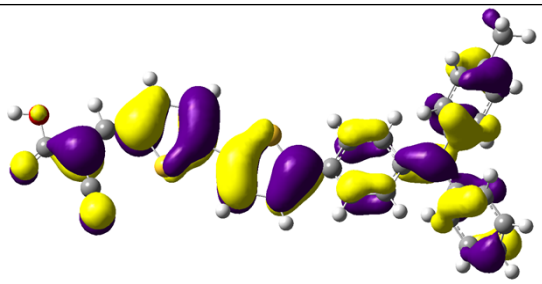
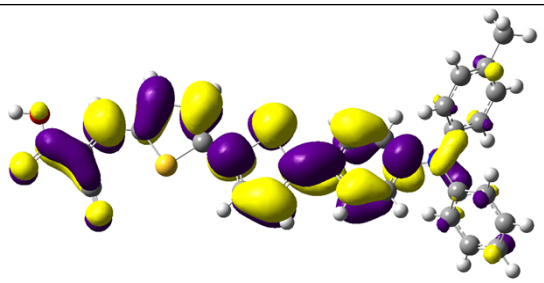
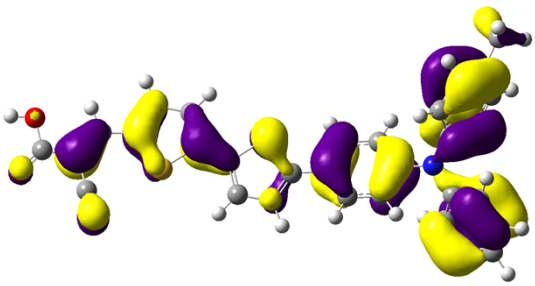
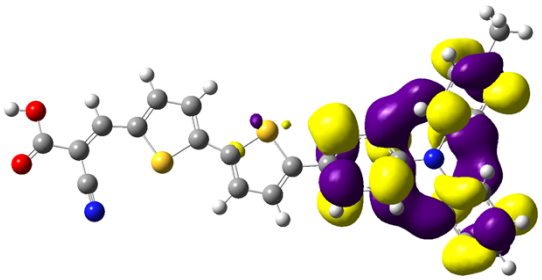
	
HOMO (−5.021 eV)	LUMO (−2.808 eV)
	
HOMO-1	LUMO+1
	
HOMO-2	LUMO+2

Figure S4. Molecular orbitals of **TPS-2** calculated by CAM//B3LYP/6-31G(d) based on the optimized ground-state geometries. THF was used as the solvent in the calculations (PCM model).

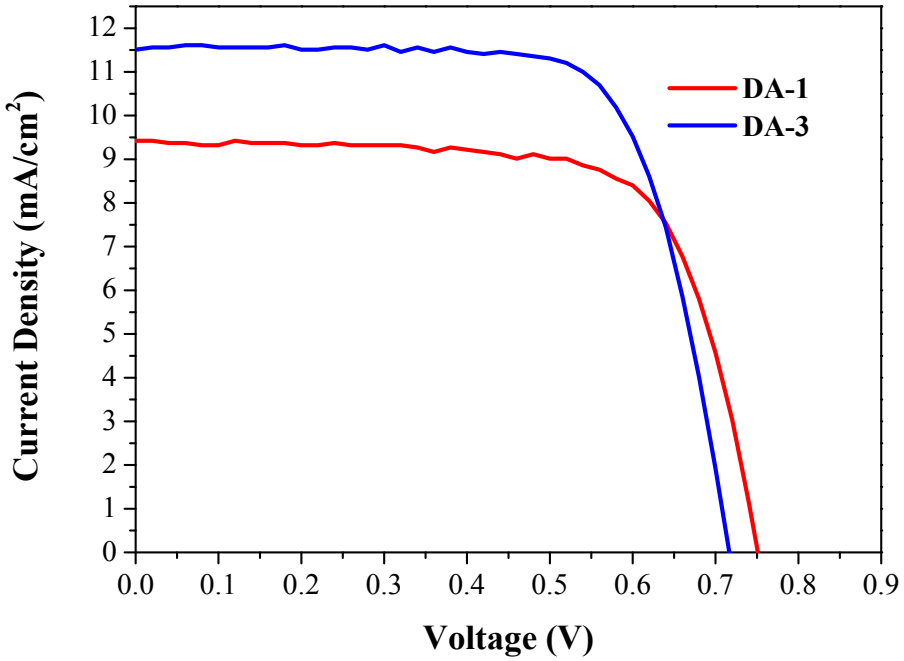


Figure S5. *J–V* curves of the DSSC devices based on **DA-1** and **DA-3** with 40 mM DCA under AM 1.5G simulated sunlight illumination.

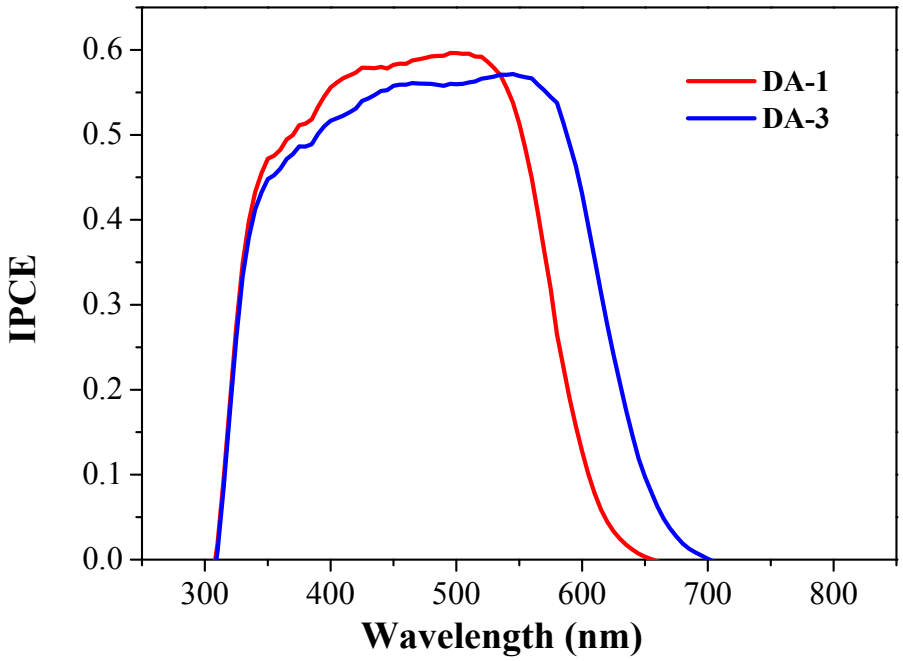


Figure S6. IPCE curves of DSSC devices based on **DA-1** and **DA-3** with 40 mM DCA.

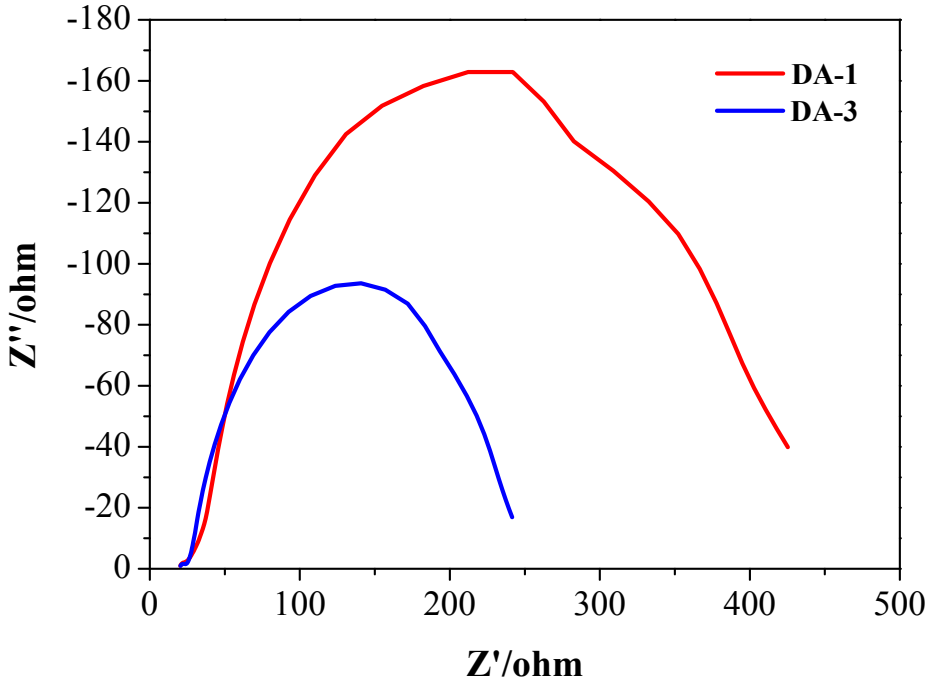


Figure S7. EIS Nyquist plots for DSSC devices based on **DA-1** and **DA-3** with 40 mM DCA under dark condition.

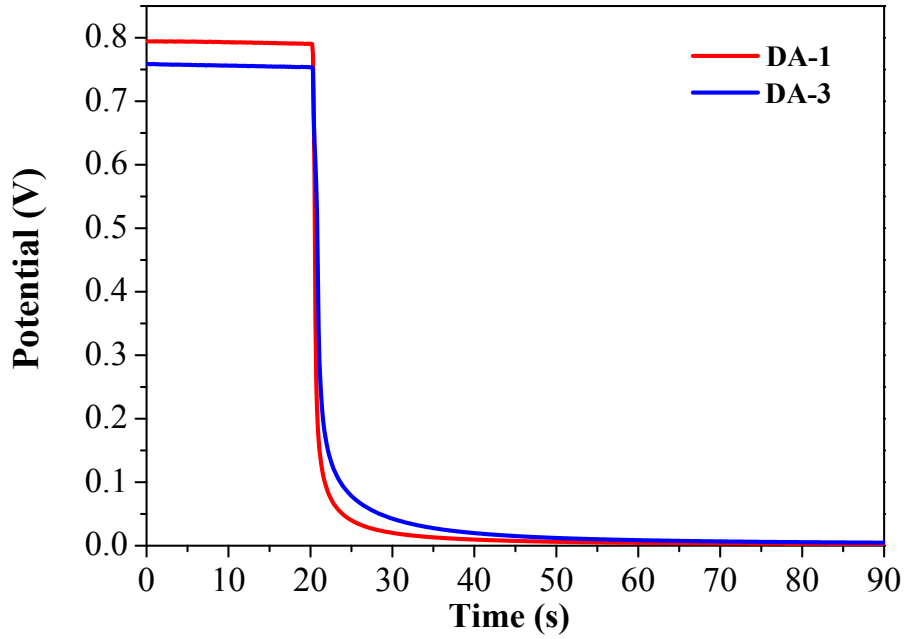


Figure S8. OCVD profiles of DSSC devices based on **DA-1** and **DA-3** with 40 mM DCA.