Electronic Supplementary Information

Conveniently synthesized isophorone dyes for high efficiency dye-sensitized solar cells: tuning photovoltaic performance by structural modification of donor group in Donor-π-Acceptor system

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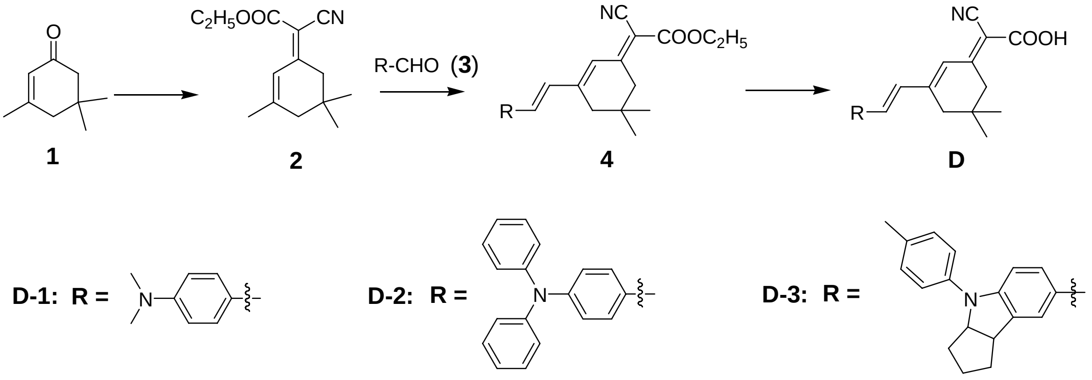
Materials and Instruments

General: The FTO conducting glass (fluorine doped SnO_2, sheet resistance < 15 Ω/square, transmission > 90% in the visible) was obtained from Geao Science and Educational Co. Ltd., China. Titanium (IV) isopropoxide, Lithium iodide, and *tert*-butylpyridine (TBP) was purchased from Aldrich. All other solvents and chemicals used were produced by Sinopharm Chemical Reagent Co., Ltd, China (reagent grade) and used as received. ^1H NMR spectra were obtained with a Bruker AM-400 spectrometer. The mass spectra were conducted on a 4700 Proteomics analyzer spectrometer.

Physical Measurements: UV-visible spectra were determined with a Varian Cary 500 spectrometer. Fluorescent spectra were recorded on Varian Cary Eclipse spectrometer. The cyclic voltammograms were determined with a Versastat II electrochemical workstation (Princeton Applied Research) using a normal three-electrodes cell with a dye-coated TiO_2 electrode as working electrode, a Pt wire auxiliary electrode, and Ag/AgCl reference electrode in saturated KCl solution, 0.1 M tetrabutylammonium hexafluorophosphoric was used as supporting electrolyte. After the measurement, ferrocene was added as the internal reference for calibration.

Fabrication and measurement of solar cells: Nanocrystalline TiO_2 electrodes were prepared following the reported procedure. (B. O'Regan and M. Grätzel, *Nature*, 1991, **353**, 737; Md. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Mueller, P. Liska, N. Vlachopoulos and M. Grätzel, *J. Am. Chem. Soc.*, 1993, **115**, 6382). The thickness of TiO_2 film was controlled by adhesive tapes with different thickness and measured by a surface profiler (Dektak Co., ltd., Model DAKTAK II). The dye-loaded electrodes were prepared by dipping TiO_2 electrodes into 0.3 mM solution of D-1, D-2 or D-3 in acetonitrile for 5 h, and a 0.5 mM solution of N719 in ethanol for 12 h, respectively. The dye-loaded TiO_2 electrode was placed on top of an FTO glass as a counter electrode, on which Pt was sputtered. The redox electrolyte was introduced into the inter-electrode space by capillary force. The photovoltaic performances of the cells reported in this paper were measured by using 0.6 M 1-methyl-3-butyl imidiazolium iodide (MBII), 0.1 M I_2, 0.05 M LiI, and 0.5 M tert-butylpyridine (TBP) in acetonitrile as electrolyte under AM 1.5 irradiation (Newport Co., ltd., 100 $mW\cdot cm^{-2}$). The light intensity of solar simulator has been calibrated by a standard silica cell (Newport Co., ltd). The photocurrent action spectra were measured with a Model SR830 DSP Lock-In Amplifier and a Model SR540 Optical Chopper and other optical system. The active area of solar cells were 0.15 cm^2 controlled by a metal mask. Each value in this paper was an average of three samples.

Synthesis of organic dyes



The product **2** was obtained as two isomers (*Z*- : *E*- = 1 : 1) by vacuum distillation (17.3 g) in 74% yield, b.p. 191-193 ºC / 19 mmHg (V. Bardakos and C. Sandris, *Org. Mag. Resonance.*, 1981, **15**, 339). All of three sensitizers were synthesized quite straightforward with the traditional Knoevenagel reaction in relatively high yield.

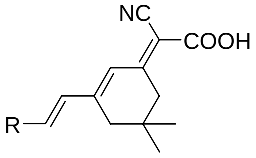
General Synthesis of dyes

The resulting compound **4** was dissolved in ethanol (90 mL). The solvent was allowed to warm to 50 °C and stirred for 5 h after the addition of $LiOH{\cdot}H_2O$ (15 g, 1.2 mol) dissolved in deionized water (90 mL). Removal most of ethanol was followed by neutralizing with 1 M HCl, and then filtered to give red solid product. The crude product was recrystallized in methylene chloride/petroleum ether to afford corresponding final product.

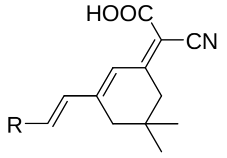
D-1 was afforded as *Z*-type products in 81% yield. mp 202-203 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.88 (s, 1H, -C=C*H*-), 7.45 (d, *J* = 8.8 Hz, 2H, =CH-*Ph*-N-), 7.00 (d, *J* = 16.0 Hz, 1H, -C*H*=CH-Ph-), 6.89 (d, *J* = 16.0 Hz, 1H, -CH=C*H*-Ph), 6.72 (d, *J* = 8.8 Hz, 2H, =CH-*Ph*-N-), 3.05 (s, 6H, -N-$(CH_3)_2$), 2.68 (s, 2H, -C=C-CH_2-), 2.46 (s, 2H, =CH-C-C*H*$_2$-), 1.09 (s, 6H, -C-(C*H*$_3$)$_2$). ^{13}C NMR (100 MHz, CDCl$_3$) δ ppm 167.9, 167.5, 155.0, 151.3, 136.9, 129.2, 126.1, 124.3, 122.8, 117.6, 112.4, 95.4, 45.1, 40.4, 39.3, 32.0, 28.2. IR (cm^{-1}, KBr): 3420, 2956, 2211, 1678, 1490, 1160. HRMS (ESI, [M + H]/z): Calcd for $C_{21}H_{24}N_2O_2$ 337.1916; Found, 337.1911.

D-2 was afforded as two isomers (*Z*- : *E*- = 1 : 1) in 74% yield. mp 160-161 ºC. ^{1}H NMR (400 MHz, CDCl$_3$) δ ppm 7.89 (s, 0.5H, *Z*-type-C=C*H*-), 7.36 (d, *J* = 7.6 Hz, 2H, *Ph*-N-Ph$_2$), 7.31-7.27 (m, 4.5H, *E*-type-C=C*H*-, Ph-N-*Ph$_2$*), 7.08-7.13 (m, 6H, Ph-N-*Ph$_2$*), 6.91-7.01 (m, 4H, -C*H*=C*H*-, -*Ph*-N-Ph$_2$), 2.99 (s, 1H, *E*-type-C=C-C*H*$_2$-), 2.68 (s, 1H, *Z*-type-C=C-C*H*$_2$-), 2.45 (s, 1H, *Z*-type-=CH-C-C*H*$_2$-), 2.43 (s, 1H, *E*-type-=CH-C-C*H*$_2$-), 1.09 (s, 3H, *Z*-type-C-(C*H*$_3$)$_2$), 1.06 (s, 3H, *E*-type-C-(C*H*$_3$)$_2$). ^{13}C NMR (100 MHz, CDCl$_3$) δ ppm 169.2, 167.5, 149.2, 147.0, 135.6, 129.5, 129.2, 128.5, 127.7, 125.8, 125.3, 125.2, 123.9, 123.8, 122.1, 116.3, 44.8, 41.2, 39.1, 31.5, 28.4, 28.2. IR (cm^{-1}, KBr): 3434, 2925, 2195, 1638, 1505, 1050. HRMS (ESI, [M + H]/z): Calcd for $C_{31}H_{32}N_2O_2$ 461.2229; Found, 461.2222.

D-3 was afforded as two isomers (*Z*- : *E*- = 1 : 1) in 78% yield. mp 146-148 ºC. ^{1}H NMR (400 MHz, CDCl$_3$) δ ppm 7.89 (s, 0.5H, *Z*-type-C=C*H*-), 7.42 (s, 0.5H, *Z*-type-=CH-*Ph*-), 7.36 (s, 0.5H, *E*-type-=CH-*Ph*-), 7.17-7.19 (m, 5H, *Ph*-N-*Ph*-CH$_3$), 7.00 (d, *J* = 16.0 Hz, 1H, -C*H*=CH-Ph-), 6.92 (s, 0.5H, *E*-type-C=C*H*-), 6.88 (d, *J* = 16.0 Hz, 1H, -CH=C*H*-Ph-), 6.79-6.81 (dd, J_1 = 3.2 Hz, J_2 = 8.0 Hz, 1H, =CH-*Ph*-), 4.87 (t, *J* = 7.0 Hz, 1H, -N-C*H*-CH-), 3.84 (t, *J* = 7.0 Hz, 1H, -N-CH-C*H*-), 3.00 (s, 1H, *E*-type-C=C-C*H*$_2$-), 2.68 (s, 1H, *Z*-type-C=C-C*H*$_2$-), 2.45 (s, 1H, *Z*-type-=CH-C-C*H*$_2$-), 2.43 (s, 1H, *Z*-type-=CH-C-C*H*$_2$-), 2.36 (s, 3H, -N-Ph-C*H*$_3$), 1.67-2.11 (m, 6H, -N-CH-$\mathrm{C}H_2$-$\mathrm{C}H_2$-$\mathrm{C}H_2$-CH-), 1.09 (s, 3H, *Z*-type-C-$(\mathrm{C}H_3)_2$), 1.06 (s, 3H, *E*-type-C-$(\mathrm{C}H_3)_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 169.1, 168.1, 167.4, 155.3, 155.2, 150.0, 139.3, 137.1, 136.9, 136.1, 136.0, 132.6, 129.9, 126.4, 126.3, 125.6, 125.0, 121.0, 107.1, 107.0, 96.1, 69.5, 45.0, 41.3, 39.3, 39.0, 35.3, 35.2, 33.4, 32.0, 31.5, 28.4, 28.2, 24.3, 20.8. IR (cm^{-1}, KBr): 3427, 2932, 2203, 1615, 1521, 1042. HRMS (ESI, [M + H]/z): Calcd for $C_{31}H_{32}N_2O_2$ 465.2542; Found, 465.2544.

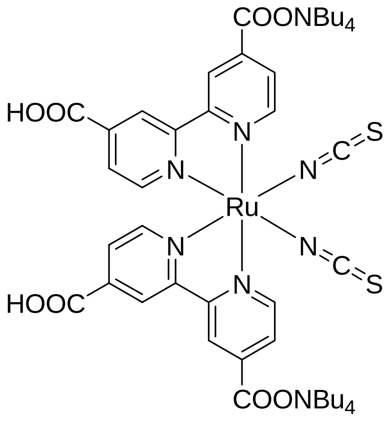


***E*-type**



***Z*-type**

D-2 and D-3 were afforded as isomers which were shown above. The isomerized double-bond was the one between the isophorone segment and cyanacetic acid. The double-bond between donor (R-) and isophorone segment was *trans*-type and confirmed through ^{1}H NMR (7.00 and 6.88 ppm, J = 16.0 Hz, take D-3 for example). Since the differences of spectral, electrochemical and photovoltaic properties between these two isomers are very little, we have not performed further separation.



N719

Fig. S1 Chemical structure of N719

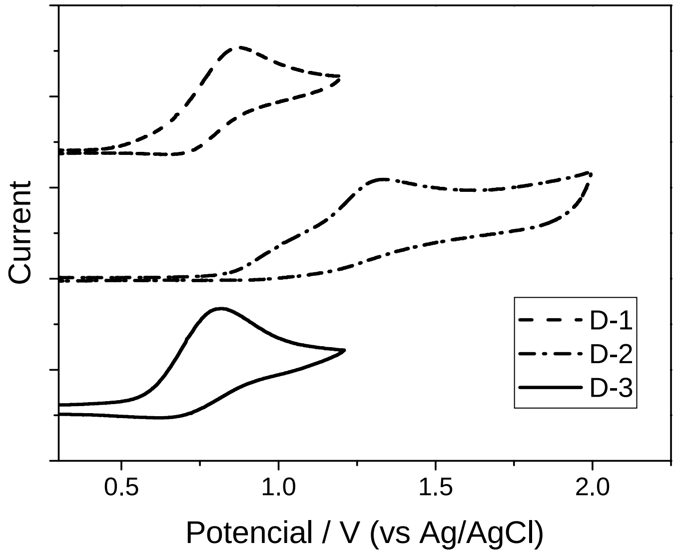


Fig. S2 Cyclic voltammetry plots of dyes D-1, D-2 and D-3 adsorbed on TiO_2 film. Scan rate: 50 mv/s

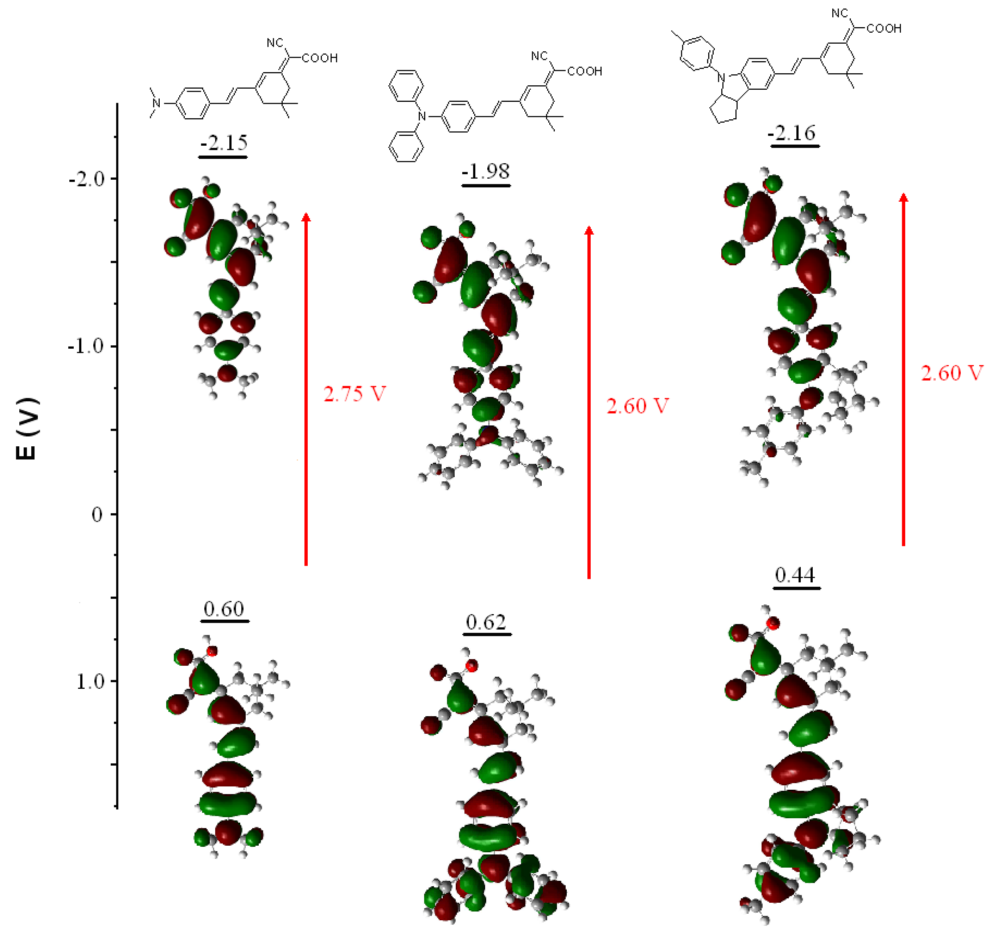


Fig. S3 Calculated HOMO and LUMO levels for D-1, D-2 and D-3.

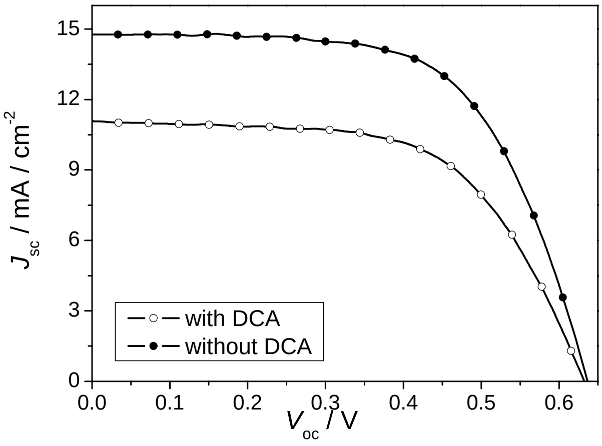


Fig. S4 Comparison of D-3-sensitized solar cells with and without DCA (1.0 mM) using 3.4 µm single layer nanocrystalline TiO_2 electrodes

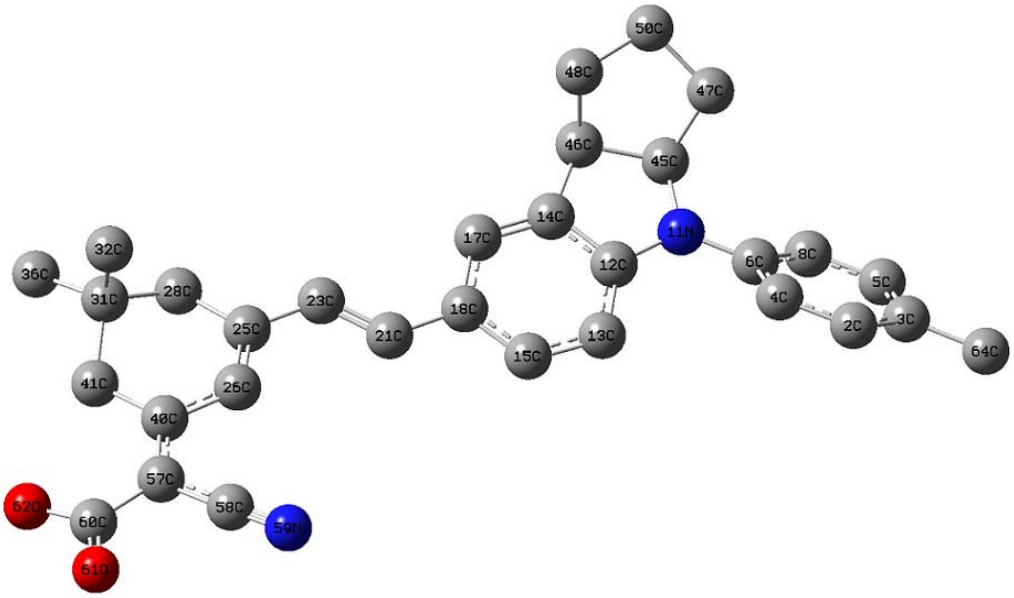


Fig. S5 Optimized ground-state geometry of D-3 calculated at the hybrid density functional theory (B3LYP) with 6-31G* basis set as implemented in the Gaussian 03 program.

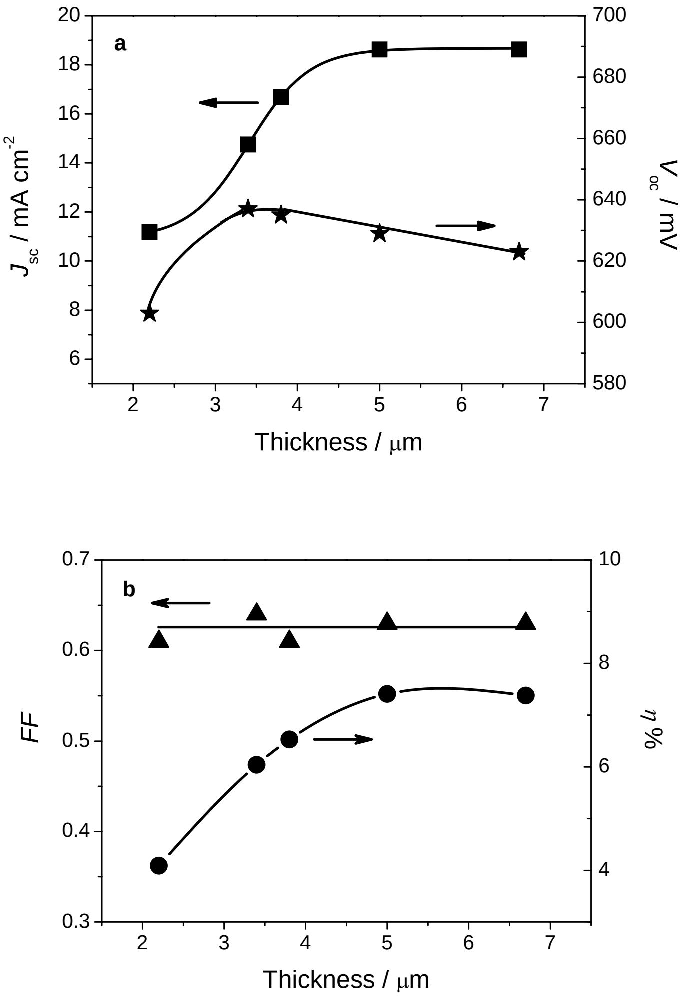


Fig. S6 Photovoltaic characteristics of solar cells based on D-3 as a function of nanocrystalline TiO_2 film thickness

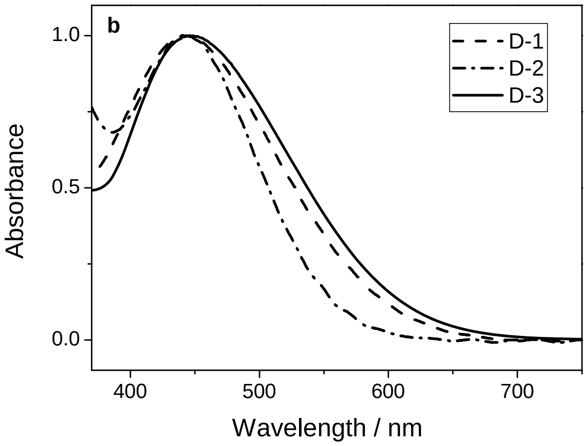


Fig. S7 Normalized absorption spectra of D-1, D-2 and D-3 in (a) acetonitrile and (b) anchored on a 3.4 μm TiO_2

Table S1. Absorption and emission properties of D-1, D-2 and D-3 measured in CH_3CN

Dyes	Absorption		Emission
	λ_{max} (nm)	ε at λ_{max} ($M^{-1}\cdot cm^{-1}$)	λ_{em} (nm)
D-1	464	32700	661
D-2	450	26900	669
D-3	497	37600	706

Table S2. Electrochemical properties of dyes D-1, D-2 and D-3

Dyes	Experimental [a] (V)			Calculated [c] (V)		
	HOMO	E_{0-0} [b]	LUMO	HOMO	E_{0-0}	LUMO
D-1	0.99	1.83	-0.84	0.60	2.75	-2.15
D-2	1.32	2.03	-0.71	0.62	2.60	-1.98
D-3	0.92	1.77	-0.85	0.44	2.60	-2.16

[a] Electrochemical properties of the dyes adsorbed on TiO_2 Films.

[b] E_{0-0} was estimated from the onset of absorption spectra of the dyes adsorbed on TiO_2 film.

[c] Calculated at the B3LYP/6-31G* level in vacuum.

Table S3. Calculated TDDFT excitation energies for the lowest transition (eV, nm), oscillator strengths (f), composition in terms of molecular orbital contributions, and experimental absorption maxima

Dyes	State	Composition [a]	E (eV, nm)	f	exp. (eV, nm)
D-1	S_1	61% H → L	2.67 (464)	1.1517	2.67 (464)
	S_2	60% H - 1 → L	3.60 (344)	0.1690	3.82 (325)
D-2	S_1	85% H → L	2.42 (513)	1.0404	2.76 (450)
	S_2	75% H - 1 → L	3.30 (375)	0.4585	4.10 (302)
D-3	S_1	63% H → L	2.47 (502)	1.2282	2.49 (497)
	S_2	60% H - 1 → L	3.39 (366)	0.3195	3.91 (317)

[a] H = HOMO, H - 1 = next highest occupied molecular orbital (HOMO - 1), L = LUMO.

[b] TDDFT excited states calculation was performed at the B3LYP/6-31G* level in vacuum with the B3LYP/6-31G* optimized ground-state geometry.

Table S4. Photovoltaic performance of DSSCs sensitized with different sensitizers (AM 1.5, 100 mW·cm^{-2})

Sensitizers	J_{sc} (mA·cm^{-2})	V_{oc} (mV)	FF	η (%)
D-1	12.33	642	0.64	5.08
D-2	11.46	643	0.66	4.93
D-3	18.63	634	0.63	7.41
N719	15.60	698	0.62	7.03