

Electronic Supplementary Information
for
**Molecular Engineering of Cocktail Co-sensitization for Efficient
Panchromatic Porphyrin-sensitized Solar Cells**

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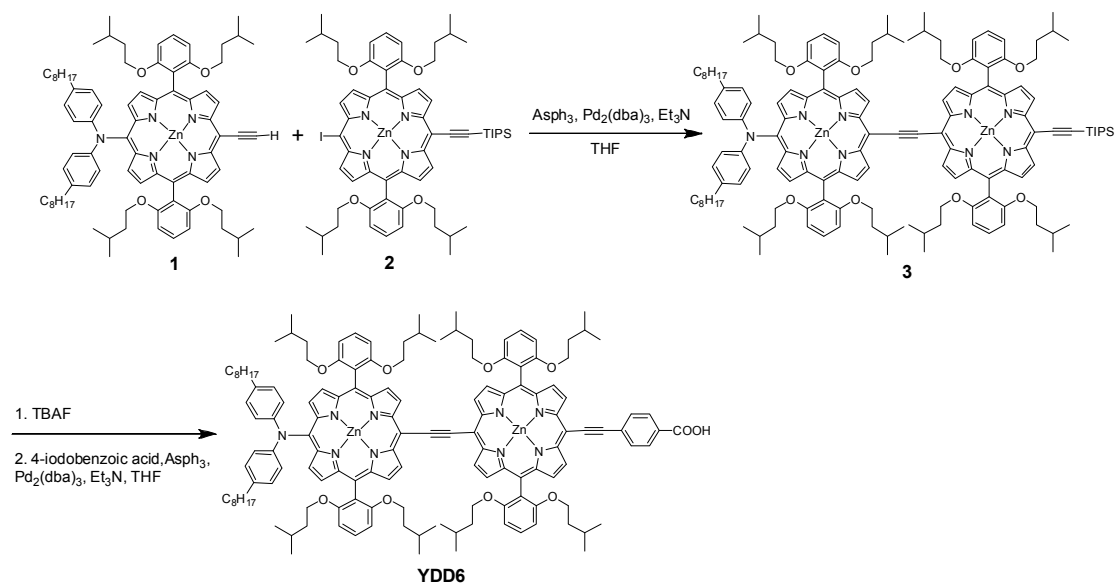
General

All reagents and solvents were obtained from commercial sources and used without further purification unless otherwise stated. CH₂Cl₂ was dried over CaH₂ and freshly distilled before use. THF was dried over sodium/benzophenone and freshly distilled before use. Tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆) was recrystallized twice from absolute ethanol and further dried for two days under vacuum. A column chromatograph contained silica gel (Merck, 70-230 Mesh ASTM). Other chemicals were titanium(IV) isopropoxide (TTIP, 97%, Aldrich), acetic acid (95%, J. T. Baker), nitric acid (69~70%, J. T. Baker), ethyl cellulose (EC, 5–15mPas, #46070, Fluka), ethyl cellulose (EC, 30–50mPas, #46080, Fluka), α -terpineol (SHOWA), titanium dioxide (ST41, 200-300 nm powder, Ishihara), H₂PtCl₆·6H₂O (99.95%, Alfa Aesar), iodine (I₂, Merck), lithium iodide (LiI, >98%, Merck), 4-*tert*-butylpyridine (TBP, >98%, Fluka), 1-methyl-3-propylimidazolium iodide (PMII, Merck), ethanol (99.5%, Aldrich), acetonitrile (>99%, Aldrich), valeronitrile (>99%, Aldrich), *tert*-butanol (99%, Aldrich), chenodeoxycholic acid (CDCA, TCI-GR), and tetrabutylammonium hydroxide (1M TBA in methanol, Acros).

Spectral and Electrochemical Measurements

¹H NMR spectra (Varian spectrometer) at 400 MHz, UV-visible spectra (Varian Cary 50), FAB-MS mass spectra (Bruker APEX II spectrometer, operating in the positive-ion detection mode) were recorded on the indicated instruments. Electrochemical tests were performed with a three-electrode potentiostat (CH Instruments, Model 750A) in THF deoxygenated on purging with pre-purified dinitrogen gas. Cyclic voltammetry experiments for porphyrin dyes were conducted with a three-electrode cell equipped with a BAS glassy carbon (area 0.07 cm²) disk as working electrode, a platinum wire as auxiliary electrode, and a Ag/AgCl (saturated) reference electrode. The reference electrode was separated from the bulk solution with a double junction filled with electrolyte solution. Potentials are reported vs. Ag/AgCl (saturated) with reference to a ferrocene/ferrocenium (Fc/Fc⁺) couple at $E_{1/2} = +0.63$ vs Ag/AgCl (saturated) at 23 °C in THF. The working electrode was polished with aluminium (0.03 μ m) on felt pads (Buehler) and treated ultrasonically for 1 min before each experiment. The reproducibility of individual potential values was within ± 5 mV.

Synthetic Procedure and Characterization



3: In an oven-dried Schlenk tube, a solution of porphyrin **1** (89 mg, 0.069 mmol), porphyrin **2** (122 mg, 0.10 mmol), $\text{Pd}_2(\text{dba})_3$ (12.7 mg, 0.014 mmol) and AsPh_3 (42.5 mg, 0.14 mmol) in a mixture of dry THF (34 mL) and Et_3N (6.8 mL) was degassed for 10 min. The reaction mixture was refluxed for 4.5 h under N_2 ; the solvent was removed under reduced pressure, and the residue was purified on a silica-gel column chromatograph with $\text{DCM}/\text{MeOH} = 20/1$ as eluent to yield porphyrin **3** (133 mg, yield 82%). ^1H NMR ($\text{CDCl}_3/\text{pyridine-d}_5$, 400 MHz): $\delta_{\text{H}} = 10.34\text{--}10.10$ (m, 4H), 9.57 (d, $J = 4.0$ Hz, 2H), 9.04 (d, $J = 4.4$ Hz, 2H), 9.00–8.86 (m, 4H), 8.81 (d, $J = 4.4$ Hz, 2H), 8.62 (d, $J = 4.4$ Hz, 2H), 7.80–7.58 (m, 4H), 7.19–6.91 (m, 12H), 6.84 (d, $J = 8.4$ Hz, 4H), 4.15–3.68 (m, 16H), 2.56–2.33 (m, 4H), 1.47–1.36 (m, 21H), 1.36–1.13 (m, 24H), 1.19–0.65 (m, 30H), 0.65–0.15 (m, 48H). ^{13}C NMR (CDCl_3 , 100 MHz) $\delta_{\text{C}} = 160.0$, 152.5, 152.2, 152.0, 151.8, 150.5, 150.4, 150.0, 147.8, 147.5, 147.2, 135.2, 134.1, 131.7, 131.6, 131.5, 130.3, 130.2, 130.1, 129.9, 129.5, 128.5, 122.8, 122.6, 122.3, 122.1, 121.5, 114.9, 113.9, 111.2, 105.2, 101.9, 100.0, 95.5, 67.2, 67.0, 39.4, 35.2, 31.9, 31.6, 29.7, 29.5, 29.2, 24.3, 24.1, 22.6, 22.1, 21.9, 19.1, 14.1, 11.9. MALDI: m/z calcd for $\text{C}_{145}\text{H}_{179}\text{N}_9\text{O}_8\text{SiZn}_2$ 2333, found 2334 $[\text{M}+1]^+$.

YDD6: To a solution of porphyrin **3** (100 mg, 0.043 mmol) in THF (10 mL) was added TBAF (1M in THF, 0.43 mL, 0.43 mmol). The solution was stirred at 23 °C for 30 min under dinitrogen. The mixture was quenched with H_2O and extracted with CH_2Cl_2 . The organic layer was dried over anhydrous Na_2SO_4 , and the solvent was removed under reduced pressure. The solution of the concentrated residue, $\text{Pd}_2(\text{dba})_3$ (7.8 mg, 0.0086 mmol), AsPh_3 (26.2 mg, 0.086 mmol) and 4-iodobenzoic acid (106 mg, 0.43 mmol) in a

mixture of dry THF (21 mL) and Et₃N (4.2 mL) was placed in a oven-dried Schlenk tube, degassed for 10 min, and refluxed for 4.5 h under N₂. After the reaction was complete as shown by TLC, the solvent was removed; the residues was purified on a silica-gel column chromatograph with DCM/MeOH = 20:1 as eluent. Recrystallization from hexane/ethanol gave **YDD6** (98 mg, yield 93%). ¹H NMR (CDCl₃/pyridine-d₅, 400 MHz): δ_H = 10.28-10.20 (m, 4H), 9.60 (d, *J* = 4.4 Hz, 2H), 9.04 (d, *J* = 4.4 Hz, 2H), 8.94 (d, *J* = 4.4 Hz, 2H), 8.92 (d, *J* = 4.4 Hz, 2H), 8.84 (t, *J* = 4.4 Hz, 2H), 8.62 (d, *J* = 4.4 Hz, 2H), 8.28 (d, *J* = 7.6 Hz, 2H), 8.04 (d, *J* = 7.6 Hz, 2H), 7.78-7.60 (m, 4H), 7.16-6.92 (m, 12H), 6.84 (d, *J* = 8.8 Hz, 4H), 4.02-3.76 (m, 16H), 2.50-2.32 (m, 4H), 1.38-1.18 (m, 24H), 1.18-1.04 (m, 6H), 1.02-0.60 (m, 24H), 0.48-0.09 (m, 48H). ¹³C NMR (CDCl₃, 100 MHz) δ_C = 175.2, 171.4, 160.0, 152.5, 152.1, 151.8, 150.5, 150.1, 144.0, 143.6, 143.3, 134.2, 133.8, 131.8, 131.6, 130.9, 130.4, 130.0, 129.6, 129.5, 128.5, 127.6, 122.0, 121.6, 121.4, 105.1, 102.2, 100.1, 67.2, 67.0, 44.8, 37.3, 31.9, 31.6, 29.7, 29.5, 29.2, 24.4, 24.1, 22.6, 22.1, 22.0, 14.1, 8.4. MALDI: *m/z* calcd for C₁₄₃H₁₆₃N₉O₁₀Zn₂ 2297, found 2298 [M+1]⁺.

Electrode Preparation and Device Fabrication

The YD2-oC8, CD4, YDD6, and their co-sensitized devices A-E were fabricated with a TiO₂ working electrode and a Pt-coated counter electrode reported elsewhere.^{S1} For the working electrode, a paste composed of TiO₂ nanoparticles (NP, particle diameter ~25 nm)^{S2} and nanorods (NR, rod length 100–300 and diameter 20–30 nm)^{S3} and prepared with a sol-gel method for a transparent nanocrystalline layer was coated onto a TiCl₄-treated FTO glass substrate (TEC 7, Hartford, USA) to obtain the required thickness of the film (~12 μm; a typical SEM image is shown in Figure S2) with repetitive screen printing of two layers of NR on top of two layers of NP. To improve the performance of the device, we screen-printed three additional scattering layers (SL, ST41 paste)^{S2} of thickness ~9 μm on the transparent active layers. TiO₂ films were crystallized with a programmed procedure: (1) heating at 80 °C for 15 min; (2) heating at 135 °C for 10 min; (3) heating at 325 °C for 30 min; (4) heating at 375 °C for 5 min; (5) heating at 450 °C for 15 min, and (6) heating at 500 °C for 15 min. After cooling in air, the sintered TiO₂ film was immersed in a freshly prepared aqueous solution of TiCl₄ (40 mM) at 70 °C for 30 min (post-TiCl₄ treatment); it was rinsed with DI water, blown with dry N₂ gas, and annealed at 400 °C for 30 min (secondary annealing). After cooling in air, the sintered TiO₂ film was immersed in a solution containing the individual dye or their mixture and CDCA in varied molar ratios (first column in Table 1)

in ethanol (5 mL, 25 °C) for a period (specified in the second column of Table 1). For the counter electrode we spin-coated the H₂PtCl₆/isopropanol solution onto a TEC 7 FTO glass substrate (typical size 1.5 × 1.5 cm²) through thermal decomposition at 385 °C for 15 min. The single-dye or the co-sensitized working electrode was assembled with the counter electrode into a cell of sandwich type and sealed with a hot-melt film (Surlyn 1706, thickness 60 μm, DuPont) heated at 90 °C. The electrolyte solution containing LiI (0.05 M), I₂ (0.05 M), PMII (1.0 M), TBP (0.5 M) in a mixture of acetonitrile and valeronitrile (volume ratio 85:15) was introduced into the space between the two electrodes, to complete the fabrication of these DSSC devices.

Dye-loading Examination

To determine the dye-loading amounts of YD2-oC8, CD4 and YDD6 on TiO₂ films for single-dye-sensitized or their co-sensitized devices, the dyes were desorbed after immersion of the sensitized film in a basic solution containing TBA (0.1 M) in methanol (3 mL). The absorption spectrum of the solution was recorded with a UV-vis spectrometer. A calibration curve for all three dyes in methanol was derived to obtain the absorption coefficient. The amounts of dye coverage on TiO₂ films (DL) shown in the third column in Table 1 were obtained from the measured absorbances in the spectra (cuvette thickness 1 cm) and the calibrated absorption coefficient of the dyes according to Beers' law. In a co-sensitized solution, the absorbances of each dye were determined first at 741 nm for YDD4, then at 645 nm for YD2-oC8, and finally at 374 nm for CD4.

Photovoltaic Characterization

The current-voltage characteristics were determined with a digital source meter (Keithley 2400, computer-controlled) with the device under one-solar AM 1.5G irradiation from a solar simulator (XES-502S, SAN-EI) calibrated with a standard silicon reference cell (Oriel PN 91150V, VLSI standards). When the device is irradiated with the solar simulator, the source meter sends a voltage (V) to the device, and the photocurrent (I) is read at each step controlled with a computer via a GPIB interface. The efficiency (η) of conversion of light to electricity is obtained with this relation,

$$\eta = \frac{J_{SC} \cdot V_{OC} \cdot FF}{P_{in}} \quad (1)$$

in which J_{SC} /mA cm⁻² is the current density measured at short circuit and V_{OC} /V is the voltage measured at open circuit. P_{in} is the input radiation power (for one-sun illumination $P_{in} = 100$ mW cm⁻²) and FF is the fill factor. For all measurements, the

DSSC devices were covered with a black mask of aperture area 0.16 cm² to ensure that the measured photocurrents were not exaggerated. The incident monochromatic efficiencies for conversion from photons to current (IPCE) spectra of the corresponding devices were measured with a system comprising a Xe lamp (PTi A-1010, 150 W), a monochromator (PTi, 1200 gr mm⁻¹ blazed at 500 nm), and a source meter (Keithley 2400, computer-controlled). A standard Si photodiode (Hamamatsu S1337-1012BQ) served as a reference to calibrate the power density of the lamp at each wavelength. Photocurrent densities of both the target device and the reference Si cell were measured under the same experimental conditions so to obtain the efficiency of the device from a comparison of the current ratio and the value of the reference cell at each wavelength. ^{S4}

Intensity-modulated Photovoltage Spectroscopy (IMVS) Measurements

The IMVS data were measured with CIMPS equipment (Zahner) at an open-circuit condition based on cw white light at six intensities (3–110 mW cm⁻²). The white light weakly absorbed by the dye molecules was driven with a slave potentiostat system (XPOT) containing a frequency-response analyzer in a frequency range 0.1 – 100 Hz; the modulated light intensity with an active feedback control of the probe intensity from a photo-detector was much smaller (~10 %) than the cw bias light intensity. A photovoltage response was measured with the master potentiostat system (IM6 or Zahnum) involving the amplitude and the phase shift between the modulated light and the voltage response under an open-circuit condition. The resulting Nyquist plot of IMVS show a nearly perfect semicircle in the lower complex plane of the IMVS spectrum because the photovoltage response lags the illumination. The electron lifetime (τ_R) characterizing the charge recombination at the TiO₂/electrolyte interface under the open-circuit condition is determined from the angular frequency at the minimum of the semicircle via the following expression,

$$\tau_R = \left(\frac{1}{\omega_{\min}} \right)_{OC} = \frac{1}{2\pi f_R} \quad (2)$$

in which f_R is the minimum-point frequency (in Hz) of the IMVS response.

Charge-extraction (CE) Measurements

The CE was measured with the same CIMPS system under the same bias light irradiation. For that experiment, the system was initially set to an open-circuit condition for 10 s for the photovoltage of the device to attain a steady state; the white light from the LED was then terminated while the device simultaneously switched to a

short-circuit condition to extract the charges generated at that bias light intensity. The current transient under the short-circuit condition was then recorded, from which the extracted charge density ($Q_{CE}/C \text{ cm}^{-2}$) was obtained on integration of the current transient as a function of time; the total charge density per volume (N_e/cm^{-3}) upon bias LED illumination under the open-circuit condition is determined with

$$N_e = \frac{Q_{CE}}{eL(1-p)} \quad (3)$$

in which e is elementary charge, L is the thickness of the TiO_2 film ($L \sim 20 \text{ }\mu\text{m}$) and p is the porosity of TiO_2 ($p \sim 0.6$).^{S5}

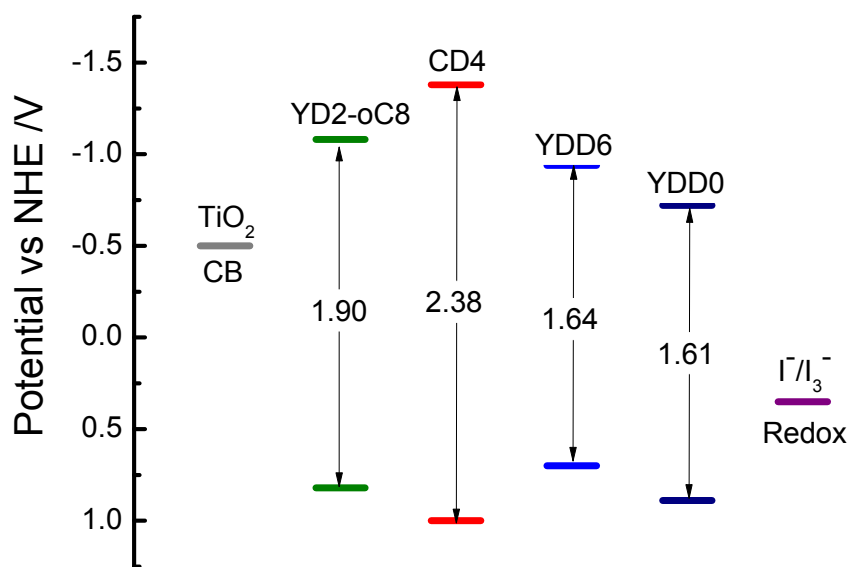
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Table S1. Optimized photovoltaic parameters of DSSC fabricated with YDD6, CD4, YD2-oC8 and their co-sensitized mixtures labeled A-E on TiO₂ films of thickness (12±9) μm under simulated AM-1.5G illumination (power 100 mW cm⁻²) and active area 0.16 cm² with a square shadow mask of size 0.25 cm².

Dye	Working Electrode ^a	J_{sc} /mA cm ⁻²	V_{oc} /mV	FF	η /%
YD2-oC8	<i>a</i>	16.45	757	0.71	8.80
	<i>b</i>	16.62	758	0.69	8.74
	<i>c</i>	16.73	760	0.70	8.88
	average	16.60±0.29	758±3	0.70±0.02	8.81±0.14
CD4	<i>a</i>	10.64	731	0.74	5.70
	<i>b</i>	10.49	738	0.76	5.91
	<i>c</i>	10.44	735	0.76	5.87
	average	10.52±0.21	734±7	0.76±0.03	5.83±0.22
YDD6	<i>a</i>	10.15	672	0.69	4.70
	<i>b</i>	9.45	671	0.75	4.75
	<i>c</i>	9.40	670	0.73	4.59
	average	9.66±0.84	671±2	0.72±0.06	4.68±0.16
A: 0/5/1	<i>a</i>	15.70	709	0.73	8.20
	<i>b</i>	16.02	707	0.72	8.12
	<i>c</i>	15.71	710	0.74	8.23
	average	15.81±0.36	708±3	0.729±0.02	8.18±0.11
B: 20/0/1	<i>a</i>	18.40	745	0.70	9.60
	<i>b</i>	18.25	742	0.71	9.56
	<i>c</i>	18.51	741	0.70	9.58
	average	18.38±0.26	743±4	0.701±0.01	9.58±0.04
C: 20/5/0	<i>a</i>	16.79	762	0.72	9.20
	<i>b</i>	17.04	762	0.70	9.12
	<i>c</i>	16.90	756	0.72	9.21
	average	16.91±0.25	760±7	0.714±0.02	9.18±0.10
D: 20/5/1	<i>a</i>	18.81	753	0.73	10.30
	<i>b</i>	19.96	751	0.72	10.75
	<i>c</i>	19.07	755	0.71	10.23
	average	19.28±1.21	753±4	0.719±0.02	10.43±0.56
E: 20/5/2	<i>a</i>	18.08	746	0.72	9.70
	<i>b</i>	17.80	747	0.72	9.61
	<i>c</i>	18.26	739	0.70	9.51
	average	18.04±0.47	744±9	0.716±0.02	9.61±0.19

^aAll TiO₂ working electrodes (labeled as *a-c*) were fabricated under the same experimental conditions; the uncertainties represent two standard errors.



S6

Figure S1. Potential-level diagram showing the upper (LUMO) and lower (HOMO) potentials for YD2-oC8, CD4, YDD6 and YDD0, and conduction band of TiO₂ and potential of the I⁻/I₃⁻ redox couple. The electrochemical properties of these dyes were investigated with cyclic voltammetry (CV) with a Fc/Fc⁺ couple as reference to produce the oxidation potential (E_{ox}) for each species; the potential level of the HOMO with respect to a normal hydrogen electrode (NHE) was determined from $E_{\text{HOMO}} = E_{\text{ox}} - E_{\text{Fc/Fc}^+} + 0.64$ V, and the potential level of LUMO was determined from $E_{\text{LUMO}} = E_{\text{HOMO}} - E_{0-0}$. The band-gap energy (eE_{0-0}) was determined from the position of the intersection of the emission with the corresponding absorption spectrum for each species.

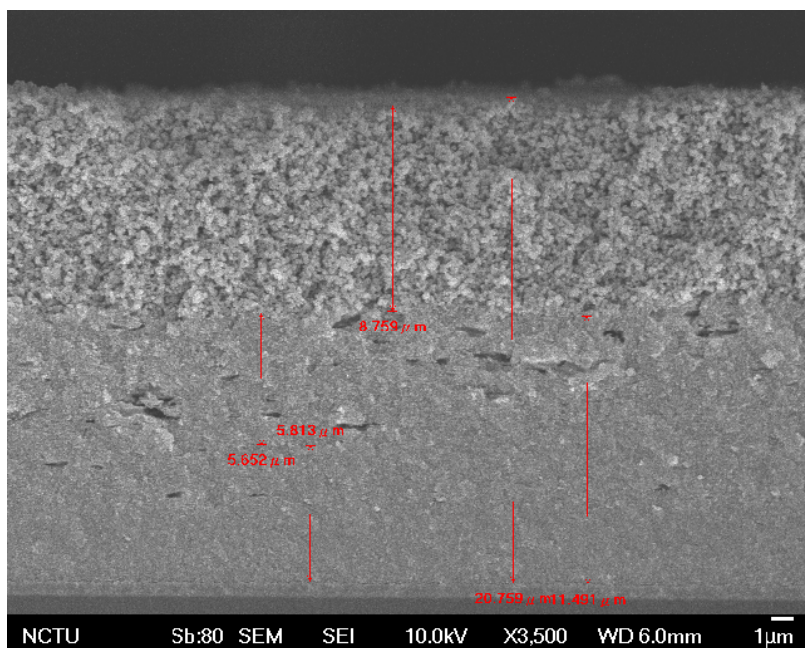


Figure S2. A typical SEM image of the TiO₂ film prepared for optimization of the device performance showing the thickness of NP, NR and SL layers.

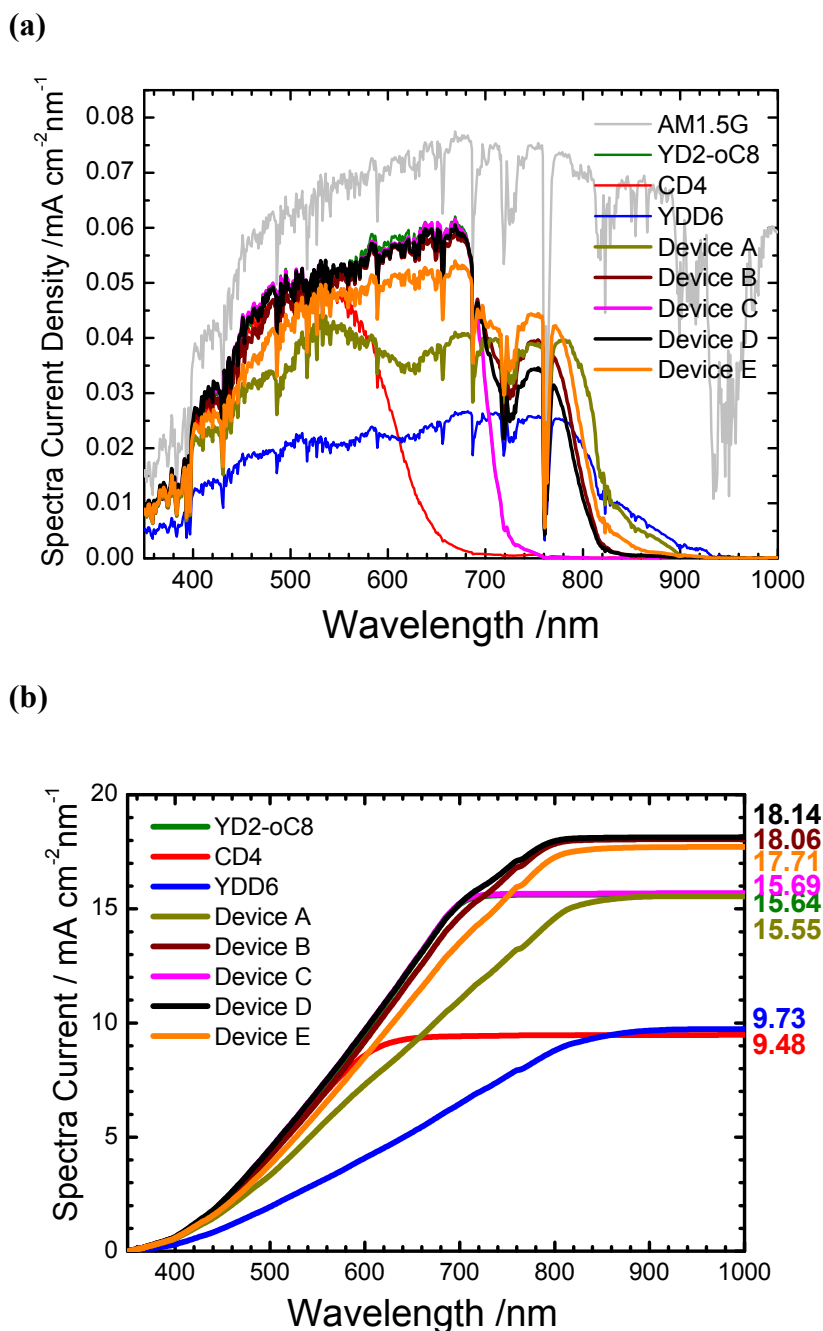


Figure S3. (a) Spectral photocurrent densities of devices made of YD2-oC8, CD4, YDD6 and co-sensitized mixtures A-E (working electrode *a*) obtained from multiplication of the AM-1.5G solar spectrum (grey curve) by the corresponding IPCE of the DSSC devices obtained from Figures 4b and 5b; (b) the corresponding integrated photocurrent densities of the devices to estimate J_{SC} according to the integral

$$J_{SC} = \int q \cdot IPCE(\lambda) \cdot F(\lambda) d\lambda .$$

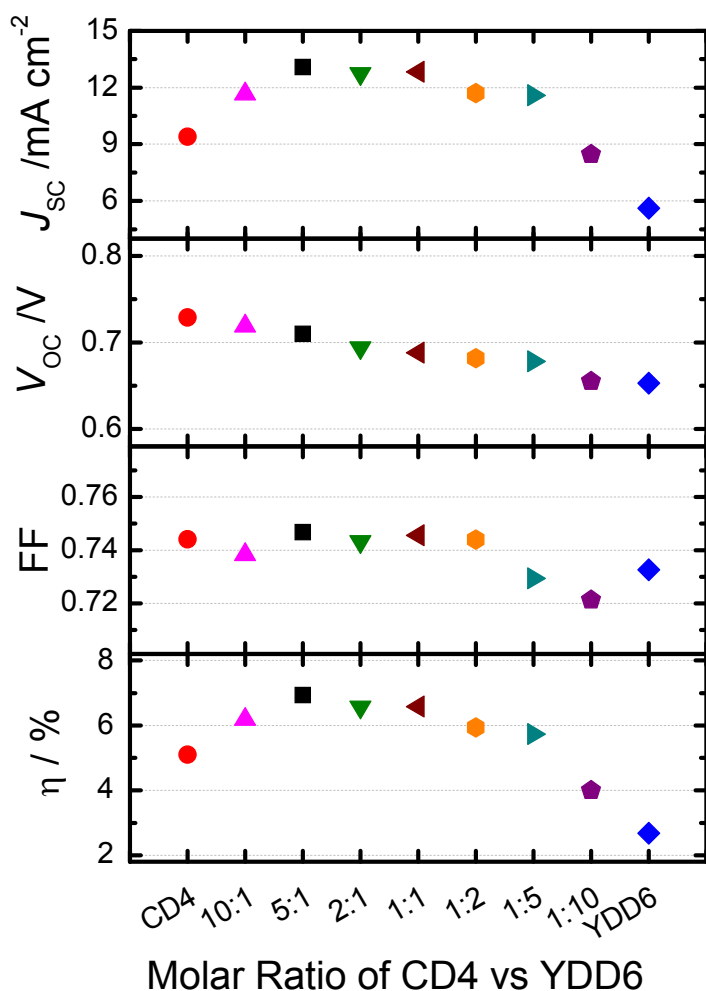


Figure S4. Preliminary photovoltaic test for devices made of CD4 and YDD6 in varied molar ratios. The devices were fabricated using thin TiO₂ films with four layers of NP (thickness ~11 μm) and two layers of SL (~5 μm) and without post-TiCl₄ treatments. The dye solutions were prepared with fixed concentrations: [CDCA] = 0.15 mM, [YDD6] = 0.03 mM; the concentrations of CD4 were varied according to the molar ratios of CD4 vs YDD6 shown on the abscissa axis of the plot.