

## Supplementary Informations

**A novel D-A- $\pi$ -A organic sensitizer containing diketopyrrolopyrrole unit with branched alkyl chain for highly efficient and stable dye-sensitized solar cells**

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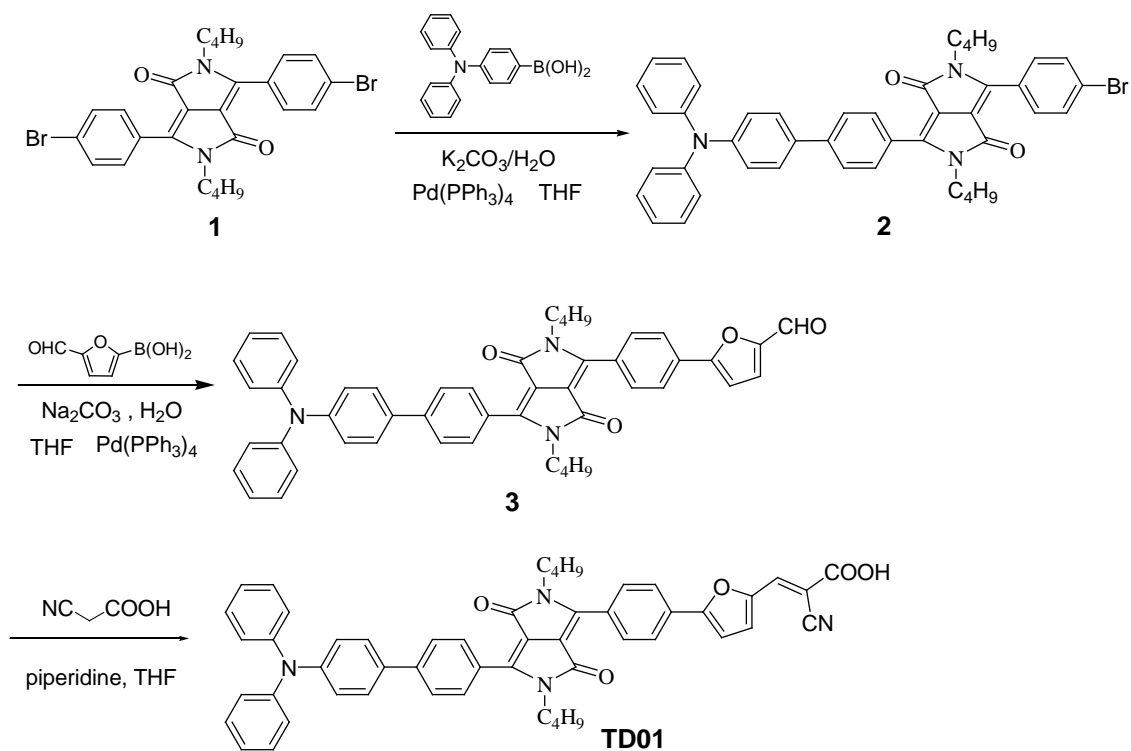
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## General

THF was pre-dried over 4 Å molecular sieves and distilled under argon atmosphere from sodium benzophenoneketyl immediately prior to use. CH<sub>2</sub>Cl<sub>2</sub> was heated under reflux with MgSO<sub>4</sub> and distilled before used. The starting material of 4-p-tolyl-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indol-7-ylboronic acid, 3,6-bis(4-bromophenyl)-2,5-dibutylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione and 3,6-bis(4-bromophenyl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione were prepared according to published procedures.<sup>[1, 2]</sup> All other solvents and chemicals used in this work were of reagent grade and used without further purification.



**Scheme 1** Synthesis procedure of **TD01**

### Synthesis of **2**

Compound **1** (0.84 g, 1.50 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (10 mg, 0.01 mmol), and K<sub>2</sub>CO<sub>3</sub> (1.65 g, 12.0 mmol) in 30 mL of THF and 5 mL of H<sub>2</sub>O were heated to 45 °C under a nitrogen atmosphere for 30 min. A solution of 4-(diphenylamino)phenylboronic acid, (0.48g, 1.65 mmol) in THF (10 mL) was added slowly, and the mixture was refluxed for further 15 h. After cooling to room temperature, the mixture was extracted with 50 mL of CH<sub>2</sub>Cl<sub>2</sub>. The organic portion was combined and removed by rotary evaporation. The residue was purified by column chromatography on silica (CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether = 1/1, v/v) to give an orange solid (0.45g). Yield: 45.2%. <sup>1</sup>H-NMR(CDCl<sub>3</sub>, 500 MHz)δ: (ppm) 7.89 (d, J = 8.28 Hz, 2H), 7.66 (m, 6H), 7.53 (d, J = 8.53 Hz, 2H), 7.28 (dd, J = 6.22 Hz, 13.81 Hz, 4H), 7.15 (d, J = 7.62 Hz, 6H), 7.06 (t, J = 7.29 Hz, 7.29 Hz, 2H), 3.78 (m, 4H), 1.51~1.65 (m, 4H), 1.20~1.35 (m, 4H), 0.86 (m, 6H).

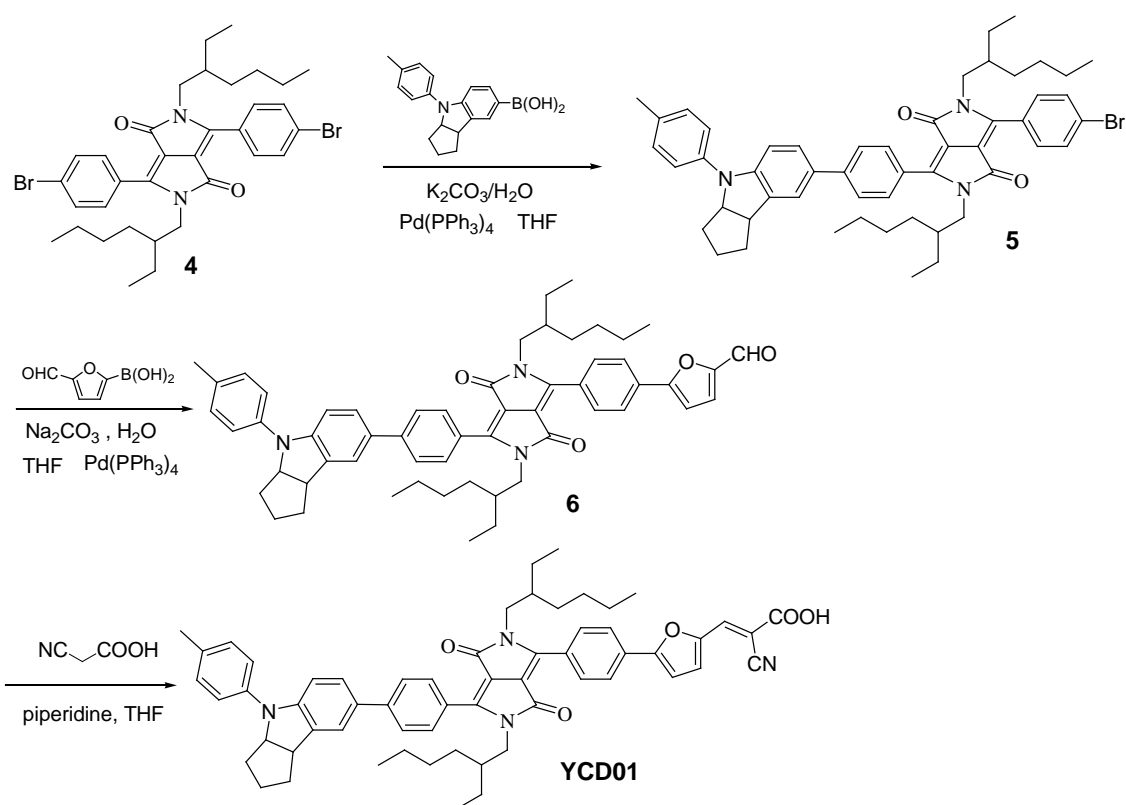
### Synthesis of **3**

Compound **2** (0.10 g, 0.14 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (10 mg, 0.01 mmol), and Na<sub>2</sub>CO<sub>3</sub> (1.02 g, 0.01 mol) in 10 mL of THF and 5 mL of H<sub>2</sub>O were heated to 45 °C under a nitrogen atmosphere for 30 min. A solution of 4-formylphenylboronic acid (0.039 g, 0.28 mmol) in THF (5 mL) was added slowly, and the mixture was refluxed for further 15 h. After cooling to room temperature, the mixture was extracted with 30 mL of CH<sub>2</sub>Cl<sub>2</sub>. The organic portion was combined and removed by rotary evaporation. The residue was purified by column chromatography on silica (CH<sub>2</sub>Cl<sub>2</sub>/ethyl acetate = 70/1, v/v) to give a red solid. Yield: 80.6%. <sup>1</sup>H-NMR(CDCl<sub>3</sub>, 500 MHz) δ: (ppm) 9.69 (s, 1H), 7.93 (m, 6H), 7.71 (d, J = 8.42 Hz, 2H), 7.52 (d, J = 8.64 Hz, 2H), 7.34 (d, J = 3.73 Hz, 1H), 7.29 (t, J = 7.87 Hz, 7.87 Hz, 4H), 7.14 (m, 6H), 7.07 (t, J = 7.32 Hz, 7.32 Hz, 2H), 6.94 (d, J = 3.72 Hz, 1H), 3.81 (dd, J = 15.14, 7.54 Hz, 4H), 1.53~1.73 (m, 4H), 1.16~1.39 (m,

4H), 0.87 (m, 6H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 191.7, 163.0, 162.7, 148.8, 148.1, 147.5, 147.0, 146.0, 143.4, 142.2, 135.7, 133.2, 129.4, 127.8, 126.8, 126.3, 124.8, 123.4, 123.3, 110.4, 109.7, 41.9, 31.7, 29.7, 20.0, 13.7.

### Synthesis of **TD01**

Compound **3** (0.08 g, 0.11 mmol), 2-cyanoacetic acid (0.094 g, 1.10mmol), and piperidine (0.5 mL) in 20 mL of THF were heated to reflux under a nitrogen atmosphere for 9 h. After cooling to room temperature, the precipitate was filtered. The residue was purified by column chromatography on silica ( $\text{CH}_2\text{Cl}_2$ /ethyl acetate/ethanol = 10/1/1, v/v/v) and then washed with solvent ( $\text{CH}_2\text{Cl}_2$ /ethanol = 1/100,v/v)to give a red solid. Yield: 97.1%.  $^1\text{H}$ NMR(500 MHz,  $\text{CDCl}_3$ )  $\delta$ : (ppm) 8.00 (d,  $J$  = 8.49 Hz, 2H), 7.89 (m, 4H), 7.74 (d,  $J$  = 8.43 Hz, 2H), 7.54 (d,  $J$  = 8.68 Hz, 2H), 7.30 (m, 6H), 7.15 (dd,  $J$  = 2.29 Hz, 8.11 Hz, 6H), 7.06 (m, 3H), 3.81 (m, 4H), 1.60 (m, 4H), 1.32 (m, 4H), 0.86 (m, 6H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 166.1, 163.3, 162.6, 158.8, 148.9, 148.6, 148.2, 147.4, 143.6, 133.1, 129.6, 129.4, 129.3, 127.8, 126.8, 125.7, 124.9, 123.4, 123.2, 115.7, 114.0, 113.3, 110.4, 109.8, 33.8, 31.9, 31.6, 31.5, 30.2, 29.7, 29.5, 29.4, 29.3, 29.2, 29.1, 29.0, 24.8, 24.7, 22.7, 20.0, 14.1, 13.6.HRMS ( $m/z$ ):  $[\text{M}-\text{H}]^-$  calcd. for ( $\text{C}_{52}\text{H}_{48}\text{N}_4\text{O}_5$ ): 803.3233; found, 803.3241.



**Scheme 2.** Synthesis procedure of YCD01

### Synthesis of **5**

The synthesis method resembles that of compound **2** and the compound was purified by column chromatography on silica ( $CH_2Cl_2$ /petroleum ether = 1/1, v/v) to give a red solid. Yield: 37.3%.  $^1H$ -NMR( $CDCl_3$ , 500 MHz)  $\delta$ : (ppm) 7.86 (d,  $J = 8.45$  Hz, 2H), 7.69 (m, 6H), 7.44 (s, 1H), 7.38 (dd,  $J = 1.79$  Hz, 8.33 Hz, 1H), 7.21 (m, 4H), 6.98 (d,  $J = 8.32$  Hz, 1H), 4.86 (m, 1H), 3.90 (td,  $J = 2.56$  Hz, 8.96 Hz, 9.15 Hz, 1H), 3.83 (dd,  $J = 1.34$  Hz, 7.14 Hz, 2H), 3.76 (dd,  $J = 3.10$  Hz, 7.15 Hz, 2H), 2.11 (m, 2H), 1.96 (m, 2H), 1.84 (m, 2H), 1.57 (m, 4H), 1.30 (s, 3H), 1.17 (m, 10H), 0.89 (m, 4H), 0.83 (m, 6H), 0.76 (m, 6H).

### Synthesis of **6**

The synthesis method resembles that of compound **3** and the compound was purified by

column chromatography on silica(CH<sub>2</sub>Cl<sub>2</sub>/ethyl acetate = 70/1, v/v) to give a red solid. Yield: 64.5%. <sup>1</sup>H NMR(500 MHz, CDCl<sub>3</sub>) δ: (ppm) 9.67 (s, 1H), 7.89 (q, J = 8.62 Hz, 8.62 Hz, 8.65 Hz, 4H), 7.83 (d, J = 8.41 Hz, 2H), 7.41 (s, 1H), 7.33 (m, 2H), 7.19 (q, J = 8.57 Hz, 8.57 Hz, 8.56 Hz, 4H), 6.92 (dd, J = 6.02 Hz, 11.46 Hz, 2H), 4.83 (m, 1H), 3.79 (m, 5H), 2.35 (s, 3H), 2.08 (m, 1H), 1.91 (m, 2H), 1.82 (m, 1H), 1.68 (m, 1H), 1.62 (m, 3H), 1.20 (m, 16H), 0.75 (m, 12H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ: 191.9, 163.1, 162.7, 149.4, 148.3, 147.0, 145.9, 144.1, 140.1, 135.8, 135.6, 131.7, 127.7, 125.7, 123.3, 120.2, 110.4, 109.5, 107.7, 69.2, 68.5, 45.4, 45.2, 45.0, 38.6, 38.4, 33.7, 28.3, 27.8, 24.5, 23.8, 22.9, 20.8, 14.0, 10.5.

### Synthesis of YCD01

The synthesis method resembles that of compound 7 and the compound was purified by column chromatography on silica(CH<sub>2</sub>Cl<sub>2</sub>/ethyl acetate/ethanol = 10/1/1, v/v/v) and then washed with solvent (CH<sub>2</sub>Cl<sub>2</sub>/ethanol = 1/100, v/v) to give a red solid. Yield: 72.9%. <sup>1</sup>H NMR(500 MHz, CDCl<sub>3</sub>) δ: (ppm) 8.12 (m, 3H), 8.04 (d, J = 8.63 Hz, 2H), 7.92 (d, J = 8.51 Hz, 2H), 7.83 (d, J = 8.28 Hz, 2H), 7.59 (m, 3H), 7.49 (d, J = 8.09, 1H), 7.22 (q, J = 8.60 Hz, 8.60 Hz, 8.57 Hz, 4H), 6.93 (d, J = 8.36 Hz, 1H), 4.90 (m, 1H), 3.88 (m, 1H), 3.79 (d, J = 6.83 Hz, 4H), 2.29 (s, 3H), 2.07 (m, 1H), 1.70~1.90 (m, 3H), 1.63 (m, 1H), 1.37 (m, 3H), 1.09 (m, 16H), 0.68 (m, 12H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ: 189.3, 168.1, 161.9, 160.7, 157.3, 154.3, 151.2, 146.2, 139.5, 139.2, 135.7, 130.8, 129.8, 129.2, 126.2, 119.6, 116.5, 111.6, 109.4, 108.8, 108.5, 107.5, 107.2, 68.3, 54.9,

48.2, 44.6, 38.8, 33.1, 27.6, 23.9, 22.1, 20.4, 13.7, 10.2. HRMS ( $m/z$ ):  $[M-H]^-$  calcd. for  $(C_{60}H_{65}N_4O_5)$ : 821.4955; found, 821.4955.

[1] O. Miyata, N. Takeda, Y. Kimura, Y. Takemoto, N. Tohnai, M. Miyata and T. Naito, *Tetrahedron*, 2006, **62**, 3629.

[2] A. R. Rabindranath, Y. Zhu, I. Heim and B. Tieke, *Macromolecules*, 2006, **39**, 8250.

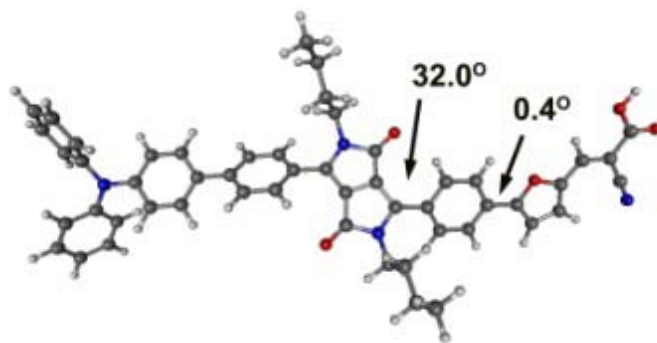
## Cell Fabrication

The DSCs were fabricated as follows. A double-layer TiO<sub>2</sub> photoelectrode (thickness 15 μm; area 0.25 cm<sup>2</sup>) was used as a working electrode. A 10 μm main transparent layer with titania particles (~20 nm) and a 6 μm scattering layer with titania particles (~400 nm) were screen-printed on the fluorine-doped tin oxide conducting glass substrate. A solution of **TD01** or **YCD01** ( $3 \times 10^{-4}$  M) in acetonitrile/tert-butyl alcohol (1/1, v/v) was used to coat the TiO<sub>2</sub> film with the dye. Deoxycholic acid (20 mM) was added to the dye solution as a co-adsorbent. The electrodes were immersed in the dye solutions and then kept at 25 °C for 24 h to adsorb the dye onto the TiO<sub>2</sub> surface. Photovoltaic measurements were performed in a two-electrode sandwich-type sealed-cell configuration. The dye-coated TiO<sub>2</sub> film was used as the working electrode, and platinum-coated conducting glass was used as the counter-electrode. The two electrodes were separated by a Surlyn spacer (50 μm thick) and sealed up by heating the polymer frame. Finally, the electrolyte consisting of 0.6 M 1-methyl-3-propylimidazolium iodide, 0.1 M LiI, 0.05 M I<sub>2</sub> and 0.5 M *tert*-butylpyridine in acetonitrile was injected into the cell and sealed with a coverglass. The current-voltage characteristics were measured using a black metal mask with an aperture area of 0.25 cm<sup>2</sup> under standard AM 1.5 sunlight (100 mW cm<sup>-2</sup>, WXS-155S-10: Wacom Denso Co. Japan) <sup>[3]</sup>. Monochromatic

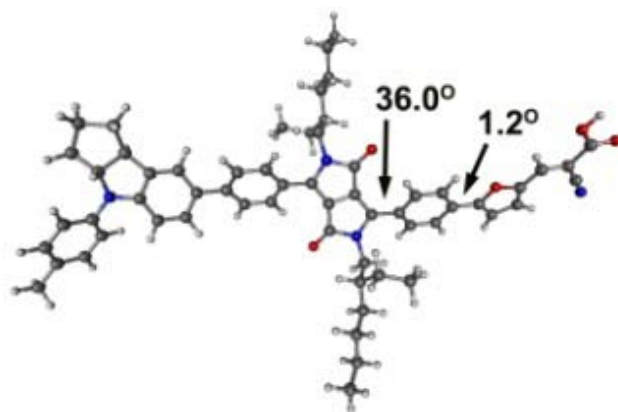


incident photon-to-current conversion efficiency spectra were measured with monochromatic incident light of  $1 \times 10^{16}$  photons  $\text{cm}^{-2}$  under  $100 \text{ mW cm}^{-2}$  in detector current mode (CEP-2000BX, Bunko-Keiki).

[3] N. Koide and L. Han, *Rev. Sci. Instrum.*, 2004, **75**, 2828.

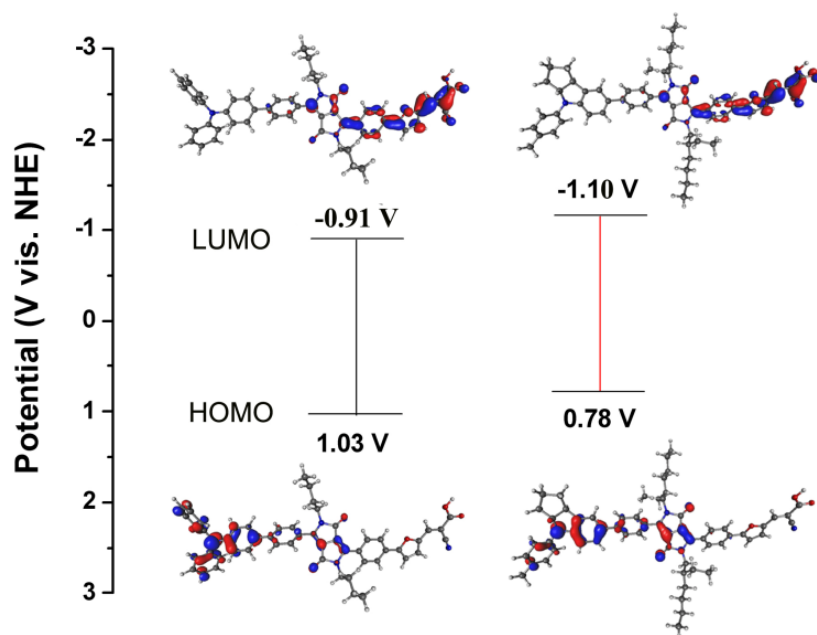


TD01

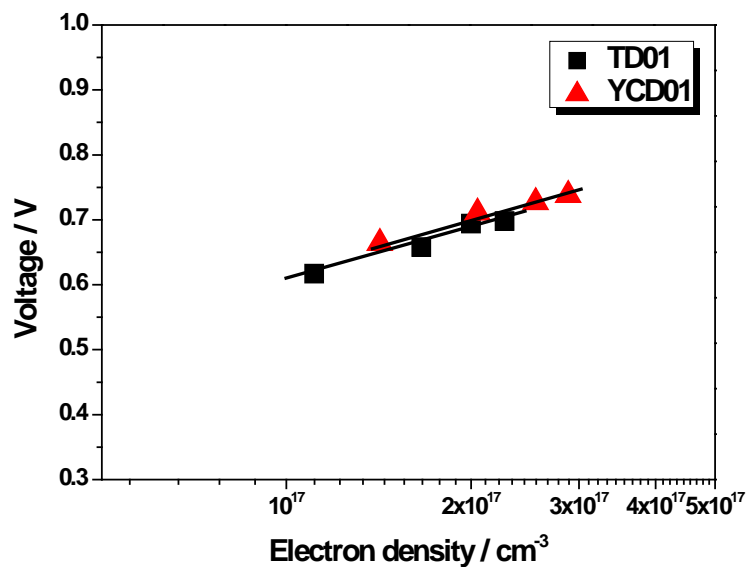


YCD01

**Figure S1.** The optimized structures of **TD01** and **YCD01** calculated at the B3LYP/6-31 G\* level of theory with Gaussian03.



**Figure S2.** Calculated frontier molecular orbitals of HOMO and LUMO and experimental energy level diagram of **TD01** (left) and **YCD01** (right).



**Figure S3.** Charge extraction of DSCs sensitized by **TD01** and **YCD01**.

**Table S1.** Optical and electrochemical properties of the dye **TD01** and **YCD01**.

Dye	$\lambda_{\text{max}}^{\text{a}}/\text{nm}$ ( $\epsilon \times 10^{-4} \text{M}^{-1} \text{cm}^{-1}$ )	$\lambda_{\text{max}}^{\text{b}}$ (nm)	HOMO <sup>c</sup> /V (vs.NHE)	$E_{0-0}^{\text{d}}$ (eV)	LUMO <sup>e</sup> /V (vs. NHE)
<b>TD01</b>	514(4.12),397(3.80), 309(3.76)	546	1.03	1.94	-0.91
<b>YCD01</b>	526(4.60),400(4.00), 326(3.60)	518	0.78	1.88	-1.10

<sup>a</sup>Absorption maximum in  $\text{CH}_2\text{Cl}_2$  solution ( $2.5 \times 10^{-5}$  M). <sup>b</sup>Absorption maximum on  $\text{TiO}_2$  film. <sup>c</sup>HOMO were measured in  $\text{CH}_2\text{Cl}_2$  with 0.1 M tetrabutylammoniumhexafluorophosphate (TBAPF<sub>6</sub>) as electrolyte (working electrode: FTO/ $\text{TiO}_2$ /dye; reference electrode: SCE; calibrated with ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) as an external reference. Counter electrode: Pt). <sup>d</sup> $E_{0-0}$  was estimated from the absorption thresholds from absorption spectra of dyes adsorbed on the  $\text{TiO}_2$  film. <sup>e</sup>LUMO is estimated by subtracting  $E_{0-0}$  to HOMO.

**Table S2.** DSCs performance of dye **YCD01** and **TD01**.

Dye	4-TBP	$J_{\text{sc}}$ ( $\text{mA cm}^{-2}$ )	$V_{\text{oc}}$ (V)	FF	$\eta$ %
<b>YCD01</b>	0	15.37	0.66	0.67	6.79
	0.5M	13.40	0.76	0.73	7.43
<b>TD01</b>	0	13.91	0.64	0.60	5.34
	0.5 M	11.05	0.69	0.68	5.18

<sup>A</sup> light intensity:  $100 \text{ mW cm}^{-2}$  simulated AM 1.5G solar light; active area:  $0.25 \text{ cm}^2$ ; thickness of  $\text{TiO}_2$  film:  $16 \mu\text{m}$ . <sup>B</sup> Dye bath: 0.3 mM in  $\text{CH}_3\text{CN}/t\text{-BuOH}$  (1:1; v/v); sensitized time: 24 h; electrolytes: 0.6 M MPImI, 0.05 M  $\text{I}_2$ , 0.1 M LiI, 0/0.5 M 4-TBP in  $\text{CH}_3\text{CN}$ .