Supporting Information for

A Novel Compact DPP Dye with Enhanced Light Harvesting and Charge Transfer Properties for Highly Efficient DSCs

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General information:

Unless otherwise noted, all solvents were treated by standard methods before use. All reagents were commercially available and used without further purification unless indicated otherwise. Thin lay all chemicals were analytical grade and used as received. NMR spectra were recorded on a BRUKER AVANCE 400 MHz instruments. The residual solvent protons (¹H) or the solvent carbons (¹³C) were used as internal standards. ¹H NMR data are presented as follows: chemical shift in ppm (δ) downfield from tetramethylsilane (multiplicity, coupling constant (Hz), integration). The following abbreviations are used in reporting NMR data: s, singlet; br.s, broad singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublets; m, multiplet. Mass spectra were taken on a Bruker Daltonics Inc. APEXII FT-ICR spectrometer. The material 1,4-diketo-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]- pyrrole (DPP) were prepared according to the literature procedures ^[1].



Scheme S1 Synthesis procedure of ICD-1 and ICD-2

Synthesis of 2

An oven-dried 250-mL one-necked flask was charged with DPP (1) (3.6 g, 8 mmol), NaH (0.48g, 20 mmol) (60% dispersion in mineral oil, in soluble bags in resealable cans) and 150 mL DMF. The mixture were stirred for 1 h at room temperature, followed by dropping 1-bromohexane (13.3 g, 80 mmol) in 30 mL of DMF. The mixture was kept for an additional 30h at room temperature and filtered. The solid was washed with 60 mL of chloroform, and the organic phase was washed with water (3*50mL) and brine (3*50mL). The combined organic phases was evaporated under reduced pressure and the residue purified by silica-gel column chromatography to give an orange-red polycrystal-line powder (2.2 g, yield =45%).^[2] ¹H NMR (CDCl₃;400MHz), δ (ppm): 0.83 (t, *J*=6.8Hz, 6H), 1.20–1.30(m, 12H), 1.52-1.58 (m, 4H), 3.72 (t, *J*=7.6Hz, 4H), 7.67 (s, 8H).

Synthesis of **3**

An oven-dried 100-mL three-necked flask was charged with Compound **2** (1.84g, 3 mmol), Pd(PPh₃)₄ (0.24g, 0.21mmol), and sodium carbonate (5.4g, 51mmol). The flask was evacuated and backfilled with nitrogen, with the operation being repeated twice. 40 mL THF and 15 mL H₂O were added and the blend was heated at 45 °C for 0.5 h, then a solution of 5-formyl-2-thiophenylboronic acid (0.47g, 3.0mmol) in 10 mL of THF was added via syringe at this time. The temperature was increased to 80°C and maintained for 16 h. ^[3] After cooling to room temperature, dichloromethane were added and the organic phase was filtered through a silica-gel. The filtrate was washed with water (3*20mL) and brine (3*20mL). The combined organic phases was dried on MgSO₄, filtered and evaporated under reduced pressure and the residue purified by silica-gel column chromatography to give an orange-red fraction corresponding to pure compound2 (0.81g. yield =42%). ¹H NMR (CDCl₃;400MHz), δ (ppm): 0.83 (m, 6H), 1.22(s, 12H), 1.55-1.60 (m, 4H), 3.71-3.80 (m, 4H), 7.50(d, *J*=4Hz, 1H), 7.65-7.71(m, 4H), 7.77(d, *J*=4Hz, 1H), 7.80(d, *J*=8.4Hz, 2H), 7.89(d, *J*=8.4Hz, 2H), 9.92 (s, 1H).

Synthesis of 4

An oven-dried 100-mL three-necked flask was charged with compound **3** (0.64g, 1.0mmol), Pd(OAc)₂ (22mg, 0.1mmol), P^tBu₃ (20mg, 0.1mmol), *bis(4-(tert-butyl)phenyl)amine* (0.37g, 1.30mmol), ^{*t*}BuONa (0.48g, 5.0mmol). The flask was evacuated and backfilled with nitrogen, with the operation being repeated twice. Then 20 mL toluene were added and the mixture was heated at 90 °C for 16h. ^[4] After cooling to room temperature, dichloromethane were added and the organic phase was filtered through a silica-gel pad. The filtrate was with water (3*20mL) and brine (3*20mL). The combined organic phases was dried on MgSO₄, filtered and evaporated under reduced pressure and the residue purified by silica-gel column chromatography to give a purple solid(0.53g, 62%), ¹H-NMR(CDCl₃, 400 MHz) δ (ppm): 0.81-0.88 (m, 6H), 1.23-1.28(m, 12H), 1.33(s, 18H), 1.61-1.74(m, 4H), 3.79 (t, *J*=7.8Hz, 4H,),7.03(d, *J*=8.8Hz, 2H), 7.13(d, *J*=8.8Hz, 4H), 7.34(d, *J*=8.8Hz, 4H), 7.49(d, *J*=4Hz, 1H), 7.77-7.82(m,5H), 7.90(d, *J*=8.8Hz, 2H), 9.92 (s, 1H).

Synthesis of ICD-1

An oven-dried 100-mL one-necked flask was charged with compound 4 (3.5×10^{-4} mol), cyanoacrylic acid (7×10^{-3} mol), 10 mL of dry THF and 0.4ml piperidine.^[3] The solution was heated to reflux for 15 h and the colour turned to

deep red. After cooling to room temperature, dichloromethane were added and the organic phase was washed with water (3*20mL) and brine (3*20mL). The combined organic phase was dried on MgSO₄, filtered and evaporated under reduced pressure and the residue purified by silica-gel column chromatography to give a purple solid (86%).¹H-NMR(DMSO, 400 MHz) δ (ppm): 0.75-0.85 (m, 6H), 1.12-1.16(m, 12H), 1.29(s, 18H), 1.47 (s, 4H), 3.71 (s, 4H), 6.84(d, *J*=8Hz, 2H), 7.10(d, *J*=8.4Hz, 4H), 7.41(d, *J*=8.4Hz, 4H), 7.77-7.80(m, 4H), 7.88(s, 4H), 8.18(s, 1H); HRMS (ESI): m/z found (M+H): 913.4696.

Synthesis of 5

An oven-dried 100-mL three-necked flask was charged with Compound **3** (0.64 g, 1 mmol), Pd(PPh₃)₄ (81 mg, 0.07 mmol), and Na₂CO₃ (2.3 g, 0.02 mol). The flask was evacuated and backfilled with nitrogen, with the operation being repeated twice. 30 mL THF and 8 mL H₂O were added and the blend was heated at 45 °C for 0.5 h, then a solution of *bis*(*4-(tert-butyl)phenyl)amino)phenyl* boronic acid (0.61 g, 1.50 mmol) in 10 mL of THF was added via syringe at this time. The temperature was increased to 80°C and maintained for 16 h. ^[3] After cooling to room temperature, dichloromethane were added and the organic phase was filtered through a silica-gel pad. The filtrate was washed with water (3*20mL) and brine (3*20mL). The combined organic phase was dried on MgSO₄, filtered and evaporated under reduced pressure and the residue purified by silica-gel column chromatography to give a red solid (0.31 g). Yield: 36%. ¹H-NMR(CDCl₃, 400 MHz) δ (ppm):0.83 (t, *J*=6.4Hz, 6H), 1.24(s, 12H), 1.33(s, 18H), 1.64-1.65 (m, 4H), 3.78-3.84 (m, 4H,),7.08(d, *J*=8.8Hz, 4H),7.12(d, *J*=8.8Hz, 2H), 7.31(d, *J*=8.8Hz, 4H), 7.50-7.52(m, 3H), 7.72(d, *J*=8.4Hz, 2H), 7.78(d, *J*=3.6Hz, 1H), 7.83(d, *J*=8.8Hz, 2H), 7.92(t, *J*=7.8Hz, 4H), 9.28(s, 1H).

Synthesis of ICD-2

An oven-dried 100-mL one-necked flask was charged with compound 5 $(3.5 \times 10^{-4} \text{ mol})$, cyanoacrylic acid $(7 \times 10^{-3} \text{ mol})$, 10 mL of dry THF and 0.4ml piperidine. The solution was heated to reflux for 15 h and the colour turned to deep red. After cooling to room temperature, dichloromethane were added and the organic phase was washed with water (3*20mL) and brine (3*20mL). The combined organic phase was dried on MgSO₄, filtered and evaporated under reduced pressure and the residue purified by silica-gel column chromatography to give a purple solid (86%). ¹H-NMR(CDCl₃, 400 MHz) δ (ppm): 0.82 (t, *J*=7.2Hz, 6H), 1.20-1.25(m, 12H), 1.33(s, 18H), 1.58 (s, 4H), 3.72-3.83 (m, 4H), 7.07-7.11(m, 6H), 7.29(d, *J*=8.8Hz, 4H), 7.47-7.50(m, 3H), 7.68-7.70(m, 3H), 7.76-7.80(m, 4H), 7.86(d, *J*=8.4Hz, 2H), 8.05(s, 1H); HRMS (ESI): m/z found (M+H): 989.5036

Dye	$\lambda_{max}^{[a]}$	3	$\lambda_{em}^{[b]}$	$E_{\theta - \theta}^{[c]}$	E _{+/0} ^[d]	$E_{+/*}^{[e]}$	J _{sc}	Voc	FF	$\pmb{\eta}^{[\mathrm{f}]}$
	[nm]	$[L \text{ mol}^{-1} \text{ cm}^{-1}]$	[nm]	[eV]	[V]	[V]	$[mA cm^{-2}]$	[mV]		[%]
ICD-1	543	48100	652	2.04	0.97	-1.07	16.65	708	0.73	8.61
	389	41900					± 0.20	± 10	± 0.02	
ICD-2	519	43200	664	2.12	0.99	-1.13	13.67	712	0.74	7.20
	393	41000					± 0.20	± 10	± 0.02	

[a] Absorption in CH₂Cl₂ solutions (1×10⁻⁵ M) at rt; [b] Emission in CH₂Cl₂ solutions (1×10⁻⁵ M) at rt; [c] $E_{0.0}$ values were estimated from the intersection of the absorption and emission spectra; [d] The oxidation potentials of the dyes were measured in CH₂Cl₂ solutions with tetrabutyl-ammoniumhexafluorophosphate (TBAPF₆, 0.1 M) as electrolyte, Pt wires as working and counter electrode, Ag/Ag⁺ as reference electrode; calibrated with ferrocene/ferrocenium (Fc/Fc⁺) as an internal reference and converted to NHE by addition of 630 mV; [e]

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The estimation was determined by subtracting $E_{0.0}$ from $E_{s+/0}$; [f] The data were recorded under AM 1.5 G simulated solar light at a light intensity of 100 mW cm⁻², and represents the average of three devices, where TiO₂ films with 11 µm thick nanocrystalline layer and 6 µm thick scattering layer were used with an electrolyte containing 0.68 M dimethyl imidiazolium iodide, 0.05 M iodine, 0.10 M LiI, 0.05 M guani-dinium thiocyanate, and 0.40 M tert-butylpyridine in a mixture of acetonitrile and valeronitrile (85/15, v/v), and each data was averaged by three parallel samples.

Fig. S2: The Geometry optimized ground state molecular structures of ICD-1 and ICD-2 with the corresponding dihedral angles between each plain.



ICD-1





DSC fabrication and characterization:

DSC fabrication: The nanocrystalline TiO₂ pastes (particle size, 20 nm) were prepared using a previously reported procedure.^[5] Fluorine doped thin oxide (FTO, 4 mm thickness, 10 ohms/sq, Nippon Sheet Glass, Japan) conducting electrodes were washed with soap and water, followed by sonication for 10 min in acetone and isopropanol, respectively. Following a drying period, the electrodes were then submerged in a 40 mM aqueous solution of TiCl₄ for 30 min at 75° C, and then washed by water and ethanol. On the electrodes, an 11 μ m thick nanocrystalline TiO₂ layer and 6 μ m thick TiO2 light scattering layer (particle size, 400 nm, PST-400C) were prepared by screen-printing method. The TiO₂ electrodes were heated at 500 °C for 30 min, followed by treating with a 40 mM aqueous solution of TiCl4 for 30 min at 75° C and subsequent sintering at 500 °C for 30 min. The thickness of TiO₂ films was measured by a profiler, Sloan, Dektak3.

The electrodes were immersed in a dye bath containing 0.2 mM ICD-1 or ICD-2 and 20 mM 3α , 7α -dihydroxy-5 β -cholic acid (chenodeoxycholic acid) in 4-*tert*-butanol/acetonitrile mixture/tetrahydrofuran (1:1:0.2, v/v) and kept for 24 h at room temperature. The dyed electrodes were then rinsed with the mixed solvent to remove excess dye. A platinum-coated counter electrode was prepared according to the reporter ^[6], and two holes were drilled on its opposite sides. The two electrodes were sealed together with a 25 µm thick thermoplastic Surlyn frame. An electrolyte solution was then introduced through one of the two holes in the counter electrode, and the holes were sealed with the thermoplastic Surlyn. The electrolyte contains 0.68 M dimethyl imidiazolium iodide, 0.05 M iodine, 0.10 M LiI, 0.05 M guanidinium thiocyanate, and 0.40 M *tert*-butylpyridine in the mixture of acetonitrile and valeronitrile (85:15, v/v). All the devices were prepared with a photoactive area of about 0.3 cm², and a metal mask of 0.165 cm² was covered on the device for photovoltaic property measurements.

Characterization: The photocurrent-voltage (*I-V*) characteristics were recorded at room temperature using a computer-controlled Keithley 2400 source meter under air mass (AM) 1.5 simulated illumination (100 mW cm⁻², Oriel, 67005). The action spectra of monochromatic incident photo-to-current conversion efficiency (IPCE) for solar cells were performed using a commercial setup (PV-25 DYE, JASCO). A 300 W Xenon lamp was employed as light source for generation of a monochromatic beam. Calibrations were performed with a standard silicon photodiode. IPCE is defined by IPCE(λ) = $hcJ_{sc}/e\varphi\lambda$, where *h* is Planck's constant, *c* is the speed of light in a vacuum, *e* is the electronic charge, λ is the wavelength in meters (m), J_{sc} is the short-circuit photocurrent density (A m⁻²), and φ is the incident radiation flux (W m⁻²).

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