

Supporting Information for:

Molecular engineering of panchromatic isoindigo sensitizers for dye-sensitized solar cell applications

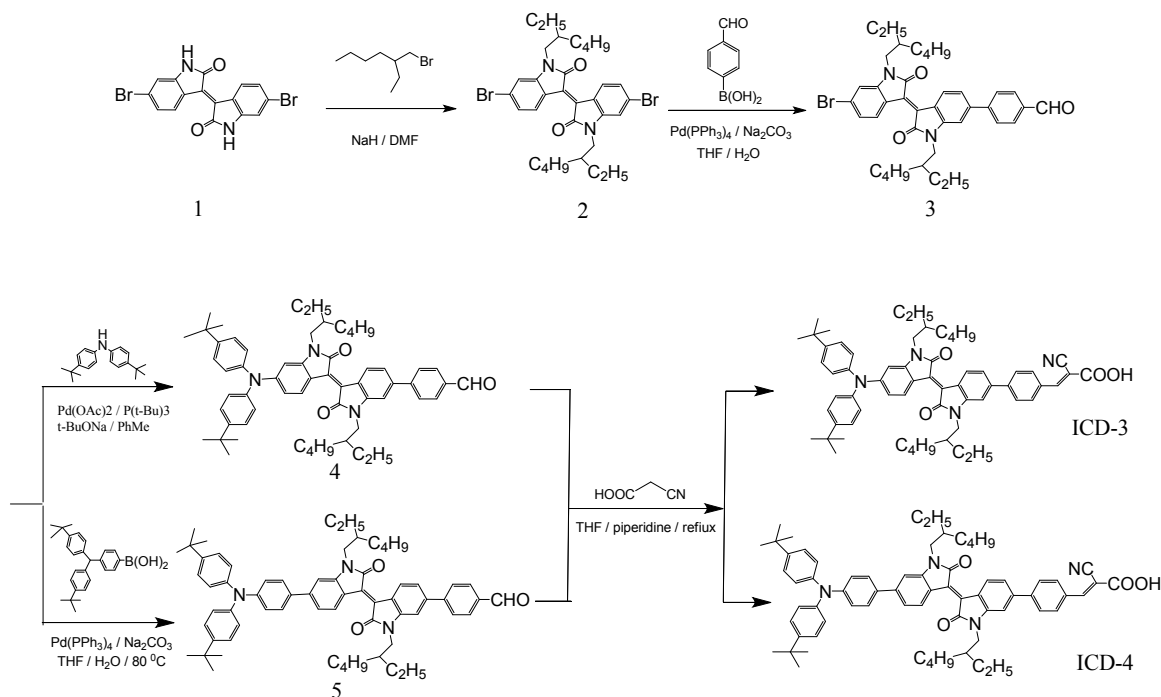
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General information:

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 (^{13}C) 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 4-(bis(4-(tert-butyl)phenyl)methyl)phenyl)boronic acid were prepared according to published procedures. ^[1]



Scheme 1 synthesis procedure of ICD-3 and ICD-4

Synthesis of 6,6'-Dibromoisindigo(1).

6-Bromooxindole (2.00g, 9.44mmol) and 6-bromoisatin (2.13g, 9.44mmol) were dissolved in AcOH (100mL), followed by the addition of conc. HCl solution (0.4mL), with the reaction mixture vigorously stirring under reflux for 24 h. After cooling to room temperature, the mixture was filtered. The solid was washed with water, ethyl alcohol and ether. After drying under a vacuum, brown powder was obtained (3.32g, 84%).^[2] ¹H NMR (CDCl₃, 400MHz) δ (ppm): 7.81(s, 2H), 7.68(d, 2H), 7.40 (s, 2H), 7.16 (s, 2H).

Synthesis of 6,6'-Dibromo-N,N'-(1-isoctyl)-isoindigo(2).

Under nitrogen, compound 1 (836mg, 2 mmol), potassium carbonate (1.65g, 12 mmol), and DMF(40mL) were dissolved in a 100mL three-necked flask, the mixture was stirred for half an hour, 3-(bromomethyl)heptane (845mg, 4.4 mmol) were added by a syringe, and then this mixture was heated to 100 °C for 18 h. After cooling to room temperature, the mixture was poured into water and extracted with CH₂Cl₂. The combined organic layers were washed with brine and water and dried with anhydrous MgSO₄, then the solvent was removed by evaporation, and the residue was purified by column chromatography using silica gel (CH₂Cl₂/petroleum ether) = 1/2 (v/v) as eluent, red powder was obtained (1.04g, 81%). ¹H NMR (CDCl₃,400MHz) δ (ppm): 9.0 (d, *J*=8.4Hz, 2H), 7.12 (d, *J*=8.8Hz, 2H), 6.83 (s, 2H), 3.55 (m, 4H), 1.78 (t, 2H), 1.29-1.35 (m, 16H), 0.90 (m, 12H).

Synthesis of 4-(6'-bromo-1,1'-bis(2-ethylhexyl)-2,2'-dioxo-[3,3'-biindolinylidene]-6-yl)benzaldehyde(3).

Compound 2 (322mg, 0.5 mmol), Pd(dba)₃ (15mg), p(o-tyl)₃ (10mg), and K₃PO₄ (1.02g, 5mmol) in 15mL of THF were heated to 40-50 °C for 30 min. A solution of (4-formylphenyl) boric acid (90mg, 0.6 mmol) in THF (5mL) was transferred to the mixture through a syringe. The mixture was then heated up to 80 °C and stirred for 12 h. After cooling to room temperature, the resulting solution was extracted with CH₂Cl₂ (3×10mL). The organic portion was combined and washed with brine and water and dried with anhydrous MgSO₄. The solvent was removed by evaporation, the residue was purified by column chromatography using silica gel (PE/CH₂Cl₂=5/1, v/v) to give a brown solid (191mg, 57%).^[3] ¹H NMR (CDCl₃,400MHz) δ (ppm): 10.08 (s, 1H), 9.24 (d, *J*=8.4Hz, 1H), 9.07 (d, *J*=8.8Hz, 1H), 7.98 (d, *J*=8.0Hz, 2H), 7.78 (d, *J*=7.6Hz, 2H), 7.31(d, *J*=8.4Hz, 1H), 7.17(d, *J*=8.4Hz, 1H), 7.00(s, 1H), 6.92(s, 1H), 3.64-3.75 (m, 4H), 1.86 (m, 2H), 1.32-1.43 (m, 16H), 0.97-0.93 (m,12H).

Synthesis of 4-(6'-(bis(4-(tert-butyl)phenyl)methyl)-1,1'-bis(2-ethylhexyl)-2,2'-dioxo-[3,3'-biindolinylidene]-6-yl)benzaldehyde (4).

Under nitrogen, compound 3 (335mg, 0.5mmol), Pd(OAc)₂ (11mg, 0.05mmol), P^tBu₃ (10mg, 0.05mmol), bis(4-(tert-butyl)phenyl)amine (190mg, 0.65mmol), ^tBuONa (240mg, 2.5mmol), and toluene (20mL) were dissolved in a 100mL three-neck flask. The mixture was stirred for half an hour at room temperature, then heated up to 90 °C and stirred for 16 h. After cooling to room temperature, the mixture was extracted with dichloromethane and the organic phase was filtered through a silica-gel pad. The combined organic layers were washed with brine and water and dried with anhydrous MgSO₄. Then the solvent was removed by evaporation and the residue was purified by column chromatography using silica gel (PE/CH₂Cl₂=2/1, v/v) to give a purple solid (256mg, 59%).^[4] ¹H NMR (CDCl₃,400MHz) δ (ppm): 10.07 (s,1H), 9.13 (d, *J*=8.4Hz, 1H), 8.96 (d, *J*=8.8Hz, 1H), 7.97 (d, *J*=8.4Hz, 2H), 7.79 (d, *J*=8.0Hz, 2H), 7.33 (d, *J*=8.8Hz, 4H), 7.30 (s, 1H), 7.14 (m, 4H), 7.00 (s, 1H), 6.52 (d, 1H), 6.27 (s, 1H), 3.74-3.71 (m, 4H), 1.89-1.75 (m, 2H), 1.33-1.21 (m, 16H), 0.93-0.75 (m,12H).

Synthesis of 4-(6'-(4-(bis(4-(tert-butyl)phenyl)methyl)phenyl)-1,1'-bis(2-ethylhexyl)-2,2'-dioxo-[3,3'-biindolinylidene]-6-yl)benzaldehyde (5).

Compound 3 (335mg, 0.5mmol), Pd(dba)₃ (15mg), p(o-tyl)₃ (10mg), and K₃PO₄ (1.02g, 5mmol) in 15mL of THF were heated to 40-50 °C for 30 min. A solution of 4-(bis (4-(tert-butyl)phenyl)methyl)phenyl boric acid (600mg, 1.5mmol) in THF (10mL) was transferred to the mixture through a syringe. The mixture was then heated to 80 °C and stirred for 12h. After cooling to room temperature, the resulting solution was extracted with CH₂Cl₂ (3×10mL). The organic portion was combined and washed with brine and water and dried with anhydrous MgSO₄. The solvent was removed by evaporation, the residue was purified by column chromatography using silica gel (PE/CH₂Cl₂=2/1, v/v) to give a purple solid (288mg, 61%). ¹H NMR (CDCl₃, 400MHz) δ (ppm): 10.07 (s, 1H), 9.26 (d, *J*=8.4Hz, 1H), 9.20 (d, *J*=8.4Hz, 1H), 7.99 (d, *J*=8.4Hz, 2H), 7.79 (d, *J*=8.0Hz, 2H), 7.51 (d, *J*=8.8Hz, 2H), 7.33-7.26 (m, 6H), 7.13-7.10 (m, 6H), 7.02 (m, 2H), 6.98 (s, 1H), 6.97 (s, 1H), 3.77-3.73 (m, 4H), 1.95-1.91 (m, 2H), 1.36-1.31 (m, 16H), 0.96-0.88 (m, 12H).

Synthesis of 3-(4-((*E*)-6'-(bis(4-(tert-butyl)phenyl)methyl)-1,1'-bis(2-ethylhexyl)-2,2'-dioxo-[3,3'-biindolinylidene]-6-yl)phenyl)-2-cyanoacrylic acid (ICD-3).

Compound 4 (87mg, 0.1mmol), 2-cyanoacetic acid (85mg, 1mmol), and ammonium acetate (120mg) in 8mL of acetic acid were heated to 120 °C for 12 h. After cooling, the mixture was poured into water. The precipitate was filtered and washed with water. The residue was purified by column chromatography using silica gel (CH₂Cl₂/ethanol=10/1, v/v) to give a dark purple solid (73mg, 78%). ¹H NMR (CDCl₃, 400MHz) δ (ppm): 12.03 (s, 1H), 9.06 (d, *J*=8.4Hz, 1H), 8.94 (d, *J*=12.8Hz, 1H), 8.37 (s, 1H), 8.16 (d, *J*=8.0Hz, 2H), 8.00 (d, *J*=8.4Hz, 2H), 7.52-7.38 (m, 5H), 7.17-7.05 (m, 5H), 6.32 (d, 1H), 6.16 (s, 1H), 3.70-3.64 (m, 4H), 2.15-2.07 (m, 2H), 1.64-1.13 (m, 16H), 0.92-0.78 (m, 12H). MS (MALDI-TOF): *m/z* found: 937.6 (M⁺).

Synthesis of 3-(4-((*E*)-6'-(4-(bis(4-(tert-butyl)phenyl)methyl)phenyl)-1,1'-bis(2-ethylhexyl)-2,2'-dioxo-[3,3'-biindolinylidene]-6-yl)phenyl)-2-cyanoacrylic acid (ICD-4).

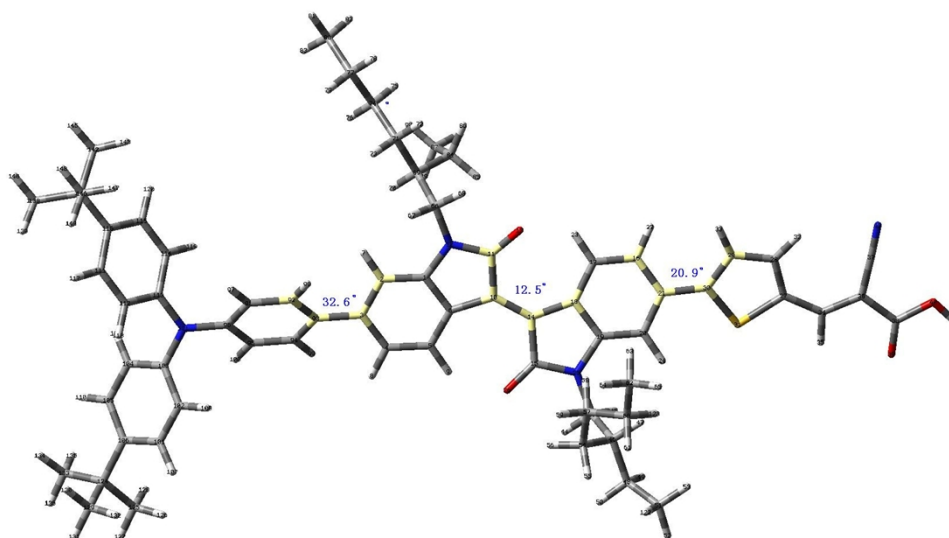
Compound 5 (94mg, 0.1mmol), 2-cyanoacetic acid (85mg, 1mmol), and ammonium acetate (120mg) in 8mL acetic acid were heated to 120 °C for 12 h. After cooling, the mixture was poured into water. The precipitate was filtered and washed with water. The residue was purified by column chromatography using silica gel (CH₂Cl₂/ethanol=10/1, v/v) to give a dark purple solid (77mg, 76%). ¹H NMR (CDCl₃, 400MHz) δ (ppm): 9.17 (s, 2H), 8.32 (s, 1H), 7.87 (s, 2H), 7.61-7.55 (m, 2H), 7.41 (s, 2H), 7.16 (t, 4H), 7.02-6.96 (m, 6H), 6.94-6.85 (m, 6H), 3.75-3.65 (m, 4H), 1.89-1.82 (m, 2H), 1.30-1.26 (m, 16H), 0.86-0.69 (m, 12H). MS (MALDI-TOF): *m/z* found: 1013.5 (M⁺).

Table 1. Photoelectrochemical properties of **ICD-3** and **ICD-4** and their solar cell performances.

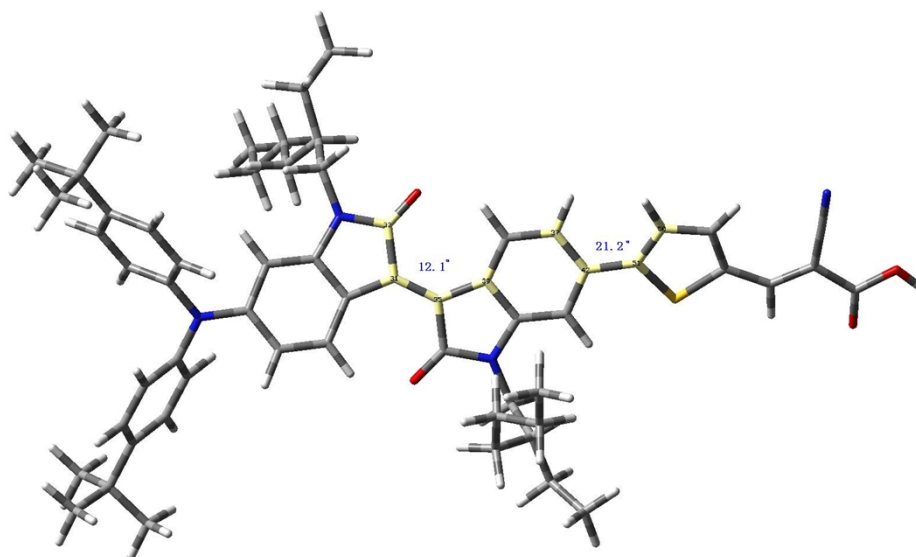
Dye	λ_{max}^a (nm)	ϵ (L mol ⁻¹ cm ⁻¹)	E_{0-0}^b (eV)	$E_{+/0}^c$ (V)	$E_{+/s}^e$ (V)	J_{sc} (mA cm ⁻²)	V_{oc} (mV)	FF	η^d (%)
ICD-3	610	22400	1.61	0.93	-0.68	17.80	624	0.68	7.55
ICD-4	565	20400	1.70	0.95	-0.75	14.67	638	0.68	6.36

^a Absorption in CH₂Cl₂ solutions (1×10⁻⁵ M) at rt.; ^b E_{0-0} values were estimated from the X-intercepts from the tangent of the absorption edges. ^c 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 The estimation was determined by subtracting E_{0-0} from $E_{s+/0}$; ^d 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.

Fig. 2: The geometry optimized ground state molecular structures of ICD-3 and ICD-4 with the corresponding dihedral angles between each plain.



ICD-4



ICD-3

DSC fabrication and characterization:

DSC fabrication: The nanocrystalline TiO₂ pastes (particle size, 20 nm) were prepared using a previously reported procedure. 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 μm thick nanocrystalline TiO₂ layer and 6μm 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-3** or **ICD-4** and 20 mM 3α,7α-dihydroxy-5β-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 published procedures [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 thermo-plastic Surlyn. The electrolyte contains 0.68 M dimethyl imidazolium 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 $IPCE(\lambda) = hcJ_{sc}/e\phi\lambda$, 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).

References:

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