

Supporting Information

**A New Type of Donor-Acceptor Dye Bridged by the Bidentate
Moieties; Metal Ion Complexation Enhancing DSSCs Performance**

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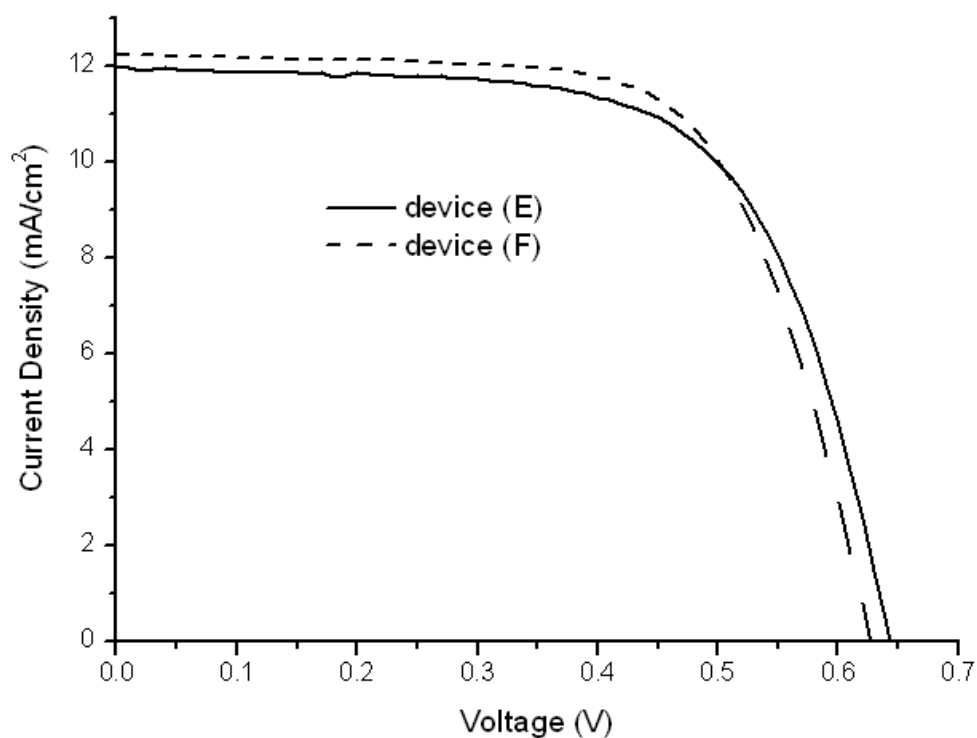


Figure S1. The photocurrent-voltage curves of **Alko1** dye employing various metal ions complexation, measured under AM 1.5G simulated sunlight at a light intensity of 100 mW/cm². See text for the description of devices (E) and (F).

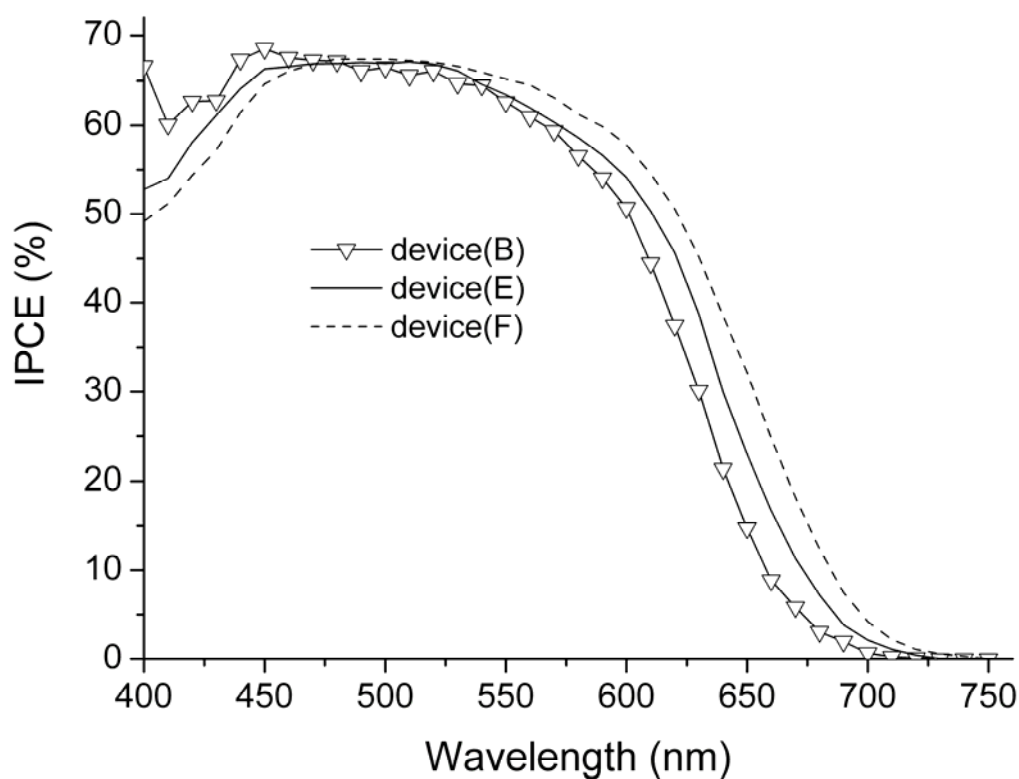


Figure S2. The incident photon-to-current conversion efficiencies (IPCEs) of **Alko1** dye employing various metal ions complexation, measured under AM 1.5G simulated sunlight at a light intensity of 100 mW/cm^2 . See text for the description of devices (B), (E) and (F).

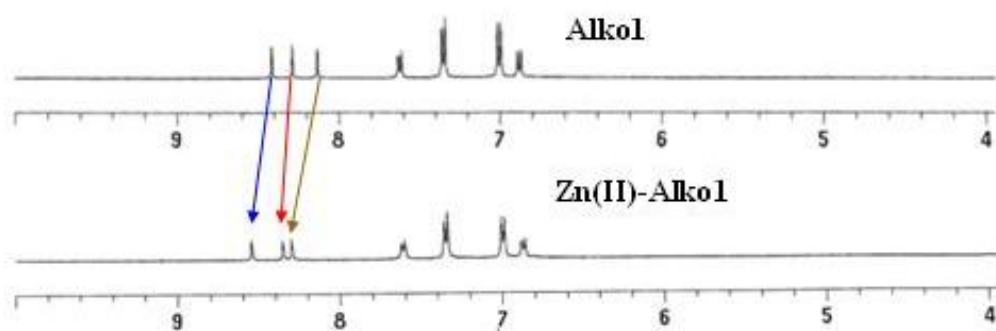


Figure S3. ^1H NMR of **Alko1** and **Zn(II)-Alko1** measured under d-DMSO (400MHz).

General procedures

All reactions were performed under nitrogen atmosphere and solvents were distilled from appropriate drying agents prior to use. All reactions were monitored using pre-coated TLC plates (0.20 mm with fluorescent indicator UV₂₅₄). Mass spectra were obtained on a JEOL SX-102A instrument operating in electron impact (EI) or fast atom bombardment (FAB) mode. ¹H and ¹³C NMR spectra were recorded on a Varian Mercury-400 or an INOVA-500 instrument.

Synthesis of 5'-bromo-2,2'-bithiazole-5-carbaldehyde (**1c**).

To a solution of **1b** (0.3 g, 0.92 mmol) in dry THF (30 mL) was added a 2.5 M solution of *n*-BuLi in hexane (0.4 mL, 1.01 mmol) dropwise at -78 °C. After this mixture was stirred at this temperature for 1 h, 4-formylmorpholine (0.10 mL, 1.01 mmol) was introduced. The resulting solution was stirred for 30 min at -78 °C and then allowed to warm up to room temperature. The reaction was quenched by HCl aqueous solution and adjusted to pH=3. The organic layer was dried (Na₂SO₄) and concentrated in vacuum. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 6/1) to obtain a pale-yellow solid (0.14 g, 56%). Spectral data of (**1**): MS (EI): *m/z* 275.88 (M)⁺. ¹H NMR (400 MHz, CDCl₃, 298 K): δ 10.08 (s, 1H), 8.42 (s, 1H), 7.86 (s, 1H). ¹³C NMR (400 MHz, CDCl₃, 298 K): δ 181.94, 166.94, 161.23, 151.59, 146.03, 140.18, 114.27.

Synthesis of 4-tert-butyl-N-(4-tert-butylphenyl)-N-phenylaniline (**2a**).

A mixture of bis(4-tert-butylphenyl)amine (10 g, 35.53 mmol), iodo-benzene (3.96 ml, 35.53 mmol), ^tBuOK (5.98 g, 53.29 mmol), P(*n*-Bu)₃ (0.72 g, 3.55 mmol) and CuI (0.34 g, 1.78 mmol) was heated under N₂ in toluene (120 mL) for 16 h. After cooling to room temperature, the crude product was extracted with CH₂Cl₂ and water. The combined organic phases were dried (MgSO₄) and the solvent was removed. It was then purified by silica gel column chromatography using hexane as the eluent to obtain pale yellow oil. The crude yellow oily product was purified by recrystallization from methanol to afford the white powder (11.15 g, 84 %). Spectral data of (**2a**): MS (EI): *m/z* 357.5 (M)⁺. ¹H

NMR (400 MHz, CDCl₃, 298 K): δ 7.26~7.19 (m, 6H), 7.14 (d, $J_{\text{H-H}} = 7.8$ Hz, 2H), 7.09 (d, $J_{\text{H-H}} = 8.4$ Hz, 4H), 7.01 (t, $J_{\text{H-H}} = 6.8$ Hz, 1H), 1.32 (s, 1H). ¹³C NMR (400 MHz, CDCl₃, 298 K): δ 148.13, 145.28, 145.03, 129.02, 125.93, 123.68, 123.28, 121.77, 34.29, 31.44.

Synthesis of 4-bromo-N,N-bis(4-tert-butylphenyl)aniline(**2b**).

To a solution of **2a** (5.0 g, 13.38 mmol) in chloroform (100 ml) was stirred under N₂ and cooled to 0°C. *N*-bromosuccinimide (2.62 g, 14.72 mmol) was added in one portion. When the color of the reaction mixture turned to green, remove the ice bath. After stirring overnight at room temperature, the reaction mixture was poured into water. The organic phase was separated and dried over anhydrous MgSO₄. After the solvent was evaporated, the crude greenish oily product was purified by recrystallization from methanol to afford white powder (5.37 g, 92 %). Spectral data of (**2b**): MS (EI): m/z 435.16 (M)⁺. ¹H NMR (400 MHz, CDCl₃, 298 K): δ 7.29~7.24 (m, 6H), 7.01 (d, $J_{\text{H-H}} = 6.4$ Hz, 4H), 6.92 (d, $J_{\text{H-H}} = 8.8$ Hz, 2H). 1.34(s, 18H). ¹³C NMR (400 MHz, CDCl₃, 298 K): δ 147.45, 146.16, 144.79, 132.06, 126.31, 126.17, 124.46, 124.21, 34.69, 31.84.

Synthesis of 4-tert-butyl-N-(4-tert-butylphenyl)-N-(4-(tributylstannyl)phenyl)aniline (**2c**).

To a solution of **2b** (0.5 g, 1.93 mmol) in dry THF (50 mL) was added a 2.5 M solution of *n*-BuLi in hexane (1.2 mL, 3 mmol) dropwise at -78 °C. After this mixture was stirred at this temperature for 1 h, tri-*n*-butyltin chloride (0.19 mL, 2.4 mmol) was introduced. The resulting solution was stirred for 30 min at -78 °C and then allowed to warm up to room temperature. The reaction was quenched by sat. NH₄Cl (30 mL). The residue was extracted with Et₂O (30mL). The organic layer was dried (MgSO₄) and concentrated in vacuum. The purity of **2c** (ca. 80%) by using ¹H NMR analysis and which used without any purification. Spectral data of (**2c**): ¹H NMR (400 MHz, CDCl₃, 298 K): δ 7.21 (d, $J_{\text{H-H}} = 7.4$ Hz, 2H), 6.51~6.63 (m, 6H). 1.64~1.52(m, 12H), 1.32~1.26 (m, 24H), 0.88(t, $J_{\text{H-H}} = 8.8$ Hz, 9H).

Synthesis of 4'-(4-(bis(4-tert-butylphenyl)amino)phenyl)-2,2'-bithiazole-5-carbaldehyde (**3**).

A mixture of **1c** (0.1 g, 0.18mmol), stannyl compounds **2c** (0.12 g, 0.18 mmol) and Pd(PPh₃)₄ (0.01 g, 0.009 mmol) was heated under N₂ in toluene (10 mL) for 16 h. Upon cooling to r.t., sat.NH₄Cl (30 mL) was added and the organic phase separated. The aqueous phase was extracted with CH₂Cl₂. The combined organic phases were dried (Na₂SO₄) and the solvent was removed. It was then purified by silica gel column chromatography using a 1:7 mixture of ethylacetate and hexane as the eluent to obtain deep red solid (0.15g, 72%). Spectral data of (**3**): MS (EI): m/z 551.21 (M)⁺. ¹H NMR (400 MHz, CDCl₃, 298 K): δ 10.06(s, 1H), 8.42(s, 1H), 8.02(s, 1H), 7.44(d, J_{H-H} = 8.4 Hz, 2H), 7.30(d, J_{H-H} = 8.4 Hz, 2H), 7.08~7.03(m, 6H). 1.34(s,18H). ¹³C NMR (400 MHz, CDCl₃, 298 K): δ 181.89, 168.30, 156.90, 151.88, 149.52, 146.98, 144.78, 144.11, 139.62, 139.16, 127.67, 126.31, 124.91, 122.30, 121.45, 34.38, 31.40.

Synthesis of (E)-3-(4'-(4-(bis(4-tert-butylphenyl)amino)phenyl)-2,2'-bithiazol-5-yl)-2- cyanoacrylic acid (**Alko1**).

Compound **3** (80 mg, 0.14 mmol) was mixed with cyanoacetic acid (23.8 mg, 0.28 mmol) and piperidine (5 drops) in mixed solvent (CH₃CN: CHCl₃=20mL:20mL) and the solution was refluxed for 6h. After cooling to RT, the crude product was extracted with CH₂Cl₂ and water. The combined organic phases was dried (Na₂SO₄) and the solvent was removed. It was then purified by silica gel column chromatography using a 3:1 mixture of ethyl acetate and methanol as the eluent to obtain red-brown solid (53.2 mg, 62%). Spectral data of (**Alko1**): MS (EI): m/z 618.21 (M)⁺. ¹H NMR (400 MHz, DMSO-d₆, 298 K): δ 8.42 (s, 1H), 8.29 (s, 1H), 8.13 (s, 1H), 7.62 (d, J_{H-H} = 8.8 Hz, 2H), 7.35 (d, J_{H-H} = 8.4 Hz, 4H), 7.02 (d, J_{H-H} = 8.4 Hz, 4H), 6.88 (d, J_{H-H} = 8.4 Hz, 2H), 1.27 (s, 18H). ¹³C NMR (400 MHz, DMSO-d₆, 298 K): δ163.16, 162.32, 157.41, 150.94, 148.93, 146.83, 144.17, 142.79, 139.98, 137.49, 134.43, 128.23, 126.85, 125.10, 122.62, 121.24, 119.30, 115.15, 39.29, 34.49.

Fabrication of DSSC and photovoltaic measurements

The Pt counter electrode was prepared by spin-coating a 50mM H₂PtCl₆ in

isopropyl alcohol on FTO glass, followed by sintering at 385 °C for 15–30 min. Transparent TiO₂ paste was prepared using published procedures.¹ The transparent TiO₂ thin film with thickness of 12 μm was first deposited on a transparent conducting oxide (F-doped SnO₂, FTO). This film was dried at 150 °C for 15 min and then a 4 μm thick layer of 400 nm TiO₂ particles (Ti-Nanoxide 300 paste from Solaronix) was deposited again by a doctor-blade method to form a square with dimension of 0.4 × 0.4 cm². Afterwards, the double-layered films were sintered at 500 °C for 30 min. After sintering, the TiO₂ films were treated with 40mM of TiCl₄ solution, rinsed with water and ethanol, and sintered at 500 °C for 30 min. After cooling to 80 °C, the TiO₂ electrode was immersed into a solution containing 0.3mM of **Alko1** dyes, 1 mM of deoxycholic acid (DCA) in mixed THF and tert-butanol solution (volume ratio: 1:1) overnight. After being rinsed with EtOH, the dye-coated TiO₂ electrode was incorporated into a sandwich cell structure with a Pt-coated FTO as counter electrode, and a film (Surlyn 1702, 25 μm) as a spacer between the electrodes. The electrolyte solution was then injected into the cell through a drilled hole in the back of the counter electrode. Lastly, the hole was sealed using a hot-melt ionomer film and a cover glass. Light-to-electricity conversion efficiency values were measured using a modified light source, 450 W Xe lamp (Oriel, 6266), an Oriel 81088 Air Mass 1.5 Global Filter and a digital source meter purchased from Keithley Instruments Inc. The incident light intensity was calibrated using a standard solar cell composed of a crystalline silicon solar cell and an IR cutoff filter (Schott, KG-5), giving the photoresponse range of amorphous silicon solar cell.

Reference

1. P. Wang, S. M. Zakeeruddin, P. Comte,; R. Charvet, R. H. Baker and M. Grätzel, *J. Phys. Chem. B*, 2003, **107**, 14336.