

Supporting information

Picolinic Acid as An Efficient Tridentate Anchoring Group Adsorbing at Lewis acid sites and Brønsted acid sites of TiO₂ Surface in Dye-Sensitized Solar Cells

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General information

All solvents were treated by standard methods before use and all chemicals were purchased from commercial suppliers and used without further purification unless indicated otherwise. *N, N*-Dimethylformamide (DMF) and tetrahydrofuran (THF) were dried and distilled from CaH₂.

The ¹H NMR and ¹³C NMR spectra were recorded on a Bruker DRX (500 MHz) NMR spectrometer with tetramethylsilane (TMS) as the internal standard. The mass spectra were measured in ESI Mass Spectrometer (LCQ Fleet).

Experimental

Fabrication of DSSCs

The working electrode (active area 0.16 cm²) was prepared by screen printing the TiO₂ paste on fluorine-doped tin oxide (FTO) glass plates (15 Ω / square). For preparation of a DSSC, FTO glass plates were cleaned in a detergent solution using an ultrasonic bath for 30 min for two times and then rinsed with water and ethanol. Then, the plates were immersed into 40 mM TiCl₄ (aqueous) at 70°C for 30 min and washed with water and ethanol. The TiO₂ paste consisted of 14 μm thick film (particle size, 20 nm, pore size 32 nm). The TiO₂ films were performed 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. Then the films were treated again with TiCl₄ at 70°C for 30 min and sintered at 500°C for 30 min. Then the working electrode were immersed into 0.2 mM dye (JA1 and JA2) solution in a mixture of THF and ethanol (THF/ethanol = 1/1) for 18 h at room temperature. For cosensitization, the porphyrin-sensitized films were washed with ethanol and dried, then immersed into 0.3 mM cosensitizer (TTR2) solution in DCM for 1.5 h at room temperature. The Pt counter electrodes were prepared on spin-coating drops of H₂PtCl₆ solution onto FTO glass

and heating at 385 °C for 20 min. The working electrode and the Pt counter electrode were then sealed with a Surllyn film (25 μm) by heating the sandwich-type cell at 110 °C. The electrolyte was introduced through pre-drilled holes in the counter electrode and was driven into the cell via vacuum backfilling, and the hole was sealed with a Surllyn film and a thin glass (0.1 mm thickness) cover by heating. The electrolyte was composed of 0.6 M 1-butyl-3-methylimidazolium iodide (BMII), 30 mM I₂, 50 mM LiI, 0.5 M tert-butylpyridine and 0.1 M guanidiniumthiocyanate (GuNCS) in a solvent mixture of acetonitrile and valeronitrile (volume ratio, 85:15).^[S1]

Characterizations of DSSCs

The photocurrent-voltage (*I-V*) curves of the DSSCs were measured on a Keithley 2400 source meter under standard global AM 1.5G solar irradiation supplied by a xenon light source (Oriel). The incident photo-to-electron conversion efficiency (IPCE) spectra of the DSSCs were measured by a DC method. The light source was a 300 W xenon lamp (Oriel 6258) coupled with a flux controller to improve the stability of the irradiance. The single wavelength was selected by a monochromator (Cornerstone 260 Oriel74125). Light intensity was measured by a NREL traceable Si detector (Oriel 71030NS) and the short circuit currents of the DSSCs were measured by an optical power meter (Oriel 70310).

Theoretical calculations

Density function theory (DFT) calculations were performed at the DFT-B3LYP/LanL2DZ level with Gaussian 09 suite of programs.

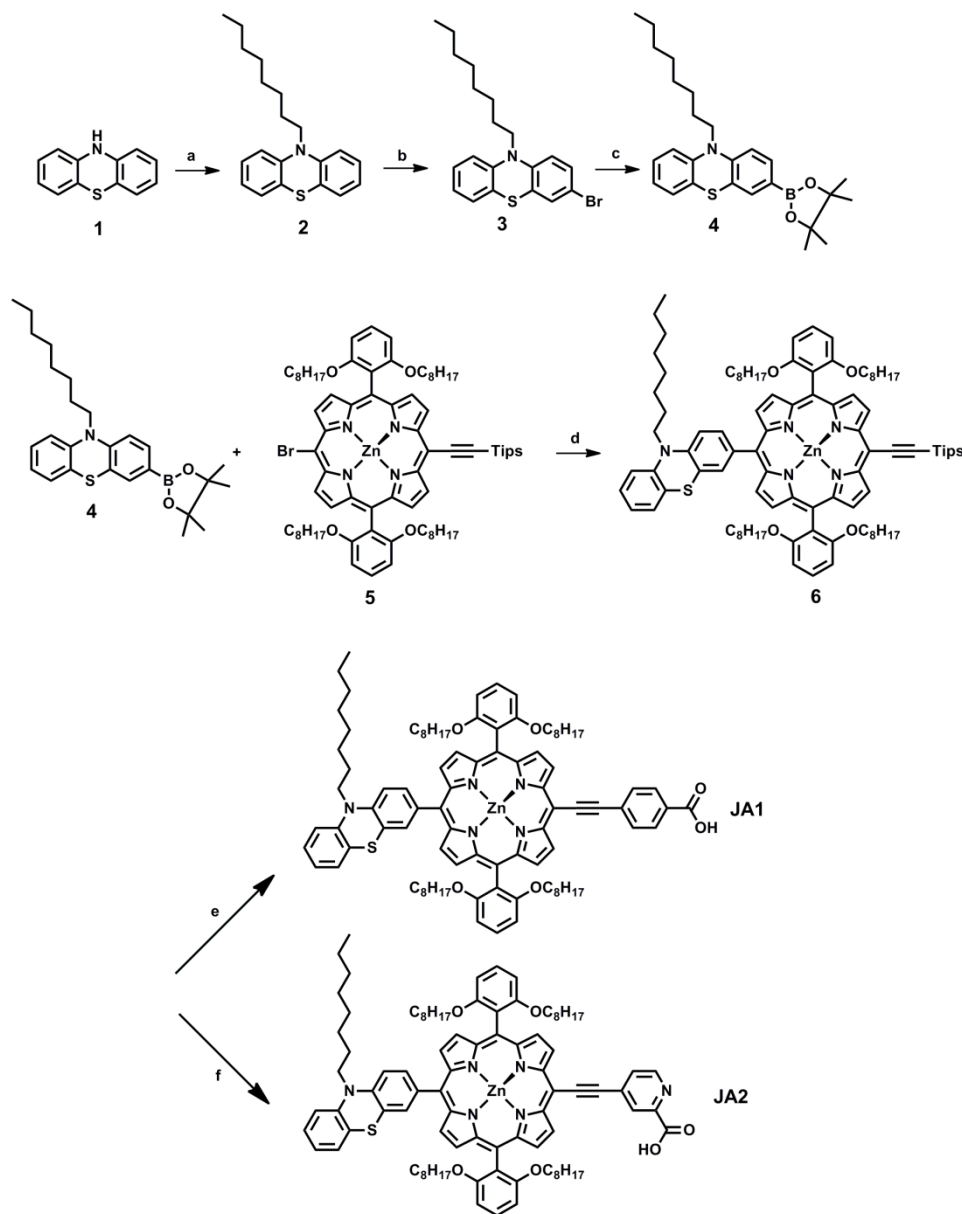
UV-Vis spectroscopy, Photoluminescence, FTIR spectra, Electrochemical properties and Measurement of dye adsorbed amounts

The UV-Vis absorption spectra were recorded on a Shimadzu UV-3600 spectrometer.

Fluorescence spectra were recorded on a Perkin Elmer LS55 spectrophotometer. FTIR spectra were recorded on a Vector22 spectrometer. The fluorescence lifetimes of the dyes were measured on a FLS920 spectrometer. Quasi-reversible oxidation and reduction waves were recorded on a Chenhua CHI660D model Electrochemical Workstation (Shanghai). Electrochemical Impedance Spectroscopy was studied using a Chenhua CHI660I model Electrochemical Workstation (Shanghai).

The dye adsorbed amounts on the TiO₂ films were measured by a Shimadzu UV-3600 spectrometer. The sensitized 4×4 mm electrodes were immersed into a 0.1 M NaOH solution in a mixed solvent (water/THF = 1/1), which resulted in desorption of each dye.

Synthesis of the dyes



Scheme S1 synthesis procedure of **JA1** and **JA2**. Reagents and conditions: a) 1-bromooctane, NaH, DMF, rt; b) NBS, DMF, rt; c) bis(pinacolato)diboron, Pd(dppf)Cl₂, KOAc, DMF, 80 °C; d) Pd(PPh₃)₄, K₂CO₃, H₂O, 1, 4-dioxane, 90 °C; e) i: TBAF, THF, rt; ii: 4-iodobenzoic acid, Pd₂(dba)₃, AsPh₃, TEA, THF, reflux; f) i: TBAF, THF, rt; ii: 4-bromopyridine-2-carboxylic acid, Pd₂(dba)₃, AsPh₃, TEA, THF, reflux.

Synthesis of compound 2

A 250 mL round bottom flask was charged with phenothiazine (5.00 g, 25.09 mmol), NaH (1.20 g, 30.11 mmol, 60%) and 100 mL of DMF. The mixture was

stirred for 30 min and 1-bromooctane (5.81 g, 30.11 mmol) was then added. The mixture was stirred overnight at room temperature. The reaction mixture was quenched with ice water and extracted with ethylacetate. The combined organic fractions were washed with brine and dried over MgSO₄. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (PE) to give the compound **2** as a viscous liquid (6.0 g, 77%). ¹HNMR (CDCl₃, 500Hz) δ_H 7.16-7.49 (m, 4H), 6.88-6.94 (m, 4H), 3.87 (s, 2H), 1.80-1.86 (m, 2H), 1.43-1.47 (m, 2H), 1.29-1.33 (m, 8H), 0.92 (t, *J* = 7.0 Hz, 3H). MS (ESI): [M + H]⁺ Calcd for C₂₀H₂₅NS, 311.48; found, 312.33.

Synthesis of compound 3

A mixture of Compound **2** (6.00 g, 19.26 mmol) in DMF (50 mL), then the NBS (3.60 g, 20.23 mmol) in a solution of DMF (30 mL) was added dropwise for 30 min. The reaction mixture was stirred overnight at room temperature. The reaction mixture was quenched with ice water and extracted with ethylacetate. The combined organic fractions were washed with brine and dried over MgSO₄. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (PE) to give the compound **3** as a viscous liquid (5.5 g, 76%). ¹HNMR (CDCl₃, 500Hz) δ_H 7.25-7.29 (m, 2H), 7.13-7.20 (m, 2H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.69-6.72 (m, 1H), 3.83 (t, *J* = 6.5 Hz, 2H), 1.77-1.83 (m, 2H), 1.41-1.46 (m, 2H), 1.29-1.32 (m, 8H), 0.92 (t, *J* = 6.5 Hz, 3H). MS (ESI): [M + H]⁺ Calcd for C₂₀H₂₄BrNS, 390.38; found, 392.17.

Synthesis of compound 4

A mixture of compound **3** (5.00 g, 12.81 mmol), bis(pinacolato)diboron (4.88 g, 19.21 mmol) and KOAc (2.51 g, 25.62 mmol) in DMF (60 mL) was added Pd(dppf)Cl₂ (0.40 g, 0.547 mmol) under dinitrogen. The mixture was heated under 80 °C for overnight. The reaction mixture was cooled to room temperature and H₂O (150 mL) was added, the mixture was extracted by EtOAc (3×50 mL). The combined

organic layers were washed with brine, dried over MgSO_4 , and evaporated in vacuo. The residue was purified by silica gel column chromatography (PE) to give the compound **4** as a yellow liquid (3.50 g, 63%). ^1H NMR (CDCl_3 , 500Hz) δ_{H} 7.62-7.65 (m, 2H), 7.14-7.18 (m, 2H), 6.92 (t, $J = 7.5$ Hz, 1H), 6.87 (d, $J = 8.0$ Hz, 2H), 3.88 (t, $J = 7.0$ Hz, 2H), 1.80-1.86 (m, 2H), 1.42-1.49 (m, 2H), 1.30-1.40 (m, 20H), 0.93 (t, $J = 6.5$ Hz, 3H). MS (ESI): $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{26}\text{H}_{36}\text{BrNO}_2\text{S}$, 437.45; found, 438.50.

Synthesis of compound **6**

Under an nitrogen, compound **5** (1.50 g, 1.16 mmol),^[S2] compound **4** (0.76 g, 1.73 mmol), K_2CO_3 (0.48 g, 3.47 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (0.22 g, 0.19 mmol) were dissolved in 1, 4-dioxane (50 mL) and H_2O (10 mL). The mixture was heated under 90°C for overnight. The reaction mixture was cooled to room temperature and extracted by CH_2Cl_2 (3×20 mL). The combined organic layers were washed with brine, dried over MgSO_4 , and evaporated in vacuo. The residue was purified by silica gel column chromatography (PE/ $\text{CH}_2\text{Cl}_2 = 4/1$) to give the compound **6** as a green solid (1.42 g, 80%). ^1H NMR (CDCl_3 , 500Hz) δ_{H} 9.80 (d, $J = 4.5$ Hz, 2H), 9.00 (d, $J = 4.5$ Hz, 2H), 8.93 (d, $J = 4.5$ Hz, 2H), 8.88 (d, $J = 4.5$ Hz, 2H), 7.99-8.02 (m, 2H), 7.73 (t, $J = 8.0$ Hz, 2H), 7.23-7.32 (m, 3H), 7.04-7.10 (m, 6H), 4.15 (s, 2H), 3.89 (t, $J = 6.0$ Hz, 8H), 2.11-2.13 (m, 2H), 1.64-1.68 (m, 2H), 1.33-1.53 (m, 29 H), 0.97-1.03 (m, 11H), 0.81-0.85 (m, 8H), 0.45-0.65 (m, 44H). ^{13}C NMR (CDCl_3 , 125 Hz) δ_{C} 160.0, 152.5, 151.0, 150.4, 149.6, 145.3, 144.6, 137.4, 133.5, 133.0, 132.1, 131.7, 130.9, 130.6, 129.7, 127.7, 127.3, 124.9, 122.5, 121.4, 115.5, 114.4, 113.2, 110.2, 105.4, 98.8, 68.7, 47.8, 31.8, 31.3, 29.4, 28.6, 27.2, 25.2, 22.7, 22.1, 19.1, 14.1, 13.8, 12.0. MS (ESI): $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{95}\text{H}_{127}\text{N}_5\text{O}_4\text{SSiZn}$, 1528.59; found, 1529.18.

Synthesis of dye **JA1**

To a solution of compound **6** (500 mg, 0.327 mmol) in anhydrous THF (20 mL) was added TBAF (0.6 mL, 1 M in THF). The solution was stirred at room temperature for 30 min under dinitrogen. The mixture was quenched with H_2O and then extracted

with CH₂Cl₂. The organic layer was dried over anhydrous MgSO₄ and the solvent was removed under reduced pressure. The residue and 4-iodobenzoic acid (324 mg, 1.31 mmol) were dissolved in a mixture of anhydrous THF (50 mL) and TEA (12 mL) under dinitrogen, then Pd₂(dba)₃ (90 mg, 0.098 mmol) and AsPh₃ (200 mg, 0.654 mmol) were added to the mixture. The solution was refluxed for 6 h. The solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (CH₂Cl₂/MeOH = 20/1), recrystallization from MeOH/Ether to give dye **JA1** (270 mg, 55%) as a green solid. ¹HNMR (CDCl₃, 500Hz) δ_H 9.70 (d, *J* = 4.4 Hz, 2H), 8.95 (d, *J* = 4.4 Hz, 2H), 8.85 (d, *J* = 4.4 Hz, 2H), 8.80 (d, *J* = 4.4 Hz, 2H), 8.20 (d, *J* = 8.4 Hz, 2H), 8.07(d, *J* = 8.0 Hz, 2H), 7.90-7.92 (m, 2H), 7.69 (t, *J* = 8.4 Hz, 2H), 7.21-7.28 (m, 2H), 7.15 (d, *J* = 8.0 Hz, 1H), 6.99-7.04 (m, 6H), 4.08 (t, *J* = 7.5 Hz, 2H), 3.83 (t, *J* = 8.0 Hz, 8H), 2.01-2.06 (m, 2H), 1.58-1.61 (m, 2H), 1.25-1.33 (m, 8H), 0.88-0.98 (m, 11H), 0.76-0.81 (m, 8H), 0.33-0.60 (m, 44H). ¹³CNMR (CDCl₃, 125 Hz) δ_C 160.0, 152.0, 151.1, 150.3, 149.6, 144.5, 132.3, 131.8, 131.2, 131.0, 130.3, 129.7, 127.3, 122.5, 121.1, 115.4, 115.0, 113.0, 105.2, 97.2, 68.6, 53.4, 47.8, 31.7, 31.3, 29.6, 29.3, 28.5, 27.1, 25.2, 22.6, 22.2, 14.1, 13.7. MS (ESI): [M - H]⁻ Calcd for C₉₃H₁₁₁N₅O₆SZn, 1492.35; found, 1490.92.

Synthesis of dye **JA2**

The preparation method was the same as that of dye **JA1**. ¹HNMR (CDCl₃, 500Hz) δ_H 9.69 (d, *J* = 4.4 Hz, 2H), 8.96 (d, *J* = 4.4 Hz, 2H), 8.83 (d, *J* = 4.4 Hz, 2H), 8.78 (d, *J* = 4.4 Hz, 2H), 7.89-7.95 (m, 2H), 7.70 (t, *J* = 8.4 Hz, 2H), 7.51-7.57 (m, 3H), 7.22-7.28 (m, 2H), 7.15 (d, *J* = 8.0 Hz, 1H), 6.98-7.04 (m, 6H), 4.08 (t, *J* = 7.5 Hz, 2H), 3.84 (t, *J* = 8.0 Hz, 8H), 2.01-2.06 (m, 2H), 1.56-1.61 (m, 2H), 1.25-1.34 (m, 8H), 0.88-0.97 (m, 11H), 0.72-0.77 (m, 8H), 0.39-0.56 (m, 44H). ¹³CNMR (CDCl₃, 125 Hz) δ_C 159.9, 152.5, 151.4, 150.4, 149.3, 145.2, 144.4, 137.0, 133.5, 132.9, 132.2, 131.9, 131.4, 130.9, 129.9, 129.4, 127.6, 127.3, 124.8, 122.5, 120.8, 115.5, 115.4, 113.3, 105.2, 68.6, 47.8, 31.7, 31.2, 30.7, 29.3, 28.6, 27.1, 25.1, 22.6, 22.1, 14.1, 13.7. MS (ESI): [M - H]⁻ Calcd for C₉₂H₁₁₀N₆O₆SZn, 1493.34; found, 1492.08.

Table S1. Percentage (%) molecular orbital contribution of the HOMO and LUMO of **JA1** and **JA2** at the DFT-B3LYP/LanL2DZ level

Dye		Phenothiazine moiety (%)	Porphyrin ring (%)	π -linker (%)	Anchoring group (%)
JA1	HOMO	13	74	12	1
	LUMO	4	66	24	6
JA2	HOMO	17	73	6	4
	LUMO	4	69	8	19

Table S2. Photovoltaic parameters of the cosensitized DSSCs obtained from different cosensitization time

Dye	Cosensitization time (h)	J_{sc} (mA cm ⁻²)	V_{oc} (mV)	FF (%)	η (%)
JA1+TTR2	1.0	13.46	717	62.6	6.04
JA1+TTR2	1.5	13.42	732	68.6	6.75
JA1+TTR2	2.0	10.27	755	66.4	5.15
JA2+TTR2	1.0	16.33	742	69.3	8.41
JA2+TTR2	1.5	17.75	755	67.0	8.98
JA2+TTR2	2.0	17.20	756	66.3	8.63

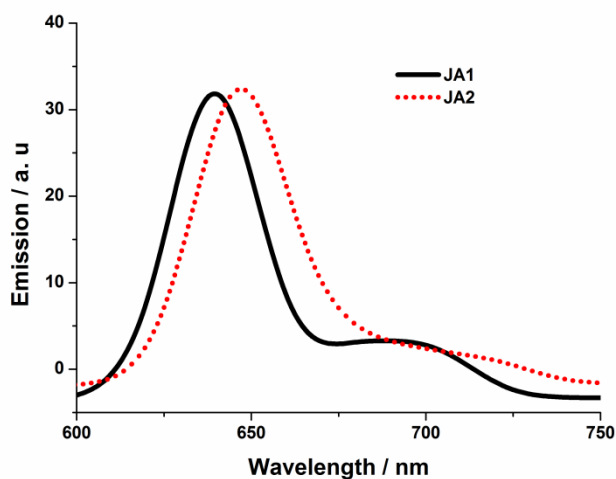


Fig. S1 Emission spectra of JA1 and JA2 in DCM.

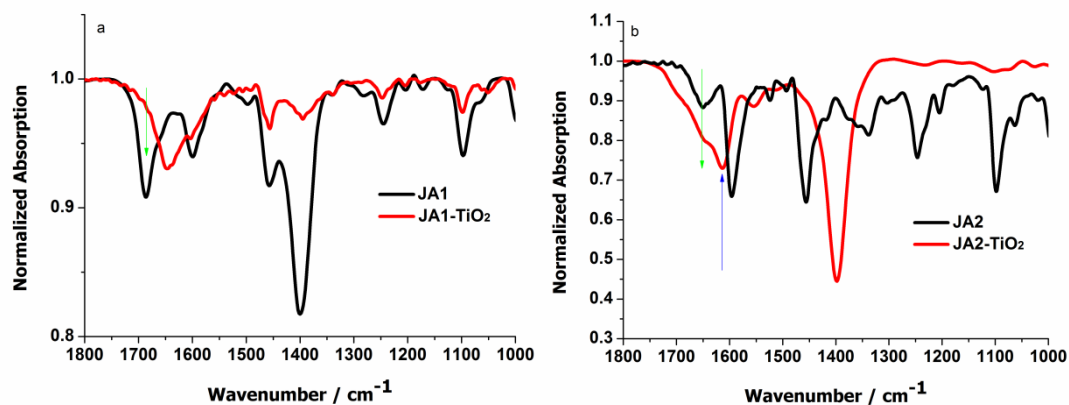


Fig. S2 FTIR spectra of dye powders (black line) and dyes adsorbed on TiO₂ films (red line), (a) JA1, (b) JA2.

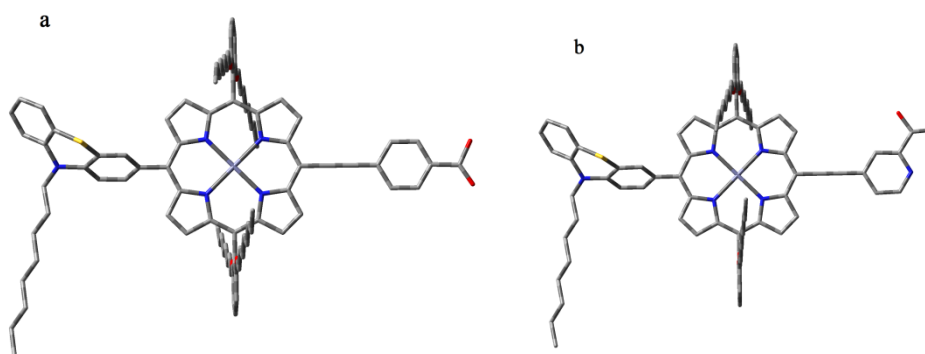


Fig. S3 The geometry optimized ground state molecular structures of (a) JA1 and (b) JA2.

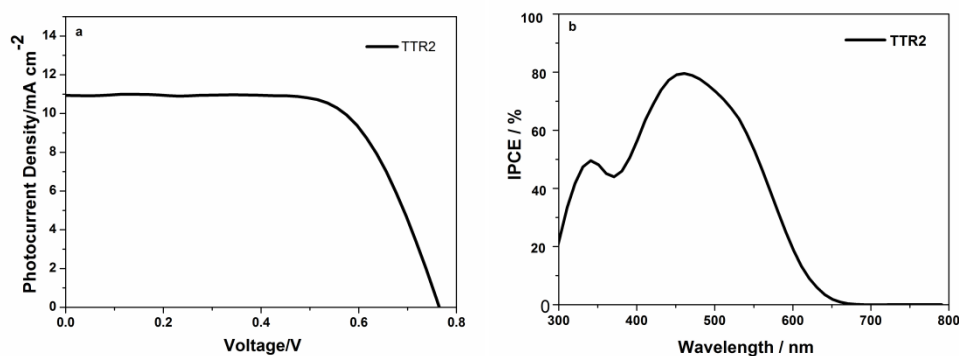


Fig. S4 (a) Current-voltage characteristics of DSSCs based on TTR2, (b) IPCE spectra of DSSCs

based on TTR2.

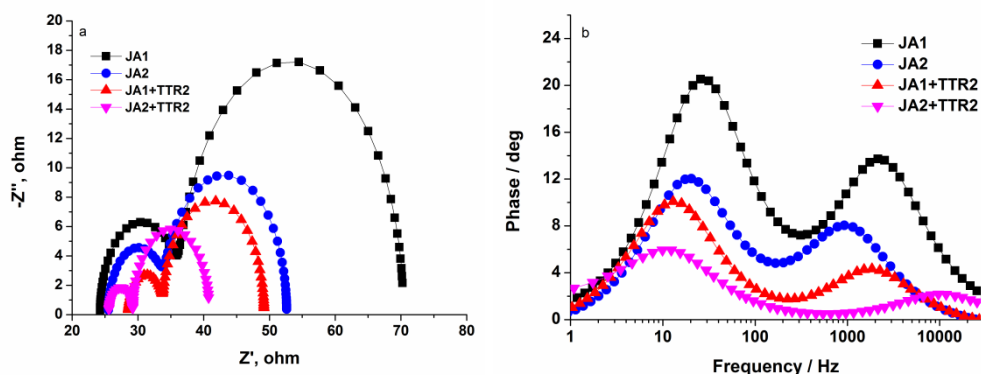


Fig. S5 The Nyquist plots (a) and Bode phase plots (b) of the DSSCs based on **JA1**, **JA2**, **JA1+TTR2** and **JA2+TTR2** observed under illumination.

References

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