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Performance improvement of dye-sensitizing solar cell by semi-rigid triarylamine-based donors

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ABSTRACT

Novel organic dyes (**IDB** and **ISB** dyes), which contain 5-phenyl-iminodibenzyl (**IDB**) and 5-phenyliminostilbene (**ISB**) as electron donors and a cyanoacrylic acid moiety as an electron acceptor and an anchoring group, connected with a thiophene as a π -conjugated system, have been synthesized and used as the sensitizers for dye-sensitized solar cells (DSSCs). The photophysical and electrochemical properties of the dyes were investigated by absorption spectrometry, cyclic voltammetry and density functional theory calculations. As demonstrated, the IDB and ISB unit exhibited stronger electron-donating ability and broader absorption spectra when coated onto TiO₂. The DSSC based on **ISB-2** consisting of **ISB** unit produced 5.83% of η ($J_{sc} = 13.14$ mA cm⁻², $V_{oc} = 0.64$ V, and ff = 0.68) under 100 mW cm⁻² simulated AM 1.5 G solar irradiation.

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1. Introduction

As a potential alternative to conventional inorganic photovoltaic devices, dye-sensitized solar cells (DSSCs), the so-called Grätzel cells [1], have attracted ever-increasing attention in the past decades. Several ruthenium-based sensitizers, such as N3, N719 and black dye [2-5], have achieved remarkable power conversion efficiency of 10-11% under AM 1.5 G irradiation. Recent attentions have focused on metal-free organic dyes as DSSC sensitizers because of their strong molar absorption coefficient, ease of structure modification, and low material cost [6]. Most metal-free dyes used for highly efficient DSSCs follow a donor-(π -spacer)-acceptor (D- π -A) architecture [7]. Generally, coumarin [8-10], indoline [11-14], triphenylamine [15-20], tetrahydroquinoline [21,22], and carbazole [23-27] have been widely employed as the electron donor unit with good performance. Carboxylic acid, cyanoacrylic acid [28-32], and rhodamine [33–35] moieties are often introduced into the $(D-\pi-A)$ system as electron acceptors to fulfill these requirements described above. The donors and the acceptors are linked by various π -conjugated spacers such as polyene, oligophenylenevinylene, oligothiophene and their derivatives. A series of indoline dyes have shown an impressive high efficiency of 9% for DSSCs [32,36].

Among various electron donors, triarylamine moieties have been investigated widely due to their prominent electron-donating ability, hole-transport properties, and prevention of direct charge recombination between TiO_2 and I_3 by the bulky aryl group covering TiO₂ surfaces [37]. Much work has been done to optimize the structure of triarylamine to improve the performance of the cells in our group [16,17,23,38]. However, one problem of triphenylamine that need to be addressed is the rotation of the phenyl rings, which causes serious energy loss. In our previous research, it was observed that as the increase of the triphenylamine units, the efficiency of the dyes decreases seriously. Hence, it can be speculated that the efficiency of the dye can be effectively increased if the phenyl rings were locked to prevent the rotation. Iminodibenzyl and iminostilbene with two phenyl rings connected by alkyl and ethylene chains have been widely used in materials of organic light-emitting diodes (OLEDs), which contribute to the achievement of high luminescence quantum yield [39,40], however, there are no report of utilizing iminodibenzyl and iminostilbene moiety as electron donor for the organic sensitizers of DSSCs. Here, we report the synthesis and characterization of four new organic dyes that contain 5-phenyl-iminodibenzyl (IDB) and 5-phenyl-iminostilbene (**ISB**) as the electron donors, thiophene as π -conjugation linkage, and cyanoacrylic acid as the electron acceptor and anchoring group, shown in Fig. 1. Thiophene and alkene as the π conjugated systems between the donor and the acceptor were



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Fig. 1. Molecular structures of IDB and ISB dyes.

extended to adjust the molecular HOMO and the LUMO energy levels of the dyes, hence red-shifting and broadening the absorption spectra with the number of π -conjugations introduced [41]. On the other hand, it was found that the bridge between the two rings can affect the performance of the sensitizer significantly. To understand the effect of the configuration to the performance of the sensitizer, TDDFT calculation was performed.

2. Experimental

2.1. General synthetic procedure and spectroscopic measurements

All chemicals were used as received from commercial sources without purification. Solvents for chemical synthesis such as dichloromethane (CH₂Cl₂), dimethylformamide (DMF) and tetrahydrofuran (THF) were purified by distillation. All chemical reactions were carried out under nitrogen atmosphere. ¹H NMR and ¹³C NMR spectra were recorded on Brucker AM-400 MHz instruments with tetramethylsilane as internal standard. HRMS were performed using a Waters LCT Premier XE spectrometer. The absorption spectra of the dyes in solution and adsorbed on TiO₂ films were measured with a Varian Cary 500 spectrophotometer.

2.2. Synthesis

2.2.1. 5-Phenyl-10,11-dihydro-5H-dibenzo[b,f]azepine (3)

A mixture of iminodibenzyl (**1**, 4 g, 20.5 mmol), iodobenzene (4.89 g, 23.9 mmol), copper powder (0.30 g, 4.6 mmol), potassium carbonate (6.93 g, 50.2 mmol), and [**1**8] crown-6 (0.33 g,1.25 mmol) was heated in 1,2-dichlorobenzene (100 ml) at 180 °C for 48 h under an atmosphere of argon. The inorganic components were removed by filtration after cooling. Then the solvent was distilled under reduced pressure, and the crude product was purified by column chromatography on silica (DCM/PE = 1/3, v/v) to give a white solid, **3** (3.57 g, 13.2 mmol, 64.4%). ¹H NMR (400 MHz, CDCl₃, δ): 7.45–7.38 (m, 2H), 7.27–7.18 (m, 6H), 7.09 (dd, *J* = 8.8, 7.3 Hz, 2H), 6.70 (t, *J* = 7.3 Hz, 1H), 6.58 (dd, *J* = 8.8, 0.9 Hz, 2H), 2.98 (s, 4H).

2.2.2. 5-Phenyl-5H-dibenzo[b,f]azepine (4)

The synthesis method resembled that of compound **3** and the crude compound was purified by column chromatography on silica (DCM/PE = 1/3, v/v) to yield a white solid, **4** (2.98 g, 11.1 mmol, 60.8%). ¹H NMR (400 MHz, CDCl₃, δ): 7.54–7.46 (m, 4H), 7.44 (d, *J* = 7.4 Hz, 2H), 7.39–7.29 (m, 2H), 7.04–6.95 (m, 2H), 6.82 (s, 2H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.26 (dd, *J* = 8.8, 0.9 Hz, 2H).

2.2.3. 5-(4-Bromophenyl)-10,11-dihydro-5H-dibenzo[b,f]azepine (5)

Compound **3** (1.94 g, 7.16 mmol) was dissolved in DMF (50 mL). While the solution was being stirred at 0 °C, *N*-bromosuccinimide (1.89 g, 10.74 mmol) was dissolved in DMF (50 mL) and added dropwise to it. And the reaction mixture was then warmed to room temperature. After being stirred for 12 h, the reaction mixture was poured into water and extracted with diethyl ether, and the combined extracts were washed with brine, dried over anhydrous magnesium sulfate, and filtered. The solvent was removed by rotary evaporation. The crude product was dissolved in hexane, and the undissolved solid was filtered. The filtrate was evaporated to dryness, and the resulting solid was washed with ethanol to yield a white solid, **5** (1.56 g, 4.47 mmol, 62.4%). ¹H NMR (400 MHz, DMSO, δ): 7.39–7.27 (m, 8H), 7.24 (d, *J* = 8.9, 2H), 6.37 (d, *J* = 8.9, 2H), 2.91 (s, 4H).

2.2.4. 5-(4-Bromophenyl)-5H-dibenzo[b,f]azepine (6)

The synthesis method resembled that of compound **5** and the resulting solid was washed with ethanol to yield a white solid, **6** (1.25 g, 3.58 mmol, 68.5%). ¹H NMR (400 MHz, CDCl₃, δ): 7.56–7.41 (m, 6H), 7.40–7.32 (m, 2H), 7.12–7.00 (m, 2H), 6.82 (s, 2H), 6.12 (d, J = 9.1 Hz, 2H).

2.2.5. 5-(4-(10,11-Dihydro-5H-dibenzo[b,f]azepin-5-yl)phenyl) thiophene-2-carbaldehyde (7)

A mixture of compound **3** (850 mg, 2.44 mmol), Pd(PPh₃)₄ (10 mg, 0.01 mmol), K₂CO₃ (270 mg, 1.96 mmol), THF (10 mL) and H₂O (5 mL) was heated to 45 °C under nitrogen atmosphere for 30 min. A stirred solution of 5-formyl-2-thiophene-boronic acid (756 mg, 4.90 mmol) in THF (5 mL) was added slowly, and the mixture was refluxed for further 12 h. After cooling to room temperature, the mixture was extracted with DCM. The organic portion was combined and removed by rotary evaporation. The residue was purified by column chromatography on silica (DCM/PE = 1/2, v/v) to give a yellow solid, **7** (434 mg, 1.14 mmol, 46.8%). ¹H NMR (400 MHz, DMSO, δ): 9.75 (s, 1H), 7.62 (d, *J* = 3.8 Hz, 1H), 7.48 (d, *J* = 8.9 Hz, 2H), 7.44–7.38 (m, 2H), 7.37–7.26 (m, 7H), 6.47 (d, *J* = 8.9 Hz, 2H), 2.94 (s, 4H).

2.2.6. 5-(4-(5H-Dibenzo[b,f]azepin-5-yl)phenyl)thiophene-2-carbaldehyde (**8**)

The synthesis method resembled that of compound **7** and the crude compound was purified by column chromatography on silica (DCM/PE = 1/2, v/v) to yield a yellow solid, **8** (352 mg, 0.93 mmol, 49.2%). ¹H NMR (400 MHz, DMSO, δ): 9.80 (s, 1H), 7.92 (d, *J* = 4.0 Hz, 1H), 7.64–7.54 (m, 6H), 7.51–7.43 (m, 4H), 7.42 (d, *J* = 4.0 Hz, 1H), 6.95 (s, 2H), 6.18 (d, *J* = 8.9 Hz, 2H).

2.2.7. 4-(10,11-Dihydro-5H-dibenzo[b,f]azepin-5-yl)benzaldehyde (9)

Phosphorus oxychloride (0.55 mL, 5.89 mmol) was added dropwise to DMF (10 mL) at 0 °C, and the mixture was stirred for 1 h at this temperature. Compound **3** (795 mg, 2.93 mmol) was added and the reaction mixture was heated to 80 °C for 8 h. The mixture was subsequently cooled to room temperature, poured into ice water, carefully neutralized with NaOH and extracted with DCM. The combined organic extract was dried over anhydrous MgSO₄ and filtered. Solvent was removed by rotary evaporation and the residue was purified by column chromatography on silica (DCM/PE = 1/1, v/v) to give a yellow solid, **9** (720 mg, 2.41 mmol, 82.1%). ¹H NMR (400 MHz, CDCl₃, δ): 9.73 (s, 1H), 7.61 (d, *J* = 9.0 Hz, 2H), 7.43–7.34 (m, 2H), 7.32–7.21 (m, 6H), 6.64 (d, *J* = 8.9 Hz, 2H), 3.00 (s, 4H).

2.2.8. 4-(5H-Dibenzo[b,f]azepin-5-yl)benzaldehyde (10)

The synthesis method resembled that of compound **9** and the crude compound was purified by column chromatography on silica (DCM/PE = 1/1, v/v) to yield a yellow solid, **10** (985 mg, 3.32 mmol, 78.4%). ¹H NMR (400 MHz, CDCl₃, δ): 9.69 (s, 1H), 7.55–7.46 (m, 8H), 7.43–7.37 (m, 2H), 6.86 (s, 2H), 6.35 (d, *J* = 8.9 Hz, 2H).

2.2.9. 5-(2-(4-(10,11-Dihydro-5H-dibenzo[b,f]azepin-5-yl)phenyl) vinyl)thiophen [41]

A mixture of compound **9** (650 mg, 2.17 mmol), t-BuOK (292 mg, 2.61 mmol) and dry THF (20 mL) was stirred at ambient temperature under nitrogen atmosphere for 1 h. 2-Thienylmethyl triphenylphosphonium chloride (1290 mg, 3.25 mmol) was dissolved in THF and added dropwise to the solution, and the reaction mixture was stirred for 1 h at ambient temperature, whereupon the mixture was heated to reflux for 24 h. The reaction mixture was allowed to cool to ambient temperature and a molar excess of water was added. The mixture was concentrated by rotary evaporator and the water phase was extracted with DCM. The organic phase was dried over MgSO₄, filtered through a plug of silica gel (DCM) and a crude intermediate was obtained (720 mg, 1.90 mmol). The crude product was used in the next step without further purification.

2.2.10. 5-(2-(4-(10,11-Dihydro-5H-dibenzo[b,f]azepin-5-yl)phenyl) vinyl)thiophen-2-carbaldehyde (11) [41]

5-(2-(4-(10,11-Dihydro-5H-dibenzo[b,f]azepin-5-yl)phenyl) vinyl)thiophen (720 mg, 1.90 mmol) was dissolved in dry THF (20 mL) and was cooled to $-78 \,^{\circ}$ C under nitrogen atmosphere. *n*-Butyl lithium (0.75 mL, 2.5 M hexane solution) was added dropwise over 10 min and the mixture was stirred at -78 °C for 1 h. The mixture was allowed to warm to 0 °C and stirred for 30 min. The mixture was once again cooled to $-78\,^\circ\text{C}$ and DMF (0.17 mL, 2.09 mmol) was added. The reaction mixture was allowed to warm to ambient temperature and stirred for 2 h. The reaction was guenched by the addition of aqueous HCl (10%, 100 mL) and extracted with DCM. The combined organic extract was dried over anhydrous MgSO₄ and filtered. Solvent was removed by rotary evaporation and the residue was purified by column chromatography on silica (DCM/ PE = 1/1, v/v) to give an orange solid, **11** (347 mg, 0.85 mmol, 45.0%). ¹H NMR (400 MHz, CDCl₃, δ): 9.77 (s, 1H), 7.52 (d, J = 3.9 Hz, 1H), 7.42 $(d, J = 7.6 \text{ Hz}, 2\text{H}), 7.29 - 7.18 \text{ (m, 6H)}, 7.11 \text{ (d, } J = 8.7 \text{ Hz}, 2\text{H}), 7.06 \text{ (d, } J = 7.6 \text{ Hz}, 2\text{H}), 7.06 \text{ (d, } J = 7.6 \text{ Hz}, 2\text{H}), 7.06 \text{ (d, } J = 7.6 \text{ Hz}, 2\text{H}), 7.06 \text{ (d, } J = 7.6 \text{ Hz}, 2\text{H}), 7.06 \text{ (d, } J = 7.6 \text{ Hz}, 2\text{H}), 7.06 \text{ (d, } J = 7.6 \text{ Hz}, 2\text{H}), 7.06 \text{ (d, } J = 7.6 \text{ Hz}, 2\text{H}), 7.06 \text{ (d, } J = 7.6 \text{ Hz}, 2\text{H}), 7.06 \text{ (d, } J = 7.6 \text{ Hz}, 2\text{H}), 7.06 \text{ (d, } J = 7.6 \text{ Hz}, 2\text{H}), 7.06 \text{ (d, } J = 7.6 \text{ Hz}, 2\text{Hz}), 7.06 \text{ (d, } J = 7.6 \text{ Hz}), 7.06 \text{ (d, } J = 7.6 \text{ Hz}), 7.06 \text{ (d, } J = 7.6 \text{ Hz}), 7.06 \text{ (d, } J = 7.6 \text{ Hz}), 7.06 \text{ (d, } J = 7.6 \text{ Hz}), 7.06 \text{ (d, } J = 7.6 \text{ Hz}), 7.06 \text{ (d, } J = 7.6 \text{ Hz}), 7.06 \text{ (d, } J = 7.6 \text{ Hz}), 7.06 \text{ (d, } J = 7.6 \text{ Hz}), 7.06 \text{$ J = 3.9 Hz, 1H), 6.63 (d, J = 12.0 Hz, 1H), 6.53 (d, J = 8.7 Hz, 2H), 6.45(d, J = 12.0 Hz, 1H), 3.00 (s, 4H).

2.2.11. 5-(2-(4-(5H-Dibenzo[bf]azepin-5-yl)phenyl)vinyl)thiophen-2-carbaldehyde (**12**)

The synthesis method resembled that of compound **11** and the crude compound was purified by column chromatography on silica (DCM/PE = 1/1, v/v) to yield a yellow solid, **12** (298 mg, 0.79 mmol,

47.8%). ¹H NMR (400 MHz, DMSO, δ): 9.82 (s, 1H), 7.89 (d, J = 3.0 Hz, 1H), 7.56 (dd, J = 15.9, 7.4 Hz, 6H), 7.46 (t, J = 6.9 Hz, 2H), 7.29 (d, J = 8.0 Hz, 3H), 7.16 (d, J = 16.1 Hz, 1H), 7.09 (d, J = 16.1 Hz, 1H), 6.94 (s, 2H), 6.14 (d, J = 8.2 Hz, 2H).

2.2.12. 3-(5-(4-(10,11-Dihydro-5H-dibenzo[b,f]azepin-5-yl)phenyl) thiophen-2-yl)-2-cyanoacrylic acid (**IDB-1**)

A mixture of compound **7** (120 mg, 0.31 mmol), 2-cyanoacetic acid (29 mg, 0.34 mmol), piperidine (0.5 mL) and THF (15 mL) was heated to reflux under nitrogen atmosphere for 6 h. Solvent was removed by rotary evaporation and the residue was purified by column chromatography on silica (DCM/ethanol = 20/1, v/v) to give a red solid, **IDB-1** (99 mg, 0.22 mmol, 71.3%). ¹H NMR (400 MHz, DMSO, δ): 7.96 (s, 1H), 7.58 (d, *J* = 3.8 Hz, 1H), 7.47 (d, *J* = 8.9 Hz, 2H), 7.44–7.40 (m, 2H), 7.39–7.27 (m, 7H), 6.50 (d, *J* = 8.9 Hz, 2H), 2.95 (s, 4H). ¹³C NMR (100 MHz, DMSO, δ): 149.40, 148.99, 142.46, 137.66, 136.39, 134.31, 131.13, 129.33, 127.60, 127.32, 126.96, 122.35, 122.10, 118.49, 112.43, 29.93. HRMS (ESI, *m/z*): [M + H]⁺ calcd for C₂₈H₂₁N₂O₂S, 449.1324; found, 449.1321.

2.2.13. 3-(5-(4-(5H-Dibenzo[b,f]azepin-5-yl)phenyl)thiophen-2-yl)-2-cyanoacrylic acid (**ISB-1**)

The synthesis method resembled that of compound **IDB-1** and the crude compound was purified by column chromatography on silica (DCM/ethanol = 20/1, v/v) to yield a red solid, **ISB-1** (102 mg, 0.23 mmol, 72.3%). ¹H NMR (400 MHz, DMSO, δ): 8.35 (s, 1H), 7.88 (d, *J* = 4.1 Hz, 1H), 7.68–7.53 (m, 6H), 7.52–7.39 (m, 5H), 6.96 (s, 2H), 6.21 (d, *J* = 8.9 Hz, 2H). ¹³C NMR (100 MHz, DMSO, δ): 163.95, 153.64, 149.61, 145.76, 141.55, 141.14, 135.55, 132.80, 130.51, 130.30, 130.16, 129.67, 127.69, 127.06, 122.74, 122.23, 117.06, 111.82. HRMS (ESI, *m/z*): $[M - H]^-$ calcd for C₂₈H₁₇N₂O₂S, 445.1011; found, 445.1006.

2.2.14. 3-(5-(4-(10,11-Dihydro-5H-dibenzo[b,f]azepin-5-yl)styryl) thiophene-2-yl)-2-cyanoacrylic acid (**IDB-2**)

The synthesis method resembled that of compound **IDB-1** and the crude compound was purified by column chromatography on silica (DCM/ethanol = 10/1, v/v) to yield a red solid, **IDB-2** (90 mg, 0.19 mmol, 68.7%). ¹H NMR (400 MHz, DMSO, δ): 8.14 (s, 1H), 7.65 (d, *J* = 3.9 Hz, 1H), 7.44–7.33 (m, 6H), 7.30 (ddd, *J* = 13.9, 7.0, 1.8 Hz, 4H), 7.24–7.16 (m, 2H), 7.00 (d, *J* = 16.1 Hz, 1H), 6.44 (d, *J* = 8.9 Hz, 2H), 2.94 (s, 4H). ¹³C NMR (100 MHz, DMSO, δ): 164.11, 149.70, 148.87, 142.55, 142.05, 137.68, 137.42, 134.10, 131.32, 131.12, 129.39, 128.15, 127.54, 127.29, 125.83, 125.61, 118.73, 117.17, 112.21, 29.94. HRMS (ESI, *m/z*): [M + H]⁺ calcd for C₃₀H₂₃N₂O₂S, 475.1480; found, 475.1485.

2.2.15. 3-(5-(4-(5H-dibenzo[b.f]azepin-5-yl)styryl)thiophene-2-yl)-2-cyanoacrylic acid (**ISB-2**)

The synthesis method resembled that of compound **IDB-1** and the crude compound was purified by column chromatography on silica (DCM/ethanol = 10/1, v/v) to yield a purple solid, **ISB-2** (103 mg, 0.22 mmol, 70.5%). ¹H NMR (400 MHz, DMSO, δ): 13.59 (s, 1H), 8.40 (s, 1H), 7.88 (d, *J* = 4.1 Hz, 1H), 7.58 (tt, *J* = 7.8, 4.1 Hz, 6H), 7.50–7.41 (m, 2H), 7.31 (dd, *J* = 6.4, 5.0 Hz, 3H), 7.21 (d, *J* = 16.1 Hz, 1H), 7.08 (d, *J* = 16.1 Hz, 1H), 6.95 (s, 2H), 6.14 (d, *J* = 8.9 Hz, 2H). ¹³C NMR (100 MHz, DMSO, δ): 163.86, 153.32, 149.14, 146.30, 141.76, 141.52, 135.63, 133.06, 132.91, 130.50, 130.31, 130.11, 129.78, 128.10, 127.59, 126.05, 125.82, 116.80, 116.73, 111.55. HRMS (ESI, *m/z*): [M – H]⁻ calcd for C₃₀H₁₉N₂O₂S, 471.1167; found, 471.1156.

2.3. Theoretical calculation

Density functional theory (DFT) calculations were conducted by using the B3LYP hybrid functional for the geometry optimizations.



Scheme 1. Synthesis of the sensitizers (IDB-1, ISB-1, IDB-2, and ISB-2).

The molecular orbital levels of HOMO and LUMO were achieved with the 6-31G(d) basis set implemented in the Gaussian 03 package.

2.4. Electrochemical measurements

The cyclic voltammograms were determined with a Versastat II electrochemical workstation (Princeton Applied Research) using a three-electrode cell with a Pt working electrode, a Pt wire auxiliary electrode, and a saturated calomel reference electrode in saturated KCl solution. The supporting electrolyte was 0.1 M TBAPF₆ (tetra-*n*-butylammonium hexafluorophosphate) in acetonitrile as the solvent.

2.5. General procedure for preparation

The dye-sensitized TiO₂ electrode was prepared by following the procedure reported in the literature [3]. TiO₂ colloidal dispersion was made employing commercial TiO₂ (P25, Degussa AG, Germany) as material. Films of nanocrystalline TiO₂ colloidal on FTO were prepared by sliding a glass rod over the conductive side of the FTO, followed by calcinations at 450 °C for 30 min. Before immersion in the dye solution, these films were immersed into a 40 mM aqueous TiCl₄ solution at 70 °C for 30 min and washed with water and ethanol. Then the films were heated again at 450 °C followed by cooling to 80 °C and soaked in dye solutions (0.3 mM in chloroform) for at least 12 h. The adsorbed TiO₂ electrode and Pt counter electrode were assembled into a sealed sandwich-type cell by heating with a hot-melt ionomer film (Surlyn 1702, DuPont). The redox electrolyte was placed in a drilled hole in the counter electrode by capillary force, and was driven into the cell by means of vacuum backfilling. Finally, the hole was sealed using a UV-melt gum and a cover glass. Two electrolytes were used for device evaluation, in which one was composed of 0.1 M lithium iodide, 0.6 M 1,2-dimethyl-3-n-propylimidazolium iodide (DMPImI), 0.1 M I₂, and

Table 1

Experimental data	for spectral and	electrochemical	l properties of the dye	s.
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 $\epsilon (M^{-1} cm^{-1})^{a}$ λ_{max} on TiO₂ (nm)^b HOMO (V) vs. NHE $E_{0-0} (\mathrm{eV})^{\mathrm{d}}$ LUMO (V) vs. NHE^e Dves $\lambda_{\max} (nm)^a$ IBD-1 422 27.000 420 1.12 2.08 -0.96 ISB-1 39,000 2.05 -0.86 470 418 1.19 IDB-2 467 466 1.05 2.03 -0.9834.000 -1.05ISB-2 498 42,000 439 0.96 2.01

^a Absorption maximum in CH₂Cl₂ solution (3×10^{-5} M).

^b Absorption maximum on TiO₂ film.

^c HOMO were measured in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as electrolyte (working electrode: FTO/TiO₂/dye; reference electrode: SCE; calibrated with ferrocene/ferrocenium (Fc/Fc⁺) as an external reference. Counter electrode: Pt).

^d E_{0-0} was estimated from the absorption thresholds from absorption spectra of dyes adsorbed on the TiO₂ film.

^e LUMO is estimated by subtracting E_{0-0} from the HOMO.

0.5 M 4-tert-butylpyridine (4-TBP) in acetonitrile, the other was composed of 0.1 M lithium iodide, 0.6 M methyl-propylimidazolum iodide (MPII) and 0.05 M I₂ in the mixed solvent of acetonitrile and 3-methoxypropionitrile (7:3, v/v).

2.6. Photoelectrochemical measurements

Photovoltaic measurements employed an AM 1.5 solar simulator equipped with a 300 W xenon lamp (Model No. 91160, Oriel). The power of the simulated light was calibrated to 100 MW/cm² using a Newport Oriel PV reference cell system (Model 91150 V). I-Vcurves were obtained by applying an external bias to the cell and measuring the generated photocurrent with a Keithley model 2400 digital source meter. The voltage step and delay time of photocurrent were 10 mV and 40 ms, respectively. Cell active area tested with a mask of 0.158 cm². The photocurrent action spectra were measured with an IPCE test system consists of a Model SR830 DSP Lock-In Amplifier and Model SR540 Optical Chopper (Stanford Research Corporation, USA), a 7IL/PX150 xenon lamp and power supply, and a 7ISW301 Spectrometer.

2.7. Electrical impedance measurements

Electrical impedance experiments were performed in the dark with CHI660C electrochemical work station, with a frequency range from 0.01 Hz to 100 kHz and a potential modulation of 10 mV. The applied bias potential is held at -0.60 V.

3. Results and discussion

3.1. Synthesis

The synthetic strategy, illustrated in Scheme 1, involves the Ullmann coupling reaction, the Suzuki coupling reaction, the Knoevenagel reaction, and the Wittig reaction to extend the



Fig. 2. Normalized absorption spectra of the IDB-1, ISB-1, IDB-2, and ISB-2 dyes in CH₂Cl₂ (a) and anchored on 6.5 μm TiO₂ films (b).

thiophene linker. The **IDB** and **ISB** as electron donors were synthesized via the Ullmann coupling reaction of iminodibenzyl and iminostilbene with iodobenzene in the presence of copper powder, potassium carbonate and [18] crown-6. Compounds **5** and **6** were obtained by bromination reaction of **IDB** and **ISB** using *N*bromosuccinimide (NBS) followed by the Michaelis–Arbuzor reaction [42,43]. The Suzuki coupling reaction was made with the respective bromides and 5-formyl-2-thiophene-boronic acid to yield the aldehydes **7** and **8**. Aldehydes **9** and **10** were prepared from **3** and **4** by means of the Vilsmeier–Haack reaction [44,45]. In the cases of linker extension by the Wittig reaction, formylation of the thiophene with *n*-BuLi and DMF was applied [41]. Finally, the target products (**IDB-1**, **ISB-1**, **IDB-2**, and **ISB-2**) were synthesized via the Knoevenagel condensation reaction of the respective aldehydes with cyanoacetic acid in the presence of piperidine, and their chemical structures were fully characterized with ¹H NMR, ¹³C NMR and HRMS.

3.2. Absorption properties in solutions and on TiO₂ film

Table 1 presents the experimental spectral and electrochemical properties of the IDB-1, ISB-1, IDB-2, and ISB-2 dyes. Normalized adsorption spectra of the dyes in dichloromethane diluted solution and on TiO₂ films were shown in Fig. 2. In dichloromethane solution, all these dyes exhibit a relatively broad and strong absorption band in the visible region corresponding to the intramolecular charge transfer (ICT) band (Fig. 2a). The absorption peaks (λ_{max}) for IDB-1, ISB-1, IDB-2, and ISB-2 located at 422, 470, 467 and 498 nm in diluted solution, respectively. Judging from that of **IDB-1** and **ISB-1**, the absorption band of **IDB-2** and **ISB-2** showed a large redshift upon increased linker conjugation. Obviously, in the series of sensitizers containing the same cyanoacetic acid unit and electron transport channels, the ICT band is dependent upon the donor units. As listed in Table 1, the red-shift by 48 or 31 nm was observed when replacing IDB unit (IDB-1 and IDB-2) with ISB unit (ISB-1 and ISB-2) in the donor moiety, indicative of the more powerful electron-donating capability of the ISB unit than that of the IDB unit.

Generally, when sensitizers are anchored onto nanocrystalline TiO₂ surface, the deprotonation and aggregation of the dye molecules affect UV-vis absorption profiles. Deprotonation and H-aggregates always result in blue-shift of absorption peak, while J-aggregates mainly lead to the red-shift of absorption peak. Like most D- π -A conjugated organic sensitizers, the ICT absorption peak of **ISB** dyes (**ISB-1** and **ISB-2**) on 6.5 μ m TiO₂ films exhibit a large blue-shift (52 and 59 nm, respectively) with respect to



Fig. 3. The optimized geometries of the IDB-1, IDB-2, ISB-1, and ISB-2 calculated with DFT on the B3LYP/6-31G(d) level.

measurements taken in dichloromethane solution (Table 1). Since the aggregation tendency is not obvious within such thin films of TiO₂, here the shift in absorption peak might be predominated by deprotonation effect. Unexpectedly, the ICT absorption peaks of **IDB** dyes (**IDB-1** and **IDB-2**) are slightly blue-shifted by only 2 nm from 422 nm in solution to 420 nm on TiO₂, and 1 nm from 467 nm in solution to 466 nm on TiO₂, respectively. Thus iminodibenzyl unit in IDB dyes countervails the deprotonation effect. It is noteworthy that the absorption spectrum of the dyes adsorbed onto 6.5 µm TiO₂ films shows a markedly broad profile, which is beneficial to light-harvesting (Fig. 2b).

3.3. Theoretical calculation

To gain insight into the geometrical properties and scrutinize the charge transfer on excitation, the ground-state geometries of the protonated dyes have been optimized in the gas phase by DFT with the Gaussian09 package [46], using the hybrid B3LYP [47] functional and the standard 6-31G(d) basis set. The TDDFT calculations were performed with MPW1 K [48] functional and 6-31G(d) basis set on the B3LYP optimized ground-state geometries. Solvation effect was included in the TDDFT calculations in CH₂Cl₂ with the nonequilibrium version of the C-PCM model [49]. As illustrated in Fig. 3, the dihedral angles between the phenyl B1 planes and the phenyl B2 planes of the **ISB** dves are higher than those of the **IDB** dyes. The phenomenon is due to the rigid iminostilbene substituent which would increase the steric strain and cause the iminostilbene moiety to twist slightly out of the plane defined by phenyl B1. The angle formed between the phenyl B1 plane and the phenyl B2 plane of the **ISB-2** is as large as 82°, which can help to inhibit the close $\pi-\pi$ aggregation. As illustrated in Fig. 4, the HOMO orbital of the dyes is primarily located at the π -framework of the donor part and thiophene group, while the electron density of the LUMO is delocalized over the thiophene group and anchoring group. Examination of the frontier orbitals of all sensitizers suggests that the HOMO-LUMO excitation would shift the electron density distribution from the donor unit to the anchoring moiety, facilitating efficient photoinduced/interfacial electron injection from excited dyes to the TiO₂ electrode.

3.4. Electrochemical properties

Fig. 5 depicts the cyclic voltammogram (CV) of IDB-1, IDB-2, ISB-1, and ISB-2, measured with four sensitizers attached to $6.5 \,\mu m$ nanocrystalline TiO₂ films deposited on conducting FTO glass in

Action spectrum, incident photon-to-electron conversion efficiency (IPCE) as a function of wavelength, was measured to evaluate the photoresponse of photoelectrode in the whole spectral





Fig. 5. Oxidative cyclic voltammetry plots of IDB-1, ISB-1, IDB-2, and ISB-2 attached to a $6.5 \,\mu$ m nanocrystalline TiO₂ film deposited on conducting FTO glass.

containing 0.1 M tetra-*n*-butylammonium MeCN hexafluorophosphate (TBAPF₆) with a 0.05 V s^{-1} scan rate. CV was employed to evaluate the redox stability and oxidation potential of the dyes. As estimated from the absorption threshold of these dyes onto TiO₂ films, the excitation transition energy (E_{0-0}) of IDB-1, IDB-2, ISB-1, and ISB-2 is 2.08, 2.03, 2.05 and 2.01 eV, respectively (Table 1). The HOMO values of IDB-1, IDB-2, ISB-1, and ISB-2 corresponding to their first redox potential were 1.12, 1.05, 1.19 and 0.96 V vs. NHE, respectively. Observed from these electrochemical data of IDB-1 and ISB-1, or IDB-2 and ISB-2, it seems that the HOMO energy level is exclusively determined by donors. The estimated excited-state potential corresponding to the LUMO levels of **IDB-1**, **IDB-2**, **ISB-1**, and **ISB-2**, calculated from $E_{\text{HOMO}} - E_{0-0}$, are -0.96, -0.98, -0.86 and -1.05 V vs. NHE, respectively. Judging from the LUMO value, the four dyes are more negative than the bottom of the conduction band of TiO_2 (-0.5 V), indicating that the electron injection process from the excited dye molecule to TiO₂ conduction band is energetically permitted [50-52].

3.5. Performances of dye-sensitized solar cells



IDB-1

ISB-1

IDB-2

ISB-2



Fig. 6. Photocurrent action spectra of the TiO₂ electrodes sensitized by IDB-1, ISB-1, IDB-2 and ISB-2

region. The IDB-1, IDB-2, ISB-1, and ISB-2 sensitizers have been used to manufacture solar cell devices by using 8 (transparent) + 4(scattering) μ m TiO₂ layers. Fig. 6 shows the IPCE obtained with a sandwich cell by using 0.1 M lithium iodide, 0.6 M methylpropylimidazolum iodide (MPII) and 0.05 M I₂ in the mixed solvent of acetonitrile and 3-methoxypropionitrile (7:3, v/v) as redox electrolyte. The photocurrent action spectra of all sensitizers exhibit very high plateaus where IPCE values reach 85%. Considering the light absorption and scattering loss by the conducting glass, the maximum efficiency for absorbed photon-to-collected electron conversion efficiency is almost unity over a broad spectral range, suggesting a very high electron injection efficiency of these dyes. Solar cells based on IDB-1 and ISB-1 showed high IPCE (85%) but not broad spectra, resulting in lower overall efficiencies due to spectral limitations. Solar cells based on IDB-2 and ISB-2 show broad IPCEs in accordance to the broad absorption spectrum achieved by increased linker conjugation.

Fig. 7 shows the current-voltage (I-V) curves of the DSSCs under standard global AM 1.5 G solar irradiation. The short-circuit photocurrent density (J_{sc}) , open-circuit voltage (V_{oc}) , and fill factor (ff) of the solar cell based on **ISB-2** are 13.14 mA cm^{-2} ,



Fig. 7. Photocurrent-voltage curves of dyes IDB-1, IDB-2, ISB-1, and ISB-2 sensitized TiO₂ electrodes under irradiation of AM 1.5 G simulated solar light (100 mW cm⁻²) with liquid electrolyte.

Table	2	
	-	

OSSC perfor	mance data	of the	dyes. ^a

Dyes	$J_{\rm sc}/{ m mA}{ m cm}^{-2}$	V _{oc} /mV	ff	η (%)
IDB-1	10.67	657	0.68	4.80
ISB-1	11.04	665	0.72	5.27
IDB-2	11.30	665	0.69	5.21
ISB-2	13.14	649	0.68	5.83
N719	16.10	689	0.67	7.47

^a Illumination: 100 mW cm⁻² simulated AM 1.5 G solar light. Electrolyte contained 0.1 M LiI, 0.6 M MPII, 0.1 M I₂, 1.0 M 4-TBP in the mixed solvent of acetonitrile and 3-methoxypropionitrile (7:3, v/v).

649 mV, and 0.68, respectively, yielding an overall conversion efficiency (n) of 5.83%. Under the same conditions, the device based on **IDB-2** shows lower J_{sc} , leading to an inferior η value of 5.21% (Table 2). For a fair comparison, the N719-sensitized DSSC was also fabricated under the same conditions and yielded *n* value of 7.47%. The higher J_{sc} values of the **IDB-2** and **ISB-2**-based cells than those of the IDB-1 and ISB-1-based cells are consistent with the values for the IPCE spectra due to the increased linker conjugation. In comparison with the IDB-1 and IDB-2-based cells, the ISB-1 and **ISB-2**-based cells show higher *J*_{sc}, respectively, reflecting the better sunlight-harvesting ability of the ISB dyes.



Fig. 8. Impedance spectra of DSSCs based on IDB-1, ISB-1, IDB-2, and ISB-2 dyes measured at -0.60 V bias in the dark. (a) Nyquist plots; and (b) Bode phase plots.

Electrochemical impedance spectroscopy (EIS) analysis was performed to elucidate the photovoltaic findings further. Fig. 8 compares the impedance spectra for IDB-1, ISB-1, IDB-2, and ISB-2-sensitized cells measured in the dark under a forward bias of -0.60 V with a frequency range of 0.1 Hz to 100 kHz. The important differences for these organic dye-sensitized solar cells are their conductivity. The Nyquist plots (Fig. 8a) show the radius of the middle semicircle to increase in the order ISB-2 < IDB-1 < IDB-**2** < **ISB-1**, indicating that the electron recombination resistance augments from ISB-2, IDB-1, IDB-2 to ISB-1 [53,54]. The electron lifetime values derived from curve fitting are 70.18, 101.52, 73.15 and 31.37 ms for IDB-1, ISB-1, IDB-2, and ISB-2-sensitized cells, respectively. The longer electron lifetime observed with ISB-1sensitized cells indicates more effective suppression of the back reaction of the injected electron with the I_3^- in the electrolyte and is reflected in the improvements on $V_{\rm oc}$. The Bode phase plots shown in Fig. 8b likewise support the differences in the electron lifetime for TiO₂ films derivatized with the four dyes and the result is agreement with the observed shit in the V_{oc} value under standard global AM 1.5 illumination.

4. Conclusion

In summary, four new organic sensitizers (IDB-1, ISB-1, IDB-2, and ISB-2) containing 5-phenyl-iminodibenzyl (IDB) and 5-phenyliminostilbene (ISB) as electron donors had been designed and synthesized for dye-sensitized solar cells. These dyes were successfully adsorbed on nanocrystalline anatase TiO₂ particles, and subsequently efficient dye-sensitized solar cells had been fabricated. It was found that the dyes containing 5-phenyl-iminostilbene (ISB) as electron donors exhibited improved photovoltaic performance compared with the ones containing 5-phenyliminodibenzyl (IDB) as electron donors. A solar cell device based on the sensitizer ISB-2 yielded a higher overall conversion efficiency up to 5.83% ($J_{sc} = 13.14 \text{ mA cm}^{-2}$, $V_{oc} = 0.64 \text{ V}$, and ff = 0.68) under 100 mW cm⁻² simulated AM 1.5 G solar irradiation. The introduction of increased linker conjugation appears to contribute to higher Isc and IPCE in DSSCs. Our findings demonstrate that the IDB and ISB organic sensitizers are promising for further improvement of the conversion efficiency of DSSCs owing to the original and versatile molecular design.

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