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5-Phenyl-iminostilbene based organic dyes for efficient dye-sensitized solar cells

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ABSTRACT

Four new 5-phenyl-iminostilbene dyes (**ISB-3**–**6**) containing electron-withdrawing benzo-[*c*][1,2,5] thiadiazole have been designed and synthesized for use as DSSCs. Their absorption properties and electrochemical and photovoltaic performances have been investigated systematically. Among these dyes, DSSCs based on a dye containing benzo-[*c*][1,2,5]thiadiazole and benzene moieties (**ISB-4**) showed the best performance: a short-circuit photocurrent density (J_{sc}) of 13.69 mA cm⁻², an open-circuit photovoltage (V_{oc}) of 722 mV, and a fill factor (FF) of 0.71, which corresponds to a power conversion efficiency (PCE) of 6.71%, under optimized conditions. Additionally, long-term stability of the **ISB-4** based DSSCs with ionic-liquid electrolytes was demonstrated under 1000 h of light soaking, the photovoltaic performance is up to 5.75%. The results suggest that 5-phenyl-iminostilbene containing dyes are promising candidates for application in DSSCs.

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1. Introduction

Dye-sensitized solar cells (DSSCs) have been considered as a promising, sustainable and environmental friendly energy device to meet the demands of mankind in the future.^{1,2} Among all the components of a DSSC, the sensitizers play the key role in achieving high power conversion efficiencies (PCEs) and have, therefore, been intensively studied. To date, DSSCs based on ruthenium-complexes have shown certified PCE values of 11.9%, whereas zinc-porphyrin co-sensitized DSSCs hold a new PCE record of 12.3%.³ Compared with metal complexes, the metal-free sensitizers have also attracted considerable scientific attention due to their low cost, facile structural modifications, easier preparation and purification.⁴ Impressive photovoltaic performances have been obtained by using organic dyes that show efficiencies exceeding 10%.⁵ Commonly, such organic sensitizers are synthesized by designing a donor- π -acceptor $(D-\pi-A)$ configuration,⁶ owing to their efficient intramolecular charge transfer (ICT) properties. Recently, a series of novel D–A– π –A organic dyes⁷ incorporating additional acceptors, such as diketopyrrolopyrrole,⁸ bithiazole,⁹ isoindigo,¹⁰ benzothiadiazole,¹¹ benzotriazole,¹² and quinoxaline¹³ into the traditional $D-\pi-A$ structure, showed more redshifted absorption than their parent analogues and thus enhanced the light-harvesting and stability.

In our previous study, a sensitizer containing a semi-rigid amine electron donor (**ISB-1**, Fig. 1) was reported. The new donor with a two-locking structure (5-phenyl-iminostilbene) was proved to be helpful to increase the molar extinction coefficient of the corresponding dyes as well as the electron lifetime of electron injected into TiO₂ conduction band.¹⁴ However, the short-circuit photocurrent density (J_{sc}) for the sensitizer still has room for improvement and optimization. In this work, we introduced the low bandgap and strong electron-withdrawing benzothiadiazole unit into the conjugation bridge to obtain four new dyes (**ISB-3–6**, Fig. 1) in an



Fig. 1. Chemical structures of ISB-3-6 and the reference dye ISB-1.



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attempt to optimize the energy levels and improve J_{sc} and PCE in DSSCs. As reported, different spacers could lead to diverse positions of the HOMO and LUMO energy levels, thus resulting in a different driving force for electron injection and tuning the short-circuit photocurrent density (J_{sc}). To enrich the research field of iminos-tilbene dyes for DSSCs and gain more information on the structure—property relationships, thiophene moiety and the benzene moiety were employed in π -spacers, respectively. Triple bonds were also inserted in π -spacers to study the influence on their photophysical and electrochemical properties and dye-sensitized solar cells (DSSCs) performance. Finally, the four sensitizers were applied to the sensitization of nanocrystalline TiO₂-based solar cells, and the effect of π -spacer linkers on the photophysical and electrochemical properties and the solar cell performance are studied.

2. Results and discussion

2.1. Synthesis

Four new dyes (**ISB-3**–**6**) containing 5-phenyl-iminostilbene (**ISB**) and 2, 1, 3-benzothiadizole (**BTD**) moieties are shown in Fig. 1. Dye **ISB-1** reported by us previously is also included for comparison. The synthetic route to the four compounds is depicted in Scheme 1. Compound **ISB** was synthesized via the Ullmann coupling reaction of iminostilbene with iodobenzene. Intermediates **1** and **5** were obtained by bromination or iodination of **ISB**. In the next step, **1** and **5** were reacted with BTD by the Suzuki or Sonogashira coupling reaction, respectively. The reaction produced the side products as well, fortunately the intermediates **2** and **7** can be easily separated by column chromatography. Then, the Suzuki coupling reaction was made with the respective bromides and 5-formylthiophen-2-yl-2-boronic acid or 4-formylphenylboronic acid to yield the aldehydes **3**, **4**, **8**, **9**, respectively. Finally, the conversion of intermediates **3**, **4**, **8**, **9** to target dyes **ISB-3**–**6** was achieved via conventional Knoevenagel condensation with 2-cyanoacetic acid. These dyes are confirmed by ¹H NMR, ¹³C NMR, and HRMS, and they also have good solubility in common organic solvents, such as methylene chloride, acetonitrile and tetrahydrofuran.

2.2. Photophysical properties

The UV/Vis absorption spectra of the dyes **ISB-3–6** and **ISB-1** in a diluted solution of CH₂Cl₂ are shown in Fig. 2a and the corresponding data are collected in Table 1. All dyes possess distinct absorption bands in the visible region (350-550 nm) that are attributed to the intramolecular charge transfer (ICT) from the 5phenyl-iminostilbene donor to the anchoring group. The absorption peaks (λ_{max}) of the dyes **ISB-1** and **ISB-3**–6 in CH₂Cl₂ are located at 470, 494, 450, 474, and 455 nm, respectively. Compared with the reference compound ISB-1, the introduction of BTD unit into the molecular frame distinctly decreases the bandgap between the HOMO and LUMO energy levels, thus results in a red-shift of almost 25 nm. Simultaneously, the absorption onset is extended by 165 nm from 535 nm (ISB-1) to 800 nm (ISB-3) in a dilute solution. The extension of the responsive wavelength is beneficial to lightharvesting and PCE. When a triple bond was added between the ISB and BTD moieties (ISB-5), although the conjugated structure is further extended, the absorption maximum is blue-shifted and the ε value is decreased relative to **ISB-3** sensitizers. This may be





Fig. 2. (a) UV-vis absorption spectra of dyes in CH_2Cl_2 ; (b) absorption spectra of dyes adsorbed on TiO_2 film.

 Table 1

 Absorption and electrochemical properties of ISB-3-6

Dyes	λ_{\max}^{a}/nm ($\varepsilon \times 10^{-4} \text{ M}^{-1} \text{ cm}^{-1}$)	λ _{max} b (nm)	HOMO ^c /V (vs NHE)	E_{0-0}^{d} (eV)	LUMO ^e /V (vs NHE)
ISB-3	494(2.45)	485	1.09	1.97	-0.88
ISB-4	450(2.89)	447	1.20	2.15	-0.95
ISB-5	474(2.21)	477	1.11	1.99	-0.89
ISB-6	455(1.19)	446	1.14	2.07	-0.94
ISB-1	470 (3.9)	418	1.19	2.05	-0.86

^a Absorption maximum in CH₂Cl₂ solution.

^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).

 $^{\rm d}$ 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} to HOMO.

attributed to the fact that, in the alkyne bridged chromophores, the carbon atoms are in both sp and sp² hybridized, which results in poorer π -orbital overlap and mismatch in energy of the π -orbitals, leading to a blue-shift and a decline of the molar extinction coefficient.

For the two dyes containing benzene moiety between the BTD unit and the cyanoacetic anchoring moiety, **ISB-4** and **ISB-6** have opposite absorption phenomena. **ISB-4** is observed a 40 nm blueshift than **ISB-3**, and the molar extinction coefficient of **ISB-4** is determined to be 28,900 M⁻¹ cm⁻¹, which is about 1.18 times of the corresponding values of **ISB-3**. This can be explained by the fact that the replacement of the thiophene moiety by benzene in the π -conjugated linker part, which leads to a strong decrease in the coplanarity between the BTD unit and the cyanoacetic anchoring

moiety. As for **ISB-6**, the absorption band shows a slight red-shift compared with **ISB-5**, and the ε value is decreased. This may be due to the influence of the triple band in the conjugation bridge.

The absorption spectra of dyes attached to the TiO_2 films display broader responses than those in solution (see Fig. 2b). The maximum absorption peaks of **ISB-3** and **ISB-4** are blue-shifted in TiO_2 films (9 nm and 3 nm), whereas those of **ISB-5** and **ISB-6** in TiO_2 films show slight red-shifting (3 nm and 1 nm) compared with their absorption spectra in CH_2Cl_2 solution. We presumed that these shifts in absorption spectra were caused by dye aggregation on the TiO_2 films. It is noteworthy that, compared with the reference compound **ISB-1** (52 nm blue-shift), the shifts of the new dyes containing BTD are much weaker, which suggest that they reduced the aggregation of sensitizers. In addition, the broadening of absorption bands and longer tailing upon dye adsorption are advantageous for device performance.

2.3. Electrochemical properties

To confirm the successful operation of DSSCs using the novel dves ISB-3-6, the electrochemical properties of the dyes were determined by cyclic voltammetry (CV) in acetonitrile using tetrabutylammonium hexafluorophosphate (TBAPF₆) as a supporting electrolyte; the data are summarized in Table 1. The HOMO levels of these dyes are 1.09 V for ISB-3, 1.20 V for ISB-4, 1.11 V for ISB-5 and 1.14 V for ISB-6 versus NHE, respectively. They are all more positive than the iodine/iodide redox potential value (0.4 V vs NHE), indicating that the oxidized dyes, formed after electron injection into the conduction band of TiO₂, could accept electrons from the electrolyte thermodynamically. The LUMO levels of sensitizer were estimated by the values of E_{0x} and the 0–0 band gaps. The latter is estimated from the absorption thresholds from absorption spectra of dyes adsorbed on the TiO₂ film. The LUMO levels of ISB-3-6 are -0.88, -0.95, -0.89, -0.94 V versus NHE, respectively. All the dyes' levels are more negative than conduction band-edge energy level of the TiO₂ electrode (-0.5 V vs NHE). These results indicate that the light-harvesting excited dyes can provide enough driving force for electron injection into the TiO₂ conduction band.¹⁵ The relatively large energy gaps between the LUMO and Ecb provide the possibility for the addition of 4-tert-butylpyridine (TBP) to the electrolyte, which can shift the E_{cb} of TiO₂ more negatively and, consequently, improve the voltage and total efficiency.¹⁶

2.4. Theoretical approach

Density functional theory (DFT) and time-dependent density functional theory (TDDFT) calculations were carried out with the Gaussian 09 package¹⁷ to achieve a better understanding of the molecular geometries and electronic distributions of the dyes. All calculations were carried out using the Gaussian 09 program with the hybrid B3LYP functional¹⁸ and the standard 6-31G(d) basis set. Time-dependent DFT calculations (TD-DFT) were performed using Gaussian 09 program with a polarizable continuum model (PCM).¹⁹ The molecular structures were optimized in vacuum, using the software Avogadro²⁰ to enter the starting geometry. Then solvation effect was taken into account into the TDDFT calculations.

Fig. 4 shows the ground-state geometries of the dyes with the dihedral angles between two neighboring conjugated segments indicated. The dihedral angles between the thienyl entity and the BTD entity (2° for **ISB-3**, 1° for **ISB-5**) are smaller than that between the phenyl entity and the BTD entity (35° for **ISB-4**, 34.5° for **ISB-6**), which is similar to the situation reported before.²¹ There is also a significant twist of the BTD from coplanarity with the phenyl entity attached to the donor (36.5° for **ISB-3**, 38.5° for **ISB-4**). In contrast, the dihedral angles between the BTD and the phenyl entity connected with the triple bond in **ISB-5** and **ISB-6** are only

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Fig. 3. The frontier orbitals of sensitizers ISB-3, ISB-4, ISB-5, and ISB-6 (isodensity=0.020 a.u.).



Fig. 4. Dihedral angles between the neighboring units.

0 and 3°, respectively. This may be explained by the fact that the extra triple bond increases the distance of the phenyl and BTD, which results the decrease the steric hindrance. It is noteworthy that, in the optimized ground-state geometries of **ISB-5**, BTD and its neighboring units (phenyl and thienyl) were almost coplanar. Such a planar configuration often causes the π - π stacking of organic dye molecules, and π -stacked aggregate usually leads to inefficient electron injection and charge recombination. The former would lead to low photocurrent and the latter would lead to the decrease of open-circuit photovoltage.

The electron distribution of the HOMOs and LUMOs of **ISB-3–6** are shown in Fig. 3. The electron density of the HOMOs are primarily located at the π -framework of the donor part, while those of the LUMOs are delocalized over the aromatic rings, thiophene or benzene moieties, and the anchoring group. Thus, the excitation from the ground-state to the excited state can move the electron distribution from the donor unit to the anchoring moiety to realize electron injection to the conduction band of TiO₂. As illustrated in Table 2, the absorption characteristics and excited state features will mainly be dominated by charge transfer transitions from the HOMO–1 to LUMO orbitals.

Table 2

TD-DFT calculated energies	and compositions	of selected transitions
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Compounds	Composition	E(nm)	f
ISB-3	99% H→L	681	0.0012
	98% H $-1 \rightarrow L$	514	1.2284
ISB-4	97% H→L	608	0.0003
	98% H $-1 \rightarrow L$	459	1.0897
ISB-5	99% $H \rightarrow L$	690	0.0148
	99% H $-1 \rightarrow L$	561	1.5279
ISB-6	98% H→L	619	0.0066
	98% H $-1 \rightarrow L$	505	1.3294

2.5. DSSCs performance

The photovoltaic characteristics of the four ISB dyes as the sensitizers in DSSCs were measured with a sandwich DSSCs cell comprising 0.1 M lithium iodide, 0.6 M methylpropylimidazolium iodide (MPII), 0.05 M I₂ and 0.5 M 4-tert-butylpyridine (4-TBP) in the mixed solvent of acetonitrile and 3-methoxypropionitrile (7:3, v/v) as the redox electrolyte. As shown in Fig. 5, the incident photon to current conversion efficiency (IPCE) spectra of ISB-3-6 are in good consistency with their absorption spectra on the TiO₂ film (Fig. 2b) and light-harvesting efficiency. All four dyes could efficiently convert the light to photocurrent in the region from 350 to 600 nm. However, the IPCE spectra of ISB-3 and ISB-4 exhibit much higher peak values and longer wavelengths than that of ISB-5 and ISB-6, especially in the range of 350–530 nm. It is notable that the onset of the IPCE of ISB-3 and ISB-4 is close to about 700 nm and the IPCE spectra data exceed 60% in the visible spectral region from 350 to 560 nm, reaching their maximum of 86% and 90% at 490 nm and 450 nm, respectively, indicating highly efficient DSSCs performances. Although the IPCE performance of the DSSC with ISB-4 is slightly narrower than those of ISB-3, the data of ISB-4 from 400 to 490 nm exceeds the corresponding data of ISB-3, leading to a better performance. This can be partially attributed to the larger molar extinction coefficient and more negative LUMO energy level of ISB-4 leading to higher electron injection efficiency. Compared with



Fig. 5. Plots of incident photon to collected electron conversion efficiency (IPCE) as a function of wavelength.

ISB-3 and **ISB-4**, IPCE value of **ISB-5** and **ISB-6** are reduced significantly, especially for **ISB-5**. This leads to the poor performance of the **ISB-5** based DSSCs in terms of photovoltage efficiency. This result can be ascribed to the fact that the lower molar absorption coefficient and the planar configuration of **ISB-5**, which has been mentioned above. So the modification in D–A– π –A configuration should be carried out carefully.

Photovoltaic tests were conducted to evaluate the potential of the ISB-3-6 dyes in DSSCs. The I-V curves of the DSSCs sensitized by the ISB-3–6 dyes are shown in Fig. 6. The detailed photovoltaic parameters are summarized in Table 3. Being consistent with the integrals of IPCEs over the standard AM 1.5 G solar emission spectrum, ISB-4 yields the highest short-circuit photocurrent density (J_{sc}) amongst these four photosensitizers. Furthermore, the V_{oc} of **ISB-4** is higher than that of the **ISB-3** based devices. This may be caused by the introduction of a benzene group, which leads to a reduction of electron recombination and improves the $V_{\rm oc}$ due to the relatively large dihedral angle between the BTD unit and the benzene-bridge (see Theoretical approach). Such a phenomenon has been also observed in other dyes.²¹ With a short-circuit photocurrent density (J_{sc}) of 12.11 mA cm⁻¹, an open-circuit photovoltage (Voc) of 673 mV and a fill factor (FF) of 0.66, an ISB-4 based cell exhibits the highest PCE (η) of 5.36%. Compared to **ISB-3** and ISB-4, ISB-5 and ISB-6 with the triple bond in the bridge, not only evokes a decline of J_{sc} but concomitantly prompts a V_{oc} decrease, leading to lower PCE.



Fig. 6. Current–voltage characteristics of DSSCs sensitized by the dyes **ISB-3–6** under irradiation of AM 1.5 G simulated solar light (100 mW cm⁻²) with liquid electrolyte.

Table 3DSSC performance data of the dyes^a

Dyes	$J_{\rm sc}/({\rm mA~cm^{-2}})$	$V_{\rm oc}/({\rm mV})$	FF	η (%)
ISB-3	11.94	657	0.66	5.16
ISB-4	12.11	673	0.66	5.38
ISB-5	3.60	545	0.71	1.39
ISB-6	7.37	636	0.61	2.86
ISB-1	11.04	665	0.72	5.27
N719	16.10	689	0.67	7.47

^a Illumination: 100 mW cm⁻² (AM 1.5 G) simulated AM 1.5 G solar light. Electrolyte contained 0.1 M Lil, 0.6 M MPII, 0.05 M I_2 , 0.5 M 4-TBP in the mixed solvent of acetonitrile and 3-methoxypropionitrile (7:3, v/v).

As we all known, the total efficiency of the dye-sensitized solar cell depends on optimization and compatibility of the semiconductor film, sensitizer, and electrolyte composition, a further optimization of DSSCs based on the dye **ISB-4** was investigated. To improve the V_{oc} of **ISB-4**, the effect of 4-*tert*-butylpyridine (4-TBP) content in the liquid electrolyte on the performance of solar cells was also investigated and the data are presented in Table 4. The

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Influence	of	4-tert-	buty	lpyrid	ine oi	n the	photov	oltaic	performance	parameters	a

Dues	$4 \text{ TDD}(\mathbf{M})$	$I /(m \Lambda cm^{-2})$	V /(mV)	EE	
Dyes	4-1BP (IVI)	$J_{sc}/(mA \ cm^{-})$	$V_{\rm oc}/(111V)$	FF	η (%)
ISB-4	0.25	12.33	649	0.65	5.23
	0.5	12.11	673	0.66	5.38
	0.8	12.00	706	0.67	5.65
	1.0	11.72	730	0.67	5.75
	1.2	9.96	738	0.71	5.24

^a Illumination: 100 mW cm⁻² simulated AM 1.5 G solar light.

value of V_{oc} for **ISB-4** increases from 649 to 738 mV, with increasing concentration of 4-*tert*-butylpyridine (0.25–1.2 M). This can be explained by the fact that the adsorption of 4-*tert*-butylpyridine on the TiO₂ surface prevents molecules from reaching the porous membrane on TiO₂, where recombination takes place. In contrast, J_{sc} value decreases progressively with increasing concentrations of 4-TBP (0.25–1.2 M) because the addition of 4-TBP can reduce the photoinduced electron injection power and the photogenerated electron concentration in the porous film. Thus, PCE can be improved by adding appropriate concentrations of 4-TBP is increased to 1.00 M, the DSSCs based on **ISB-4** gives the best performance.

To further optimize the solar cell performance of **ISB-4**, the effect of chenodeoxycholic acid (CDCA) content as coadsorbent was also investigated and the data are reported in Table 5. The value of V_{oc} for **ISB-4** increases from 730 to 746 mV, when the concentration of CDCA increases from 0 to 10 mM, whereas the value of J_{sc} for **ISB-4** initially increases and then decreases. It is known that the addition of CDCA could reduce the aggregation of the dye on the TiO₂ surface, thereby reducing the deactivation due to quenching of intermolecular excited-electron aggregation and increasing the injection efficiency of the excited state photoelectron to the TiO₂ conduction band.²² On the other hand, dyes and CDCA are adsorbed competitively by the TiO₂ surface, which will reduce the amount of coverage of the dye. Thus, excess CDCA (10 mM) reduces the performance of the solar cells based on **ISB-4**.

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Effect of CDCA on the photovoltaic performances of ISB-3-6ª

Dyes	CDCA	$J_{\rm sc}/({\rm mA~cm^{-2}})$	$V_{\rm oc}/({\rm mV})$	FF	η (%)
ISB-4	0	11.72	730	0.67	5.75
	5	12.56	738	0.68	6.26
	10	12.38	746	0.66	6.04

^a Illumination: 100 mW cm⁻² simulated AM 1.5 G solar light, Electrolyte contained 0.1 M Lil, 0.6 M MPII, 0.05 M I₂, 1.0 M 4-TBP in the mixed solvent of acetonitrile and 3-methoxypropionitrile (7:3, v/v).

To maximize the device performance, DSSCs were fabricated by employing different thickness of TiO₂ films with the dye **ISB-4** and the data are reported in Table 6. Both the films were containing a 6 μ m scattering TiO₂ layer to avoid the reflection and absorption losses in the FTO substrate. As illustrated in Table 6 and Fig. S4, the short-circuit photocurrent density (*J*_{sc}) is increased from 12.58 to 13.69 mA cm⁻² when changing the nanocrystalline TiO₂ film thickness from 7.0 to 10.0 μ m, which also decreases the open circuit photovoltage (*V*_{oc}) from 738 mV to 722 mV. The enhancement of *J*_{sc} could be ascribed to the increased amount of dyes adsorbed on TiO₂ films because of thicker films of TiO₂, and the decline of the *V*_{oc} is due to the dye aggregation on the TiO₂ surface area, which can

Current-voltage characteristics of DSSCs with various TiO2 films based on ISB-4

Dyes	TiO ₂ films	$J_{\rm sc}/({\rm mA~cm^{-2}})$	$V_{\rm oc}/({\rm mV})$	FF	η (%)
ISB-4	Film A ^a	12.58	738	0.67	6.24
	Film B ^b	13.69	722	0.68	6.71

 a Film A was comprised of 7 μm nanocrystalline TiO₂ and 6 μm scattering TiO₂. b Film B was comprised of 10 μm nanocrystalline TiO₂ and 6 μm scattering TiO₂.

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provide additional charge recombination sites and enhance the dark current. $^{\rm 23}$

2.6. Stability measurements

Long-term stability is a vital parameter for sustained cell operation. Substitution of the liquid electrolyte by a solvent-free ionic liquid allows the determination of the stability of the photovoltaic performance over an extended period of time. For the evaluations, ISB-4 was utilized as sensitizers in ionic liquid electrolyte DSSCs. The photovoltaic parameters were J_{sc} =10.65 mA cm⁻², V_{oc} =673 mV, FF=0.68, and η =4.91% under standard global AM 1.5 solar light conditions (100 mW cm⁻²) shown in Fig. S3. The device was subjected to long-term stability tests under the irradiance of AM 1.5 G full sun visible-light soaking at 60 °C. The detailed photovoltaic parameters of the device during the aging process are plotted in Fig. 7. The PCE of ISB-4 containing devices remained at 97% of the initial value under both the thermal and the light soaking stress for over 1000 h. This demonstrates that the amount of dye on the TiO₂ surface remained intact after long time light soaking. To the best of our knowledge, this is the first test for stability test of DSSCs based on iminostilbene dyes.



Fig. 7. Stability test photovoltaic parameter (J_{sc} , V_{oc} , ff, and η) variations with aging time for the device based on ISB-4 sensitized TiO₂ film with quasi-solid-state electrolyte during successive one sun visible-light soaking at 60 °C.

2.7. Electrochemical impedance spectroscopy

To further elucidate the photovoltaic properties of these dyes, electrochemical impedance spectroscopy (EIS) was performed. EIS analysis of the DSSCs made with these sensitizers was carried out in the dark under a forward bias of -0.60 V with a frequency range of 0.1 Hz–100 kHz. The Nyquist plots (Fig. 8a) show the radius of the middle semicircle to decrease in the order of **ISB-4**>**ISB-3 ~ISB-6**>**ISB-3**. The result appears to be roughly consistent with the increase of V_{oc} in the DSSCs based on **ISB-3**–**6**. The electron lifetime values derived from Bode phase plots (Fig. 8b) are 18.99, 207.90, 4.55, and 14.41 ms for **ISB-3**–**6** sensitized cells, respectively. The longer electron lifetime indicates more effective suppression of the back reaction of the injected electron with the I₃ in the electrolyte and is reflected in the improvements on V_{oc} . So electron lifetime values are agreement with the V_{oc} values under standard global AM 1.5 illumination.

3. Conclusion

In summary, four new organic D–A– π –A dyes (**ISB-3–6**), comprising a 5-phenyl-iminostilbene as the electron donor, a cyanoacrylic acid as the anchoring group, benzothiadiazole as the core,



Fig. 8. Impedance spectra for DSSCs based on dyes **ISB-3**–6 measured at –0.60 V bias in the dark. (a) Nyquist plots; (b) Bode phase plots.

and different π spacers, were successfully synthesized and demonstrated as efficient sensitizers for DSSCs. The auxiliary electron withdrawing units, benzothiadiazole unit, facilitates the electron migration direction to the electron acceptor, which results in a redshift of the absorption spectrum leading to an increase of the *I*_{sc}. The introduction of an acetylenyl between the 5-phenyl-iminostilbene and benzothiadiazole neither extends the light-harvesting ability of the dyes, nor improves the PCE. The limited π -orbital overlap is not beneficial to the intramolecular charge transfer. Among the four dyes, DSSCs based on **ISB-4**, containing a phenyl as π spacers exhibit the best photovoltaic performance, after the optimization of the DSSCs, the PCE runs up to 6.71% (J_{sc} =12.74 mA cm⁻², V_{oc} =784 mV, FF=0.73) under AM 1.5 irradiation (100 mW cm⁻²). Most importantly, long-term stability of the ISB-4 based DSSCs with ionic-liquid electrolytes under 1000 h of light soaking was demonstrated, ISB-4 exhibited a PCE of 5.75%. All of the results reveal that the iminostibene-based dyes are promising sensitizer because of their good photoresponse in the visible region, good long-term stability under one sun soaking, and appropriate lowest unoccupied molecular orbital (LUMO) level matching the conduction band of TiO₂.

4. Experimental section

4.1. Materials and reagents

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.

4.2. Photophysical and electrochemical measurements

The absorption spectra of the dyes in solution and adsorbed on TiO_2 films were measured with a Varian Cary 500 spectrophotometer. Emission spectra of sensitized dyes in solution were measured with Varian Cary Eclipse. The oxidation potentials of dyes adsorbed on TiO_2 films were measured in a normal three-electrode electrochemical cell. TiO_2 films stained with sensitizer were used as the working electrode, a platinum wire was the counter electrode, and a regular calomel electrode in saturated KCl solution was the reference electrode. The measurements were performed using a potentiostat/galvanostat model K0264 (Princeton Applied Research). The supporting electrolyte was 0.1 M TBAPF6 (tetra-*n*-butylammoniumhexafluorophosphate) in acetonitrile as the solvent. The ferrocenium/ferrocene (Fc/Fc⁺) redox couple was used as an external potential reference. The potentials versus NHE were calibrated by addition of 630 mV to the potentials versus Fc/Fc⁺.³

4.3. Photovoltaic performance 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 cm^{-2} by a Newport Oriel PV reference cell system (Model 91150V). J-V curves 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. The photocurrent action spectra were measured with an IPCE test system consists of a Model SR830 DSP Lock-In Amplifier and a Model SR540 Optical Chopper (Stanford Research Corporation, USA), a 7IL/PX150 xenon lamp and power supply, and a 7ISW301 Spectrometer. The electrochemical impedance spectroscopy (EIS) measurements of all the DSSCs were performed using a Zahner IM6e Impedance Analyzer (ZAHNER-Elektrik GmbH & CoKG, Kronach, Germany). The frequency range is 0.1 Hz-100 kHz. The applied voltage bias is -0.60 V. The magnitude of the alternative signal is 10 mV.

4.4. Synthesis

All sensitizers were synthesized quite straightforward with the traditional Knoevenagel reaction in relatively high yield. The synthetic routes as well as detailed synthesis of intermediates are list in Scheme 1 (Supplementary data).

4.4.1. Synthesis of **ISB-3**. A mixture of compound **3** (159 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/ methanol=20/1, v/v) to yield a deep red solid, **ISB-3** (120 mg, 0.21 mmol, 72.8%). ¹H NMR (400 MHz, DMSO, δ): 8.33 (s, 1H), 8.26–8.14 (m, 2H), 7.94 (d, *J*=3.8 Hz, 1H), 7.73 (t, *J*=8.6 Hz, 3H), 7.68–7.55 (m, 6H), 7.54–7.44 (m, 2H), 6.98 (s, 2H), 6.28 (d, *J*=8.8 Hz, 2H). ¹³C NMR (100 MHz, DMSO, δ): 163.87, 152.82, 151.72, 148.83, 145.62, 143.51, 141.89, 137.40, 136.96, 135.74, 133.21, 130.53, 130.37, 130.10, 129.92, 129.60, 127.57, 127.41, 127.27, 125.95, 125.88, 122.60, 117.85, 111.29. HRMS (ESI, *m*/*z*): [M–H][–] calcd for C₃₄H₁₉N₄O₂S₂, 579.0949; found, 579.0952.

4.4.2. Synthesis of **ISB-4**. The synthesis method resembles that of compound **ISB-3** and the crude compound was purified by column

chromatography on silica (DCM/methanol=20/1, v/v) to yield a red solid, **ISB-4** (108 mg, 0.19 mmol, 68.7%). ¹H NMR (400 MHz, DMSO, δ): 8.39 (s, 1H), 8.22–8.12 (m, 4H), 7.97 (d, *J*=7.5 Hz, 1H), 7.74 (d, *J*=7.5 Hz, 1H), 7.69 (d, *J*=8.7 Hz, 2H), 7.65–7.55 (m, 6H), 7.47 (t, *J*=7.2 Hz, 2H), 6.97 (s, 2H), 6.27 (d, *J*=8.8 Hz, 2H). ¹³C NMR (100 MHz, DMSO, δ): 163.31, 153.39, 153.28, 153.13, 148.77, 141.96, 141.11, 135.79, 133.33, 130.97, 130.74, 130.55, 130.39, 130.11, 129.98, 129.64, 129.46, 129.20, 129.03, 127.56, 126.15, 116.34, 111.29. HRMS (ESI, *m/z*): [M–H][–] calcd for C₃₆H₂₁N₄O₂S, 573.1385; found, 573.1380.

4.4.3. *Synthesis of* **ISB-5**. The synthesis method resembles that of compound **ISB-3** and the crude compound was purified by column chromatography on silica (DCM/methanol=10/1, v/v) to yield a deep red solid, **ISB-5** (93 mg, 0.15 mmol, 60.3%). ¹H NMR (400 MHz, DMSO, δ): 8.21 (d, J=3.9 Hz, 1H), 8.16–8.08 (m, 2H), 7.85 (d, J=7.6 Hz, 1H), 7.80 (d, J=3.9 Hz, 1H), 7.67–7.55 (m, 6H), 7.48 (t, J=7.3 Hz, 2H), 7.30 (d, J=8.7 Hz, 2H), 6.98 (s, 2H), 6.21 (d, J=8.7 Hz, 2H). ¹³C NMR (100 MHz, DMSO, δ): 154.25, 150.92, 149.16, 141.45, 139.05, 135.55, 134.85, 132.52, 132.17, 130.56, 130.31, 130.23, 129.71, 128.19, 127.72, 126.37, 125.16, 115.83, 111.48, 110.39, 97.92, 84.70. HRMS (ESI, *m/z*): [M–H]⁻ calcd for C₃₆H₁₉N₄O₂S₂, 603.0949; found, 603.0947.

4.4.4. Synthesis of **ISB-6**. The synthesis method resembles that of compound **ISB-3** and the crude compound was purified by column chromatography on silica (DCM/methanol=10/1, v/v) to yield a red solid, **ISB-6** (85 mg, 0.14 mmol, 58.4%). ¹H NMR (400 MHz, DMSO, δ): 8.15 (d, *J*=8.5 Hz, 2H), 8.08–8.00 (m, 3H), 7.95 (d, *J*=7.5 Hz, 1H), 7.91 (d, *J*=7.4 Hz, 1H), 7.68–7.55 (m, 6H), 7.52–7.43 (m, 2H), 7.31 (d, *J*=8.9 Hz, 2H), 6.98 (s, 2H), 6.21 (d, *J*=8.9 Hz, 2H). ¹³C NMR (100 MHz, DMSO, δ): 163.37, 154.47, 152.27, 149.11, 147.31, 141.49, 138.49, 135.56, 133.09, 132.48, 132.14, 131.50, 130.55, 130.30, 130.21, 129.70, 129.56, 129.39, 128.24, 127.69, 118.95, 116.09, 113.18, 111.49, 110.48, 97.25, 84.47. HRMS (ESI, *m/z*): [M–H][–] calcd for C₃₈H₂₁N₄O₂S, 597.1385; found, 597.1390.

4.5. Preparation of photovoltaic devices

A screen-printed double layer of TiO₂ particles was used as photoelectrode. A 7-µm thick film of 13-nm-sized TiO₂ particles (Ti-Nanoxide T/SP) was first printed on the FTO conducting glass and further coated by a 6-µm thick second layer of 400-nm lightscattering anatase particles (Ti-Nanoxide 300). Sintering was carried out 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 for 30 min followed by cooling to 80 °C and dipping into a 3×10^{-4} M solution of dye in acetonitrile for 12 h at room temperature. To prepare the counter electrode, the Pt catalyst was deposited on the cleaned FTO glass by coating with a drop of H₂PtCl₆ solution (20 mM 2-propanol solution) with the heat treatment at 400 °C for 15 min. A hole (0.6 mm diameter) was drilled on the counter electrode by a drill press. The perforated sheet was cleaned by ultrasound in an ethanol bath for 10 min. About the assemblage of DSSCs, the dye-covered TiO₂ electrode and Ptcounter electrode were assembled into a sandwich type cell and sealed with a hot-melt gasket of 25 µm thickness made of the ionomer Surlyn 1702 (DuPont). The electrolyte was introduced into the cell via vacuum backfilling. Finally, the hole was sealed with a selfadhesive silver film.

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Supplementary data

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