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Synthesis and photovoltaic properties of new [1,2,5]thiadiazolo[3,4c]pyridine-based organic Broadly absorbing sensitizers for dyesensitized solar cells

Weijiang Ying ^{a,†}, Xiaoyu Zhang ^{a,†}, Xin Li^b, Wenjun Wu^a, Fuling Guo^a, Jing Li^{a,*}, Hans Ågren^b, Jianli Hua^{a,*}

^a Key Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science and Technology, Shanghai 200237, China ^b Department of Theoretical Chemistry and Biology, School of Biotechnology, KTH Royal Institute of Technology, Stockholm 10691, Sweden

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ABSTRACT

In this paper, by introducing [1,2,5]thiadiazolo[3,4-*c*]pyridine (PT) as an auxiliary acceptor into the molecular design of organic sensitizers, we have synthesized four new dyes (**PT1–PT4**) for dye-sensitized solar cells (DSSCs) with triphenylamine or *N*,*N*-diphenylthiophen-2-amine as the donor units and thiophene or benzene as the π -bridges, respectively. All the structures, optical and electro-chemical properties were fully characterized. Nanocrystalline TiO₂ dye-sensitized solar cells were also fabricated using these dyes. Among them, **PT2**-based DSSCs showed the highest overall conversion efficiency of 6.11% with *V*_{oc}=668 mV, *J*_{sc}=12.61 mA cm⁻² and a fill factor (FF)=0.74 after a chenodeoxycholic acid (CDCA) treatment under standard illumination condition (100 mW cm⁻² simulated AM 1.5 solar light).

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1. Introduction

Dye-sensitized solar cells (DSSCs) have drawn extensive attention as a promising alternative to traditional silicon-based solar cells during the past two decades due to their low-cost fabrication and relatively high performance.¹ The sensitizers, which have a crucial effect on the performance of DSSCs, are basically divided into two big groups, that is, metal complexes and organic dyes.² Ruthenium (Ru) complexes, as one of the most successful metalcomplex sensitizers, have roughly reached the photoelectric conversion efficiency of 10-12% under the standard measurement conditions.⁴ To date, a record efficiency of 12.3% has been kept by using zinc–porphyrin-based sensitizer.⁵ On the other hand, metalfree organic sensitizers have also attracted increasing attention due to their high molar extinction coefficients, tunable absorption properties, relatively high efficiency and low cost. Owing to the sensitizers' intramolecular charge-transfer (ICT) property, the donor $-\pi$ bridge-acceptor (D $-\pi$ -A) configuration is often used in the design of organic sensitizers.⁶ Recently, a renewed configuration has been put forward by introducing an additional electron-

* Corresponding authors. Tel.: +86 21 64250940; fax: +86 21 64252758 (J.H.), Tel./fax: +86 21 64252758(J.L.); e-mail addresses: lijhy@ecust.edu.cn (J. Li), jlhua@ ecust.edu.cn (J. Hua).

[†] These authors contributed equally to this work.

0040-4020/\$ – see front matter \odot 2014 Published by Elsevier Ltd. http://dx.doi.org/10.1016/j.tet.2014.04.039 withdrawing unit between the donor and the π -bridge as an internal acceptor, which is known as the D–A– π –A configuration.⁷ It has been reported that sensitizers with those auxiliary acceptor units, such as benzothiadiazole,⁸ benzotriazole,⁹ quinoxaline,¹⁰ diketopyrrolopyrrole,¹¹ pyrido[3,4-*b*]pyrazine,¹² and thieno[3,4-*c*] pyrrole-4,6-dione,¹³ have displayed several advantages involving tuning of the molecular energy levels, red-shifting of the chargetransfer absorption band, and improvement of photovoltaic performance and stability.

[1,2,5]Thiadiazolo[3,4-*c*]pyridine (PT), with the only molecular difference of nitrogen atom on the pyridine ring from benzothiadiazole (BT), has a higher electron affinity than BT. PT-based polymers have been widely used in the fields of field-effect transistors (FET) and bulk heterojunction (BHJ) solar cells.¹⁴ It is notable that, in 2011, Heeger and his co-workers reported the highest conversion efficiency of 6.7% for solution-processed small molecular solar cells of that time by incorporating PT as the acceptor unit inside the small molecule, indicating that PT is a promising electron acceptor unit.^{15,16}

Triphenylamine, however, as a good hole-transport group, is limited by its relatively narrow absorption range. It is reported recently that replacing one benzene ring of triphenylamine with a thiophene ring can improve its electron-donating ability and broaden the absorption spectrum, by which the overall conversion efficiency of 7.64% was reached.¹⁷ This report inspired us to do some

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further investigation into the application of *N*,*N*-diphenylthiophen-2-amine as the donor moiety to dye-sensitized solar cells. So in this paper, we have designed and synthesized four D–A– π –A featured organic sensitizers **PT1–PT4** using PT as the auxiliary acceptor unit, triphenylamine or *N*,*N*-diphenylthiophen-2-amine between the donor unit and thiophene or benzene as the π -bridge (see Scheme 1). The photovoltaic performance was also measured and analyzed. According to our expectation, the absorption spectra of the dyes would be broadened and even extended into NIR region.



Scheme 1. Molecular structures of the dyes PT1-PT4.

2. Results and discussion

2.1. Synthetic procedures

Scheme 2 depicts the synthesis of PT dyes. 2,5-Dibromopyridine-3,4-diamine (1) was synthesized by refluxing the commercially available 3,4-diaminopyridine in a mixture of hydrobromic acid and bromine. The crucial intermediate (2) was obtained by the subsequent cyclization reaction according to published procedures.¹⁸ Stille coupling reaction of PT with N,N-diphenyl-4-(tributylstannyl)aniline and N,N-diphenyl-5-(tributylstannyl)thiophen-2-amine resulted in the compounds **3** and **6**, respectively. In the next step, Suzuki coupling reaction of 3 and 6 with 5formylthiophen-2-ylboronic acid and 4-formylphenyl-boronic acid afforded the corresponding aldehyde precursors (4, 5, 7, 8), respectively. Finally, the target products PT1-PT4 were synthesized via Knoevenagel condensation of respective aldehydes with cyanoacetic acid in the presence of ammonium acetate. In the Stille coupling reaction, preferential oxidative coupling occurred at the more electron deficient 4-carbon position of pyridine derivates leading to the pyridal N-atoms proximal to the donor unit.¹⁹ It is important to highlight the regiochemistry of 3 and 6, where the Natoms of pyridine rings of each PT acceptor unit are orientated towards the donor moiety (proximal configuration). This conformation is observed from the corresponding ¹H NMR, as the δ data of the benzene and thiophene attached to the PT-core shifted to the downfield (8.40-8.50 ppm), which was affected by the N-atoms of pyridine rings (see Supplementary data). Such a phenomenon has also been observed in other small molecules containing pyridine rings.^{12,15} Also, it can be confirmed by the molecular weight of compounds 3 and 6. The four organic PT-based sensitizers were fully characterized with elemental analysis, ¹H NMR, ¹³C NMR, and HRMS (see Supplementary data).

2.2. Optical and electrochemical properties

The absorption spectra of the four dyes in the CH_2Cl_2 solvent are shown in Fig. 1. From the absorption spectra, we can see that all the dyes exhibit three major absorption bands. The former absorption bands of **PT1–PT4** are typical triarylamine absorptions, peaking at the range of 305–320 nm, which can be attributed to π – π *



Scheme 2. The synthetic procedures of the dyes PT1-PT4.



Fig. 1. Absorption spectra of PT1-PT4 dyes in CH₂Cl₂.

transitions caused by the conjugation of PT and donor mojety. The middle absorption bands of PT1 and PT3 peak at 415 nm and 430 nm while that of PT2 and PT4 peak at 360 nm and 373 nm, respectively, suggesting these bands can be ascribed to localized aromatic $\pi - \pi^*$ transitions caused by the conjugation of PT and thiophene or benzene moiety of the π -bridge.²⁰ The latter absorption band can be assigned to the intramolecular chargetransfer (ICT) between the donor and acceptor moiety.^{12,21} The maximum absorption wavelengths of **PT1–PT4** were 535, 500, 620 and 575 nm, respectively. With the same donor moieties, the 35 nm red-shift of PT1 compared with PT2 and 45 nm red-shift of PT3 compared with PT4 in the absorption spectra can be contributed to the different π -bridges. Fig. 1 is also an evidence of that the changing of donor unit can cast a notable influence on the absorption spectrum. As a matter of fact, replacing triphenylamine unit with N,N-diphenylthiophen-2-amine unit resulted in 75-85 nm bathochromic shift among the four dyes, which



Fig. 2. Absorption spectra of PT1-PT4 dyes on 2 µm transparent TiO₂ films.

expanded the absorption wavelength range efficiently. According to the optimized structures from density functional theory (DFT) calculations, the pyridine segment together with the thiadiazole unit is prone to form H-bonding with the proximal thiophene or phenyl rings, leading to nearly full planarity. The only fragment that would cause twisting is the distal phenyl ring. These features are clearly represented in Fig. 3, Fig. S2 and Table S2. It appears that the stronger electron-donating ability of *N*,*N*-diphenylthiophen-2amine than triphenylamine is mainly responsible for the bathochromic shifts. Unfortunately, this was on the expense of the molar extinction coefficient, which may affect the light harvesting efficiency. The cut-off wavelength of **PT3** reached 740 nm, indicating that narrow-energy-gap groups and strong electrondonating moieties can broaden the absorption spectrum, even to the near-infrared region.



Fig. 3. The electron distribution in HOMO and LUMO levels of PT1-PT4 dyes.

Absorption spectra of **PT1–PT4** dyes on transparent TiO_2 films are shown in Fig. 2. The maximum absorption wavelengths of

PT1–PT4 on the TiO₂ films were 503, 476, 554 and 524 nm, which were blue-shift 32, 24, 66 and 51 nm compared with that in CH_2Cl_2 , respectively. To our knowledge, this may be caused by two reasons: (1) the deprotonation of carboxylic acid when it absorbs on the surface of TiO₂, since the formed carboxylate—TiO₂ unit is a weaker electron acceptor than carboxylic acid; (2) the H-aggregation of dyes. We noted that dyes with triphenylamine donor units were less hypochromatic-shifted than those with *N*,*N*-diphenylth-iophen-2-amine donor units. This may be the result of the non-planar molecular configuration of triphenylamine, which reduced the H-aggregation. However, the absorption spectra were broaden when the dyes were absorbed on the TiO₂ films, which was beneficial to the light harvesting. All the absorption data are listed in Table 1.

Table 1

Optical	l properties	and e	lectroc	hemica	l properties	of t	the c	lyes	PT	I-P	Τ4
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Dye	$\lambda_{max}^{a}/nm (\epsilon \times 10^{-4} \text{ M}^{-1} \text{ cm}^{-1})$	λ _{max} ^b TiO ₂ /nm	HOMO ^c /V (vs NHE)	$E_{0-0}^{\rm d}/{\rm eV}$	LUMO ^e /V (vs NHE)
PT1	308(0.68), 415(0.35), 535(0.73)	503	1.13	1.97	-0.84
PT2	313(1.35), 360(0.67), 500(0.94)	476	1.13	2.07	-0.94
РТЗ	315(0.35), 430(0.33), 620(0.61)	554	0.97	1.78	-0.81
PT4	317(0.36), 373(0.27), 575(0.55)	524	0.97	1.90	-0.93

^a Absorption maximum in CH₂Cl₂ solution.

^b Absorption maximum on TiO₂ film(without CDCA).

 $^{\rm c}$ HOMO energy levels were measured in CH₂Cl₂ with 0.1 M tetra-n-buty-lammoniumhexafluorophosphate (TBAPF₆) as electrolyte (working electrode: Pt; reference electrode: SCE; calibrated with ferrocene/ferrocenium (Fc/Fc⁺)).

^d E_{0-0} was estimated from the intercept of the normalized absorption and emission spectra of the dyes, $E_{0-0}=1240/\lambda$.

 $^{\rm e}\,$ LUMO energy levels were estimated by subtracting $E_{\rm 0-0}$ from the HOMO energy level.

One of the conditions that a good sensitizer has to meet is its lowest unoccupied molecular orbital (LUMO) energy level have to be higher than the conduction band energy level (E_{cb}) of TiO₂ so that the excited electrons can be injected into the conduction band efficiently, and its highest occupied molecular orbital (HOMO) must be lower than the redox potential of the electrolyte so that the oxidized dyes can be reduced by accepting the electrons from the redox species in the electrolyte. To estimate the feasibility of the electron injection into the conduction band of TiO₂ and dye regeneration, cyclic voltammetry (CV) plots were recorded in CH₂Cl₂ solution with 0.1 M tetra-n-butylammoniumhexafluorophosphate $(TBAPF_6)$ as electrolyte with a three-electrode system (working electrode: Pt; counter electrode: Pt wire; reference electrode: saturated calomel electrode; calibrated with ferrocene/ferrocenium (Fc/Fc⁺) as an internal reference, the results were converted to those for the normal hydrogen electrode (NHE)). The cyclic voltammograms of PT1-PT4 are shown in Fig. S1. The redox potentials (E_{ox}) of **PT1–PT4**, which were corresponding to the HOMO energy levels, were located at 1.13, 1.13, 0.97, and 0.97 V versus NHE, respectively. The same HOMO energy levels of PT1 and PT2 along with PT3 and PT4 indicated that the HOMO energy level mainly depended on the donor moiety. The reason for higher HOMO energy levels of PT3 and PT4 compared to that of PT1 and PT2 can be attributed to the stronger electron-donating ability of N,N-diphenylthiophen-2-amine unit than that of triphenylamine unit. The stronger electron-donating ability the donor unit has, the higher HOMO energy level the sensitizer has. The parameters of electrochemical properties of PT1-PT4 can be found in Table 1. The zerozero transition energies (E_{0-0}) of the four dyes were estimated from the intercept of the normalized absorption and emission spectra, which were 1.97, 2.07, 1.78, and 1.90 eV, respectively. The LUMO energy levels, calculated from $E_{\text{HOMO}} - E_{0-0}$, were -0.84, -0.94, -0.81, and -0.93 V versus NHE, respectively. The LUMO values are much more negative than the Fermi level of TiO₂ (-0.5 V vs NHE),

ensuring an efficient electron injection process from the excited state of the dyes into the TiO_2 electrode. And the HOMO values are much more positive than the redox potential of I^-/I_3^- (0.4 V vs NHE), which assure an efficient dye regeneration process. Cyclic voltammetry proves that **PT1–PT4** can be applied to DSSCs in theory.

2.3. Molecular orbital calculations

To further study the processes of intermolecular electron transfer and the properties of absorption spectrum caused by exited states, DFT calculations were carried out to optimize the structures of compounds **PT1–PT4** at the B3LYP/6-31G* level of theory using the Gaussian 09 program packages.^{22,23} With solvent effects of CH₂Cl₂ taken into account by the polarizable continuum model (PCM),²⁴ the lowest singlet excited states (S1) of the sensitizer dyes were simulated by time-dependent (TD) DFT calculations employing the range-separated CAM-B3LYP functional.²⁵

The calculated parameters of the lowest excitation processes are shown in Table S1, including the energies of excited states, oscillator strengths and the contribution components of molecular orbitals. The obtained lowest excitation process of each compound corresponds to charge-transfer (CT) from HOMO to LUMO, that is, electronic transition from the donor moiety to the cyanoacrylic acid acceptor moiety, which ensures effective injection of electrons into TiO₂. According to Table S1, **PT1** and **PT2** had two components (HOMO \rightarrow LUMO and HOMO-1 \rightarrow LUMO) for S₀ \rightarrow S₁ transition while **PT3** and **PT4** had only one component (HOMO \rightarrow LUMO), owing to different nature of the donor units. The maximum absorption peaks caused by the electron transition from HOMO to LUMO were 524, 476, 577 and 528 nm, consistent with the experimental data.

The electron distributions in HOMO and LUMO levels of PT1-PT4 dyes are displayed in Fig. 3, from which we can see that the HOMOs of PT1 and PT2 are largely localized on the triphenylamine donor units, and a small part of them are on the π -bridge through the PT moiety. Whilst, the HOMOs of PT3 and PT4 show extension to the *N*,*N*-diphenylthiophen-2-amine, PT and π -bridge, leaving low electron density on the donor moiety, which goes against the electron transfer from the donor unit to the acceptor unit. Meanwhile, the LUMOs of four dyes are concentrated on the PT, π -bridge and cyanoacrylic acid acceptor moiety. This indicates that PT plays a role of an electron trap. When the dyes adsorb on the surface of TiO₂, the photoinduced electrons on the donor part can flow to the PT heterocycle smoothly, then to the cyanoacrylic acid moiety, and finally into the conduction band of TiO₂. The Cartesian coordinates of optimized geometries are provided in Supplementary data.

2.4. Photovoltaic performance of DSSCs

Fig. 4 shows the incident photon-to-electron conversion efficiency (IPCE) as a function of incident wavelength for DSSCs based on these dyes. The maximum IPCE values of DSSCs based on **PT1** and **PT2** are about 60%, while **PT3** and **PT4** are about 45%. Even though the IPCE spectra of **PT3** and **PT4** have red-shifted compared with that of **PT1** and **PT2**, the corresponding IPCE values in the range of 470–610 nm are much smaller, which lead to the lower short circuit current densities. After the treatment with 20 mM chenodeoxycholic acid (CDCA), the IPCE values of **PT2** in the region of 400–600 nm are increased by about 20%. Moreover, the IPCE spectrum is also broadened a little. Therefore, the relatively high J_{sc} and η have been obtained.

The photovoltaic performance of DSSCs is characterized under the AM1.5 simulated sunlight (100 mW cm⁻²). All the values of the short circuit current density (J_{sc}), the open circuit voltage (V_{oc}), fill



Fig. 4. The IPCE spectra for DSSCs sensitized by the dyes PT1-PT4 and 20 mM CDCAtreated PT2.

factor (FF) and the overall conversion efficiency (η) are tabulated in Table 2. And the I-V curves are illustrated in Fig. 5. There are three possible reasons of why the performance of triphenylamine-based DSSCs is better than that of N,N-diphenylthiophen-2-amine-based DSSCs: (1) The molar extinction coefficients of **PT1** and **PT2** are higher, which enable them to harvest the sunlight more efficiently. (2) According to the DFT calculations, the HOMOs of PT3 and PT4 extend from *N*,*N*-diphenylthiophen-2-amine to PT and π -bridge, leaving low electron density on the donor moiety, which goes against the electron transfer from the donor unit to the acceptor unit. This can also be reflected by the IPCE spectra; (3) The distinct $V_{\rm oc}$ decreases of DSSCs based on **PT3** and **PT4** might be the main reason for the low conversion efficiencies. Since the planarity of the compound became better by replacing the benzene ring by a thiophene ring, the dye aggregation and the electron recombination might not be restricted effectively, resulting in decreasing V_{oc} .

To optimize the performance of PT2-based DSSCs, we carried out CDCA treatments with different concentrations.²⁶ All the data are tabulated in Table 2. CDCA acts as a co-adsorbent with spatial configuration to reduce the dye aggregation effectively, thus can enhance the electron injection efficiency of the dye and J_{sc} . I-Vcurves of cells based on PT2 co-sensitized with CDCA of different concentrations are presented in Fig. 6. When the concentration of CDCA increased from 0 to 20 mM, the J_{sc} increased while V_{oc} decreased slightly, and the overall conversion efficiency was enhanced. Especially when the concentration of CDCA increased from 0 to 10 mM, the I_{sc} rose from 7.72 to 11.44 mA cm⁻², which was a strong evidence that CDCA can reduce the dye aggregation and increase the electron injection efficiency. However, when the concentration increased to 30 mM, the J_{sc} dropped and V_{oc} barely changed, resulting in a decrease of the overall conversion efficiency. This might be the result of the excess CDCA, which reduced the adsorption of the dye. Eventually, with the 20 mM CDCA treatment, PT2-based DSSCs obtained the highest conversion efficiency of 6.11%.

2.5. Electrochemical impedance spectroscopy

The electrochemical impedance spectroscopy (EIS) was engaged in further study upon the effect of different donors and π -bridges on V_{oc} in DSSCs. The impedance spectra of DSSCs were obtained at -0.70 V bias in the dark within the frequency range from 0.1 Hz to 100 Hz.

 $R_{\rm s}$, $R_{\rm res}$, and $R_{\rm CE}$ represent the series impedance, the charge-transfer impedances at the interface of TiO₂/dye/electrolyte and the interface of Pt/electrolyte, respectively (see Table S3). In Fig. 7a, the biggest semicircle corresponds to the $R_{\rm res}$. It is known that generally

Table 2
Photocurrent-voltage characteristics of untreated DSSCs based on PT1-PT4 and
CDCA with different concentrations of 10, 20 and 30 mM co-adsorbed DSSCs based
on PT2

Dye	CDCA (mM)	$J_{\rm sc}$ (mA cm ⁻²)	$V_{\rm oc}~({\rm mV})$	FF	η (%)
PT1	0	7.58	484	0.65	2.40
PT2	0	7.72	727	0.75	4.23
	10	11.44	656	0.73	5.45
	20	12.61	668	0.73	6.11
	30	10.99	680	0.74	5.51
PT3	0	5.70	324	0.50	0.94
PT4	0	5.76	385	0.55	1.23

Illumination condition: AM 1.5 G simulated sunlight (100 mW cm⁻²). Electrolyte: 0.05 M I₂, 0.5 M Lil in acetonitrile and 3-methoxypropionitrole (7:3, v/v).



Fig. 5. The *I*–*V* performance of solar cells sensitized by PT1–PT4 dyes.



Fig. 6. *I*–*V* curves of cells based on **PT2** co-sensitized with different concentrations of CDCA.

the bigger this semicircle is, the higher R_{res} is, which will restrain the recombination of electrons. According to Table S3, the R_s and R_{CE} of the four dyes are similar to each other. However, when it comes to R_{res} , we can find the values showing the order of **PT3**<**PT4**<**PT1**<**PT2**, which indicates that their electron transfer resistances at the interface of TiO₂/dye/electrolyte are in the same order. From the Bode phase plots (Fig. 7b), the calculated electron lifetimes of **PT3**, **PT4**, **PT1** and **PT2** are 0.03, 0.05, 0.06 and 3.38 ms, respectively. It's interesting that **PT2** has a much longer electron lifetime than the others. This suggests that **PT2** can inhibit the dark current and reduce the electron recombination, thus we can obtain a relatively high open circuit voltage. The V_{oc} data of **PT3**, **PT4**, **PT1**



Fig. 7. The impedance spectra (a) Nyquist plots and (b) Bode phase plots and (c) equivalent circuits for DSSCs based on **PT1–PT4** dyes measured at -0.70 V bias in the dark. The lines of (a) and (b) show theoretical fits using the equivalent circuits (c).

and **PT2** are 324, 385, 484 and 727 mV, respectively, which are completely consistent with the sequence of the electron lifetime.

3. Conclusions

In summary, a series of new sensitizers (**PT1–PT4**) containing [1,2,5]thiadiazolo[3,4-*c*]pyridine moiety as the auxiliary acceptor were designed and synthesized. By replacing the triphenylamine unit with *N*,*N*-diphenylthiophen-2-amine, the absorption range was further broadened. Their absorption spectra, electrochemical and photovoltaic properties and photovoltaic performance were fully characterized. Electrochemical measurement data indicate that the tuning the LUMO and HOMO energy levels can be conveniently accomplished by tuning the donor and π -bridge moiety. All of these dyes were employed as sensitizers for DSSC photovoltaic performance test, **PT2**-based DSSC showed the best conversion efficiency of 6.11% (J_{sc} =12.61 mA cm⁻², V_{oc} =668 mV, FF=0.74) after treatment with 20 mM CDCA under standard global AM 1.5 solar light condition.

4. Experimental

4.1. Instruments and characterization

A Brücker AM 400 spectrometer was employed to obtain ¹H NMR and ¹³C NMR spectra. Mass spectra were measured using an

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ESI mass spectrometer. A Varian Cary 500 spectrophotometer was utilized to measure the UV—vis spectra. The cyclic voltammograms of dyes were obtained with a Versastat II electrochemical work-station (Princeton applied research) using a normal three-electrode system (a Pt working electrode, a Pt wire counter electrode, and a regular calomel reference electrode in saturated KCl solution).

The photovoltaic characterization was performed on the setup that constitutes a 450 W Xenon lamp (Oriel), a Schott K113 Tempax sunlight filter (Präzisions Glas & Optik GmbH), and a source meter (Keithley 2400), which applies potential bias and measures the photogenerated current. IPCE was measured using an SR830 lockin amplifier, a 300 W xenon lamp (ILC Technology) and a Gemini-180 double monochromator (Jobin-Yvon Ltd.). The EIS measurements were carried out using a Zahner IM6e Impedance Analyzer (ZAH-NER-Elektrik GmbH & CoKG, Kronach, Germany) under the applied voltage bias of -0.70 V. The frequency range is 0.1 Hz-100 kHz and the magnitude of the alternating signal is 10 mV.

4.2. Fabrication of dye-sensitized solar cells

Two layers of Dyesol 90-T TiO₂ paste and a scattering layer were screen-printed onto the FTO glass and sintered up to 500 °C. After the treatment of 40 mM TiCl₄ in deionized water at room temperature for 12 h, the photoanode was calcinated at 450 °C for 30 min. The photoanodes were cooled down to 80 °C and immersed in a solution of CDCA with different concentrations in ethanol for 6 h before in a 3×10^{-4} M dye bath in CH₂Cl₂ solution for 12 h at room temperature. After rinsed with ethanol, the dye-sensitized photoanodes were sealed with platinized counter electrode. Surlyn (Dupont, 25-µm-thick) was used as a binder and a spacer. The electrolytes were introduced to the cells via pre-drilled holes in the counter electrodes. The compositions of the electrolyte were as follows: 0.05 M iodine, and 0.5 M lithium iodide in acetonitrile/3-methoxypropionitrole (7:3, v/v). The active area of DSSCs was 0.25 cm².

4.3. Materials and reagents

Fluorine-doped SnO₂ conducting glass (FTO glass, transparency >90%, sheet resistance 15 Ω /sq) was obtained from the Geao Science and Educational Co. Ltd. of China. Acetonitrile, tetra-*n*-butyl ammonium hexafluorophosphate (TBAPF₆), 4-*tert*-butylpyridine (4-TBP), and lithium iodide were bought from Fluka and iodine (99.999%) was purchased from Alfa Aesar. The starting materials *N*,*N*-diphenyl-4-(tributylstannyl)aniline and *N*,*N*-diphenyl-5-(tributylstannyl)thiophen-2-amine were prepared according to published procedures.²⁷ All other solvents and chemicals used in this work were of reagent grade and used without further purification.

4.4. 2,5-Dibromopyridine-3,4-diamine (1)

The mixture of 3,4-diaminopyridine (5.45 g, 50 mmol) with 48% hydrobromic acid (24 mL) in a 50 mL flask was heated to reflux while stirring. After adding bromine (8 mL, 155.7 mmol) dropwise, the reaction mixture was heated for 16 h at 80 °C then cooled down to the room temperature. The mixture was filtered and washed with a saturated solution of Na₂S₂O₃ (150 mL), NaHCO₃ (150 mL) and finally water (150 mL). The residue was first purified by flash chromatography using PE (petroleum ether)/EA (ethyl acetate)=1:2 (v/v) as eluent and recrystallized in ethanol to give 4 g orange solid. (Yield: 30%). ¹H NMR (400 MHz, DMSO-*d*₆, ppm): δ =7.53 (s, 1H), 5.99 (s, 2H), 5.05 (s, 2H); ¹³C NMR (100 MHz, DMSO-*d*₆, ppm): δ =140.66, 140.45, 129.81, 128.30, 106.24.; HRMS (ESI, *m/z*): [M+H]⁺ calcd for (C₅H₅N₃Br₂), 264.8850; found, 264.8844.

4.5. 7-Bromo-4-chloro-[1,2,5]thiadiazolo[3,4-c]pyridine (2)

The mixture of 2,5-dibromopyridine-3,4-diamine (2 g, 7.5 mmol) with 40 mL thionyl chloride in a 100 mL flask was heated to reflux for 16 h then cooled to the room temperature. The excess of thionyl chloride was evaporated and the crude product was dissolved with 15 mL CH₂Cl₂. The CH₂Cl₂ layer was washed using a saturated solution of NaHCO₃ (50 mL) and water (50 mL). The organic layer was dried with MgSO₄ and the solvent was removed under reduce pressure. The residue was purified by flash chromatography using PE (petroleum ether)/DCM (dichloromethane)=2:1 (v/v) to obtain 1.57 g of pale yellow needles. (Yield: 84%). ¹H NMR (400 MHz, CDCl₃, ppm): δ =8.56 (s, 1H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ =156.10, 148.48, 145.19, 144.62, 110.88; HRMS (ESI, *m/z*): [M+H]⁺ calcd for (C₅H₂N₃SClBr), 249.8841; found, 249.8855.

4.6. 4-(7-Bromo-[1,2,5]thiadiazolo[3,4-c]pyridin-4-yl)-*N*,*N*-diphenylaniline (3)

A mixture of compound 2 (498 mg, 2 mmol), N,N-diphenyl-4-(tributylstannyl)aniline (1.1 g, 2.1 mmol), 20 mg bis(triphenylphosphine)palladium(II) dichloride (PdCl₂(PPh₃)₂) in 20 mL of argon-saturated dimethylformamide (DMF) was heated to 95 °C under Ar for 12 h. After cooling to room temperature, the mixture was poured into 100 mL of water and extracted with CH_2Cl_2 (3×20 mL). The combined organic layers were washed with water and brine, dried with anhydrous MgSO₄ and the solvent was removed under reduce pressure. The crude product was purified by flash chromatography with (PE/DCM=2:1 to 1:1, v/v) to yield 687 mg red solid. Yield: 75%. ¹H NMR (400 MHz, CDCl₃, ppm): δ=8.74 (s, 1H), 8.48 (d, J=8 Hz, 2H), 7.43–7.30 (m, 4H), 7.21–7.16 (m, 6H), 7.14–7.10 (m, 2H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ =156.65, 152.38, 149.41, 146.79, 130.94, 129.16, 128.14, 125.28, 123.67, 122.24, 121.19, 113.69, 107.92; HRMS (ESI, m/z): $[M+H]^+$ calcd for (C₂₃H₁₆N₄SBr), 459.0279; found, 459.0275.

4.7. 5-(4-(4-(Diphenylamino)phenyl)-[1,2,5]thiadiazolo[3,4-*c*] pyridin-7-yl)thiophene-2-carbaldehyde (4)

5-Formylthiophen-2-ylboronic acid (156 mg, 1.0 mmol), Pd(PPh₃)₄ (20 mg) and 2 M K₂CO₃ (aq, 5 mL) were added into the solution of compound 3 (229 mg, 0.5 mmol) in 15 mL THF. The mixture was heated at 80 °C under Ar for 12 h. The mixture was cooled to room temperature and diluted with 100 mL water and 100 mL of CH₂Cl₂. The organic layer was separated and washed with brine. After drying with anhydrous MgSO₄, the solvent was evaporated. The residue was purified by flash chromatography with PE/DCM=2:1 to 1:1 (v/v) to give a red solid (100 mg). Yield: 41%. ¹H NMR (400 MHz, CDCl₃, ppm): δ=9.99 (s, 1H), 9.03 (s, 1H), 8.60 (d, *J*=8 Hz, 2H), 8.20 (d, *J*=4 Hz, 1H), 7.87 (d, *J*=4 Hz, 1H), 7.35–7.31 (m, 4H), 7.22-7.18 (m, 6H), 7.15-7.12 (m, 2H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ =182.74, 165.14, 155.16, 152.58, 146.68, 144.24, 142.36, 136.43, 130.87, 129.27, 127.63, 125.58, 124.21, 121.01; HRMS (ESI, m/z): $[M+H]^+$ calcd for (C₂₈H₁₉N₄OS₂), 491.1000; found, 491.0992.

4.8. 4-(4-(4-(Diphenylamino)phenyl)-[1,2,5]thiadiazolo[3,4-*c*] pyridin-7-yl)benzaldehyde (5)

Compound **5** was synthesized in a similar way to **4**. The crude product was purified by flash chromatography with PE/DCM=1:1 to 1:2 (v/v) to give a red solid. Yield: 78%. ¹H NMR (400 MHz, CDCl₃, ppm): δ =10.12 (s, 1H), 8.84 (s, 1H), 8.58 (d, *J*=8 Hz, 2H), 8.21 (d, *J*=8 Hz, 2H), 8.07 (d, *J*=4 Hz, 2H), 7.35–7.31 (m, 4H), 7.23–7.20 (m, 6H), 7.14–7.11 (m, 2H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ =191.62, 156.47, 150.34, 149.43, 146.79, 143.45, 140.71, 135.88, 131.06, 130.01,

129.63, 129.19, 125.75, 124.32, 121.20; HRMS (ESI, m/z): $[M+H]^+$ calcd for (C_{30}H_{21}N_4OS), 485.1436; found, 485.1435.

4.9. 5-(7-Bromo-[1,2,5]thiadiazolo[3,4-*c*]pyridin-4-yl)-*N*,*N*-diphenylthiophen-2-amine (6)

A mixture of compound **2** (498 mg, 2 mmol), *N*,*N*-diphenyl-5-(tributylstannyl)thiophen-2-amine (1.08 g, 2.0 mmol), PdCl₂(PPh₃)₂ (20 mg) in 20 mL of argon-saturated DMF was heated at 95 °C under Ar for 12 h. After cooling to room temperature, the mixture was poured into 100 mL of water and extracted with CH₂Cl₂ (3×20 mL). The combined organic layers were washed with water and brine, dried with anhydrous MgSO₄ and the solvent was removed under reduce pressure. The crude product was purified by flash chromatography with PE/DCM=2:1 to 1:1 (v/v) to yield 687 mg purple solid. Yield: 85%. ¹H NMR (400 MHz, CDCl₃, ppm): δ =8.47 (d, *J*=8 Hz, 1H), 8.45 (s, 1H), 7.35–7.33 (m, 4H), 7.31–7.29 (m, 4H), 7.19–7.16 (m, 2H), 6.58 (d, *J*=4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ =156.25, 147.83, 146.45, 144.61, 133.38, 129.61, 129.26, 125.35, 124.96, 123.20, 115.84; HRMS (ESI, *m/z*): [M+H]⁺ calcd for (C₂₁H₁₄N₄S₂Br), 464.9843; found, 464.9846.

4.10. 5-(4-(5-(Diphenylamino)thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-c]pyridin-7-yl)thiophene-2-carbaldehyde (7)

5-Formylthiophen-2-yl boronic acid (156 mg, 1.0 mmol), Pd(PPh₃)₄ (20 mg) and 2 M K₂CO₃ (aq, 5 mL) were added into the solution of compound 6 (232 mg, 0.5 mmol) in 15 mL THF. The mixture was heated at 80 °C under Ar for 12 h. The solution was cooled to room temperature, and extracted with 100 mL water and 100 mL of CH₂Cl₂. The organic layer was separated and washed with brine. After drying with anhydrous MgSO₄, the solvent was evaporated. The residue was purified by flash chromatography with PE/DCM=2:1 to 1:1 (v/v) to give a purple solid (136 mg). Yield: 55%. ¹H NMR (400 MHz, CDCl₃, ppm): δ =9.96 (s, 1H), 8.76 (s, 1H), 8.56 (d, J=4 Hz, 1H), 8.12 (d, J=4 Hz, 1H), 7.84 (d, J=4 Hz, 1H), 7.39–7.36 (m, 4H), 7.34–7.32 (m, 4H), 7.22–7.19 (m, 2H), 6.60 (d, J=4 Hz, 1H); ¹³C NMR(100 MHz, CDCl₃, ppm): δ=182.67, 160.74, 154.88, 148.34, 148.01, 146.46, 146.00, 142.69, 134.66, 129.61, 125.40, 125.09, 116.70, 115.54; HRMS (ESI, m/z): $[M+H]^+$ calcd for (C₂₆H₁₇N₄OS₃), 497.0565; found, 497.0532.

4.11. 4-(4-(5-(Diphenylamino)thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-c]pyridin-7-yl)benzaldehyde (8)

Compound **8** was synthesized in similar way to **7**. The crude product was purified by flash chromatography with PE/DCM=1:1 to 1:2 (v/v) to give a purple solid. Yield: 77%. ¹H NMR (400 MHz, CDCl₃, ppm): δ =10.09 (s, 1H), 8.58 (s, 1H), 8.56 (d, *J*=4 Hz, 1H), 8.15 (d, *J*=8 Hz, 2H), 8.03 (d, *J*=8 Hz, 2H), 7.39–7.36 (m, 4H), 7.35–7.32 (m, 4H), 7.21–7.17 (m, 2H), 6.62 (d, *J*=4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ =195.82, 159.82, 156.04, 148.74, 146.63, 143.70, 140.90, 134.09, 129.92, 129.03, 124.92, 122.23, 115.85; HRMS (ESI, *m*/*z*): [M+H]⁺ calcd for (C₂₈H₁₉N₄OS₂), 491.1000; found, 491.0977.

4.12. 2-Cyano-3-(5-(4-(4-(diphenylamino)phenyl)-[1,2,5]thiadiazolo-[3,4-*c*]pyridin-7-yl)thiophen-2-yl)acrylic acid (PT1)

Cyanoacetic acid (85 mg, 1 mmol) and ammonium acetate (120 mg) were added into the solution of compound **4** (98 mg, 0.2 mmol) in acetic acid (10 mL). The reaction mixture was heated to reflux under Ar for 12 h. The solution was cooled to room temperature and diluted with 100 mL of water and 100 mL of CH₂Cl₂ was added. The organic layer was separated and washed with brine and water. After drying with anhydrous MgSO₄, the solvent was evaporated. The residue was purified by flash chromatography with

DCM/ethanol=10;1 (v/v) to yield 87 mg red solid. Yield: 76%. ¹H NMR (400 MHz, THF-*d*₈, ppm): δ =9.02 (s, 1H), 8.66 (d, *J*=8 Hz, 2H), 8.32 (s, 1H), 8.20 (d, *J*=4 Hz, 1H), 7.90 (d, *J*=4 Hz, 1H), 7.24–7.20 (m, 4H), 7.10–7.08 (m, 4H), 7.04–6.99 (m, 4H); ¹³C NMR (100 MHz, THF-*d*₈, ppm): δ =162.79, 154.41, 151.20, 150.61, 148.72, 144.96, 141.61, 137.23, 130.61, 127.08, 125.12, 123.57, 120.26, 118.07; HRMS (ESI, *m*/*z*): [M+H]⁺ calcd for(C₃₁H₂₀N₅O₂S₂), 558.1058; found, 558.1058. Anal. Calcd for C₃₁H₁₉N₅O₂S₂: C 66.77, H 3.43, N 12.56. Found C 66.58, H 3.52, N 12.39.

4.13. 2-Cyano-3-(4-(4-(diphenylamino)phenyl)-[1,2,5]thiadiazolo-[3,4-c]pyridin-7-yl)phenyl)acrylic acid (PT2)

A procedure similar to that for the dye **PT1** but with compound **5** (96 mg, 0.2 mmol) instead of compound **4** giving the dye **PT2** as a red solid (100 mg, yield: 91%). ¹H NMR (400 MHz, THF-*d*₈, ppm): δ =8.54 (s, 1H), 8.47–8.43 (m, 2H), 8.42 (s, 1H), 8.00–7.95 (m, 4H), 7.20–7.16 (m, 4H), 7.09–7.05 (m, 4H), 7.03–6.99 (m, 4H); ¹³C NMR (100 MHz, THF-*d*₈, ppm): δ =168.31, 156.43, 153.16, 146.88, 143.39, 136.38, 133.02, 129.15, 128.71, 125.67, 124.24, 120.97, 118.20; HRMS (*m/z*): [M+H]⁺ calcd for (C₃₃H₂₂N₅O₂S), 552.1494; found, 552.1491. Anal. Calcd for C₃₃H₂₁N₅O₂S: C 71.85, H 3.84, N 12.70. Found C 71.67, H 3.99, N 12.61.

4.14. 2-Cyano-3-(5-(4-(5-(diphenylamino)thiophen-2-yl)-[1,2,5]-thiadiazolo[3,4-c]pyridin-7-yl)thiophen-2-yl)acrylic acid (PT3)

A procedure similar to that for the dye **PT1** but with compound **7** (100 mg, 0.2 mmol) instead of compound **4** giving the dye **PT3** as a purple solid (93 mg, yield: 82%). ¹H NMR (400 MHz, THF- d_8 , ppm): δ =8.74 (s, 1H), 8.45 (d, *J*=4 Hz, 1H), 8.30 (s, 1H), 8.11 (d, *J*=4 Hz, 1H), 7.88 (d, *J*=4 Hz, 1H), 7.29–7.25 (m, 4H), 7.23–7.21 (m, 4H), 7.10–7.07 (m, 2H), 6.48 (d, *J*=4 Hz, 1H); ¹³C NMR (100 MHz, THF- d_8 , ppm): δ =167.65, 156.82, 146.95, 145.25, 144.76, 142.29, 137.35, 133.65, 129.21, 124.76, 120.30, 115.16; HRMS (*m*/*z*): [M+H]⁺ calcd for (C₂₉H₁₈N₅O₂S₃), 564.0623; found, 564.0623. Anal. Calcd for C₂₉H₁₇N₅O₂S₃: C 61.79, H 3.04, N 12.42. Found C 61.63, H 3.16, N 12.30.

4.15. 2-Cyano-3-(4-(4-(5-(diphenylamino)thiophen-2-yl)-[1,2,5]-thiadiazolo[3,4-c]pyridin-7-yl)phenyl)acrylic acid (PT4)

A procedure similar to that for the dye **PT1** but with compound **8** (100 mg, 0.2 mmol) instead of compound **4** giving the dye **PT4** as a purple solid (94 mg, yield: 84%). ¹H NMR (400 MHz, THF- d_8 , ppm): δ =8.58 (s, 1H), 8.45 (d, *J*=4 Hz, 1H), 8.21 (d, *J*=8 Hz, 2H), 8.11 (d, *J*=8 Hz, 1H), 7.28–7.24 (m, 4H), 7.22–7.20 (m, 4H), 7.09–7.05 (m, 2H), 6.50 (d, *J*=4 Hz, 1H); ¹³C NMR (100 MHz, THF- d_8 , ppm): δ =160.33, 157.29, 154.18, 143.35, 139.33, 133.80, 132.03, 129.15, 127.37, 124.76, 122.00; HRMS (*m*/*z*): [M+H]⁺ calcd for (C₃₁H₂₀N₅O₂S₂), 558.1056; found, 558.1058. Anal. Calcd for C₃₁H₁₉N₅O₂S₂: C 66.77, H 3.43, N 12.56. Found C 66.64, H 3.54, N 12.42.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2014.04.039.

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