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Molecular design of new organic sensitizers based on thieno[1,4]benzothiazine for dye-sensitized solar cells†

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A novel thieno[1,4]benzothiazine donor has been developed for the first time to construct metal-free organic sensitizers, which exhibit dramatically red-shifted absorptions than phenothiazine-based dyes. Under AM 1.5G irradiation, the conversion efficiency of the new dye **TBT-1**-based DSSC (η = 7.6%) approximates to that of the phenothiazine-based **PT-C$_6$**, indicating thieno[1,4]benzothiazine would be a promising electron donor for the construction of organic optoelectronic materials.

Introduction

Dye-sensitized solar cells (DSSCs) have attracted much attentions since Grätzel and coworkers reported Ru-based sensitizers in 1991.[1] At present, DSSCs based on Ru complex sensitizers, such as N3, N719, black dye, and C101, have reached overall photoelectric conversion efficiencies (PCEs) of over 11%.[2] Most recently, a new benchmark for DSSCs with 13% efficiencies has also been made by using a zinc(II) porphyrin dye with the cobalt(II/III) redox shuttle.[3] Compared with metal complexes, metal-free organic sensitizers have many advantages including lower cost, easier preparation and purification, and higher structural flexibility.[4,5] Moreover, organic sensitizers usually show higher molar extinction coefficients than Ru complexes.[5]

   The basic design strategy of organic sensitizers is to construct the donor-π-acceptor (D-π-A) structure.[2e,6] Based on this strategy, a variety of electron donors such as triphenylamine,[7] carbazole,[8] fluorene,[9] indoline,[10] tetrahydroquinoline,[11] and phenothiazine[12] have been employed to develop highly efficient organic dyes. Among various donors, phenothiazine exhibits an especially strong electron-donating ability due to its electron-rich sulfur and nitrogen atoms. Furthermore, its non-planar heteroanthracene structure with a butterfly conformation in the ground state can also inhibit dye aggregation and the intermolecular excimer formation.[12] Recently, a simple

phenothiazine-based dye (**PT-C$_6$**) has been developed and showed a PCE of 8.18%, which exceeds the reference N719 (7.73%) under the same conditions.[12d] However, the relatively short-wavelength absorption band (300–600 nm) hinders the harvest of more lower-energy photons. We conceived that replacing one of the two electron-neutral benzene rings of phenothiazine framework with an electron-rich thiophene would not only endow the resulting thieno[1,4]benzothiazine with stronger electron-donating ability than phenothiazine, which might reduce the band gap of sensitizer and lead to a red-shifted absorption band, but also be favourable to keeping the new dyes slim.[12d] Density functional theory (DFT) calculations demonstrated that the replacement of the benzene ring of phenothiazines by thiophene would reduce molecular HOMO–LUMO energy gaps (Fig. 1).
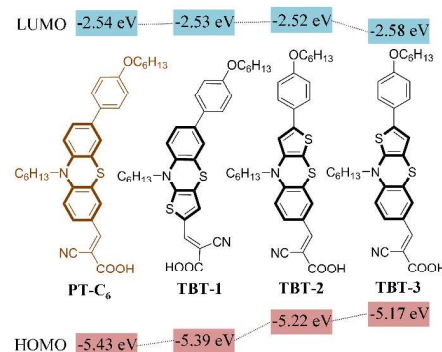
Fig. 1 Calculated HOMO and LUMO energy levels of phenothiazine and thieno[1,4]benzothiazine-based dyes. Alkyl chains were replaced by methyl groups due to their limited contribution to the electronic structures of skeletons.

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Results and discussion

Synthetic routes
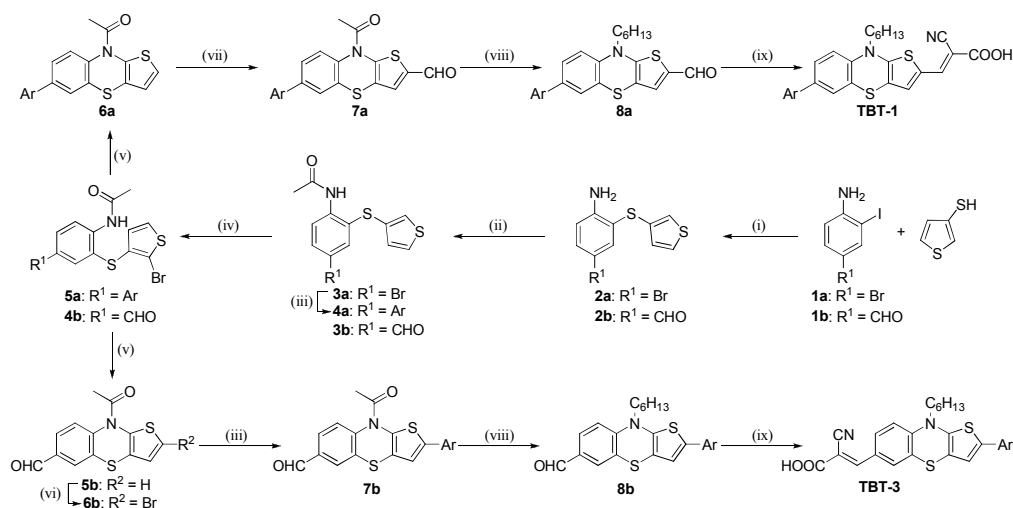
Scheme 1 Synthetic routes for **TBT-1** and **TBT-3**. Reaction conditions: (i) CuI, L-proline, K_3PO_4, EtOH/H_2O. (ii) Acetyl chloride, NEt_3, CH_2Cl_2. (iii) Pd(PPh$_3$)$_4$, K_2CO_3, ArB(OH)$_2$, dioxane/H_2O. (iv) NBS, HOAc/CH_2Cl_2. (v) CuI, N,N-dimethylglycine, K_3PO_4, dioxane or DMF. (vi) NBS, HOAc/CH_2Cl_2. (vii) POCl$_3$, DMF, DCE. (viii) K_2CO_3, DMF/H_2O; K_2CO_3, C_6H_{13}Br, DMF. (ix) Cyanoacetic acid, piperidine, CHCl$_3$. Ar = 4-(hexyloxy)phenyl.

The Scheme 1 shows the synthetic strategy of thieno[1,4]-benzothiazine-based dyes. Thieno[3,2-b][1,4]benzothiazines **6a** and **5b** were synthesized by an intermolecular Cu-catalysed Ullmann coupling of 2-iodoaniline **1a** or **1b** with thiophene-3-thiol, followed by a regioselective bromination at C2-position of thiophene and an intramolecular Ullmann reaction of amide with 2-bromothiophene. The Vilsmeier formylation at C2-position of **6a** and subsequent Knoevenagel condensation reaction with cyanoacetic acid provided **TBT-1**. The bromination of **5b**, Suzuki coupling with 4-(hexyloxy)phenyl boronic acid and Knoevenagel condensation gave **TBT-3**. It is noteworthy that the aldehyde group at C6-position of **5b** needs to be incorporated prior to the construction of the thieno[3,2-b][1,4]benzothiazine framework due to the competition of C6-, C2-, and C3-position formylation. Fortunately, the aldehyde group does not need to be protected throughout the synthetic route of **TBT-3**, which averts extra protection and deprotection steps. The thieno[2,3-b][1,4]benzothiazine-based dye **TBT-2** was obtained by using the similar synthetic strategy (Scheme S1, ESI†).

UV-vis absorption properties

The UV-vis absorption spectra of organic dyes in CH_2Cl_2 solution (1×10^{-5} M) are displayed in Fig. 2a and the detailed spectroscopic data are listed in Table 1. Each of these compounds exhibits two absorption bands, appearing at ca. 300–400 nm and 400–700 nm, respectively. The short-wavelength absorption band is assigned to localized aromatic π-π* transition, and the long-wavelength absorption band to a charge-transfer (CT) transition. Both absorption bands of these new dyes **TBT-1**–**TBT-3** are distinctly red-shifted than that of the phenothiazine-based **PT-C$_6$**, which may be favorable to the

harvest of more lower-energy photons. The molar extinction coefficient of **TBT-3** in the short-wavelength region exceeds 4 $\times 10^4$ M^{-1} cm^{-1}, while the molar extinction coefficient of **TBT-1** in the long-wavelength region exceeds 3×10^4 M^{-1} cm^{-1}, which is greater than that of **PT-C$_6$**. The absorption spectra of **TBT-1**–**TBT-3** on TiO$_2$ films are shown in Fig. 2b. All dyes on the film exhibit a blue-shifted absorption about 18–38 nm with respect to those in solution, which may be attributed to deprotonation of the carboxylic acid and H-type of aggregation.[12e,13]
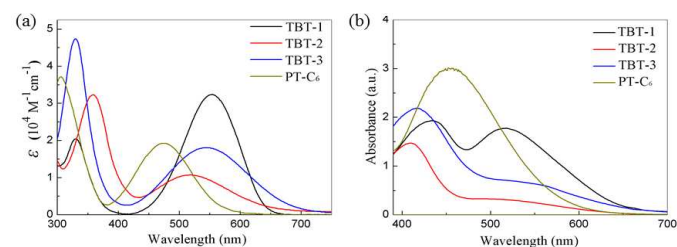
Fig. 2 Absorption spectra of **TBT-1**, **TBT-2**, **TBT-3**, and **PT-C$_6$** (a) in CH_2Cl_2 solution (1×10^{-5} M) and (b) on optically transparent 7 μm thick TiO$_2$ film.

Electrochemical properties

To evaluate the possibility of electron transfer from the photoexcited dyes to the TiO$_2$ conduction band (CB), the electrochemical properties of these new dyes in CH_2Cl_2 were investigated by cyclic voltammetry (Table 1 and Fig. S1, ESI†). The ground oxidation potential (E_{ox}) corresponding to the highest occupied molecular orbital (HOMO) are 0.84, 0.73, and 0.66 V (vs NHE), respectively. The zero−zero band gaps (E_{0-0}) estimated from the onset of the absorption spectra are 1.94,

1.90, and 1.80 eV, respectively. The excited-state oxidation potential (E_{ox}^*) corresponding to the lowest unoccupied molecular orbital (LUMO), calculated from $E_{ox} - E_{0-0}$, are −1.10, −1.17 and −1.14 V, respectively. The HOMO levels of the three dyes (**TBT-1**–**TBT-3**) are more positive than that of I^-/I_3^- redox couple (0.42 V vs NHE), ensuring that the oxidized dyes formed after electron injection into the CB of TiO_2 can regenerated by the electrolyte. Similarly, the LUMO levels of these dyes were more negative than the conduction-band-edge energy level (E_{CB}) of the TiO_2 (−0.5 V vs NHE), indicating a sufficient driving force for electron injection from the oxidized dyes to the TiO_2 films.

Table 1 Photophysical and electrochemical properties of dyes

Dye	λ_{max}^a (nm) (ε [$\times 10^4$ M^{-1} cm^{-1}])		λ_{max}^b (nm)	E_{ox}^c (V)	E_{0-0}^d (Ev)	E_{ox}^{*e} (V)
TBT-1	330(2.04)	554(3.24)	516	0.84	1.94	-1.10
TBT-2	358(3.23)	518(1.07)	500	0.73	1.90	-1.17
TBT-3	330(4.74)	543(1.80)	514	0.66	1.80	-1.14
PT-C$_6$	305(3.71)	475(1.92)	450	-	-	-

[a] Absorption peaks (λ_{max}) and molar extinction coefficients (ε) were measured in CH_2Cl_2 (1×10^{-5} M). [b] Absorption peaks (λ_{max}) were measured on TiO_2 film. [c] Oxidation potential were measured in CH_2Cl_2 containing 0.1 M (n-C$_4$H$_9$)$_4$NPF$_6$ with a scan rate of 100 mV s^{-1} (vs Fc$^+$/Fc). [d] E_{0-0} was determined from the onset of absorption spectrum. [e] $E_{ox}^* = E_{ox} - E_{0-0}$.

Theoretical chemical calculations

DFT calculations were performed at B3LYP/6-31G(d) level with Gaussian 03. The optimized structures of side view and electron density distribution of the HOMOs and LUMOs were shown in Fig. 3. From the optimized structures, the configurations of these three **TBT** dyes all exhibit butterfly shapes which were coincident with **PT-C$_6$**. In addition, the electron density distributions of the HOMOs of these new dyes were found to be largely located on the thiazine core, whereas the electron density distributions of the LUMOs were mostly delocalized on the cyanoacrylic acid segment and partly on the thiazine moiety. The partial orbital overlap between the donor and acceptor would be favorable to the fast charge transition from the HOMO to the LUMO.[14]
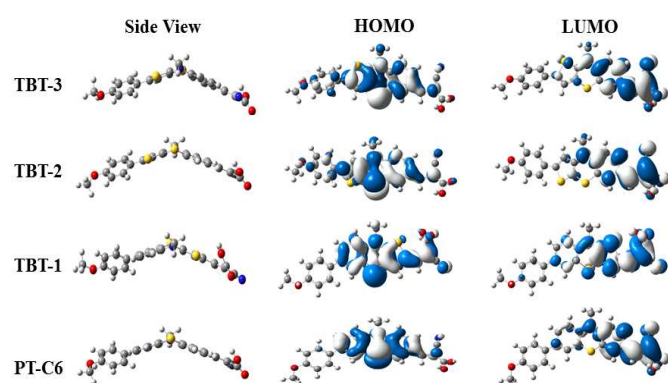

Fig. 3 The optimized geometries and the electron distributions of dyes.

Photovoltaic properties

The DSSCs were fabricated with these thieno[1,4]benzo-thiazine-based dyes on TiO_2 films in conjunction with the I^-/I_3^- electrolyte. The photovoltaic parameters were measured under AM 1.5G standard testing condition (100 mW cm^{-2}) and the photocurrent–voltage (J–V) plots are shown in Fig. 4b. The cell based on **TBT-1** exhibits the highest conversion efficiency (η) of 7.6% (J_{SC} = 19.56 mA cm^{-2}, V_{OC} = 0.64 V, and FF = 0.61) (Table 2). However, the cells based on **TBT-2** and **TBT-3** show much lower PCEs of 3.0% (J_{SC} = 8.79 mA cm^{-2}, V_{OC} = 0.56 V, and FF = 0.61) and 4.1% (J_{SC} = 11.64 mA cm^{-2}, V_{OC} = 0.58 V, and FF = 0.61) under the same condition, respectively (Table 2). The dramatically reduced conversion efficiencies for cells based on **TBT-2** and **TBT-3** can also be predicted by the low IPCE spectra with 45% and 55% at 430 nm, respectively, in contrast to the IPCE of 65% for **TBT-1** (Fig. 4a). Moreover, **TBT-2** and **TBT-3** show poor solubility in most of common solvents, which may be due to molecular aggregation. Therefore, the performances of the DSSCs in the presence of the co-adsorbent chenodeoxycholic acid (CDCA) were studied. However, after addition of CDCA, the PCEs of all the **TBT**-based DSSCs were slightly decreased, which suggested the aggregation is not a main reason for the low PCEs of **TBT-2** and **TBT-3**-based cells. Upon addition of CDCA, the significant decrease of J_{SC} shows that CDCA may lower the adsorption amount of dyes on the TiO_2 surface.[15a,c] Meanwhile, the slightly increased V_{OC} also shows that CDCA can somewhat suppress the aggregation of dyes (Fig. S2, ESI†).[15b,c]

Subsequently, dye adsorption amounts on TiO_2 photoanodes were obtained by using 0.1 M NaOH aqueous-THF (1:1) mixture solutions to desorb the dye on photoanode for 10 min and measuring their UV-vis spectra. The calculated adsorption amount was listed in Table 2 (and see Fig. S3, ESI†). The adsorption amounts of **TBT-1**, **TBT-2**, **TBT-3** and **PT-C$_6$** on TiO_2 are 2.33×10^{-7}, 2.65×10^{-7}, 3.75×10^{-7} and 4.77×10^{-7} mol cm^{-2}, respectively. Notably, although **TBT-1** exhibited the lowest adsorption amount on TiO_2, it has the highest light-absorption intensity (Fig. 2). The light harvesting efficiency (LHE) of dyes, which are calculated from the absorption spectra of dye-loaded 7 μm thick TiO_2 film, also show that **TBT-1** possesses the best LHE among the three **TBT** dyes (Fig. S4, ESI†). Thus, we speculate that this much higher LHE of **TBT-1** compared to those of **TBT-2** and **TBT-3** is one of the main reasons for its relatively good DSSCs performance.
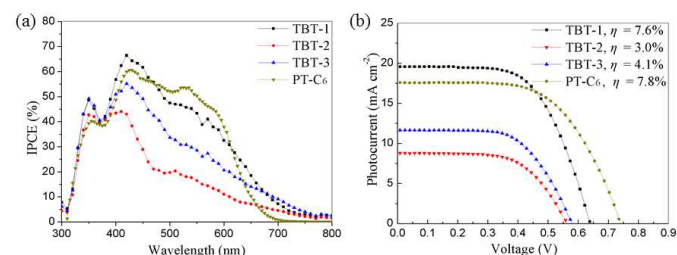
**Fig. 4** (a) IPCE curves. (b) J−V plots under simulated AM 1.5G irradiation.

Table 2 Photovoltaic parameters of DSSCs based on **TBT-1-3** and **PT-C_6** dyes[a]

Dye	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF	η (%)	R_{rec}[b] (Ω cm^{-1})	Dye amount[c] (10^{-7} mol cm^{-2})
TBT-1	19.56	0.64	0.61	7.6	50.6	2.33
TBT-2	8.79	0.56	0.61	3.0	26.1	2.65
TBT-3	11.64	0.58	0.61	4.1	30.9	3.75
PT-C_6	17.57	0.74	0.60	7.8	126.8	4.77

[a] Measured under AM 1.5G irradiation with working area of 0.4×0.4 cm^2 on a FTO substrate at room temperature. Dyes were maintained at 0.5 mM in THF solution for **TBT** dyes and in CH$_2$Cl$_2$ for **PT-C_6**. Electrolyte: LiI (0.1 M), I$_2$ (0.05 M), 1,2-dimethyl-3-propylimidazolium iodide (DMPII, 0.6 M), and 4-*tert*-butylpyridine (0.5 M) in acetonitrile. [b] EIS was performed in the dark conditions under forward bias of −0.73 V and the parameters were fitted from Z-View software. [c] Dyes adsorption amount on TiO$_2$ were obtained by using 0.1 M NaOH aqueous-THF (1:1) mixture solutions to desorb the dye on photoanode for 10 min and recording their UV-vis spectra.

Electrochemical impedance spectroscopy

To get an elucidation of the difference in the value of V_{oc}, electrochemical impedance spectroscopy (EIS) of the **TBT**-based DSSCs was performed in dark conditions under forward bias of −0.73 V and the parameters were fitted from Z-View software (Fig. 5). The calculated R_{rec} values listed in Table 2 show an increasing order of **TBT-2** < **TBT-3** < **TBT-1** < **PT-C_6** which is coincidence with the increased value of V_{oc} in the DSSCs based on these dyes. The first smaller semicircle (R_{ce}) is ascribed to charge transfer at the counter electrode/electrolyte interface, while the second bigger semicircle (R_{rec}) is attributed to charge transfer at the TiO$_2$/dye/electrolyte interface.[13] It is noteworthy that a larger R_{rec} value means a slower charge recombination rate. The suppression of charge recombination improves the V_{oc} value. The **TBT-1** device exhibits the largest R_{rec} among these **TBT** sensitized cells and, thus, is more beneficial for the suppression of charge recombination, which was reflected in its better performance of DSSCs.[12e]
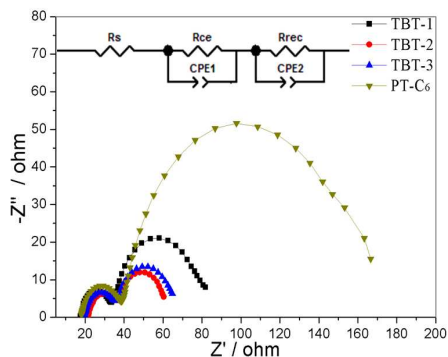
Fig. 5 Electrochemical impedance Nyquist plots of the DSSCs measured under forward bias of −0.73 V in dark conditions.

Conclusion

In summary, we have developed an efficient approach for the synthesis of thieno[1,4]benzothiazine-based sensitizers. The resulting new sensitizers show dramatically red-shifted absorptions than phenothiazine-based dyes, which is favourable to the harvest of more lower-energy photons. Due to the much higher LHE of **TBT-1** compared to those of **TBT-2** and **TBT-3**, the **TBT-1**-based DSSC exhibits the highest conversion efficiency among the three newly designed dyes, which approximate to phenothiazine-based **PT-C_6** under the same fabrication condition. These results indicate that thieno[1,4]benzothiazine is a promising electron donor like phenothiazine, which may also be an ideal candidate for the construction of organic optoelectronic materials.

Experimental section

Materials and reagents

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Pt-counter electrode was purchased from OPV Tech (China) Co., Ltd. Two types of TiO$_2$ films were purchased from OPV Tech (China) Co., Ltd.: 1) A 7 µm thick film of 20 nm TiO$_2$ particles as the absorbing layer coated on a FTO glass substrate with dimensions of 1.0×1.0 cm^2 was used in the determination of absorption spectra of organic dyes; 2) A 13 µm thick film of 20 nm TiO$_2$ particles as the absorbing layer and a 5 µm thick film of 400 nm TiO$_2$ particles as the scattering layer coated on a FTO glass substrate with dimensions of 0.4×0.4 cm^2 were used in the preparation of DSSCs. The reference dye **PT-C_6** was synthesized according to the reported method.[12d]

Analytical characterization

NMR spectra were obtained on a Bruker AV II-400 MHz spectrometer. High-resolution mass spectra (HRMS) were obtained with a Waters-Q-TOF-Premier (ESI). Elemental analyses were performed with an EA Flash 1112 analyzer. Melting points were measured with XRC-1 and are uncorrected. NMR (400 MHz) chemical shifts were measured relative to CDCl$_3$ and DMSO-d_6 as the internal reference (CDCl$_3$: δ = 7.26 ppm; DMSO-d_6: δ = 2.50 ppm). The ^{13}C NMR (100 MHz) chemical shifts were given using CDCl$_3$ or DMSO-d_6 as the internal standard (CDCl$_3$: δ = 77.16 ppm; DMSO-d_6: δ = 39.52 ppm). Absorption spectra in solvent were detected on a HITACHI U-2910 absorption spectrophotometer and absorption spectra on TiO$_2$ film were recorded on a Shimazu UV-3600 absorption spectrophotometer. The cyclic voltammetry (CV) measurements were performed on LK2005A electrochemical workstation.

Fabrication of cells and photovoltaic characterization

The TiO$_2$ photoanode was dipped into the solution containing 0.5 mM dye sensitizers in THF for 36 h. After rinsing with CH$_2$Cl$_2$ and EtOH, the photoanode was adhered with 30 μm thick polyimide tape (*Parafilm*, Sigma-Aldrich) and a square aperture of 0.36 cm^2 was placed on top of the counter electrode. The photoanode and the counter electrode were tightly clipped together to form a cell. Electrolyte was then injected into the seam between the two electrodes. The electrolyte employed was composed of 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII), 0.1 M lithium iodide (LiI), 0.05 M iodine (I$_2$), and 0.5 M 4-*tert*-butylpyridine dissolved in acetonitrile.

Photoelectro-chemical characterizations on the solar cells were performed by using an Oriel Class AAA solar simulator (Oriel 94023A, Newport Corp.). Photo-current-voltage characteristics of the DSSCs were recorded with a potentiostat/galvanostat (Keithley Series 2400 SourceMeter, Keithley Instruments, Inc.) at a light intensity of 100 mW cm^{-2} calibrated by an Oriel reference solar cell (Oriel 91150V, Newport Corp.). The monochromatic quantum efficiency was recorded through a monochromator (Oriel 77890, Newport Corp.) under short-circuit condition. Electrochemical impedance spectroscopy (EIS) was recorded by an Autolab PGSTAT 30/302 electrochemical workstation (Eco Chemie B.V., Amsterdam, the Netherlands) under dark conditions over a frequency range of 0.1−10^5 Hz with an amplitude of −0.73V, and the parameters were fitted from Z-View software (v3.1, Scribner Associates, Inc.)

Synthesis of dye TBT-1[16]

4-Bromo-2-iodoaniline (1a)

This material was prepared according to the reported procedure.[17] In a 50 mL flask, 4-bromoaniline (5.90 g, 34.2 mmol), molecular iodine (4.25 g, 16.8 mmol) and cyclohexane (25.0 mL) were charged and the contents were heated to 50 °C. After confirming the contents become homogeneous, 30% aqueous solution of hydrogen peroxide (1.92 g, 16.8 mmol) was added at the speed of 0.02 mol min^{-1}. Further, the reaction was carried out for 2 hours under stirring, 7.4% (wt%) aqueous solution of Na$_2$SO$_3$ (25.00 g) was added to the reaction mixture. Then the mixture was quenched with water and extracted with EtOAc two times. The combined organic layers were washed with water and dried over anhydrous Na$_2$SO$_4$. After removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (10/1, v/v) as the eluent to give the product as a white solid (6.63g, 65% yield). M.p.: 70-72 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ = 4.11 (s, 2H), 6.62 (d, J = 8.8 Hz, 1H), 7.22 (dd, J = 8.4, 2.4 Hz, 1H), 7.73 (d, J = 2.0 Hz, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ = 84.2, 110.0, 115.7, 132.2, 140.5, 146.1 ppm.

4-Bromo-2-(thiophen-3-ylthio)aniline (2a)

This compound was prepared according to the reported method with some modification.[18] To a mixture of compound **1a** (6.09 g, 20.0 mmol), CuI (384 mg, 2.0 mmol), L-proline (464 mg, 4.0 mmol), and K$_3$PO$_4$·7H$_2$O (10.14 g, 30.0 mmol) in H$_2$O/EtOH (1/1, v/v, 100 mL), thiophene-3-thiol (2.49 g, 21.0 mmol) was added slowly. The mixture was vigorously stirred

and heated at 110 °C for 10 hours. After cooling the solution, EtOH was removed under vacuum. Then the mixture was quenched with water and extracted with EtOAc two times. The combined organic layers were washed with saturated Na$_2$CO$_3$ and water, respectively, dried over anhydrous Na$_2$SO$_4$. After removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (8/1, v/v) as the eluent to give the product as yellow oil (5.28 g, 92% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ = 4.30 (s, 2H), 6.63 (d, J = 8.8 Hz, 1H), 6.90 (dd, J = 4.8 Hz, 1.2 Hz, 1H), 7.01 (dd, J = 2.8 Hz, 1.2 Hz, 1H), 7.24 (dd, J = 8.4 Hz, 2.4 Hz, 1H), 7.31 (dd, J = 4.8 Hz, 2.8 Hz, 1H), 7.51 (d, J = 2.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$) δ = 109.5, 116.9, 118.7, 122.5, 126.9, 128.5, 130.6, 133.2, 137.5, 146.9 ppm. HRMS (ESI$^+$): calcd for C$_{10}$H$_9$BrNS$_2$ [M+H]$^+$ 285.9360, found 285.9362.

N-(4-Bromo-2-(thiophen-3-ylthio)phenyl)acetamide (3a)

2a (25.70 g, 90.0 mmol) was diluted in 150 mL CH$_2$Cl$_2$ together with Et$_3$N (25.0 mL, 180.0 mmol). Acetyl chloride (12.7 mL, 180.0 mmol) was added dropwise at room temperature under strong magnetic stirring overnight. Then the mixture was quenched with water and extracted with CH$_2$Cl$_2$ two times. The combined organic layers were washed with brine and water, respectively, dried over anhydrous Na$_2$SO$_4$. After removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (5/1, v/v) as the eluent to give the product as a white solid (18.90 g, 64% yield). M.p.: 120-122 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.12 (s, 3H), 6.87 (d, J = 4.8 Hz, 1H), 7.10 (d, J = 1.6 Hz, 1H), 7.36 (dd, J = 4.8 Hz, 2.8 Hz, 1H), 7.45 (dd, J = 8.8 Hz, 2.0 Hz, 1H), 7.59 (s, 1H), 8.04 (br. s, 1H), 8.24 (d, J = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 24.9, 116.6, 122.7, 124.39, 124.44, 127.7, 128.7, 129.0, 133.0, 136.5, 137.7, 168.4 ppm. HRMS (ESI$^+$): calcd for C$_{12}$H$_{11}$BrNOS$_2$ [M+H]$^+$ 327.9465, found 327.9471.

N-(4'-(Hexyloxy)-3-(thiophen-3-ylthio)biphenyl-4-yl)acetamide (4a)

A mixture of compound **3a** (8.24 g, 25.0 mmol), 4-(hexyloxy)phenylboronic acid (6.80 g, 30.0 mmol), Pd(PPh$_3$)$_4$ (1.45 g, 1.25 mmol) and K$_2$CO$_3$ (8.63 g, 62.5 mmol) were dissolved in dioxane/H$_2$O (8/1, v/v, 270 mL). Then, the mixture was heated at 85 °C for 12 h under a N$_2$ atmosphere. After cooling the solution, dioxane was removed under vacuum. The reaction mixture was poured into water and extracted with EtOAc two times. The combined organic layers were washed with water and dried over anhydrous Na$_2$SO$_4$. After removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (5/1; v/v) as the eluent to give the product as a white solid (6.39 g, 60% yield). M.p.: 96-98 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.91 (t, J = 6.8 Hz, 3H), 1.32-1.37 (m, 4H), 1.45-1.49 (m, 2H), 1.76-1.83 (m, 2H), 2.13 (s, 3H), 3.98 (t, J = 6.4 Hz, 2H), 6.89 (d, J = 4.4 Hz, 1H), 6.93-6.96 (m, 2H), 7.03 (d, J = 1.6 Hz, 1H), 7.33 (dd, J = 4.8 Hz, 2.8 Hz, 1H), 7.46 (d, J = 8.8 Hz, 2H), 7.57 (dd, J = 8.8 Hz, 2.0 Hz, 1H), 7.73 (d, J = 1.6 Hz, 1H), 8.14 (s, 1H), 8.39 (d, J = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz,

CDCl$_3$): δ = 14.2, 22.8, 24.9, 25.9, 29.4, 31.7, 68.3, 115.0, 121.5, 122.3, 122.7, 127.3, 127.9, 128.3, 128.5, 130.5, 132.0, 132.9, 137.3, 137.6, 159.0, 168.4 ppm. HRMS (ESI$^+$): calcd for C$_{24}$H$_{28}$NO$_2$S$_2$ [M+H]$^+$ 426.1561, found 426.1568.

N-(3-(2-Bromothiophen-3-ylthio)-4'-(hexyloxy)biphenyl-4-yl)acetamide (5a)

To a stirred solution of **4a** (4.35 g, 10.0 mmol) in the mixture of HOAc/CH$_2$Cl$_2$ (1/1, v/v, 160 mL), NBS (1.87 g, 10.5 mmol) was added slowly in portions. After this addition, the mixture was stirred at room temperature for 6 hours. Then the mixture was quenched with water and extracted with EtOAc two times. The combined organic layers were washed with water, saturated Na$_2$CO$_3$ and water, respectively, dried over anhydrous Na$_2$SO$_4$. After removal of the solvent under vacuum, the residue was crystalized by ether/EtOH to give the product as a white solid (4.78 g, 95% yield). M.p.: 102-104 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.91 (t, J = 7.2 Hz, 3H), 1.33-1.37 (m, 4H), 1.44-1.51 (m, 2H), 1.76-1.83 (m, 2H), 2.18 (s, 3H), 3.99 (t, J = 6.4 Hz, 2H), 6.59 (d, J = 6.0 Hz, 1H), 6.94-6.98 (m, 2H), 7.19 (d, J = 5.6 Hz, 1H), 7.47 (d, J = 8.8 Hz, 2H), 7.58 (dd, J = 8.4 Hz, 1.6 Hz, 1H), 7.79 (d, J = 1.6 Hz, 1H), 8.14 (s, 1H), 8.40 (d, J = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 14.2, 22.8, 25.0, 25.9, 29.4, 31.7, 68.3, 111.9, 115.0, 121.5, 121.6, 127.2, 127.9, 128.9, 129.5, 131.86, 131.90, 133.4, 137.2, 137.9, 159.0, 168.5 ppm. HRMS (ESI$^+$): calcd for C$_{24}$H$_{27}$BrNO$_2$S$_2$ [M+H]$^+$ 504.0667, found 504.0669.

1-(6-(4-(Hexyloxy)phenyl)-9H-benzo[b]thieno[2,3-e][1,4]thiazin-9-yl)ethanone (6a)

A mixture of compound **5a** (1.27 g, 2.5 mmol), CuI (48 mg, 0.25 mmol), N,N-dimethylglycine hydrochloride (35 mg, 0.25 mmol) and K$_3$PO$_4$ (1.08 g, 5.0 mmol) were dissolved in DMF (40 mL) under an N$_2$ atmosphere and heated at 135 °C for 20 hours. After cooling, water was added and extracted with CH$_2$Cl$_2$ two times. The combined organic layers were washed with water and dried over anhydrous Na$_2$SO$_4$. After removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (5/1; v/v) as the eluent to give the product as a colourless solid (0.87 g, 82% yield). M.p.: 33-35 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.92 (t, J = 6.8 Hz, 3H), 1.33-1.38 (m, 4H), 1.44-1.51 (m, 2H), 1.77-1.84 (m, 2H), 2.41 (s, 3H), 3.99 (t, J = 6.4 Hz, 2H), 6.81 (d, J = 5.6 Hz, 1H), 6.95-6.98 (m, 2H), 7.18 (d, J = 5.6 Hz, 1H), 7.29-7.40 (m, 1H), 7.44 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 7.46-7.50 (m, 2H), 7.53 (d, J = 2.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 14.1, 22.7, 23.3, 25.8, 29.3, 31.6, 68.1, 114.9, 123.3, 125.1, 126.0, 128.1, 131.5, 132.7, 136.1, 136.9, 139.8, 159.2, 169.3 ppm. HRMS (ESI$^+$): calcd for C$_{24}$H$_{26}$NO$_2$S$_2$ [M+H]$^+$ 424.1405, found 424.1407.

9-Acetyl-6-(4-(hexyloxy)phenyl)-9H-benzo[b]thieno[2,3-e][1,4]thiazine-2-carbaldehyde (7a)

To a solution of **6a** (425 mg, 1 mmol) and dry DMF (115 μL, 1.5 mmol) in dry dichloroethane (DCE, 6.0 mL) in an ice water bath, POCl$_3$ (185 μL, 2.0 mmol) was added dropwise below 0 °C. The reaction was stirred to room temperature and then heated to 80 °C for 24 hours. The mixture was quenched with diluted NaOH and extracted with CH$_2$Cl$_2$. The organic phase

was washed with water and dried over anhydrous MgSO$_4$. After removal of the solvent under vacuum, the residue was purified by column chromatograph using petroleum ether/EtOAc (5/1, v/v) to give the product as a pale white solid (216 mg, 48% yield). M.p.: 90-92 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.91 (t, J = 7.2 Hz, 3H), 1.33-1.37 (m, 4H), 1.44-1.51 (m, 2H), 1.77-1.84 (m, 2H), 2.44 (s, 3H), 4.00 (t, J = 6.4 Hz, 2H), 6.96-6.99 (m, 2H), 7.24-7.26 (m, 1H), 7.46-7.50 (m, 4H), 7.53 (d, J = 2.0 Hz, 1H), 9.81 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 14.2, 22.8, 23.4, 25.9, 29.3, 31.7, 68.3, 115.1, 125.7, 125.8, 126.5, 128.2, 131.06, 131.09, 131.4, 135.7, 140.0, 140.7, 145.0, 159.5, 169.1, 182.9 ppm. HRMS (ESI$^+$): calcd for C$_{25}$H$_{26}$NO$_3$S$_2$ [M+H]$^+$ 452.1354, found 452.1359.

9-Hexyl-6-(4-(hexyloxy)phenyl)-9H-benzo[b]thieno[2,3-e][1,4]thiazine-2-carbaldehyde (8a)

A mixture of compound **7a** (113 mg, 0.25 mmol) and K$_2$CO$_3$ (173 mg, 1.25 mmol) were dissolved in DMF/H$_2$O (4/1, v/v, 5.0 mL) under an N$_2$ atmosphere and heated to 85 °C overnight. After cooling the solution, the solvent was removed under vacuum. Then, the residue was dissolved in anhydrous DMF under an N$_2$ atmosphere and followed by the addition of n-C$_6$H$_{13}$Br (88 μL, 0.63 mmol). The mixture was kept at 85 °C for 12 hours under an N$_2$ atmosphere. Then the mixture was quenched with water and extracted with EtOAc two times. The combined organic layers were washed with water and dried over anhydrous Na$_2$SO$_4$. After removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (20/1, v/v) as the eluent to give the product as a yellow solid (99 mg, 80% yield). M.p.: 36-38 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.91 (t, J = 7.2 Hz, 6H), 1.30-1.39 (m, 8H), 1.42-1.50 (m, 4H), 1.76-1.88 (m, 4H), 3.74 (t, J = 7.6 Hz, 2H), 3.98 (t, J = 6.4 Hz, 2H), 6.74 (d, J = 8.4 Hz, 1H), 6.92-6.95 (m, 2H), 7.12 (d, J = 2.0 Hz, 1H), 7.13 (s, 1H), 7.24 (dd, J = 8.8 Hz, J = 2.4 Hz, 1H), 7.39-7.43 (m, 2H), 9.54 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 14.0, 14.1, 22.60, 22.64, 25.7, 25.8, 26.4, 29.2, 31.4, 31.6, 51.2, 68.1, 109.0, 114.5, 114.9, 120.8, 125.6, 125.7, 127.4, 130.3, 131.4, 134.4, 137.3, 138.9, 155.8, 158.9, 180.4 ppm. HRMS (ESI$^+$): calcd for C$_{29}$H$_{36}$NO$_2$S$_2$ [M+H]$^+$ 494.2187, found 494.2183.

(E)-2-Cyano-3-(9-hexyl-6-(4-(hexyloxy)phenyl)-9H-benzo[b]thieno[2,3-e][1,4]thiazin-2-yl)acrylic acid (TBT-1)

This compound was prepared according to the reported method with some modification.[19] To a stirred solution of **8a** (49 mg, 0.1 mmol) and cyanoacetic acid (27 mg, 0.3 mmol) in CHCl$_3$ (8.0 mL) was added piperidine (70 μL, 0.75 mmol). The resulting mixture was refluxed for 20 hours under an N$_2$ atmosphere, then cooled to room temperature and acidified with 2 M hydrochloric acid aqueous solution. The solution was extracted with CHCl$_3$. Then the organic phase was washed with water and dried over anhydrous Na$_2$SO$_4$. After removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel using petroleum ether/EtOAc/HOAc (100:50:1, v/v/v) to give the product as a golden solid (40 mg, 71% yield). M.p.: 177-179 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.84-0.89 (m, 6H), 1.29-1.31 (m,

8H), 1.39-1.43 (m, 4H), 1.67-1.77 (m, 4H), 3.82 (t, J = 7.2 Hz, 2H), 3.97 (t, J = 6.4 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 7.03 (d, J = 8.8 Hz, 1H), 7.27 (d, J = 2.0 Hz, 1H), 7.38 (dd, J = 8.4 Hz, J = 2.0 Hz, 1H), 7.48 (s, 1H), 7.54 (d, J = 8.4 Hz, 2H), 8.11 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 13.9, 14.0, 22.0, 22.1 25.2, 25.4, 25.6, 28.7, 30.7, 31.1, 50.9, 67.5, 89.6, 108.9, 114.8, 115.8, 117.7, 119.5, 122.6, 124.7, 125.5, 127.2, 130.2, 136.4, 137.2, 137.6, 145.2, 155.3, 158.5, 164.7 ppm. HRMS (ESI$^+$): calcd for $C_{32}H_{37}N_2O_3S_2$ [M+H]$^+$ 561.2246, found 561.2244. Anal. calcd for $C_{32}H_{36}N_2O_3S_2$ (%): C, 68.54; H, 6.47; N, 5.00; S, 11.43. found: C, 68.35; H, 6.48; N, 5.46; S, 11.17.

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Notes and references

1 B. O'Regan and M. Grätzel, *Nature*, 1991, **353**, 737.

2 (*a*) M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Müller, P. Liska, N. Vlachopoulos and M. Grätzel, *J. Am. Chem. Soc.*, 1993, **115**, 6382; (*b*) M. K. Nazeeruddin, P. Péchy and M. Grätzel, *Chem. Commun.*, 1997, 1705; (*c*) M. K. Nazeeruddin, S. M. Zakeeruddin, R. Humphry-Baker, M. Jirousek, P. Liska, N. Vlachopoulos, V. Shklover, C.-H. Fischer and M. Grätzel, *Inorg. Chem.*, 1999, **38**, 6298; (*d*) F. Gao, Y. Wang, D. Shi, J. Zhang, M. Wang, X. Jing, R. Humphry-Baker, P. Wang, S. M. Zakeeruddin and M. Grätzel, *J. Am. Chem. Soc.*, 2008, **130**, 10720; (*e*) A. Mishra, M. K. R. Fischer and P. Bäuerle, *Angew. Chem., Int. Ed.*, 2009, **48**, 2474.

3 S. Mathew, A. Yella, P. Gao, R. Humphry-Baker, B. F. E. Curchod, N. Ashari-Astani, I. Tavernelli, U. Rothlisberger, M. K. Nazeeruddin and M. Grätzel, *Nat. Chem.*, 2014, **6**, 242.

4 (*a*) B.-G. Kim, K. Chung and J. Kim, *Chem.–Eur. J.*, 2013, **19**, 5220; (*b*) S. Ahmad, E. Guillén, L. Kavan, M. Grätzel and M. K. Nazeeruddin, *Energy Environ. Sci.*, 2013, **6**, 3439.

5 (*a*) A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo and H. Pettersson, *Chem. Rev.*, 2010, **110**, 6595; (*b*) Y.-S. Yen, H.-H. Chou, Y.-C. Chen, C.-Y. Hsu and J. T. Lin, *J. Mater. Chem.*, 2012, **22**, 8734.

6 (*a*) Z. Ning, Y. Fu and H. Tian, *Energy Environ. Sci.*, 2010, **3**, 1170; (*b*) J. N. Clifford, E. Martínez-Ferrero, A. Viterisi and E. Palomares, *Chem. Soc. Rev.*, 2011, **40**, 1635.

7 M. Liang and J. Chen, *Chem. Soc. Rev.*, 2013, **42**, 3453.

8 B. Liu, B. Wang, R. Wang, L. Gao, S. Huo, Q. Liu, X. Li and W. Zhu, *J. Mater. Chem. A*, 2014, **2**, 804.

9 A. Yella, R. Humphry-Baker, B. F. E. Curchod, N. A. Astani, J. Teuscher, L. E. Polander, S. Mathew, J.-E. Moser, I. Tavernelli, U. Rothlisberger, M. Grätzel, M. K. Nazeeruddin and J. Frey, *Chem. Mater.*, 2013, **25**, 2733.

10 Y. Cui, Y. Wu, X. Lu, X. Zhang, G. Zhou, F. B. Miapeh, W. Zhu and Z.-S. Wang, *Chem. Mater.*, 2011, **23**, 4394.

11 Y. Hao, X. Yang, J. Cong, H. Tian, A. Hagfeldt and L. Sun, *Chem. Commun.*, 2009, 4031.

12 (*a*) W. Wu, J. Yang, J. Hua, J. Tang, L. Zhang, Y. Long and H. Tian, *J. Mater. Chem.*, 2010, **20**, 1772; (*b*) S. H. Kim, H. W. Kim, C. Sakong, J. Namgoong, S. W. Park, M. J. Ko, C. H. Lee, W. I. Lee and J. P. Kim, *Org. Lett.*, 2011, **13**, 5784; (*c*) Z. Wan, C. Jia, Y. Duan, L. Zhou, Y. Lin and Y. Shi, *J. Mater. Chem.*, 2012, **22**, 25140; (*d*) Y. Hua, S. Chang, D. Huang, X. Zhou, X. Zhu, J. Zhao, T. Chen, W.-Y. Wong and W.-K. Wong, *Chem. Mater.*, 2013, **25**, 2146; (*e*) Y. Hua, S. Chang, J. He, C. Zhang, J. Zhao, T. Chen, W.-Y. Wong, W.-K. Wong and X. Zhu, *Chem.–Eur. J.*, 2014, **20**, 6300; (*f*) W.-I. Hung, Y.-Y. Liao, C.-Y. Hsu, H.-H. Chou, T.-H. Lee, W.-S. Kao and J. T. Lin, *Chem.–Asian J.*, 2014, **9**, 357; (*g*) W.-I. Hung, Y.-Y. Liao, T.-H. Lee, Y.-C. Ting, J.-S. Ni, W.-S. Kao, J. T. Lin, T.-C. Wei and Y.-S. Yen, *Chem. Commun.*, 2015, **51**, 2152.

13 (*a*) Y. J. Chang and T. J. Chow, *J. Mater. Chem.*, 2011, **21**, 9523; (*b*) Z.-S. Huang, H.-L. Feng, X.-F. Zang, Z. Iqbal, H. Zeng, D.-B. Kuang, L. Wang, H. Meier and D. Cao, *J. Mater. Chem. A*, 2014, **2**, 15365.

14 W. Zeng, Y. Cao, Y. Bai, Y. Wang, Y. Shi, M. Zhang, F. Wang, C. Pan and P. Wang, *Chem. Mater.*, 2010, **22**, 1915.

15 (*a*) K. Hara, Y. Dan-oh, C. Kasada, Y. Ohga, A. Shinpo, S. Suga, K. Sayama and H. Arakawa, *Langmuir*, 2004, **20**, 4205; (*b*) H.-P. Lu, C.-Y. Tsai, W.-N. Yen, C.-P. Hsieh, C.-W. Lee, C.-Y. Yeh and E. W.-G. Diau, *J. Phys. Chem. C*, 2009, **113**, 20990; (*c*) Z. Iqbal, W.-Q. Wu, H. Zhang, P.-L. Hua, X. Fang, D.-B. Kuang, L. Wang, H. Meier and D. Cao, *Dyes Pigm.*, 2013, **99**, 299.

16 Experimental procedures and characterization data of **TBT-2** and **TBT-3** see the Supplementary Information.

17 Y. Takashi, S. Yoshifumi and T. Kazuo, JP 2008/247746, 2008.

18 W. Deng, Y. Zou, Y.-F. Wang, L. Liu and Q.-X. Guo, *Synlett*, 2004, 1254.

19 N. Cai, R. Li, Y. Wang, M. Zhang and P. Wang, *Energy Environ. Sci.*, 2013, **6**, 139.