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## ARTICLE

# Dithienopyrrolobenzothiadiazole-Based Organic Dyes for Efficient Dye-Sensitized Solar Cells

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,  
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Four novel D- $\pi$ -A metal-free organic dyes **DTP1-4** containing a dithienopyrrolobenzothiadiazole (DTPBT) unit were synthesized and applied for dye-sensitized solar cells, where DTPBT was employed as  $\pi$ -spacer for the first time. The photophysical, electrochemical and photovoltaic properties of the dyes were systematically investigated. The dyes **DTP1-4** showed broad absorption spectra and high molar extinction coefficient, resulting in high light harvesting efficiency. In addition, the impacts of donors and thiophene unit as additional  $\pi$ -spacer were also studied. The results showed that the dye **DTP4** with triphenylamine as the donor exhibited better photovoltaic performance than **DTP1-3** with phenothiazine as the donor. Linking position of the thiophene unit to DTPBT unit significantly influenced the photovoltaic performance. A power conversion efficiency of 7.55% with 1 mM CDCA as co-adsorbent under simulated AM 1.5 G illumination was reached by the DSSC sensitized by the dye **DTP4**. These results indicate that the DTPBT-based organic dye is a promising candidate for efficient DSSCs.

## Introduction

In recent years, enormous attention has been paid to the research of dye-sensitized solar cells (DSSCs).<sup>1,2</sup> As we all know, sensitizer, as one of the key component of DSSCs, plays a pivotal role in achieving higher power conversion efficiency. It plays a critical function in light harvesting and electron injection. Up to date, DSSCs incorporating ruthenium based sensitizers and zinc-porphyrin based co-sensitizers have reached high efficiency over 11%<sup>3,4</sup> and 12%<sup>5,6</sup>, respectively.

Metal-free organic dyes have gained a great deal of attention for their unique advantages, such as facile fabrication procedure, high molar extinction coefficients as well as environment-friendliness.<sup>7-10</sup> Overall conversion efficiency of up to 10% has been achieved from liquid DSSCs by employing pure organic dyes.<sup>11,12</sup> The donor- $\pi$ -conjugation-acceptor (D- $\pi$ -A) configuration of the organic dyes is the most researched architecture, owing to its efficient intramolecular charge transfer (ICT) properties. In the past decades, many efforts have focused on the electron donor units like triphenylamine, carbazole, phenothiazine, and indoline.<sup>13-20</sup> At the same time, many groups have explored various  $\pi$ -bridges in the D- $\pi$ -A dyes, such as thiophene, furan, benzene and pyrrole.<sup>21-27</sup> Moreover, some electron-withdrawing groups acting as auxiliary acceptors have been introduced into DSSCs to tune the energy level, broaden the absorption spectra and improve the stability of the device.<sup>28-34</sup>

The  $\pi$ -bridge plays an important role in organic dyes. It links the donor and the acceptor, adjusts the HOMO-LUMO levels and extends the absorption range.<sup>2</sup> Since the  $\pi$ -bridge is the passageway which can facilitate the electron migration from donor to acceptor,

its geometry should be relatively planar rather than distorted. Recently, Cheng et al. synthesized a novel nitrogen-bridged donor-acceptor multifused dithienopyrrolobenzothiadiazole (DTPBT) by intramolecular Cadogan annulation,<sup>35</sup> and used it as a monomer to prepare a copolymer which was successfully applied in polymer solar cells.<sup>36</sup> DTPBT shows good coplanarity and a donor-acceptor-donor structure, which might be expected to be a good  $\pi$ -spacer in the organic dye. Moreover, the large planar structure of DTPBT might be beneficial to enhance the molar extinction coefficient of the dyes, which can increase the light-harvesting ability of the DSSCs. However, to the best of our knowledge, there is no report about DTPBT-based organic dyes for DSSCs.

In this paper, we designed and synthesized four novel D- $\pi$ -A metal-free organic dyes **DTP1-4** with DTPBT unit as a  $\pi$ -spacer (Fig. 1). In order to study the impacts of donors and additional  $\pi$ -spacer, phenothiazine and triphenylamine were introduced as the electron-donor, and thiophene unit was linked to cyanoacrylic acid and *N*-octyl-phenothiazine unit, respectively. In addition, two alkyl chains were incorporated at the *N*-position of the DTPBT unit, which not only might improve the solubility of the dye, but also reduce the intermolecular aggregation and suppress the charge recombination on TiO<sub>2</sub> interface.<sup>37,38</sup> The photophysical, electrochemical and photovoltaic properties of the four dyes were systematically

investigated.

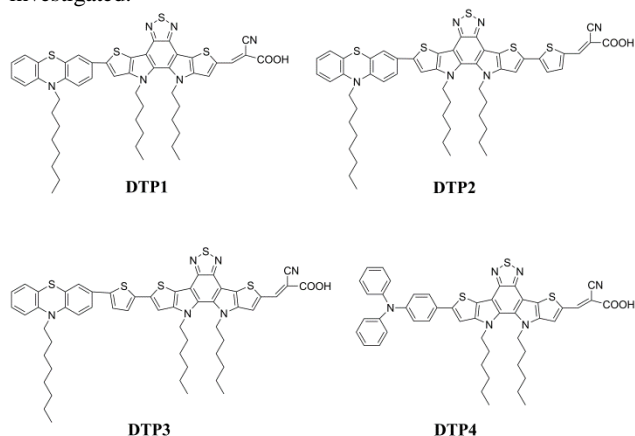
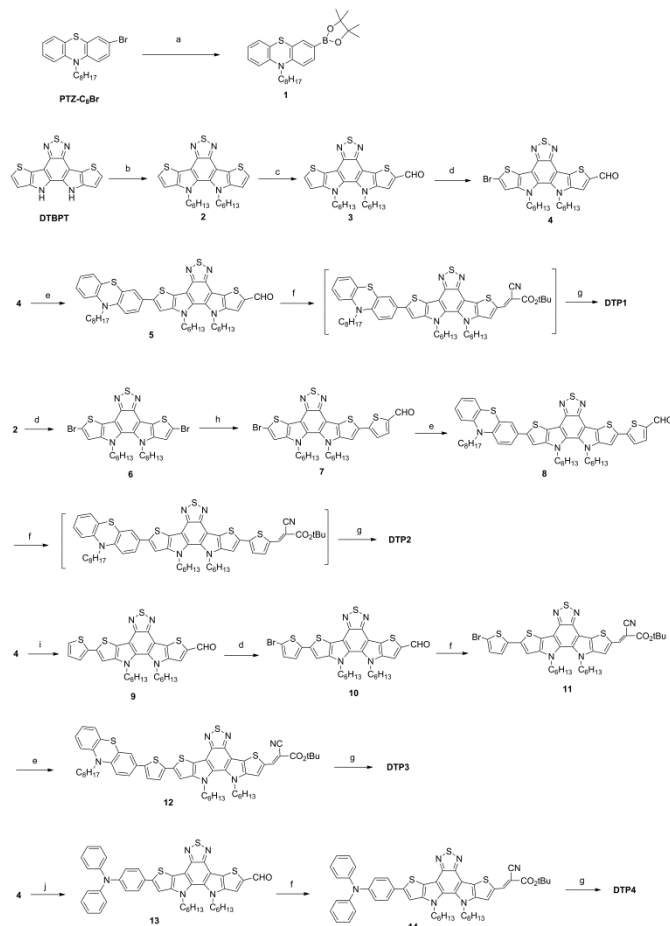


Fig 1. Chemical structures of the sensitizers DTP1-4.

## Results and discussion

### Synthesis of the materials



**Scheme 1** Synthetic route for **DTP1-4**: (a) 4,4,4',4',5,5,5',5'- octamethyl-2,2'-bi(1,3,2-dioxaborolane), KOAc, Pd(dppf)Cl<sub>2</sub>, dioxane; (b) 1-bromohexane, KOH, KI, DMSO; (c) DMF, POCl<sub>3</sub>, 1,2-dichloroethane; (d) NBS, THF; (e) **1**, K<sub>2</sub>CO<sub>3</sub>, Pd(PPh<sub>3</sub>)<sub>4</sub>, THF; (f) *tert*-butyl 2-cyanoacetate, ammonium acetate, acetic acid, toluene; (g) trifluoroacetic acid; (h) (5-formylthiophen-2-yl)boronic acid, K<sub>2</sub>CO<sub>3</sub>, Pd(PPh<sub>3</sub>)<sub>4</sub>, THF; (i) thiophen-2-ylboronic acid, K<sub>2</sub>CO<sub>3</sub>, Pd(PPh<sub>3</sub>)<sub>4</sub>, THF; (j) 4-(diphenylamino)phenylboronic acid, K<sub>2</sub>CO<sub>3</sub>, Pd(PPh<sub>3</sub>)<sub>4</sub>, THF.

The synthetic route of the dyes **DTP1-4** is depicted in Scheme 1. 3-Bromo-10-octyl-10*H*-phenothiazine (PTZ-C<sub>8</sub>Br)<sup>39</sup> and DTPBT<sup>35</sup> were synthesized according to the references. *N*-alkylation of DTPBT gave compound **2**. The aldehyde **3** was prepared from **2** by Vilsmeier-Haack reaction and then converted to **4** through bromination with *N*-bromosuccinimide (NBS). The aldehydes **5**, **9**, **12** and **13** were synthesized by Suzuki-Miyaura reaction. The Knoevenagel condensation reactions of **5** and **13** with *tert*-butyl 2-cyanoacetate afforded their cyanoacetates, respectively. The cyanoacetates were hydrolysed with trifluoroacetic acid to give the target products **DTP1** and **DTP4**, respectively. **DTP2** was prepared from **2** through one bromination reaction, two Suzuki coupling reactions, a Knoevenagel condensation and a hydrolysis reaction. **DTP3** with one thiophene unit between phenothiazine and DTPBT was prepared in a similar manner from **9**. All the new compounds were verified by <sup>1</sup>H NMR, <sup>13</sup>C NMR and HRMS.

In order to determine the *E/Z* geometry of the double bonds in the products of the Knoevenagel condensation reactions, we used the *J*-HMBC method to determine the geometry of the double bond of the intermediate **14** as a model.<sup>40,41</sup> The *J*-HMBC measurement showed that the olefinic proton has a vicinal coupling constant (<sup>3</sup>*J*<sub>CH</sub>) of 5.5 Hz to the carbonyl carbon, which means *cis* standing to the carboxy group (see supporting information). Therefore, the trisubstituted double bond of **14** is *E*-configuration.

### Photophysical properties

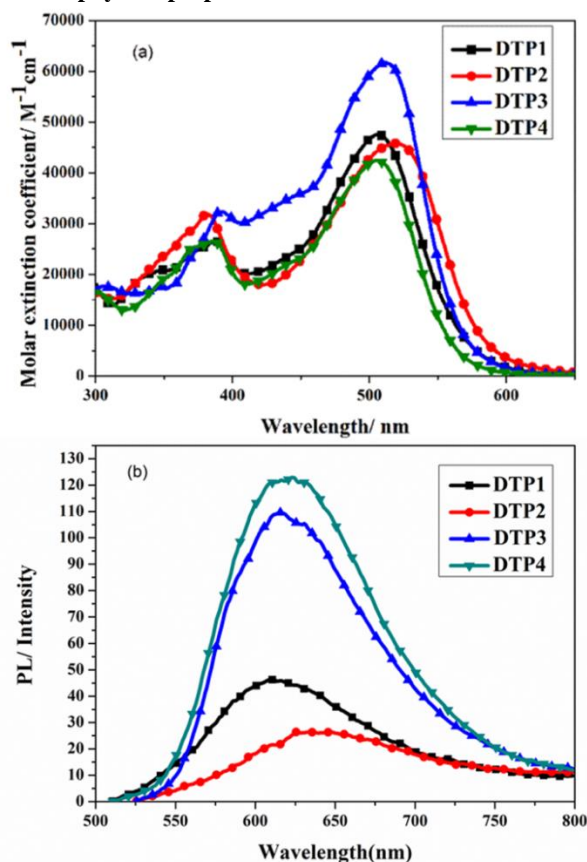


Fig. 2 Absorption spectra (a) and emission spectra (b) of **DTP1-4** in CH<sub>2</sub>Cl<sub>2</sub>/MeOH solutions.

The UV-vis absorption and emission spectra of **DTP1-4** in CH<sub>2</sub>Cl<sub>2</sub>/MeOH (1:1) solution (2 × 10<sup>-5</sup> M) are shown in Fig. 2 and the corresponding photophysical data are listed in Table 1. In the

**Table 1** Photophysical and electrochemical parameters of the dyes **DTP1-4**.

Dye	$\lambda_{max}/nm^a / (\epsilon/M^{-1} cm^{-1})$	$\lambda_{max}$ on TiO <sub>2</sub> (nm)	$\lambda(nm)^b$	HOMO <sup>c</sup> (eV)	LUMO <sup>d</sup> (eV)	$E_{0-0}$ <sup>e</sup> (eV)
<b>DTP1</b>	507(47520)	500	554	-5.06	-2.82	2.24
<b>DTP2</b>	519(45765)	494	568	-5.05	-2.87	2.18
<b>DTP3</b>	512(61680)	476	558	-5.05	-2.83	2.22
<b>DTP4</b>	505(42425)	502	557	-5.19	-2.96	2.23

<sup>a</sup> Absorption maximum of dyes measured in CH<sub>2</sub>Cl<sub>2</sub>/MeOH (1:1) with concentration  $2 \times 10^{-5}$  M.  $\epsilon$ : Molar extinction coefficient at  $\lambda_{max}$ .

<sup>b</sup>  $\lambda$  intersection obtained from the cross point of normalized absorption and emission spectra in CH<sub>2</sub>Cl<sub>2</sub>/MeOH (1:1) solution.

<sup>c</sup> HOMO of the dyes by cyclic voltammetry in 0.1 M tetrabutylammonium perchlorate in MeCN solutions as supporting electrolyte, Ag/AgCl as the reference electrode and Pt as counter electrode, scanning rate: 50 mV s<sup>-1</sup>.

<sup>d</sup> LUMO was calculated by HOMO +  $E_{0-0}$ .

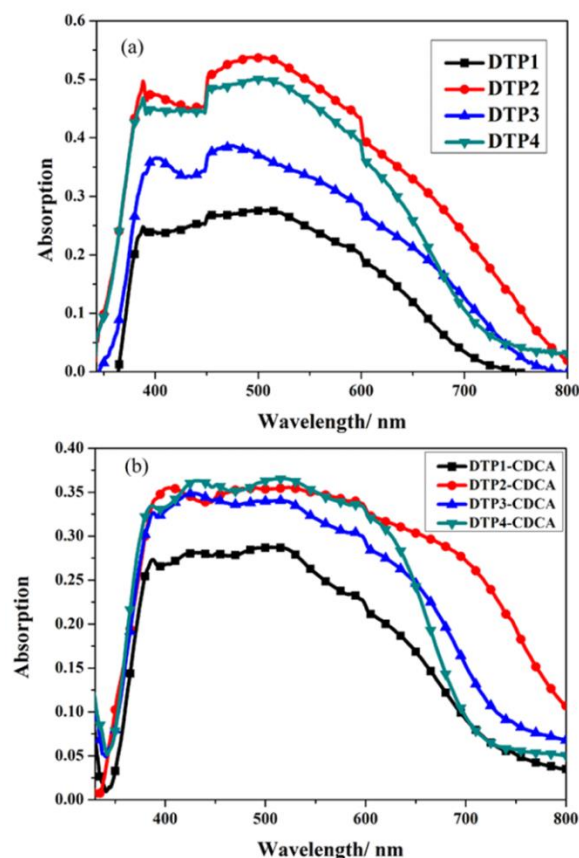
<sup>e</sup>  $E_{0-0} = 1240/\lambda$  intersection.

UV-vis spectra of the dyes in solution, the four dyes exhibit two distinct bands in the range of 300-400 nm and 500-550 nm, respectively. The maximum absorption wavelengths of **DTP1**, **DTP2**, **DTP3** and **DTP4** are 507 (molar extinction coefficient ( $\epsilon$ ) = 47520 M<sup>-1</sup> cm<sup>-1</sup>), 519 ( $\epsilon$  = 45765 M<sup>-1</sup> cm<sup>-1</sup>), 512 ( $\epsilon$  = 61680 M<sup>-1</sup> cm<sup>-1</sup>) and 505 nm ( $\epsilon$  = 42425 M<sup>-1</sup> cm<sup>-1</sup>), respectively. In comparison with **DTP1**, the  $\lambda_{max}$  of **DTP2** and **DTP3** display a red-shift of 12 and 5 nm, respectively. This phenomenon can be ascribed to the inserted thiophene extending the  $\pi$ -conjugation system, which enhances the extent of electron delocalization over the whole molecule. It is worth noting that the four dyes exhibit high molar extinction coefficients from  $4.2 \times 10^4$  to  $6.2 \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup>, which indicates that the four organic dyes have good light-harvesting ability. Additionally, the high values of  $\epsilon$  may be attributed from the incorporation of the large planar structure of DTPBT.<sup>42-44</sup>

The absorption spectra of **DTP1-4** on 16  $\mu$ m thick TiO<sub>2</sub> films are shown in Fig. 3a. Upon adsorption to the TiO<sub>2</sub> films, a broadening spectrum can be found for four dyes compared with the spectrum in the solution, which is beneficial to light-harvesting and  $J_{sc}$  enhancement. In addition, the absorption peaks of **DTP1-4** are observed to be blue-shift about 7, 25, 36 and 3 nm with respect to those in the solution, respectively. Such a hypsochromic shift on the TiO<sub>2</sub> films can be mainly attributed to deprotonation of the carboxylic acid and *H*-type of aggregation.<sup>19</sup> Obviously, the absorption bands of **DTP2** (25 nm) and **DTP3** (36 nm) adsorbed on TiO<sub>2</sub> films display larger blue-shifts compared with **DTP1** (7 nm) and **DTP4** (3 nm), which indicates that the two dyes with one thiophene inserted in the  $\pi$ -spacer have a higher degree of  $\pi$ -stacked aggregation on the TiO<sub>2</sub> films.<sup>45</sup> As we all know, chenodeoxycholic acid (CDCA) can work as an anti-aggregation compound in the DSSCs device. Thus, as shown in the Fig. 3b, after adding CDCA as the co-adsorbent on the TiO<sub>2</sub> films, the four dyes present a red-shift of absorption spectra compared with those without CDCA on the TiO<sub>2</sub>. The concentration dependent absorption spectra of the four dyes in the solution were conducted (Fig. S1). When the concentration of the four dyes increased from  $5 \times 10^{-7}$  M to  $5 \times 10^{-5}$  M, bathochromic shifts of the maximum absorption wavelengths were observed, which was due to the aggregation of the organic molecules.<sup>46</sup>

### Electrochemical properties

Cyclic voltammetry (CV) was carried out to investigate the possibility of electron transfer from sensitizer molecule to TiO<sub>2</sub> and the regeneration of sensitizer (Fig. 4, Table 1). The estimated ground state oxidation potentials corresponding to the highest occupied molecular orbital (HOMO) levels of **DTP1-4**, calculated from the equation  $E_{HOMO} = -(E_{ox}(dye) - E_{ox}(Fc/Fc^+) + 4.80)$  eV, are -5.06, -5.05, -5.05 and -5.19 eV, respectively. It is clear that a larger gap between the HOMO level of triphenylamine based dye **DTP4** and I<sup>-</sup>/I<sub>3</sub><sup>-</sup> redox couple (-4.6 eV vs. vacuum)<sup>29</sup> than phenothiazine based dyes **DTP1-3** may imply that the oxidized **DTP4** can be more



**Fig. 3** Absorption spectra of **DTP1-4** on TiO<sub>2</sub> films (a) and with CDCA on TiO<sub>2</sub> films (b).

effectively regenerated. The energy gap  $E_{0-0}$  between HOMO level and LUMO level (2.24 eV, 2.18 eV, 2.22 eV and 2.23 eV for **DTP1**, **DTP2**, **DTP3** and **DTP4**) were calculated from the intersection points of normalized UV-vis absorption and emission spectra of the sensitizers. **DTP2** exhibits the lowest HOMO–LUMO energy gap among the dyes, which, in turn, corresponds well with the red shift of the absorption spectrum. It can be confirmed by the UV–vis absorption spectrum.<sup>47,48</sup> The lowest unoccupied molecular orbitals (LUMO), calculated from HOMO +  $E_{0-0}$ , are, -2.82, -2.87, -2.83 and -2.96 eV for **DTP1**, **DTP2**, **DTP3** and **DTP4**, respectively. Compared with **DTP1**, when the donor is changed from phenothiazine to triphenylamine, **DTP4** exhibits more negative value of HOMO, which may be due to the stronger electron-donating ability of phenothiazine than that of triphenylamine. Similar results were discovered in several pioneer works.<sup>49,50</sup> The LUMO levels of these dyes are much more positive than the titania conduction band

edge ( $-4.0$  eV vs. vacuum),<sup>51</sup> which implies that the electron injection from the excited dyes into  $\text{TiO}_2$  is energetically permitted.

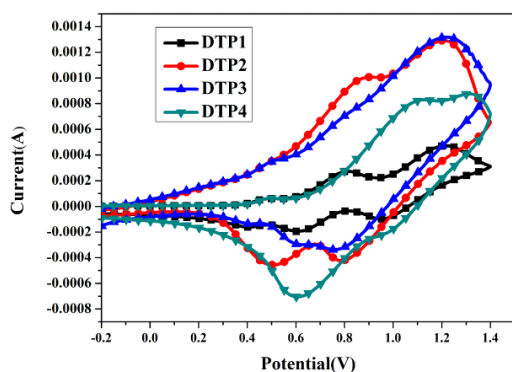


Fig. 4 Cyclic voltammetry of **DTP1-4**.

### Molecular orbital calculations

Density functional theory (DFT) calculations at B3LYP/6-31G\* level with the Gaussian 03W program package were carried out to further understand the geometrical configuration and electron distributions of the four sensitizers (Table 2). According to the optimized structures, the electron distributions in the HOMO levels of the four dyes mainly concentrate on the electron donor and extend to the  $\pi$ -spacer, while predominantly locate on the cyanoacetic acid segment and partly on the DTBPT unit in the LUMO levels. These kinds of electron distributions facilitate electron injection from the dyes to the  $\text{TiO}_2$  surface. In the optimized structures of the four dyes, the DTPBT unit exhibits almost a planar construction. The dihedral angles between DTBPT and phenothiazine or triphenylamine are  $24.52^\circ$  for **DTP1**,  $24.38^\circ$  for **DTP2** and  $25.06^\circ$  for **DTP4**, respectively. The torsional angles between DTBPT and thiophene are  $2.78^\circ$ ,  $9.07^\circ$  for **DTP2** and **DTP3**, respectively. The torsional degree of the entire **DTP2** molecule is less than that of **DTP3**. The result is consistent with the UV-vis absorption spectra in the solution. Compared with **DTP3**, **DTP2** generates a red-shift of CT band about 7 nm. Based on the calculations, we can find that the four dyes exhibit well coplanar geometries, leading to effective  $\pi$ -conjugation throughout the molecules. This can facilitate the charge transfer, while increase the likelihood of dye aggregation and electron recombination.<sup>52</sup>

Time dependent density functional theory (TDDFT) calculations were carried out to understand the electronic transition assignments and excitation energies, and the data are collected in Table S1. Taking **DTP1** as an example, two distinct bands in the absorption spectra are produced from several kinds of electron excitation. The low energy band located at 507 nm is ascribed to HOMO  $\rightarrow$  LUMO (77.7%) and HOMO-1  $\rightarrow$  LUMO (15.8%) transitions. The other band in the range of 350-400 nm is composed of HOMO-1  $\rightarrow$  LUMO (9.8%), HOMO-1  $\rightarrow$  LUMO+1 (16.9%) and HOMO  $\rightarrow$  LUMO+1 (66.7%). From the view of the data, the maximum absorptions of **DTP1-4** mainly come from the transition from HOMO to LUMO and partially from HOMO-1  $\rightarrow$  LUMO. In addition, the simulated  $\lambda_{max}$  of the four dyes have the similar values to the experimental data, which shows the accuracy of this theoretical calculation.

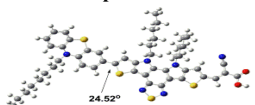
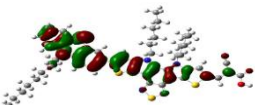

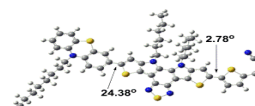
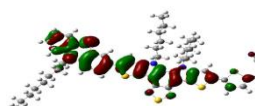
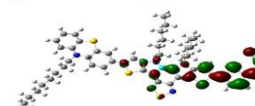
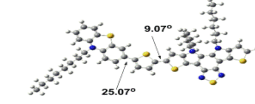
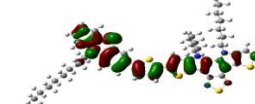

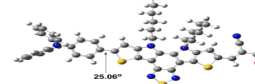


### Adsorption amount

The dye loading amounts of the dyes on  $\text{TiO}_2$  surface ( $16 \mu\text{m}$ ) were obtained by desorbing the dyes from the films by dipping them into an aqueous solution of NaOH and THF (1:1) for 30 min and measuring the absorbance of the desorbed dye solutions (Table 3).<sup>53</sup> The dye loading amounts of **DTP1**, **DTP2**, **DTP3** and **DTP4** are  $3.65 \times 10^{-7}$ ,  $4.46 \times 10^{-7}$ ,  $3.43 \times 10^{-7}$  and  $4.45 \times 10^{-7}$  mol  $\text{cm}^{-2}$ , respectively. **DTP2** and **DTP4** with higher loading amounts than **DTP1** and **DTP3** exhibit stronger UV-vis absorption on the  $\text{TiO}_2$  films. The adsorption amounts of **DTP1** and **DTP3** are lower than that of **DTP4** because the *N*-octyl-phenothiazine and *N*-octyl-phenothiazine-thiophene units have larger molecular configuration than triphenylamine. Although **DTP1** and **DTP3** have similar structure to **DTP2**, their loading amounts are lower because a large configuration moiety near the acceptor decreases adsorption.<sup>54</sup>

### Photovoltaic performance of DSSCs

The photoresponse properties of the device sensitized by **DTP1-4** were evaluated by incident photon-to-current conversion efficiency (IPCE) spectra, as shown in Fig. 5. All the four dyes exhibit a broad spectral response range from 400 to 750 nm, indicating that all the dyes can efficiently convert the visible light into photocurrent. The broad spectral ranges are well agreed with the UV-vis absorption on  $\text{TiO}_2$  films (Fig. 3a). The IPCE value of **DTP4** is over than 70% from 430 to 630 nm with a maximum IPCE value of 78% at 470 nm, which shows a higher IPCE value than the other three dyes. This result is also in good accordance with the  $J_{sc}$  variation obtained in  $J$ -

Table 2 The optimized structure and electron distribution in HOMO and LUMO levels of the dyes **DTP1-4**.

Dye	Optimized structure	HOMO	LUMO
<b>DTP1</b>			
<b>DTP2</b>			
<b>DTP3</b>			
<b>DTP4</b>			

$V$  (current-voltage) measurements. On the other hand, **DTP1**, **DTP2** and **DTP3** get maximum IPCE values of 68% at 480 nm, 49% at 490 nm and 60% at 490 nm, respectively. From the absorption spectra (Fig. 2), **DTP2** and **DTP3** show a good light harvesting ability but

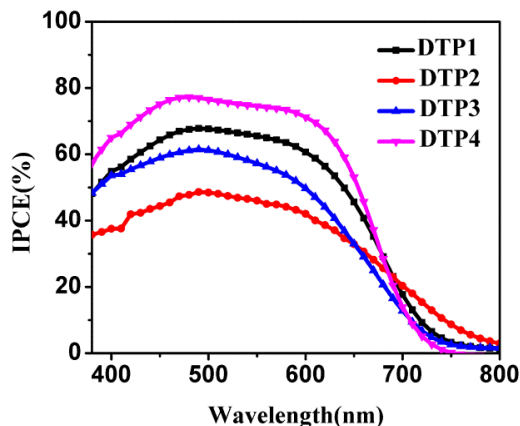


Fig. 5 IPCE spectra of the DSSCs based on DTP1-4.

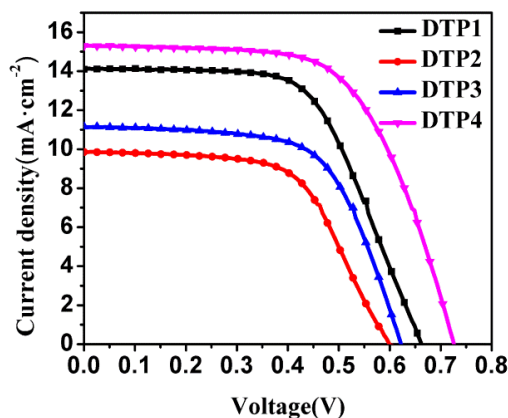


Fig. 6  $J$ - $V$  curves of the DSSCs based on DTP1-4.

lower IPCE values compared to **DTP1** and **DTP4**. IPCE is a product of the electron injection efficiency, light-harvesting efficiency and charge collection efficiency. For a dye-loaded film with the thickness over 10  $\mu\text{m}$ , light harvesting efficiency can be considered to be 100%.<sup>46</sup> Therefore, in comparison with **DTP1** and **DTP4**, the thiophene unit of **DTP2** and **DTP3** caused the significant decrease of IPCE values due to more serious intermolecular aggregation, leading to lower charge injection efficiency.<sup>42</sup> On the basis of aforementioned photo-physical properties analysis, **DTP2** and **DTP3** adsorbed on  $\text{TiO}_2$  show larger blue-shift appearance than **DTP1** and **DTP4** by comparison of  $\lambda_{\text{max}}$  of four dyes in the solution.

**Table 3** Photovoltaic performance parameters of the DSSCs based on **DTP1-4**.

Dye	$J_{\text{sc}}$ (mA $\text{cm}^{-2}$ )	$V_{\text{oc}}$ (mV)	$\eta$ (%)	$FF$	Dye loading amount (mol $\text{cm}^{-2}$ )
<b>DTP1</b>	12.54	664	5.02	0.60	$3.65 \times 10^{-7}$
<b>DTP2</b>	9.86	599	3.54	0.60	$4.46 \times 10^{-7}$
<b>DTP3</b>	11.15	622	4.39	0.63	$3.43 \times 10^{-7}$
<b>DTP4</b>	15.30	726	6.86	0.62	$4.45 \times 10^{-7}$

The detailed photovoltaic parameters of short-circuit photocurrent ( $J_{\text{sc}}$ ), open-circuit photovoltage ( $V_{\text{oc}}$ ), fill factor ( $FF$ ) and overall conversion efficiency ( $\eta$ ) are listed in Fig. 6 and Table 3. The device sensitized by **DTP4** shows the best efficiency of 6.86% with a  $J_{\text{sc}}$  of 15.30  $\text{mA}/\text{cm}^2$ , a  $V_{\text{oc}}$  of 726 mV and an  $FF$  of 0.62. The other three cells based on dyes **DTP1**, **DTP2** and **DTP3** exhibit efficiencies of 5.02%, 3.54% and 4.39%, respectively. In particular, the DSSC based on **DTP4** presents the highest  $\eta$  due to its highest  $J_{\text{sc}}$  and  $V_{\text{oc}}$ . The higher  $J_{\text{sc}}$  of **DTP4** can be ascribed to the higher dye loading capacity, less intermolecular aggregation and more efficient regeneration of the oxidized dye. This result is in good agreement with the IPCE spectra. The highest  $V_{\text{oc}}$  value of **DTP4** can be explained by that triphenylamine unit has the similar structure to the propeller which is better to restrain aggregation and retard charge recombination. Besides, faster regeneration of oxidized **DTP4** molecule than the other three dyes will suppress the back electron transfer from the  $\text{TiO}_2$  to the oxidized dye. **DTP4** with triphenylamine as the donor shows better cell performance than **DTP1** with *N*-octyl-phenothiazine. The reason is that **DTP4** has a larger dye loading amount, and a higher value of HOMO level which ensures efficient regeneration of the oxidized dye. The DSSCs based on **DTP2** displays a relatively poor performance with the lowest values of  $J_{\text{sc}}$  and  $V_{\text{oc}}$ , which may be ascribed to increase of dark current and aggregation. In comparison of the three dyes **DTP1**, **DTP2** and **DTP3**, it is easy to find that when a thiophene ring is inserted, no matter near the acceptor or close to the donor, the overall conversion efficiency is dropped, due to more intermolecular aggregation. Furthermore, this aggregation has deleterious effect on electron transfer from the donor to  $\text{TiO}_2$ .<sup>55,56</sup> In addition, there have been many examples illustrating that dyes with sulfur-containing thiophene units have a stronger interaction with  $I_3^-$ , leading to more facile charge recombination and lower  $V_{\text{oc}}$ .<sup>57</sup> From another perspective, this result suggests that DTPBT is already an efficient  $\pi$ -bridge, and it is no longer necessary to extend the conjugation system by increasing the  $\pi$ -bridge length.

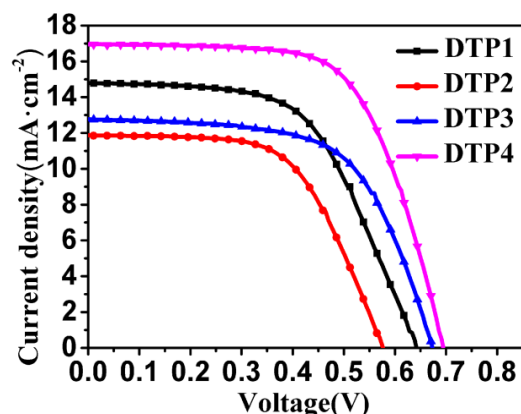


Fig. 7  $J$ - $V$  curves of the DSSCs based on DTP1-4 with 1 mM CDCA.

**Table 4** Photovoltaic performance parameters of the DSSCs based on **DTP1-4** with 1 mM CDCA.

Dye	$J_{\text{sc}}$ (mA $\text{cm}^{-2}$ )	$V_{\text{oc}}$ (mV)	$\eta$ (%)	$FF$
<b>DTP1</b>	14.79	642	5.42	0.57
<b>DTP2</b>	11.87	577	4.07	0.59
<b>DTP3</b>	12.76	673	5.31	0.62
<b>DTP4</b>	16.95	694	7.55	0.64

Due to strong intermolecular interactions,  $\pi$ - $\pi$  stacking of organic dyes always occurs, causing inefficient electron

injection and low power conversion efficiency.<sup>58</sup> It has been verified that CDCA (chenodeoxycholic acid) can prevent the aggregation of dyes, and then improve the performance of the solar cells.<sup>59</sup> Therefore, the performances of the DSSCs in the presence of co-adsorbent CDCA are studied (Fig.7, Table 4). After addition of CDCA, the short-circuit photocurrents and power conversion efficiencies of **DTP1-4** were improved significantly. The apparently enhancement of the DSSC performances is attributed to the hamper of dye aggregation, improving the electron injection efficiency. Suppression of dye aggregation was also supported by the red shift of the absorption spectra of the four dyes on the TiO<sub>2</sub> films when CDCA was added (Fig. 3). As shown in Table 4, a power conversion efficiency of 7.55% ( $J_{sc} = 16.95 \text{ mA cm}^{-2}$ ,  $V_{oc} = 694 \text{ mV}$ ,  $FF = 0.64$ ) for **DTP4** was obtained with 1 mM CDCA as co-adsorbent.

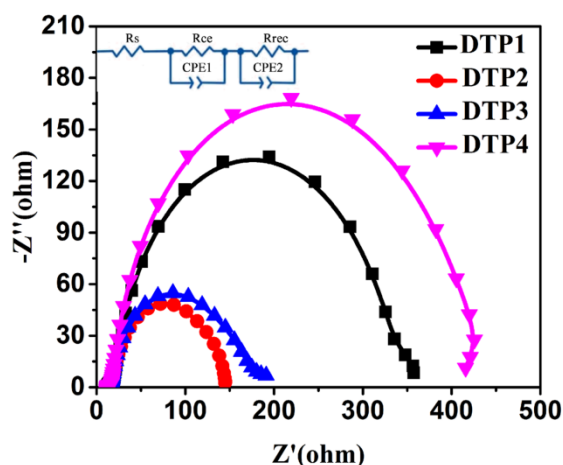


Fig. 8 Electrochemical impedance spectra (Nyquist plot) of the DSSCs based on **DTP1-4** in the dark by using the equivalent circuit (inset).

Table 5 Parameters obtained by fitting the impedance spectra of the DSSCs with **DTP1-4**.

Dye	$R_{ce}$ ( $\Omega \text{ cm}^{-2}$ )	$R_{rec}$ ( $\Omega \text{ cm}^{-2}$ )	CPE2 ( $\mu\text{F}$ )	$\tau_r$ (ms)
<b>DTP1</b>	6.888	330.0	848.7	280.1
<b>DTP2</b>	5.181	128.9	815.4	105.1
<b>DTP3</b>	5.189	160.4	943.9	151.4
<b>DTP4</b>	5.611	409.7	756.7	310.1

To further understand the relationship between the charge transfer process and photovoltaic properties of the DSSCs, electrochemical impedance spectroscopy (EIS) was measured in the dark. The Nyquist plots for the DSSCs based on **DTP1-4** are displayed in Fig. 8, and the corresponding data are listed in Table 5. The first semicircle ( $R_{ce}$ ) is attributed to charge transfer at the counter electrode/electrolyte interface, while the second semicircle ( $R_{rec}$ ) is accorded to charge transfer at the TiO<sub>2</sub>/dye/electrolyte interface.<sup>60</sup> Similar  $R_{ce}$  values are obtained in the low frequency region ( $6.888 \Omega \text{ cm}^{-2}$  for **DTP1**,  $5.181 \Omega \text{ cm}^{-2}$  for **DTP2**,  $5.189 \Omega \text{ cm}^{-2}$  for **DTP3** and  $5.611 \Omega \text{ cm}^{-2}$  for **DTP4**) by using the same counter electrode and electrolyte. On the other hand, the diverse dyes adsorbed on the TiO<sub>2</sub> films cause the difference of  $R_{rec}$ . Obviously, the values of the large semicircles decrease in the order of **DTP4** ( $409.7 \Omega \text{ cm}^{-2}$ ) > **DTP1** ( $330.0 \Omega \text{ cm}^{-2}$ ) > **DTP3** ( $160.4 \Omega \text{ cm}^{-2}$ ) > **DTP2** ( $128.9 \Omega \text{ cm}^{-2}$ ). It is known to all, a smaller  $R_{rec}$  indicates a faster charge recombination and a larger dark current.<sup>61</sup> Hence, the largest  $R_{rec}$  observed in **DTP4**

sensitized cells indicates that **DTP4** possesses more effective suppression of the recombination of the injected electron with  $I_3^-$  in the electrolyte. The electron lifetimes calculated by fitting the equation  $\tau_r = R_{rec} \times \text{CPE2}$  (CPE2, chemical capacitance)<sup>62</sup> are 280.1, 105.1, 151.4 and 310.1 ms for **DTP1**, **DTP2**, **DTP3** and **DTP4**, respectively. The trend of electron lifetime is in the order of **DTP4** > **DTP1** > **DTP3** > **DTP2**, which is well in accordance to the  $V_{oc}$  values obtained in  $J-V$  curves. The EIS results show that the thiophene unit may interact with the redox, which drives  $I_3^-$  to approach the TiO<sub>2</sub> surface and facilitates the electron recombination. Moreover, the longer electron lifetime of **DTP4** compared to the other three phenothiazine based dyes is associated with the more effective suppression of the back reaction of the injected electron with  $I_3^-$  in the electrolyte, leading to a higher  $V_{oc}$ .

## Conclusions

In summary, we explored four novel metal-free organic dyes **DTP1-4** with DTPBT unit as  $\pi$ -spacer. The dyes exhibit broad photo-spectral response and high molar extinction coefficients ( $4.2 - 6.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ), resulting in good solar cell performance. Triphenylamine as the electron-donor brings better photovoltaic performance compared with phenothiazine. DTPBT is already an efficient  $\pi$ -bridge by itself, and it is no longer necessary to extend the conjugation system of the dye by increasing the  $\pi$ -bridge length. Introduction of thiophene unit to extend the  $\pi$ -bridge conjugation leads serious intermolecular aggregation and decreases of the electron lifetime. The DTPBT-based dyes have well coplanar geometry and exhibit effective electron separation from HOMO levels to LUMO levels, which is confirmed by DFT and TDDFT calculations. Under standard global AM 1.5 G solar light illumination conditions, the DSSC sensitized by **DTP4** yielded the highest conversion efficiency of 6.86%, and achieved an efficiency of 7.55% with 1 mM CDCA as co-adsorbent. The results indicate that the DTPBT-based organic dyes are promising candidates for efficient DSSCs.

## Experiments

### Materials and instruments

All reagents were purchased from Aladdin, Adamas and J&K. THF and dioxane were distilled over sodium under argon atmosphere; other solvents of reagent-grade were dried over 4A molecular sieve. All reactions were performed under argon and monitored by TLC. The silica gel (200-300 or 300-400 mesh) was used in the column chromatography. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker 400 MHz instrument with the solvents of CDCl<sub>3</sub>, DMSO-*d*<sub>6</sub> and THF-*d*<sub>8</sub>. The melting point was measured on a SGW X-4B microscopic melting point apparatus. The absorption and emission spectra of organic dyes in CH<sub>2</sub>Cl<sub>2</sub>/methanol (v/v=1:1) solution ( $2 \times 10^{-5} \text{ M}$ ) were measured on a Shimadzu UV-2450 spectrophotometer and a Fluorolog III photoluminescence spectrometer, respectively. The absorption spectra of dyes adsorbed on TiO<sub>2</sub> were tested on a UV-3010 spectrophotometer. The dye loading amounts were conducted by desorbing the dyes from TiO<sub>2</sub> films with 0.1 M NaOH in THF/H<sub>2</sub>O (1:1) and measuring UV-Vis spectrum. Electrochemical redox potentials were obtained by cyclic voltammetry (CV), using three electrode cells on an electrochemistry workstation (e-corder (ED 401) potentiostat). The dye adsorbed TiO<sub>2</sub> films were used as working electrodes, the Ag/AgCl (3 M in KCl) as a reference electrode and a platinum wire as the counter electrode. The supporting electrolyte was 0.1 M TBAPF<sub>6</sub> in MeCN. The ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple (4.80 eV vs. vacuum) acted as the standard. The photocurrent-photovoltage characteristics

were performed on a Keithley 2400 source meter under simulated AM 1.5 G (100 mW cm<sup>-2</sup>) illumination with a solar light simulator (Oriel, Model: 91192). The incident photon-to-current conversion efficiency (IPCE) spectra were carried out on a Spectral Products DK240 monochromator from 400 to 800 nm region. The electrochemical impedance spectra (EIS) were measured on Zahner Zennium electrochemical workstation under the dark condition.

### Synthesis of dyes

#### 10-Octyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10H-phenothiazine (1).

To a mixture of 3-bromo-10-octyl-10H-phenothiazine (1.17 g, 3 mmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (1.52 g, 6 mmol), and KOAc (588 mg, 6 mmol) in dioxane, Pd(dppf)Cl<sub>2</sub> (150 mg, 0.2 mmol) was added. The reaction mixture was stirred under argon at 100 °C for 24 h. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, v/v=20:1) to give **1** as a faint yellow liquid in 77% yield (1.01 g). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.49–7.47 (m, 1H), 7.33 (s, 1H), 7.21–7.17 (m, 1H), 7.14–7.12 (m, 1H), 7.01–6.92 (m, 3H), 3.88–3.85 (m, 2H), 1.67–1.64 (m, 2H), 1.35 (m, 2H), 1.26 (s, 12H), 1.18 (m, 8H), 0.81–0.79 (m, 3H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 147.4, 144.1, 134.2, 132.9, 127.6, 127.1, 123.4, 122.9, 122.7, 116.0, 115.3, 83.5, 46.4, 31.0, 28.5, 28.4, 26.0, 25.9, 24.6, 22.0, 13.9. HRMS (ESI, m/z): [M + H]<sup>+</sup> calcd for C<sub>26</sub>H<sub>37</sub>BNO<sub>2</sub>S: 438.2637, found: 438.2640.

#### 10,11-Dihexyl-10,11-dihydrodithieno[2',3':4,5]pyrrolo[3,2-*e*:2'3'-g][2,1,3]benzothiadiazole (2).

To a mixture of DTBPT (1.00 g, 3.06 mmol), 1-bromohexane (3.03 g, 18.3 mmol) and potassium iodide (30 mg, 0.18 mmol) in DMSO (50 mL) was added potassium hydroxide (1.71 g, 30.6 mmol) in one portion under argon. The reaction mixture was stirred for 16 h at 80 °C. After cooling to room temperature, the reaction was quenched by water, extracted with ethyl acetate and washed with water. The combined organic layer was dried over MgSO<sub>4</sub>. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, v/v=10:1) to give **2** as an organic solid in 70% yield (1.06 g), mp 148–150 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.43 (d, *J* = 5.2 Hz, 2H), 7.18 (d, *J* = 5.2 Hz, 2H), 4.50 (t, *J* = 7.8 Hz, 4H), 1.87–1.79 (m, 4H), 1.18–1.09 (m, 12H), 0.79–0.75 (m, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 147.5, 145.5, 132.1, 126.8, 121.2, 111.8, 110.9, 50.4, 31.2, 30.0, 26.3, 22.4, 13.8. HRMS (ESI, m/z): [M + H]<sup>+</sup> calcd for C<sub>26</sub>H<sub>31</sub>N<sub>4</sub>S<sub>3</sub>: 495.1705, found: 495.1711.

#### 10,11-Dihexyl-10,11-dihydrodithieno[2',3':4,5]pyrrolo[3,2-*e*:2'3'-g][2,1,3]benzothiadiazole-2-carbaldehyde (3).

To a solution of **2** (140 mg, 0.28 mmol) and dry DMF (0.11 mL, 1.42 mmol) in 1,2-dichloroethane (15 mL), POCl<sub>3</sub> (0.13 mL, 1.42 mmol) was added slowly over 20 min at 0 °C under argon. Then the bath was heated to 70 °C and maintained for 3 h. After cooling to room temperature, 0.1 M sodium hydroxide aqueous solution (10 mL) was added, and the mixture was extracted three times with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic fractions were washed with brine and dried over MgSO<sub>4</sub>. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, v/v=6:1) to give **3** as a yellow solid in 82.6% yield (121 mg), mp 144–146 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.95 (s, 1H), 7.78 (s, 1H), 7.51 (d, *J* = 5.2 Hz, 1H), 7.19 (d, *J* = 5.2 Hz, 1H), 4.54–4.49 (m, 4H), 1.90–1.81 (m, 4H), 1.20–1.12 (m, 12H), 0.80–0.76 (m, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 182.8, 147.5, 147.2, 146.6, 144.1, 143.2, 135.4, 130.5, 128.8, 128.5, 121.2, 119.5, 113.0, 111.7, 110.0, 50.5, 50.4, 31.2,

30.2, 26.3, 26.3, 22.4, 13.8, 13.8. HRMS (ESI, m/z): [M + H]<sup>+</sup> calcd for C<sub>27</sub>H<sub>31</sub>N<sub>4</sub>OS<sub>3</sub>: 523.1655, found: 523.1659.

#### 8-Bromo-10,11-dihexyl-10,11-dihydrodithieno[2',3':4,5]pyrrolo[3,2-*e*:2'3'-g][2,1,3]benzothiadiazole-2-carbaldehyde (4).

To a solution of **3** (137 mg, 0.26 mmol) in THF (10 mL), NBS (92.6 mg, 0.52 mmol) was added in one portion. The reaction mixture was stirred for 12 h at room temperature, and quenched by water. The solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> for three times, and the combined organic solution was washed with brine and dried over MgSO<sub>4</sub>. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, v/v=6:1) to give **4** as a yellow solid in 65% yield (102 mg), mp 219–221 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.92 (s, 1H), 7.72 (s, 1H), 7.18 (s, 1H), 4.48–4.40 (m, 4H), 1.89–1.80 (m, 4H), 1.25–1.15 (m, 12H), 0.82–0.80 (m, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 182.9, 147.3, 147.1, 144.2, 144.2, 143.4, 135.2, 129.6, 128.8, 121.3, 119.4, 115.3, 114.9, 112.7, 110.2, 50.5, 50.5, 31.2, 30.2, 30.2, 26.3, 26.3, 22.4, 22.4, 13.8. HRMS (ESI, m/z): [M + H]<sup>+</sup> calcd for C<sub>27</sub>H<sub>30</sub><sup>79</sup>BrN<sub>4</sub>OS<sub>3</sub>: 601.0760, found: 601.0766; [M + H]<sup>+</sup> calcd for C<sub>27</sub>H<sub>30</sub><sup>81</sup>BrN<sub>4</sub>OS<sub>3</sub>: 603.0740, found: 603.0750.

#### 10,11-Dihexyl-8-(10-octyl-10H-phenothiazin-3-yl)-10,11-dihydrodithieno[2',3':4,5]pyrrolo[3,2-*e*:2'3'-g][2,1,3]benzothiadiazole-2-carbaldehyde (5).

To a mixture of **4** (150 mg, 0.25 mmol), 10-octyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10H-phenothiazine (131 mg, 0.3 mmol) and K<sub>2</sub>CO<sub>3</sub> aqueous solution (2 M, 0.38 mL) in THF (15 mL), Pd(PPh<sub>3</sub>)<sub>4</sub> (29 mg, 0.025 mmol) was added. The reaction mixture was stirred for 18 h under argon at 70 °C. After cooling to room temperature, the reaction mixture was quenched by water, extracted with CH<sub>2</sub>Cl<sub>2</sub> three times and the combined organic layers were washed with brine then dried over MgSO<sub>4</sub>. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, v/v=6:1) to give **5** as a red solid in 65% yield (135.2 mg), mp 149–151 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.87 (s, 1H), 7.68 (s, 1H), 7.37 (s, 1H), 7.33–7.31 (m, 1H), 7.19–7.14 (m, 2H), 7.08 (s, 1H), 6.96–6.92 (m, 1H), 6.87–6.85 (m, 1H), 6.80–6.78 (m, 1H), 4.49–4.39 (m, 4H), 3.85 (t, *J* = 6.8 Hz, 2H), 1.87–1.78 (m, 6H), 1.46–1.41 (m, 2H), 1.26–1.24 (m, 20H), 0.89–0.82 (m, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 182.7, 147.3, 147.3, 146.6, 146.2, 144.8, 144.6, 144.0, 143.0, 135.3, 129.5, 129.1, 128.9, 127.4, 127.4, 125.1, 124.4, 123.8, 122.6, 119.6, 119.4, 115.5, 115.4, 112.8, 109.8, 105.9, 50.4, 50.3, 47.6, 31.8, 31.3, 30.3, 29.70, 29.2, 27.0, 26.8, 26.4, 22.6, 22.5, 14.1, 13.9. HRMS (APCI, m/z): [M + H]<sup>+</sup> calcd for C<sub>47</sub>H<sub>54</sub>N<sub>5</sub>OS<sub>4</sub>: 832.3206, found: 832.3206.

#### 2,8-Dibromo-10,11-dihexyl-10,11-dihydrodithieno[2',3':4,5]pyrrolo[3,2-*e*:2'3'-g][2,1,3]benzothiadiazole (6).

To a solution of **2** (125 mg, 0.253 mmol) in THF (15 mL), NBS (112 mg, 0.63 mmol) was added in one portion at 0 °C. The flask was wrapped with aluminum foil and stirred for 1 h at 0 °C, and then stirred for another 2 h at room temperature. Water was added to quench reaction. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> for three times. The combined organic solution was washed with brine and dried over MgSO<sub>4</sub>. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, v/v=30:1) to give **6** as a yellow solid in 93.8% yield (155 mg), mp 155–157 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.20 (s, 2H), 4.42–4.39 (m, 4H), 1.83–1.76 (m, 4H), 1.22–1.09 (m, 12H), 0.80–0.77 (m, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 147.1, 143.2, 130.8, 121.2, 115.0, 113.6, 110.7, 50.4, 31.2, 30.1, 26.3, 22.4, 13.8. HRMS (ESI, m/z): [M + H]<sup>+</sup> calcd for C<sub>26</sub>H<sub>29</sub><sup>79</sup>Br<sup>79</sup>BrN<sub>4</sub>S<sub>3</sub>: 650.9916, found: 650.9928; [M + H]<sup>+</sup> calcd for C<sub>26</sub>H<sub>29</sub><sup>79</sup>Br<sup>81</sup>BrN<sub>4</sub>S<sub>3</sub>: 652.9896, found: 652.9895.



**5-(8-Bromo-10,11-dihexyl-10,11-dihydrodithieno[2',3':4,5]pyrrolo[3,2-*e*:2'3'-g][2,1,3]benzothiadiazole-2-yl)thiophene-2-carbaldehyde (7).**

To a mixture of **6** (235 mg, 0.36 mmol), (5-formylthiophen-2-yl)boronic acid (45 mg, 0.29 mmol) and K<sub>2</sub>CO<sub>3</sub> aqueous solution (2 M, 0.54 mL) in THF (15 mL), Pd(PPh<sub>3</sub>)<sub>4</sub> (41.4 mg, 0.036 mmol) was added. The reaction mixture was stirred for 10 h under argon at 70 °C. After cooling to room temperature, the reaction mixture was quenched by water, extracted with CH<sub>2</sub>Cl<sub>2</sub> three times and the combined organic layers were washed with brine, and then dried over MgSO<sub>4</sub>. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, v/v=5:1) to give **7** as a red solid in 40% yield (80 mg), mp 152–154 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.88 (s, 1H), 7.69 (d, *J* = 4.0 Hz, 1H), 7.38 (s, 1H), 7.32 (d, *J* = 4.0 Hz, 1H), 7.22 (s, 1H), 4.50–4.42 (m, 4H), 1.87–1.79 (m, 4H), 1.21–1.12 (m, 12H), 0.82–0.77 (m, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 182.3, 148.2, 147.2, 145.1, 143.6, 141.3, 137.6, 136.6, 132.5, 130.5, 123.7, 122.5, 121.4, 115.0, 114.2, 111.53, 110.7, 110.1, 50.5, 50.5, 31.2, 30.1, 26.3, 26.3, 22.4, 22.4, 13.8. HRMS (ESI, *m/z*): [M + H]<sup>+</sup> calcd for C<sub>31</sub>H<sub>32</sub><sup>79</sup>BrN<sub>4</sub>S<sub>4</sub>: 683.0637, found: 683.0638; [M + H]<sup>+</sup> calcd for C<sub>31</sub>H<sub>32</sub><sup>81</sup>BrN<sub>4</sub>S<sub>4</sub>: 685.0618, found: 685.0612.

**5-(10,11-Dihexyl-8-(10-octyl-10*H*-phenothiazin-3-yl)-10,11-dihydrodithieno[2',3':4,5]pyrrolo[3,2-*e*:2'3'-g][2,1,3]benzothiadiazole-2-yl)thiophene-2-carbaldehyde (8).**

The synthetic procedure for **8** was similar to that of **5** in 43% yield, mp 190–192 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.73 (s, 1H), 7.52–7.51 (m, 1H), 7.35–7.32 (m, 2H), 7.18–7.13 (m, 4H), 7.05 (s, 1H), 6.95–6.92 (m, 1H), 6.86–6.84 (m, 1H), 6.77–6.75 (m, 1H), 4.29–4.23 (m, 4H), 3.80 (t, *J* = 7.1 Hz, 2H), 1.84–1.79 (m, 6H), 1.45–1.40 (m, 2H), 1.25 (m, 20H), 0.89–0.84 (m, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 182.2, 148.2, 147.4, 147.2, 146.0, 145.4, 144.8, 144.8, 144.7, 144.6, 140.9, 137.6, 136.1, 132.4, 130.3, 129.4, 127.4, 127.4, 125.2, 124.4, 123.9, 123.3, 122.5, 122.3, 119.7, 115.4, 111.5, 110.1, 109.9, 106.2, 50.2, 50.2, 47.6, 31.8, 31.4, 31.3, 30.3, 30.3, 29.7, 29.2, 27.0, 26.8, 26.4, 26.4, 22.6, 22.5, 14.1, 13.9. HRMS (APCI, *m/z*): [M + H]<sup>+</sup> calcd for C<sub>51</sub>H<sub>56</sub>N<sub>5</sub>O<sub>5</sub>S<sub>5</sub>: 914.3083, found: 914.3080.

**10,11-Dihexyl-8-(thiophene-2-yl)-10,11-dihydrodithieno[2',3':4,5]pyrrolo[3,2-*e*:2'3'-g][2,1,3]benzothiadiazole-2-carbaldehyde (9).**

The synthetic procedure for **9** was similar to that of **5**, except thiophen-2-ylboronic acid instead of 10-octyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10*H*-phenothiazine, in 76% yield, mp 187–189 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.97 (s, 1H), 7.80 (s, 1H), 7.32 (m, 1H), 7.30–7.29 (m, 1H), 7.24 (s, 1H), 7.10–7.08 (m, 1H), 4.54–4.48 (m, 4H), 1.91–1.82 (m, 4H), 1.23–1.13 (m, 12H), 0.81–0.79 (m, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 182.7, 147.2, 146.1, 144.1, 143.2, 140.1, 138.0, 135.1, 129.8, 128.7, 128.1, 124.8, 123.8, 119.8, 119.4, 112.7, 109.9, 107.5, 50.4, 50.3, 31.3, 30.3, 29.7, 26.4, 22.5, 13.9. HRMS (ESI, *m/z*): [M + H]<sup>+</sup> calcd for C<sub>31</sub>H<sub>33</sub>N<sub>4</sub>O<sub>5</sub>: 605.1532, found: 605.1533.

**8-(5-Bromothiophen-2-yl)-10,11-dihexyl-10,11-dihydrodithieno[2',3':4,5]pyrrolo[3,2-*e*:2'3'-g][2,1,3]benzothiadiazole-2-carbaldehyde (10).**

To a solution of **9** (115 mg, 0.19 mmol) in THF, NBS (41 mg, 0.23 mmol) was added in one portion. The reaction mixture was stirred at 0 °C for 12 h. After that water was added to quench the reaction, and the reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> three times. The combined organic solution was washed by water, and then dried over MgSO<sub>4</sub>. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, v/v=5:1) to give **10** as a deep yellow solid in 92% yield (119 mg), mp 195–197 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.99 (s, 1H), 7.82 (s, 1H), 7.18 (s, 1H), 7.07–7.04 (m, 2H), 4.55–4.48 (m, 4H), 1.92–1.80 (m, 4H), 1.20–1.14 (m, 12H), 0.80–

0.77 (m, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 182.8, 147.4, 147.3, 146.0, 144.3, 143.4, 139.5, 138.8, 135.2, 130.9, 130.3, 128.9, 124.0, 120.2, 119.4, 112.9, 111.5, 110.4, 107.9, 50.5, 50.5, 31.2, 30.2, 26.3, 26.3, 22.4, 13.8. HRMS (ESI, *m/z*): [M + H]<sup>+</sup> calcd for C<sub>31</sub>H<sub>32</sub><sup>79</sup>BrN<sub>4</sub>O<sub>5</sub>: 683.0637, found: 683.0638; [M + H]<sup>+</sup> calcd for C<sub>31</sub>H<sub>32</sub><sup>81</sup>BrN<sub>4</sub>O<sub>5</sub>: 685.0618, found: 685.0625.

**(E)-tert-Butyl-3-(8-(5-bromothiophen-2-yl)-10,11-dihexyl-10,11-dihydrodithieno[2',3':4,5]pyrrolo[3,2-*e*:2'3'-g][2,1,3]benzothiadiazole-2-yl)-2-cyanoacrylate (11).**

A mixture of **10** (133 mg, 0.195 mmol), *tert*-butyl 2-cyanoacetate (82.6 mg, 0.585 mmol), ammonium acetate (45.1 mg, 0.585 mmol) and acetic acid (2 mL) in toluene (15 mL) was stirred under argon at 130 °C for 3 h. After cooling to room temperature, water was added and the reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were dried over MgSO<sub>4</sub> and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, v/v=6:1) to give **11** as a red solid in 89% yield (140 mg), mp 162–164 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.20 (s, 1H), 7.96 (s, 1H), 7.13 (s, 1H), 7.03 (m, 2H), 4.53–4.46 (m, 4H), 1.93–1.76 (m, 4H), 1.60 (s, 9H), 1.23–1.12 (m, 12H), 0.82–0.76 (m, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 162.2, 147.2, 147.1, 146.1, 146.0, 144.9, 139.5, 138.9, 136.1, 135.0, 130.9, 130.0, 129.5, 123.9, 120.1, 118.3, 116.9, 112.8, 111.5, 110.1, 107.7, 97.8, 83.1, 50.5, 50.4, 31.3, 31.2, 30.9, 30.3, 30.1, 29.7, 26.4, 26.3, 22.5, 22.4, 13.9, 13.8. HRMS (APCI, *m/z*): [M + H]<sup>+</sup> calcd for C<sub>38</sub>H<sub>41</sub><sup>79</sup>BrN<sub>5</sub>O<sub>2</sub>S<sub>4</sub>: 806.1321, found: 806.1319; [M + H]<sup>+</sup> calcd for C<sub>38</sub>H<sub>41</sub><sup>81</sup>BrN<sub>5</sub>O<sub>2</sub>S<sub>4</sub>: 808.1304, found: 808.1303.

**(E)-tert-Butyl-3-(5-(10,11-dihexyl-8-(10-octyl-10*H*-phenothiazin-3-yl)thiophen-2-yl)-10,11-dihydrodithieno[2',3':4,5]pyrrolo[3,2-*e*:2'3'-g][2,1,3]benzothiadiazole-2-yl)acrylate (12).**

To a mixture of **11** (110 mg, 0.136 mmol), 10-octyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10*H*-phenothiazine (77 mg, 0.177 mmol) and K<sub>2</sub>CO<sub>3</sub> aqueous solution (2 M, 0.20 mL) in THF (15 mL), Pd(PPh<sub>3</sub>)<sub>4</sub> (21 mg, 0.018 mmol) was added. The reaction mixture was stirred for 18 h under argon at 70 °C. After completion of reaction, the reaction mixture was poured into cold water, extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 20 mL), and dried over MgSO<sub>4</sub>. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, v/v=5:1) to give **12** as a deep yellow solid in 45% yield (63 mg), mp 88–90 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.06 (s, 1H), 7.64 (s, 1H), 7.22–7.21 (m, 2H), 7.18–7.12 (m, 2H), 6.99–6.98 (m, 1H), 6.95–6.90 (m, 3H), 6.84–6.82 (m, 1H), 6.72–6.70 (m, 1H), 4.39–4.30 (m, 4H), 3.78 (t, *J* = 7.1 Hz, 2H), 1.88–1.87 (m, 4H), 1.80–1.75 (m, 2H), 1.58 (s, 9H), 1.42–1.40 (m, 2H), 1.26 (m, 20H), 0.89–0.85 (m, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 162.2, 147.2, 147.1, 146.3, 146.0, 144.7, 144.7, 144.6, 142.5, 140.3, 136.2, 135.8, 135.1, 129.7, 129.6, 128.1, 127.4, 125.1, 124.5, 124.4, 124.0, 123.9, 122.7, 122.5, 119.8, 118.5, 116.9, 115.4, 115.3, 112.9, 109.8, 106.7, 97.3, 83.0, 50.4, 50.3, 47.6, 31.8, 31.4, 31.3, 30.4, 30.2, 29.7, 29.3, 29.2, 28.1, 27.0, 26.8, 26.5, 26.4, 22.7, 22.6, 22.5, 14.1, 14.0, 13.9. HRMS (APCI, *m/z*): [M + H]<sup>+</sup> calcd for C<sub>58</sub>H<sub>65</sub>N<sub>6</sub>O<sub>2</sub>S<sub>5</sub>: 1037.3767, found: 1037.3757.

**8-(4-(Diphenylamino)phenyl)-10,11-dihexyl-10,11-dihydrodithieno[2',3':4,5]pyrrolo[3,2-*e*:2'3'-g][2,1,3]benzothiadiazole-2-carbaldehyde (13).**

The synthetic procedure for **13** was similar to that of **5**, except 4-(diphenylamino)phenylboronic acid instead of 10-octyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10*H*-phenothiazine, in 71% yield, mp 179–181 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.93 (s, 1H), 7.75 (s, 1H), 7.58–7.56 (m, 2H), 7.32–7.28 (m, 5H), 7.17–7.15 (m, 4H), 7.12–7.05 (m, 4H), 4.50–4.49 (m, 4H), 1.87–1.86 (m, 4H), 1.26–1.21 (m, 12H), 0.81–0.79 (m, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 182.7, 147.8, 147.4, 147.4, 147.4, 146.9, 146.9, 144.1,

143.1, 135.4, 129.6, 129.4, 128.9, 128.7, 126.4, 124.8, 123.4, 123.3, 119.8, 119.4, 113.2, 109.8, 106.2, 50.5, 50.4, 31.3, 30.2, 26.4, 22.4, 13.9. HRMS (APCI, m/z): [M + H]<sup>+</sup> calcd for C<sub>45</sub>H<sub>44</sub>N<sub>5</sub>O<sub>5</sub>: 766.2703, found: 766.2695.

**(E)-tert-Butyl 2-cyano-3-(8-(4-(diphenylamino)phenyl)-10,11-dihexyl-10,11-dihydro-[1,2,5]thiadiazolo[3,4-*e*]thieno[2',3':4,5]pyrrolo[3,2-*g*]thieno[3,2-*b*]indol-2-yl)acrylate (14).**

A mixture of **13** (93 mg, 0.105 mmol), *tert*-butyl 2-cyanoacetate (51.4 mg, 0.363 mmol), ammonium acetate (28.0 mg, 0.363 mmol) and acetic acid (2 mL) in toluene (15 mL) was stirred under argon at 130 °C for 3 h. After cooling to room temperature, the reaction was quenched by water and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 20 mL). The organic layer was dried over MgSO<sub>4</sub> and evaporated by reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, v/v=5:1) to give **14** as a black solid in 88% yield (95 mg), mp 223–225 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.08 (s, 1H), 7.69 (s, 1H), 7.52–7.50 (m, 2H), 7.31–7.27 (m, 4H), 7.18 (s, 1H), 7.15–7.13 (m, 4H), 7.09–7.05 (m, 4H), 4.50–4.37 (m, 4H), 1.92–1.84 (m, 4H), 1.57 (s, 9H), 1.26–1.23 (m, 12H), 0.85–0.81 (m, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 162.2, 147.7, 147.6, 147.4, 147.1, 147.1, 145.9, 144.7, 135.7, 135.4, 129.6, 129.5, 129.4, 128.7, 126.5, 124.8, 123.4, 123.3, 119.8, 118.4, 116.9, 113.3, 109.6, 106.3, 97.3, 82.9, 50.5, 31.4, 31.3, 30.3, 30.1, 29.7, 28.1, 26.5, 26.3, 22.5, 22.4, 13.9, 13.9. HRMS (APCI, m/z): [M+H]<sup>+</sup> calcd for C<sub>52</sub>H<sub>53</sub>N<sub>6</sub>O<sub>2</sub>S<sub>3</sub>: 889.3387, found: 889.3381.

**(E)-2-Cyano-3-(10,11-dihexyl-8-(10-octyl-10*H*-phenothiazin-3-yl)-10,11-dihydrodithieno[2',3':4,5]pyrrolo[3,2-*e*:2'3'-*g*] [2,1,3]benzothiadiazole-2-yl)acrylic acid (DTP1).**

A mixture of **5** (120 mg, 0.144 mmol), *tert*-butyl 2-cyanoacetate (61.1 mg, 0.432 mmol), ammonium acetate (33.3 mg, 0.432 mmol) and acetic acid (2 mL) in toluene was stirred under argon at 130 °C for 3 h. After cooling to room temperature, the reaction mixture was quenched by water, extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 20 mL). The organic layer was dried over MgSO<sub>4</sub> and evaporated by reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, v/v=6:1) to give a black solid. The resulting black solid was dissolved in trifluoroacetic acid (15 mL), and stirred at room temperature for 4 h. After that deionized water (100 mL) was added to the mixture, and the resulting black solid **DTP1** was collected by filtration. The black solid was then washed by water (100 mL) three times, and the final product of **DTP1** as a black solid was obtained. The yield for the two steps is 53% (69 mg), mp 240–242 °C. <sup>1</sup>H NMR (400 MHz, THF-*d*<sub>8</sub>) δ 8.24 (s, 1H), 7.86 (s, 1H), 7.49–7.42 (m, 2H), 7.41–7.39 (m, 1H), 7.17–7.11 (m, 2H), 6.96–6.88 (m, 3H), 4.62–4.52 (m, 4H), 3.90–3.87 (m, 2H), 1.99–1.93 (m, 4H), 1.84–1.77 (m, 2H), 1.48–1.43 (m, 2H), 1.30–1.21 (m, 20H), 0.89–0.80 (m, 9H). <sup>13</sup>C NMR (100 MHz, THF-*d*<sub>8</sub>) δ 164.4, 148.4, 148.2, 148.1, 147.4, 147.2, 145.8, 145.8, 145.5, 137.1, 136.2, 130.5, 130.5, 130.1, 128.1, 128.0, 126.3, 125.4, 125.0, 124.6, 123.3, 121.3, 120.5, 117.2, 116.4, 113.9, 110.5, 107.9, 97.3, 51.2, 51.2, 48.1, 32.7, 32.3, 32.2, 31.2, 31.0, 30.2, 30.2, 27.7, 27.7, 27.3, 27.2, 23.5, 23.4, 23.3, 14.4, 14.3, 14.2. HRMS (ESI, m/z): [M – H]<sup>–</sup> calcd for C<sub>50</sub>H<sub>53</sub>N<sub>6</sub>O<sub>2</sub>S<sub>4</sub>: 897.3118, found: 897.3123.

**(E)-2-Cyano-3-(5-(10,11-dihexyl-8-(10-octyl-10*H*-phenothiazin-3-yl)-10,11-dihydrodithieno[2',3':4,5]pyrrolo[3,2-*e*:2'3'-*g*] [2,1,3]benzothiadiazole-2-yl)thiophene-2-yl)acrylic acid (DTP2).**

**DTP2** was synthesized from **8** with the same procedure as that of **DTP1** as a black solid in 50% yield, mp 236–238 °C. <sup>1</sup>H NMR (400 MHz, THF-*d*<sub>8</sub>) δ 8.24 (s, 1H), 7.63–7.62 (m, 1H), 7.60 (s, 1H), 7.47–7.46 (m, 1H), 7.45 (s, 1H), 7.41–7.38 (m, 1H), 7.27–7.26 (m, 1H), 7.17–7.10 (m, 2H), 6.94–6.87 (m, 3H), 4.59–4.52 (m, 4H), 3.87 (t, *J* = 7.0 Hz, 2H), 1.91 (m, 4H), 1.83–1.76 (m, 2H), 1.49–1.42 (m, 2H),

1.28–1.22 (m, 20H), 0.88–0.85 (m, 3H), 0.83–0.79 (m, 6H). <sup>13</sup>C NMR (100 MHz, THF-*d*<sub>8</sub>) δ 163.2, 147.8, 147.5, 147.2, 146.5, 145.5, 145.3, 145.1, 144.9, 144.6, 139.7, 135.9, 134.1, 132.5, 130.3, 129.8, 127.2, 127.1, 125.4, 124.3, 124.1, 123.5, 123.3, 122.3, 122.1, 119.5, 116.0, 115.5, 111.6, 110.7, 110.1, 106.9, 97.8, 50.1, 47.1, 31.8, 31.3, 30.1, 29.7, 29.3, 29.2, 26.8, 26.8, 26.3, 26.2, 22.6, 22.4, 13.5, 13.3. HRMS (ESI, m/z): [M – H]<sup>–</sup> calcd for C<sub>54</sub>H<sub>55</sub>N<sub>6</sub>O<sub>2</sub>S<sub>5</sub>: 979.2996, found: 979.2984.

**(E)-2-Cyano-3-(10,11-dihexyl-8-(5-(10-octyl-10*H*-phenothiazin-3-yl)thiophen-2-yl)-10,11-dihydrodithieno[2',3':4,5]pyrrolo[3,2-*e*:2'3'-*g*] [2,1,3]benzothiadiazole-2-yl)acrylic acid (DTP3).**

A solution of **12** (100 mg, 0.096 mmol) in trifluoroacetic acid (15 mL) was stirred at room temperature for 4 h. After completion of reaction, the mixture was poured into deionized water (100 mL). The black solid residue was collected by filtration. The black solid was then washed by water (3 × 100 mL), and the final product **DTP3** was obtained as black solid in 80% yield (75 mg), mp 224–226 °C. <sup>1</sup>H NMR (400 MHz, THF-*d*<sub>8</sub>) δ 8.29 (s, 1H), 7.91 (s, 1H), 7.39–7.37 (m, 2H), 7.33 (s, 1H), 7.20–7.14 (m, 4H), 6.99–6.91 (m, 3H), 4.61–4.55 (m, 4H), 3.92 (t, *J* = 6.9 Hz, 2H), 2.00–1.99 (m, 4H), 1.87–1.81 (m, 2H), 1.51–1.46 (m, 2H), 1.33 (m, 20H), 0.93–0.85 (m, 9H). <sup>13</sup>C NMR (100 MHz, THF-*d*<sub>8</sub>) δ 163.4, 147.3, 147.2, 146.6, 146.4, 144.9, 144.8, 144.6, 142.3, 139.9, 136.5, 136.3, 134.9, 129.8, 129.1, 128.4, 127.2, 127.1, 125.4, 124.6, 124.3, 124.1, 123.6, 123.0, 122.3, 120.5, 119.6, 116.3, 115.5, 112.7, 109.7, 107.4, 96.5, 50.3, 50.2, 47.1, 31.8, 31.4, 31.3, 30.3, 30.1, 29.7, 29.2, 29.2, 26.8, 26.7, 26.3, 26.2, 22.5, 22.5, 22.4, 13.5, 13.3, 13.3. HRMS (ESI, m/z): [M – H]<sup>–</sup> calcd for C<sub>54</sub>H<sub>55</sub>N<sub>6</sub>O<sub>2</sub>S<sub>5</sub>: 979.2996, found: 979.2995.

**(E)-2-Cyano-3-(8-(4-(diphenylamino)phenyl)-10,11-dihexyl-10,11-dihydrodithieno[2',3':4,5]pyrrolo[3,2-*e*:2'3'-*g*] [2,1,3]benzothiadiazole-2-yl)acrylic acid (DTP4).**

**DTP4** was synthesized from **13** with the same procedure as that of **DTP1** as a black solid in 56% yield, mp 255–257 °C. <sup>1</sup>H NMR (400 MHz, THF-*d*<sub>8</sub>) δ 8.30 (s, 1H), 7.97 (s, 1H), 7.60–7.58 (m, 2H), 7.52 (s, 1H), 7.29–7.25 (m, 4H), 7.13–7.11 (m, 4H), 7.08–7.02 (m, 4H), 4.66–4.59 (m, 4H), 2.00–1.92 (m, 4H), 1.25–1.17 (m, 12H), 0.82–0.78 (m, 6H). <sup>13</sup>C NMR (100 MHz, THF-*d*<sub>8</sub>) δ 163.4, 147.7, 147.6, 147.4, 147.4, 147.2, 147.1, 146.4, 144.7, 136.2, 135.3, 129.7, 129.2, 126.3, 124.5, 123.4, 123.1, 120.4, 119.7, 116.2, 113.2, 109.6, 106.9, 96.5, 50.3, 50.3, 31.3, 31.2, 30.1, 29.9, 29.6, 26.3, 26.2, 22.4, 22.3, 13.3, 13.2. HRMS (APCI, m/z): [M + H]<sup>+</sup> calcd for C<sub>48</sub>H<sub>45</sub>N<sub>6</sub>O<sub>2</sub>S<sub>3</sub>: 833.2761, found: 833.2751.

### Fabrication of dye-sensitized solar cells

The fabrication of the dye-sensitized solar cells was carried out according to the previously reported procedures.<sup>56,63</sup> Fluorine-doped tin oxide (FTO) glasses were washed with detergent, water, ethanol and acetone in an ultrasonic bath to remove dirt and debris. Anatase TiO<sub>2</sub> nanoparticles (20 nm) were prepared through a hydrothermal treatment with a precursor solution containing Ti(OBu)<sub>4</sub> (10 mL), ethanol (20 mL), acetic acid (18 mL) and deionized water (50 mL). The TiO<sub>2</sub> powder (1.0 g) was ground for 40 min in the mixture of ethanol (8.0 mL), acetic acid (0.2 mL), terpineol (3.0 g) and ethyl cellulose (0.5 g) to form homogeneous slurry. Finally, the slurry was sonicated for 15 min in an ultrasonic bath to form a viscous white TiO<sub>2</sub> paste. Then the TiO<sub>2</sub> photoanodes (about 16 μm thickness) were prepared via screen-printing process onto FTO glass. The prepared films were annealed through a procedure (325 °C for 5 min, 375 °C for 5 min, 450 °C for 15 min, and 500 °C for 15 min) to remove the organic substances. Then TiO<sub>2</sub> films were soaked in 0.04 M TiCl<sub>4</sub> aqueous solution for 30 min at 70 °C to improve the photocurrent and photovoltaic performance. The treated films were rinsed with deionized water, ethanol and then sintered again at 520 °C for 30 min. After cooling to 80 °C, the films were immersed in a

$3.0 \times 10^{-4}$  M solution of the dyes for 24 h (0.3 mM dye in  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  (1:1)). For the co-adsorption, chenodeoxycholic acid (CDCA) was added into the dye solution at a concentration of 1 mM. Afterward these films were washed with  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  (1:1) and dried. The dye-loaded  $\text{TiO}_2/\text{FTO}$  glass films were assembled into a sandwiched type together with Pt/FTO counter electrode. The active area of the dye-coated  $\text{TiO}_2$  film was  $0.16 \text{ cm}^2$ .

## Acknowledgements

We gratefully acknowledge the financial support of the National Natural Science Foundation of China (21272079, 20873183 and 21072064), the Natural Science Foundation of Guangdong Province, China (10351064101000000, S2012010010634) and the Fund from Guangzhou Science and Technology Project, China (2012J4100003).

## Notes and references

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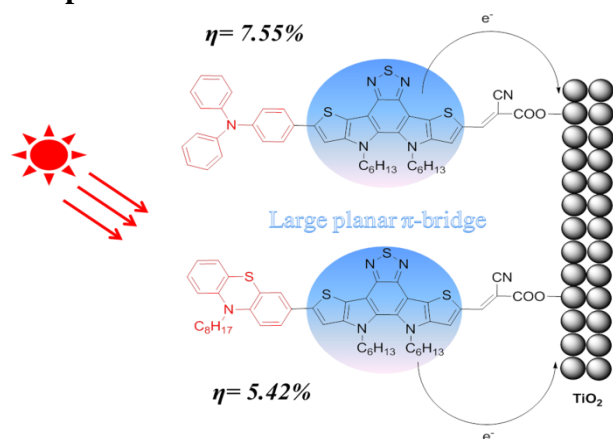
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† Electronic Supplementary Information (ESI) available: concentration dependent absorption spectra in the solution, theoretical approach data,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra. See DOI: 10.1039/b000000x/

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## Graphical abstract



Organic dyes with a large planar dithienopyrrolobenzothiadiazole unit as  $\pi$ -bridge for efficient DSSCs.