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Four new substituted dihydro-indolo[2,3-b]carbazole donor based organic dyes containing thiophene (or benzothiadiazole) or thieno[3,2-b]thiophene were synthesized and successfully applied in dye-sensitized solar cells. It was found that these dyes could achieve high molar extinction coefficients and the DSSCs based on these dyes displayed good performance and high photo-stabilty.

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## Efficient and stable DSSC sensitizers based on substituted dihydroindolo[2,3-b]carbazole donor with high molar extinction coefficients

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Four novel metal-free organic sensitizers based on 5,7-dihexyl-6,12-diphenyl-5,7-dihydroindolo[2,3b]carbazole (**DDC**) donor have been synthesized. Their optical/electrochemical properties, dye-sensitized solar cell (DSSCs) performances and photo-stability upon successive irradiation for 30 min have been <sup>10</sup> investigated. The optical data indicates that all these dyes showed a high molar extinction coefficient (5.6 -  $6.3 \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup>). Under standard global AM 1.5 solar light condition, the **DDC4** sensitized cell gave a short circuit photocurrent density ( $J_{sc}$ ) of 14.81 mA cm<sup>-2</sup>, an open circuit voltage ( $V_{oc}$ ) of 0.688 V, and a fill factor (*FF*) of 0.69, corresponding to an overall efficiency ( $\eta$ ) of 7.03%. The benzothiadiazole units and thieno[3,2-b]thiophene (**TT**) in the  $\pi$  spacer were found to increase the photo-stability of the <sup>15</sup> corresponding dyes and these dyes based on this donor are promising candidates for the further application in DSSCs.

#### Introduction

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With the depletion of fossil energy, the energy problems are more and more needed to be confronted with and solved day by <sup>20</sup> day.<sup>1</sup> Among several promising candidates, dye-sensitized solar cells (DSSCs) based on Ru-complex dyes have been reported with light-to-electricity efficiency ( $\eta$ ) as high as 11.5 %.<sup>2</sup> However, Ru-complex dyes are not suitable for cost-effective and environmentally friendly photovoltaic systems since they contain

<sup>25</sup> the noble metal ruthenium which may limit their widespread application in DSSCs.<sup>3</sup> Compared with metal complexes, organic dyes have the advantages of environmental friendliness, higher structural flexibility, lower cost, easier preparation and purification, etc.<sup>4</sup> Most organic dyes are composed of a donor-π-<sup>30</sup> acceptor (D-π-A) dipolar structure due to its effective photo-

induced intramolecular charge transfer characteristics.<sup>5</sup>

The molar extinction coefficient of sensitizers in the visible light region ( $\varepsilon$ ) is an important factor that influences the DSSCs efficiency. Generally, a high  $\varepsilon$  means a good light harvesting <sup>35</sup> ability, thus it will contribute to a large short-circuit current density ( $J_{sc}$ ).<sup>5e</sup> The photo-stability of dyes is also an important factor and it will pose a great influence on the long-term stability of DSSCs.<sup>6</sup> As to be promisingly applied in the future DSSCs, a donor should help the corresponding dyes to produce a high  $\varepsilon$  in <sup>40</sup> order to harvest photoelectrons as many as possible. Besides, the donor should be able to stabilize the oxidized dyes upon light irradiation in order to reinforce the photo-stability of dyes.<sup>6</sup> In

addition, the synthesis and purification of the donor should be easy. However, as far as we know, donors based on the above 45 factors in DSSCs were seldom designed. Considering this point,

here, we report a new donor 5,7-dihexyl-6,12-diphenyl-5,7dihydroindolo[2,3-b]carbazole (DDC) with easier preparation and purification process. The considerations are as follows: 1) carbazole is an excellent donor which has very strong electron <sup>50</sup> donating ability.<sup>7</sup> The new donor **DDC** contains two fused carbazole units and can be expected to have stronger donating ability; 2) the two fused carbazole units consists of a large  $\pi$ plane, which could desirably delocalize the generated cation as well as reinforce the photo-stability of the corresponding dyes.<sup>8</sup> 55 The effective conjugation of these two fused carbazole units could be expected to contribute to a high molar extinction coefficient; 3) the two alkyl chains attached on the two nitrogen atoms will efficiently improve the solubility in common organic solvents; 4) with the coefficient of both the free rotation of two 60 phenyl rings connected to the indolo[3, 2-b]carbazole core and the nonlinear structure of this donor, a controlled aggregation on  $TiO_2$  could be anticipated; 5) the synthesis and purification of this new donor by our methodology (In the synthesis part) is very easy. As to the  $\pi$ -spacer, benzothiadiazole can stabilize the 65 charge-separated excited-state,<sup>9</sup> therefore, high photo-stability of dyes could be accessible.<sup>10</sup> In addition, as an electronwithdrawing group in the  $\pi$ -spacer part, benzothiadiazole could result in the striking red-shift of absorption spectrum of the corresponding dyes.<sup>9</sup> Thieno[3,2-b]thiophene (TT) is an excellent 70  $\pi$ -spacer, it has been reported that the **TT** compound offers better  $\pi$ -conjugation and smaller geometric relaxation energy upon oxidation.<sup>11</sup> However, as far as we know, the photo-stability of dves containing TT moiety as  $\pi$ -spacer has not been reported. therefore the investigation on photo-stability of TT containing 75 dyes seems interesting. Based on the above considerations, four new dyes based on DDC donor (Scheme 1), containing

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benzothiadiazole (or thiophene) and **TT** (or thiophene) as  $\pi$ -spacer, 2-cyanoacetic acid as acceptor, were designed and synthesized. In order to investigate whether the two fused carbazole units from the donor is good for the DSSCs 5 performance and stability of dyes upon light irradiation, **CBZ** with N-alkyl carbazole unit donor, was also synthesized as the reference dye.



Scheme 1 Molecular structures of dyes (DDC1-DDC4 and CBZ).



DDB1, DDB2, DDB3, DDB4, CBA 2-cyano acetic acid\_ piperdine, THF DDC1, DDC2, DDC3, DDC4, CBZ Scheme 2 Synthetic route to dyes DDC1-DDC4 and CBZ.

#### **Results and discussion**

Synthesis

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The synthetic route to the four dyes DDC1-DDC4 containing 15 DDC moiety and reference dve CBZ with carbazole moiety were depicted in Scheme 2. The intermediate 1 was obtained from the condensation reaction of 1 H-indole and benzaldehyde under the catalysis of iodine in CH<sub>3</sub>CN, which employed the procedure previously reported by Mohit L. Deb. <sup>12a</sup> However, the products 20 obtained were identified as not the reported product DDCX, but the product (compound 1 in Scheme 2) exhibiting a different configuration where two nitrogen atoms connected with the central six-membered ring are in ex situ for each other. Moreover, the central six-membered ring was not aromatized. The real 25 structure was identified as 1 which was directly characterized by NMR and indirectly by **DDC** which was further characterized by X-ray crystallography (Fig. 1). The DDC were synthesized by the alkylation of 1, followed by the oxidation reaction by DDQ. The synthesis of DDC was very simple with high yields and the 30 purification did not necessarily employ the column chromatography, suggesting that its synthesis could be carried out in mass production. The bromination of DDC gave the key intermediate DDC-Br. The intermediates B1, B2 were synthesized according to our previous work.<sup>9b</sup> B3 and B4 were 35 obtained by repeated bromination and Suzuki Coupling reaction and the starting material 3 was synthesized by four step reactions according to previous report.<sup>12b</sup> The final products were obtained via Suzuki coupling of DDC-Br with B1-B4, followed by the condensation with cyanoacetic acid in the presence of a catalytic 40 amount of piperidine in THF. The procedure to synthesis reference dye CBZ from easily obtained intermediate 8 was very similar to that of DDC1. The purification of intermediates was performed by flash column chromatography and subsequent HPLC. All the intermediates and target dyes were characterized 45 by standard spectroscopic methods including <sup>1</sup>H NMR, <sup>13</sup>C NMR and HRMS. Clearly, except the intermediates 1 and 2 which are



not very stable in solution, all the intermediates are fairly stable.

Fig. 1 Crystal structure of DDC (CCDC 933739).

#### 50 Optical properties

UV/Vis absorption spectra of the five dyes in a diluted solution of THF ( $1 \times 10^{-5}$  M) are shown in Fig. 2(a) and their absorption data are listed in Table 1. In the visible light region, the dyes **DDC1-DDC4** all exhibit three absorption bands: the major and broad <sup>55</sup> absorption band is located at 440-650 nm with the maximum absorption at 453, 522, 464, 522 nm, respectively, which is ascribed to the charge transfer (CT) transition between the donor

and the acceptor,<sup>13</sup> the high intensity of this band is wellcorrelated with the large value of oscillator strength (Table 1); the other two narrower absorption bands which are not completely separated off are located at 350-440 nm and the maximum s absorption are almost located at the same positions around 402 and 421 nm, respectively, which may be resulted from the localized aromatic  $\pi$ — $\pi^*$  transitions.<sup>13</sup> The intensity of  $\pi$ — $\pi^*$ transitions is higher than that of the charge-transfer transitions. The reference dye **CBZ** displays only one absorption band at <sup>10</sup> 350-650 nm with the maximum absorption at 461 nm which is slightly red-shifted compared to CT band of **DDC1**. For the dyes **DDC1-DDC4**, the corresponding maximum molar extinction

coefficients for CT band are quite high, they are  $6.31 \times 10^4$ ,  $5.63 \times 10^4$ ,  $5.97 \times 10^4$  and  $5.95 \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup>, respectively, which 15 exhibit striking enhancement compared to that for the dye **CBZ** ( $3.61 \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup>). The maximum molar extinction coefficients for the two absorption bands of **DDC1-DDC4** at 350-440 nm are also very high, reaching up around  $5 \times 10^4$  and  $7 \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup>.



Fig. 2 (a) UV-Vis absorption spectra of DDC1-DDC4 and CBZ in THF  $(1 \times 10^{-5} \text{ M})$ ; (b) absorption spectra of DDC1-DDC4 and CBZ adsorbed on TiO<sub>2</sub> film.

The high molar extinction coefficients for **DDC1-DDC4**<sup>25</sup> indicated that these dyes have good light harvesting ability. A correspondingly thinner nanocrystalline film was allowed so as to avoid the decrease in the film's mechanical strength. This also

benefits the electrolyte diffusion in the film and reduces the recombination possibility of the light induced charges during <sup>30</sup> transportation.<sup>14</sup> As to the CT bands for these dyes, three points were noteworthy: 1) the introduction of **TT** unit instead of thiophene unit did not surely result in obvious red shifted absorption bands, such as **DDC4** compared to **DDC2**; 2) as expected, the benzo[c][1,2,5]thiadiazole unit results in obvious <sup>35</sup> red shifted, the reason of which were discussed in previous report;<sup>10</sup> 3) The dyes possessing electron withdrawing groups, i.e., **DDC4** and **DDC2** displayed slightly lower values of molar extinction coefficients of CT band compared to the others, i.e., **DDC1** and **DDC3**, the similar situation was reported before.<sup>10</sup>

<sup>40</sup> The absorption spectra of **DDC1–DDC4** and **CBZ** on thin transparent films (8 μm thick) after 12 h adsorption in THF solution are shown in Fig. 2(b) and the absorption data are listed in Table 1. It could be seen that in 350-440 nm region, the absorption peaks for **DDC1–DDC4** and **CBZ** on the TiO<sub>2</sub> films <sup>45</sup> are located at almost the same positions as that from the solution spectra. However, in 440-700 nm region, the absorption peaks for **DDC2–DDC4** and **CBZ** on the TiO<sub>2</sub> films are located at 517, 458, 514 and 436 nm, correspondingly blue-shifted by 5, 6, 8 and 25 nm, respectively, from the solution, while the absorption peak

<sup>50</sup> for **DDC1** is red-shifted by 14 nm. Such blue shift and red shift have been reported in many other organic dyes on TiO<sub>2</sub> electrodes.<sup>15</sup>

#### **Electrochemical properties**

Fig. S2 depicts the typical cyclic voltammogram of DDC1-55 DDC4 and CBZ, measured with five sensitizers attached to a 8 µm nanocrystalline TiO<sub>2</sub> film deposited on conducting FTO glass in CH<sub>3</sub>CN containing 0.1 M TBAPF<sub>6</sub> as the supporting electrolyte with a 0.1V s<sup>-1</sup> scan rate and the results are listed in Table 1. Each new donor containing dyes (DDC1-DDC4) 60 displayed two major semi-reversible waves: the lower voltage one is ascribed to the oxidation of the donor, while the higher one could be ascribed to the oxidation of the oligothiophene and benzothiadiazole moieties ( $\pi$  spacer).<sup>16</sup> The carbazole donor based dye (CBZ) presented only a wave which is derived from 65 the oxidation of carbazole moiety (donor). The HOMO level energies decreased slightly in the order of CBZ (1.45) > DDC2 $(0.91) > DDC3 (0.86) > DDC4 (0.85) \approx DDC1 (0.85)$  (the values are ones vs. NHE), thus the HOMO levels of these dyes were sufficiently lower than that of electrolyte pair I  $^{-}/I_{3}$   $^{-}$  (ca. 0.40 V), 70 which ensured a smooth electron flow from the electrolyte to the dyes. It is noteworthy that the HOMO levels of the new donor based dyes DDC1-DDC4 were much higher than that of CBZ based on carbazole donor, suggesting that the donating ability of the new donor was much stronger than that of carbazole donor. <sup>75</sup> The LUMO levels were estimated by the values of  $E_{ox}$  and the  $E_{0-}$ o band gaps, which were estimated at the intersection of absorption and emission spectra. A trend appeared as CBZ (-0.69 > **DDC2** (-1.00) > **DDC4** (-1.09) > **DDC1** (-1.16)  $\approx$ DDC3 (-1.16). All these levels were considerably higher than the

 $_{\rm 80}$  conductive band level of TiO<sub>2</sub> (ca. -0.5 V), indicating that the excited-state electrons injection of all five dyes are guaranteed to be efficient.

#### **Computational analysis**

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Table 1 Optical and electrochemical of DDC1-DDC4 and CBZ.										
Dye	Calculated	$f^{a}$	$\lambda_{\max}^{b}/nm$	$\lambda_{max}^{c}/nm$ on TiO <sub>2</sub>	$E_{0-0}^{d}$	$E_{HOMO}^{e}(V)$	$E_{\text{LUMO}}^{f}(V)$			
	energy		$(\varepsilon^{g}/10^{4} M^{-1} cm^{-1})$							
	(eV, nm)									
DDC1	$2.80, 443^{h}$	1.76	404 (5.77), 426 (7.87), 453 (6.31)	402, 427, 467	2.01	0.85	-1.16			
DDC2	2.60, 477	1.20	402 (6.08), 421 (7.34), 522 (5.63)	401, 420, 517	1.91	0.91	-1.00			
DDC3	2.76, 449	2.04	403 (5.09), 427 (6.85), 464 (5.97)	403, 427, 458	2.02	0.86	-1.16			
DDC4	2.55, 486	1.51	401 (5.77), 421 (7.02), 522 (5.95)	401, 422, 514	1.94	0.85	-1.09			
CBZ	2.91, 425	1.48	461 (3.61)	436	2.14	1.45	-0.69			
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<sup>*a*</sup> Oscillator strengths at CT bands calculated by DFT/B3LYP; <sup>*b*</sup> Absorption maximum in THF solution; <sup>*c*</sup> Absorption maximum on TiO<sub>2</sub> film; <sup>*d*</sup>  $E_{0-0}$ : 0 \_ 0 transition energy measured at the intersection of absorption and emission spectra; <sup>*e*</sup> HOMOs were measured in CH<sub>3</sub>CN containing 0.1 M (n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NPF<sub>6</sub> with a scan rate of 100 mV s<sup>-1</sup> (working electrode: Pt; reference electrode: SCE); calibrated with ferrocene/ferrocenium (Fc/Fc+) as an external reference. Counter electrode: Pt wire. <sup>*f*</sup>  $E_{LUMO}$  was calculated by  $E_{ox} - E_{0-0}$ ; <sup>*s*</sup> Absorption coefficient; <sup>*h*</sup> Wavelength of the calculated oscillator strength in vacuo.

To gain deep insight into the electronic distribution of the frontier <sup>5</sup> and other close-lying orbitals as well as the geometrical configuration of these dyes, density functional theory (DFT) calculations were carried out. In the calculations, the long alkyl chains in these compounds were replaced by ethyl groups to save computational time while preserving their steric effect. The <sup>10</sup> hybrid B3LYP functional<sup>17</sup> and the Ahlrichs split valence SVP basis set <sup>18</sup> was employed to optimize molecular geometries of the dyes and to compute their frontier molecular orbitals, using the ORCA program package.<sup>19</sup> Subsequent time-dependent DFT (TDDFT) calculations were performed to gain information of the <sup>15</sup> lowest singlet excited states of the sensitizer dyes, using the Coulomb-attenuated CAM-B3LYP <sup>20</sup> functional and the SVP

basis set implemented in Gaussian 09 program package. The charge distribution in the frontier molecular orbitals is depicted in Fig. S1. As shown in the graphs, in the above four <sup>20</sup> sensitizers, the HOMO level is localized mostly at indolo[3,2,*b*]carbazole moiety (D), while the LUMO is localized mostly at oligothiophene units ( $\pi$ ) and the anchoring cyanoacrylic acid (A) group. The electron distributions of both D and A are heavily coupled with the orbitals in the central bridge ( $\pi$ ) and the <sup>25</sup> desirable shift of electron density from D to A once upon photo excitation is obvious, suggesting that the electron transfer from the donor part to the acceptor units would be efficient once upon photoexcitation. The calculated oscillator strength (*f*) is shown in Table 1. The *f* values for the lowest energy transitions, the CT <sup>30</sup> transitions, are all very high, ranging from 1.20 to 2.04. The

results are roughly consistent with the absorptivity measured in solutions except for **DDC2**.

The geometrical configuration of these dyes is shown in Fig. 3. In the ground state, all these dyes are not totally planar. The

- <sup>35</sup> dihedron angles between the indolo[3,2,-*b*]carbazole moiety and the two phenyl rings connected to the central core of the donor were near to 90°, suggesting that these two phenyl rings may help to suppress dye aggregation when dyes are loaded on TiO<sub>2</sub> films. For **DDC1-DDC4**, those possessing withdrawing groups-
- <sup>40</sup> benzothiadiazole units are obviously twisted more between the donor part and benzothiadizole units compared to the others, i. e. such as **DDC2** and **DDC1**, this phenomenon was reported by some previous articles.<sup>21</sup>

#### 45 DSSCs performance



Fig. 3 Dihedral angles between the neighbouring units.

To investigate the light harvesting ability of DDC1-DDC4 and CBZ, DSSCs based on dye-sensitized TiO<sub>2</sub> (12 µm) films and the 50 electrolyte in the experimental section were fabricated and the performances were measured. Fig. 4(a) shows the action spectra of incident photon-to-current conversion efficiency (IPCE) for DSSCs with these dyes when  $CH_3CN$  (AV): DMF (v/v 3:1) was used as the solvent for dye loading. The IPCE exceeds 60 % in 55 the range 360-570 nm for DDC1, 390-430 and 510-540 nm for DDC2, 350-610 nm for DDC4 and 395-510 nm for CBZ, with the highest value of 74.8 % at 470 nm for DDC1, 61.6 % at 420 nm for DDC2, 77.2 % at 430 nm for DDC4 and 66.0 % at 440 nm for CBZ, respectively. However, the highest value of 60 IPCE for DDC3 was only 58.9 % at 410 nm. Among these five dyes, it could be easily seen that the IPCE for DDC3 displayed poorest performance with low IPCE values and narrow IPCE spectra, while the IPCE for DDC4 exhibited the best performance with high IPCE values at broad spectra region, indicating that

<sup>65</sup> DDC4 sensitized TiO2 electrode would generate a higher

conversion yield compared to other four dyes. Except for **DDC3**, the IPCE performances of the dyes based on the new donor all displayed better than that of **CBZ** based on carbazole donor. One explanation is that the molar extinction coefficients of the dyes <sup>5</sup> based on the new donor were much higher than that of **CBZ** based on carbazole donor. Generally, a high molar extinction coefficient means a good light harvesting ability, suggests that it would be helpful to convert light to electricity more efficiently,<sup>22</sup> thus that the high molar extinction coefficients would facilitate

<sup>10</sup> the new donor based dyes to display good IPCE perormance.



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**Fig. 4** The performances of DSSCs sensitized by **DDC1-DDC4** and **CBZ**: (a) IPCE spectra for DSSCs based on **DDC1-DDC4** and **CBZ** with dye 15 baths in CH<sub>3</sub>CN (AV): DMF ( $\nu/\nu$  3:1) or CHCl<sub>3</sub>: EtOH ( $\nu/\nu$  1:3); (b) I-V curves for DSSCs based on **DDC1-DDC4** and **CBZ** with dye baths in AV: DMF ( $\nu/\nu$  3:1) or CHCl<sub>3</sub>: EtOH ( $\nu/\nu$  1:3) upon AM 1.5 solar light irradiation and I-V curves for DSSCs based on **DDC1-DDC4** and **CBZ** with dye baths in AV: DMF ( $\nu/\nu$  3:1) under dark condition.

- Note: 1) the order of the IPCE spectrum of the new four dyes based cells DDC4 > DDC1 > DDC2 > DDC3 was consistent with the order of the dye loading amount in practical devices (Table 1S); 2) compared to the absorption spectra of sensitized films, the IPCE spectra were broadened significantly. This 25 phenomenon could be ascribed to the scattering effect of the large
- particles in the film and the reflective effect of the Pt counter

the IPCE values. Fig. 4(b) presents the photocurrent-voltage (J-V) plots of DSSCs based on these dyes, along with that of CBZ 30 for comparison. The detailed parameters, i.e., short circuit current  $(J_{sc})$ , open-circuit photovoltage  $(V_{oc})$ , fill factor (FF), and solar-to- electricity conversion efficiency  $(\eta)$  measured under AM 1.5 solar light (100 mW cm<sup>-2</sup>) are summarized in Table 2. When the mixture solvents AV: DMF (v/v 3:1) were used as the solvent 35 for dye baths, the DSSCs based on DDC1-DDC4 and CBZ exhibited inferior conversion efficiency of 6.09%, 5.55%, 4.11%, 6.40% and 4.90%. The larger  $J_{sc}$  of the DDC1 sensitized solar cell as compared with that of the solar cell based on CBZ demonstrates the beneficial influence of the high molar extinction 40 coefficients of DDC1 in solution. The superior performance of DDC1 sensitized solar cell presented an advantage of the new donor. The lower  $J_{sc}$  of the **DDC2** sensitized solar cell as compared with that of DDC1 could be ascribed to the much lower IPCE values although DDC2 had broad IPCE spectra. The 45 **DDC3** sensitized DSSCs performed very poor with low  $J_{sc}$  and

electrode. Moreover, the electrolyte could also pose influence on

- $V_{oc}$ . The low  $J_{sc}$  may be resulted from the low electron injection yield from LUMO levels into TiO<sub>2</sub> conduction band. The low  $V_{oc}$  implied that there were severe charge recombination between the electrolytes and the oxidized dyes. Among these five dyes, the <sup>50</sup> **DDC4** based DSSCs gave the best performance, with  $J_{sc}$  of 13.96
- <sup>55</sup> DDC4 ones a based based based are best performance, while  $y_{sc}$  of 15.56mA cm<sup>-2</sup>, an  $V_{oc}$  of 0.674 V, and a *FF* of 0.68, corresponding to an overall conversion efficiency ( $\eta$ ) of 6.40%. The large  $J_{sc}$  could be attributed to the high IPCE values and the broad IPCE spectra. However,  $V_{oc}$  of **DDC4** sensitized solar cell was not high and one <sup>55</sup> possible reason is because of the existence of benzothiadiazole, which were reported for many times previously.<sup>23</sup> The low  $V_{oc}$  of **DDC2** was also consistent with this observation. Based on that **DDC1** and **DDC4** sensitized solar cells displayed better performance among the five dyes, the two dyes based DSSCs <sup>60</sup> with dye loading in CHCl<sub>3</sub>: EtOH (v/v 1:3) were fabricated and the performances were measured. The reason why the mixture solvents CHCl<sub>3</sub>: EtOH (v/v 1:3) were chosen as the dye baths solvents was based on the consideration that many dyes based DSSCs fabricated with dye baths in these mixture solvents.<sup>96</sup>

Fig. 2 The performances	of DSSCs based of	on <b>DDC1-DDC4</b> and <b>CBZ</b> .
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Dye	Solvents	$J_{\rm sc}/{\rm mAcm}^{-2}$	$V_{oc}/V$	FF (%)	$\eta$ (%)
DDC1	AV: DMF (v/v 3:1)	11.95	0.768	66	6.09
DDC2	AV: DMF (v/v 3:1)	11.57	0.707	68	5.55
DDC3	AV: DMF (v/v 3:1)	9.40	0.644	68	4.11
DDC4	AV: DMF (v/v 3:1)	13.96	0.674	68	6.40
CBZ	AV: DMF (v/v 3:1)	10.28	0.713	67	4.90
DDC1	CHCl <sub>3</sub> : EtOH (v/v 1:3)	12.28	0.754	67	6.24
DDC4	CHCl <sub>3</sub> : EtOH (v/v 1:3)	14.81	0.688	69	7.03

As shown in Table 2, the photovoltaic performance for DSSCS <sup>70</sup> based on **DDC1** and **DDC4** both exhibited better when CHCl<sub>3</sub>: EtOH ( $\nu/\nu$  1:3) were used as the solvents for dye loading compared with using AV: DMF ( $\nu/\nu$  3:1) as the solvents for dye loading. The reason why the two dyes performed well in CHCl<sub>3</sub>: EtOH ( $\nu/\nu$  1:3) was very complicated including that the <sup>75</sup> diversified interactions among the dyes, solvents, electrolytes and semiconductor surface could alter the optical and chemical Journal of Materials Chemistry A Accepted Manuscript

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properties of dyes and semiconductor. Also, the solvent effect could pose an influence on the adsorbed amount of dyes on TiO<sub>2</sub> films.<sup>24</sup> Noted that **DDC4** based DSSCs fabricated with dye baths in CHCl<sub>3</sub>: EtOH (v/v 1:3) exhibited a very good performance with  $_{5}$   $\eta$  enhanced up to 7.03 % with  $J_{\rm sc}$  of 14.81 mA cm<sup>-2</sup>,  $V_{\rm oc}$  of 0.69 V and the FF of 0.69. The good performance of DDC4 sensitized solar cell suggests that DDC4 is a promising candidate for application in DSSCs.

#### Electrochemical impedance spectroscopy



Fig. 5 Impedance spectra of DSSCs based on DDC1-DDC4 and CBZ with dye baths in AV: DMF (v/v 3:1) measure at bias -0.70 V in the dark. 15 (a) Nyquist plots; and (b) bode phase plots.

To further clarify the dyes effect on the  $V_{oc}$  in the DSSCs sensitized by these dyes, electrochemical impedance spectroscopy (EIS) of the DSSCs made with these sensitizers was performed. The Nyquist plots of the DSSCs based on the seven 20 dyes under a forward bias of -0.70V in the dark with a frequency

- range of 0.1 Hz to 100 kHz are shown in Fig. 5(a). The Bode phase was also shown in Fig. 5(b). Two semicircles were observed in the Nyquist plots. The smaller semicircle at high frequency is assigned to the redox charge-transfer response at the
- 25 Pt/electrolyte interface. The large one at the intermediate frequency represents the electron-transfer impedance at the

TiO<sub>2</sub>/dye/electrolyte interface. It is related to the charge recombination rate, generally, a smaller R<sub>rec</sub> indicates a faster charge recombination and therefore a larger dark current (Shown  $_{30}$  in Fig. 4(b). The radius of the biggest semicircle  $R_{\rm rec}$  values decreased in the order of DDC1 > DDC2 > CBZ >DDC3~DDC4. The result appears to be roughly consistent with the increase of  $V_{oc}$  in the DSSCs based on **DDC1–DDC4** and CBZ. In Bode phase plots, the peak position of the middle 35 frequency is related to the electron lifetime and a shift to low frequency corresponds to a longer electron life-time. Thus, according to the Fig. 5(b), the order of the corresponding electron DDC1>DDC2≈CBZ>DDC4>DDC3 further lifetimes approximately support the order of the  $V_{oc}$  of DSSCs based on 40 these dyes.

#### Stability of the sensitizers

The stability of dyes is an essentially important factor considering the practical application in DSSCs, because the stability of dyes will greatly influence the lifetime of the corresponding DSSCs. <sup>45</sup> To evaluate the photo-stability of these dyes, the methodology by Katoh and coworkers were employed.<sup>6</sup> Sensitizers adsorbed on 8 µm TiO<sub>2</sub> films without redox electrolyte were successively irradiated upon AM 1.5 solar light for 30 min. Fig. 6 shows the absorption curves of dyes DDC1-DDC4 and CBZ upon light 50 irradiation of AM 1.5 solar light (30 min). Obviously, sensitizers based on the new donor are stable enough without any distinct absorption peak shift and the variations of absorbance in CT bands before and after irradiation are very small. Nevertheless, the maximum absorbance variations in CT bands for 55 benzothiadiazole-incorporated DDC2 and DDC4 before and after irradiation is smaller than that for oligothiophene-containing DDC1 and DDC3, suggesting that the benzothiadiazolecontaining DDC2 and DDC4 are more stable than that DDC1 and DDC3. This phenomenon is well consistent with the similar 60 situation reported before.<sup>10</sup> What's more, from the comparison of DDC1 and DDC3, it could be observed that the introduction of **TT** instead of thiophene could increase the photo-stability of the corresponding dyes. The comparison of DDC2 and DDC4 showed the same phenomenon. Finally, incorporating 65 benzothiadiazole unit and **TT** unit as  $\pi$ -spacer, both of which are helpful to stabilize the oxidized dyes upon light irradiation, DDC4 displayed the best photo-stability with very small absorption variations in CT band. It is noteworthy that the percentage of the maximum absorbance variations in CT bands 70 for CBZ based on carbazole donor is much larger than that for the new donor based **DDC1** which has the similar structure (9.0% for CBZ, 4.1% for DDC1), indicating that the new donor are much more capable of stabilizing oxidized state of dyes than that the carbazole donor. The good photo-stability of dyes DDC2-75 DDC4 further supports this viewpoint.

To investigate the temperature effects on the physics of the dyes, absorption curves of dyes on TiO<sub>2</sub> films which were kept for 30 min at different temperatures (25°C, 40°C, 50°C and 60°C) were measured. As shown in Fig. 4S, dyes on TiO<sub>2</sub> films at these 80 four temperatures were fairly thermo-stable with the percentage of the maximum absorbance variations in CT bands no more than 1.5 % before and after heating.

30

#### Conclusions

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In summary, four dyes (DDC1-DDC4) based on the new donor with two fused carbazole units, containing benzothiadiazole (or thiophene) and TT (or thiophene) as  $\pi$ -spacer, 2-cyanoacetic acid 5 as acceptor, were successfully synthesized and demonstrated as efficient sensitizers for DSSCs. The results showed that the synthesis and purification of this new donor with two fused carbazole units were simple. The large and effective conjugation of the new donor contributed to a high molar extinction

10 coefficient of the corresponding dyes which is in favour of the dyes harvesting more photoelectrons. The comparison between **DDC1** and **CBZ**, no matter from the  $J_{sc}$  or from the  $V_{oc}$ , both suggested that the donor has some advantages over carbazole donor for the corresponding DSSCs. Derived from the broad 15 absorption spectrum and efficient electron injection into the conduction band of TiO<sub>2</sub>, **DDC4** with the large  $J_{sc}$ , exhibited the best performance overall efficiency of 7.03 % among these dyes  $(J_{\rm sc} \text{ of } 14.81 \text{ mA cm}^2, V_{\rm oc} \text{ of } 0.69 \text{ V} \text{ and } FF \text{ of } 0.69)$ . As to the photo-stability of these dyes, the new donor facilitated the 20 corresponding dyes to stabilize the oxidized state once upon the light irradiation. To the  $\pi$ -spacer, the introduction of benzothiadiazole unit was once again proved to increase the photo-stability of the corresponding dyes in this system. Most importantly, the influence of the introduction of TT unit in  $\pi$ -25 spacer on the photo-stability of the corresponding dyes has firstly

been examined and in this system, the introduction of TT could strikingly reinforce the photo-stability of the corresponding dyes.









**Fig. 6** Absorption curves of dyes **DDC1-DDC4** and **CBZ** on 8  $\mu$ m TiO<sub>2</sub> films upon light irradiation of AM 1.5 solar light (30 min) at ambient temperature;  $\Delta A_{max}$ : the maximum absorbance variations in CT bands 5 before and after irradiation (30 min); A: the maximum absorbance in CT bands before irradiation;  $\Delta A_{max}/A$ : the percentage of the maximum absorbance variations in CT bands upon light irradiation (30 min).

#### **Experimental section**

#### Materials and Reagents:

- 10 Optically transparent FTO conducting glass (F-doped SnO, transmission > 90% in the visible, sheet resistance 15 $\Omega$  square<sup>-1</sup>, Geao Science and Educational Co. Ltd. of China) was washed with detergent, redistilled water, ethanol, choloroform and acetone successively under supersonication for 30 min each 15 before use. Titania pastes of Ti-Nanoxide T/SP and Ti-Nanoxide 300 were obtained from Geao Science and Educational Co. Ltd. of China. Reagent grade LiI, I2 (purity > 99.999%), TiCl4, acetonitrile (AV), 1,2-dimethyl-3-propylimidazolium iodide (DMPII), Tetra-n-butylammonium hexafluorophosphate 20 (TBAPF<sub>6</sub>), 4-tert-butylpyridine (TBP), chloroform, N, Ndimethylformamide (DMF), ethanol (C<sub>2</sub>H<sub>5</sub>OH), 2.4 M BuLi solution in hexane and the reaction catalyst Pd(PPh<sub>3</sub>)<sub>4</sub> were used as received without further purification from commercial sources. Acetonitrile with HPLC purity was purchased from SK
- 25 Chemicals. THF was pre-dried over sodium and distilled under argon atmosphere from sodium benzophenone ketyl immediately prior to use. All other chemicals were used as received without further purification.

#### Instruments and Characterization

- <sup>30</sup> The new compounds were characterized by <sup>1</sup>H NMR (400 MHz), <sup>13</sup>C NMR (100 MHz) and Mass. NMR spectra were obtained on a Brucker AM 400 spectrometer and Mass spectra were recorded on an ESI mass spectrometer. Elemental analyses were measured by German elementar vario EL III. The UV-Vis absorption
- <sup>35</sup> spectra of the dyes solutions and dye-loaded films were measured with a Varian Cary 500 spectrophotometer. The cyclic voltammograms of dyes were obtained from a Versastat II electrochemical workstation (Princeton applied research). The conventional three electrode configuration was employed with a <sup>40</sup> dye-loaded film as working electrode, a Pt wire counter electrode,
- and a regular calomel reference electrode in saturated KCl

solution. The supporting electrolyte was 0.1M TBAPF<sub>6</sub> in AV. The scan rate was 100 mV s<sup>-1</sup>. The potential of the reference electrode was calibrated by ferrocene and all the potential data in <sup>45</sup> this paper are relative to normal hydrogen electrode (NHE). The electrochemical impedance spectroscopy (EIS) measurements of all the DSSCs were carried out under dark using a Zahner IM6e Impedance Analyzer (ZAHNER-Elektrik GmbH & CoKG, Kronach, Germany). The spectra were scanned in a frequency <sup>50</sup> range of 0.1-10<sup>5</sup> Hz with applied potential set at open circuit of the corresponding DSSCs. The alternate current amplitude was set at 10 mV.

#### Measurements:

Photovoltaic measurements were performed by an AM 1.5 solar simulator A 300 W xenon lamp (Model No. 91160, Oriel) was used as the light source. The work curves of the cell were obtained under the following conditions: 1) the power of the simulated light was calibrated to 100 mW cm<sup>-2</sup> by a reference Si solar cell; 2) Cell active area was tested with a mask of 0.25 cm<sup>-2</sup> <sup>60</sup> was used to cover around the cell active area. The photocurrent action spectra were obtained through an IPCE test system with a model SR830 DSP Lock. A 7IL/PX150 xenon lamp was used as the light source and the IPCE spectra were recorded on a 7ISW301 spectrometer.

#### 65 Fabrication of DSSCs

To a well-cleaned FTO conducting glass, thin  $TiO_2$  films (12 µm) consisting of a transparent layer (Ti-Nanoxide T/SP) and a 4 µm scattering layer (Ti-Nanoxide 300) were coated using a screen printing technique <sup>18</sup>, followed by calcinated at 500°C under an 70 air flow in muffle for 30 min. After cooling down to the ambient temperature, the obtained films were immersed in 0.05 M aqueous TiCl<sub>4</sub> solution for 30 min at 75 °C, then washed with redistilled water and anhydrous ethanol consecutively, followed by annealed at 450 °C for 30 min. After cooling down, the 75 obtained films were immersed into the dye solution (0.1 M in the required solvents) for 12 h. After dyes loaded on the films, the working electrodes were rinsed with chloroform and anhydrous ethanol respectively. The Pt-counter electrodes were made by depositing ~100 nm thick Pt on the conductive surface and two <sup>80</sup> holes (0.8-mm diameter) were drilled by Drill-press. The working and Pt-counter electrodes were assemble into a sandwich type solar cell and sealed with a hot-melt gasket of 25µm thickness. The electrolyte was injected into the cell from the holes and the fabrication of the solar cells was finally finished by sealing the 85 holes using a UV-melt gum. The electrolytes was composed of 0.1 M lithium iodide, 0.6 M 1,2-dimethyl-3- propylimidazolium iodide (DMPII), 0.05 M I<sub>2</sub>, 0.5 M 4-tertbutylpyridine (4-TBP) in

#### Synthesis:

#### 5'-(5,11-dihexyl-6,12-diphenyl-5,11-dihydroindolo[3,2b]carbazol-2-vl)-[2,2'-bithiophene]-5-carbaldehyde (DDB1)

acetonitrile (AV) as a liquid electrolyte.

In a dry flask, 1.6 M n-BuLi in hexane (2.4 ml, 3.85 mmol) was added dropwise to a solution of compound **3** (1.0 g, 2.57 mmol) in THF at -78 °C under a N<sub>2</sub> atmosphere. After stirring for 1.5 h <sup>95</sup> at this temperature, triisopropyl borate (1.5 ml, 6.43 mmol) was added dropwise and the mixture was allowed to warm to r.t followed by stirring for 2 h. Then compound **B1** (701 mg, 2.57 mmol), K<sub>2</sub>CO<sub>3</sub> (1.38 g, 10 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (50 mg, 0.05 mmol), water (5mL), and THF (15mL) was added and the mixture was warmed to reflux after the flask was recharged with N<sub>2</sub>. After refluxing for 4h, the mixture was allowed to cool down s to r.t. and then washed with water. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed by using a rotary evaporator. The crude materials was purified by silica gel column chromatography using a petroleum and dichloromethane mixture as the eluent to obtain the desired product as an orange 10 solid 1.54 g, 20%. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>), δ: 9.90 (s,

<sup>10</sup> Solid 1.54 g, 20%. If NMR (400 MHz, DMSO4*a*<sub>6</sub>), 0. 9.90 (s, 1H), 8.03 (t, J = 4.7 Hz, 1H), 7.85 – 7.78 (m, 3H), 7.76 – 7.68 (m, 8H), 7.53 (dd, J = 6.7, 3.0 Hz, 1H), 7.51 – 7.43 (m, 3H), 7.37 – 7.28 (m, 1H), 7.09 (t, J = 4.7 Hz, 1H), 6.78 (t, J = 7.6 Hz, 1H), 6.54 (d, J = 1.7 Hz, 1H), 6.37 (d, J = 7.8 Hz, 1H), 3.96 – 3.87 (m, 1s 2H), 3.85 – 3.76 (m, 2H), 1.53 – 1.37 (m, 4H), 1.19 (dd, J = 14.6, 7.3 Hz, 4H), 1.12 – 1.04 (m, 4H), 0.87 – 0.80 (m, 10H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>), δ: 183.00, 149.21, 148.66, 143.16, 143.09, 141.50, 139.40, 139.20, 138.19, 133.61, 133.36, 133.09, 131.14, 129.89, 129.65, 129.05, 128.91, 127.88, 126.15, 124.14, 123.93, <sup>20</sup> 123.86, 123.75, 123.70, 123.53, 123.13, 123.03, 122.69, 120.49, 118.98, 118.72, 118.67, 109.21, 108.92, 45.24, 45.11, 32.09, 29.46, 29.40, 27.00, 23.20, 14.65. HRMS (m/z): [M + H]<sup>+</sup> calcd

for  $C_{51}H_{49}N_2OS_2$ , 769.3286; found, 769.3287. Compound **DDB2-DDB5** were synthesized by the same

<sup>25</sup> procedure as described for C1 5-(7-(5,11-dihexyl-6,12-diphenyl-5,11-dihydroindolo[3,2b]carbazol-2-yl)benzo[c][1,2,5]thiadiazol-4-yl)thiophene-2carbaldehyde (DDB2)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$ : 9.99 (s, 1H), 8.22 (d, *J* = 4.0 Hz, <sup>30</sup> 1H), 8.08 (dd, *J* = 8.6, 1.7 Hz, 1H), 8.00 (d, *J* = 7.5 Hz, 1H), 7.86 (d, *J* = 4.0 Hz, 1H), 7.77 – 7.73 (m, 2H), 7.71 (dd, *J* = 6.5, 3.0 Hz, 2H), 7.67 – 7.61 (m, 5H), 7.57 (d, *J* = 7.4 Hz, 1H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 8.6 Hz, 1H), 7.34 (s, 1H), 7.29 (s, 1H), 7.23 (d, *J* = 1.6 Hz, 1H), 6.83 (s, 1H), 6.54 (d, *J* = 7.8 Hz, 1H), 35 3.88 – 3.80 (m, 4H), 1.23 (dd, *J* = 14.6, 7.4 Hz, 4H), 1.18 – 1.09 (m, 4H), 0.94 – 0.82 (m, 10H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$ : 183.06, 154.01, 152.70, 149.40, 142.98, 142.84, 142.47, 138.86, 138.61, 136.94, 136.25, 132.68, 132.57, 130.54, 130.52, 129.17, 129.03, 128.28, 128.17, 127.76, 127.51, 126.72, 126.37, 126.28, <sup>40</sup> 125.46, 123.76, 123.49, 123.28, 122.88, 122.61, 122.46, 118.33, 118.12, 118.01, 108.38, 108.29, 44.64, 44.47, 31.47, 28.82, 28.74, 26.37, 22.57, 14.04. HRMS (*m*/*z*): [M + H]<sup>+</sup> calcd for C<sub>53</sub>H<sub>49</sub>N<sub>4</sub>OS<sub>2</sub>, 821.3348; found, 821.3344.

5-(5-(5,11-dihexyl-6,12-diphenyl-5,11-dihydroindolo[3,2-45 b]carbazol-2-yl)thiophen-2-yl)thiophene-2-

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carbaldehyde (DDB3)
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<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), \delta: 9.95 (s, 1H), 7.89 (s, 1H), 7.74 (s, 5H), 7.69 (dd, J = 6.7, 3.1 Hz, 2H), 7.65 (d, J = 2.3 Hz, 3H), 7.61 – 7.57 (m, 1H), 7.35 (s, 2H), 7.27 (s, 2H), 7.21 (d, J = 3.7
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- <sup>50</sup> Hz, 1H), 6.87 (d, J = 3.8 Hz, 1H), 6.83 (dd, J = 9.7, 5.5 Hz, 1H), 6.71 (d, J = 1.5 Hz, 1H), 6.53 (d, J = 7.7 Hz, 1H), 3.88 (dd, J =16.1, 7.0 Hz, 2H), 3.80 (dt, J = 9.1, 6.5 Hz, 2H), 1.55 – 1.48 (m, 4H), 1.22 (s, 4H), 1.16 – 1.09 (m, 4H), 0.86 (t, J = 7.2 Hz, 10H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>),  $\delta$ : 182.74, 147.74, 146.78, 146.40, 55 144.12, 142.44, 142.31, 138.70, 138.48, 137.07, 133.45, 132.65,
- 132.36, 130.42, 129.13, 128.91, 128.86, 128.29, 128.17, 126.36, 125.41, 123.41, 123.29, 123.02, 122.96, 122.81, 122.40, 122.31, 121.82, 119.68, 118.24, 117.98, 117.94, 114.71, 108.48, 108.18,

44.51, 44.38, 31.36, 31.35, 28.72, 28.65, 26.27, 26.26, 22.47, 60 22.45, 13.91. HRMS (m/z):  $[M + H]^+$  calcd for  $C_{53}H_{48}N_2OS_3$ , 824.2929; found, 824.2927.

5-(7-(5,11-dihexyl-6,12-diphenyl-5,11-dihydroindolo[3,2b]carbazol-2-yl)benzo[c][1,2,5]thiadiazol-4-yl)thieno[3,2b]thiophene-2-carbaldehyde (DDB4)

<sup>65</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), δ: 10.00 (s, 1H), 8.50 (s, 1H), 8.11 – 8.06 (m, 1H), 7.99 (s, 1H), 7.93 (s, 1H), 7.75 (s, 2H), 7.69 (s, 2H), 7.67 – 7.62 (m, 5H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.48 – 7.39 (m, 2H), 7.37 – 7.32 (m, 1H), 7.28 (d, *J* = 6.6 Hz, 1H), 7.22 (d, *J* = 1.6 Hz, 1H), 6.84 (t, *J* = 7.4 Hz, 1H), 6.54 (d, *J* = 7.9 Hz, 1H), 70 3.89 – 3.80 (m, 4H), 1.56 – 1.48 (m, 4H), 1.24 – 1.19 (m, 4H), 1.13 (d, *J* = 7.3 Hz, 4H), 0.86 (q, *J* = 7.2 Hz, 10H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>), δ: 183.02, 153.95, 152.47, 148.09, 146.64, 145.11, 142.73, 142.44, 138.82, 138.77, 138.56, 135.56, 132.65, 132.55, 130.49, 130.45, 129.03, 128.91, 128.86, 128.16, 128.02, 75 127.09, 126.58, 126.29, 126.24, 125.35, 123.80, 123.64, 123.40, 122.84, 122.83, 122.55, 122.37, 119.74, 118.26, 118.03, 117.94, 108.24, 108.20, 44.55, 44.39, 31.37, 31.35, 29.59, 28.72, 28.63, 26.26, 22.45, 22.44, 13.90, 13.88. HRMS (*m*/z):  $[M + H]^+$  calcd for C<sub>55</sub>H<sub>49</sub>N<sub>4</sub>OS<sub>3</sub>, 877.3069; found, 877.3063.

#### <sup>80</sup> 5'-(9-hexyl-9H-carbazol-3-yl)-[2,2'-bithiophene]-5carbaldehyde (CBA)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$ : 9.81 (s, 1 H), 8.27 (s, 1 H), 8.09 (d, J =7.7 Hz, 1 H), 7.67 (dd, J =8.5, 1.5 Hz, 1 H), 7.63 (d, 1 H, J= 3.9 Hz), 7.44 (dd, J =9.3, 5.7 Hz, 1 H), 7.37 (d, J =2.6 Hz, 1 H), 85 7.35 (d, J =3.0 Hz, 1 H), 7.32 (d, J =3.8 Hz, 1 H), 7.25 (d, J =3.8 Hz, 1 H), 7.22 (d, J =4.0 Hz, 2 H), 4.26 (t, J =7.2 Hz, 2 H), 1.83 (dt, J =15.1, 7.5 Hz, 2 H), 1.34 (ddd, J =10.4, 7.7, 4.6 Hz, 2 H), 1.26 - 1.17 (4 H, m), 0.84 - 0.78 (3 H, m). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>),  $\delta$ : 182.24, 147.89, 147.61, 141.02, 140.89, 140.33, 90 137.33, 133.64, 127.19, 126.11, 124.48, 123.87, 123.44, 123.28, 122.88, 122.59, 120.45, 119.19, 117.72, 109.04, 108.92, 43.15, 31.46, 28.85, 26.85, 22.43, 13.88. HRMS (m/z): [M + H]<sup>+</sup> calcd for C<sub>27</sub>H<sub>26</sub>NOS<sub>2</sub>, 444.1456; found, 444.1459.

#### (E)-2-cyano-3-(5'-(5,11-dihexyl-6,12-diphenyl-5,11-95 dihydroindolo[3,2-b]carbazol-2-yl)-[2,2'-bithiophen]-5yl)acrylic acid (DDC1)

A mixture of DDB1 (384mg, 0.5mmol), 2-cyanoacetic acid (160mg, 2 mmol ) and 2 drops of piperidine in 20ml THF was refluxed for 4h under N<sub>2</sub> atmosphere. After cooled to r.t., the 100 solvent was removed in vacuo. The residual was dissolved in 200 ml dichloromethane and washed with redistilled water for 3 times. The combined organic layer was dried over anhydrous MgSO<sub>4</sub> and then filtered. The filtrate was concentrated using rotary evaporator. The crude product was chromatographed on <sup>105</sup> silica gel and firstly using pure dichloromethane as the eluent to exclude the impurities and then using THF and methanol mixture (1:1) as the eluent to obtain the pure product as a red solid (382 mg, 90%). <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ),  $\delta$ : 8.26 (d, J = 1.2Hz, 1H), 7.88 - 7.82 (m, 1H), 7.81 - 7.75 (m, 3H), 7.73 - 7.64 110 (m, 8H), 7.43 (t, J = 7.0 Hz, 4H), 7.32 (t, J = 7.7 Hz, 1H), 7.05 (d, J = 3.8 Hz, 1H), 6.78 (t, J = 7.6 Hz, 1H), 6.53 (d, J = 1.3 Hz, 1H), 6.36 (d, J = 8.0 Hz, 1H), 3.95 - 3.84 (m, 2H), 3.81 - 3.71 (m, 2H), 1.50 - 1.36 (m, 4H), 1.16 (dd, J = 9.2, 5.2 Hz, 4H), 1.11 - 1.161.02 (m, 4H), 0.88 - 0.79 (m, 10H). <sup>13</sup>C NMR (126 MHz, THF-115  $d_8$ ),  $\delta$ : 141.43, 141.22, 137.67, 131.92, 131.42, 131.12, 129.36, 129.21, 128.03, 127.63, 127.30, 126.80, 125.50, 123.96, 122.29, (E)-2-cyano-3-(5-(7-(5,11-dihexyl-6,12-diphenyl-5,11dihydroindolo[3,2-b]carbazol-2-yl)benzo[c][1,2,5]thiadiazol-4-yl)thiophen-2-yl)acrylic acid (DDC2)

- <sup>10</sup> <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ),  $\delta$ : 8.57 (s, 1H), 8.30 (t, J = 6.0Hz, 2H), 8.12 (d, J = 4.0 Hz, 1H), 8.06 – 8.01 (m, 1H), 7.70 (d, J= 12.6 Hz, 9H), 7.65 (dd, J = 8.1, 3.5 Hz, 1H), 7.61 – 7.54 (m, 2H), 7.43 (s, 1H), 7.31 (d, J = 7.5 Hz, 2H), 6.78 (t, J = 7.7 Hz, 1H), 6.37 (d, J = 7.9 Hz, 1H), 3.83 (d, J = 5.1 Hz, 4H), 1.50 –  $_{15}$  1.38 (m, 4H), 1.18 (dd, J = 16.5, 7.4 Hz, 4H), 1.09 (ddd, J = 12.3, 8.5, 5.9 Hz, 4H), 0.83 (dd, J = 15.9, 7.3 Hz, 10H). <sup>13</sup>C NMR (126) MHz, THF-d<sub>8</sub>), δ: 161.88, 152.66, 151.49, 147.46, 144.30, 141.79, 141.50, 137.84, 136.79, 135.19, 134.70, 131.47, 131.41, 129.41, 127.97, 127.69, 126.98, 126.86, 126.50, 126.29, 125.56, 20 125.24, 124.99, 123.91, 122.65, 122.23, 121.84, 121.68, 121.47, 121.03, 117.15, 117.11, 116.50, 114.49, 106.92, 43.11, 42.94, 30.26, 27.50, 27.41, 25.05, 23.63, 21.29, 12.17. HRMS (m/z): [M -  $H_{1}^{+}$  calcd for  $C_{56}H_{48}N_5O_2S_2$ , 886.3249; found, 886.3251. Anal. Calcd for C<sub>56</sub>H<sub>49</sub>N<sub>5</sub>O<sub>2</sub>S<sub>2</sub>: C, 75.73; H, 5.56; N, 7.89. Found: C, 25 75.61; H, 5.90; N, 7.76.
- Compound **DDC3-DDC5** were synthesized by the same procedures as described above for DDC1 using corresponding carbaldehyde (**DDB3–DDB4**)

#### (E)-2-cyano-3-(5-(5-(5,11-dihexyl-6,12-diphenyl-5,11-30 dihydroindolo[3,2-b]carbazol-2-yl)thiophen-2-yl)thion[3,2b]thiophen-2-yl)acrylic acid (DDC3)

<sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ),  $\delta$ : 8.27 (s, 1H), 8.08 (s, 1H), 7.91 (s, 1H), 7.81 (t, J = 7.5 Hz, 2H), 7.77 – 7.67 (m, 9H), 7.45 (dd, J = 8.7, 2.9 Hz, 2H), 7.38 (d, J = 3.7 Hz, 1H), 7.33 (s, 1H), 35 7.08 (d, J = 3.8 Hz, 1H), 6.78 (s, 1H), 6.51 (d, J = 1.4 Hz, 1H), 6.37 (d, J = 8.1 Hz, 1H), 3.97 – 3.87 (m, 2H), 3.84 – 3.73 (m, 2H), 1.51 – 1.39 (m, 4H), 1.21 – 1.13 (m, 4H), 1.07 (dd, J = 9.6, 5.0 Hz, 4H), 0.88 – 0.80 (m, 10H). <sup>13</sup>C NMR (126 MHz, THF- $d_8$ ),  $\delta$ : 145.82, 145.06, 143.69, 141.40, 141.04, 137.65, 136.92, 40 136.36, 132.77, 131.35, 131.06, 129.34, 129.21, 127.94, 127.60, 127.14, 126.76, 124.64, 123.96, 122.42, 122.16, 121.75, 121.55,

- 121.18, 121.02, 120.42, 118.21, 116.97, 116.92, 116.45, 113.42, 107.15, 106.86, 42.86, 30.24, 30.08, 28.44, 27.47, 27.34, 25.01, 24.96, 21.26, 12.17, 12.13. HRMS (*m/z*):  $[M H]^+$  calcd for <sup>45</sup> C<sub>56</sub>H<sub>48</sub>N<sub>3</sub>O<sub>2</sub>S<sub>3</sub>, 890.2909; found, 890.2912. Anal. Calcd for
- $C_{56}H_{48}N_3O_2S_3$ ; 890.2909; 100110, 890.2912. Anal. Carcu 101  $C_{56}H_{49}N_3O_2S_3$ : C, 75.39; H, 4.71; N, 5.54. Found: C, 75.54; H, 4.78; N, 5.39.

#### (E)-2-cyano-3-(5-(5-(5,11-dihexyl-6,12-diphenyl-5,11dihydroindolo[3,2-b]carbazol-2-yl)thiophen-2-yl)thieno[3,2-50 b]thiophen-2-yl)acrylic acid (DDC4)

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>),  $\delta$ : 8.59 (s, 1H), 8.18 (d, *J* = 7.6 Hz, 2H), 8.10 (s, 1H), 8.04 (dd, *J* = 7.0, 2.9 Hz, 1H), 7.73 (d, *J* = 3.2 Hz, 9H), 7.67 – 7.62 (m, 1H), 7.60 (d, *J* = 7.4 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.31 (s, 2H), 6.78 (t, *J* = 7.5 Hz, 1H), 6.38 (d, 55 *J* = 7.9 Hz, 1H), 3.92 – 3.77 (m, 4H), 1.45 (m, 4H), 1.21 – 1.14 (m, 4H), 1.09 (d, *J* = 7.2 Hz, 4H), 0.88 – 0.79 (m, 10H). <sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>),  $\delta$ : not sufficiently soluble to obtain a spectrum. HRMS (*m*/*z*): [M - H]<sup>+</sup> calcd for C<sub>58</sub>H<sub>48</sub>N<sub>5</sub>O<sub>2</sub>S<sub>3</sub>,

942.2970; found, 942.2983. Anal. Calcd for  $C_{58}H_{49}N_5O_2S_3$ : C, <sup>60</sup> 73.78; H, 5.23; N, 7.42. Found: C, 73.53; H, 5.47; N, 7.14.

(E)-2-cyano-3-(5'-(9-hexyl-9H-carbazol-3-yl)-[2,2'bithiophen]-5-yl)acrylic acid (CBZ)

<sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ),  $\delta$ : 8.58 (s, 1H), 8.50 (s, 1H), 8.29 (d, J = 7.8 Hz, 1H), 8.00 (d, J = 4.0 Hz, 1H), 7.85 (d, J = 8.2

- <sup>65</sup> Hz, 1H), 7.72 7.60 (m, 5H), 7.49 (t, J = 7.6 Hz, 1H), 7.24 (t, J = 7.5 Hz, 1H), 4.42 (t, J = 6.9 Hz, 2H), 1.82 1.73 (m, 2H), 1.25 (dt, J = 12.3, 6.7 Hz, 6H), 0.81 (t, J = 6.9 Hz, 3H). <sup>13</sup>C NMR (126 MHz, DMSO- $d_6$ ),  $\delta$ : 163.68, 147.29, 146.16, 146.09, 141.45, 140.57, 140.00, 133.47, 132.59, 128.35, 126.22, 124.33, 123.87,
- <sup>70</sup> 123.82, 123.62, 122.69, 122.01, 120.76, 119.15, 117.54, 116.68, 109.87, 109.52, 42.37, 30.94, 28.47, 26.10, 21.98, 13.79. HRMS (*m/z*):  $[M H]^+$  calcd for  $C_{30}H_{25}N_2O_2S_2$ , 509.1357; found, 509.1365. Anal. Calcd for  $C_{30}H_{26}N_2O_2S_2$ : C, 70.56; H, 5.13; N, 5.49. Found: C, 70.79; H, 5.17; N, 5.24.

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#### Notes and references

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- † Electronic Supplementary Information (ESI) available: (1) The frontier orbital plots of the HOMO and LUMO of these dyes; (2) Cyclic
- ss voltammograms of dyes attached on 8 µm TiO<sub>2</sub> films; (3) Crystal structure of **DDC**; (4) Absorption curves of dyes on TiO<sub>2</sub> films which were kept for 30 min at different temperatures (25°C, 40°C, 50°C and 60°C); (5) Adsorbed amount of **DDC1-DDC4** and **CBZ** under the following two conditions: The mixture solvents CH<sub>3</sub>CN: DMF (v:v=3:1) and v:v=0 and v=0 and v=0.
- <sup>90</sup> were used as the solvents for dye-loading; the TiO<sub>2</sub> films are consisted of 8 μm (T/SP); (6) Crystallography of **DDC**; (7) Synthetic procedure of intermediate **DDC-Br**, **4-7** and **B3-B4**. See DOI: 10.1039/b000000x/
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