Electronic Supplementary Information (ESI)

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

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1. **Fig. S1** The frontier orbital plots of the HOMO and LUMO of these dyes.

2. **Fig. S2** Cyclic voltammograms of dyes attached on 8 μm TiO_2 films.

3. **Fig. S3** Crystal structure of **DDC**.

4. **Fig. S4** Absorption curves of dyes on TiO_2 films which were kept for 30 min at different temperatures (25^{o}C, 40^{o}C, 50^{o}C and 60^{o}C).

5. **Table 1** Adsorbed amount of **DDC1-DDC4** and **CBZ** under the following two conditions: The mixture solvents CH_3CN: DMF (*v*:*v*= 3:1) were used as the solvents for dye-loading; the TiO_2 films are consisted of 8 μm (T/SP).

6. Crystallography of **DDC**.

7. Synthetic procedure of intermediate **DDC-Br, 4-7** and **B3-B4.**

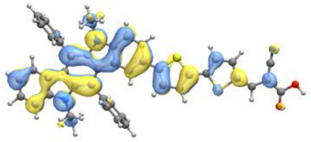
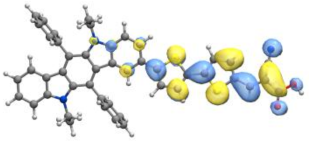
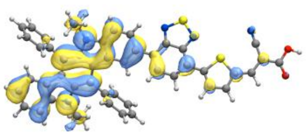
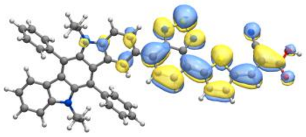
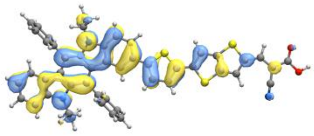
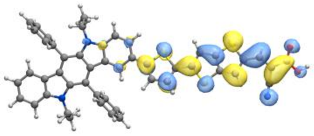
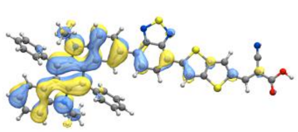
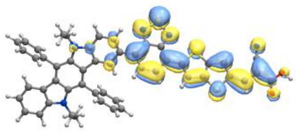
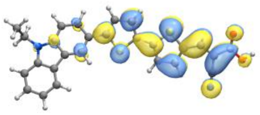
Compound	HOMO	LUMO
DDC1		
DDC2		
DDC3		
DDC4		
CBZ		

Fig. S1 The frontier orbital plots of the HOMO and LUMO of these dyes

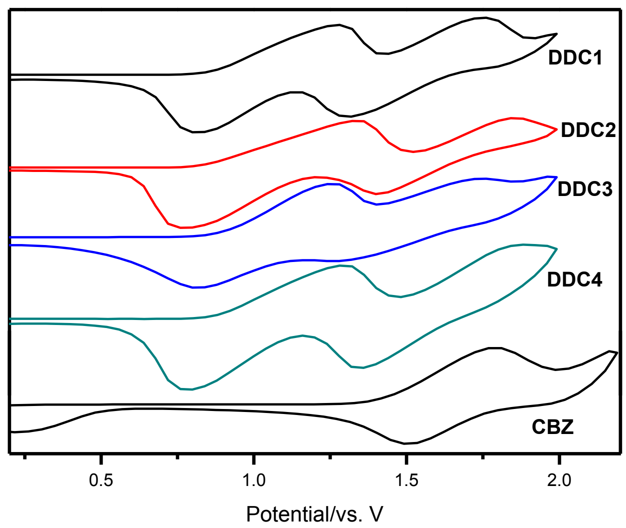


Fig. S2 Cyclic voltammograms of dyes attached on 8 μm TiO_2 films.

Crystallography of DDC

Single crystal of **DDC** suitable for X-ray analyses was obtained by slow evaporation of their corresponding solutions in hexane at room temperature.

Crystal data for **1a**: $C_{84}H_{88}N_4$, Mw=1153.58 g·mol^{-1}, 0.256×0.153×0.076 mm^3, *Monoclinic*, *P2(1)/c*, a = 12.364(3), b = 22.542(5), c = 12.548(3) Å, β= 106.993(5)°, V=3344.7(12) Å^3, F(000)=1240, ρ_{calcd}=1.145 Mg/m^3, $\mu(MoK\alpha)$=0.066 mm^{-1}, T=293(2) K, 20404 data were measured on a Bruker SMART Apex diffractometer, of which 13088 were uinque (R_{int}=0.0413); 853 parameters were refined against Fo^2 (all data), final wR_2=0.1269, S=1.026, $R_1(I>2\sigma(I))$=0.0574, largest final difference peak/hole= +0.152/-0.142 eÅ^{-3}. Structure solution by direct methods and full-matrix least-squares refinement against F^2 (all data) using SHELXTL.

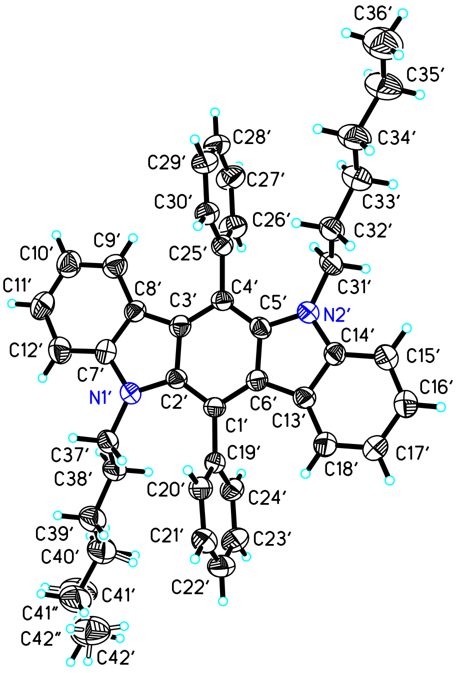


Fig. S3 Crystal structure of **DDC.**

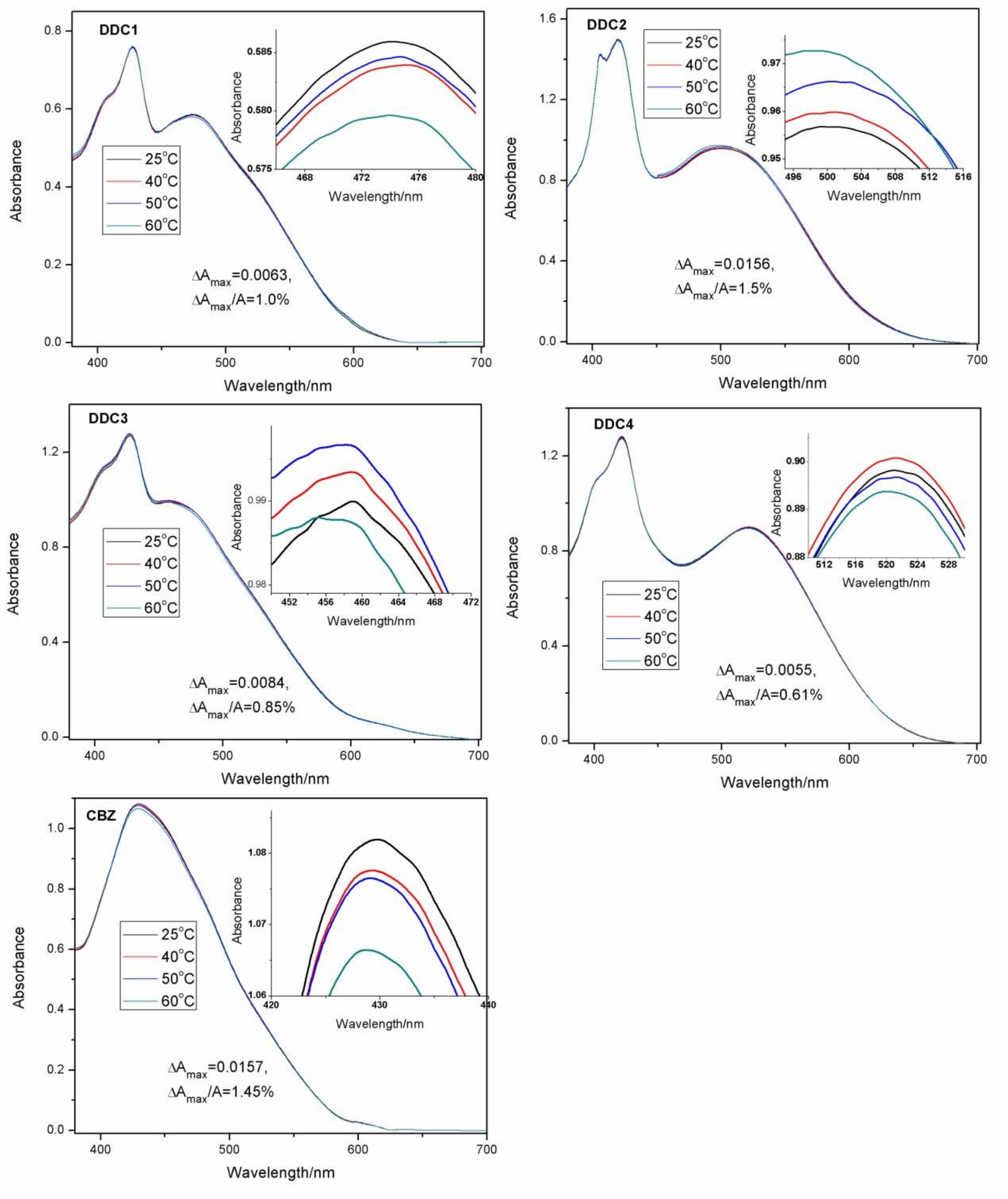


Fig. S4 Absorption curves of dyes on TiO_2 films which were kept for 30 min at different temperatures (25^{o}C, 40^{o}C, 50^{o}C and 60^{o}C), respectively; ΔA_{max}: the maximum absorbance variations in CT bands before and after heating; A: the maximum absorbance in CT bands before heating; ΔA_{max}/A: the percentage of the maximum absorbance variations in CT bands upon heating.

Table. S1 Adsorbed amount of **DDC1-DDC4** and **CBZ** under the following two conditions: The mixture solvents CH_3CN: DMF (*v*:*v*= 3:1) were used as the solvents for dye-loading; the TiO_2 films are consisted of 8 μm (T/SP).

Dye	Adsorbed amount (mol cm^{-2})
DDC1	4.21×10^{-8}
DDC2	4.08×10^{-8}
DDC3	3.40×10^{-8}
DDC4	4.79×10^{-8}
CBZ	4.19×10^{-8}

Synthesis:

6,12-diphenyl-5,6,11,12-tetrahydroindolo[3,2-b]carbazole (**1**)

Equimolar amounts of 1*H*- indole (23.4 g, 0.2 mol) and benzaldehyde (21.2 g, 0.2 mol) were added to a round-bottomed flask containing MeCN (500 mL). I_2 (0.52 g, 2 mol%) was added to the mixture and it was refluxed for 30 min. The solid compound obtained was filtered, dried, and recrystallized from DMF. The yield is 30 g, 75%. ^{1}H NMR (400 MHz, DMSO), δ: 10.69 (s, 2H), 7.35 – 7.31 (m, 4H), 7.29 (d, *J* = 7.3 Hz, 3H), 7.25 (d, *J* = 6.8 Hz, 2H), 7.22 (s, 1H), 7.21 – 7.16 (m, 2H), 7.07 (d, *J* = 7.9 Hz, 2H), 6.97 – 6.91 (m, 2H), 6.82 – 6.74 (m, 2H), 5.69 (s, 2H).

5,11-dihexyl-6,12-diphenyl-5,11-dihydroindolo[3,2-b]carbazole (**DDC**)

A mixture of **1** (10.2 g, 25 mmol), NaOH (10 g, 0.25 mol)and DMSO (1 L) were added to a round-bottomed flask and stirred for 30 min, then 2-bromino hexane (8.2 g, 50 mmol) was added dropwise to the reaction mixture. The reaction was stirred at ambient temperature for 12 h. The mixture was poured into water, then filtered and dried. The crude product was dissolved in $CHCl_3$ (200 ml). DDQ (11.4 g, 50 mmol) was added portionally at r.t. and then stirred for 30 min, the reaction mixture was filtered off and the filter-cake was rinsed with $CHCl_3$. The filtrate was condensed and then decolorized by activated clay under refluxed conditions for 1 h, then filtered off, again, the obtained filtrate was condensed, the residue was recrystallized from ethanol to yield light yellowish green powder 4.8 g, 33%. ^{1}H NMR (400 MHz, DMSO), δ: 7.75 – 7.64 (m, 10H), 7.44 – 7.39 (m, 2H), 7.33 – 7.27 (m, 2H), 6.76 (t, *J* = 7.3 Hz, 2H), 6.38 – 6.33 (m, 2H), 3.79 (dd, *J* = 8.6, 7.6 Hz, 4H), 1.49 – 1.36 (m, 4H), 1.17 (dd, *J* = 13.9, 7.0 Hz, 4H), 1.12 – 1.02 (m, 4H), 0.88 – 0.80 (m, 10H).

2-bromo-5,11-dihexyl-6,12-diphenyl-5,11-dihydroindolo[3,2-b]carbazole (**DDC-Br**)

A mixture of **DCC** (5.76 g, 10 mmol), NBS (1.97 g, 11 mmol) and CCl_4 (50 ml) were added to a round-bottomed flask and heated to reflux for 4 h. After cooling down, the mixture was washed with water for 3 times. The combined organic layer was concentrated using a rotary evaporator. The residue was recrystallized from hexane. An yellowish green solid was obtained with a yield of (5.37 g, 82%).

thieno[3,2-b]thiophene-2-carbaldehyde (4)

Under a nitrogen atmosphere, a solution of diisopropylamine (2.1 ml, 15 mmol) in anhydrous THF (20 ml) was added to a dried three-necked flask. The reaction mixture was cooled to 0^oC, then 2.4 M BuLi in hexane (6.2 ml, 15 mmol) was injected into the mixture slowly and then continuously stirred for 1 h before the solution of **3** in THF (10 ml) was added dropwise. After stirred for 1 h again, DMF (2.3 ml, 30 mmol) was added slowly. The mixture was stirred for another 1 h and then allowed to increased to the r.t. Water was added. The mixture was extracted with CH_2Cl_2 and the combined organic layer was vaporized. The residue was recrystallized from hexane. A brown solid was obtained with a yield of 0.924 g, 55%. ^1H NMR (400 MHz, $CDCl_3$), δ: 9.98 (s, 1H), 7.96 (s, 1H), 7.71 (d, *J* = 5.3 Hz, 1H), 7.41 – 7.29 (m, 1H)

5-bromothieno[3,2-b]thiophene-2-carbaldehyde (5)

A solution of NBS (1.96 g, 10 mmol) in DMF (20 ml) were added dropwise to the solution of **4** (1.68 g, 10 mmol) in DMF (30 ml) at ambient temperature and then the reaction was stirred for 2 h. The reaction mixture was poured into water and filtered off. The brown solid was obtained with a yield of 1.98 g, 80%. ^1H NMR (400 MHz, $CDCl_3$), δ: 9.97 (d, *J* = 2.6 Hz, 1H), 7.85 (s, 1H), 7.36 (s, 1H).

5-(thiophen-2-yl)thieno[3,2-b]thiophene-2-carbaldehyde (6)

In a 100 mL three-necked round-bottom flask, compound **5** (2.48 g, 10 mmol) obtained above, K_2CO_3 (6.9 g, 50 mmol), $Pd(PPh_3)_4$ (50mg), water (25 ml), and THF (75ml) were heated to 45ºC for 1h under an argon atmosphere. Then, (2-thienyl)boronic acid (1.89 g, 15 mmol) dissolved in 10 mL THF was added and the reaction was stirred at 45 ºC for 4 h. The mixture was washed with water and extracted with chloroform. The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated using a rotary evaporator. The residue was purified by column chromatography on silica to yield the product as a yellow powder (1.0 g, 40%).

5-(5-bromothiophen-2-yl)thieno[3,2-b]thiophene-2-carbaldehyde (**B3**)

B3 was synthesized from **6** by the same procedure as described for **6**. The yield is 80%.^{1}H NMR (400 MHz, DMSO), δ: 9.90 (s, 1H), 8.02 (d, *J* = 4.0 Hz, 1H), 7.93 (s, 1H), 7.72 (s, 1H), 7.58 (d, *J* = 3.9 Hz, 1H).

2-(5-bromothieno[3,2-b]thiophen-2-yl)-1,3-dioxolane (**7**)

A mixture of **5** (2.47 g, 10 mmol), Me_3SiCl (6.8 ml, 50 mmol) and CH_2Cl_2 (50 ml) was stirred at r.t., and ethane-1,2-diol (2.8 ml, 50 mmol) was slowly added. The reaction mixture was heated to reflux for 4 h. After cooling down, the mixture was washed with water and extracted with CH_2Cl_2. The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated using a rotary evaporator. The residue was recrystallized from ethanol to give a yield of (2.18 g, 75%).

5-(7-bromobenzo[c][1,2,5]thiadiazol-4-yl)thieno[3,2-b]thiophene-2-carbaldehyde (**B4**)

In a dry flask, 2.4 M n-BuLi in hexane (6.2 ml, 15 mmol) was added dropwise to a solution of compound **7** (2.66 g, 10 mmol) in THF at -78 ^{o}C under a N_2 atmosphere. After stirring for 1.5 h at this temperature, triisopropyl borate (6.5 ml, 50 mmol) was added dropwise and the mixture was allowed to warm to r.t followed by stirring for 2h. Then compound 4,7-dibromobenzo[c][1,2,5]thiadiazole (2.94 g, 10 mmol), K_2CO_3 (6.9 g, 50 mmol), $Pd(PPh_3)_4$ (50 mg, 0.05 mmol), water (25 mL), and THF (75mL) was added and the mixture was warmed to reflux after the flask was recharged with N_2. After refluxing for 4h, the mixture was allowed to cool down to r.t. and then washed with water. The organic layer was dried over anhydrous Na_2SO_4 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 a yellow solid. The solid was added to a mixture of THF (20 ml) and 6 M HCl (20 ml) and the reaction mixture was heated to reflux for 4h. The mixture was refluxed and extracted with CH_2Cl_2. The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated. The residue was recrystallized from EtOH to give a orange solid with a yield of 1.1 g, 29%. .^{1}H NMR (400 MHz, $CDCl_3$), δ: 10.01 (s, 1H), 8.50 (s, 1H), 7.98 (s, 1H), 7.94 – 7.90 (m, 1H), 7.79 (d, *J* = 7.7 Hz, 1H).