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Improving photovoltaic performance by installing alkyl chains perpendicular to π -conjugated plane of organic dye for dye-sensitized solar cells

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We demonstrate that employing long alkyl chains perpendicular to π -conjugated backbone's plane is a ¹⁰ promising strategy to construct efficient organic sensitizers for dye-sensitized solar cells (DSSCs) with efficient photovoltaic performance. The perpendicular alkyl chains have been suggested as superior alternatives to those parallel alkyl chains for preventing intermolecular interactions in D- π -A dyes, therefore co-adsorption with deoxycholic acid (DCA) can be avoided. DSSCs employing iodine/iodide electrolytes and an organic dye **LJ-8** with long alkyl chains perpendicular to its π -conjugated plane ¹⁵ produced high photovoltage of 0.801 V and high conversion efficiency over 8%.

Introduction

As a promising alternative to conventional photovoltaic devices, dye-sensitized solar cells (DSSCs) have received considerable attention and investigation with the aim of low cost and high 20 efficiency.¹ During the past two decades, tremendous research

- ²⁰ efficiency.²⁰ During the past two decades, tremendous research efforts have been devoted to develop efficient sensitizers which play a crucial role in DSSCs.² So far, there are mainly two kinds of sensitizers, involving metal-complexes and metal-free organic dyes.³ Metal-complexes such as ruthenium(II)–polypyridyl
- ²⁵ complexes (N3, N719, and black dye) and metal porphyrins, possess broad absorption spectra extending into the near-IR region and produce solar-to-electrical energy conversion efficiencies (η) of up to 13% under AM1.5 irradiation.⁴ However, the shortage of noble metal resource and the environmental
- ³⁰ issues would greatly limit their application prospect. In contrast, metal-free organic dyes have been gradually considered as more promising candidates for DSSCs due to their advantageous

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features, such as low costs, easier tunable absorptions, bandgaps and electrochemical properties through variation of the ³⁵ molecular structure, which typically consists of a donor- π acceptor (D- π -A) system.⁵ Besides expanding the light absorption edge of the organic dyes for efficient light harvesting associated with short-circuit photocurrent,⁶ valid concept toward high η of DSSCs based on them is minimizing the interficial ⁴⁰ losses with respect to open-circuit photovoltage.⁷ The low photovoltage is partially caused by dye aggregation resulting in intermolecular charge transfer, and charge recombination between injected electrons and acceptors (dye cation and I₃⁻

- ions).⁸ Coadsorption with bulk molecules, such as deoxycholic ⁴⁵ acid (DCA), 1-decylphosphonic acid (DPA), cyclodextrins (CD) has been frequently employed to supress dye-aggregation to improve efficiency.⁹ However, the co-adsorption strategy requires strict optimization of the adsorption conditions (e.g. solvent, dye and additive concentrations), reduces the dye
- ⁵⁰ coverage rate and is hard to drive the orderly assembling (one to one match) on the TiO₂ surface.¹⁰ As another solution, molecular engineering of organic sensitizers by introduction of long alky chains in the dye backbone has been intensively investigated.¹¹ However, this strategy claimed the consideration of the chain
- ⁵⁵ length and number, as well as the substitution position. For instance, a famous dye MK-2 with four hexylthiophene groups made a successful advance for retarding charge recombination by molecular engineering and achieved efficient photovoltaic performance,^{11a} but its analogues MK-4, MK-5, MK-7, MK-8
- ⁶⁰ can not perform efficiently.^{12a} Moreover, alkyl chains can not suppress the intermolecular interactions completely due to their orientation, and in some case, the alkylation decreases the efficiencies in comparison with the pristine dyes.¹² Therefore, the development of valid method for the suppression of dye

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aggregation is still a big challenge. Herein, we envisage that substituents being perpendicular to the π -conjugated backbone may be a superior strategy to construct efficient dyes toward high efficiency without additive engineering.

In order to confirm our assumption, we employ the oligothiophene as π -conjugated backbone, which was often used to develop efficient sensitizers for DSSCs. On the other hand, it had been investigated that the phenyl substituent is almost perpendicular to the thiophene plane in 3-phenylthiophene due to ¹⁰ its inherent cross-conjugation properties.¹³ Therefore, it is reasonable to install alky chains on the phenyl group in β positions of thiophene moieties to be perpendicular to the π conjugated backbone. In this context, we design three new D- π -A dyes employing substituted oligothiophene as π -spacer for ¹⁵ DSSCs, and investigated the relationship between substituents and photovoltaic performance, particularly focus on the effect of the orientation of the alky chains on the photovoltaic performance.



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Scheme 1 Molecular structures and synthetic routes of circle chain embracing D-π-A dyes LJ-7, LJ-8 and LJ-9.

Results and discussion

The synthesis of three D- π -A dyes LJ-7, LJ-8 and LJ-9 was achieved *via* bromination, Suzuki coupling and Knoevenagel condensation reactions in a moderated yield by rational routes

- ²⁵ shown in Scheme 1. Two substituted bithiophene derivates 1a and 1b were prepared according to the reported method.¹⁴ Compound 5 was used as received from chemical companies without further purification. Bromination of the substituted bithiophene 1a and 1b by NBS produced the desired compound
- ³⁰ 2a and 2b,¹⁵ respectively. Compound 2a, 2b and 5 were reacted with 5-formylthiophene-2-boronic acid to synthesize aldehyde 3a, 3b and 6,¹⁶ respectively. Suzuki coupling between the resulted aldehydes (3a, 3b and 6) and 9-ethyl-9H-carbazol-3-ylboronic acid obtain dye precusors 4a, 4b and 7, which were converted to
- ³⁵ dyes LJ-7, LJ-8 and LJ-9 as black solids via Knoevenagel condensation, respectively. The structures of desired organic

sensitizers were confirmed by ¹H and ¹³C NMR spectroscopy as well as mass spectrometry.





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Fig. 2 Absorption spectra of LJ-7, LJ-8 and LJ-9 anchored on a transparent TiO_2 film with or without DCA.

The absorption spectra of three new D-π-A dyes LJ-7, LJ-8 5 and LJ-9 in dichloromethane are shown in Fig. 1, and the data are summarized in Table 1. These three new dyes LJ-7, LJ-8 and LJ-9 exhibit two distinct absorption bands: the longer wavelength absorption band in the visible region (440-500 nm) that can be assigned to an intramolecular charge transfer (ICT) 10 from the carbazole donating group to the cyanoacrylic acid anchoring moiety; the shorter wavelength absorption band in the UV region (360~400 nm) is originated from the π - π * electron transitions of the conjugated molecules as well as the overlapped $n-\pi^*$ electron transitions. There was no obvious difference 15 between the absorption spectra of LJ-7 and LJ-8. Owing to the longer alky chains in the electron-donating aromatic substituents on conjugated oligothiophene backbone, dye LJ-8 exhibts a slight bathochromic shift as well as a little higher molar extinction coefficient (ε) in comparison with its analogue LJ-7. 20 Whereas the spectra of LJ-9 shows an ~50 nm bathochromic shift and a lower ε value relative to those of LJ-7 and LJ-8. Without regard to the solvent effect, we suggest the different kinds of substituted group on conjugated oligothiophene backbone in dye LJ-9 and the former two dyes (LJ-7 and LJ-8)

25 lead to significant diversity of the configuration of the dye

Table 1 Ontirel and Daday Demonstrate of Deves I I 7 I I 9

skeleton, which will be further disscussed in the DFT calculation details (*vide infra*). All these three new D-π-A dyes LJ-7, LJ-8 and LJ-9 exhibit similar emission in CH₂Cl₂ solution but different stokes shifts (Fig. S1, ESI†). Among these three new ³⁰ dyes, dye LJ-9 exhibits the largest stokes shift, which indicates significant structural reorganization of dye molecule upon photoexcitation and the large degree of rotational freedom in dye LJ-9.¹⁷ On the contrary, dye LJ-8 exhibits the smallest stokes shift probably due to its relative rigid configuration of dye ³⁵ molecule.

The UV-vis absorption spectra of dyes LJ-7, LJ-8 and LJ-9 adsorbed on TiO₂ films with or without DCA are shown in Fig. 2. The λ_{max} for the dye-loaded TiO₂ films are also listed in Table 1. After being adsorbed on TiO₂ film, The maximum absorption of these dyes anchored on TiO₂ film exhibits approximately 40 nm hypochromatic shift in comparison with that in solution, respectively. Such blue shift would be assigned to the solvent

effect and/or deprotonation of the carboxylic acid in the anchoring process.¹⁸ The influence of the co-adsorption of DCA ⁴⁵ on the TiO₂ surface on the absorption spectra has been

- investigated (Fig. 2). After coadsorption with DCA, the intensity of the ICT band for these three new dyes reduces, which would must be attributed to the decrease of the dye-loading amount during the DCA coadsorption.^{8b} Both dipping in the solution
- ⁵⁰ with and without DCA, dialkoxyphenyl substituted dyes LJ-7 and LJ-8 perform fine absorption peaks similar to those in solution, suggesting that the steric hindrance of dialkoxyphenyl groups are effective to supress the intermolecular interactions effectively. Whereas, the situation of dye LJ-9 employing two
- ⁵⁵ hexyl chains are slightly different. Without co-adsorption, the absorption spectrum of LJ-9 is broadened. The results suggests that the hexyl groups on the conjugated oligothiophene backbone of dye LJ-9 are not effective enough to supress the intermolecular interaction and/or dye aggregation on the TiO₂
 ⁶⁰ surface, which will be prevented by means of coadsorption with DCA. The probable reason is further disscussed by molecular structure analysis (*vide infra*).

I able I	Optical and	i Redox P	arameters	of Dyes L	J-/, LJ-ð	, and LJ-9

Dye	$^{a}\lambda_{max}/nm (\epsilon/L mol^{-1} cm^{-1})$	$^{b}\lambda_{max}/nm$	^e S ^{+/0} /V (vs NHE)	^f S ^{+/*} /eV (vs NHE)	${}^{g}E_{0-0}/V$
LJ-7	492(31800), 360(20950)	451°	0.97	-1.09	2.06
		451 ^d			
LJ-8	498(32880), 361(22420)	453°	0.93	-1.12	2.05
		453 ^d			
LJ-9	440(27110), 332(19780)	416 ^c	1.01	-1.14	2.15
		412 ^d			

a) The absorption spectra were measured in CH_2Cl_2 solution (2 × 10⁻⁵ M). b) measured on TiO₂ film. c) TiO₂ films were dipping in a 0.3 mM solution of

⁶⁵ dye in CH₃CN/*n*-BuOH (1/1, v/v). d) TiO₂ films were dipping in a mixture of dye (0.3 mM) and DCA (20 mM) in CH₃CN/*n*-BuOH (1/1, v/v). e) The S⁺/0 corresponding to the ground-state oxidation potential (vs NHE) in CH₂Cl₂ internally calibrated with ferrocene. f) S⁺/* = S⁺/0 - $E_{0.0}$, where $E_{0.0}$ is the zero-zero transition energy. g) $E_{0.0}$ values were estimated from the intersection between the normalized absorption and emission spectra in CH₂Cl₂ (Fig. S1, ESI[†]).



Fig. 3 Cyclic voltammograms of dyes LJ-7, LJ-8, and LJ-9 in CH₂Cl₂/TBAHFP (0.1 M), $[c] = 1 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, 293 K, scan rate = 100 mV·s⁻¹.

⁵ Cyclic voltammetry (CV) was carried out in CH₂Cl₂ containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAHFP) as a supporting electrolyte to investigate the electrochemical properties of three new D- π -A dyes LJ-7, LJ-8 and LJ-9. As shown in Fig. 3, all these dyes exhibit two ¹⁰ reversible oxidative waves. Due to these three new employing same donor part and similar D- π -A skeleton, their HOMO levels corresponding to the first oxidation potentials exhibit little difference, increase in the order of LJ-8 (0.93 V) < LJ-7 (0.97 V) < LJ-9 (1.01 V), which was associated with the electron-¹⁵ donoating ability of the corresponding substituent on the conjugated oligothiophene backbone in these three dyes. The energy-level diagram of dyes, the electrolyte and TiO₂ was shown in Fig. S2. The HOMO levels of these three dyes are all more positive than the Nernst potential of Ir/I₃ redox couple (0.4 V) with S

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- ²⁰ V vs NHE), ensuring regeneration of the oxidized dyes by I after electron injection, with the driving force of $0.53 \sim 0.61$ V, respectively. The LUMO levels corresponding to the excited state redox potentials of these three dyes (-1.09 to -1.14 V vs NHE) are sufficiently more negative than the conduction band of V(0.50)
- $_{25}$ TiO₂ (-0.5 V vs NHE), ensuring sufficient driving force (0.59 ~ 0.64 V) for electron injection from the excited dyes to the conduction band of TiO₂. These results suggested the potential application of these three new sensitizers in dye-sensitized solar cells.^{5e}
- To explain the different absorption properties between dialkyoxyphenyl substituted dye (LJ-7 or LJ-8) and hexyl substituted dye LJ-9, we further investigate the optimized configuration of dyes LJ-8 and LJ-9 by density functional theory (DFT) caculation. The optimized ground-state geometries
- as and the dihedral angles between the π -conjugated units indicated that the configurations of the bithiophene units connecting the donor moieties were different in dyes **LJ-8** and **LJ-9** (Figure S3). Two flexible hexyl β -substituents in **LJ-9** caused large dihedral twisting of the bithiophene units (torsion angle, 62.5°). In
- ⁴⁰ contrast, in **LJ-8**, the two dibutoxyphenyl groups and the bithiophene backbone seem to be restrained each other and hamper the rotation around the thiophene-thiophene bond, so that the thiophene units were relative rigid and twist would be restricted, which facilitated ICT, as suggested by the absorption
- ⁴⁵ properties described above. As shown in Fig. S3, the hexyl chains are horizontal to their corresponding thiophene planes in

dye LJ-9, they can not prevent the intermolecular π - π interaction and/or dye aggregation completely eventhough two thiophene units are twisted, which was suggested by the broaden absorption $_{50}$ spectra on TiO₂ film in the presence of coadsorption with DCA. However, four butyl chains are located on two sides of thiophene planes and perpendicular to the π -conjugated backbone in dye LJ-8, which are effective to supress the intermolecular interaction and/or charge transfer. Moreover, DFT calculations 55 of dyes LJ-7, LJ-8 and LJ-9 are carried out at the B3LYP/6-31G** level to gain further insight into their frontier molecular orbitals. As shown in Fig. S4 (ESI⁺), LUMOs show localized electron distributions through the cyanoacrylic acid and its adjacent π -spacer, whereas HOMOs are mainly delocalized from 60 the donor parts to the oligothiophene π -spacer. Hence, both orbitals provide sufficient overlap between donor and acceptor to guarantee a fast charge transfer transition.

The device fabrication and characterization were performed according to our previous method,^{15,16} which was detailed in ⁶⁵ supporting information (ESI[†]). Photovoltaic characteristics of the DSSCs based on dyes **LJ-7**, **LJ-8** and **LJ-9** and the influences of DCA co-adsorption on their photovoltaic performances have been investigated,¹⁹ employing a solution of 0.6 M 1-propyl-2,3-dimethylimidazolium iodide, 0.05 M I₂, 0.1 ⁷⁰ M LiI and 0.5 M *tert*-butylpyridine (TBP) in acetonitrile as electrolyte. The device performance statistics of them were provided in Fig. S5, which suggested that the reproductivity of devices based on pristine dyes was slightly better than those with DCA coadsorption.



Fig. 4 IPCE spectra of DSSCs based on dyes LJ-7, LJ-8 and LJ-9 with/without DCA coadsorption.

The onset wavelength of IPCE spectra shift toward the red region in the order LJ-9 < LJ-7 < LJ-8 cells (Fig. 4), in accord ⁸⁰ with the absorption spectra observed for the dye-loaded TiO₂ films. DSSCs based on dialkoxyphenyl substituted dyes LJ-7 and LJ-8 without coadsorption perform similar maximum IPCE value observed in the range of 400~600 nm in comparison with those under coadsorption with DCA. However, in the case of 85 hexyl substituted dye LJ-9, the IPCE value was increased after the coadsorption with DCA. These results implied that alkyl chains perpendicular to π -conjugated plane of dyes LJ-7 and LJ-8 are efficient to retard the dye-aggregation and/or intermolecular interaction for efficient electron injection, 90 whereas that in LJ-9 should be achieved by coadorption with DCA. This phenomena was similar with that reported previously.^{8b} As shown in Fig. S6, integrated photocurrent values

calculated from IPCE of DSSCs based on LJ-7, LJ-7-DCA, LJ-8, LJ-8-DCA, LJ-9 and LJ-9-DCA were 12.85 mA·cm⁻², 12.54 mA·cm⁻², 13.1 mA·cm⁻², 12.28 mA·cm⁻², 10.27 mA·cm⁻² and 10.88 mA·cm⁻², respectively. The result closed to the short-Table 2 Photovoltaic performance for DSSCs based on dyes LJ-7, LJ-8 and LJ-9^a

s circuit current density (J_{SC}) of their corresponding devices measured by *J-V* characterizations at the 100 mW cm⁻², simulated AM1.5G conditions (Table 2, Fig. 5).

Dyes	DCA[mM]	$J_{\rm SC} [{\rm mA} \cdot {\rm cm}^{-2}]$	$V_{\rm OC}$ [V]	FF	η [%]	Dye-loading amount
						[10 ⁻⁷ mol·cm ⁻²]
LJ-7	0	12.94	0.738	0.734	7.01	2.01
LJ-7	20	12.78	0.747	0.758	7.24	1.89
LJ-8	0	13.05	0.801	0.766	8.01	1.92
LJ-8	20	12.51	0.751	0.753	7.07	1.73
LJ-9	0	9.96	0.715	0.711	5.06	1.94
LJ-9	20	10.57	0.751	0.727	5.77	1.82

10 a) Measurements were performed under AM 1.5 irradiation on the DSSC devices with 0.2304 cm² active surface. J_{SC} , short-circuit current density; V_{OC} , open-circuit voltage; FF, fill factor; η , conversion efficiency.



Fig. 5 *J-V* curves of DSSCs based on **LJ-7**, **LJ-8** and **LJ-9** with/without DCA coadsorption.

- ¹⁵ The open-circuit voltages (V_{OC}) of DSSCs based on the pristine dyes **LJ-7**, **LJ-8** and **LJ-9** are 0.738 V, 0.801 V and 0.715 V, respectively. After coadsorption with DCA, V_{OC} of DSSCs based on **LJ-7** and **LJ-9** increase to 0.747 V and 0.751 V, respectively, whereas that of **LJ-8** based device decrease to
- ²⁰ 0.751. The different influence of DCA coadsorption on the V_{OC} of DSSCs based on these three dyes implied that various effect of coadsorption on charge recombination rates, which were further investigated by the measurement of electron lifetimes (τ_e) in the conduction band of TiO₂ by means of intensity-modulated ²⁵ photovoltage spectroscopy (IMVS). As shown in Fig. 6, the τ_e
- values of the DSSCs based on pristine dyes vary in the order of LJ-8 > LJ-7 > LJ-9, suggesting that the long alkyl chains perpendicular to π -conjugated plane of organic dyes (LJ-7 and LJ-8) are superior to those in parallel mode (dye LJ-9) for
- $_{\rm 30}$ suppression of charge recombination between I_3^- and injected electron in ${\rm Ti}O_2.$



Fig. 6 Electron lifetime (τ_e) as a function of V_{OC} for DSSCs based on dyes LJ-7, LJ-8 and LJ-9 with and without DCA coadsorption.

- As shown in Fig. 7, we proposed the possible mechanisms of the influence of DCA on the dye adsorption on the TiO₂ surface and the photovoltaic properties. For dyes LJ-7 and LJ-8, intermolecular energy transfer may be prevented by the steric hindrance being perpendicular to π-conjugated plane of organic 40 dyes even without DCA, leading to a high IPCE value. On the other hand, upon coadsorption with DCA during the dipping process, the photocurrent decreased slightly. This is probably attributed to the decrease in dye loading amount on the TiO₂ surface because the DCA molecules occupied a part of the TiO₂ surface area. In contrast, dye LJ-9 with two hexyl groups attaching on the dye backbone can not retard the intermolecular interactions and/or dye aggregation on the TiO₂ surface
- completely without DCA, which resulted in the photocurrent and photovoltage loss due to the intermolecular energy transfer and ⁵⁰ excited-state quenching of the dye, as well as serious charge
- recombination.²⁰ After co-adsorption with DCA, it is expected that the intermolecular energy-transfer between dye **LJ-9** molecules was efficiently suppressed, and the photocurrent was therefore improved eventhough dye loading amount decrease.
- ⁵⁵ The enhancement of V_{OC} of devices based **LJ-7** and **LJ-9** after DCA coadsorption was mainly attributed to the increasing blocking effect. In the case of **LJ-8**, two long alkyl chains being pendecular to the dye backbone would assemble a dense blocking layer *via* crosslinking effect, and was sufficient to ⁶⁰ retard the charge recombination between I₃⁻ and injected electron

in TiO₂, which resulted in a high V_{OC} over 0.8 V. However, when DCA molecules were coadsorbed on the TiO₂ surface with **LJ-8** lead to the decrease of V_{OC} , probably owing to the reducing dye-

loading amount and deteriorated blocking effect.



Fig. 7 Schematic drawings of LJ-7, LJ-8 and LJ-9 adsorbed on the TiO₂ surface (a) without and (b) with DCA (ET: energy transfer).

Conclusion

- ¹⁰ In summary, we have successfully developed three new D- π -A dyes **LJ-7**, **LJ-8** and **LJ-9** bearing substituted oligothiophene as π -spacer, cyanoacrylic acid as the acceptor moieties for high-efficiency DSSCs. Due to the preferable orientation for blocking effect, the long alkyl chains being pendicular to the dye ¹⁵ backbone seems to be superior to those attaching on backbone in parallel for suppressing charge recombination, which resulted in high photovoltage. Moreover, the long alkyl chains in pendicular
- was also superior to those attaching dye backbone directly for reducing the twist effect between conjugated planes, which gain ²⁰ braoder light harvesting and resulting high photocurrent. As a result, a high V_{OC} over 0.8V and high power conversion
- efficiency over 8% were achieved in **LJ-8** based devices through molecular egineering by the present strategy. The strategy described here should give a significant enlightenment for ²⁵ molecular design of organic semiconductors in photoelectronic
- field, particularly involving light harvesting and intermolecular interaction.

Experimental

Synthesis and characterization

- Preparation of Compond 2a. To a stirred solution of compound 1a (200 mg, 0.46 mmol) in AcOH/CHCl₃ (10 mL/20 mL) was added NBS (171 mg, 0.96 mmol) portionwise at 0 °C. The reaction mixture was stirred for 2 hours and then treated with water (50 mL), extracted twice with CH₂Cl₂ (40 mL × 2).
 The combined organic layers were washed twice with water and once with brine, dried over anhydrous sodium sulfate. After
- evaporation of the solvent under reduced pressure, The residue was treated with MeOH (15 mL), the solid was collected by filtration, and dried under vacuum to yield the desired product **2a**
- ⁴⁰ as a white powder (246 mg, 91%). ¹H NMR (CDCl₃, 400 MHz): δ 7.14 (t, J = 8.4 Hz, 2H), 6.79 (s, 2H), 6.38 (d, J = 8.4 Hz, 4H), 3.56 (s, 12H). ¹³C NMR (CDCl₃, 400 MHz): δ 157.45, 134.74, 133.76, 130.88, 128.35, 112.51, 109.64, 103.82, 55.25. ESI (m/z): Calcd for C₂₄H₂₀Br₂O₄S₂, 593.92 (M)⁺; found, 893.92.
- ⁴⁵ Preparation of Compond 2b. To a stirred solution of compound 1b (303 mg, 0.5 mmol) in AcOH/CHCl₃ (15 mL/30 mL) was added NBS (178 mg, 1.0 mmol) portionwise at 0 °C. The reaction mixture was stirred for 2 hours and then treated with ice water (40 mL), extracted twice with CH₂Cl₂ (50 mL × 2).
 ⁵⁰ The combined organic layers were washed twice with water and once with brine, dried over anhydrous sodium sulfate. After evaporation of the solvent under reduced pressure, The residue was treated with MeOH (10 mL), and the solid was collected by filtration, and dried under vacumm to yield compund 2b as a ⁵⁵ white powder (340 mg, 89%). ¹H NMR (CDCl₃, 400 MHz): δ

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7.03 (t, J = 8.4 Hz, 2H), 6.73 (s, 2H), 6.29 (d, J = 8.4 Hz, 4H), 3.65-3.72 (m, 8H), 1.50-1.57 (m, 8H), 1.23-1.35 (m, 8H), 0.89 (t, J = 7.2 Hz, 12H). ¹³C NMR (CDCl₃, 400 MHz): δ 157.42, 134.80, 134.33, 131.60, 128.65, 113.16, 108.98, 104.43, 67.68, 31.19, 5 19.19, 13.90. ESI (m/z): Calcd for C₃₆H₄₄Br₂O₄S₂, 762.10 (M)⁺; found, 762.10.

Preparation of Compond 3a. To a stirred solution of compound 2a (240 mg, 0.404 mmol) in THF/H₂O (40 mL/10 mL) was added 5-Formyl-2-thiopheneboronic acid (63 mg, 0.404 10 mmol), potassium carbonate (167 mg, 1.21 mmol), followed by $Pd(PPh_3)_4$ (46 mg, 0.04 mmol) as a catalyst at room temperature. The reaction mixture was stirred at 40 °C under argon atmosphere for 4 h. Evaporation of the solvent under reduced pressure and the residue was treated with water (50 mL), 15 extracted twice with CH_2Cl_2 (50 mL \times 2). The combined organic layers were washed twice with water and once with brine, dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the residue was purified by chromatography using hexane/EA (10/1, v/v) as an eluent to yield compound 3a 20 as an orange solid (116 mg, 46%). ¹H NMR (CDCl₃, 400 MHz): δ 9.84 (s, 1H), 7.63 (d, J = 3.6 Hz, 1H), 7.14-7.18 (m, 4H), 6.85 (s, 1H), 6.40-6.43 (m, 4H), 3.59 (s, 6H), 3.58 (s, 6H); ¹³C NMR (CDCl₃, 400 MHz): δ 182.47, 158.17, 147.84, 141.27, 137.44, 135.51, 134.79, 133.96, 132.82, 131.87, 131.46, 130.53, 129.24, 25 123.78, 112.68, 110.28, 103.96, 55.61. ESI (m/z): Calcd for C₂₉H₂₃BrO₅S₃, 625.99 (M⁺); found, 648.98 [M+Na]⁺.

Preparation of Compond 3b. To a stirred solution of compound **2b** (320 mg, 0.42 mmol) in THF/H₂O (40 mL/10 mL) was added 5-Formyl-2-thiopheneboronic acid (66 mg, 0.42 30 mmol), potassium carbonate (174 mg, 1.26 mmol), followed by $Pd(PPh_3)_4$ (48 mg, 0.042 mmol) as a catalyst at room temperature. The reaction mixture was stirred at 40 °C under argon atmosphere for 4 h. Evaporation of the solvent under reduced pressure and the residue was treated with water (40 mL), $_{35}$ extracted twice with CH₂Cl₂ (50 mL × 2). The combined organic layers were washed twice with water and once with brine, dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the residue was purified by chromatography with hexane/EA (10/1, v/v) as an eluent to yield compound **3b** as 40 an orange solid (160 mg, 48%). ¹H NMR (CDCl₃, 400 MHz): δ 9.81 (s, 1H), 7.62 (d, J = 4.2 Hz, 1H), 7.11-7.12 (m, 2H), 7.05 (t, J = 8.4 Hz, 1H), 7.03 (t, J = 8.4 Hz, 1H), 6.78 (s, 1H), 6.30 (d, J) = 8.4 Hz, 2H), 6.28 (d, J = 8.4 Hz, 2H), 3.65-3.75 (m, 8H), 1.48-1.54 (m, 8H), 1.22-1.32 (m, 8H), 0.87 (t, J = 7.2 Hz, 6H), 0.82 (t,

- ⁴⁵ *J* = 7.2 Hz, 6H); ¹³C NMR (CDCl₃, 400 MHz): δ 182.40, 157.30, 148.15, 140.90, 137.56, 135.71, 134.83, 134.57, 132.49, 132.12, 132.05, 131.80, 131.43, 130.89, 129.22, 123.15, 113.11, 109.47, 104.40, 67.63, 31.16, 19.13, 13.81. ESI (m/z): Calcd for $C_{41}H_{47}BrO_5S_3$, 794.18 (M⁺); found, 817.17 [M+Na]⁺.
- Preparation of Compond 4a. To a stirred solution of compound 3a (100 mg, 0.159 mmol) in 1,4-dioxane/H₂O (20 mL/5 mL) was added 9-ethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (61 mg, 0.191 mmol), potassium carbonate (66 mg, 0.477 mmol), followed by
- ⁵⁵ Pd(PPh₃)₄ (18 mg, 0.016 mmol) as a catalyst at room temperature. The reaction mixture was stirred at 90 °C under argon atmosphere overnight. Evaporation of the solvent under reduced pressure and the residue was treated with water (40 ml),

extracted twice with CH₂Cl₂ (40 mL \times 2). The combined organic ⁶⁰ layers were washed twice with water and once with brine, dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the residue was purified by chromatography with PE/EA (5/1, v/v) as an eluent to yiled compound **6** as an orange solid (85 mg, 72%). ¹H NMR (CDCl₃, 400 MHz), δ : 9.83 ⁶⁵ (s, 1H), 8.26 (d, *J* = 1.6 Hz, 1H), 8.10 (d, *J* = 7.6 Hz, 1H), 7.67

(d, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H), 7.64 (d, J = 4.0 Hz, 1H), 7.46-7.49 (m, 1H), 7.41 (d, J = 8.0 Hz, 1H), 7.37 (d, J = 8.8 Hz, 1H), 7.13-7.24 (m, 6H), 6.42 (d, J = 1.6 Hz, 2H), 6.40 (d, J = 1.6 Hz, 2H), 4.37 (q, J = 7.2 Hz, 2H), 3.59 (s, 6H), 3.58 (s, 6H), 1.44 (t, J70 = 7.2 Hz, 3H). ¹³C NMR (CDCl₃, 400 MHz), δ : 182.51, 157.86, 148.37, 143.00, 140.86, 140.46, 139.46, 137.63, 137.33, 132.22, 132.09, 131.70, 131.28, 131.16, 128.83, 128.69, 126.88, 126.01, 125.80, 124.03, 123.40, 122.98, 120.65, 119.09, 117.51, 113.99, 113.31, 108.70, 104.09, 55.45, 37.74, 13.93. ESI (m/z): Calcd for 75 C₄₃H₃₅NO₅S₃, 741.17 (M)⁺; found, 741.17.

Preparation of Compond 4b. To a stirred solution of compound **3b** (70 mg, 0.088 mmol) in 1,4-dioxane/H₂O (20 mL/5 mL) was added 9-ethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (43 mg, 0.132 mmol),

- ⁸⁰ potassium carbonate (37 mg, 0.264 mmol), followed by $Pd(PPh_3)_4$ (12 mg, 0.01 mmol) as a catalyst at room temperature. The resulting mixture was stirred at 90 °C under argon atmosphere overnight. Evaporation of the solvent under reduced pressure and the residue was treated with water (40 ml),
- $_{85}$ extracted twice with CH_2Cl₂ (40 mL \times 2). The combined organic layers were washed twice with water and once with brine, dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the residue was purified by chromatography with PE/EA (5/1, v/v) as an eluent to yield compound **6** as an
- ⁹⁰ orange solid (61 mg, 76%). ¹H NMR (CDCl₃, 400 MHz), δ: 9.83
 (s, 1H), 8.26 (d, J = 1.6 Hz, 1H), 8.09 (d, J = 7.6 Hz, 1H), 7.657.68 (m, 2H), 7.46-7.48 (m, 1H), 7.37-7.42 (m, 2H), 7.22-7.24 (m, 1H), 7.19 (s, 1H), 7.16 (d, J = 4.0 Hz, 1H), 7.14 (s, 1H),
 7.00-7.05 (m, 2H), 6.30 (d, J = 1.2 Hz, 2H), 6.28 (d, J = 1.2 Hz,
- ⁹⁵ 2H), 4.38 (q, J = 7.2 Hz, 2H), 3.65-3.76 (m, 8H), 1.51-1.62 (m, 8H), 1.47 (t, J = 7.2 Hz, 3H), 1.24-1.37 (m, 8H), 0.80-0.84 (m, 12H). ¹³C NMR (CDCl₃, 150 MHz), δ: 182.51, 157.26, 148.76, 142.22, 140.62, 140.45, 139.38, 137.81, 137.86, 132.33, 132.02, 131.44, 128.30, 128.12, 127.60, 126.05, 125.95, 123.84, 122.96, ¹⁰⁰ 120.52, 119.07, 117.28, 114.37, 113.55, 108.67, 104.41, 104.33, 67.57, 37.75, 31.31, 31.28, 19.27, 13.90. ESI (m/z): Calcd for C₄₃H₃₅NO₅S₃, 909.36 (M)⁺; found, 909.36.

Preparation of Compond 6. To a stirred solution of compound 5 (300 mg, 0.612 mmol) in THF /H₂O (40 mL/10 mL) ¹⁰⁵ was added 5-Formyl-2-thiopheneboronic acid (95 mg, 0.612 mmol), potassium carbonate (253 mg, 1.837 mmol), followed by Pd(PPh₃)₄ (69 mg, 0.06 mmol) as a catalyst at room temperature. The reaction mixture was stirred at 50 °C under argon atmosphere for 2 h. Evaporation of the solvent under reduced ¹¹⁰ pressure and the residue was treated with water (40 mL), extracted with CH₂Cl₂ (50 mL × 2). The combined organic layers were washed twice with water and once with brine, dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the residue was purified by chromatography ¹¹⁵ with hexane/EA (10/1, v/v) as an eluent to yield compound **3a** as an orange solid (140 mg, 44%). ¹H NMR (CDCl₃, 600 MHz): δ

9.86 (s, 1H), 7.66 (d, J = 4.2 Hz, 1H), 7.22 (d, J = 3.6 Hz, 1H), 7.21 (s, 1H), 6.94 (s, 1H), 2.47-2.50 (m, 4H), 1.51-1.57 (m, 4H), 1.23-1.30 (m, 12H), 0.84-0.88 (m, 6H); ¹³C NMR (CDCl₃, 400 MHz): δ 182.44, 146.90, 144.43, 143.76, 141.78, 137.23, 135.87, s 131.58, 129.57, 129.04, 127.55, 124.15, 112.58, 31.57, 30.54, 30.50, 29.03, 28.98, 28.88, 22.54, 14.03. ESI (m/z): Calcd for C₂₅H₃₁BrOS₃, 522.07 (M⁺); found, 522.07.

Preparation of Compond 7. To a stirred solution of compound 6 (130 mg, 0.249 mmol) in 1,4-dioxane/H₂O (25 10 mL/5 mL) was added 9-ethyl-3-(4,4,5,5-tetramethyl-1,3,2dioxaborolan-2-yl)-9H-carbazole (96 mg, 0.3 mmol), potassium carbonate (103 mg, 0.747 mmol), followed by Pd(PPh₃)₄ (24 mg, 0.02 mmol) as a catalyst at room temperature. The reaction mixture was stirred at 90 °C under argon atmosphere overnight. 15 Evaporation of the solvent under reduced pressure and the residue was treated with water (30 ml), extracted twice with CH_2Cl_2 (30 mL \times 2). The combined organic layers were washed twice with water and once with brine, dried over anhydrous sodium sulfate. After removing the solvent under reduced 20 pressure, the residue was loaded onto silica gel column and purified by chromatography with PE/EA (5/1, v/v) as an eluent to yield compound 7 as an orange solid (114 mg, 72%). ¹H NMR $(CDCl_3, 600 \text{ MHz}), \delta: 9.87 \text{ (s, 1H)}, 8.32 \text{ (d, } J = 1.2 \text{ Hz}, 1\text{H}), 8.14$ $(d, J = 7.8 \text{ Hz}, 1\text{H}), 7.72 (dd, J_1 = 8.4, J_2 = 1.8 \text{ Hz}, 1\text{H}), 7.67 (d, J_1 = 1.8 \text{ Hz}, 1\text{H}), 7.67 (d, J_1 = 1.8 \text{ Hz}, 1\text{Hz}), 7.67 (d, J_1 = 1.8 \text{ Hz}), 7.67 (d, J_1 = 1.8 \text{ Hz}), 7.67 (d, J_1 = 1.8 \text{ Hz}), 7.67 (d, J_1 = 1.8 \text$ $_{25} J = 4.2 \text{ Hz}, 1 \text{H}$, 7.49 (t, J = 7.8 Hz, 1 H), 7.42 (t, J = 8.4 Hz, 2 H), 7.24-7.27 (m, 3H), 4.39 (q, J = 7.2 Hz, 2H), 2.60 (q, J = 8.4 Hz, 4H), 1.62-1.67 (m, 4H), 1.46 (t, J = 7.2 Hz, 3H), 1.26-1.36 (m, 12H), 0.86-0.92 (m, 6H). ¹³C NMR (CDCl₃, 400 MHz), δ: 182.51, 147.43, 145.78, 143.82, 143.75, 141.46, 140.45, 139.65, 30 137.43, 135.16, 131.59, 127.78, 126.06, 125.64, 125.29, 123.99, 123.93, 123.76, 123.42, 122.90, 120.61, 119.13, 117.67, 108.77, 108.71, 37.71, 31.69, 31.63, 30.76, 30.64, 29.29, 29.20, 29.11, 29.02, 22.62, 22.59, 14.11, 14.09, 13.86. ESI (m/z): Calcd for C₃₉H₄₃NOS₃, 637.25 (M)⁺; found, 637.25.

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- Preparation of dye LJ-7. A solution of compound 4a (74 mg, 0.1 mmol) in anhydrous CHCl₃ (15 mL) was added cyanoacetic acid (26 mg, 0.3 mmol), followed by piperidine (51 mg, 0.6 mmol) as a base at room temperature. The resulting solution was stirred at 70 °C for 8 h. After being cooled to room temperature,
- ⁴⁰ the reaction mixture was treated with water (30 mL) and acidified with 1 M aqueous hydrochloric acid (10 mL), extracted twice with CHCl₃ (20 mL × 2). The combined organic layers were washed twice with water and once with brine, dried over anhydrous sodium sulfate. After removing the solvent under ⁴⁵ reduced pressure, the residue was purified by chromatography
- with CH₂Cl₂/CH₃OH (15/1, v/v) as an eluent to yield the desired dye **LJ-7** as a black solid (62 mg, 76%). ¹H NMR (DMSO-d₆, 400 MHz), δ : 8.36 (d, *J* = 2.0 Hz, 1H), 8.33 (s, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 4.0 Hz, 1H), 7.62 (s, 1H), 7.60 (s, 1H),
- ⁵⁰ 7.45-7.52 (m, 2H), 7.32-7.37 (m, 3H), 7.19-7.25 (m, 3H), 6.67 (d, J = 1.6 Hz, 2H), 6.65 (d, J = 1.6 Hz, 2H), 4.44 (q, J = 7.2 Hz, 2H), 3.63 (s, 6H), 3.62 (s, 6H), 1.32 (t, J = 7.2 Hz, 3H). ¹³C NMR (DMSO-d₆, 400 MHz), δ : 158.52, 142.72, 140.57, 139.52, 135.97, 133.38, 132.45, 132.01, 130.85, 130.60, 130.50, 130.34, for 126.77, 126.69, 124.93, 124.71, 123.75, 123.21, 121.20, 110.55
- $_{55}$ 126.77, 126.69, 124.93, 124.71, 123.75, 123.21, 121.20, 119.55, 117.35, 113.59, 112.99, 110.20, 104.86, 60.29, 56.03, 55.97, 37.62, 14.62, 14.25. ESI (m/z): Calcd for C_{46}H_{36}N_2O_6S_3, 808.17 (M⁺); found, 808.16.

Preparation of dye LJ-8. A solution of the compound **4b** (55 mg, 0.06 mmol) in anhydrous CHCl₃ (15 mL) was added cyanoacetic acid (15 mg, 0.18 mmol), followed by piperidine (30 mg, 0.36 mmol) as a base at room temperature. The resultinig mixture was stirred at 70 °C for 10 h. After being cooled to room temperature, the reaction mixture was treated with water (30 mL) est and acidified with 1 M aqueous hydrochloric acid (10 mL), extracted twice with CHCl₃ (30 mL × 2). The combined organic layers were washed twice with water and once with brine, dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the residue was purified by chromatography with CH₂Cl₂/CH₃OH (15/1, v/v) as an eluent to yield the desired

- dye **LJ-8** as a black solid (50 mg, 84%). ¹H NMR (DMSO-d₆, 400 MHz), δ : 8.34 (d, J = 1.6 Hz, 1H), 8.24 (s, 1H), 8.16 (d, J = 7.6 Hz, 1H), 7.78 (d, J = 3.6 Hz, 1H), 7.857.65 (m, 3H), 7.45 (m, 1H), 7.32 (d, J = 4.0 Hz, 1H), 7.22 (t, J = 7.6 Hz, 1H), 7.18 (s, 1H), 7.15 (c, 1H), 7.05 7.12 (c, 2H), (42.6) Hz, 1H), 7.18 (s, 1H), 7.15 (c, 1H), 7.15 (c, 2H), (42.6) Hz, 1H), 7.18 (c, 2H), (42.6) Hz, 1H), (42.6)
- ⁷⁵ 1H), 7.15 (s, 1H), 7.05-7.12 (m, 2H), 6.42 (d, J = 0.8 Hz, 2H), 6.39 (d, J = 0.8 Hz, 2H), 4.45 (q, J = 7.2 Hz, 2H), 3.67-3.78 (m, 8H), 1.45-1.55 (m, 8H), 1.17-1.34 (m, 11H), 0.73-0.77 (m, 12H). ¹³C NMR (DMSO-d₆, 400 MHz), δ: 157.22, 141.85, 140.55, 139.50, 132.99, 132.04, 131.23, 129.38, 129.20, 127.93, 126.67,
- $_{80}$ 125.41, 124.18, 123.57, 123.15, 122.58, 120.97, 119.57, 117.07, 113.82, 113.12, 110.20, 109.90, 108.79, 105.00, 70.50, 67.49, 60.77, 37.62, 31.27, 19.19, 14.29, 14.13. ESI (m/z): Calcd for $C_{58}H_{60}N_2O_6S_3, 976.36~(M^+);$ found, 976.35.
- **Preparation of LJ-9.** A solution of the aldehyde **7** (90 mg, so 0.141 mmol) in anhydrous CHCl₃ (25 mL) was added cyanoacetic acid (24 mg, 0.282 mmol), followed by piperidine (48 mg, 0.564 mmol) as a base at room temperature. The resulting mixture was stirred at 70 °C for 10 h. After being cooled to room temperature, the reaction mixture was treated ⁹⁰ with water (30 mL) and acidified with 1 M aqueous hydrochloric acid (10 mL), extracted twice with CHCl₃ (30 mL × 2). The combined organic layers were washed twice with water and once with brine, dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the residue was purified by ⁹⁵ chromatography with CH₂Cl₂/CH₃OH (15/1, v/v) as an eluent to yield the desired dye **LJ-9** as a brown solid (82 mg, 83%). ¹H
- NMR (DMSO-d₆, 600 MHz), δ : 8.48 (d, J = 1.8 Hz, 1H), 8.33 (s, 1H), 8.23 (d, J = 7.8 Hz, 1H), 7.85 (d, J = 3.6 Hz, 1H), 7.73 (dd, J_1 = 8.4, J_2 = 1.2 Hz, 1H), 7.60-7.63 (m, 2H), 7.48-7.52 (m, 3H),
- ¹⁰⁰ 7.47 (t, J = 7.8 Hz, 1H), 7.22 (t, J = 7.8 Hz, 1H), 4.44 (q, J = 7.2 Hz, 2H), 2.53-2.57 (m, 4H), 1.55-1.63 (m, 4H), 1.32 (t, J = 7.2 Hz, 3H), 1.20-1.24 (m, 12H), 0.77-0.81 (m, 6H). ¹³C NMR (DMSO-d₆, 600 MHz), δ : 163.78, 145.62, 144.01, 140.59, 139.78, 135.36, 135.24, 130.50, 128.50, 126.62, 125.27, 125.23,
- 105 124.89, 124.65, 124.05, 123.24, 122.65, 121.13, 119.51, 117.64, 110.09, 109.79, 37.60, 31.43, 31.38, 30.37, 30.28, 29.16, 28.92, 28.86, 22.51, 22.43, 14.30, 14.15. ESI (m/z): Calcd for $C_{42}H_{44}N_2O_2S_3$, 704.26 (M⁺); found, 704.25.

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We demonstrate that installing alkyl chains perpendicular to π -conjugated plane is a promising strategy to construct efficient sensitizers for DSSCs.

