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Photophysical characteristics and photosensitizing abilities of thieno[3,2-b] thiophene-Based photosensitizers for photovoltaic and photocatalytic applications

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ABSTRACT

Six donor $-\pi$ - acceptor (D- π -A) organic dyes based on thieno [3,2-b] thiophene π -linker comprising different alkyl side chains were synthesized and characterized. Their photophysical and electrochemical properties were studied and their corresponding performances as photosensitizers (PSs) in dye-sensitized solar cells (DSSCs) and photocatalytic hydrogen production systems were also investigated. A power conversion efficiency (PCE) of 5.25 % in DSSCs and a decent H₂ turnover number (TON) of 5170 (48 h) in platinized TiO₂ hydrogen production system were demonstrated. The results indicated that alkyl chain engineering is one of the crucial steps in designing a superior photosensitizer.

1. Introduction

Environmental problems such as global warming and energy crisis have led to the urgency of utilization of renewable energy resources in the past two decades [1]. Solar power is a promising clean energy source for the community because of its tremendous amount of supply from the sun [2]. Other than inorganic solar cells, dye-sensitized solar cell (DSSC) has been regarded as another potential candidate to be adopted in large scale application. In DSSCs, apart from the electrolytes and nanostructured titania film, the role of photosensitizer (PS) is utterly significant to the device performance [3–5]. In recent years, organic dyes with high molar extinction coefficients (ε) have attracted attention since they are low-cost in production and flexible in molecular modifications. Stable organic PSs are able to compete with polypyridyl ruthenium complexes in terms of the device performance [6-13]. In 2019, Sun et al.

reported a triazatruxene-based donor $-\pi$ - acceptor $-\pi$ - acceptor' $(D-\pi-A-\pi-A')$ organic dye, which was claimed to overcome the hurdle of electron-injection energy losses and achieved a champion power conversion efficiency (PCE) of 13.6 % in a single dve-sensitized DSSC device at that time [14].

In addition to DSSCs, photocatalytic water splitting [15], which converts water molecules (feedstock) into hydrogen (fuel) and oxygen through a light-driven catalytic process, has been regarded as another solar energy research direction, because nature provides us with abundant amount of feedstock and the fuel is obtained without the discharge of carbon-containing species during the energy conversion. In principle, water splitting reaction is equivalent to the sum of two redox half-reactions [16]. For the cathodic side, a workable system comprises an PS for exciton formation, a pathway for charge separation, a catalyst for hydrogen generation, aqueous protons and a sacrificial electron

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donor (SED) for providing electrons [17]. Similar to the case in DSSCs, PS also plays a pivotal role in the cathodic reaction and affects the activity, stability and production cost of the photocatalytic systems. Therefore, the performance of a wide variety of PSs has been investigated in the past decade [18–24].

Herein, six new organic dyes based on thieno[3,2-*b*]thiophene π -linker are reported (Fig. 1). These six compounds are composed of cyanoacrylic acid which acts as an anchoring group attached to TiO₂ as well as an electron-withdrawing unit. For the π -linker, thieno[3,2-*b*] thiophene and the congener with one more 3-hexylthiophene group are selected due to their strong intramolecular charge transfer (ICT) property and intense absorption in visible light region as reported in the literature [25–27]. 9-Substituted carbazoles with three different alkyl chains (i.e., octyl, ethylhexyl and hexyl) are chosen to act as the donor moiety because of the appropriate HOMO energy level and the ease of alkyl chain alteration [28]. The synthetic procedures are simple and all the products can be purified by column chromatography. The photophysical and electrochemical properties of the organic PSs were studied and their corresponding performances in photocatalytic hydrogen production as well as DSSCs were also investigated.

2. Results and discussion

2.1. Synthesis and characterization

The structures of new organic photosensitizers are shown in Fig. 1. The corresponding synthetic routes are depicted in Scheme 1. The key intermediate 2,5-dibromothieno[3,2-b]thiophene 2 was prepared according to the published procedures [29]. Compound 2 was then reacted with *n*-butyllithium and dimethylformamide according to the general Bouveault aldehyde synthetic procedure to get the compound 3 with around 50 % yield. Palladium-catalyzed Suzuki coupling reaction was then performed to react aryl bromide 3 with different alkylated carbazole-based arylboronic acids to prepare organic dye precursors 4a-4c. On the other hand, compound 6 was synthesized by Suzuki coupling reaction using compound 2, followed by Vilsmeier-Haack reaction. The organic dye precursors 7a-7c were obtained by Suzuki coupling reactions with compound 6 utilizing corresponding arylboronic acids. Finally, all the organic dyes **5a**–**5c** and **8a**–**8c** were prepared by Knoevenagel condensation using cyanoacetic acid from the respective aldehyde precursors. All the target organic PSs were soluble in common organic solvents, such as chloroform and tetrahydrofuran (THF) and were characterized by ¹H and ¹³C NMR spectroscopies (Figures S1-S12) and Matrix-assisted Laser Desorption Ionization Time-of-flight (MALDI-TOF) mass spectrometry. In particular, the downfield singlet peak located at around δ 8.5 ppm is a characteristic peak of the proton on the carbon-carbon double bond of cyanoacrylic

acid. All of the corresponding organic precursors were also characterized by ¹H and ¹³C NMR spectroscopy. The singlet peak located at around δ 10.0 ppm refers to the proton of aldehyde in the corresponding precursors.

2.2. Photophysical properties

The UV/Vis absorption spectra of all the organic dyes in CH₂Cl₂ solution are shown in Fig. 2 and the corresponding data are summarized in Table 1. All of the dyes exhibit two major distinct broad absorption bands in the range of 300 - 600 nm. The ε of these organic dyes are relatively high as compared to those of standard ruthenium dyes due to the rigid and planar thieno [3,2-*b*] thiophene π -linker [30]. The absorption bands at short wavelengths (centered at 301 - 352 nm) are ascribed to the $\pi \rightarrow \pi^*$ transitions of chromophores. The low-energy broad absorption bands (centered at 459 - 502 nm) are attributed to the intramolecular charge transfer (ICT) from the donor to acceptor, hence providing an efficient charge separation at the excited state. Dyes 8a-8c show a significant red shift in the ICT transition as compared to 5a-5c, which implies that embedding one more thiophene ring can increase the light-harvesting ability efficiently. In addition, the ε of these dyes are in the order of 5a < 5b < 5c and 8a < 8b < 8c. The highest ε was achieved by 8c with the value of 5.81×10^4 M-¹ cm-¹. No significant influence is observed on the absorption wavelength regarding the nature of alkyl chains. Although the absorption maxima of the ICT bands of 5a-5c vary, the onsets of absorption peaks are almost the same.

2.3. Electrochemical properties

Besides light harnessing ability, suitable energy-offsets of the dye molecules between the nanostructured TiO₂, redox electrolytes and SED are necessary for the high performance DSSC and photocatalytic system. If the lowest unoccupied molecular orbital (LUMO) of the photosensitizer is more positive than that of the conduction band edge of TiO₂ while the corresponding highest occupied molecular orbital (HOMO) is more negative than the redox potential of redox couples (i.e., I^-/I_3^-) and SED, the electron injection and charge separation would be efficient at the interface [31] in DSSCs and photocatalytic hydrogen production system, respectively. To investigate such electron and charge transfer, cyclic voltammetry (CV) was performed in PS solution using glassy carbon electrode as the working electrode, platinum wire as the counter electrode and Ag/Ag⁺ as the reference electrode in dichloromethane containing 0.1 M tetrabutylammonium hexafluorophosphate at a scan rate of 100 mV s^{-1} . Under these conditions, the reversible oxidation potential ($E_{1/2}$) of ferrocene was 0.25 V versus Ag/Ag⁺. The corresponding behaviors of the PSs (irreversible onset oxidation potential) in CV are recorded in Figure S13 and tabulated in Table 2.



Fig. 1. The chemical structures of organic photosensitizers 5a-5c and 8a-8c.



Scheme 1. Synthetic routes of 5a-5c and 8a-8c. Ar-B(OH)₂ = 9-octylcarbazolylboronic acid or 9-(2-ethylhexyl)carbazolylboronic acid or 9-hexylcarbazolylboronic acid; Ar'-B(OH)₂ = (4-hexylthiophen-2-yl)boronic acid.



Fig. 2. UV/Vis absorption spectra of 5a-5c and 8a-8c in CH₂Cl₂ at 293 K.

Table 1

UV/Vis absorption data of 5a-5c and 8a-8c in CH_2Cl_2 at 293 K.

	· · · · · · · · · · · · · · · · · · ·		- 2-2		
Dye	$\lambda_{\rm max}$ /nm ($arepsilon$ /10	$\lambda_{\rm max}$ /nm (ϵ /10 ⁴ M ⁻¹ cm ⁻¹)			
5a	302 (1.81)	352 (1.00)	472 (4.58)	534	
5b	301 (2.46)	349 (1.07)	459 (5.27)	528	
5c	302 (2.36)	351 (1.35)	470 (5.37)	537	
8a	309 (2.70)		500 (4.25)	585	
8b	309 (2.36)		499 (4.32)	582	
8c	309 (3.00)		502 (5.81)	585	

According to the results, the conduction band edge of TiO₂ (-4.4 eV) is more negative than LUMO of all our organic dyes (ranging from -2.93 to -2.80 eV), thereby facilitating an efficient electron injection [32]. On the other hand, the HOMO energy levels of our dyes (ranging from -5.19 to -5.02 eV) are more negative than the redox potentials of I^-/I_3^- electrolyte (-4.45 eV) and ascorbic acid (SED, -4.65 eV, pH ~ 4),

Table 2Electrochemical data and energy levels of 5a-5c and 8a-8c.

Dye	$E_{\rm Ox}^{\rm onset}$ /V	HOMO ^a /eV	E_{g}^{b} /eV	$E_{\mathrm{ox}^*}^{\mathrm{c}}/\mathrm{V}$	LUMO ^d /eV
5a	0.64	-5.19	2.32	-1.68	-2.87
5b	0.60	-5.15	2.35	-1.75	-2.80
5c	0.59	-5.14	2.31	-1.72	-2.83
8a	0.49	-5.04	2.12	-1.63	-2.92
8b	0.47	-5.02	2.13	-1.66	-2.89
8c	0.50	-5.05	2.12	-1.62	-2.93

^a Calculated from $-(E_{Ox}^{onset} + 4.55)$.

^b Energy bandgap (E_g) was determined from the onset of absorption spectrum.

^c $E_{\text{ox}^*} = E_{\text{Ox}}^{\text{onset}} - E_{\text{g}}$.

^d LUMO = HOMO + E_g

which ensures an efficient dye regeneration [33,34]. The first irreversible oxidation wave observed was ascribed to the removal of an electron from the carbazole donor [35]. The embedded electron-rich 3-hexylthiophene in **8a**–**8c** dramatically decreases the oxidation potential as compared to **5a**–**5c**, due to the elongation of π -conjugated length in the former, hence rising the HOMO levels as well as reducing the HOMO-LUMO gap.

2.4. Computational studies

To explain the structural properties of the dyes and understand the possibility of charge transfer from donor to acceptor on electronic excitation, the optimized structures of six dyes were calculated geometrically using the density functional theory (DFT) with Gaussian 09 program. The optimized structures and electron densities of HOMOs and LUMOs of the dyes are shown in Supporting information. From Figures S14–S19, the electron density of the HOMO is mainly distributed along the carbazole donor to adjacent thieno[3,2-b]thiophene for 5a-5c and to its adjoining hexylthiophene unit for 8a-8c, while the electron density of the LUMO is mainly localized on the cyanoacrylic acid group and adjacent functionalized thiophenes. This phenomenon suggested that a well-inductive electron tendency from carbazole donor

to the cyanoacrylic acceptor. It is clear that the HOMO - LUMO excitation induced by light irradiation in our dyes could move the electron distribution from the carbazole moiety to the cyanoacrylic moiety effectively, and the photoinduced electrons can be efficiently transferred from the dye to the TiO₂ surface in charge separation. In this system, the planar structure can enhance the π -conjugation through the skeleton backbone, increasing the degree of electronic resonance between donor and acceptor moieties in the molecules and facilitating the electron transfer from donor to cyanoacrylic acceptor. However, the planarity increases the stacking of the dye molecules, resulting in more dye aggregation and electron recombination. From the contour plots (Figures S14–S19), it is clearly shown that all the alkylated chains are free of intramolecular steric hinderance, flexible and able to twirl towards different directions. This could effectively suppress the intermolecular stacking, therefore the geometric structure might effectively retard the charge recombination and enhance the open-circuit photovoltage (V_{oc}) in DSSC. In addition, the calculated HOMO and LUMO from time-dependent density functional theory (TD-DFT) further confirm that the differences in alkyl chains do not have significant influence on the HOMO and LUMO energy levels. The embedded thiophene unit in 8a-8c can elevate the HOMO energy level, resulting in the enhancement of light absorption property for the corresponding compounds by reducing the energy gap between HOMO/LUMO transition.

2.5. Photovoltaic performance

DSSCs with an effective area of 0.20 cm² were fabricated by adsorbing our new organic photosensitizers onto nanocrystalline anatase TiO₂ as the photoanode and using the liquid electrolyte consisting of 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII), 0.1 M LiI, 0.05 M I₂ in a mixture of acetonitrile and 4-*tert*-butylpyridine (volume ratio, 1:1). All the DSSCs were tested under standard conditions of AM 1.5 G, 100 mW cm⁻². The basic device performance parameters, such as short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF) and power conversion efficiencies (PCEs), are collected in Table 3. Figs. 3 and 4 demonstrate the photocurrent density – voltage curves (J–V curves) and incident-photon-to-current conversion efficiency (IPCE) spectra, respectively.

The highest PCE of 5.25 % ($J_{sc} = 12.32 \text{ mA cm}^{-2}$, $V_{oc} = 0.680 \text{ V}$ and FF = 0.626) was achieved by **8a**, attaining 66 % of the PCE of standard ruthenium dye N719-based cell (PCE = 7.91 %), fabricated and measured under the same condition. PCEs of DSSCs based on 5a-5c, 8b and 8c are 3.95 %, 3.49 %, 2.91 %, 5.01 % and 4.58 %, respectively. The IPCE values of 5a-5c and 8a-8c exceed 50 % in the range of 350 - 500 nm and 400 - 550 nm, respectively. Dyes **5a**-**5c**, with a shorter π -conjugation length, have lower PCEs than those of **8a**-**8c** due to the narrower IPCE spectral response, which is also reflected from the lower $J_{\rm sc}$ values of 5a–5c. The almost double $J_{\rm sc}$ values of dyes 8a–8c as compared to those of 5a-5c can be ascribed to the following factors. Firstly, the red-shifted ICT absorption bands of 8a-8c lead to a broader harnessing of sunlight. In addition, the attached hexyl chain present in the π -linker of **8a**-**8c** might weaken the intermolecular π -stacked aggregation, thus facilitating the electron injection process and increasing the J_{sc} values. Moreover, these hexyl chains may play another role in

Table 3

Photovoltaic performance of DSSCs with different photosensitizers (5a–5c, 8a–8c and N719) under AM 1.5 G sunlight illumination.

Dye	$J_{\rm sc}$ /mA cm $^{-2}$	$V_{\rm oc}$ /V	FF	PCE /%	$R_{ m rec}$ / Ω cm ⁻¹
5a	8.61	0.672	0.683	3.95	_
5b	8.00	0.657	0.664	3.49	_
5c	7.69	0.652	0.579	2.91	_
8a	12.32	0.680	0.626	5.25	141.59
8b	11.51	0.692	0.629	5.01	152.55
8c	10.64	0.672	0.641	4.58	140.29
N719	15.83	0.701	0.713	7.91	-



Fig. 3. Photocurrent density – voltage (J-V) plots obtained with 5a-5c, 8a-8c and N719.



Fig. 4. Incident photon-to-current efficiency (IPCE) curves obtained with 5a-5c, 8a-8c and N719.

which their hydrophobic property and steric hindrance may block the approach of the hydrophilic electrolytes (i.e., iodide/triiodide ions) to the hydrophilic surface of TiO₂, thereby inducing the charge recombination suppression and resulting in larger V_{oc} values of **8a**–**8c** as compared to **5a**–**5c** [36,37]. This alkyl chain effect is also profound for the carbazole ring in which the V_{oc} rises from 0.652 V to 0.672 V and from 0.672 V to 0.692 V as the alkyl chain on carbazole changed from hexyl chain to octyl chain (**5c** vs **5a**) or 2-ethylhexyl chain (**8c** vs **8b**), respectively.

In order to elucidate the interfacial charge recombination process in DSSCs, electrochemical impedance spectroscopy (EIS) has been applied under dark condition for the selected dyes 8a-8c with higher PCEs and the results are recorded in Figure S20. An ideal EIS Nyquist plot shows three semi-circles and these semicircles are referring to electrochemical reactions among (I) Pt/electrolyte interface, (II) charge transfer at the TiO₂/dye/electrolyte interface and (III) Warburg diffusion processes (I^{-}/I_{3}^{-}) , respectively. However, the impedance of a DSSC device will change with the device potential, therefore different shapes and patterns of the curves regarding the impedance signal can be observed while the applied bias voltage varies. In the Figure S20, the semi-circle revealed the resistance of electron recombination (R_{rec}) of process (II) at the interface for 8a-8c [38]. The calculated R_{rec} values are summarized in Table 3. The R_{rec} (Ω /cm) value increases in the order of 8c (140.29) < 8a (141.59) < 8b (152.55), therefore 8b is the most effective dye to suppress charge recombination while 8c suffers from the most conspicuous charge recombination. This conforms to their measured increasing order of $V_{\rm oc}$ and supports that 2-ethylhexyl chain, as compared to hexyl and octyl chains, is more effective to weaken the interaction between electrolyte and TiO₂ in such a structure framework.

2.6. Light-driven hydrogen generation

In view of the light-harvesting capability of **5a–5c** and **8a–8c** in 450–550 nm region demonstrated from the IPCE spectra (Fig. 4), we anticipated that **5a–5c** and **8a–8c** could be utilized in light-driven H₂ production from water. Herein, we carried out the photocatalytic H₂ production investigation by adopting the same system to these six $D-\pi$ –A organic dyes. Also, a reference dye **Eosin Y**, which has been used to study light-driven H₂ production in many different photocatalytic systems was also examined for comparison [39–41].

Detailed procedures for the preparation of platinized TiO₂, attachment of PS onto the platinized TiO₂ and photocatalytic reaction studies are referred to the Experimental section. In short, each PS was loaded onto the TiO₂ using sonication for 30 min, the 'active' photocatalytic reaction mixture was then retrieved by centrifugation and dried before the H₂ production experiments. The dye-loading percentage for each PS was estimated by comparing the absorbance value of low-energy absorption peak before and after the dye adsorption and all these carboxylate anchor-based PSs were found to attach onto the composite completely. The photocatalytic reactions were carried out in 5 mL aqueous ascorbic acid (AA, 0.5 M) solution at pH 4.0 with AA serving as the sacrificial electron donor (SED). The photocatalytic system in 25 mL reaction flasks was continuously radiated with green light-emitting diodes (ca. 520 nm) and the headspace of each sample was qualitatively and quantitatively analyzed by gas chromatography (GC) by the end of illumination. The GC analysis of hydrogen generation was conducted after 16, 24, 40 and 48 h of irradiation using methane as an internal standard to calibrate the hydrogen measurement. Hydrogen generation curves (vs. time) for 5a-5c, 8a-8c, Eosin Y and blank are exhibited in Fig. 5 and the corresponding data (TON, TOF, TOF_i, Activity_i and AQY_i%) are tabulated in Table 4.

All $D-\pi-A$ organic dyes present in this study potently facilitate the light-driven H₂ production (> 7 mL over 48 h) while the system without PS (blank) only produced ~ 0.5 mL of H₂. Overall, the TON and TOF of the six studied photosensitizers exceed the reference dye **Eosin Y** by approximately 10 times and this shows a pronounced effect in protons reduction, especially in consideration of the simplicity of their chemical structures. Among the six organic dyes, the best TON of 5170 and TOF of 108 h⁻¹ in 48 h are achieved by **8c**. The highest TOF_i of 155 h⁻¹ and AQY_i of 5.0 % are attained by **5c**. The apparent decrease in H₂ evolution rate of the six dyes after 20 h of irradiation is probably ascribed to the

700 5 600 5b 5c 89 500 8b 8c 400 H₂ (µmol) Eosin Y blank 300 200 100 0 24 32 40 8 16 48 Time (hour)

Fig. 5. Photocatalytic H₂ generation curves of dye-sensitized systems (**5a–5c**, **8a–8c**, **Eosin Y** and blank) under green LED irradiation (50 mW).

Table 4

Photocatalytic H ₂ generation data with different	photosensitizers over 48 h.
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Dye	H ₂ /mL	TON ^a	TOF ^b /h ⁻¹	TOF _i ^c / h ⁻¹	$\begin{array}{l} Activity_i^d/\mu mol\\ g^{-1} \ h^{-1} \end{array}$	AQY _i % ^e
5a	10.5	3500	72.9	124	155,000	3.97
5b	7.22	2410	50.2	89.2	112,000	2.87
5c	13.7	4570	95.2	155	194,000	5.00
8a	11.1	3700	77.1	118	148,000	3.83
8b	11.7	3900	81.3	137	171,000	4.42
8c	15.5	5170	108	148	185,000	4.79
Eosin	1.06	354	7.4	12.0	15,000	0.35
Y						
Blank	0.45	-	-	-	10,400	0.23

^a Turnover number (TON) of H_2 is calculated as number of mole of H_2 produced over the number of mole of PS attached to platinized TiO₂. And the dyeloading value for **5a–5c**, **8a–8c** and **Eosin Y** were all measured to be close to 100 %.

^b Turnover frequency (TOF) is calculated per hour.

^c Initial turnover frequency (TOF_i) in the first 16 h.

^d Initial photocatalytic activity (Activity_i) is defined as number of micromole of H_2 evolved per gram of platinum loaded per hour.

^e Initial apparent quantum vield percentage (AQY_i).

decrease of AA concentration and dye degradation [42,43]. PS **8c**, with a longer π -linker, is considered to be more stable in the photolysis condition and more persistent in photocatalytic efficiency than **5c** throughout the two-day experiment.

According to Table 4, 5c and 8c, both with a hexyl chain attached to the carbazole group, show higher TON and TOF than other PSs with octyl chains. This comparison indicates that the shorter alkyl chain on the donor moiety may favor the photocatalytic reduction of aqueous protons by promoting the interaction among the photocatalyst (i.e., dyesensitized platinized TiO₂ nanoparticles), aqueous protons and AA [44]. Besides, by comparing each set of the two molecules with the same donor moiety but different π -linkers, the PS with a longer π -linker exhibits a higher photocatalytic efficiency than that with a shorter π -bridge. This trend corresponds to the UV/Vis absorption spectra (Fig. 2) and IPCE spectra (Fig. 4), the increased photocatalytic efficiencies of 8a-8c are attributed to the wider light absorption bands in green light region, especially from 550 to 600 nm. In contrast, 5a-5c with blue-shifted absorption bands would lower the photons utilization from this region, thus producing smaller amount of H₂ in the same duration. Therefore, 8c, which possesses a shorter alkyl chain on the donor moiety and more intense light absorption in the green light region, displays the largest H₂ evolution amount.

2.7. Conclusion

A series of D- π -A organic photosensitizers based on thieno[3,2-b] thiophene π -linker has been designed and synthesized. All these PSs were fully characterized by spectroscopic studies. The best performance in DSSCs (PCE = 5.25 %) was achieved by dye 8a with a thieno[3,2-b] thiophene-based π -linker linked between an octyl chain-functionalized carbazole donor and cyanoacrylic acid acceptor. For the H₂ generation, the largest H2 TON of 5170 (48 h) was achieved by the 8c-anchored platinized TiO₂ system, whereas 8c possesses a hexyl chainfunctionalized carbazole group. From these results, it was found that the modification of alkyl chain in donor moiety in the confined $D-\pi-A$ framework is crucial to attain a significant variation in efficiency no matter in light-driven H₂ generation or DSSCs. Therefore, it could be anticipated that alkyl chain engineering is one of the necessary step in designing a superior photosensitizer, because the length, orientation and bulkiness of alkyl chain(s) would dramatically change the interactions between PS and other variable components at the charge separation interface.

3. Experimental section

3.1. Materials and reagents

All reactions were performed under an inert nitrogen atmosphere with the use of a Schlenk line. Glassware was dried in oven prior to use. Commercially available reagents were used without purification unless otherwise stated. All the reagents for the chemical synthesis were purchased from Sigma-Aldrich and Acros Organics. Solvents were purified by distillation over appropriate drying agents. All reactions were monitored by thin-layer chromatography (TLC) with Merck pre-coated aluminum plates. Products were separated and purified by column chromatography using silica gel (230 - 400 mesh) purchased from Merck.

3.2. Instrumentation

Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were recorded on an Autoflex Bruker MALDI-TOF system. Proton and carbon NMR spectra were measured in CDCl₃/DMSO-d₆/THF-d₈ on a Bruker Ultra-shield 400 MHz FT-NMR spectrometer and tetramethylsilane (TMS) was used as an internal standard for calibrating the chemical shift. UV/Vis absorption spectra were recorded on a Hewlett Packard 8453 spectrometer in CH₂Cl₂ solution at 293 K. Electrochemical measurements were conducted on Potentiostat/Galvanostat/EIS Analyzer model Parstat 4000 at a scan rate of 100 mV s⁻¹.

3.3. Computational details

All the calculations in this work were carried out using Gaussian 09 package [45]. The ground state geometries of all the dyes in dichloromethane ($\varepsilon = 8.93$) were optimized using the density functional theory (DFT) with hybrid functional PBE0 and the solvation effects were included using the integral equation formalism [46,47] (IEF) version of the polarizable continuum [48,49] (PCM) model. The frequency calculations were then performed to confirm each optimized structure was the real minimum without imaginary vibration frequency. The time-dependent DFT (TD-DFT) was used to calculate vertically excited singlet-state energies. The 6–31 G(d) basis set was adopted. The absorption profiles were calculated using the Multiwfn program [50] as a sum of Gaussian-shaped bands with full width at half maximum (FWHM) equal to 0.667 eV.

3.4. Fabrication and characterization of DSSCs

All the anode films of DSSCs were made under the same standard manner and composed of a 12 µm thick transparent layer (TiO₂ with diameter of 20 nm) and a 6 µm thick scattering layer (TiO₂ nanoparticles with a diameter of 200 nm). Doctor-blade technique was utilized to prepare photoanode (TiO₂) films. First, a TiO₂ paste (20 nm) layer of ~ 6 µm was doctor-bladed onto a FTO conducting glass and then relaxed at room temperature for 3 min before heated at 150 °C for 6 min; this procedure was repeated once to achieve a film thickness of $\sim 12 \ \mu m$ and the resulting surface was finally coated with a scattering layer ($\sim 6 \ \mu m$) of TiO₂ paste (200 nm). Then, the electrodes were gradually heated under an air flow at 275 °C for 5 min, 325 °C for 5 min, 375 °C for 5 min, and 470 °C for 30 min to remove polymers and generate a three dimensional TiO₂ nanoparticle network. After that, the sintered films were soaked into 0.02 M TiF₄ aqueous solution for 45 min at 70 $^\circ$ C, washed with deionized water, and further annealed at 450 $^\circ C$ for 30 min. After cooling down to ~80 °C, the electrodes were immersed into a 5 \times 10^{-4} M concentration of corresponding dye bath in acetonitrile/tertbutyl alcohol (volume ratio, 1:1) and maintained in the dark for 15 h. Afterwards, the electrodes were rinsed with ethanol to remove the nonadsorbed dyes and dried in the air. Pt counter electrodes were prepared

by sputtering method at 15 mA for 90 s at a power of 150 W. Two holes (0.75 mm in diameter) were predrilled in the FTO glass for introducing the electrolyte. The dye-adsorbed TiO₂ electrode and Pt-counter electrode were assembled into a sandwich type cell and sealed with a hotmelt parafilm at about 100 °C. The liquid electrolyte consisting of 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII), 0.1 M LiI, 0.05 M I2 in a mixture of acetonitrile and 4-tert-butylpyridine (volume ratio, 1:1) was introduced into the cell through the drilled holes at the back of the counter electrode. At last, the holes were sealed by parafilm and covering glass (0.1 mm thickness) at elevated temperature. The effective areas of all the TiO₂ electrodes were ~ 0.20 cm². The current – voltage (J-V) characteristics of the assembled DSSCs were measured by a semiconductor characterization system (Keithley 236) at room temperature in air under the spectral output from solar simulator (Newport 94023A) using an AM 1.5 G filter with a light power of 100 mW cm⁻². IPCEs of DSSCs were recorded in the Solar Cell QE/IPCE Measurement System (Zolix Solar Cell Scan 100) using dc mode. CHI 660D electrochemical workstation was used to characterize the electrochemical properties of the DSSCs. Electrochemical impedance spectroscopy (EIS) was recorded under dark conditions over a frequency range of $0.1 - 10^5$ Hz with an ac amplitude of 10 mV and the parameters were calculated from Z-View software (v2.1b, Scribner Associates, Inc.).

3.5. Preparation of platinized TiO₂

For a 0.5 wt-% platinized TiO₂ sample, addition of 40 mL methanol to 1.6 g of titanium(IV) oxide nanopowder (anatase, < 25 nm particle size, 99.7 % trace metals basis, Sigma-Aldrich) and 0.1 mL of H₂PtCl₆ aqueous solution (8 wt. %) created slurry which was then subjected to radiation from a 300 W coated Hg lamp (HF300PD, EYE Lighting) under vigorously stirring for 24 h. The resulting crude product had a grayish colour. Platinized TiO₂ was then retrieved by centrifugation at 3500 rpm for 5 min and washed three times with methanol. The obtained material was dried under vacuum at \sim 60 °C in darkness for 8 h.

3.6. Adsorption of photosensitizer onto platinized TiO₂

20 mg of the prepared platinized TiO_2 was added to 2.5 mL of 50 μ M photosensitizer dichloromethane solution, the mixture was then evenly sonicated for 30 min. The solution gradually became colourless while the solid became orange/red in colour. The dye-loaded solid was then retrieved by centrifugation at 3500 rpm for 5 min. The supernatant was removed carefully using a dropper and the pellet at the bottom was dried under vacuum for two to three hours in darkness. At the end, the whole dried pellet was directly utilized in the photocatalytic reaction without further characterization. The dye-loading percentage was estimated by comparing the absorbance of low energy absorption peak between the supernatant and original photosensitizer solution.

3.7. Light-driven H_2 production studies

A 25 mL pear-shaped flask was placed above stirrers and the flask was sealed with a rubber septum. The photocatalytic reaction mixture with a stir bar was then purged with a mixture of argon/methane (80:20 mol%) for 15 min. The methane present in the gas mixture was served as an internal standard for GC analysis. The reaction mixture was steadily stirred and directly radiated from the bottom with green (520 nm) light-emitting diodes inside a just-fit container which blocks the stray light from the environment. The light power was measured using a thermal sensor and power meter (Model: BIM-7203–0100 F & BIM-7001; Hangzhou Brolight Technology Co., Ltd.) and giving an estimated value of 50 mW for each reaction. At the end of the experiment, head-spaces of the flasks were characterized by GC to examine the amount of hydrogen produced. The amount of hydrogen evolved was determined using GC (Agilent 6890 Series GC System with a molecular sieve 5 Å column and TCD detector) by the end of radiation and were quantified

referring to a calibration plot of integrated amount of hydrogen relative to that of methane (Figure S21). In the course of a 48 -h radiation, samples were taken at four different time points from the reaction mixtures of each photosensitizer and blank. The LED radiation is assumed to be monochromatic at emission maximum (520 nm) and the corresponding apparent quantum yield values for each PS could be estimated according to the equation shown below.

$$AQY(\%) = \frac{\text{rate of } H_2 \quad \text{production} \times 2}{\text{rate of incident photons}} \times 100\%$$
(1)

3.8. Synthesis

2,5-Dibromothieno [3,2-b] thiophene (2): Thieno[3,2-b] thiophene **1** (1 g, 7.131 mmol) was dissolved in THF (40 mL) at room temperature and the solution was cooled to 0 °C. NBS (2.547 g, 14.262 mmol) was then added in ten portions at 0 °C. The reaction mixture was slowly warmed to room temperature and was stirred for 12 h. The mixture was then poured into cold water (100 mL) and extracted with diethyl ether (3 × 80 mL). The organic layers were washed with water (100 mL) twice and dried over Na₂SO₄. Removal of solvents gave **2** as a pure white solid (2.1 g, 7.047 mmol, 99 % yield). ¹H NMR (400 MHz, CDCl₃): δ = 7.29 (s, 2H, Ar) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 138.29, 121.76, 113.62 (Ar) ppm. HRMS (MALDI-TOF, *m*/z): [M⁺] 295.7957; calcd for (C₆H₂Br₂S₂) 295.7965.

5-Bromothieno [3,2-b] thiophene-2-carbaldehyde (3): To a twonecked round-bottom flask containing 2 (0.7 g, 2.348 mmol) in 20 mL dry THF, n-BuLi (0.978 mL, 2.348 mmol, 2.4 M in hexane) was added dropwisely at -78 °C. After the reaction mixture was stirred for 15 min, dimethylformamide (0.271 mL, 3.532 mmol) was added. The reaction mixture was then warmed up gradually to room temperature and was stirred for 30 min. To the reaction mixture, an excess amount of 2 M HCl (aq) (10 mL) was introduced, while the mixture was stirred for another 1 h. The reaction was quenched by pouring it into water, followed by extraction using ethyl acetate. The organic layer was dried over anhydrous Na₂SO₄ and the solvent was then removed under reduced pressure. The crude product was subjected to flash column chromatography with hexane/CH₂Cl₂ (2:1) as eluent. Product **3** (0.284 g, 1.149 mmol) was obtained as a pale-yellow oil in 49 % yield. ¹H NMR (400 MHz, CDCl₃): δ = 9.98 (s, 1H, CHO), 7.85 (s, 1H, Ar), 7.36 (s, 1H, Ar) ppm; ¹³C NMR (100 MHz, CDCl₃): $\delta = 183.28$ (CHO), 144.72, 144.54, 139.35, 128.20, 122.91, 120.95 (Ar) ppm. HRMS (MALDI-TOF, m/z): [M⁺] 245.8811; calcd for (C7H3BrOS2) 245.8809.

General synthetic procedure of 4a-4c: A mixture of 3 (94 mg, 0.38 mmol), (9-octylcarbazolyl)/ (9-(2-ethylhexyl)carbazoyl)/ (9-hexylcarbazolyl)boronic acid (0.76 mmol), Pd(PPh₃)₄ (22 mg, 0.019 mmol) and 2 M K₂CO₃ (2 mL) in THF (20 mL) was heated to reflux under a N₂ atmosphere overnight. The reaction mixture was poured into water, followed by extraction using ethyl acetate. The organic layer was dried over anhydrous Na₂SO₄ and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using a 1:1 mixture of CH₂Cl₂ and hexane as eluent to afford **4a-4c** as orange red solids, respectively.

5-(9-Octyl-9H-carbazol-3-yl)thieno [3,2-*b***] thiophene-2-carbaldehyde (4a): 0.112 g; 66 % yield. ¹H NMR (400 MHz, CDCl₃): \delta = 9.96 (s, 1H, CHO), 8.38 (s, 1H, Ar), 8.15 (d, 1H,** *J* **= 8 Hz, Ar), 7.93 (s, 1H, Ar), 7.77 (d, 1H,** *J* **= 8.4 Hz, Ar), 7.58 (s, 1H, Ar), 7.53 – 7.43 (m, 4H, Ar), 4.32 (t, 2H,** *J* **= 7.2 Hz, alkyl), 1.89 – 1.88 (m, 2H, alkyl), 1.35 – 1.19 (m, 10H, alkyl), 0.88 – 0.84 (m, 3H, alkyl) ppm; ¹³C NMR (100 MHz, CDCl₃): \delta = 183.05 (CHO), 154.95, 147.34, 143.70, 141.03, 140.84,137.45, 129.37, 126.38, 124.80, 124.21, 123.44, 122.64, 120.58, 119.48, 118.32, 114.44, 109.29, 109.14 (Ar), 43.31, 31.79, 29.37, 29.17, 29.00, 27.31, 22.61, 14.07 (alkyl) ppm. HRMS (MALDI-TOF,** *m***/z): [M⁺] 445.1532; calcd for (C₂₇H₂₇NOS₂) 445.1534.**

5-(9-(2-Ethylhexyl)-9H-carbazol-3-yl)thieno [3,2-b] thiophene-2-carbaldehyde (4b): 0.15 g; 89 % yield. ¹H NMR (400 MHz, CDCl₃): δ = 9.73 (s, 1H, CHO), 8.14 (d, 1H, J = 1.6 Hz, Ar), 7.98 (d, 1H, J = 7.6 Hz, Ar), 7.64 (s, 1H, Ar), 7.54 – 7.52 (m, 1H, Ar), 7.40 – 7.36 (m, 1H, Ar), 7.31 – 7.26 (m, 2H, Ar), 7.21 – 7.13 (m, 2H, Ar), 4.00 – 3.92 (m, 2H, alkyl), 1.95 – 1.89 (m, 1H, alkyl), 1.33 – 1.168 (m, 8H, alkyl), 0.81 – 0.74 (m, 6H, alkyl) ppm; ¹³C NMR (100 MHz, CDCl₃): $\delta = 183.02$ (CHO), 154.85, 147.28, 143.60, 141.45, 141.25, 137.35, 129.38, 126.35, 124.68, 124.06, 123.32, 122.60, 120.52, 119.46, 118.09, 114.26, 109.50, 109.43 (Ar), 47.51, 39.44, 31.02, 28.82, 24.42, 23.09, 14.09, 10.94 (alkyl) ppm. HRMS (MALDI-TOF, m/z): [M⁺] 445.1529; calcd for (C₂₇H₂₇NOS₂) 445.1534.

5-(9-Hexyl-9H-carbazol-3-yl)thieno [**3,2-b**] thiophene-2-carbaldehyde (4c): 0.13 g; 82 % yield. ¹H NMR (400 MHz, CDCl₃): δ = 9.88 (s, 1H, CHO), 8.30 (d, 1H, *J* = 1.6 Hz, Ar), 8.14 (d, 1H, *J* = 8 Hz, Ar), 7.78 (s, 1H, Ar), 7.70 – 7.67 (m, 1H, Ar), 7.56 – 7.52 (m, 1H, Ar), 7.46 – 7.42 (m, 2H, Ar), 7.37 – 7.28 (m, 2H, Ar), 4.26 (t, 2H, *J* = 8 Hz, alkyl), 1.91 – 1.83 (m, 2H, alkyl), 1.40 – 1.28 (m, 6H, alkyl), 0.95 – 0.92 (m, 3H, alkyl) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 183.02 (CHO), 154.86, 147.27, 143.58, 140.99, 140.76, 137.35, 129.38, 126.37, 124.71, 124.09, 123.36, 122.63, 120.58, 119.47, 118.16, 114.28, 109.22, 109.14 (Ar), 43.23, 31.58, 28.96, 26.97, 22.58, 14.06 (alkyl) ppm. HRMS (MALDI-TOF, *m*/z): [M⁺] 417.1125; calcd for (C₂₅H₂₃NOS₂) 417.1121.

5-(5-Bromothieno [3,2-b] thiophen-2-yl)-3-hexylthiophene-2carbaldehyde (6): A mixture of 2 (1 g, 3.355 mmol), (4-hexylthiophen-2-yl)boronic acid (0.711 g, 3.355 mmol), Pd(PPh₃)₄ (193 mg, 0.168 mmol) and 2 M K₂CO₃ (6 mL) in THF (30 mL) was heated to reflux under a N2 atmosphere overnight. The reaction mixture was poured into water, followed by extraction using ethyl acetate. The organic layer was dried over anhydrous Na₂SO₄. The solvent was then removed under reduced pressure. In order to remove the residue of palladium catalyst, the organic fraction was filtered by short column chromatography on silica gel using a 1:3 mixture of CH2Cl2 and hexane as eluent to afford the filtered crude product which was immediately subjected to the Vilsmeier-Haack reaction. Next, to a two-necked round-bottom flask containing dry DMF (0.936 g, 12.818 mmol), POCl₃ (1.961 g, 12.818 mmol) was added dropwisely by syringe at 0 °C, Vilsmeier-Haack reagent was produced. A solution of the filtered crude product (0.494 g) in dry CH₂Cl₂ (20 mL) was added dropwise to the prepared Vilsmeier-Haack reagent under N2 atmosphere. The mixture was stirred for 15 min at 0 °C and overnight at 65 °C. After cooling, the reaction was poured into aqueous NaOH solution slowly in an ice bath with stirring for 30 min, the resulting mixture was then extracted with CH₂Cl₂ and H₂O. The organic fraction was dried over anhydrous Na₂SO₄ and the solvent was removed under reduced pressure. A yellow oil was yielded, which was purified by column chromatography on silica gel with hexane/CH₂Cl₂ (3:2 v/v) as the eluent to give **6** as a yellow oil (0.228 g, 0.552 mmol, 16)% yield). ¹H NMR (400 MHz, CDCl₃): δ = 9.98 (s, 1H, CHO), 7.36 (d, 1H, *J* = 0.4 Hz, Ar), 7.20 (d, 1H, *J* = 0.8 Hz, Ar), 7.05 (s, 1H, Ar), 2.91 (t, 2H, *J* = 7.6 Hz, alkyl), 1.72 – 1.65 (m, 2H, alkyl), 1.42 – 1.31 (m, 6H, alkyl), 0.908 - 0.873 (m, 3H, alkyl) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 181.45 (CHO), 153.83, 145.63, 140.09, 138.45, 137.23, 136.24, 126.68, 122.18, 117.46, 115.31 (Ar), 31.55, 31.34, 29.00, 28.57, 22.55, 14.06 (alkyl) ppm. HRMS (MALDI-TOF, *m*/z): [M⁺] 411.9629; calcd for (C₁₇H₁₇BrOS₃) 411.9625.

General synthetic procedure of 7a–7c: A mixture of 6 (76 mg, 0.184 mmol), (9-octylcarbazolyl)/ (9-(2-ethylhexyl)carbazolyl)/ (9-hexylcarbazolyl) boronic acid (0.368 mmol), Pd(PPh₃)₄ (11 mg, 0.009 mmol) and 2 M K₂CO₃ (2 mL) in THF (20 mL) was heated to reflux under a N₂ atmosphere for overnight. The reaction mixture was poured into water, followed by extraction using ethyl acetate. The organic layer was dried over anhydrous Na₂SO₄. Then, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using a 1:1 mixture of CH₂Cl₂ and hexane as eluent to afford **7a–7c** as red solids.

3-Hexyl-5-(5-(9-octyl-9H-carbazol-3-yl)thieno [3,2-b] thiophen-2-yl)thiophene-2-carbaldehyde (7a): 72 mg; 64 % yield. ¹H NMR (400 MHz, CDCl₃): δ = 9.91 (s, 1H, CHO), 8.24 (d, 1H, *J* = 1.6 Hz, Ar), 8.06 (d, 1H, *J* = 7.6 Hz, Ar), 7.65 – 7.63 (m, 1H, Ar), 7.42 – 7.38 (m, 3H, Ar), 7.34 – 7.31 (m, 2H, Ar), 7.19 – 7.18 (m, 1H, Ar), 6.99 (s, 1H, Ar), 4.21 (t, 2H, *J* = 7.2 Hz, alkyl), 2.84 (t, 2H, *J* = 7.6 Hz, alkyl), 1.81 – 1.78 (m, 2H, alkyl), 1.65 – 1.61 (m, 2H, alkyl), 1.33 – 1.16 (m, 16H, alkyl), 0.85 – 0.77 (m, 6H, alkyl) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 181.42 (CHO), 154.01, 149.79, 146.63, 140.98, 140.97, 140.43, 138.30, 136.20, 135.69, 126.20, 126.14, 125.36, 124.04, 123.39, 122.69, 120.57, 119.28, 118.37, 117.88, 113.99, 109.18, 109.03 (Ar), 43.27, 31.80, 31.58, 31.37, 29.38, 29.18, 29.04, 29.01, 28.60, 27.32, 22.62, 22.57, 14.08 (alkyl) ppm. HRMS (MALDI-TOF, *m*/z): [M⁺] 611.2350; calcd for (C₃₇H₄₁NOS₃) 611.2350.

5-(5-(9-(2-Ethylhexyl)-9H-carbazol-3-yl)thieno [3,2-b] thiophene-2-yl)-3-hexylthiophene-2-carbaldehyde (7b): 85 mg; 75 % yield. ¹H NMR (400 MHz, CDCl₃): δ = 9.85 (s, 1H, CHO), 8.15 (d, 1H, *J* = 1.6 Hz, Ar), 8.00 (d, 1H, *J* = 7.6 Hz, Ar), 7.54 (dd, 1H, *J* = 8.4, 1.6 Hz, Ar), 7.40 – 7.36 (m, 1H, Ar), 7.29 – 7.26 (m, 3H, Ar), 7.21 (d, 1H, *J* = 8.4 Hz, Ar), 7.17 – 7.15 (m, 1H, Ar), 6.90 (s, 1H, Ar), 4.00 – 3.97 (m, 2H, alkyl), 2.76 (t, 2H, *J* = 7.6 Hz, alkyl), 1.96 – 1.90 (m, 1H, alkyl), 1.59 – 1.53 (m, 2H, alkyl), 1.29 – 1.13 (m, 14H, alkyl), 0.82 – 0.75 (m, 9H, alkyl) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 181.35 (CHO), 153.99, 149.74, 146.61, 141.42, 140.97, 140.87, 138.22, 136.17, 135.53, 126.15, 126.03, 125.28, 123.91, 123.31, 122.68, 120.51, 119.26, 118.30, 117.66, 113.85, 109.41, 109.32 (Ar), 47.49, 39.45, 31.61, 31.36, 31.03, 29.07, 28.85, 28.59, 24.43, 23.09, 22.61, 14.12, 14.08, 10.93 (alkyl) ppm. HRMS (MALDI-TOF, *m*/z): [M⁺] 611.2353; calcd for (C₃₇H₄₁NOS₃) 611.2350.

3-Hexyl-5-(5-(9-hexyl-9H-carbazol-3-yl)thieno [3,2-*b***] thiophen-2-yl)thiophene-2-carbaldehyde (7c):** 80 mg; 74 % yield. ¹H NMR (400 MHz, CDCl₃): $\delta = 10.01$ (s, 1H, CHO), 8.35 (d, 1H, J = 2 Hz, Ar), 8.16 (d, 1H, J = 7.6 Hz, Ar), 7.77 – 7.74 (m, 1H, Ar), 7.53 – 7.50 (m, 3H, Ar), 7.46 – 7.42 (m, 2H, Ar), 7.31 – 7.28 (m, 1H, Ar), 7.10 (s, 1H, Ar), 4.33 (t, 2H, J = 7.2 Hz, alkyl), 2.97 – 2.93 (m, 2H, alkyl), 1.92 – 1.89 (m, 2H, alkyl), 1.74 – 1.72 (m, 2H, alkyl), 1.44 – 1.31 (m, 12H, alkyl), 0.95 – 0.89 (m, 6H, alkyl) ppm; ¹³C NMR (100 MHz, CDCl₃): $\delta = 181.44$ (CHO), 154.03, 149.79, 146.64, 140.98, 140.97, 140.43, 138.30, 136.20, 135.61, 126.21, 126.16, 125.36, 124.05, 123.39, 122.69, 120.57, 119.28, 118.39, 117.90, 114.01, 109.18, 109.03 (Ar), 43.28, 31.58, 31.38, 29.03, 28.98, 28.61, 26.98, 22.57, 22.56, 14.09, 14.02 (alkyl) ppm. HRMS (MALDI-TOF, *m*/z): [M⁺] 583.2031; calcd for (C₃₅H₃₇NOS₃) 583.2037.

General synthetic procedure of 5a–5c and 8a–8c: A mixture of each dye precursors (4a–4c and 8a–8c) and cyanoacetic acid (10 M equivalents) in acetic acid (8 mL) was refluxed in the presence of ammonium acetate (25 mg) overnight under a N₂ atmosphere. After cooling, the reaction mixture was washed with water and extracted with CHCl₃. The solvent was then removed under reduced pressure and the crude compound was purified by column chromatography on silica gel eluting with CHCl₃ followed by CHCl₃/MeOH (10:1, v/v) to give the corresponding products 5a–5c and 8a–8c.

(*E*)-2-Cyano-3-(5-(9-octyl-9H-carbazol-3-yl)thieno [3,2-*b*] thiophen-2-yl)acrylic acid (5a): 125 mg; 97 % yield; red solid. ¹H NMR (400 MHz, DMSO-*d*₆): $\delta = 8.59$ (d, 1H, J = 1.6 Hz, Ar), 8.57 (s, 1H, C = CH-), 8.33 - 8.28 (m, 2H, Ar), 8.06 (d, 1H, J = 0.4 Hz, Ar), 7.87 - 7.85 (m, 1H, Ar), 7.71 (d, 1H, J = 8.4 Hz, Ar), 7.64 (d, 1H, J = 8.4 Hz, Ar), 7.53 - 7.48 (m, 1H, Ar), 7.28 - 7.24 (m, 1H, Ar), 4.43 (t, 2H, J = 6.8 Hz, alkyl), 1.80 - 1.77 (m, 2H, alkyl), 1.26 - 1.18 (m, 10H, alkyl), 0.83 - 0.79 (m, 3H, alkyl) ppm; ¹³C NMR (100 MHz, THF-d₈): $\delta = 162.92$ (COOH), 154.25, 147.65, 146.00, 140.73, 140.52, 137.42, 136.36, 129.73, 125.67, 124.51, 123.50, 123.09, 122.31, 119.95, 118.78, 117.46, 115.45, 114.01, 108.97, 108.69, 97.58 (Ar), 42.33, 31.40, 28.99, 28.80, 28.54, 26.73, 22.11, 13.02 ppm (alkyl). HRMS (MALDI-TOF, *m*/z): [M⁺] 512.1585; calcd for (C₃₀H₂₈N₂O₂S₂) 512.1592.

(*E*)-2-Cyano-3-(5-(9-(2-ethylhexyl)-9H-carbazol-3-yl)thieno [3,2-b] thiophen-2-yl)acrylic acid (5b): 145 mg; 84 % yield; red solid. ¹H NMR (400 MHz, DMSO- d_6): $\delta = 8.60$ (d, 1H, J = 1.2 Hz, Ar), 8.57 (s, 1H, C = CH–), 8.34 – 8.28 (m, 2H, Ar), 8.06 (s, 1H, Ar), 7.863 (dd, 1H, J = 8.8, 1.6 Hz, Ar), 7.67 (d, 1H, J = 8.4 Hz Ar), 7.60 (d, 1H, J = 8 Hz, Ar), 7.53 – 7.49 (m, 1H, Ar), 7.28 – 7.25 (m, 1H, Ar), 4.30 (d, 2H, J = 7.2 Hz, alkyl), 2.02 – 1.99 (m, 1H, alkyl), 1.35 – 1.16 (m, 8H, alkyl), 0.86 (t, 3H, J = 7.2 Hz, alkyl), 0.78 (t, 3H, J = 6.8 Hz, alkyl) ppm; ¹³C NMR (100 MHz, THF-d₈): δ = 162.84 (COOH), 154.22, 147.69, 146.08, 141.11, 140.91, 137.40, 136.34, 129.84, 125.66, 124.49, 123.47, 123.03, 122.27, 119.93, 118.80, 117.41, 115.42, 109.23, 108.94, 97.42 (Ar), 67.42, 46.60, 38.98, 30.46, 28.30, 22.57, 12.97, 9.82 ppm (alkyl). HRMS (MALDI-TOF, m/z): [M⁺] 512.1590; calcd for (C₃₀H₂₈N₂O₂S₂) 512.1592.

(*E*)-2-Cyano-3-(5-(9-hexyl-9H-carbazol-3-yl)thieno [3,2-*b*] thiophen-2-yl)acrylic acid (5c): 150 mg; 99 % yield; red solid. ¹H NMR (400 MHz, DMSO-*d*₆): $\delta = 8.60$ (d, 1H, J = 1.6 Hz, Ar), 8.56 (s, 1H, C = CH–), 8.33 – 8.28 (m, 2H, Ar), 8.07 (s, 1H, Ar), 7.88 – 7.86 (m, 1H, Ar), 7.73 (d, 1H, J = 8.8 Hz, Ar), 7.65 (d, 1H, J = 8 Hz, Ar), 7.53 – 7.49 (m, 1H, Ar), 7.28 – 7.24 (m, 1H, Ar), 4.44 (t, 2H, J = 7.2 Hz, alkyl), 1.81 – 1.77 (m, 2H, alkyl), 1.30 – 1.20 (m, 6H, alkyl), 0.81 (t, 3H, J = 6.8 Hz, alkyl) ppm; ¹³C NMR (100 MHz, THF-d₈): $\delta = 162.96$ (COOH), 154.22, 147.63, 145.99, 140.70, 140.48, 137.38, 136.33, 129.73, 125.66, 124.47, 123.47, 123.05, 122.29, 119.94, 118.77, 117.42, 115.48, 113.96, 108.94, 108.67, 97.56 (Ar), 42.31, 31.18, 28.49, 26.36, 22.07, 12.97 ppm (alkyl). HRMS (MALDI-TOF, m/z): [M⁺] 484.1284; calcd for (C₂₈H₂₄N₂O₂S₂) 484.1279.

(*E*)-2-Cyano-3-(3-hexyl-5-(5-(9-octyl-9H-carbazol-3-yl)thieno [3,2-*b*] thiophen-2-yl)thiophen-2-yl)acrylic acid (8a): 79 mg; 99 % yield; dark purple solid. ¹H NMR (400 MHz, DMSO- d_6): $\delta = 8.54$ (s, 1H, C = CH–), 8.29 – 8.26 (m, 2H, Ar), 7.99 (s, 1H, Ar), 7.92 (s, 1H, Ar), 7.82 – 7.80 (m, 1H, Ar), 7.68 – 7.62 (m, 2H, Ar), 7.53 – 7.47 (m, 2H, Ar), 7.26 – 7.23 (m, 1H, Ar), 4.41 (t, 2H, J = 6.8 Hz, alkyl), 2.80 (t, 2H, J= 7.2 Hz, alkyl), 1.79 – 1.76 (m, 2H, alkyl), 1.63 – 1.60 (m, 2H, alkyl), 1.30 – 1.18 (m, 16H, alkyl), 0.89 – 0.79 (m, 6H, alkyl) ppm; ¹³C NMR (100 MHz, THF- d_8): $\delta = 163.34$ (COOH), 154.83, 149.59, 144.99, 141.92, 140.90, 140.63, 140.02, 138.08, 135.38, 128.49, 125.48, 125.00, 124.95, 123.16, 122.97, 122.33, 119.88, 118.58, 116.89, 115.65, 113.57, 108.79, 108.57, 96.69 (Ar), 42.27, 31.40, 31.16, 30.70, 29.00, 28.81, 28.55, 28.24, 26.72, 22.12, 22.09, 13.04 ppm (alkyl). HRMS (MALDI-TOF, m/z): [M⁺] 678.2401; calcd for (C₄₀H₄₂N₂O₂S₃) 678.2408.

(*E*)-2-Cyano-3-(5-(5-(9-(2-ethylhexyl)-9H-carbazol-3-yl)thieno [3,2-*b*] thiophen-2-yl)-3-hexylthiophen-2-yl)acrylic acid (8b): 80 mg; 85 % yield; dark purple solid. ¹H NMR (400 MHz, DMSO- d_6): $\delta =$ 8.53 (s, 1H, C = CH–), 8.28 – 8.25 (m, 2H, Ar), 7.93 (s, 1H, Ar), 7.89 (s, 1H, Ar), 7.81 – 7.78 (m, 1H, Ar), 7.66 – 7.57 (m, 2H, Ar), 7.52 – 7.48 (m, 2H, Ar), 7.27 – 7.23 (m, 1H, Ar), 4.27 (d, 2H, *J* = 7.2 Hz, alkyl), 2.77 (t, *J* = 7.2 Hz, alkyl), 2.01 – 1.98 (m, 1H, alkyl), 1.61 – 1.59 (m, 2H, alkyl), 1.32 – 1.14 (m, 14H, alkyl), 0.87 – 0.86 (m, 9H, alkyl) ppm; ¹³C NMR (100 MHz, THF- d_8): $\delta =$ 164.38 (COOH), 154.20, 149.31, 144.41, 141.37, 140.98, 140.71, 140.37, 138.01, 135.54, 128.71, 125.44, 124.97, 124.87, 123.12, 122.88, 122.30, 119.85, 118.58, 118.26, 116.78, 116.22, 113.52, 108.98, 108.80, 98.14 (Ar), 46.51, 38.93, 31.21, 30.65, 30.42, 28.59, 28.27, 22.55, 22.11, 13.09, 12.99, 9.83 ppm (alkyl). HRMS (MALDI-TOF, *m*/*z*): [M⁺] 678.2403; calcd for (C₄₀H₄₂N₂O₂S₃) 678.2408.

(*E*)-2-Cyano-3-(3-hexyl-5-(5-(9-hexyl-9H-carbazol-3-yl)thieno [3,2-*b*] thiophen-2-yl)thiophen-2-yl)acrylic acid (8c): 81 mg; 91 % yield; dark purple solid. ¹H NMR (400 MHz, DMSO- d_6): δ = 8.55 (s, 1H, C = CH–), 8.30 – 8.26 (m, 2H, Ar), 8.02 (s, 1H, Ar), 7.94 (s, 1H, Ar), 7.84 – 7.81 (m, 1H, Ar), 7.66 (d, 1H, *J* = 8.4 Hz, Ar), 7.63 (d, 1H, *J* = 8.4 Hz, Ar), 7.54 (s, 1H, Ar), 7.52 – 7.47 (m, 1H, Ar), 7.27 – 7.23 (m, 1H, Ar), 4.42 (t, 2H, *J* = 7.2 Hz, alkyl), 2.81 (t, *J* = 7.6 Hz, alkyl), 1.80 – 1.75 (m, 2H, alkyl), 1.64 – 1.59 (m, 2H, alkyl), 1.35 – 1.21 (m, 12H, alkyl), 0.89 – 0.79 (m, 6H, alkyl) ppm; ¹³C NMR (100 MHz, THF- d_8): δ = 163.23 (COOH), 154.90, 149.63, 145.03, 141.99, 140.93, 140.66, 140.06, 138.12, 135.39, 128.52, 125.50, 125.08, 124.98, 123.19, 123.00, 122.34, 119.88, 118.64, 118.60, 116.94, 115.58, 113.64, 108.82, 108.58, 96.64 (Ar), 42.28, 31.21, 31.17, 30.74, 28.55, 28.53, 28.25, 26.39, 22.09, 13.05, 12.99 ppm (alkyl). HRMS (MALDI-TOF, m/z): [M⁺] 650.2099; calcd for (C₃₈H₃₈N₂O₂S₃) 650.2095.

Declaration of Competing Interest

The authors report no declarations of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jphotochem.2020. 112979.

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