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Significantly Improved Performance of Dye-Sensitized Solar Cell by Optimizing

Organic Dyes with Pyrrole as the Isolation Spacer and Utilizing Alkyl Chain

Engineering

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The conversion efficiencies of dye sensitized solar cells were largely enhanced by organic dyes bearing pyrrole as the isolation spacer and alkyl chain engineering, which afforded an efficient strategy to suppress the charge recombination together with the increased light-harvesting ability by the optimization of intramolecular and interfacial charge transfer.



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Significantly Improved Performance of Dye-Sensitized Solar Cell by Optimizing Organic Dyes with Pyrrole as the Isolation Spacer and Utilizing Alkyl Chain Engineering

Jinfeng Wang,^a Siwei Liu,^a Zhaofei Chai,^a Kai Chang,^a Manman Fang,^a Mengmeng Han,^a Yiyi Wang,^a Sheng Li,^b Hongwei Han,^b Qianqian Li,^{*a} Zhen Li^a

The optimization of interfacial and intramolecular charge transfer of organic dyes is crucial to the photovoltaic performance of dye-sensitized solar cells. In this text, the efficient strategy was afforded by the introduction of alkylated pyrrole as isolation spacer into the organic dyes. The interfacial charge transfer can be organized by the tunable alkyl chains as the barrier layer to inhibit the electron recombination, and the pull-push system can be strengthened by the incorporation of electron-withdrawing unit (benzothiadiazole) and electron-rich moieties (pyrrole) into the conjugated bridge simultaneously, resulting in the excellent light-harvesting capability. Therefore, the high conversion efficiency of LI-124 with suitable alkyl chains and 9.70% was achieved by device optimization.

> cannot be well combined to generate the synergistic effect. For instance, it is an efficient approach to broaden the

> absorption spectra of organic dyes by the introduction of an

electron-withdrawing unit into the conjugated bridge as the

auxiliary acceptor (A'), but the A' moieties can also act as the

"electron trap" to aggravate the electron recombination. 16-19

Thus, with the aim to achieve the high conversion efficiencies,

the balance of these two effects should be controlled by the

well-designed molecular structures. Apart from the

modulation of electronic properties of A' units by different

building blocks ²⁰⁻²², in our previous study, the steric hindrance

effect was applied into the isolation spacers between

benzothiadiazole (A') and cyanoacrylic acid (A), which was

conducted by the linkage of different substituents to β -

position of thiophene ring (Figure 1). With the increased sizes

of substituents, the involved dihedral angles were enlarged

with poorer conjugation effect, the electron back reaction can

be inhibited efficiently, as proved by the increased lifetimes of

electrons in TiO₂ film. Accordingly, the conversion efficiencies

of corresponding DSCs increased from 3.44% to 6.48%,

affording an efficient way to suppress the electron

recombination by the partially twisted strategy. $^{\rm 23}$ However, on

the other hand, the absorption spectra became narrowed with the onset wavelength blue-shifted from 693 to 626 nm (Chart S1), leading to the lower light harvesting abilities. Thus, the

improvement of photovoltaic performance is limited by the

similar trends of input power and energy loss. Is it possible to

obtain the decreased charge recombination and the increased

light-harvesting ability simultaneously?

Introduction

Converting sunlight into electrical energy is considered to be the most effective way to solve the energy crisis and environmental problems.¹⁻⁴ Dye-sensitized solar cells (DSCs) have attracted much attention in both academic and industrial fields because of their low cost and simple construction.⁵⁻¹⁰ In the development of DSCs, the dye sensitizer engineering is proved as an efficient approach to adjust the light-harvesting ability and regulate the electron processes in devices, resulting in the improved the photovoltaic performance.¹¹⁻¹⁴ Until now, the conversion efficiency of 14.3% as a record was achieved by an organic dye with electron donor- π -bridge-electron acceptor (D- π -A) structure,¹⁵ which highlighted the superiority of these pull-push systems with high polarities.

Generally, the optimization of D- π -A structures has focused on the following two aspects: (1) the modulation of intrinsic electron property to strengthen the intramolecular charge transfer (CT), with the aim to harvest more sunlight as the input energy; (2) the adjustment of molecular configurations to optimize the interfacial charge transfer, including the suppression of dye aggregation and electron recombination as the energy loss. However, in most cases, the above two points

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Figure 1. The comparison between organic dyes with different isolation groups and the functionality of alkyl chains in different positions. CT: Charge transfer.

Actually, this combine effect is hard to be realized by the modification of thienyl unit as the common building block of organic dyes for the steric hindrance effect. As a similar fivemembered ring to thiophene, pyrrole affords an additional function site at the nitrogen atom, which can incorporate various substituents with nearly no influence on the intramolecular CT effect of conjugated system, as proved by our previous study. ²⁴⁻²⁸ Also, pyrrole with the electron-rich property can act as the electron donor (D') to the adjacent A' unit, leading to the reversed charge transfer. It can relieve the electron-trapping effect of A' unit to some extent,²⁹ indicating the key role of pyrrole to the intramolecular CT effect of organic dyes as the isolation spacer.

Besides, the interfacial CT in DSCs can be optimized by the well-organized molecular arrangements of organic dyes on the TiO_2 surface, which can be conducted by the alkyl chain engineering. It plays the key role to the molecular morphology by the adjustable packing modes and intermolecular interactions, and has been applied into many fields, including organic field-effect transistors (OFETs),³⁰ organic light-emitting diodes (OLEDs)³¹ and organic photovoltaic devices (OPVs),^{32,33}

Scheme 1. Synthetic routes of sensitizers



Figure 2. Absorption spectra of dyes in CH_2Cl_2 solution (30 μ M) (A) and on TiO₂ films (6 μ m) (B).

and so on. In DSCs, the alkyl chains are mostly linked to the electron donor moieties of organic dyes, which can act as the first barrier layer to inhibit the dye aggregation and block the electron recombination.³⁴⁻⁴⁰ Recently, the largely increased conversion efficiency is achieved by cyclopentadithiophenebased organic dyes from 4.74% to 9.07% (Chart S2),⁴¹ mainly due to the dual protection of the two barrier layers from alkyl chains in conjugated bridge. These indicated that the alkyl chains as the side chains in organic dyes play the essential role to the interfacial CT, which were varied with the different linkage positions.

Combined with the function of pyrrole and alkyl chains, a series of organic dyes (LI-121-LI-125) with pyrrole as the isolation spacer were designed and synthesized with the alkyl chain engineering from methyl to dodecyl (Figure 1). Through the replacement of thiophene in dye LI-80 with N-methyl pyrrole moiety, the improved photovoltaic performance was obvious with the increased conversion efficiency from 3.44% to 4.27%. Furthermore, the highest conversion efficiency of 8.75% was achieved by LI-124 with N-decyl pyrrole as the isolation spacer, which can further increase to 9.70% by device optimization, indicating the great functionality of alkyl chains engineering. These alkyl chains play the essential role to the regulation of dye molecular arrangement and electron process at the dye/TiO₂/electrolyte interface, but have nearly no adverse effect on the conjugated effect of molecular skeleton for their perpendicular geometry to pyrrole ring, as proved by the similar absorption spectra of these organic dyes. Thus, an efficient method is afford to achieve the high conversion efficiency by the suppression of electron recombination with



Reagents and conditions: (i) NaH, RBr, THF; (ii) [Ir(COD)Cl]₂,4,4'-ditert-butyl-2,2'-dipyridyl, (Bpin)₂, cyclohexane, 60° C, 12h. (iii) K₂CO₃, Pd(PPh₃)₄, THF/H₂O, reflux, 12h; (iv) POCl₃, DMF, ClCH₂CH₂Cl, 0^oC to rt, 10h; (v) cyanoacrylic acid, piperidine, CH₃CN, reflux, 12h.



Figure 3. Energy-level diagram of sensitizers, electrolyte and TiO_2. ΔG_1 : energy gap for electron injection; ΔG_2 : energy gap for regeneration of the oxidized dyes.

the increased light-harvesting abilities, which can be applied to various organic dyes to promote the development of DSCs.

Results and discussion

Synthesis of the Sensitizers

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The alkyl chain engineering is the common strategy to tune the molecular morphology in the aggregated state. In this text, various alkyl moieties with different lengths were linked to the nitrogen atom of pyrrole ring, which was located near the cyanoacrylic acid moiety as the electron acceptor and anchoring group. In this case, these flexible chains closed to the TiO₂ surface can act as the second barrier layer after the first insulation effect by the alkyl chains linked to the electron donor, with the aim to further inhibit the electron recombination. Besides, the absorption behaviors of organic molecules on TiO_2 in the aggregated state can be adjustable by different alkyl moieties as the side chains. Moreover, the conjugated effect of the whole molecule has maintained in spite of varied alkyl moieties, affording an efficient strategy to reduce the energy loss in DSCs without any unfavorable effect on the light-harvesting ability. It is mainly related to the particular structure of pyrrole with the functional site on nitrogen atom, which is hardly to be realized in the similar moieties, including thiophene and furan. Thus, a series of organic dyes (LI-121-LI-125) based on pyrrole with alkyl chain modification have been synthesized (Scheme 1). After the alkylation of pyrrole with different chains, the corresponding heteroarylboronates were obtained by the followed C-H activation, which can be linked to the main light-harvesting moieties with bromine atoms (Ar-Br) by Suzuki coupling reaction. Then, through the introduction of aldehyde group by Vilsmeier-Haack reaction, the organic dyes were obtained by the Knoevenagel condensation of compound 4a-e and cyanoacrylic acid, which were well characterized by ¹H NMR, ¹³C NMR, ESI and EA.

Optical Properties

All of the organic dyes with the same conjugated skeleton show the similar absorption spectra as single molecules (in dilute solutions) and in the aggregated states (in TiO₂ films) (Figure 2), indicating that the alkyl chain engineering does not affect ICT and molecular configuration of conjugated system. There are two main absorption bands in the range of 350-700



Figure 4. J-V characteristic curves (A) and IPCEs (B) for DSCs based on dye LI-121-LI-125

nm. The peak located at 380 nm is assigned to the π - π * transitions of aromatics, while the other one located at 517 nm is attributed to the ICT through the whole molecule, providing efficient charge-separation at the excited state. Once these dyes were adsorbed onto the nanocrystalline TiO₂ film, the obvious red-shift of absorption spectra was observed in comparison with those in solution, mainly attributing to the interactions between TiO₂ and organic dyes, together with their intermolecular interactions in the aggregated state. With the increased thickness of TiO_2 films (from 6 to 9 μ m), the absorption spectra can be further extended (Figure S1). These broader absorption regions are beneficial to the enhancement of light-harvesting capability, leading to the improved photovoltaic performance.

Electrochemical Properties

Regardless of the different lengths of alkyl chains substituted to the nitrogen atom of pyrrole, the electrochemical properties of these dyes were similar with each other (Figure 3). The reversible redox process were observed for these organic dyes by cyclic voltammetry (Figure S2 and Table S1). The first oxidation potentials (E_{ox}) (0.8 V vs NHE), were significantly more positive than that of the liquid electrolyte $I - / I_3$ redox potential (0.4 V vs NHE), indicating that the oxidized dyes could be efficiently regenerated for the enough driving force. The excited state oxidation potentials (E_{ox}^{*}) (-1.2 V vs NHE), estimated from E_{ox} and zero-zero transition energy (E_{0-0}) , were more negative than the conduction band-edge of TiO_2 (*E_{CB}*) for thermodynamically favored electron injection.⁴² Thus, dye LI-121-LI-125 can act as the efficient organic dyes for the well-matched energy levels and chemical stability.

Theoretical Calculations

Through the incorporation of pyrrole moiety as the isolation spacer into the organic dyes, the conjugated skeleton of dye LI-121-LI-125 exhibited the almost planar geometry with the small dihedral angle of 30.5° between benzothiadiazole and pyrrole (Table S2), which is proved by the density functional theory (DFT) calculation at B3LYP/6-31G* level.43 The efficient charge transfer in the push-pull structure can be observed with the almost separated HOMO and LUMO. Also, the extent of charge separation upon excitation was estimated by natural bond orbital analysis (Figure S3). These dyes were grouped into four segments, including triarylamine-thiophene (TPA-Th), benzothiadiazole (BT), isolation spacer (IS), and cyanoacrylic acid (CAA). The charge differences (Δq , $S_0 \rightarrow S_1$) showed that the prominent charge transfer occurred between TPA-Th and

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Figure 5. The molecular arrangements of organic dyes on the TiO₂ surface with different alkyl chains

BT, acting as the main light-harvesting unit. Moreover, compared to the analogue **LI-80** with thiophene as the isolation group, the electron-rich property of pyrrole in **LI-121** can promote ICT effect for the larger charge differences, which was beneficial to the light harvesting.

Photovoltaic Performance

The current-voltage (*J-V*) curves of solar cells in conjunction with an iodine electrolyte (0.05 M I₂, 0.2 M Lil, 0.6 M DMPII, 0.1 M GuNCS and 0.5 M 4-TBP in acetonitrile) were measured under standard AM 1.5G conditions (100 mW cm⁻²) (Figure 4A and Table S3). With the involved alkyl chains lengthened from methyl to dodecyl, the open circuit voltages (V_{oc}) of the corresponding DSCs firstly increased from 598 to 674 mV, then decreased to 618 mV. Also, their short-current densities (J_{sc}) exhibited the similar trend, and the highest conversion efficiency of 8.75% is achieved by DSC based on **LI-124** with decyl modification. It is mainly related to the various aggregated states of organic dye on the TiO₂ film, which can be partially demonstrated by the different dye-loading amounts with alkyl chain engineering.

The largest dye-loading amount of **LI-121** (3.29×10^{-8} mol cm⁻² μ m⁻¹) with methyl modification meant the densely packed molecules on the TiO₂ surface. In this case, the severe dye aggregates were usually formed for the strong intermolecular interactions with the short contact of the adjacent molecules, resulting in the inhomogeneous distribution of organic dyes on the TiO₂ surface (Figure 5). Thus, the severe electron recombination may occur at the bare TiO₂ surface, leading to the lower *V*_{oc} of **LI-121**. Also, the possible intermolecular energy transfer can be induced with the excited state quenching, resulting in the photocurrent loss. ^{44,45} With the

increased length of alkyl moieties as the side chains, the distances among the organic dyes can be enlarged, accompanied with the decreased intermolecular interactions, as demonstrated by the decreased dye- loading amount of LI-124 (2.80×10⁻⁸ mol cm⁻² μ m⁻¹). Thus, the arrangement of organic dyes on the $\rm TiO_2$ surface could be regulated with the almost homogeneous packing modes, which is beneficial to the light-harvesting and the inhibition of electron recombination, leading to the improved photovoltaic performance. However, when the length of involved alkyl chains increased to some extent, the ample sizes of organic molecules may largely decrease the amount of dyes on the TiO₂ surface, leading to the lower light harvesting efficiencies. Also, the barrier effect for the suppression of electron recombination can be weakened with the decreased amount of alkyl chains. Thus, LI-125 bearing the longest alkyl chains (dodecyl) exhibited the moderate conversion efficiency. Accordingly, decyl moiety is proved as the suitable side chain to realize the increase of J_{sc} and V_{oc} at the same time, resulting in the best photovoltaic performance of LI-124. The density of photogenerated electrons could also be analyzed from IPCE, as shown in Figure 4B. The IPCE curves of these organic dyes exhibited the similar shape with different IPCE values, which was mainly related to the varied electron collection efficiencies with different alkyl chains modification. Dye LI-123 and LI-124 bearing octyl and decyl moieties exhibited the higher values for the well-organized molecular arrangement and dual insulation effect by the alkyl chains in electron donor and isolation spacer together (Figure 5).

Besides, the energetic and dynamic origins of different V_{oc}



Figure 6. Charge density (A) and electron lifetime (B) at open circuit as a function of V_{oc} for DSCs based on LI-121-LI-125-sensitized solar cells.



Figure 7. The changes of photovoltaic parameters of dye LI-121-LI-125 by alkyl chain engineering

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can be investigated and understood in detail by charge extraction (CE) method and intensity-modulated photovoltage spectroscopy (IMVS). Since the related DSCs were fabricated with the same electrolyte, V_{oc} is mainly determined by the electron quasi-Fermi-level ($E_{F,n}$) of dye-loaded TiO₂ film, which associated with conduction band (E_{CB}) and the density of free charge.⁴⁶ As shown in Figure 6A, the shifts in E_{CB} was much different with the alkyl chain engineering of organic dyes. The up-shift of conduction band to a greater extent was conducted by dye LI-121, which was related to their orientation and arrangement on the TiO₂ surface as mentioned above. However, it did not result in the enhancement of V_{oc} values, mainly due to the shorter electron lifetime of LI-121-sensitized TiO₂ film, as shown in Figure 6B. While DSCs based on dye LI-123 and LI-124 exhibited the longer electron lifetime, meaning the lower electron recombination rate. Thus, the suitable alkyl chains closed to the TiO₂ surface indeed can act as the efficient barrier layer to further inhibit the contact of electrolyte with electron in TiO₂ film, which is beneficial to the suppression of charge recombination. Accordingly, electrochemical impedance spectroscopy (EIS), which was performed in the dark under a forward bias of -0.69 V (Figure S4), showed the similar trend with IMVS measurement, further confirming the important role of alkyl chains substituted to pyrrole moiety.

Thus, with different alkyl moieties applied into the organic dyes as the side chains, the well-organized molecular alignment can be achieved by the adjustable intermolecular interactions and dye-loaded amounts, which can be considered as the chemical optimization of organic dyes. On the other hand, the physical doping can be conducted by the introduction of chenodeoxycholic acid (CDCA), which is the common coadsorbent to inhibit the dye aggregation on the TiO₂ surface. When it was applied into DSC based on dye LI-124 with suitable alkyl chains, the high conversion efficiency of 9.70% was achieved by the incorporation of CDCA with low concentration (1 mM) (Figure 7 and S5-S8), which was mainly attributed to the combine effect of chemical optimization and physical doping. Under the same conditions, the conversion efficiency of N719 was 8.26% with J_{sc} of 16.76 mA cm⁻², V_{ac} of 683 mV and FF of 0.72 (Table S3), meaning that the superiority of organic dyes LI-124 with reasonable molecular structure and the potential higher conversion efficiency by device



Figure 8. The storage stability of DSC based on LI-124

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optimization.

The storage stability of DSCs based on these dyes were investigated, and values for J_{scr} , V_{ocr} , *FF* and η were recorded over a period of 500 h. Taking **LI-124**-sensitized solar cell with the best photovoltaic performance as the example, the overall efficiency remained 91% after 500 h of aging in the air (Figure 8). Also, other dyes exhibited the excellent storage stabilities (Figure S9 and S10), indicating organic dyes on the TiO₂ surface remained intact after long time aging. Also, under continuous full sunlight irradiation at standard AM 1.5G conditions, the dye-sensitized films almost keep intact for 15 h, as proved by the similar absorption spectra and photographs (Figure S11-13), further confirming their good photo-stabilities. Besides, they possessed excellent thermal stability with the decomposition temperatures (the 5% of weight lost) higher than 220 °C (Figure S14).

Based on these excellent photovoltaic performance, some strategies can be proposed to optimize the molecular design of organic dyes in DSCs (Figure 9). As discussed above, once the A' units were introduced into the conjugated bridges of organic dyes with D- π -A structure to broaden the light harvest regions, it is essential to insert isolation spacers between the A' and A moieties to suppress the possible "electron trap" effect. In the previous study, some aromatic rings were employed, such as thienyl, phenyl, and so on. ²³ However, when some alkyl chains were substituted to inhibit the charge recombination, the steric hindrance can result in the partially twisted configuration of organic dyes, leading to the decreased light-harvesting capability. In this text, alkylated pyrrole was incorporated as the isolation spacers with the adjustable lengths of alkyl chains, which can act as the second barrier layer closed to the TiO₂ surface, after the first insulation by the alkyl chains linked to electron donor part. Meanwhile, the light harvesting region was maintained, since nearly no steric hindrance would be caused by the alkyl chains linked to the nitrogen atom of pyrrole. Thus, the intramolecular charge transfer of organic dyes can increase by the addition of electron-withdrawing unit and electron-rich ring to harvest more sunlight, and the interfacial charge transfer can be



Figure 9. The strategy for molecular design of efficient organic dyes in dye-sensitized solar cells.

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optimized by the alkyl chain engineering closed to the TiO_2 surface, which can adjust the molecular arrangement of organic dyes as the aggregated state and act as efficient contact inhibitor, to suppress the interfacial charge recombination. Therefore, the high conversion efficiency can be gained by the increased input energy and reduced energy loss, which were conducted by the optimization of molecular configuration and alignment, and pull-push electronic property of organic dyes. In the further research, more isolation spacers near the electron acceptor will be exploited to extend the conjugated system and organize the interfacial charge transfer together, with the aim to achieve the better photovoltaic performance.

Conclusions

A series of organic dyes with alkylated pyrrole moieties as the isolation spacers were designed and synthesized, with the enhanced light-harvesting ability and inhibited charge recombination in dye sensitized solar cells. With the adjustment of alkyl chains closed to the TiO_2 surface, the interfacial charge transfer was optimized by the well-organized molecular arrangement and formation of contact inhibitor. Accordingly, the highest conversion efficiency can be achieved as 9.70% for **LI-124** with decyl-substituted pyrrole as the isolation spacer. Also, with the investigation of relationship between molecular structure and photovoltaic performance, some strategies were proposed to promote the development of DSCs by efficient organic dyes.

Experimental

Materials and Instrumentation:

Tetrahydrofuran (THF) was dried over and distilled from K-Na alloy under an atmosphere of dry argon. All solvents were analytical grade and used without further purification. Compound 1a (Nmethylpyrrole) was purchased without further purification. Compound Ar-Br were synthesized according to our previous work. 23 ^1H and ^{13}C spectra were obtained with a Bruker 300 MHz spectrometer or Bruker Avance III HD 400 MHz using tetramethylsilane (TMS; δ = 0 ppm) as internal standard. Elemental analyses were performed by a 73 CARLOERBA-1106 microelemental analyzer. ESI-MS spectra were recorded with a Finnigan LCQ advantage mass spectrometer. UV-visible spectra were on a Shimadzu UV-2550 spectrometer conducted dichloromethane. Electrochemical cyclic voltammetry was performed with a CHI 660 voltammetric analyzer with Pt disk, Pt plate, and Ag/Ag^{\dagger} electrode as working electrode, counter electrode, and reference electrode, respectively, in nitrogen-purged anhydrous CH₂Cl₂ with tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte (scanning rate: 100 mV/s). The ferrocene/ferrocenium redox couple was used for potential calibration.

DSC device fabrication and measurement

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fluorine doped tin oxide (FTO) conducting glass (3.2 mm thickness, 7-8 ohms/sq) which were cleaned with detergent, water, ethanol and acetone respectively and irradiated under O₃ for 18 min, then immersed in TiCl₄ solution (40 mM) for 30 min at 70 °C. After being cooled to room temperature, they were washed with deionized water and ethanol three times respectively and dried. The photoanodes (16 µm thickness), which consist of 12 µm layer of mesoporous TiO₂ (18 NR-T, 18-20 nm, Dyesol) and 4 μ m scatter layer (18 NR-AO, 20 - 450 nm, Dyesol), were prepared using the screen printing technique and gradually heated under airflow at 325 °C for 5 min, 375 °C for 5 min, 450 °C for 15 min and 500 °C for1 h. After the film being cooled to room temperature, they were immersed in TiCl₄ solution (40 mM) for 30 min at 70 $^{\circ}$ C once again, then washed and annealed at 500 $^{\circ}$ C for 30 min. After the TiO₂ film being cooled to 80 °C, they were immersed in dye bath (0.3 mM) in mixture solution (CH₃CN/t-BuOH/CHCl₃ = 2/2/1) for 18 h in dark condition. Then, the sensitized electrodes were washed with corresponding solvents and dried in air. Counter electrodes were prepared by thermal deposition: FTO glass (2.2 mm thickness, 7-8 ohms/sq) with two small holes were cleaned as photocathodes, 10 μ L solution of H₂PtCl₆ (10 mM) in isopropyl alcohol were dispersed on FTO glass and heated at 400 °C for 30 min. After then, dve absorbed photoanodes and Pt-counter electrode were assembled into a sandwich type cell and sealed with a hot-melt gasket (25 µm thickness) made by the ionomer Surlyn 1702 (DuPont). The electrolyte consisted of 0.05 M $\rm I_2,~0.2~M$ Lil, 0.6 M DMPII, 0.1 M GuNCS and 0.5 M 4-TBP in acetonitrile were injected into cells by the two small holes after assembled. Lastly, the two holes were sealed with a Surlyn sheet (50 µm thickness) and a thin ITO glass covered by heating.

The DSC devices were fabricated according to literatures. ^{45,47} A

Photovoltaic measurement were conducted under AM 1.5 solar simulator (Model 94023A equipped with a 450 W xenon arc lamp, Newport Co). It was calibrated with a normal silicon solar cells before measurement. Keithley model 2400 digital source meter were connected with light source to get J-V curves when applying an external bias to the cell. Incident photon-current conversion efficiency (IPCE) was recorded on a DC Power Meter (Model 2931-C equipped with a 300 W xenon arc lamp, Newport Co.) under irradiation with a motorized monochromator (Oriel). Some electrochemical properties were obtained by Modulab XM PhotoEchem system such as IMVS (intensity modulated photovoltage spectroscopy), CE (charge extraction), EIS (electrochemical impedance spectroscopy). IMVS and CE were measured under a white light emitting diode (LED) array. CE were conducted in dark with different potential biases with a frequency range from 1 Hz to 100 kHz.

The measurement of the dye loading amounts

The dye loading amounts (DLA) were measured by two steps, firstly, the desorption of organic dyes from TiO₂ films were conducted by the immersion of dye-sensitized TiO₂ films into the solution (3.0 mL) of NaOH (0.1 M)/THF (v/v, 1/1). Then, the concentrations (c) of these solutions were determined by standard curves of organic dyes under the same conditions. Accordingly, DLA values were calculated by a mathematical equation: DLA = $(c \times v)/(0.25 \text{ cm}^2 \times 16 \mu\text{m})$, v was

the volume of desorption solution (3.0 mL), 0.25 cm² was the area of TiO₂ film, 16 μ m was the thickness of TiO₂ film.

General synthesis of compound 1b-e

Under an atomsphere of nitrogen, a mixture of pyrrole (1.0 equiv) and RBr (1.5 equiv) in dry THF (30 mL) was placed in a 200 mL round-bottom and cooled to -20 °C. Then NaH (3.0 equiv) dissolved in THF (10 mL) was added slowly and the mixture was stirred at -20 °C for 1h, then 65 °C for 12h. The solid was filtered out, and the solvent was poured into water and extracted with chloroform for three times. The combined organic layers were dried with anhydrous sodium sulfate. After the solvent was evaporated, the crude products were purified by flash column chromatography.

1b: Pyrrole (670 mg, 10 mmol), C₆H₁₃Br (2.48 g, 15.0 mmol), NaH (720 mg, 30.0 mmol). Brown oil (730 mg, 48.0%). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 6.66 (s, 2H, ArH), 6.15 (s, br, 2H, ArH), 3.87 (t, J = 7.2 Hz, 2H, -NCH₂-), 1.74 (m, 2H, -CH₂-), 1.29 (m, 6H, -CH₂-), 0.89 (s, br, 3H, -CH₃).

1c: Pyrrole (720 mg, 10.7 mmol), $C_8H_{17}Br$ (3.10 g, 16.0 mmol), NaH (770 mg, 32.1 mmol). Brown oil (832 mg, 43.4%). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 6.63 (s, 2H, ArH), 6.14 (s, 2H, ArH), 3.78 (t, *J* = 7.5 Hz, 2H, -*N*CH₂-), 1.69 (m, 2H, -CH₂-), 1.27 (m, 10H, -CH₂-), 0.89 (s, br, 3H, -CH₃).

1d: Pyrrole (700 mg, 10.4 mmol), $C_{10}H_{21}Br$ (3.45 g, 15.6 mmol), NaH (749 mg, 31.2 mmol). Brown oil (679 mg, 31.5%). ¹H NMR (300 MHz, CDCl₃) δ (ppm):6.65 (s, 2H, ArH), 6.14 (s, 2H, ArH), 3.77 (t, *J* = 7.2 Hz, 2H, -NCH₂-), 1.70 (m, 2H, -CH₂), 1.27 (m, 14H, -CH₂), 0.89 (s, br, 3H, -CH₃).

1e: Pyrrole (910 mg, 13.6 mmol), $C_{12}H_{25}Br$ (5.08 g, 20.4 mmol), NaH (979 mg, 4.8 mmol). Brown oil (972 mg, 30.3%). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 6.67 (s, 2H, ArH), 6.14 (s, 2H, ArH), 3.77 (s, br, 2H, -*N*CH₂-), 1.71 (m, 2H, -CH₂), 1.27 (m, 18H, -CH₂), 0.89 (s, br, 3H, -CH₃). **General synthesis of compound 2a-e**

Under an atomsphere of nitrogen, a mixture of **1a-e** (1.0 equvi), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (1.2 equvi), $[Ir(COD)CI]_2$ (0.05 equvi) and 4,4'-ditert-butyl-2,2'-dipyridyl (0.05 equvi) in degassed cyhexane was (60 mL) stirred at 65 °C for 14 h. The mixture were poured into water (100 mL) then extracted with dichloromethane. The organic layers were collected and evaporated under reduced pressure, and the crude products were used directly without further purification.

General synthesis of compound 3a-e

Under an atomsphere of nitrogen, a mixture of compound **ArBr** (1.0 equvi), compound **2a-e** (5.0 equvi), Pd(PPh₃)₄ (0.05 equiv) and K₂CO₃ (5 equvi) in 30 mL solvent (THF/H₂O = 5/1) was placed in 100 mL dry Schlenk tube and refluxed for 12 hours. The mixture was poured into water and extracted with chloroform for three times. The combined organic layers were dried with anhydrous sodium sulfate. After the solvent was evaporated, the crude products were purified by column chromatography.

3a: ArBr (225 mg, 0.30 mmol), compound **2a** (310 mg, 1.50 mmol), red solid (200 mg, 90%). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 8.15 (m, 2H, ArH), 7.70 (d, 1H, *J* = 6.6 Hz, ArH), 7.59 (d, 2H, *J* = 8.7 Hz, ArH), 7.49 (s, 1H, ArH), 7.06 (d, 5H, *J* = 8.4 Hz, ArH), 6.94 (d, 4H, *J* = 8.4 Hz, ArH), 6.81 (d, 2H, *J* = 7.8 Hz, ArH), 6.41(s, 1H, ArH), 6.55 (m, 1H, ArH), 6.20 (s, br, 1H, ArH), 3.95 (m, 4H, -OCH₂-), 3.69 (s, 3H, -NCH₃), 1.72 (s, br, 4H, -CH₂-), 1.43-1.32 (m, 12H, -CH₂-), 0.89 (s, br, 6H, -

CH₃).

3b: ArBr (200 mg, 0.27 mmol), compound **2b** (374 mg, 1.35 mmol), red solid (289 mg, 78%). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 8.14-8.09 (m, 2H, ArH), 7.66 (d, 1H, *J* = 7.2 Hz, ArH), 7.57 (d, 2H, *J* = 8.4 Hz, ArH), 7.49 (s, br, 1H, ArH), 7.05 (d, 5H, *J* = 6.6 Hz, ArH), 6.92 (d, 4H, *J* = 8.7 Hz, ArH), 6.80 (d, 2H, *J* = 7.2 Hz, ArH), 6.41(s, br, 1H, ArH), 6.20 (s, br, 1H, ArH), 3.94 (m, 6H, -OCH₂-, -NCH₂-), 1.70 (m, 6H, -CH₂-), 1.42-1.23 (m, 18H, -CH₂-), 0.88 (s, br, 9H, -CH₃).

3c: ArBr (224 mg, 0.30 mmol), compound **2c** (458 mg, 1.5 mmol), red solid (200 mg, 79.4%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.13 (d, 1H, J = 4.0 Hz, ArH), 7.89 (d, 1H, J = 8.0 Hz, ArH), 7.55-7.50 (m, 3H, ArH), 7.30 (d, 1H, J = 4.0 Hz, ArH), 7.09 (d, 4H, J = 8.0 Hz, ArH), 7.96-6.91 (m, 3H, ArH), 6.86 (d, 4H, J = 8.0 Hz, ArH), 6.50 (d, 1H, J = 4.0 Hz, ArH), 6.34 (t, 1H, J = 4.0 Hz, ArH), 3.98-3.94 (m, 6H, -OCH₂-, NCH₂-), 1.80-1.77 (m, 4H, -CH₂-), 1.62 (m, 2H, -CH₂-), 1.49-1.33 (m, 12H, -CH₂-), 1.21-1.10 (m, 10H, -CH₂-), 0.93-0.80 (m, 9H, CH₃).

3d: ArBr (265 mg, 0. 35 mmol), compound **2d** (583 mg, 1.75 mmol), red solid (207 mg, 68.1%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.12 (d, 1H, *J* = 4.0 Hz, ArH), 7.87 (d, 1H, *J* = 8.0 Hz, ArH), 7.55-7.44 (m, 3H, ArH), 7.28 (d, 1H, *J* = 4.0 Hz, ArH), 7.08 (d, 4H, *J* = 8.0 Hz, ArH), 6.98-6.88 (m, 3H, ArH), 6.84 (d, 4H, *J* = 8.0 Hz, ArH), 6.48 (d, 1H, *J* = 4.0 Hz, ArH), 6.35-6.29 (m, 1H, ArH), 4.05-3.84 (m, 6H, -OCH₂-, NCH₂-), 1.80-1.75 (m, 4H, -CH₂-), 1.63-1.58 (m, 2H, -CH₂-), 1.49-1.33 (m, 12H, -CH₂-), 1.21-1.10 (m, 14H, -CH₂-), 0.93-0.83 (m, 9H, -CH₃).

3e: ArBr (265 m, 0. 35 mmol), compound **2e** (632 mg, 1.75 mmol), red solid (178 mg, 56.9%), ¹H NMR (400 MHz, CDCl₃) δ (ppm): δ 8.04 (d, 1H, *J* = 4.0 Hz, ArH), 7.82 (d, 1H, *J* = 8.0 Hz, ArH), 7.48-7.41 (m, 3H, ArH), 7.23 (t, 1H, *J* = 4.0 Hz, ArH), 6.99 (d, 4H, *J* = 8.0 Hz ArH), 6.84-6.82 (m, 3H, ArH), 6.77 (d, 4H, *J* = 8.0 Hz, ArH), 6.33 (m, 1H, ArH), 6.19 (m, 1H, ArH), 3.85 (m, 6H, -OCH₂-, *N*CH₂-), 172-1.65 (m, 4H, -CH₂-), 1.52-1.47 (m, 2H, -CH₂-), 1.40-1.25 (m, 12H, -CH₂-), 1.16-1.00 (m, 18H, -CH₂-), 0.85-0.75 (m, 9H, -CH₃).

General synthesis of compound 4a-e

Under an atomsphere of nitrogen, fresh distilled DMF (3.0 equvi) and POCl₃ (2.0 equvi) were added into round-bottom flask and stirred at 0 °C. After the resultant solution turn to glassy solid. compound **3** (1.0 equvi) dissolved in 1,2-dichloroethane (10 mL) was added dropwise. The solution was warmed to room temperature and sirred for 12 h. then poured into Na₂CO₃ solution (1 M, 50 mL), and stirred for another 2 h. The mixture was extracted with chloroform for three times. The combined organic layers were dried with anhydrous sodium sulfate. After the solvent was evaporated, the crude product was purified by column chromatography.

4a: 3a (200 mg, 0.27 mmol), DMF (59 mg, 0.81 mmol), POCl₃ (83 mg, 0.54 mmol), red solid (130 mg, 62.6%). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 9.66 (s, 1H, -CHO), 8.17 (d, 2H, *J* = 5.1 Hz, ArH), 7.92 (d, 1H, *J* = 7.2 Hz, ArH), 7.64 (d, 2H, *J* = 7.2 Hz, ArH), 7.50 (d, 2H, *J* = 8.8 Hz, ArH), 7.31(d, 2H, *J* = 3.9 Hz, ArH), 7.10 (d, 4H, *J* = 9.0 Hz, ArH), 6.95 (d, 2H, *J* = 9.0 Hz, ArH), 6.85 (d, 4H, *J* = 8.7 Hz, ArH), 6.59 (d, 1H, *J* = 3.9 Hz, ArH), 6.85 (m, 6H, -*N*CH₂-, -OCH₂-), 1.80-1.76 (m, 4H, -CH₂-), 1.47-1.25 (m, 12H, -CH₂-), 0.92 (s, br, 6H, -CH₃).

4b: 3b (270 mg, 0.33 mmol), DMF (73 mg, 1.00 mmol), POCl₃ (101 mg, 0.66 mmol), red oil (180 mg, 65.0%). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 9.62 (s, 1H, -CHO), 8.21 (m, 2H, ArH), 7.83 (d, 1H, *J* = 8.0 Hz, ArH), 7.59 (d, 2H, *J* = 8.7 Hz, ArH), 7.51 (s, br, 1H, ArH), 7.25 (d, 1H, *J* = 8.4 Hz, ArH), 7.05 (d, 4H, *J* = 8.4 Hz, ArH), 6.80 (d, 2H, *J* = 7.8 Hz, ArH), 6.56 (d, 1H, *J* = 8.4 Hz, ArH), 4.30 (s, br, 2H, -NCH₂-), 3.92

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(m, 4H, -OCH₂-), 1.69 (m, 6H, -CH₂-), 1.41-1.23 (m, 18H, -CH₂-), 0.88 (m, 9H, -CH₃).

4c: **3c** (190 mg, 0.23 mmol), DMF (50 mg, 0.69 mmol), POCl₃ (71 mg, 0.46 mmol), red oil (143 mg, 71.9%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 9.63 (s, 1H, CHO), 8.19 (d, 1H, *J* = 3.9 Hz, ArH), 7.92 (d, 1H, *J* = 7.4 Hz, ArH), 7.62 (d, 1H, *J* = 7.5 Hz, ArH), 7.57-7.46 (m, 2H, ArH), 7.31 (d, 1H, *J* = 4.0 Hz, ArH), 7.15-7.05 (m, 5H, ArH), 6.95 (d, 2H, *J* = 8.8 Hz, ArH), 6.85 (d, 4H, *J* = 8.0 Hz, ArH), 6.52 (d, 1H, *J* = 8.0 Hz, ArH). 4.39-4.29 (m, 2H, -NCH₂-), 3.95 (t, 4H, *J* = 6.5 Hz, -OCH₂-), 1.78 (m, 4H, -CH₂-), 1.39 (m, 12H, -CH₂-), 1.22 (m, 2H, -CH₂-), 1.19-0.98 (m, 10H, -CH₂-), 0.92 (t, 6H, *J* = 4.5 Hz, -CH₃), 0.84 (m, 3H, -CH₃).

4d: 3d (200 mg, 0.23 mmol), DMF (50 mg, 0.69 mmol), POCl₃ (71 mg, 0.46 mmol), red oil (156 mg,75.7%). ¹H NMR (400 MHz, CDCl₃) δ (ppm):9.63 (s, 1H, -CHO), 8.19 (d, 1H, J = 4.0 Hz, ArH), 7.92 (d, 1H, J = 8.0 Hz, ArH), 7.62 (d, 1H, J = 8.0 Hz, ArH), 7.54-7.47 (m, 2H, ArH), 7.31 (d, 1H, J = 4.0 Hz, ArH), 7.14-7.03 (m, 5H, ArH), 6.95 (d, 2H, J = 8.8 Hz, ArH), 6.85 (m, 4H, ArH), 6.52 (d, 1H, J = 8.0 Hz, ArH), 4.41-4.25 (m, 2H, -NCH₂-), 3.95 (t, 4H, J = 6.5 Hz, -OCH₂-), 1.79 (m, 4H, -CH₂-), 1.58-1.33 (m, 12H, -CH₂-), 1.20 (m, 2H, -CH₂-), 1.20-0.97 (m, 14H, -CH₂-), 0.97-0.78 (m, 9H, -CH₃).

4e: 3e (170 mg, 0.19 mmol), DMF (42 mg, 0.57 mmol), POCl₃ (58 mg, 0.38 mmol), red oil (123 mg,70.3%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 9.63 (s, 1H, CHO), 8.19 (d, 1H, J = 4.0 Hz, ArH), 7.92 (d, 1H, J = 8.0 Hz, ArH), 7.62 (d, 1H, J = 8.0 Hz, ArH), 7.50 (d, J = 8.0, 2H, ArH), 7.31 (d, 1H, J = 4.0 Hz, ArH), 7.12-7.07 (m, 5H, ArH), 6.95 (d, 2H, J = 8.8 Hz, ArH), 6.85 (d, 4H, J = 8.0 Hz, ArH), 6.52 (d, 1H, J = 8.0 Hz, ArH), 4.34 (t, 2H, J = 8.0 Hz, -NCH₂-), 3.95 (t, 4H, J = 8.0 Hz, -CH₂-), 1.17 (m, 2H, -CH₂-), 1.15-1.01 (m, 18H, -CH₂-), 0.93-0.83(m, 9H, -CH₃).

General synthesis of sensitizers

A mixture of compound **4a-e** (1.0 equiv), cyanoacrylic acid (3.0 equiv) and catalytic amount of piperidine in 10 mL solvent (MeCN/THF = 4/1) were placed in a 50 mL dry round-bottom with a condensation tube. The mixture was refluxed for 16 h, then pour into hydrochloric acid solution (50 mL, 2 M). The crude product was extracted with chloroform for three times, and the combined organic layer were dried with anhydrous sodium sulfate. After the solvent was evaporated, the crude product was purified by column chromatography.

LI-121: 4a (165 mg, 0.21 mmol), cyanoacrylic acid (53 mg, 0.63 mmol). Black solid (110 mg, 62.8%). ¹H NMR (300 MHz, DMSO- d_6) δ (ppm): 8.17 (m, 2H, ArH, -CH=), 8.05 (s, 1H, ArH), 7.78 (d, 1H, *J* = 7.2 Hz, ArH), 7.58 (d, 2H, *J* = 8.4 Hz, ArH), 7.51 (s, br, 1H, ArH), 7.43 (s, br, 1H, ArH), 7.05 (d, 4H, *J* = 8.4 Hz, ArH), 6.93 (d, 4H, *J* = 8.4 Hz, ArH), 6.80 (d, 2H, *J* = 9.0 Hz, ArH), 6.72 (s, 1H, ArH), 3.94 (m, 4H, OCH₂-), 3.66 (s, 3H, -NCH₃), 1.70 (m, 4H, -CH₂-), 1.41-1.23 (m, 12H, -CH₂-), 0.88 (m, 6H, -CH₃). ¹³C NMR (100 MHz, THF- d_8) δ (ppm): 165.21, 157.11, 155.01, 153.14, 149.99, 147.77, 141.26, 140.04, 139.94, 137.65, 131.69, 130.80, 130.72, 128.80, 127.76, 127.19, 126.76, 125.12, 123.60, 123.43, 120.88, 119.12, 117.81, 116.13, 115.86, 95.32, 68.84, 33.21, 32.68, 30.39, 26.84, 23.63, 14.50. MS (ESI, m/z): calcd for C₄₉H₄₉N₅O₄S₂, 835.3; Found, 835.3; Anal. Calcd for C₄₉H₄₉N₅O₄S₂: C, 70.39; H, 5.91; N, 8.38; S, 7.67; Found: C, 69.93; H, 5.78; N, 8.71; S, 7.58.

LI-122: **4b** (160 mg, 0.19 mmol), cyanoacrylic acid (48 mg, 0.57 mmol). Black solid (127 mg, 73.8%). ¹H NMR (300 MHz, DMSO- d_6) δ

(ppm): 8.20 (m, 3H, ArH, -CH=), 7.81 (d, 1H, J = 8.1 Hz, ArH), 7.67 (d, 1H, J = 8.7 Hz, ArH), 7.58 (d, 2H, J = 9.0 Hz, ArH), 7.52 (d, 1H, J = 8.4 Hz, ArH), 7.05 (d, 4H, J = 8.1 Hz, ArH), 6.92 (d, 4H, J = 8.4 Hz, ArH), 6.80 (m, 3H, ArH), 4.18 (m, 2H, -NCH₂-), 3.94 (m, 4H, -OCH₂-), 1.69 (m, 6H, -CH₂-), 1.41-1.23 (m, 18H, -CH₂-), 0.89 (m, 9H, -CH₃). ¹³C NMR (75 MHz, CDCl₃ and DMSO- d_6) δ (ppm): 165.57, 155.74, 153.82, 151.98, 148.76, 146.72, 139.94, 139.45, 138.64, 136.29, 130.80, 129.91, 128.21, 127.95, 126.89, 126.34, 125.25, 124.25, 122.67, 122.35, 119.71, 119.10, 117.75, 115.31, 94.36, 83.41, 68.10, 45.05, 31.58, 30.92, 29.65, 29.28, 26.03, 25.74, 25.05, 22.61, 14.16, 13.93. MS (ESI, m/z): calcd for C₅₄H₅₉N₅O₄S₂, 905.4; Found, 905.4. Anal. Calcd for C₅₄H₅₉N₅O₄S₂: C, 71.57; H, 6.56; N, 7.73; S, 7.08; Found: C, 71.43; H, 6.85; N, 7.65; S, 7.11.

LI-123: 4c (140 mg, 0.16 mmol), cyanoacrylic acid (40 mg, 0.48 mmol). Black solid (97 mg, 65.1%). ¹H NMR (400 MHz, DMSO- d_6) δ (ppm): 8.16 (m, 2H, ArH, -CH=), 8.07 (s, 1H, ArH), 7.78 (d, 1H, J = 7.2 Hz, ArH), 7.58 (d, 2H, J = 8.4 Hz, ArH), 7.50(s, br, 1H, ArH), 7.45 (s, br, 1H, ArH), 7.05 (d, 4H, J = 8.7 Hz, ArH), 6.92 (d, 4H, J = 8.4 Hz, ArH), 6.80 (d, 2H, J = 8.7 Hz, ArH), 6.64 (d, 1H, J = 3.9 Hz, ArH), 4.06 (s, br, 2H, -NCH₂-), 3.94 (t, 3H, J = 6.0 Hz, -OCH₂-), 1.73-1.68 (m, 5H, -CH₂-, -CH-), 1.41-1.30 (m, 16H, -CH₂-), 0.88 (m, 16H, -CH₂-, -CH₃). ¹³C NMR (100 MHz, THF- d₈) δ (ppm): 165.21, 156.72, 154.66, 152.74, 149.61, 147.34, 140.87, 139.43, 138.86, 137.24, 131.43, 130.29, 129.18, 128.42, 127.37, 126.80, 126.39, 124.78, 123.66, 123.21, 120.52, 118.89, 117.72, 117.55, 115.75, 95.84, 68.45, 45.38, 39.85, 32.45, 32.36, 32.30, 30.02, 29.66, 29.51, 26.94, 26.46, 23.26, 23.16, 14.13. MS (ESI, m/z): calcd for $C_{56}H_{63}N_5O_4S_2$, 933.4; Found, 933.4. Anal. Calcd for C₅₆H₆₃N₅O₄S₂: C, 71.99; H, 6.80; N, 7.50; S, 6.86; Found: C, 72.16; H, 6.61; N, 7.26; S, 6.61.

LI-124: 4d (150 mg, 0.17 mmol), cyanoacrylic acid (43 mg, 0.51 mmol). Black solid (102 mg, 62.6%). 1 H NMR (400 MHz, DMSO- d_{6}) δ (ppm): 8.21-8.15 (m, 3H, ArH, -CH=), 7.81 (d, 1H, J = 7.5 Hz, ArH), 7.67 (d, 1H, J = 4.3 Hz, ArH), 7.58 (d, 2H, J = 8.7 Hz, ArH), 7.51 (d, 1H, J = 3.9 Hz, ArH), 7.05 (d, 4H, J = 8.9 Hz, ArH), 6.92 (d, 4H, J = 9.0 Hz, ArH), 6.80 (d, 2H, J = 8.8 Hz, ArH), 6.76 (d, 1H, J = 4.3 Hz, ArH), 4.19 (s, br, 2H, -NCH₂-), 3.94 (t, 4H, J = 6.4 Hz, -OCH₂-), 1.75-1.66 (m, 4H, -CH₂-), 1.51-0.95 (m, 28H, -CH₂-), 0.90-0.74 (m, 9H, -CH₃). ¹³C NMR (100 MHz, THF- d_8) δ (ppm): 164.87, 156.73, 154.65, 152.74, 149.63, 147.42, 140.88, 139.72, 139.23, 137.22, 131.49, 130.31, 129.10, 128.53, 127.36, 126.79, 126.38, 124.74, 123.59, 123.19, 120.52, 119.07, 117.37, 115.73, 115.67, 95.08, 68.43, 45.37, 32.51, 32.45, 32.29, 30.10, 30.01, 29.97, 29.90, 29.52, 26.91, 26.45, 23.24, 23.21, 14.13, 14.09. MS (ESI, m/z): calcd for C₅₈H₆₇N₅O₄S₂, 961.5; Found, 961.5.Anal. Calcd for C58H67N5O4S2, C, 72.39; H, 7.02; N, 7.28; S, 6.66; Found: C, 72.05; H, 7.15; N, 7.55; S, 6.45.

LI-125: 4e (120 mg, 0.13 mmol), cyanoacrylic acid (33 mg, 0.39 mmol). Black solid (80 mg, 62.0%). ¹H NMR (400 MHz, DMSO- d_6) δ (ppm): 8.23-8.14 (m, 3H, ArH, -CH=), 7.79 (d, J = 7.5 Hz, 1H, ArH), 7.68 (d, J = 4.4 Hz, 1H, ArH), 7.55 (d, J = 8.6 Hz, 2H, ArH), 7.48 (d, J = 3.8 Hz, 1H, ArH), 7.03 (d, J = 8.8 Hz, 4H, ArH), 6.91 (d, J = 8.9 Hz, 4H, ArH), 6.79-6.75 (m, 3H, ArH), 4.19 (s, br, 2H, -NCH₂-), 3.93 (t, J = 6.3 Hz, 4H, -OCH₂-), 1.68 (m, 4H, -CH₂-), 1.44-1.08(m, 32H, -CH₂-), 0.89-0.74 (m, 9H, -CH₃). ¹³C NMR (100 MHz, CDCl₃ and DMSO- d_6) δ (ppm): 167.67, 155.71, 153.88, 151.97, 148.69, 146.48, 139.99, 136.77, 136.71, 136.38, 130.48, 129.59, 128.61, 127.47, 126.81, 126.31, 125.40, 124.23, 123.07, 122.60, 119.79, 116.98, 115.34, 114.53, 68.14, 44.60, 31.81, 31.68, 31.50, 29.53, 29.43, 29.22,

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28.77, 26.14, 25.66, 22.57, 22.52, 18.49, 14.13, 14.07. MS (ESI, m/z): calcd for $C_{60}H_{71}N_5O_4S_2$, 990.5; Found, 990.6. Anal. Calcd for $C_{60}H_{71}N_5O_4S_2$, C, 72.77; H, 7.23; N, 7.07; S, 6.47; Found: C, 72.89; H, 7.33; N, 6.90; S, 6.67.

Conflicts of interest

There are no conflicts to declare.

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