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Introduction

In the last decade, there has been great interest in the potential of dye-sensitized solar cells (DSSCs), with their high performance of energy conversion, simple device manufacture, and low production cost,^{1–4} to compete with conventional inorganic photovoltaic modules. Among all of the DSSC photosensitizers being developed to date, the ruthenium complexes and zinc porphyrins are the most outstanding candidates for commercialization because

^a Institute of Molecular Functional Materials, Department of Chemistry, Partner State Key Laboratory of Environmental and Biological Analysis and Institute of Advanced Materials, Hong Kong Baptist University, Waterloo Road, Kowloon Tong, Hong Kong, P. R. China. E-mail: clamho@hkbu.edu.hk, rwywong@hkbu.edu.hk

^b State Key Laboratory of Molecular Reaction, Dynamics Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116012, P. R. China. E-mail: klhan@dicp.ac.cn

^c Department of Materials Science and Engineering, University of Science and Technology of China, 96 Jinzhai Road, Hefei, Anhui 230026, P. R. China. E-mail: tchenmse@ustc.edu.cn

^d Department of Physics, The Chinese University of Hong Kong, Shatin, Hong Kong, P. R. China

- ^e HKBU Institute of Research and Continuing Education,
- Shenzhen Virtual University Park, Shenzhen, 518057, P. R. China
- ^f Department of Applied Physics and Chemistry, University of Taipei, Taipei 100, Taiwan. E-mail: yhlo@utaipei.edu.tw
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Po-Yu Ho,^a Chi-Ho Siu,^a Wai-Hong Yu,^a Panwang Zhou,^b Tao Chen,*^{cd} Cheuk-Lam Ho,*^{ae} Lawrence Tien Lin Lee,^d Ying-Hsuan Feng,^f Jianyong Liu,^b Keli Han,*^b Yih Hsing Lo*^f and Wai-Yeung Wong*^{ae}

A series of new D- π -A organic photosensitizers **7a**-**7d** featuring a novel starburst electron donor unit and uncommon selenophene containing π -linker were synthesized, characterized, and applied for fabrication of dye-sensitized solar cells (DSSCs). Dyes **11d**-**13d** with thiophene or phenyl ring as the π -linker also were synthesized for comparison. The best power conversion efficiency (PCE) of 6.67% was attained for **11d** with a relatively high open-circuit voltage (V_{oc}) of 0.825 V using conventional I^{-}/I_{3}^{-} redox electrolyte in DSSCs, and this value reaches about 84% of the device based on standard dye **N719** (7.91%) under the same device fabrication conditions. Electrochemical impedance spectroscopy (EIS) and open-circuit voltage decay (OCVD) were applied to verify the findings. All the results suggest that starburst electron donor design strategy can be used to minimize dye aggregation on TiO₂ and to slow down the charge recombination kinetics in DSSCs to improve the photovoltaic performance. Effects of using selenophene as the π -linker building block on the photovoltaic parameters also were explored and evaluated.

of their high power conversion efficiency (PCE) of over 11% and long-term stability.^{5,6} As alternatives to metal-containing dyes, a number of organic photosensitizers also have been reported recently, such as coumarin dyes,⁷ indoline dyes,^{8,9} and triaryl-amine dyes.^{10–12} Compared with the metal-containing complexes, organic dyes have advantages of higher structural design flexibility, lower production cost, and easier preparation and purification.^{13–19}

It is well known that the photosensitizer has a pivotal role in the performance of DSSCs. To boost the performance of organic dyes, the chemical structures have to be modified to combat against the narrow absorption band and dye aggregation on TiO₂.^{9,20} To achieve this goal effectively, the structure-property relationship must be elucidated so that structural modification can be accomplished in the correct direction. In general, most organic dyes are featured in a rod shaped donor- π -acceptor $(D-\pi-A)$ framework, but this configuration favors formation of aggregate on the surface of nanostructured TiO₂ and intermolecular guenching of molecules is induced.²¹ It is reported that simple phenothiazine-based dyes with a non-planar butterfly conformation are able to inhibit the dye aggregation and the formation of intermolecular excimers, hence phenothiazine-based dyes lead to some high performance DSSC devices (PCE > 6%).²¹⁻²⁴ Also, the electron-donating property attributed by the electronrich sulfur and nitrogen atoms in the phenothiazine ring facilitates the electron delocalization from donor to acceptor.²⁵ However, these simple phenothiazine-based dyes have relatively short



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 π -conjugation length and this limits the absorption coverage of photovoltaic cells in the long wavelength region.

On the other hand, novel dianchoring A– π –D– π –A frameworks^{26–28} have been fully utilized in DSSCs. The dianchoring dyes were able to increase the electron injection efficiency and inhibit charge recombination simultaneously, so overall performances were improved compared with the single anchoring congeners.^{29,30} Regarding this point, a simple molecular design with a D– π –A framework, which can inhibit charge recombination and broaden light absorption coverage effectively at the same time, is still required for further development.

The bulky starburst electron donor is a potential solution to resolve such difficulty in molecular design. Several groups have reported that starburst donor-based organic dyes can increase open-circuit voltage (V_{oc}) by inhibiting charge recombination on the dye layer interface, and increase the short-circuit current density (J_{sc}) by expanding and strengthening the light absorption within the solar spectrum.^{31–37} In this study, seven organic dyes were synthesized with different donor and π -linker combinations, in particular with the new starburst triarylamine donor (Fig. 1 and 2). For the electron donor units, disubstituted triphenylamine donor with two 9-hexylcarbazole units at the 3-position was used for comparison with some other reported donor building blocks. For the π -linker, selenophene was selected to further extend the π -conjugation because of its high electron donating effect and its uniqueness in DSSC studies.³⁸ Dyes with thiophene or phenyl ring as π -linker also were synthesized for comparison.³⁹ Cyanoacrylic acid acts as the electron acceptor to constitute the intramolecular charge transfer (ICT) absorption band and to facilitate electron injection into the conduction band of titanium dioxide. This electron-deficient moiety also corresponds with the anchoring unit on the surface of TiO₂. The synthetic procedures were straightforward, and all the products were purified easily by column chromatography. The photophysical and electrochemical properties of these organic photosensitizers were studied and the corresponding performances of DSSCs with traditional liquid electrolyte-based device structure also were investigated.



Results and discussion

Synthesis and characterization

The structures of new organic photosensitizers are shown in Fig. 1 and 2. Their corresponding synthetic routes are depicted in Schemes 1 and 2 and Scheme S1 (ESI[†]). The key intermediate 2,5-dibromoselenophene (2) was prepared by bromination of selenophene (1) with N-bromosuccinimide according to a previously published method.⁴⁰ Subsequently, compound 2 was reacted with 3-hexylthiophene-2-boronic acid under palladiumcatalyzed Suzuki coupling reaction conditions to yield compound 3. Then, aldehyde precursor 4 was obtained by the Vilsmeier-Haack reaction. Bromination of 4 with N-bromosuccinimide under acidic conditions yielded brominated 5. The organic dye precursors 6a-6d were prepared by a Suzuki coupling reaction of 5 with the corresponding arylboronic acids. Finally, Knoevenagel condensation using cyanoacetic acid was performed to prepare organic photosensitizers 7a-7d with high yields of around 90%. For 11d-13d, the key intermediates 11b-13b were obtained by either bromination using N-bromosuccinimide or iodination using potassium iodide and potassium iodate of 11a-13a under acidic conditions. Eventually, organic photosensitizers 11d-13d were prepared





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Scheme 1 Synthetic routes of 7a-7d.

by a Suzuki coupling reaction of 11b-13b with (9-hexylcarbazolyl)boronic acid and subsequent Knoevenagel condensation in high yield. All the organic precursors were characterized by ¹H and ¹³C NMR spectroscopy. The singlet peak positioned at around δ 10.0 ppm refers to the proton of aldehyde on the corresponding organic aldehyde precursors. All the target organic dyes were soluble in common organic solvents, such as dichloromethane, chloroform, tetrahydrofuran and dimethyl sulfoxide, and were characterized by matrix-assisted laser desorption ionization timeof-flight (MALDI-TOF) mass spectrometry and ¹H NMR spectroscopy. In their ¹H NMR spectra, the downfield singlet peaks positioned at around δ 8.5 ppm are the specific peaks of the proton on the carbon-carbon double bond of cyanoacrylic acid. Complete conversion of aldehyde precursors to the target organic dyes could be indicated by the disappearance of the singlet peak positioned at around δ 10.0 ppm and the presence of a new singlet peak positioned at δ 8.5 ppm.

Photophysical properties

The UV/Vis absorption spectra of all the organic photosensitizers in CH_2Cl_2 solution are depicted in Fig. 3, and the corresponding data are summarized in Table 1. All these organic dyes possess two main structureless broad absorption bands in the range of 300-600 nm. The molar extinction coefficients (10000- $70\,000 \text{ mol}^{-1} \text{ cm}^{-1}$) of these photosensitizers are comparable with other D- π -A starburst donor-based dyes reported in the literature,^{31–36,41,42} and dyes 7a–7d, 11d and 12d possess much higher molar extinction coefficients than those of standard ruthenium dyes.⁴³ The absorption bands at short wavelength (centered at 340-362 nm) are assigned to the localized aromatic π - π * transitions and the low-energy broad absorption bands (centered at 458-511 nm) refer to the intramolecular charge transfer (ICT) from electron donor to electron acceptor. It is evidenced that the replacement of terminal donor (7a-7d) or π -linker (7d, 11d–13d) in such a framework modulates the absorption profiles of organic dyes, including the localized π - π * transitions band and especially the ICT bands. The peak absorption wavelengths of ICT bands are red-shifted in the order of 13d (458 nm) < 12d (478 nm) < 11d (480 nm) < 7d (511 nm). This is most probably correlated with the diminishing electron donating strength of π -linkers in the order of 2,5-bis(4-hexylthiophen-2-yl)selenophene > 3,4'-dihexyl-2,2'bithiophene > 3-hexylthiophene > phenyl ring. Importantly, the adoption of starburst donor units in 7b-7d (with smaller optical band gap values) allows us to broaden the absorption coverage and to enhance the absorption intensity compared



Scheme 2 Synthetic routes of **11d–13d**.



Fig. 3 UV/Vis absorption spectra of 7a-7d and 11d-13d in CH_2Cl_2 at 293 K.

with the non-starburst donor organic dye 7a bearing alkylated carbazole.

Electrochemical properties

To identify high performance photosensitizers for DSSCs, the optimal energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) must be attained. Cyclic voltammetry (CV) was used to calculate

Table 1 UV/Vis absorption data of 7a-7d and 11d-13d in CH_2Cl_2 at 293 K

$\lambda_{ m max}~(\epsilon/10^4~{ m M}^{-1}~{ m o})$	$E_{\rm g,opt}^{a}/{\rm eV}$	
352 (1.23)	507 (3.64)	2.10
344(5.62) 362(2.45)	510 (5.12) 503 (6.79)	2.07
345 (6.24)	511 (4.05)	2.04
346 (5.38) 341 (5.11)	480 (2.30) 478 (1.84)	2.15
	$\begin{array}{c} \lambda_{\max} \left(\epsilon / 10^4 \text{ M}^{-1} \text{ o} \right. \\ 352 \left(1.23 \right) \\ 344 \left(5.62 \right) \\ 362 \left(2.45 \right) \\ 345 \left(6.24 \right) \\ 346 \left(5.38 \right) \\ 341 \left(5.11 \right) \\ 240 \left(\epsilon 55 \right) \end{array}$	$\begin{array}{c c} \lambda_{\max} \ (\epsilon/10^4 \ M^{-1} \ cm^{-1})/nm \\ \hline 352 \ (1.23) & 507 \ (3.64) \\ 344 \ (5.62) & 510 \ (5.12) \\ 362 \ (2.45) & 503 \ (6.79) \\ 345 \ (6.24) & 511 \ (4.05) \\ 346 \ (5.38) & 480 \ (2.30) \\ 341 \ (5.11) & 478 \ (1.84) \\ 240 \ (2.55) & 458 \ (1.11) \\ \end{array}$

 a Optical band gap was determined from the onset of absorption in $\rm CH_2 Cl_2.$

the values and hence to examine the energy offsets of the dye molecules between the semiconducting TiO₂ film and the redox electrolytes (Fig. S8 and S9, ESI[†]). If the conduction band edge of TiO₂ was significantly more negative than the energy level of LUMO of the photosensitizers, this would favor the electron injection process because of the larger driving force for charge separation. If the redox potential of redox shuttle (iodide/triiodide ions) in the electrolyte was considerably more positive than the HOMO energy level of the dye, efficient dye regeneration would occur. Both of these processes are necessary to afford charge separation at the interface for energy conversion. CV was performed with the corresponding photosensitizer films on the glassy carbon electrode, platinum wire as the counter electrode, and Ag/Ag⁺ as the reference electrode in acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate at a scan rate of 100 mV s^{-1} . The results of these organic dyes are shown in Table 2.

Table 2 Electrochemical data and energy levels of 7a-7d and 11d-13d

Dye	$E_{\mathrm{Ox}}^{\mathrm{onset}}\left(\mathrm{V}\right)$	$HOMO^{a}$ (eV)	$E_{\mathrm{Red}}^{\mathrm{onset}}\left(\mathrm{V}\right)$	$LUMO^{b}$ (eV)	$E_{\rm g,ec}^{c}$ (eV)
7a	0.55	-5.28	-1.26	-3.47	1.81
7 b	0.52	-5.25	-1.25	-3.48	1.77
7c	0.52	-5.25	-1.27	-3.46	1.79
7d	0.44	-5.17	-1.27	-3.46	1.71
11d	0.43	-5.16	-1.33	-3.40	1.76
12d	0.51	-5.24	-1.28	-3.45	1.79
13d	0.47	-5.20	-1.34	-3.39	1.81

^{*a*} Calculated from $-(E_{\text{Ox}}^{\text{onset}} + 4.73)$. ^{*b*} Calculated from $-(E_{\text{Red}}^{\text{onset}} + 4.73)$. ^{*c*} Electrochemical band gap was obtained from the energy difference between HOMO and LUMO levels.

The first observed oxidation is ascribed to removal of an electron from the electron-rich units in the molecule, and the reduction wave observed is an indication of electron gain to the electron-deficient moiety. The LUMO energy levels of all the organic dyes (ranging from -3.39 to -3.48 eV) are more positive than that of the energy level of the conduction band edge of titanium dioxide (-4.4 eV), thus ensuring a prompt electron injection process.44 On the other hand, the redox potential of iodide/triiodide ions (-4.95 eV) is more positive than the HOMO energy levels of all the organic dyes (ranging from -5.28 to -5.16 eV), thereby facilitating efficient reduction of the oxidized dye.45 It was found that the electrochemical band gaps of 7a-7d and 11d-13d obtained in the film state conform to the trends of optical band gaps (7a > 7c > 7b > 7dand 13d > 12d > 11d > 7d) obtained from their absorption spectra. This further confirms that replacement of terminal donor and π -linker in the D- π -A framework controls the magnitude of the HOMO-LUMO gap.

Computational studies

The ground state geometries of all the dyes were optimized using the DFT method (Fig. S1-S7, ESI⁺). From the results, we observed that the triarylamine moiety in starburst shaped dyes 7b, 7d, 11d-13d has a propeller geometry and the cyanoacrylic acid is coplanar with the thienyl moiety or phenyl unit. On the other hand, the electrons in the HOMO levels of the compounds are distributed over the electron-donating moiety, that is the triarylamine and/or carbazole fragment. Conversely, the LUMO levels of the compounds showed that electrons are distributed over the cyanoacrylic acid moiety of the dyes. Thus, we anticipated that efficient photoinduced charge separation and relatively stronger anchoring power would enhance the degree of electron injection to the TiO₂ electrode. Furthermore, we found that a π -conjugated linker, such as 2,5-bis(4-hexylthiophen-2-yl)selenophene, 3,4'-dihexyl-2,2'-bithiophene, 3-hexylthiophene and phenyl ring, as well as cyanoacrylic acid moieties, are involved in the frontier molecular orbitals. It was also shown that the energy levels of the LUMOs of the compounds are dependent on the nature of the π -conjugated linker in the compounds, whereas the energy levels of the HOMOs are not affected significantly by the identities of the π -conjugated linker which are consistent with the CV results. For example, the energy levels of the LUMO of 7d and 11d are -2.83 eV and

-2.73 eV, respectively (Table S2, ESI†). The decrease in energy level of LUMO for 7d can be attributed to the more extended delocalization of electrons for the selenophene moiety in the LUMO of 7d compared with 11d.

Photovoltaic performance

All the DSSCs with an effective area of 0.126 cm² were prepared according to conventional procedures, as described in the Experimental section, and tested under standard conditions (AM 1.5G, 100 mW cm⁻²). The DSSCs were fabricated by anchoring our new organic dyes and reference dye **N719** accordingly onto nanocrystalline anatase TiO₂ as the photoanode and the liquid electrolyte consisting of 0.1 M LiI, 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII), 0.05 M I₂ in a mixture of acetonitrile and 4-*tert*-butylpyridine (volume ratio, 1:1). Their basic device performance parameters, such as PCE, V_{oc} , short-circuit current density (J_{sc}), and fill factor (FF) are depicted in Table 3. Fig. 4 and 5 display the photocurrent density-voltage curves (J-V curves) and incident-photon-tocurrent conversion efficiency (IPCE) spectra, respectively.

The highest PCE of 6.67% ($J_{sc} = 11.22 \text{ mA cm}^{-2}$, $V_{oc} = 0.825 \text{ V}$, FF = 0.721) was obtained with dye 11d, attaining 84% of the reference ruthenium dye N719-based cell (PCE = 7.91%) measured under the same conditions. The PCEs of DSSCs based on other organic dyes are in the range of 3.04–6.60%. The I_{sc} , V_{oc} , and FF values are in the range of 5.60-13.77 mA cm⁻², 0.660-0.825 V, and 0.703–0.751, respectively. Impressively, the $V_{\rm oc}$ of **11d** exceeds the value of **N719** (V_{oc} = 0.701 V) by 0.124 V and this Voc value is remarkably high among the iodide/triiodide redox couple-based DSSCs.³⁹ Notably, the $V_{\rm oc}$ values of all starburst donor-based dyes are higher than that of the non-starburst donor-based dye 7a, and this implies that such starburst donor molecular design can effectively improve the photovoltaic performance of D- π -A dyes by elevating the V_{oc} . Moreover, 7a-7d with selenophene as the elongated π -linker unit present higher J_{sc} values than do 11d-13d, implying that uncommon selenophene may be a useful π -linker building block to augment the J_{sc} . Meanwhile, the action response range of IPCE spectra among the seven new organic photosensitizers is around 310-700 nm and the IPCE curves conform well to the absorption profiles of organic dyes after taking the common J-aggregate formation of organic dyes into consideration.46 The IPCE values exceed 50% from 400 to 550 nm for all the organic dyes, except for 13d. In addition, the maximum IPCE value attained by 12d is larger than

Table 3Photovoltaic performance of DSSCs with different photosensitizers(7a-7d, 11d-13d and N719) under AM 1.5G sunlight illumination

Dye	$J_{ m sc}~({ m mA~cm^{-2}})$	$V_{\rm oc}$ (V)	FF	PCE (%)
7a	13.77	0.660	0.706	6.41
7b	12.89	0.701	0.705	6.37
7c	13.13	0.692	0.724	6.57
7d	13.21	0.706	0.703	6.53
11 d	11.22	0.825	0.721	6.67
12d	10.66	0.824	0.751	6.60
13d	5.60	0.770	0.704	3.04
N719	15.83	0.701	0.713	7.91



Fig. 4 Photocurrent density-voltage (*J*-*V*) plots obtained with **7a-7d**, **11d-13d**, and **N719**.



Fig. 5 Incident photon-to-current efficiency (IPCE) curves obtained with 7a–7d, 11d–13d, and N719.

65% at 475 nm, but the corresponding IPCE curve rolls off sharply from 600 to 650 nm. And this explains the low J_{sc} value attained compared with 7**a**-7**d** and **11d**, which have more intense action responses within 600–700 nm in the long wavelength region. In other words, this accounts for the higher J_{sc} values attained by 7**a**-7**d**.

This result indicates that broadening the light harvesting region by elongating π -conjugation length and placing π -linkers with increasing electron donating power (phenyl ring < 3-hexyl-thiophene < 3,4'-dihexyl-2,2'-bithiophene < 2,5-bis(4-hexyl-thiophen-2-yl)selenophene) is an effective way to increase the $J_{\rm sc}$ in the order **13d** < **12d** < **11d** < **7d**. This is in agreement with most traditional D– π -A organic photosensitizers found in the literature.⁴⁷ On the other hand, it is reasonable to expect that the $J_{\rm sc}$ values of **7a–7d** vary much less because of their very similar absorption properties. Besides, the $V_{\rm oc}$ values measured in these dyes are highly dependent on the selection of terminal donor. The $V_{\rm oc}$ values of all starburst donor-based

dyes (7b–7d and 11d–13d) are higher than that of the nonstarburst donor-based dye 7a, and this is ascribed to the following. Firstly, the prolongation of rod-like D– π –A molecules in 7a may facilitate the charge recombination of electrons to I₃⁻ with the formation of dye-aggregates, thus reducing the V_{oc} .^{34,48,49} Secondly, charge recombination may also occur between electrolyte and the semiconducting TiO₂ photoanode, thus reducing the theoretical potential difference between the electrolyte and TiO₂.⁵⁰ To suppress these two unfavorable processes, starburst structural design of donor was used to prevent the π -stacked aggregation and to form a compact hydrophobic layer between the hydrophilic I⁻/I₃⁻ redox electrolyte and the surface of TiO₂, which can block the backward electron transfer for maintaining a high V_{oc} value.

To assess the interfacial charge recombination process in DSSCs, electrochemical impedance spectroscopy (EIS) was used under dark conditions for 7a-7d and 11d-13d, with the corresponding data shown in Table 4, and Fig. 6 and 7. In the EIS Nyquist plot, seven semicircles for 7a-7d and 11d-13d were recorded. This plot reveals the resistance of electron recombination (R_{rec}) at the interfaces between the redox couples/sensitizers/ TiO₂.⁵¹ If the radius of the semicircle is shorter, a smaller value of $R_{\rm rec}$ will be calculated from the Nyquist plot, and this implies that the recombination kinetics is faster. The R_{rec} values of 7b-7d and 11d-13d, which consist of starburst donor, are larger than that of non-starburst donor-based 7a, thereby suggesting that 7a suffers from more serious charge recombination while 11d is most potent to restrain the charge recombination. Simultaneously, these results match the trend of their Voc values, and disubstituted triphenylamine linked with two 9-hexylcarbazole units at the 3-position as a novel starburst donor is potent to weaken the dye aggregation on TiO2 and also the interaction between liquid electrolyte (I^{-}/I_{3}^{-}) and TiO₂ in these D- π -A photosensitizers.

In addition to the EIS Nyquist plot, an EIS Bode plot was used to extract the angular frequency ($\omega_{\rm rec}$) at the mid-frequency peak using the equation below, in which $f_{\rm max}$ correlates to the peak frequency.

$$\tau_{\rm e} = \frac{1}{\omega_{\rm rec}} = \frac{1}{2\pi f_{\rm max}}$$

From the equation, the electron lifetimes (τ_e) of DSSCs can be estimated.⁴² The τ_e estimation reflects the charge recombination rate at the interface of DSSCs.^{52,53} Interestingly, the τ_e values of dyes **7a–7d** with selenophene as part of the π -linker

Table 4 Parameters obtained by fitting the EIS spectra of the DSSCs with dyes **7a-7d**, **11d-13d** and **N719**

Dye	$R_{\rm rec} \left(\Omega \ {\rm cm}^{-1}\right)$	$f_{ m max}({ m Hz})$	$\tau_{\rm e}~({\rm ms})$
7a	126.6	39.36	4.0
7b	218.6	26.80	5.9
7c	270.3	16.43	9.7
7d	191.2	19.37	8.2
11d	3270.5	1.48	107.5
12d	3181.9	1.54	103.3
13 d	1790.7	2.48	64.2
N719	93.5	4.54	35.1



Fig. 6 EIS Nyquist plots for DSSCs based on **7a–7d**, **11d–13d**, and **N719** under darkness.



Fig. 7 EIS Bode plots for DSSCs based on 7a-7d, 11d-13d, and N719 under darkness.

are much smaller than those of 11d-13d without selenophene in their structures. Furthermore, the $R_{\rm rec}$ values of 11d-13d are larger than those of 7a-7d by one order of magnitude and this doubly confirms that selenophene plays a pivotal role in determining the photovoltage by varying the charge recombination kinetics. This phenomenon indicates that the presence of selenophene drives the decline of $V_{\rm oc}$ regardless of the structure of the terminal donor, hence some unknown interactions induced by selenophene are expected to occur so as to enhance the charge recombination process and hence lower the $V_{\rm oc}$. Recently, a similar result was reported using selenophenecontaining Ru complex photosensitizer, and the corresponding findings were ascribed to adduct formation between oxidized iodide(s) and the selenophene moiety in the photosensitizer.⁵⁴ Spectroscopic studies identified that a 4-fold-larger and second-order rate constant measured for the reaction between triiodide ions and TiO_2 (e⁻) accounted for this phenomenon, as compared with the use of thiophene as the π -conjugated linker.



Fig. 8 Open-circuit voltage decay profiles of DSSCs based on 7a-7d, 11d-13d, and N719.

To further analyze the kinetics of charge recombination of DSSC devices, open-circuit voltage decay (OCVD) was used to illustrate the electron lifetime (τ_n), which is estimated from the OCVD curve from a steady state to equilibrium in darkness.⁵⁵ The OCVD profiles of **7a–7d** and **11d–13d** are depicted in Fig. 8. The equation shown below interprets the relationship between τ_n and OCVD curves, where *e*, *T*, and k_B denote the electron charge, temperature, and Boltzmann constant, respectively.⁵⁶

$$\tau_{\rm n} = -\frac{k_{\rm B}T}{e} \left(\frac{{\rm d}V_{\rm oc}}{{\rm d}t}\right)^{-1}$$

The slope of the decay curve in the OCVD plot correlates the τ_n value, and the less steep curve suggests the longer electron lifetime accordingly. It is obvious that the curves of **7d** and **11d–13d** with disubstituted triphenylamine linked with two 9-hexylcarbazole units at the 3-position as starburst donor are less steep than those of **7a–7c** and **N719**. This provides a strong evidence to support the interfacial charge recombination improvement by the novel starburst donor structure, thus prolonging the electron lifetime (τ_n) and elevating the V_{oc} value in each of the organic photosensitizers. Again, weakening the dye aggregation and formation of the protective, compact and hydrophobic layer between hydrophilic redox couples and the TiO₂ photoanode using starburst donor molecular design might best explain such variation in the photovoltaic performance.

Conclusions

A series of new D– π –A organic photosensitizers based on starburst triarylamine donor and selenophene-containing π -linker were designed and synthesized, with investigations made of the effects of combinations of new or reported electron donors and π -linkers. All the photosensitizers were fully characterized by spectroscopic studies. The PCEs of these organic dyes ranged from 3.04% to 6.67% under standard conditions (AM 1.5G, 100 mV cm⁻²). The best performance of the device is

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achieved using the dye 11d with a novel starburst donor structure, with PCE value attaining 84% of that of N719-based DSSC (7.91%) fabricated under the same conditions. The corresponding Voc achieved for 11d is 0.825 V and this is greater than that of N719 (0.710 V) by 0.124 V. All the photovoltaic performances were verified using IPCE curves, EIS, and OCVD studies. The influences towards DSSCs driven by selenophene as a π -linker unit were explored and evaluated. It is evident that the selection of starburst donor is essential to modulate both light harnessing ability and the charge recombination process at the interfaces, thus accounting for a clear improvement in device performance. Although the device performance obtained is not as high as that of standard ruthenium complex photosensitizer, elucidation of the structure-property relationship is worthwhile for future improvements towards better organic photosensitizers, particularly in the design of organic dyes with high $V_{\rm oc}$. Synthesis of new starburst donor-based organic dyes with broader light harvesting regions, and their DSSC fabrication, is now ongoing in our group.

Experimental

Materials and reagents

All reactions were performed under an inert N_2 atmosphere with the use of a Schlenk line. Glassware was dried in an oven prior to use. Commercially available reagents were used without purification unless otherwise stated. All the reagents for chemical synthesis were purchased from Acros Organics, Sigma-Aldrich, and Tokyo Chemical Industry Co., Ltd (TCI). Solvents were purified by distillation over suitable drying agents. All the reactions were monitored by thin-layer chromatography (TLC) with Merck pre-coated aluminum plates. Products were purified and separated by column chromatography with silica gel (230–400 mesh) purchased from Merck.

Instrumentation

Proton and carbon NMR spectra were measured in CDCl_3 or DMSO-d_6 on a Bruker Ultra-shield 400 MHz FT-NMR spectrometer, and tetramethylsilane (TMS) was used as an internal standard for calibrating the chemical shift. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were performed on an Autoflex Bruker MALDI-TOF system. Electrochemical measurements were conducted using a Potentiostat/Galvanostat/EIS Analyzer model Parstat 4000 at a scan rate of 100 mV s⁻¹. UV/Vis absorption spectra were performed on a Hewlett Packard 8453 spectrometer in CH_2Cl_2 solution at 293 K.

Computational details

All the calculations in this work were carried out using the Gaussian 09 package.⁵⁷ The ground state geometries of all the dyes in dichloromethane ($\varepsilon = 8.93$) were optimized using the density functional theory (DFT) method with hybrid functional PBE0, and the solvation effects were included using the integral equation formalism^{58,59} (IEF) version of the polarizable

continuum^{60,61} (PCM) model. Frequency calculations were then performed to confirm that each optimized structure was the real minimum without imaginary vibration frequency. The time-dependent DFT (TD-DFT) method was used to calculate vertically excited singlet-state energies. The 6-31G(d) basis set was adopted. The absorption profiles were calculated using the Multiwfn program⁶² as a sum of Gaussian-shaped bands with the full width at half maximum (FWHM) equal to 0.667 eV.

Fabrication and characterization of DSSCs

All the anode films for the DSSCs were made using the same standard manner, and were composed of a 12 µm-thick transparent layer (TiO₂ with diameter of 20 nm) and 6 µm-thick scattering layer (TiO₂ nanoparticles with a diameter of 200 nm). The doctor-blade technique was used to prepare photoanode (TiO₂) films. First, a layer of ~6 μ m TiO₂ paste (20 nm) was doctor-bladed onto the FTO conducting glass and then relaxed at room temperature for 3 min before heating 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 by a scattering layer ($\sim 6 \mu m$) of TiO₂ paste (200 nm). 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 threedimensional TiO2 nanoparticle network. After that, the sintered films were soaked with 0.02 M TiF₄ aqueous solution for 45 min at 70 °C, washed with deionized water, and further annealed at 450 °C for 30 min. After cooling down to \sim 80 °C, the electrodes were immersed into a 5 imes 10⁻⁴ M dye bath in acetonitrile/ tert-butyl alcohol (volume ratio, 1:1) for the dyes 7a-7d, 11d-13d and maintained in the dark for 12 h. Afterwards, the electrodes were rinsed with ethanol to remove the nonadsorbed dyes and dried in the air. Pt counter electrodes were prepared by the 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 hot-melt parafilm at about 100 °C. Liquid electrolyte consisting of 0.6 M 1,2-dimethyl-3propylimidazolium 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. 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 $\sim 0.126 \text{ cm}^2$. The current density-voltage (J-V) characteristics of the assembled DSSCs were measured using a semiconductor characterization system (Keithley 236) at room temperature in air under the spectral output from solar simulator (Newport) using an AM 1.5G 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. A 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 0.1-10⁵ Hz with an ac amplitude

of 10 mV, and the parameters were calculated from Z-View software (v2.1b, Scribner Associates, Inc.). For the open-circuit voltage decay (OCVD) measurements, the cell was first illuminated for 20 s to achieve a steady voltage, and then the illumination was turned off for 90 s and the OCVD curve was obtained.

Synthetic procedures

2,5-Bis(3-hexylthiophenyl)selenophene (3). A mixture of 2^{40} (1.207 g, 4.179 mmol), 3-hexylthiophenyl-2-boronic acid (1.95 g, 9.194 mmol), Pd(PPh₃)₄ (241 mg, 0.209 mmol) and 2 M aqueous solution of K₂CO₃ (5 mL) in THF (40 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 then removed under reduced pressure. The residue was purified by column chromatography on silica gel using a 1:10 mixture of CH₂Cl₂ and hexane as eluent to afford compound 3 (0.62 g, 1.337 mmol) as a pale yellow solid. ¹H NMR (400 MHz, CDCl₃): δ = 7.17 (s, 2H, Ar), 6.94 (s, 2H, Ar), 6.79 (s, 2H, Ar), 2.57 (t, 4H, J = 7.6 Hz, alkyl), 1.66–1.58 (m, 4H, alkyl), 1.37–1.32 (m, 12H, alkyl), 0.91–0.88 (t, 6H, I = 6.8 Hz, alkyl); ¹³C NMR (100 MHz, $CDCl_3$): $\delta = 144.20$, 141.17, 139.04, 126.00, 125.62, 119.28 (Ar), 31.69, 30.53, 30.37, 29.01, 22.64, 14.14 ppm (alkyl).

3-Hexyl-5-(5-(3-hexylthiophen-2-yl)selenophenyl)thiophene-2-carbaldehyde (4). The Vilsemier Haack reagent was first prepared in a two-necked round-bottom flask containing dry DMF (0.489 g, 6.685 mmol). POCl₃ (0.246 g, 1.604 mmol) was added dropwise by syringe at 0 °C. A solution of 3 (0.62 g, 1.337 mmol) in dry CH₂Cl₂ (20 mL) was added dropwise to the prepared Vilsmeier-Haack reagent under a N₂ atmosphere. The mixture was stirred for 15 minutes at 0 °C and then heated overnight at 70 °C. After cooling, the reaction was poured into NaOH(aq) solution slowly in an ice bath with stirring for 30 minutes, then the resulting mixture was extracted with CH₂Cl₂ and H₂O. The organic fraction was dried over anhydrous Na₂SO₄. The solvent was then removed under reduced pressure and an orange oil was obtained, which was purified by column chromatography on silica gel with hexane/ CH_2Cl_2 (1:1 v/v) as the eluent to give 4 as an orange solid (0.597 g, 1.214 mmol). ¹H NMR (400 MHz, CDCl₃): δ = 10.00 (s, 1H, CHO), 7.42 (d, 1H, J = 4 Hz, Ar), 7.25 (d, 1H, J = 4 Hz, Ar), 7.02 (s, 1H, Ar), 6.99 (s, 1H, Ar), 6.88 (s, 1H, Ar), 2.94 (t, 2H, J = 7.6 Hz, alkyl), 2.60 (t, 2H, J = 7.6 Hz, alkyl), 1.75-1.61 (m, 4H, alkyl), 1.39-1.34 (m, 12H, alkyl), 0.93-0.90 ppm (m, 6H, alkyl); ¹³C NMR (100 MHz, CDCl₃): δ = 181.55 (CHO), 153.99, 148.01, 144.61, 144.47, 139.06, 138.42, 135.79, 129.05, 126.90, 126.39, 126.24, 120.29 (Ar), 31.67, 31.57, 31.39, 30.48, 30.37, 29.01, 28.99, 28.57, 22.63, 22.56, 14.13, 14.09 ppm (alkyl)

5-(5-(5-Bromo-4-hexylthiophen-2-yl)selenophen-2-yl)-3-hexylthiophene-2-carbaldehyde (5). NBS (0.214 g, 1.2 mmol) was slowly added to a solution of 4 (0.562 g, 1.143 mmol) in a mixture of $CHCl_3$ (10 mL) and acetic acid (10 mL) at 0 °C under darkness. After the mixture was stirred at room temperature overnight, the reaction was terminated by the addition of water. The reaction mixture was then extracted with CH_2Cl_2 and water. The organic extract was dried over anhydrous Na₂SO₄ and the solvent was removed under reduced pressure to yield an orange oil, which was purified by column chromatography on silica gel with hexane/CH₂Cl₂ (1:1 v/v) as the eluent to give 5 as an orange solid (0.627 g, 1.099 mmol). ¹H NMR (400 MHz, CDCl₃): $\delta = 9.98$ (s, 1H, CHO), 7.38 (d, 1H, J = 4 Hz, Ar), 7.17 (d, 1H, J = 4 Hz, Ar), 6.97 (s, 1H, Ar), 6.84 (s, 1H, Ar), 2.91 (t, 2H, J = 7.6 Hz, alkyl), 2.54 (t, 2H, J = 7.6 Hz, alkyl), 1.71–1.65 (m, 2H, alkyl), 1.62–1.55 (m, 2H, alkyl), 1.40–1.30 (m, 12H, alkyl), 0.91–0.88 ppm (m, 6H, alkyl); ¹³C NMR (100 MHz, CDCl₃): $\delta = 181.55$ (CHO), 153.94, 147.67, 143.34, 143.31, 139.58, 138.18, 136.02, 128.98, 127.06, 126.52, 125.71, 109.10 (Ar), 31.61, 31.57, 31.38, 29.64, 29.59, 29.00, 28.91, 28.57, 22.61, 22.56, 14.12, 14.08 ppm (alkyl).

General synthetic procedures of 6a-6d

A mixture of 5 (60 mg, 0.105 mmol), and each of the corresponding aromatic boronic acid (0.126 mmol), Pd(PPh₃)₄ (6 mg, 0.005 mmol), and 2 M aqueous solution of K_2CO_3 (1 mL) in THF (20 mL) was heated to reflux under a N_2 atmosphere overnight. The reaction mixture was poured into water, followed by extraction using ethyl acetate. The organic layer was dried over anhydrous Na_2SO_4 . Then, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using a 2:1 mixture of CH_2Cl_2 and hexane as eluent to yield **6a–6d** as an orange red oil.

Compound 6a. 72 mg (89% yield). ¹H NMR (400 MHz, CDCl₃): δ = 10.01 (s, 1H, CHO), 8.19 (s, 1H, Ar), 8.14 (d, 1H, J = 8 Hz, Ar), 7.58–7.51 (m, 2H, Ar), 7.47–7.43 (m, 3H, Ar), 7.31–7.27 (m, 2H, Ar), 7.12 (s, 1H, Ar), 7.00 (s, 1H, Ar), 4.34 (t, 2H, J = 7.2 Hz, alkyl), 2.94 (t, 2H, J = 7.6 Hz, alkyl), 2.73 (t, 2H, J = 8 Hz, alkyl), 1.96–1.89 (m, 2H, alkyl), 1.76–1.69 (m, 4H, alkyl), 1.44–1.30 (m, 22H, alkyl), 0.96–0.88 ppm (m, 9H, alkyl), ¹³C NMR (100 MHz, CDCl₃): δ = 180.39 (CHO), 152.94, 147.10, 143.74, 139.81, 138.86, 138.70, 138.17, 137.50, 134.93, 134.60, 128.13, 126.47, 125.95, 125.70, 124.98, 124.77, 123.47, 121.96, 121.61, 119.99, 119.40, 118.05 (Ar), 42.19, 30.76, 30.61, 30.53, 30.32, 29.96, 28.35, 28.17, 28.16, 27.97, 27.78, 27.51, 26.30, 21.58, 25.53, 13.05 ppm (alkyl).

Compound 6b. 87 mg (76% yield). ¹H NMR (400 MHz, CDCl₃): $\delta = 9.97$ (s, 1H, CHO), 7.52–7.46 (m, 8H, Ar), 7.39 (d, 1H, J = 4 Hz, Ar), 7.32–7.30 (m, 2H, Ar), 7.21–7.18 (m, 5H, Ar), 7.16–7.14 (m, 2H, Ar), 7.02 (s, 1H, Ar), 6.97–6.93 (m, 5H, Ar), 3.98 (t, 4H, J = 6.4 Hz, alkyl), 2.90 (t, 2H, J = 7.6 Hz, alkyl), 2.65 (t, 2H, J = 8 Hz, alkyl), 1.83–1.76 (m, 4H, alkyl), 1.72–1.60 (m, 4H, alkyl), 1.49–1.26 (m, 24H, alkyl), 0.93–0.86 ppm (m, 12H, alkyl); ¹³C NMR (100 MHz, CDCl₃): $\delta = 181.47$ (CHO), 158.55, 153.99, 148.08, 147.23, 146.00, 144.57, 139.41, 138.77, 138.34, 136.03, 135.82, 135.74, 132.90, 129.79, 129.17, 127.71, 127.51, 126.83, 126.00, 124.95, 123.02, 114.83 (Ar), 68.12, 31.67, 31.65, 31.59, 31.39, 30.94, 29.32, 29.23, 29.03, 28.93, 28.59, 25.79, 22.66, 22.65, 22.59, 14.16, 14.10 ppm (alkyl).

Compound 6c. 40 mg (42% yield). ¹H NMR (400 MHz, CDCl₃): δ = 9.90 (s, 1H, CHO), 8.17 (d, 1H, *J* = 1.6 Hz, Ar), 8.1 (d, 1H, *J* = 1.2 Hz, Ar), 7.62–7.60 (m, 1H, Ar), 7.55–7.53 (m, 2H, Ar), 7.46 (dd, 1H, *J* = 8.4, 2 Hz, Ar), 7.38–7.32 (m, 3H, Ar), 7.17

(d, 1H, J = 4 Hz, Ar), 7.01 (s, 1H, Ar), 6.94–6.92 (m, 2H, Ar), 6.89 (s, 1H, Ar), 4.23 (t, 2H, J = 7.2 Hz, alkyl), 3.94 (t, 2H, J = 6.4 Hz, alkyl), 2.83 (t, 2H, J = 7.6 Hz, alkyl), 2.63 (t, 2H, J = 8 Hz, alkyl), 1.84–1.70 (m, 4H, alkyl), 1.65–1.56 (m, 4H, alkyl), 1.43–1.15 (m, 28H, alkyl), 0.86–0.74 ppm (m, 12H, alkyl); ¹³C NMR (100 MHz, CDCl₃): $\delta = 181.50$ (CHO), 158.24,154.03, 148.19, 144.82, 140.36, 140.02, 139.75, 139.25, 138.57, 136.00, 135.67, 134.40, 132.48, 129.21, 128.20, 127.56, 127.11, 126.89, 126.79, 126.38, 125.85, 125.35, 124.61, 123.20, 123.18, 121.10, 118.44, 114.87, 109.11, 108.84 (Ar), 68.16, 43.39, 31.84, 31.66, 31.60, 31.39, 31.02, 29.42, 29.35, 29.22, 29.10, 29.04, 28.88, 28.59, 27.38, 25.81, 22.67, 22.65, 22.59, 14.11 ppm (alkyl).

Compound 6d. 119 mg (92% yield). ¹H NMR (400 MHz, CDCl₃): δ = 10.01 (s, 1H, CHO), 8.36 (d, 2H, *J* = 1.6 Hz, Ar), 8.18 (d, 2H, *J* = 7.6 Hz, Ar), 7.76 (dd, 2H, *J* = 8.4, 1.6 Hz, Ar), 7.71 (d, 4H, *J* = 8.8 Hz, Ar), 7.54–7.35 (m, 12H, Ar), 7.30–7.26 (m, 6H, Ar), 7.08 (s, 1H, Ar), 7.00 (s, 1H, Ar), 4.35 (t, 4H, *J* = 7.2 Hz, alkyl), 2.94 (t, 2H, *J* = 7.6 Hz, alkyl), 2.72 (t, 2H, *J* = 7.6 Hz, alkyl), 1.97–1.89 (m, 4H, alkyl), 1.77–1.66 (m, 4H, alkyl), 1.45–1.30 (m, 24H, alkyl), 0.96–0.89 ppm (m, 12H, alkyl); ¹³C NMR (100 MHz, CDCl₃): δ = 181.47 (CHO), 153.98, 148.09, 147.37, 145.85, 144.57, 140.88, 139.79, 139.37, 138.69, 138.42, 137.16, 135.95, 135.68, 131.65, 129.77, 129.15, 128.07, 127.68, 127.52, 126.79, 125.96, 125.76, 125.11, 124.84, 123.33, 122.94, 122.86, 120.39, 118.85, 118.46, 108.91, 108.82 (Ar), 43.22, 31.66, 31.60, 31.56, 31.36, 30.94, 29.71, 29.22, 29.00, 28.91, 28.55, 27.00, 22.66, 22.63, 22.56, 14.14, 14.07, 14.03 ppm (alkyl).

3,4'-Dihexyl-[2,2'-bithiophene]-5-carbaldehyde (9). A mixture of 8 (0.460 g, 1.671 mmol), 3-hexylthiophenyl-2-boronic acid (0.425 g, 2.005 mmol), Pd(PPh₃)₄ (97 mg, 0.084 mmol), and 2 M K_2CO_3 (2 mL) in THF (30 mL) was heated to reflux under a N_2 atmosphere 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 9 (0.545 g, 1.504 mmol) as a pale yellow oil. ¹H NMR (400 MHz, CDCl₃): δ = 9.82 (s, 1H, CHO), 7.58 (s, 1H, Ar), 7.11 (d, 1H, J = 1.6 Hz, alkyl), 7.01 (d, 1H, J = 1.2 Hz, alkyl), 2.79 (t, 2H, J = 7.6 Hz, alkyl), 2.62 (t, 2H, J = 7.6 Hz, alkyl), 1.70-1.60 (m, 4H, alkyl), 1.42-1.26 (m, 12H, alkyl), 0.91-0.87 ppm (m, 6H, alkyl); ¹³C NMR (100 MHz, $CDCl_3$): $\delta = 182.63$ (CHO), 144.15, 141.82, 140.15, 140.08, 139.00, 134.58, 128.88, 122.19 (Ar), 31.66, 31.60, 30.38, 30.29, 29.28, 29.13, 28.96, 22.61, 22.60, 14.10, 14.07 ppm (alkyl).

5'-Bromo-3,4'-dihexyl-[2,2'-bithiophene]-5-carbaldehyde (10). NBS (0.396 g, 2.227 mmol) was slowly added to a solution of 9 (0.769 g, 2.121 mmol) in a mixture of $CHCl_3$ (25 mL) and acetic acid (3 mL) at 0 °C under darkness. After the mixture was stirred at room temperature overnight, the reaction was terminated by the addition of water. The reaction mixture was then extracted with CH_2Cl_2 and water. The organic extract was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure to yield a yellow oil, which was purified by column chromatography on silica gel with hexane/ CH_2Cl_2 (2:1 v/v) as the eluent to give **10** as a yellow oil (0.922 g, 2.088 mmol). ¹H NMR (400 MHz, CDCl₃): δ = 9.82 (s, 1H, CHO), 7.57 (s, 1H, Ar), 6.96 (s, 1H, alkyl), 2.74 (t, 2H, *J* = 7.6 Hz, alkyl), 2.57 (t, 2H, *J* = 7.6 Hz, alkyl), 1.69–1.56 (m, 4H, alkyl), 1.40–1.31 (m, 12H, alkyl), 0.91–0.88 ppm (m, 6H, alkyl); ¹³C NMR (100 MHz, CDCl₃): δ = 182.62 (CHO), 142.99, 140.55, 140.42, 138.87, 134.33, 128.31, 111.24 (Ar), 31.59, 30.30, 29.61, 29.49, 29.26, 29.11, 28.88, 22.59, 14.10, 14.07 ppm (alkyl).

General synthetic procedures of 11a-13a

A mixture of **10** (400 mg, 0.906 mmol) or **8** (400 mg, 1.453 mmol) or 4-bromobenzaldehyde (600 mg, 3.243 mmol), (4-(diphenylamino)phenyl)boronic acid (1.5 molar equivalents), Pd(PPh₃)₄ (112 mg, 0.097 mmol), and 2 M aqueous solution of K_2CO_3 (2 mL) in THF (30 mL) was heated to reflux under 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 and the residue was purified by column chromatography on silica gel using a 1:1 mixture of CH₂Cl₂ and hexane as eluent to yield **11a–13a** as an orange oil.

Compound 11a. 173 mg (32% yield). ¹H NMR (400 MHz, CDCl₃): δ = 9.70 (s, 1H, CHO), 7.51 (s, 1H, Ar), 7.19–7.13 (m, 6H, Ar), 7.16–7.14 (m, 5H, Ar), 7.11–7.04 (m, 4H, Ar), 2.82 (t, 2H, *J* = 7.6 Hz, alkyl), 2.67 (t, 2H, *J* = 8 Hz, alkyl), 1.73–1.60 (m, 4H, alkyl), 1.43–1.27 (m, 12H, alkyl), 0.91–0.86 ppm (m, 6H, alkyl); ¹³C NMR (100 MHz, CDCl₃): δ = 182.58 (CHO), 147.55, 147.42, 141.95, 140.31, 139.88, 139.73, 139.24, 139.06, 132.26, 130.08, 129.84, 129.40, 127.31, 124.84, 123.37, 122.83 (Ar), 31.65, 30.91, 30.29, 29.44, 29.20, 29.16, 28.74, 22.63, 14.13 ppm (alkyl).

Compound 12a. 545 mg (85% yield). ¹H NMR (400 MHz, CDCl₃): δ = 9.82 (s, 1H, CHO), 7.59 (s, 1H, Ar), 7.31–7.27 (m, 6H, Ar), 7.04–7.02 (m, 4H, Ar), 6.98–6.92 (m, 4H, Ar), 2.57 (t, 2H, *J* = 8 Hz, alkyl), 1.56–1.48 (m, 2H, alkyl), 1.25–1.13 (m, 6H, alkyl), 0.79–0.74 ppm (m, 3H, alkyl); ¹³C NMR (100 MHz, CDCl₃): δ = 181.64 (CHO), 147.85, 147.32, 146.08, 139.33, 138.61, 137.81, 128.75, 128.40, 125.47, 124.05, 123.37, 121.13 (Ar), 30.52, 29.65, 27.99, 27.65, 21.51, 13.05 ppm (alkyl).

Compound 13a. 953 mg (84% yield). ¹H NMR (400 MHz, CDCl₃): δ = 9.88 (s, 1H, CHO), 7.79 (d, 2H, *J* = 8.4 Hz, Ar), 7.58 (d, 2H, *J* = 8 Hz, Ar), 7.41 (d, 2H, *J* = 8.8 Hz, Ar), 7.18 (t, 4H, *J* = 7.6 Hz, Ar), 7.07 (d, 6H, *J* = 8.4 Hz, Ar), 6.99 (t, 2H, *J* = 7.2 Hz, Ar); ¹³C NMR (100 MHz, CDCl₃): δ = 191.68 (CHO), 148.54, 147.46, 146.45, 134.87, 132.81, 130.50, 129.69, 128.25, 126.96, 125.05, 123.73, 123.28 ppm (Ar).

5'-(4-(Bis(4-iodophenyl)amino)phenyl)-3,4'-dihexyl-[2,2'bithiophene]-5-carbaldehyde (11b). A mixture of 11a (0.403 g, 0.665 mmol), KI (166 mg, 0.998 mmol) and KIO₃ (142 mg, 0.665 mmol) in acetic acid (20 mL) and water (2 mL) was stirred overnight at 80 °C. After cooling, the reaction mixture was washed with water and extracted with CHCl₃. Then, the solvent was removed under reduced pressure and the crude compound was purified by column chromatography on silica gel eluting with CH₂Cl₂/hexane (1:1, v/v) to give product **11b** (0.406 g, 0.473 mmol). ¹H NMR (400 MHz, CDCl₃): δ = 9.79 (s, 1H, CHO), 7.57 (s, 1H, Ar), 7.55–7.52 (m, 4H, Ar), 7.33–7.31 (m, 2H, Ar), 7.16 (s, 1H, Ar), 7.08 (d, 2H, *J* = 8.4 Hz, Ar), 6.88–6.85 (m, 4H, Ar), 2.82 (t, 2H, J = 8 Hz, alkyl), 2.66 (t, 2H, J = 8 Hz, alkyl), 1.72–1.60 (m, 4H, alkyl), 1.43–1.26 (m, 12H, alkyl), 0.90–0.86 ppm (m, 6H, alkyl); ¹³C NMR (100 MHz, CDCl₃): $\delta = 182.49$ (CHO), 146.76, 146.32, 141.66, 140.01, 139.92, 139.70, 139.36, 139.20, 138.50, 132.69, 130.16, 130.10, 128.82, 126.30, 123.88, 86.66 (Ar), 31.70, 31.69, 30.94, 30.33, 29.49, 29.24, 29.20, 28.81, 22.74, 22.68, 14.26, 14.22 ppm (alkyl).

5-(4-(Bis(4-bromophenyl)amino)phenyl)-4-hexylthiophene-2carbaldehyde (12b). NBS (0.441 g, 2.48 mmol) was slowly added to a solution of 12a (0.545 g, 1.24 mmol) in CHCl₃ (25 mL) at 0 °C under darkness. After the mixture was stirred at room temperature overnight, the reaction was terminated by the addition of water. The reaction mixture was then extracted with CH₂Cl₂ and water. The organic extract was dried over anhydrous Na₂SO₄ and the solvent was removed under reduced pressure to yield a yellow oil, which was purified by column chromatography on silica gel with hexane/CH₂Cl₂ (2:1 v/v) as the eluent to give 12b as a yellow oil (0.709 g, 1.187 mmol). ¹H NMR (400 MHz, $CDCl_3$: δ = 9.70 (s, 1H, CHO), 7.53 (s, 1H, Ar), 7.27–7.20 (m, 6H, Ar), 6.97–6.95 (m, 2H, Ar), 6.90–6.86 (m, 4H, Ar), 2.57 (t, 2H, J = 8 Hz, alkyl), 1.56-1.49 (m, 2H, alkyl), 1.26-1.15 (m, 6H, alkyl), 0.76 ppm (t, 3H, J = 6.8 Hz, alkyl); ¹³C NMR (100 MHz, CDCl₃): $\delta =$ 182.68 (CHO), 148.23, 147.40, 145.95, 140.78, 139.99, 138.80, 132.67, 130.18, 127.94, 126.27, 123.12, 116.56 (Ar), 31.62, 30.76, 29.09, 28.76, 22.62, 14.18 ppm (alkyl).

4'-(Bis(4-iodophenyl)amino)-[1,1'-biphenyl]-4-carbaldehyde (13b). A mixture of 13a (0.529 g, 1.514 mmol), KI (377 mg, 2.271 mmol) and KIO₃ (324 mg, 1.514 mmol) in acetic acid (20 mL) and water (2 mL) was stirred overnight at 80 °C. After cooling, the reaction mixture was washed with water and extracted with CHCl₃. Then, the solvent was removed under reduced pressure and the crude compound was purified by column chromatography on silica gel eluting with CH₂Cl₂/ hexane (1 : 1, v/v) to give product 13b (0.210 g, 0.349 mmol) as a yellow oil. ¹H NMR (400 MHz, CDCl₃): δ = 10.04 (s, 1H, CHO), 7.94 (d, 2H, *J* = 8.4 Hz, Ar), 7.72 (d, 2H, *J* = 8 Hz, Ar), 7.59–7.53 (m, 6H, Ar), 7.15–7.13 (m, 2H, Ar), 6.89–6.87 (m, 4H, Ar); ¹³C NMR (100 MHz, CDCl₃): δ = 191.84 (CHO), 147.21, 146.72, 146.28, 138.50, 134.96, 134.34, 130.37, 128.37, 127.09, 126.32, 124.15, 86.65 ppm (Ar).

General synthetic procedures of 11c-13c

A mixture of **11b** (88 mg, 0.103 mmol) or **12b** (120 mg, 0.200 mmol) or **13b** (210 mg, 0.349 mmol), (9-hexylcarbazolyl)boronic acid (3 molar equivalents), $Pd(PPh_3)_4$ (10 mg, 0.008 mmol), and 2 M aqueous solution of K_2CO_3 (1 mL) in THF (20 mL) was heated to reflux under N₂ atmosphere 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 3:2 mixture of CH₂Cl₂ and hexane as eluent to yield **11c–13c** as an orange oil.

Compound 11c. 95 mg (84% yield). ¹H NMR (400 MHz, CDCl₃): δ = 9.71 (s, 1H, CHO), 8.23 (d, 2H, *J* = 1.6 Hz, Ar), 8.05 (d, 2H, *J* = 7.6 Hz, Ar), 7.62 (dd, 2H, *J* = 8.4, 1.6 Hz, Ar), 7.59–7.57 (m, 4H, Ar), 7.46 (s, 1H, Ar), 7.41–7.35 (m, 4H, Ar), 7.33–7.27

(m, 4H, Ar), 7.26–7.22 (m, 4H, Ar), 7.17–7.14 (m, 4H, Ar), 7.09 (s, 1H, Ar), 4.21 (t, 4H, J = 7.2 Hz, alkyl), 2.73 (t, 2H, J = 7.6 Hz, alkyl), 2.62 (t, 2H, J = 8 Hz, alkyl), 1.83–1.76 (m, 4H, alkyl), 1.61–1.56 (m, 4H, alkyl), 1.33–1.18 (m, 24H, alkyl), 0.83–0.76 ppm (m, 12H, alkyl); ¹³C NMR (100 MHz, CDCl₃): δ = 182.62 (CHO), 147.56, 145.86, 142.01, 140.91, 140.44, 139.88, 139.83, 139.69, 139.29, 139.08, 137.24, 132.26, 131.67, 130.14, 129.92, 128.13, 127.27, 125.82, 125.19, 124.89, 123.37, 122.97, 122.85, 120.44, 118.90, 118.51, 108.97, 108.87 (Ar), 43.25, 31.70, 31.65, 30.98, 30.32, 29.48, 29.24, 29.05, 28.82, 27.05, 22.72, 22.67, 22.62, 14.20, 14.17, 14.10 ppm (alkyl).

Compound 12c. 161 mg (86% yield). ¹H NMR (400 MHz, CDCl₃): δ = 9.72 (s, 1H, CHO), 8.23 (d, 2H, *J* = 1.6 Hz, Ar), 8.04 (d, 2H, *J* = 7.6 Hz, Ar), 7.61 (dd, 2H, *J* = 8.8, 1.6 Hz, Ar), 7.59–7.57 (m, 4H, Ar), 7.51 (s, 1H, Ar), 7.40–7.35 (m, 3H, Ar), 7.33–7.32 (m, 2H, Ar), 7.30–7.25 (m, 3H, Ar), 7.23–7.21 (m, 4H, Ar), 7.16–7.12 (m, 4H, Ar), 4.19 (t, 4H, *J* = 7.2 Hz, alkyl), 2.61 (t, 2H, *J* = 7.6 Hz, alkyl), 1.82–1.74 (m, 4H, alkyl), 1.58–1.51 (m, 2H, alkyl), 1.30–1.14 (m, 18H, alkyl), 0.82–0.76 ppm (m, 9H, alkyl); ¹³C NMR (100 MHz, CDCl₃): δ = 182.80 (CHO), 149.12, 148.45, 145.62, 140.94, 140.39, 139.89, 139.73, 138.93, 137.62, 131.62, 129.93, 128.21, 126.56, 125.85, 125.50, 124.90, 123.41, 122.99, 122.27, 120.44, 118.94, 118.54, 108.99, 108.89 (Ar), 43.26, 31.67, 31.65, 30.79, 29.14, 29.05, 28.82, 27.05, 22.65, 22.62, 14.17, 14.09 ppm (alkyl).

Compound 13c. 150 mg (51% yield). ¹H NMR (400 MHz, CDCl₃): δ = 10.04 (s, 1H, CHO), 8.33 (d, 2H, *J* = 1.2 Hz, Ar), 8.15 (d, 2H, *J* = 7.6 Hz, Ar), 7.96–7.94 (m, 2H, Ar), 7.78–7.76 (m, 2H, Ar), 7.73 (dd, 2H, *J* = 8.8, 1.6 Hz, Ar), 7.69–7.67 (m, 4H, Ar), 7.60–7.58 (m, 2H, Ar), 7.48–7.42 (m, 6H, Ar), 7.34–7.29 (m, 6H, Ar), 7.27–7.25 (m, 2H, Ar), 4.33 (t, 4H, *J* = 7.2 Hz, alkyl), 1.92–1.89 (m, 4H, alkyl), 1.44–1.26 (m, 12H, alkyl), 0.89–0.83 ppm (m, 6H, alkyl); ¹³C NMR (100 MHz, CDCl₃): δ = 191.91 (CHO), 148.45, 146.71, 145.78, 140.92, 139.85, 137.39, 134.68, 132.73, 131.64, 130.38, 128.14, 128.11, 126.92, 125.80, 125.23, 124.86, 123.38, 123.13, 122.96, 120.41, 118.89, 118.51, 108.94, 108.85 (Ar), 43.26, 31.61, 29.01, 27.02, 22.57, 14.03 ppm (alkyl).

General synthetic procedures of 7a-7d and 11d-13d

A mixture of each of the corresponding dye precursors **6a–6d** and **11c–13c** and cyanoacetic acid (10 molar 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 extracted with CHCl₃ and water. Then, the solvent was removed under reduced pressure and the crude compound was purified by column chromatography on silica gel eluting with CHCl₃ and then CHCl₃/MeOH (10:1, v/v) to give the desired products **7a–7d** and **11d–13d**.

Compound 7a. 75 mg (97% yield); dark purple solid. ¹H NMR (400 MHz, DMSO-d₆): δ = 8.29 (s, 1H, C=CH-), 8.25-8.22 (m, 2H, Ar), 7.71-7.64 (m, 3H, Ar), 7.55-7.46 (m, 4H, Ar), 7.39 (s, 1H, Ar), 7.26-7.22 (m, 1H, Ar), 4.43 (t, 2H, J = 6.8 Hz, alkyl), 2.79 (t, 2H, J = 7.6 Hz, alkyl), 2.69 (t, 2H, J = 7.2 Hz, alkyl), 1.81-1.78 (m, 2H, alkyl), 1.65-1.60 (m, 4H, alkyl), 1.31-1.19 (m, 22H, alkyl), 0.89-0.76 ppm (m, 9H, alkyl). HRMS (MALDI-TOF, m/z): [M⁺] 836.2891; calcd for (C₄₈H₅₆N₂O₂S₂Se) 836.2948.

Compound 7b. 81 mg (88% yield); dark purple solid. ¹H NMR (400 MHz, DMSO-d₆): δ = 8.26 (s, 1H, C=CH-), 7.65 (d, 1H, *J* = 3.6 Hz, Ar), 7.59–7.55 (m, 8H, Ar), 7.46 (s, 1H, Ar), 7.42–7.36 (m, 3H, Ar), 7.34 (s, 1H, Ar), 7.13 (d, 4H, *J* = 8.4 Hz, Ar), 7.08 (d, 2H, *J* = 8.4 Hz, Ar), 6.98 (d, 4H, *J* = 8.8 Hz, Ar), 3.98 (t, 4H, *J* = 6.4 Hz, alkyl), 2.77 (t, 2H, *J* = 7.2 Hz, alkyl), 2.62 (t, 2H, *J* = 7.2 Hz, alkyl), 1.75–1.68 (m, 4H, alkyl), 1.60–1.58 (m, 4H, alkyl), 1.42–1.24 (m, 24H, alkyl), 0.90–0.82 ppm (m, 12H, alkyl). HRMS (MALDI-TOF, *m*/*z*): [M⁺] 1154.3167; calcd for (C₇₀H₇₈N₂O₄S₂Se) 1154.4568.

Compound 7c. 40 mg (92% yield); dark purple solid. ¹H NMR (400 MHz, CDCl₃): δ = 8.39 (s, 1H, C=CH-), 8.27 (d, 1H, *J* = 1.2 Hz, Ar), 8.19 (d, 1H, *J* = 1.6 Hz, Ar), 7.72–7.70 (m, 1H, Ar), 7.66–7.64 (m, 2H, Ar), 7.56–7.54 (m, 1H, Ar), 7.51 (d, 1H, *J* = 4 Hz, Ar), 7.47–7.42 (m, 2H, Ar), 7.28–7.27 (m, 1H, Ar), 7.11 (s, 1H, Ar), 7.05–7.02 (m, 3H, Ar), 4.33 (t, 2H, *J* = 6.8 Hz, alkyl), 4.04 (t, 2H, *J* = 6.8 Hz, alkyl), 2.80 (t, 2H, *J* = 7.6 Hz, alkyl), 2.72 (t, 2H, *J* = 8 Hz, alkyl), 1.96–1.85 (m, 4H, alkyl), 1.69–1.64 (m, 4H, alkyl), 1.54–1.26 (m, 28H, alkyl), 0.96–0.85 ppm (m, 12H, alkyl). HRMS (MALDI-TOF, *m*/*z*): [M⁺] 1012.3496; calcd for (C₆₀H₇₂N₂O₃S₂Se) 1012.4150.

Compound 7d. 101 mg (80% yield); dark purple solid. ¹H NMR (400 MHz, CDCl₃): δ = 8.31 (s, 1H, C=CH-), 8.29 (d, 2H, *J* = 1.6 Hz, Ar), 8.11 (d, 2H, *J* = 7.6 Hz, Ar), 7.68–7.62 (m, 6H, Ar), 7.48–7.44 (m, 2H, Ar), 7.41–7.38 (m, 4H, Ar), 7.28– 7.13 (m, 12H, Ar), 6.98 (s, 1H, Ar), 6.94 (s, 1H, Ar), 4.26 (t, 4H, *J* = 7.2 Hz, alkyl), 2.77 (t, 2H, *J* = 7.2 Hz, alkyl), 2.62 (t, 2H, *J* = 7.6 Hz, alkyl), 1.89–1.82 (m, 4H, alkyl), 1.66–1.59 (m, 4H, alkyl), 1.42–1.25 (m, 24H, alkyl), 0.94–0.84 ppm (m, 12H, alkyl). HRMS (MALDI-TOF, *m*/*z*): [(M + H)⁺] 1301.5270; calcd for (C₈₂H₈₅N₄O₂S₂Se) 1301.5274.

Compound 11d. 99 mg (89% yield); dark red solid. ¹H NMR (400 MHz, DMSO-d₆): $\delta = 8.50$ (d, 2H, J = 1.6 Hz, Ar), 8.40 (s, 1H, C=CH-), 8.26 (d, 2H, J = 7.6 Hz, Ar), 7.91 (s, 1H, Ar), 7.82–7.77 (m, 6H, Ar), 7.68 (d, 2H, J = 8.4 Hz, Ar), 7.63 (d, 2H, J = 8.4 Hz, Ar), 7.50–7.46 (m, 4H, Ar), 7.36 (s, 1H, Ar), 7.28 (d, 4H, J = 8.8 Hz, Ar), 7.25–7.17 (m, 4H, Ar), 4.43 (t, 4H, J = 7.2 Hz, alkyl), 2.82 (t, 2H, J = 7.6 Hz, alkyl), 2.74–2.70 (m, 2H, alkyl), 1.82–1.77 (m, 4H, alkyl), 1.66–1.61 (m, 4H, alkyl), 1.34–1.22 (m, 24H, alkyl), 0.88–0.81 ppm (m, 12H, alkyl). HRMS (MALDI-TOF, m/z): [M⁺] 1170.6682; calcd for (C₇₈H₈₂N₄O₂S₂) 1170.5879.

Compound 12d. 166 mg (95% yield); dark red solid. ¹H NMR (400 MHz, DMSO-d₆): $\delta = 8.48$ (d, 2H, J = 1.6 Hz, Ar), 8.38 (s, 1H, C=CH-), 8.24 (d, 2H, J = 7.6 Hz, Ar), 7.90 (s, 1H, Ar), 7.81–7.76 (m, 6H, Ar), 7.66 (d, 2H, J = 8.8 Hz, Ar), 7.61 (d, 2H, J = 8 Hz, Ar), 7.49–7.45 (m, 4H, Ar), 7.28 (d, 4H, J = 8.4 Hz, Ar), 7.23–7.16 (m, 4H, Ar), 4.41 (t, 4H, J = 6.8 Hz, alkyl), 2.71 (t, 2H, J = 7.6 Hz, alkyl), 1.82–1.75 (m, 4H, alkyl), 1.61–1.56 (m, 2H, alkyl), 1.32–1.20 (m, 18H, alkyl), 0.86–0.79 ppm (m, 9H, alkyl). HRMS (MALDI-TOF, m/z): [(M + H)⁺] 1005.5955; calcd for (C₆₈H₆₉N₄O₂S) 1005.5136.

Compound 13d. 132 mg (80% yield); dark red solid. ¹H NMR (400 MHz, DMSO-d₆): δ = 8.48 (d, 2H, *J* = 0.8 Hz, Ar), 8.33 (s, 1H, C=CH-), 8.24 (d, 2H, *J* = 7.6 Hz, Ar), 8.11 (d, 2H, *J* = 8.4 Hz, Ar),

7.88 (d, 2H, J = 8.4 Hz, Ar), 7.79–7.73 (m, 8H, Ar), 7.63–7.59 (m, 4H, Ar), 7.48–7.44 (m, 2H, Ar), 7.25–7.15 (m, 8H, Ar), 4.38 (t, 4H, J = 6.4 Hz, alkyl), 1.78–1.75 (m, 4H, alkyl), 1.27–1.18 (m, 12H, alkyl), 0.81–0.78 ppm (m, 6H, alkyl). HRMS (MALDI-TOF, m/z): [M⁺] 914.4616; calcd for ($C_{64}H_{58}N_4O_2$) 914.4560.

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