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Synthesis of sensitizers containing donor cascade of triarylamine and dimethylarylamine moieties for dye-sensitized solar cells

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Four triarylamine derivatives (**XS6–9**) containing *N*,*N*-dimethylaryl amine units as secondary electron-donating groups are designed and synthesized. These dyes were applied into nanocrystalline TiO_2 dye-sensitized solar cells through standard operations. For a typical device the maximal monochromatic incident photon-to-current conversion efficiency (IPCE) can reach 93%, with a short-circuit photocurrent density (J_{sc}) 10.8 mA cm^{-2}, an open-circuit photovoltage (V_{oc}) 690 mV, and fill factor (FF) 0.61, which corresponds to an overall conversion efficiency of 4.54%.

1. Introduction

For the past two decades, more and more attentions from both academia and industry have been paid to the development of dye-sensitized solar cells (DSSCs) because of their simple structure, low incident-light-angle, and potential for low-cost manufacturing.[1,2] The ruthenium complexes used as sensitizers for cells have achieved power conversion efficiencies above 11%.[3] In comparison with ruthenium complexes, the DSSCs based on organic dyes have also been remarkably improved due to their organic structural variation, high molar extinction coefficients, and low-cost preparation.[4] Recently, the highest overall photoelectric conversion efficiency of solar cells using organic dyes as sensitizers has reached 9%, which indicated the promising perspective of organic dyes for cells. Great effort has been made on the design of new organic dyes in order to obtain excellent sensitizers with high power conversion efficiency and long-term stability.[5–8]

Most organic dyes contain a structure of donor-π-acceptor moieties. 2-Cyanoacrylic acid or rhodanine moiety acts as the electron acceptor while amines act as the electron donor. These two parts are connected by π-conjugated systems, such as methene or thiophene unit, thereby forming a D–π-A structure. Great progress has been made through variation of functionalized thiophene units for the π-conjugated systems.[9] Another important approach on the design of organic dyes is the changes in the electron-donating nature and amine unit for the donor moiety. Various amines, such as coumarin,[10] indoline,[11] oligoene,[12] hemicyanine, and cyanine[13] have been used and exhibited good performances of DSSCs. Organic dyes derived from triphenylamine (TPA) with TPA as the electron donor and 2-cyanoacrylic acid as the electron acceptor afforded a 3.3% of power conversion efficiency.[14] Its analogy dyes based on diphenylvinyl triarylamine improved the power conversion efficiency to 5.47%,[15] which showed that expansion of π-electron systems conjugated with phenyl ring of TPA had obvious effect on the performance of DSSCs and gave high power conversion efficiency. On the other hand, organic dyes with D–D–π-A structure based on triphenylamine and carbazole are reported by several groups.[16] Their studies suggested that great performance of organic dyes with D–D–π-A structure over the simple D–π-A configuration can be achieved by molecular design. Furthermore, introducing a secondary electron donor into the dye molecule can increase electron-density of donor and enhance molar extinction coefficient, which resulted in high overall conversion efficiency.[12c,17] Based on these strategies, we designed and synthesized four new triarylamine derivatives **XS6–9** containing *N*,*N*-dimethylaryl amine moieties as secondary electron-donating groups. Both triarylamine and *N*,*N*-dimethylaryl amine constructed a D–D–π-A structure with electron donor cascade in dyes. We are especially interested in the strong electron donor of *N*,*N*-dimethylaryl amine, which may be possible to induce efficient light-induced charge separation. Here, we wish to report the synthesis, characterization, and photovoltaic properties of these new organic dyes (Scheme 1).

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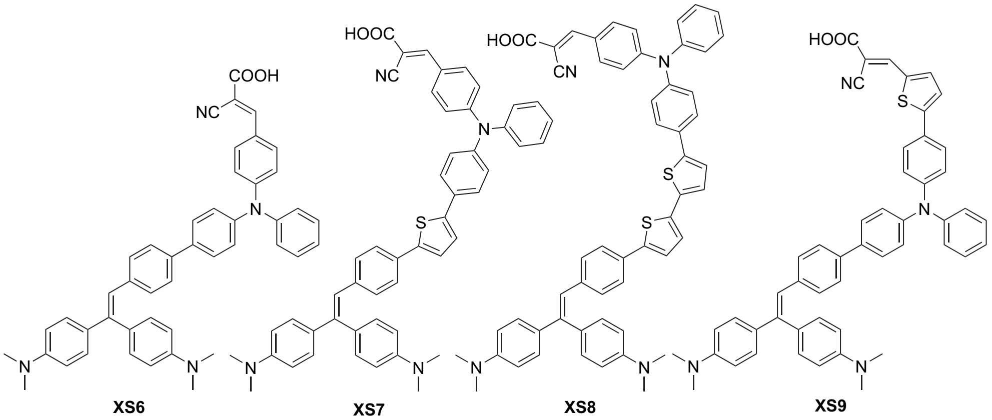


Scheme 1. Structure of dyes (**XS6–9**).

2. Results and discussion

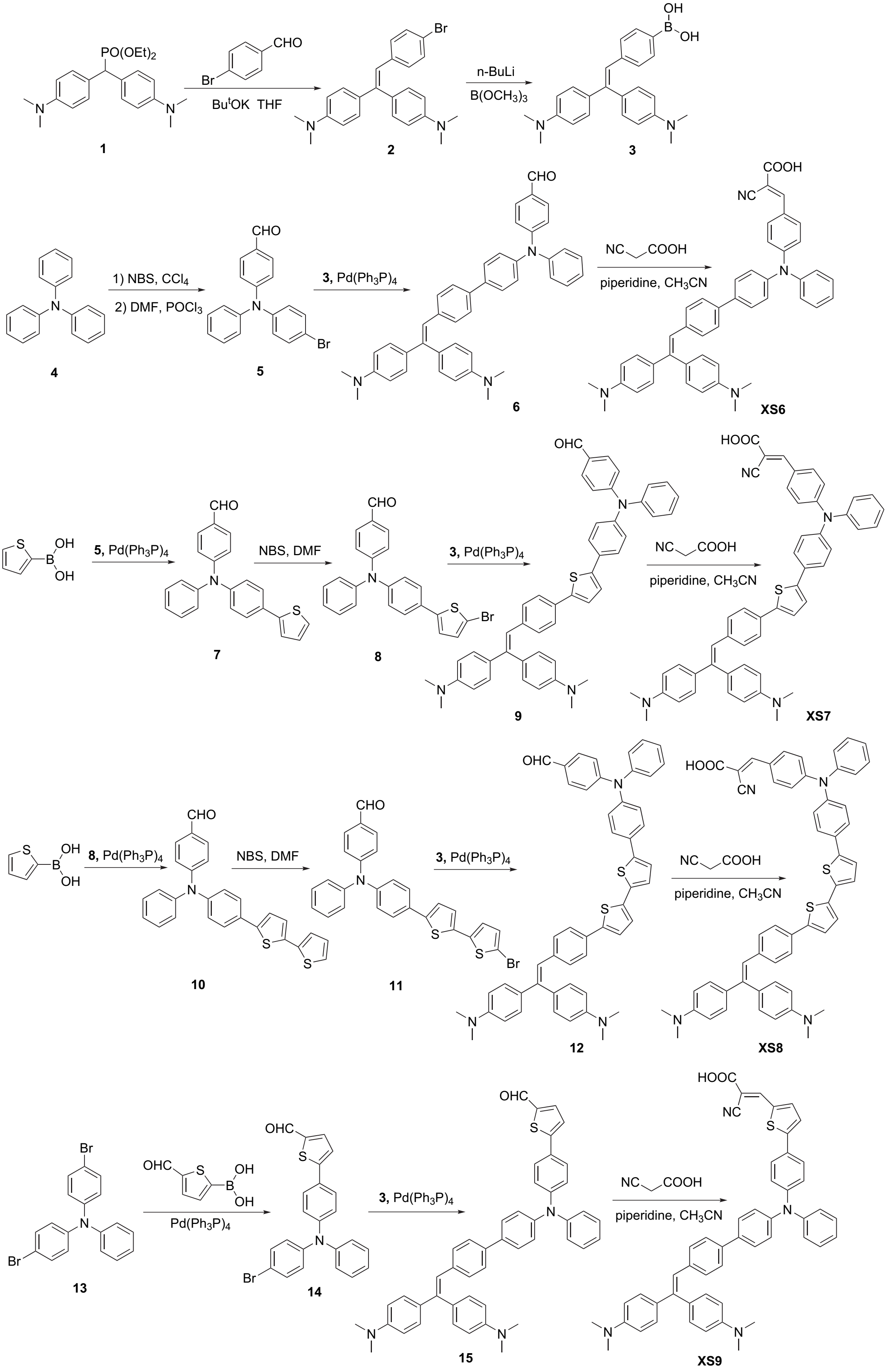
The synthetic routes of four organic dyes **XS6–9** are shown in Scheme 2. Phosphonate **1** was used as starting material to react with 4-bromobenzaldehyde in the presence of Bu^tOK to give intermediate **2**. Treatment of the intermediate **2** with *n*-BuLi and trimethyl borate afforded a key intermediate 4-(2,2-bis(4-(dimethylamino)phenyl)vinyl)phenylboronic acid (**3**). 4-((4-Bromophenyl)(phenyl)amino)benzaldehyde (**5**) was prepared from triphenylamine via bromonation reaction with NBS and Vilsmeier–Haack reaction with $POCl_3$ in DMF according to literature procedure.[18] Treatment of the boronic acid **3** with the aldehyde **5** through Suzuki coupling reaction gave an important intermediate aldehyde **6**. Then the target dye **XS6** was obtained via Knoevenagel condensation reaction of the aldehyde **6** with cyanoacetic acid in the presence of a catalytic amount of piperidine. The dyes **XS7–9** were obtained according to the similar procedures of **XS6**, and their synthesis routes are summarized in Scheme 2. These dyes containing thiophene unit were desired to induce a red shift of the absorption spectrum by expansion of π-electron systems conjugated with phenyl ring of TPA. All the intermediates and target dyes (**XS6–9**) were characterized by standard spectroscopic methods.

The UV–vis and emission spectra of organic dyes in chloroform solution are displayed in Figure 1, together with the spectra of the corresponding sensitizers absorbed on TiO_2 film. The four dyes show strong absorption bands at around 350–450 nm. **XS6** and **XS9** display two visible bands, appearing at 387/432 nm and 384/463 nm, respectively. The second absorption peak (463 nm) for **XS9** is red-shifted in comparison with that of **XS6**, which is due to the introduction of thiophene moiety, manifesting the effect of thiophene unit in increasing conjugation. For **XS7**, one of the corresponding absorptions is red-shifted to 416 nm, which is ascribed to the thiophene unit between triarylamine and *N*,*N*-dimethylaryl amine moieties, extending the π-conjugation system. The other absorption is appearing as a shoulder peak at around 432 nm. When bi-thiophene units are introduced to form **XS8**, the corresponding absorption peak is further red-shifted and overlaps the other peak, therefore look like one peak. It is notable that the molar extinction coefficients (ε) of these four dyes **XS6–9** are 124,800, 194,000, 263,700, and 90,100 $M^{-1}\,cm^{-1}$, respectively, which are very high in comparison with ruthenium complexes. The dyes containing thiophene unit between triarylamine and *N*,*N*-dimethylaryl amine, such as **XS7–8**, gave much higher molar extinction coefficient than that of dyes **XS6** and **XS9**. The greater absorption coefficient of organic dyes indicates a good ability of light harvesting and allows for a thinner nanocrystalline film. Adsorption of the dyes **XS6–9** onto a TiO_2 electrode was observed to broaden the absorption spectrum and to red-shifted. When the dyes were excited within respective π–π* bands in an air-equilibrated chloroform solution at 298 K, they exhibited strong luminescence maximum of 522–575 nm.

Electrochemical properties of the dyes **XS6–9** are listed in Table 1. The redox potentials of these dyes were obtained by cyclic voltammetric (CV) curve with 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile solution. The dyes absorbed on TiO_2 films showed quasi-reversible couples. The oxidation potentials (E_{ox}) of **XS6–9** on nanocrystalline TiO_2 electrodes are 1.09, 1.14, 1.46, and 0.97 V versus NHE, respectively. These E_{ox} value are more positive than the I_3^-/I^- redox potential (~0.4 V vs NHE), and indicate that the oxidized dyes formed from respective electrons injection into the conduction band of TiO_2 will favorably accept electrons from I^- ions in thermodynamic property. The reduction potentials (E_{red}) of the dyes are calculated from the oxidation potentials and the E_{0-0} determined from the intersection of absorption and emission spectra. The excited-state oxidation potentials of the four dyes are calculated to be −1.32, −1.28, −0.97, and −1.41 V, respectively. They are much more negative than the conduction band of TiO_2 at approximately −0.5 V versus NHE.[19] Therefore, the four dyes used as sensitizers will have sufficient driving force for electron transfer from the excited dye molecules to the conduction band of TiO_2 electrode.

The photovoltaic performance was measured at 100 $mW\,cm^{-2}$ under AM 1.5 conditions. The incident monochromatic photon-to-current conversion efficiency (IPCE) was obtained with a sandwich cell using 0.6 M 1,2-dimethyl-3-*n*-propylimidazolium iodide (DMPImI), 0.1 M LiI, 0.05 M I_2, and 0.5 M tertbutylpyridine in acetonitrile solution. The IPCE data of dyes **XS6–9** plotted as a function of wavelength are shown in Figure 2. The four dyes as sensitizers produced a strikingly high maximum IPCE value. The IPCE value for **XS6** reached 86% at 460 nm, and the dyes **XS7–9** reached 88%, 90%, and 93%, respectively. The high maximum IPCE value for these four dyes may be tentatively ascribed to high electron injection efficiency and charge separation efficiency because of the D–D–π-A structure with strongly electron donor unit of *N*,*N*-dimethylaryl amine. Unfortunately, the IPCE spectrum for the four dyes was responded at about 400–550 nm in wavelength, which is consistent with the absorption spectra on the TiO_2 film. Their lack of broad absorption in the visible spectrum will result in low power conversion efficiency.

The corresponding photocurrent–voltage curves are shown in Figure 3, and the overall conversion efficiencies (η) for these DSSCs are listed in Table 2. The performance of **XS6** in DSSCs showed a shortcircuit current (J_{sc}) of 7.8 $mA\,cm^{-2}$, an open-circuit voltage (V_{oc}) of 680 mV, and an overall conversion efficiency (η) of 3.29%.



Scheme 2. Synthesis of organic dyes (**XS6–9**).

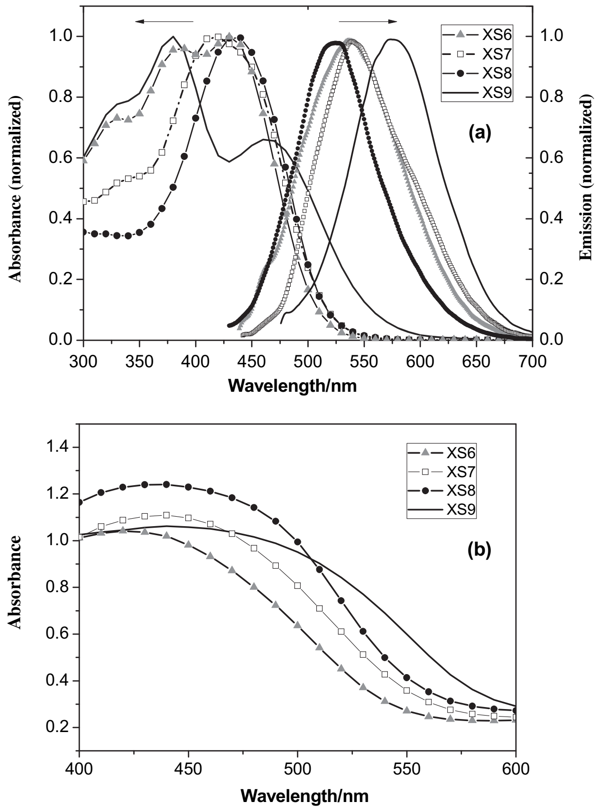


Figure 1. Absorption and emission spectra of dyes **XS6–9** in chloroform (1×10^{-5} M) (a) and on TiO_2 film (b).

Table 1
Optical properties and electrochemical properties of four dyes

Dye	λ_{max},[a] nm (ε, $M^{-1}\,cm^{-1}$)	E_{0-0}/eV[b]	E_{ox}/V versus NHE[c]	E_{red}/V versus NHE[d]
XS6	387 (120,400), 432 (124,800)	2.41	1.09	−1.32
XS7	416 (199,900), 432(194,000)	2.42	1.14	−1.28
XS8	434 (263,700)	2.43	1.46	−0.97
XS9	384 (134,800), 463 (90,100)	2.38	0.97	−1.41

[a] Absorption and emission spectra were measured in chloroform.

[b] E_{0-0} values were calculated from intersect of the normalized absorption and the emission spectra (λ_{int}): $E_{0-0}=1240/\lambda_{int}$.

[c] The oxidation potentials (vs NHE) of dyes were measured in CH_3CN with tetrabutylammonium perchlorate (TBAP, 0.1 M) as supporting electrolyte.

[d] E_{red} was calculated from $E_{ox}-E_{0-0}$.

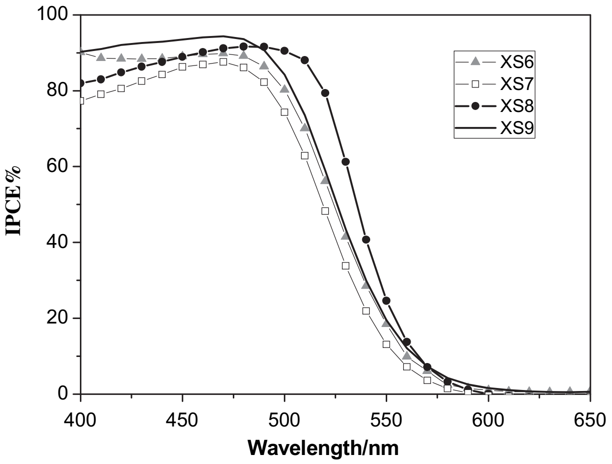


Figure 2. IPCE spectra for DSSCs based on the dyes **XS6–9**.

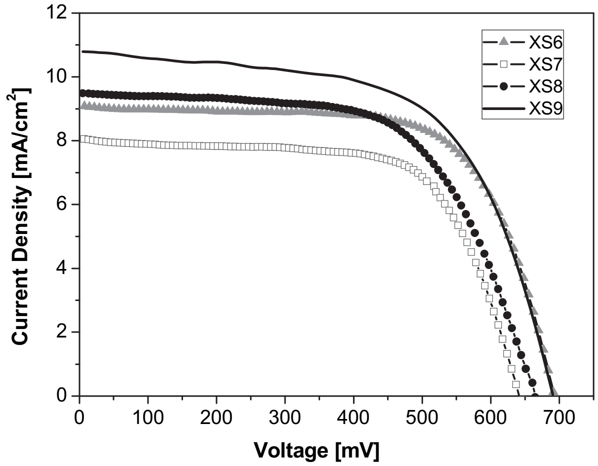


Figure 3. Current–potential (*I–V*) curves for the dyes **XS6–9**.

Table 2
Photovoltaic performance of DSSCs sensitized with the four dyes[a]

Dye	J_{sc}/mA cm^{-2}	V_{oc}/mV	*FF*	η/%
XS6	9.1	693	0.64	4.04
XS6	7.8	680	0.62	3.29[b]
XS7	8.2	644	0.65	3.43
XS8	9.5	658	0.64	4.00
XS9	10.8	690	0.61	4.54
N719	14.2	714	0.63	6.39[a]

[a] Photovoltaic performances of DSSCs were measured under irradiation of AM 1.5 G simulated solar light (100 mW cm^{-2}) at room temperature with a 0.16 cm^2 working area. The thickness of the TiO_2 film was 9 μm.

[b] Chenodeoxycholic acid was not employed as co-adsorbate.

When CDCA was employed as a co-adsorbate, the overall conversion efficiency was improved into 4.04% with higher J_{sc} and V_{oc} value. The DSSCs based on **XS7** showed relatively lower J_{sc} and V_{oc}, resulting in a lower η value of 3.43%. The dye **XS9** shows the highest overall conversion efficiency of 4.54% among the four dyes, which resulted from the largest shortcircuit current and high open-circuit voltage. The high efficiency of **XS9** dye is mainly attributed to more sufficient driving force for the photo-induced electron transfer from the excited dye molecules to the conduction band of TiO_2 electrode and broader absorption in visible spectrum. These results suggest that a suitable structure of **XS9** with thiophene located between TPA donor and cyanoacrylic acceptor is responsible for its prominent solar-to-electrical conversion efficiency. With this structure, the **XS9** exhibited broadening light response, leading to broad IPCE response and high photovoltaic performance. A slightly higher V_{oc} value of **XS6** and **XS9** compared to **XS7–8** may be ascribed to the lower E_{ox} value, which might be beneficial for retarding the electron transfer from TiO_2 to the oxidized dye or electrolyte, resulting in enhancing open-circuit voltage.[20] For a fair comparison, the N719-sensitized TiO_2 solar cell showed an efficiency of 6.39%, with a J_{sc} of 14.2 mA cm^{-2}, a V_{oc} of 714 mV, and a fill factor (*FF*) of 0.63.

To get further insight into the molecular structure and electron distribution of **XS9**, density functional theory (DFT) calculations were made on a B3LYP/6-31 G level with Gaussian 03.[21] Figure 4 shows the electron distribution of the HOMO and LUMO of **XS9**. It is obviously that, the HOMO of **XS9** is localized over the diphenylvinyl unit and the LUMO is localized over the cyanoacrylic unit through thiophene, indicating that the HOMO–LUMO excitation moves the electron distribution from the diphenylvinyl unit to the cyanoacrylic acid moiety, thus allowing an efficient photo-induced electron transfer from the dye to the TiO_2 electrode under light irradiation.

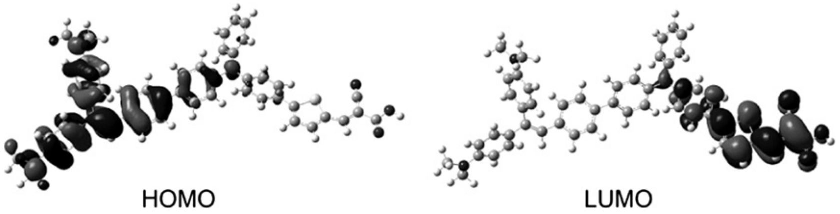


Figure 4. The frontier molecular orbitals of the HOMO and LUMO calculated at B3LYP/6-31+G (D) level of **XS9**.

In summary, we have designed and synthesized four organic sensitizers containing donor cascade of triarylamine and *N*,*N*-dimethylaryl amine moieties. The dyes gave high molar extinction coefficient and high maximum IPCE value (93%). These results imply that synthesis of sensitizer containing a secondary electron-donating group is a possible alternative to produce excellent IPCE value with high electron injection efficiency and charge separation efficiency. The power conversion efficiency of the DSSCs based on the **XS9** reached 4.54%. The lower efficiency of these four dyes compared to literature reports (η=9%) is mainly ascribed to the lack of broad absorption in the visible spectrum. It is possible to develop highly efficient organic sensitizers through expansion of π-electron systems between TPA donor and acceptor to broaden spectral response. The more conjugated organic dyes by functionalized thiophene units were desired to induce broader absorption in the visible spectrum, and these works are now in progress.

3. Experimental section

3.1. Materials and instruments

The FTO conducting glass (fluorine doped SnO_2, sheet resistance 10 Ω/square, transmission >90% in the visible) was obtained from Nippon Sheet Glass, Hyogo, Japan, and cleaned by a standard procedure. All reactions and manipulations were carried out under argon atmosphere with the use of Schlenk techniques. Diethyl ether and THF were distilled from Na/benzophenone under nitrogen atmosphere. Dichloromethane and chloroform were distilled from calcium hydride under nitrogen atmosphere. Titanium (IV) isopropoxide and tertbutylpyridine were purchased from Aldrich. Lithium iodide was purchased from Alfa. The starting materials diethyl bis(4-(dimethylamino)phenyl)methylphosphonate (**1**) and 4-bromo-*N*-(4-bromophenyl)-*N*-phenylbenzenamine (**13**) were synthesized following the known procedure.[11,22]

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-300 or AM-400 spectrometer. Mass spectra were recorded on a LCQ AD (Thermofinnigan, USA) mass spectrometer. The melting point was taken on a RY-1 thermometer and temperatures were uncorrected.

3.2. Photophysical and electrochemical measurements

The absorption spectra of the dyes either in solution or on the adsorbed TiO_2 films was measured by HITACHI U-3310 spectrophotometer. Adsorption of the dye on the TiO_2 surface was done by soaking the TiO_2 electrode in a dry chloroform solution of the dye (standard concentration 3×10^{-4} M) at room temperature for 24 h. Fluorescence measurement was carried with a HITACHI F-4500 fluorescence spectrophotometer. FT-IR spectra were obtained with a Bio-Rad FTS 135 FT-IR instrument.

Electrochemical measurements were performed at room temperature under Ar atmosphere on a Voltammetric Analyzer (Metrohm, μAutolab III) with polymer coated ITO glass as the working electrode, and platinum (Pt) plate as the counter electrode, using Ag/Ag$^+$ (nonaqueous) electrode as reference electrode with a scan rate of 50 mV/s. Tetrabutylammonium perchlorate (TBAP, 0.1 mol/L) and acetonitrile were used as supporting electrolyte and solvent, respectively. The measurements were calibrated using ferrocene as standard. The redox potential of ferrocene internal reference was taken as 0.63 V versus NHE. The solutions were purged with argon and stirred for 15 min before the measurements.

3.3. Fabrication of DSSCs

TiO_2 colloid was prepared according to the literature,[23] which was used for the preparation of the nanocrystalline films. The TiO_2 paste consisting of 18 wt % TiO_2, 9 wt % ethyl cellulose and 73 wt % terpineol was firstly prepared, which was printed on a conducting glass using a screen printing technique. The thickness of the TiO_2 film was controlled by selection of screen mesh size and repetition of printing. A second layer of commercial TiO_2 (P25) anatase particles was applied. The film was dried in air at 120 °C for 30 min and calcined at 500 °C for 30 min under flowing oxygen before cooling to room temperature. The heated electrodes were impregnated with a 0.05 M titanium tetrachloride solution in a water-saturated desiccator at 70 °C for 30 min and then recalcined at 500 °C for 30 min. The as-prepared TiO_2 electrode was stained by immersing it into a dye solution containing 300 μM dye sensitizers and 2 mM chenodeoxycholic acid (CDCA) in a mixture of chloroform and methanol (volume ratio 10/1) for 24 h. The CDCA was employed as a co-adsorbate to prevent dye aggregations on the TiO_2 surface. Pt catalyst was deposited on the FTO glass by coating with a drop of H_2PtCl_6 solution (40 mM in ethanol) with the heat treatment at 395 °C for 15 min to give photoanode. The photocathode (the dye-deposited TiO_2 film) was placed on top of the counter electrode and was tightly clipped together to form a cell. Electrolyte was then injected into the seam between two electrodes. The electrolyte employed was a solution of 0.6 M 1,2-dimethyl-3-*n*-propylimidazolium iodide (DMPImI), 0.1 M LiI, 0.05 M I_2, and 0.5 M tertbutylpyridine in acetonitrile.

3.4. Characterization of DSSCs

The photocurrent–voltage (I–V) characteristics of solar cells were carried out using a Keithley 2400 digital source meter controlled by a computer and a standard AM 1.5 solar simulator-Oriel 91160–1000 (300 W) SOLAR SIMULATOR 2×2 BEAM. The active electrode area was 0.16 cm^2. The action spectra of monochromatic incident photon-to-current conversion efficiency (IPCE) for solar cells were performed by using a commercial setup (QTest Station 2000 IPCE Measurement System, CROWNTECH, USA).

3.5. The detailed experimental procedures and characterization data

*3.5.1. 4,4′-(2-(4-Bromophenyl)ethane-1,1-diyl)bis(N,N-dimethylaniline) (**2**).* To a suspension of diethyl bis(4-(dimethylamino) phenyl) methylphosphonate (**1**) (1.5 g, 3.6 mmol) in 20 mL dry THF at 0 °C under N_2, Bu^{t}OK (0.6 g, 5.4 mmol) was added and the mixture turned yellow. The mixture was stirred at this temperature for 1 h before 4-bromobenzaldehyde (0.686 g, 3 mmol) dissolved in 10 ml dry THF was added dropwise. The mixture was stirred at 0 °C for 1 h and moved into room temperature for another 12 h. Saturated NH_4Cl was added and the resulting mixture was extracted with EtOAc (3×20 mL). The combined extracts were washed with water and dried over $MgSO_4$. After filtration and removal of the solvent under vacuum, the crude product was recrystallized from petroleum to give a yellow product (0.909 g, 60%). Mp: 162–163 °C. IR (KBr): 2992, 2888, 2804, 1888, 1606 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.45 (d, J=8.4 Hz, 2H), 7.26–7.22 (m, 4H), 6.93 (d, J=8.4 Hz, 2H), 6.67 (d, J=8.4 Hz, 5H), 2.98 (s, 6H), 2.96 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.2, 149.9, 143.8, 137.8, 132.1, 130.9, 130.8, 128.8, 128.1, 122.4, 119.2, 112.3, 112.0, 40.6, 40.5. HRMS (ESI) calcd for $C_{24}H_{25}N_2Br$ (M^+): 420.1201, found: 420.1196.

*3.5.2. 4-(2,2-Bis(4-(dimethylamino)phenyl)vinyl) phenylboronic acid (**3**).* A solution of compound **2** (0.421 g, 1.0 mmol) in dry THF (10 mL) was cooled to −78 °C. To this solution *n*-BuLi (0.42 mL, 2.7 M in hexane, 1.134 mmol) was added dropwise through a dropping funnel. The mixture was stirred at this temperature for 3 h before 7.8 g of trimethyl borate (0.28 mL, 2.5 mmol) dissolved in 20 mL of dry THF was added in a dropwise manner. The solution was allowed to warm to room temperature and stirred for 12 h. The reaction was quenched with saturated NH_4Cl, extracted with chloroform and dried over $MgSO_4$. After filtration and removal of the solvent under vacuum, the product was purified by a silica gel column (petroleum/ethyl acetate=3:1 as eluent) to give a kelly powder (0.27 g, 70% yield). Mp: 67–69 °C. IR (KBr): 3479, 3416, 3242, 1610, 1519 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.32–7.27 (m, 4H), 7.14–7.10 (m, 5H), 6.73–6.70 (m, 4H), 3.03(s, 3H), 3.00 (s, 3H), 2.99 (s, 3H), 2.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.6, 149.3, 131.4, 130.6, 130.0, 129.3, 128.9, 128.5, 127.9, 115.0, 112.9, 112.3, 112.2, 112.1, 40.9, 40.7, 40.68, 40.60. HRMS (ESI) calcd for $C_{24}H_{27}BN_2O_2$ (M+H^+): 387.2244, found: 387.2257.

*3.5.3. 4-((4-Bromophenyl)(phenyl)amino) benzaldehyde (**5**)*[22b]. A mixture of *N*-bromosuccinimide (5.34 g, 30 mmol), triphenylamine (**4**) (7.65 g, 30 mmol), and 80 mL of CCl_4 was refluxed for 4 h. After cooling to room temperature, the precipitate was filtered off and recrystallized from EtOH to give 4-bromo-*N*,*N*-diphenylaniline as a buff powder (8.747 g, 89.9% yield). To a solution of 4-bromo-*N*,*N*-diphenylaniline (3.849 g, 11.87 mmol) in anhydrous DMF (12 mL, 152 mmol) at 0 °C under N_2 atmosphere was added $POCl_3$ (4.33 mL, 29 mmol) dropwise and stirred for 1 h. Subsequently, the mixture was heated at 50 °C for 12 h. The mixture was cooled and poured into an ice-water with vigorous stirring. After neutralization with NaOH, the mixture was further stirred at 70 °C for 1 h. After cooling and extraction with ethyl acetate, the organic fractions were combined and dried over $MgSO_4$. The resulting solid was purified by column chromatography on silica gel (petroleum/ethyl acetate=5:1 as eluent) to give a buff powder (4.157 g, 99.4% yield). IR (KBr): 1686, 1604, 1588, 1576, 1505, 1487, 818 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 9.85 (s, 1H), 7.71 (d, J=8.0 Hz, 2H), 7.47 (d, J=8.0 Hz, 2H), 7.39–7.35 (m, 2H), 7.23–7.16 (m, 3H), 7.07–7.03 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.4, 152.9, 145.9, 145.4, 132.8, 131.4, 130.2, 129.9, 127.4, 126.3, 125.4, 120.0, 117.7.

*3.5.4. 4-((4′-(2,2-Bis(4-(dimethylamino) phenyl)vinyl)biphenyl-4-yl)(phenyl)amino) benzaldehyde (**6**).* A mixture of compound **5** (0.352 g, 1 mmol), 4-(2,2-bis(4-(dimethy lamino)phenyl)vinyl)phenylboronic acid (**3**) (0.425 g, 1.1 mmol), $Pd(PPh_3)_4$ (50 mg, 0.042 mmol), aqueous 1 M Na_2CO_3 (3 mL), and 10 mL DME was refluxed for 18 h under N_2. Ethyl acetate was added before cooling down to room temperature. The organic layer was separated and washed three times with water, dried over anhydrous $MgSO_4$, and filtered. After removing the solvent, the resulting solid was purified by column chromatography on silica gel (petroleum/ethyl acetate=10:1 as eluent) as a yellow powder (45%). Mp: 128–129 °C. IR (KBr): 3449, 3030, 2886, 2799, 1689, 1608 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 9.82 (s, 1H), 7.70 (d, J=8.7 Hz, 2H), 7.53 (d, J=7.6 Hz, 2H), 7.39–7.33 (m, 4H), 7.28–7.25 (m, 2H), 7.21–7.05 (m, 11H), 6.78 (s, 1H), 6.72–6.67 (m, 4H), 3.00 (s, 6H), 2.98 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.5, 153.3, 150.1, 149.8, 146.2, 145.1, 143.2, 138.0, 137.5, 137.1, 132.4, 131.4, 129.8, 129.4, 128.8, 128.6, 127.9, 126.4, 126.3, 126.2, 125.2, 123.3, 119.7, 112.4, 112.1, 40.6, 40.5. HRMS (ESI) calcd for $C_{43}H_{40}N_3O$ (M+H^+): 613.3093, found: 613.3090.

*3.5.5. 3-(4-((4′-(2,2-Bis(4-(dimethylamino) phenyl)vinyl)biphenyl-4-yl)(phenyl)amino)phenyl)-2-cyanoacrylic acid (**XS6**).* To a solution of compound **6** (0.184 g, 0.3 mmol) and cyanoacetic acid (0.042 g, 0.5 mmol) in acetonitrile (10 mL) was added dichlormethane (5 mL) and piperidine (50 μL). The solution was refluxed for 24 h. After cooling the solution, the solvent was removed in vacuo. The pure product was obtained by silica gel chromatography (CH_2Cl_2/MeOH=10:1 as eluent) as an orange powder in 92% yield. Mp: 176–179 °C. IR (KBr): 3434, 2210, 1592 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ 7.87–7.85 (m, 3H), 7.79 (d, J=8.7 Hz, 2H), 7.62 (d, J=8.4 Hz, 2H), 7.43 (d, J=8.4 Hz, 2H), 7.37 (d, J=7.5 Hz, 2H), 7.20–7.07 (m, 9H), 6.93 (d, J=7.5 Hz, 2H), 6.76 (s, 1H), 6.71 (d, J=8.7 Hz, 2H), 6.66 (d, J=8.7 Hz, 2H), 2.92 (s, 6H), 2.90 (s, 6H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 165.1, 150.8, 150.6, 150.5, 148.6, 146.8, 146.1, 143.5, 138.3, 137.2, 136.4, 132.2, 132.1, 132.0, 131.6, 130.8, 130.4, 129.2, 128.4, 128.3, 126.7, 126.6, 126.4, 125.9, 123.2, 121.2, 120.2, 113.2, 112.8, 44.4. HRMS (EI) calcd for $C_{45}H_{40}N_4$ ($[M-CO_2]^+$): 636.3253, found: 636.3259.

*3.5.6. 4-(Phenyl(4-(thiophen-2-yl)phenyl)amino) benzaldehyde (**7**).* A mixture of compound **5** (3.52 g, 10 mmol), thiophen-2-ylboronic acid (1.408 g, 11 mmol), $Pd(PPh_3)_4$ (300 mg, 0.255 mmol), aqueous 1 M Na_2CO_3 (25 mL), and 45 mL DME was refluxed for 18 h under N_2. Ethyl acetate (20 mL) was added before cooling down to room temperature. The organic layer was separated and washed three times with water, dried over anhydrous $MgSO_4$, and filtered. After removing the solvent, the resulting solid was purified by column chromatography on silica gel (petroleum/ethyl acetate=5:1 as eluent) to give a yellow powder (2.84 g, 86% yield). Mp: 126–127 °C. IR (KBr): 2739, 1685, 1585 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 9.82 (s, 1H), 7.70 (d, J=7.4 Hz, 2H), 7.57 (d, J=6.7 Hz, 2H), 7.38–7.33 (m, 2H), 7.28–7.15 (m, 7H), 7.14–7.06(m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.6, 153.3, 146.2, 145.7, 143.9, 131.5, 131.3, 130.0, 129.8, 128.3, 127.4, 126.6, 126.4, 125.5, 125.0, 123.2, 120.1. HRMS (ESI) calcd for $C_{23}H_{18}NOS$ (M+H^+): 356.1104, found: 356.1109.

*3.5.7. 4-((4-(5-Bromothiophen-2-yl)phenyl) (phenyl)amino)benzaldehyde (**8**).* Compound **7** (6.606 g, 9.379 mmol) and NBS (1.669 g, 9.379 mmol) were dissolved in DMF (100 mL) and stirred at room temperature for 24 h. The mixture was poured into water (100 mL) and leading to a precipitate yellow solid. The precipitate was filtered and purified by chromatography on silica gel (petroleum/ethyl acetate=5:1 as eluent) to give a yellow solid (4.01 g, 98% yield). Mp: 107–109 °C. IR (KBr): 2803, 1695, 459 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 9.83 (s, 1H), 7.72 (d, J=6.9 Hz, 2H), 7.46 (d, J=6.7 Hz, 2H), 7.39–7.34 (m, 2H), 7.22–7.06 (m, 7H), 7.05–7.00 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.6, 153.2, 146.1, 145.3, 133.1, 131.5, 131.2, 130.3, 129.9, 127.7, 127.0, 126.6, 126.2, 125.6, 123.3, 120.3, 111.5. HRMS (ESI) calcd for $C_{23}H_{17}NOSBr$ (M+H^+): 434.0209, found: 434.0197.

*3.5.8. 4-((4-(5-(4-(2,2-Bis(4-(dimethylamino) phenyl)vinyl)phenyl)-thiophen-2-yl)phenyl)(phenyl) amino)benzaldehyde (**9**).* The product was synthesized according to the procedure for synthesis of compound **6**, giving an orange powder of the product in 84% yield. Mp: 126–128 °C. IR (KBr): 2795, 1748, 1508 cm^{-1}. ^1H NMR (300 MHz,

$CDCl_3$): δ 9.82 (s, 1H), 7.70 (d, J=6.9 Hz, 2H), 7.55 (d, J=6.7 Hz, 2H), 7.40–7.33 (m, 4H), 7.27–7.20 (m, 5H), 7.18–7.11 (m, 5H), 7.07 (d, J=4.4 Hz, 5H), 6.74–6.65 (m, 5H), 2.99 (s, 6H), 2.97 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.6, 153.3, 150.3, 150.0, 146.2, 142.3, 138.5, 132.5, 131.6, 131.2, 130.1, 130.0, 129.7, 129.0, 128.7, 126.9, 126.6, 126.4, 125.5, 125.1, 124.2, 123.8, 123.4, 120.1, 112.6, 112.2, 40.7. HRMS (ESI) calcd for $C_{47}H_{42}N_3OS$ (M+H$^+$): 696.3043, found: 696.3018.

*3.5.9. 3-(4-((4-(5-(4-(2,2-Bis(4-(dimethylamino) phenyl)vinyl)phenyl)-thiophen-2-yl)(phenyl) amino)phenyl))-2-cyanoacrylic acid (**XS7**).* The product was synthesized according to the procedure for synthesis of **XS6**, giving an orange powder of the product in 92% yield. Mp: 174–175 °C. IR (KBr): 3565, 3446, 1791, 1772, 1749, 1700, 1683, 1653 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (s, 1H), 7.87 (d, J=7.6 Hz, 2H), 7.55 (d, J=7.6 Hz, 2H), 7.41–7.36 (m, 5H), 7.28–7.02 (m, 15H), 6.79–6.76 (m, 4H), 3.02 (s, 6H), 3.00 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.4, 154.2, 152.1, 149.8, 149.6, 145.6, 144.9, 143.9, 143.0, 142.1, 138.1, 133.2, 131.4, 129.9, 129.8, 129.6, 129.1, 128.8, 126.7, 126.5, 126.2, 126.0, 125.6, 124.9, 124.0, 123.6, 119.7, 112.9, 112.6, 79.1, 40.8. HRMS (ESI) calcd for $C_{50}H_{43}N_4O_2S$ (M+H$^+$): 763.3101, found: 763.3090.

*3.5.10. 4-((4-(2,2′-Bithiophen-5-yl)phenyl) (phenyl)amino)benzaldehyde (**10**).* A mixture of compound **8** (2.118 g, 4.88 mmol), $Pd(PPh_3)_4$ (150 mg, 0.127 mmol), thiophen-2-ylboronic acid (0.687 g, 5.37 mmol), aqueous 1 M Na_2CO_3 (15 mL), and 25 mL DME was refluxed for 18 h under N_2. Ethyl acetate (10 mL) was added before cooling down to room temperature. The organic layer was separated and washed three times with water, dried over anhydrous $MgSO_4$, and filtered. After removing the solvent, the resulting solid was purified by column chromatography on silica gel (petroleum/ethyl acetate=5:1 as eluent) to give a yellow powder (1.489 g, 70%). Mp: 170–172 °C. IR (KBr): 3742, 3687, 2816, 1506 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.83 (s, 1H), 7.72 (d, J=6.6 Hz, 2H), 7.55 (d, J=6.9 Hz, 2H), 7.39–7.33 (m, 2H), 7.26–7.12 (m, 9H), 7.10–7.02 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.6, 153.2, 146.2, 145.8, 142.5, 137.6, 136.9, 131.6, 130.8, 130.1, 129.8, 128.1, 127.0, 126.6, 126.3, 125.6, 124.9, 124.7, 123.9, 123.8, 120.2. HRMS (ESI) calcd for $C_{27}H_{20}NOS_2$ (M+H$^+$): 438.0981, found: 438.0973.

*3.5.11. 4-((4-(5′-Bromo-2,2′-bithiophen-5-yl)phenyl)(phenyl)amino)benzaldehyde (**11**).* Compound **10** (2.149 g, 4.919 mmol) and NBS (0.876 g, 4.919 mmol) were dissolved in DMF (50 mL) and stirred at room temperature for 24 h. The mixture was poured into water (50 mL) and leading to precipitate yellow solid. The precipitate was filtered and purified by chromatography on silica gel (petroleum/ethyl acetate=5:1 as eluent) to give a yellow solid (2.371 g, 93%). Mp: 144–146 °C. IR (KBr): 3528, 3419, 1792, 1749, 1717, 1653, 1604 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.83 (s, 1H), 7.72 (d, J=7.2 Hz, 2H), 7.52 (d, J=6.6 Hz, 2H), 7.39–7.34 (m, 2H), 7.26–7.11 (m, 6H), 7.10–7.05 (m, 3H), 6.99 (d, J=3.9 Hz, 1H), 6.93 (d, J=3.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.6, 153.2, 146.1, 146.0, 143.1, 135.8, 131.5, 130.9, 130.5, 130.1, 129.9, 127.0, 126.6, 126.2, 125.6, 125.1, 123.9, 123.8, 120.3. HRMS (ESI) calcd for $C_{27}H_{19}NOS_2Br$ (M+H$^+$): 516.0086, found: 516.0071.

*3.5.12. 4-((4-(5′-(4-(2,2-Bis(4-(dimethylamino) phenyl)vinyl)phenyl)-2,2′-bithiophen-5-yl) phenyl)(phenyl)amino)benzaldehyde (**12**).* The product was synthesized according to the procedure for synthesis of compound **6**, giving a salmon pink powder of the product in 52% yield. Mp: 201–202 °C. IR (KBr): 2803, 1756, 1506 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.82 (s, 1H), 7.70 (dd, J=6.8, 2.0 Hz, 2H), 7.53 (dd, J=6.5, 2.0 Hz, 2H), 7.38–7.33 (m, 4H), 7.27–7.22 (m, 2H), 7.20–7.11 (m, 11H), 7.07 (d, J=7.5 Hz, 4H), 6.73–6.65 (m, 5H), 2.99 (s, 6H), 2.96 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.7, 153.2, 150.3, 150.0, 146.2, 145.7, 143.7, 143.6, 142.3, 138.6, 137.1, 136.2, 132.4, 131.6, 131.2, 130.8, 130.1, 130.0, 129.8, 129.0, 128.7, 126.9, 126.6, 126.3, 125.6, 125.2, 124.8, 124.6, 124.0, 123.5, 123.4, 120.2, 112.6, 112.2, 40.7. HRMS (ESI) calcd for $C_{51}H_{44}N_3OS_2$ (M+H$^+$): 778.2920, found: 778.2918.

*3.5.13. 3-(4-((4-(5′-(4-(2,2-Bis(4-(dimethylamino) phenyl)vinyl)phenyl)-2,2′-bithiophen-5-yl)phenyl) (phenyl)amino)phenyl)-2-cyanoacrylic acid (**XS8**).* The product was synthesized according to the procedure for synthesis of **XS6**, giving a salmon pink powder of the product in 68% yield. Mp: 233–234 °C. IR (KBr): 3649, 3446, 2215, 1653, 1608 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.93 (br s, 1H), 7.59–7.57 (m, 2H), 7.28–7.25 (m, 2H), 7.16–7.08 (m, 7H), 6.95–6.88 (m, 13H), 6.58–6.49 (m, 6H), 2.82 (s, 6H), 2.80 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.5, 151.7, 150.6, 149.9, 149.6, 145.6, 143.0, 141.8, 138.0, 136.5, 135.8, 132.3, 132.1, 131.2, 130.9, 130.1, 129.6, 128.6, 126.5, 126.1, 125.6, 125.1, 124.7, 124.4, 124.3, 123.6, 123.2, 120.3, 118.7, 112.7, 112.3, 112.0, 41.2. HRMS (ESI) calcd for $C_{54}H_{45}N_4O_2S_2$ (M+H$^+$): 845.2978, found: 845.2976.

*3.5.14. 5-(4-((4-Bromophenyl)(phenyl)amino) phenyl)thiophene-2-carbaldehyde (**14**).* A mixture of 4-bromo-*N*-(4-bromophenyl)-*N*-phenylbenzenamine (**13**) (0.806 g, 2 mmol), $Pd(PPh_3)_4$ (60 mg, 0.050 mmol), 5-formylthiophen-2-ylboronic acid (0.343 g, 2.2 mmol), aqueous 1 M Na_2CO_3 (6 mL), and 20 mL DME was refluxed for 18 h under N_2. Ethyl acetate (10 mL) was added before cooling down to room temperature. The organic layer was separated and washed three times with water, dried over anhydrous $MgSO_4$, and filtered. After removing the solvent, the resulting solid was purified by column chromatography on silica gel (petroleum/ethyl acetate=10:1 as eluent) to give a yellow powder (0.342 g, 39.4% yield). Mp: 132–134 °C. IR (KBr): 2796, 1663, 1591 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.88 (s, 1H), 7.74 (d, J=4.0 Hz, 1H), 7.55 (dd, J=6.8, 1.6 Hz, 2H), 7.41 (d, J=6.4 Hz, 2H), 7.40–7.18 (m, 3H), 7.15–7.07 (m, 5H), 7.02 (d, J=6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.6, 154.2, 148.6, 146.6, 141.6, 137.7, 132.7, 129.7, 127.4, 126.8, 126.3, 125.3, 125.2, 124.3, 123.9, 122.9, 116.2. HRMS (ESI) calcd for $C_{23}H_{17}NOSBr$ (M+H$^+$): 434.0209, found: 434.0201.

*3.5.15. 5-(4-((4′-(2,2-Bis(4-(dimethylamino) phenyl)vinyl)biphenyl-4-yl)(phenyl)amino)phenyl) thiophen-2-carbaldehyde (**15**).* The product was synthesized according to the procedure for synthesis of compound **6**, giving a yellow powder of the product in 42% yield. Mp: 204–205 °C. IR (KBr): 1654, 1608, 815 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.83 (s, 1H), 7.69 (d, J=3.9 Hz, 1H), 7.52–7.45 (m, 4H), 7.36–7.31 (m, 2H), 7.29–7.23 (m, 6H), 7.16–7.06 (m, 10H), 6.75 (s, 1H), 6.69–6.65 (m, 4H), 2.98 (s, 6H), 2.94 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 182.0, 154.3, 149.9, 148.9, 145.8, 137.7, 137.5, 136.2, 132.5, 131.4, 129.7, 129.5, 128.8, 127.6, 127.3, 126.0, 125.3, 125.1, 124.1, 123.4, 123.0, 122.7, 112.5, 112.2, 41.3. HRMS (ESI) calcd for $C_{47}H_{42}N_3OS$ (M+H$^+$): 696.3043, found: 696.3049.

*3.5.16. 3-(5-(4-((4′-(2,2-Bis(4-(dimethylamino) phenyl)vinyl)-biphenyl-4-yl)(phenyl)amino) phenyl)thiophen-2-yl)-2-cyanoacrylic acid (**XS9**).* The product was synthesized according to the procedure for synthesis of **XS6**, giving an orange powder of the product in 42.4% yield. Mp: >300 °C. IR (KBr): 2942, 2211, 1595, 1561, 1518, 1491 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.27 (br s, 1H), 7.49 (s, 1H), 7.31–7.28 (m, 2H), 7.24–7.13 (m, 8H), 7.07–7.02 (m, 5H), 6.99–6.96 (m, 5H), 6.89–6.87 (m, 2H), 6.73 (s, 1H), 6.65 (d, J=6.9 Hz, 4H), 2.93 (s, 6H), 2.86 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.5, 152.3, 149.8, 149.5, 148.1, 146.6, 145.6, 145.2, 142.7, 138.1, 137.4, 137.1, 135.7, 134.6, 132.5, 131.3, 129.7, 129.4, 128.7, 127.4, 127.1, 126.4, 125.9, 125.2, 124.8, 123.9, 123.5, 123.1, 122.5, 118.6, 112.7, 112.4, 41.3, 41.2. HRMS (ESI) calcd for $C_{50}H_{43}N_4O_2S$ (M+H$^+$): 763.3101, found: 763.3101.

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