Tetrahedron 69 (2013) 190–200

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Triazine dyes as photosensitizers for dye-sensitized solar cells

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ARTICLE INFO

Article history:
Received 13 June 2012
Received in revised form 9 October 2012
Accepted 16 October 2012
Available online 23 October 2012

Keywords:
Triazine
Triphenylamine
Dye-sensitized solar cells

ABSTRACT

A new series of triazine-containing donor–π-acceptor organic sensitizers (**TCT-**(**7**–**19**)) with broad absorptions and high molar extinction coefficients have been designed and synthesized based on our previous work. All these dyes were completely characterized by ^{1}H NMR, ESI-MS, EA, IR, UV–vis, and cyclic voltammetry. The photovoltaic performances of dye-sensitized solar cells (DSSCs) based on these dyes were investigated. The effect of conjugating length and terminating groups on the absorption properties and photovoltaic performances were discussed. An overall photon-to-electron conversion efficiency of 3.69% was achieved with the DSSC based on the dye **TCT-13** (J_{sc}=7.76 mA cm^{-2}, V_{oc}=691 mV, FF=68.8%) under AM 1.5G illumination (100 mW/cm^2).

1. Introduction

Due to the energy crisis, a variety of light-harvesting devices have been intensively investigated in recent years.[1] Among these devices, dye-sensitized solar cells (DSSCs) have received considerable attention since Gratzel's pioneering report in 1991.[2] Ruthenium-based dyes (such as N3, N719, and black dye) have been considered as the most efficient sensitizers, which have reached the promising solar-energy-to-electricity conversion efficiencies of 11% under AM 1.5 irradiation.[3] In view of the limited ruthenium resource, however, sensitizers based on non-Ru system are sorely needed. In this regard, conjugated donor–π-acceptor (D–π-A) chromophores have been intensively investigated as promising candidates due to their large molar extinction coefficient, tunable absorption wavelength, facile synthesis, and lower cost.[4] Recently, Gratzel's group reported the porphyrin-sensitized solar cells with the highest solar-energy-to-electricity conversion efficiencies of 12.3%.[5]

π-Conjugated compounds based on triazine have been studied as an attractive candidate in functional photoelectric materials owing to the intriguing structural and electronic properties of triazine moiety.[6] Structurally, triazine unit is a symmetric core with three active substituted places, which is promising for derivation through organic synthesis.[7] Moreover, triazine unit is a typical electron-accepting unit and would be able to improve the electron-injection and electron-transportation abilities of its conjugated derivates.[8] In our previous work, a new type of D–π-A organic sensitizers utilizing triazine as π spacer has been developed for DSSCs.[9] The cyanoacrylic acid dye **TCT-1** with two electron donating triphenylamine moieties exhibits better photovoltaic performance than other dyes with one donor moiety. The DSSC based on **TCT-1** shows a high open-circuit photovoltage (V_{oc}) of 757 mV, which is comparative with some reported excellent dyes. However, its short-circuit photocurrent densities (J_{sc}) is quite low (3.33 mA cm^{-2}) due to its narrow absorption. Based on these results, we decided to tailor the chemical structure to optimize their photovoltaic properties. The molecular structures of the new sensitizers designed and synthesized in this work are given in Figs. 1–3. Red-shifted and broadened absorptions were realized, DSSCs with better photovoltaic performance have been obtained. The correlations between structure, absorption, and photovoltaic performance were discussed.

2. Results and discussion

Increasing the conjugation length is an effective way to expand the absorption of D–π-A chromophores.[10] Therefore, we synthesized a series of π-conjugated linker between the triphenylamine and triazine in **TCT-1** according to the synthetic protocol illustrated in Schemes 1–3. Double aryl substitutions of the cyanuric chloride with the corresponding Grignard reagents gave **2a**,**b**. Compounds **3a**,**b** were obtained by bromination of **2a**,**b** using NBS.[11] The reactions of **3a**,**b** with triethyl phosphate in the presence of Lewis acid afford the Horner reagents **4a**,**b**.[12] The aldehydes **6a**,**b** were readily prepared by Suzuki coupling between 4-bromotriphenylamine and the aromatic

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http://dx.doi.org/10.1016/j.tet.2012.10.046

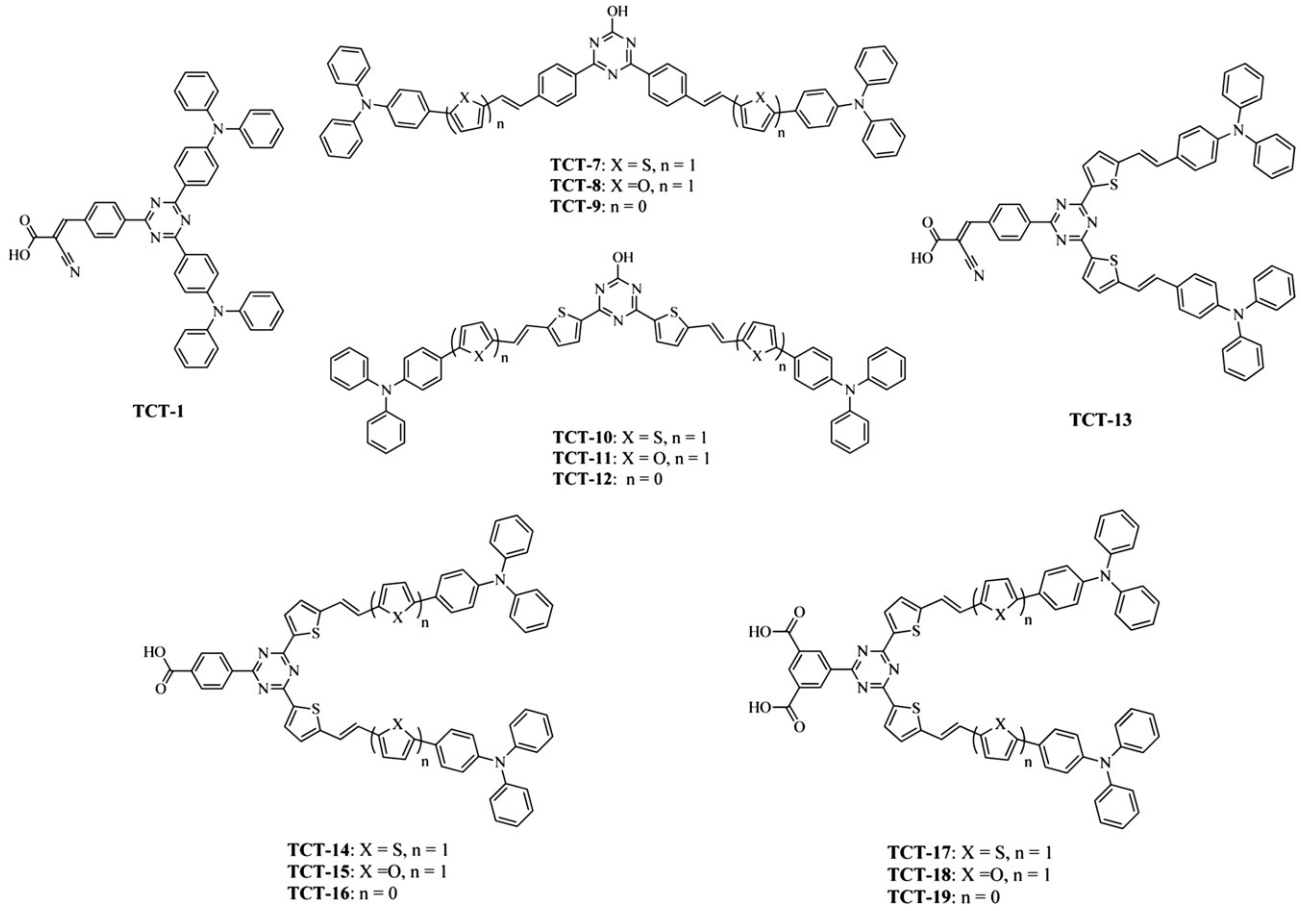


Fig. 1. Molecular structure of **TCT** dyes.

boron acids (**5a**,**b**). Compound **6c** was purchased from commercial suppliers and used as received. The subsequent reactions between **4a**,**b** and **6a**–**c** were carried out in anhydrous THF using sodium hydride as base. However, the Horner–Wadsworth–Emmons reactions didn't occur as expected. Instead, the chlorine was substituted by hydroxyl in the reaction to give **TCT-**(**7**–**12**) (Schemes 1 and 2). In order to obtain the mono-chlorine substituted triazine compounds, we also investigated other mild conditions, which may favor the Horner–Wadsworth–Emmons reactions. Unfortunately, only compound **7** was obtained in low yield (20%) from **4b** and **6c** when *t*-BuOK was used as base at 0 °C. Other reactions resulted in either no reaction or extremely low yields. The subsequent Suzuki coupling with 4-formylphenylboronic acid was performed to give compound **8** in moderate yield. Finally, the **TCT-13** was obtained through Knoevenagel reaction (Scheme 3).[13]

To compare with the hydroxyl dyes (**TCT-**(**7**–**12**)), we also designed and synthesized a series of dyes (**TCT-**(**14**–**19**)) with one or two carboxyl groups. The target compounds were synthesized in moderated overall yield through the routes described in Schemes 4 and 5. Suzuki coupling between **2b** and 4-ethoxycarbonylphenylboronic acid affords compound **9**, which was transformed to Horner reagent **13** through bromination and substitution by triethyl phosphate successively. The Horner–Wadsworth–Emmons reactions between **13** and **6a**–**c** and subsequent hydrolysis were carried out in THF using sodium hydride as base in one-pot to afford the desired mono-carboxyl dyes **TCT-**(**14**–**16**), respectively. The dyes **TCT-**(**17**–**19**) with two carboxyl groups were synthesized in a similar way.

The absorption spectra of **TCT-7**, **TCT-10**, **TCT-13**, **TCT-14**, **TCT-16**, **TCT-17**, and **TCT-19** in DMF are representatively presented in Fig. 2a, while the detailed parameters of all **TCT** dyes are collected in Table 1. All the **TCT** dyes show a strong absorption maximum in the visible region corresponding to intramolecular charge transfer absorption. In comparison with **TCT-1**, **TCT-13** exhibits 60 nm bathochromic shift owing to its longer conjugation as well as introducing another donor (thiophene unit), which enhance the intramolecular charge separation tendency. Similarly, **TCT** dyes containing additional furan rings exhibit significant bathochromic shift in absorption spectra as compared to their analogues.[10a] **TCT-10** and **TCT-11** with the longest conjugation length show the maximum red-shift in absorption peak (around 500 nm), which are comparable to the black dye.[3b] The dyes with two carboxyl groups (**TCT-**(**17**–**19**)) show similar absorption characteristics as those of the mono-carboxyl ones (**TCT-**(**14**–**16**)) without a distinct bathochromic shift. The absorption spectra of adsorbed **TCT** dyes on TiO_2 films are very similar to **TCT** dyes in DMF solution while the absorption peak wavelengths are red-shifted by 40–70 nm relatively (Fig. 2b). Such a red-shift is attributable to aggregation of the dyes on TiO_2 electrode as reported previously.[4c]

Cyclic voltammetry experiments were conducted on triazine dyes at room temperature to investigate their electrochemical properties. Both quasi-reversible oxidation and reversible reduction processes were observed in DMF solutions with 0.1 M *n*-Bu_4NClO_4 as a supporting electrolyte. The first oxidation potentials (E_{ox}), corresponding to the HOMO level of dyes, were calculated by using the oxidation potential (after being converted to the potential relative to the standard hydrogen electrode potential, NHE) and the Ag/AgCl energy level of −4.44 eV (relative to the vacuum level) as the standard.[14] The LUMO levels of sensitizer were estimated by the values of E_{ox} and the E_{0-0} band gaps, while the latter were estimated from the absorption spectra (absorption edge) of the compounds. The data are

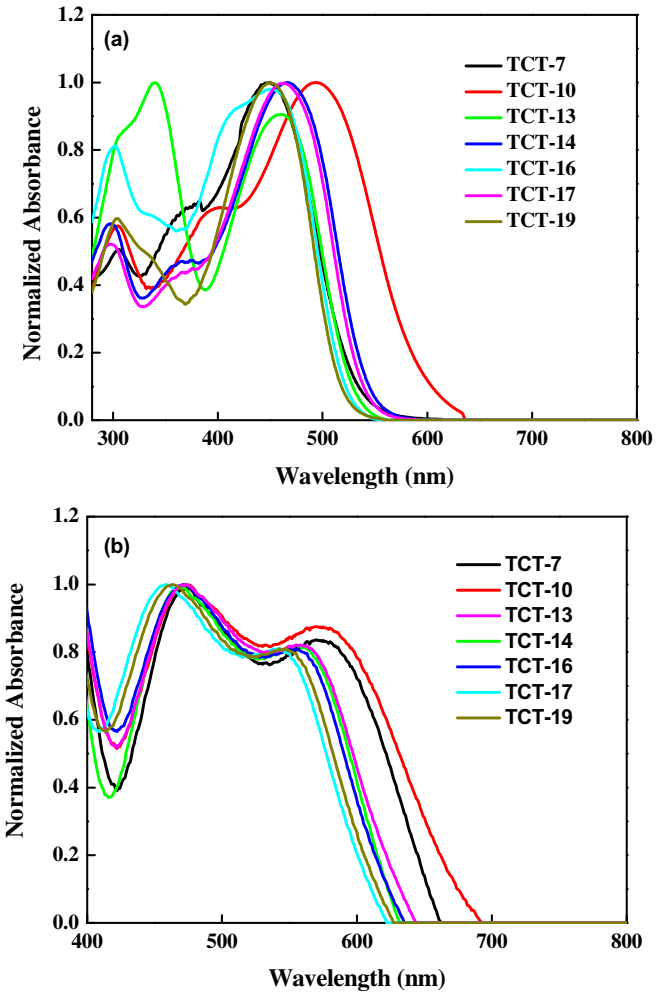


Fig. 2. Absorption of **TCT** dyes 2×10^{-5} M (a) in DMF and on TiO_2 film (b).

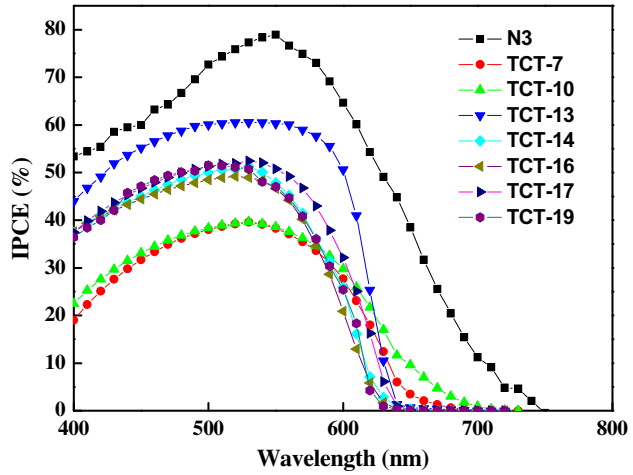


Fig. 3. IPCE values for DSSCs based on the **TCT** and **N3** dyes.

summarized in Table 1. The LUMO energy levels for these dyes are higher than the energy level of TiO_2 conduction band (−0.5 V vs NHE), indicating that these dyes can inject electrons to conduction band of TiO_2 electrode in their potential DSSCs applications.[15]

The photovoltaic performance of these dyes as the sensitizers for DSSCs was evaluated with a sandwich DSSC cell with 0.05 M iodine, 0.5 M LiI, and 0.05 M *tert*-butylpyridine in acetonitrile and *tert*-butanol (1:1, v/v) as the redox electrolyte (details of the device fabrication and characterization are described in the Experimental). The incident photon-to-current conversion efficiency (IPCE) spectra of **TCT-7**, **TCT-10**, **TCT-13**, **TCT-14**, **TCT-16**, **TCT-17**, and **TCT-19** are representatively depicted in Fig. 3. The photo-to-current conversion areas of these dyes lie in the range of 400–650 nm, which match well with the absorption spectra. The IPCE spectra of **TCT** dyes containing additional thiophene or furan rings extend to longer wavelengths as compared to their analogues. This feature is in agreement with the trend in absorption spectra.[16] The DSSCs based on **TCT-13** show IPCE >50% from 420 nm to 600 nm and IPCE maxima of 60% around 500 nm, which are the best among **TCT-**(**7**–**19**) and also better than that of **TCT-1**.

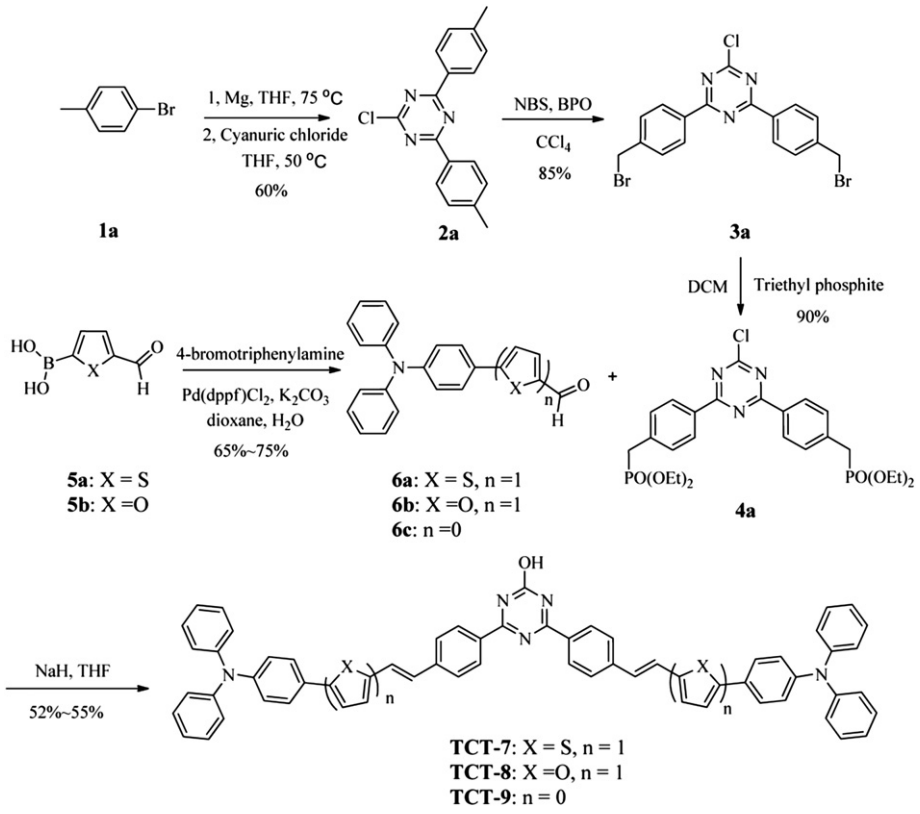
The photocurrent–voltage curves of **TCT-7**, **TCT-10**, **TCT-13**, **TCT-14**, **TCT-16**, **TCT-17**, and **TCT-19** are representatively shown in Fig. 4, while the detailed photovoltaic parameters of all **TCT** dyes were listed in Table 2. The short-circuit photocurrent densities (J_{sc}) are 3.07–7.76 mA cm^{-2}, and the open-circuit photovoltages (V_{oc}) are in the range from 0.583 V to 0.691 V. The solar-energy-to-electricity conversion yield values (η) of **TCT** dyes vary from 1.20% to 3.69%.

Two interesting observations can be made by comparing the absorption spectra of **TCT-**(**7**–**19**) with their photovoltaic performances. Firstly, the **TCT** dyes with terminating hydroxyl groups show poor photovoltaic performances in spite that they exhibit good absorption characteristics, indicating a lower electron-injecting efficiency from the LUMO orbital of the sensitizers to the conduct band of the TiO_2 through hydroxyl group.[17] Secondly, the di-carboxyl dye (e.g., **TCT-19**) exhibits better DSSCs performance than the corresponding mono-carboxyl ones (e.g., **TCT-16**), due to their better anchoring on the semiconductor surface, which results in higher electron-injecting efficiency into TiO_2.[18]

In **TCT-13**, the carboxyl and cyano groups are directly connected to −CH=CH− unit, which may play an important role in effective electron-injection into the conduction band of TiO_2, resulting the better photovoltaic performance as compared to other **TCT** dyes. In order to get further insight into this issue, frontier orbital calculations with density functional theory (DFT) methods were performed.[19] **TCT-13**, **TCT-16**, and **TCT-19** were chosen as the model compounds since they have the same conjugated length between triphenylamine moieties and triazine moieties. Fig. 5 shows the frontier molecular orbitals of **TCT-13**, **TCT-16**, and **TCT-19**. The highest occupied molecular orbitals (HOMOs) of these dyes are similar and mainly located in the electron donating triphenylamine moiety. However, the lowest unoccupied molecular orbitals (LUMOs) of **TCT-13** exhibit differences from those of **TCT-16** and **TCT-19**. For **TCT-13**, the LUMO is mainly distributed in triazine and cyanoacetic acid moieties, indicating that the HOMO–LUMO excitation moves the electron distribution from the triphenylamine moiety to the triazine and cyanoacetic acid unit, thus allowing an efficient photo-induced electron transfer from the dye to the TiO_2 electrode under light irradiation. In contrast, the LUMO orbitals of **TCT-16** and **TCT-19** are mainly located on triazine and thiophene moieties. Therefore, the excited electrons cannot be directly injected into the conduction band of TiO_2. They have to get across the phenyl moiety before injecting into the conduction band of TiO_2 via carboxyl groups, resulting in the relatively lower photovoltaic performance.

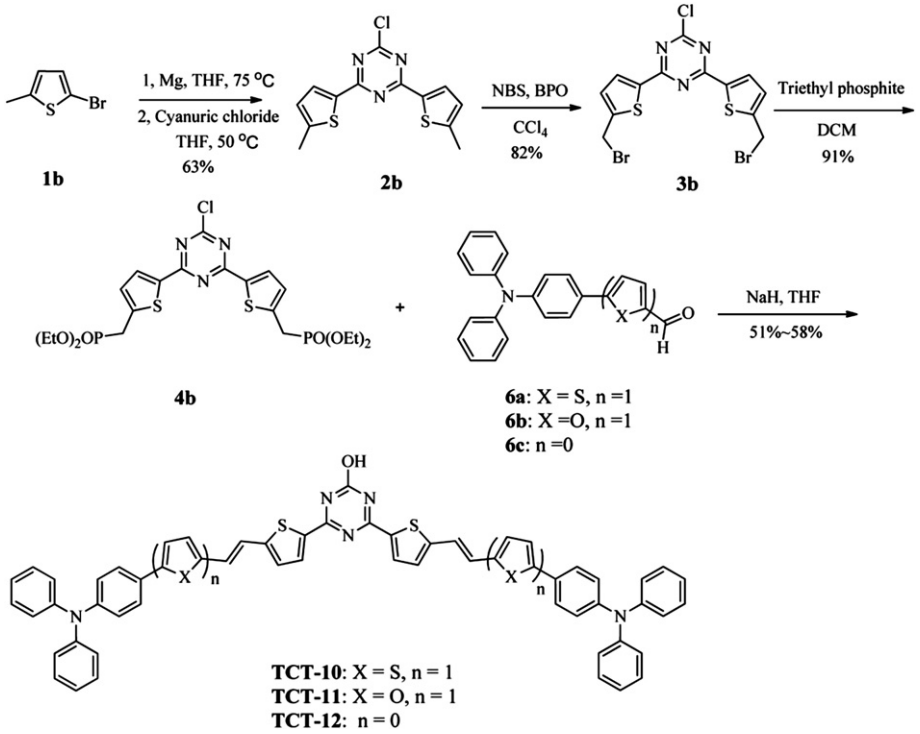
3. Conclusions

To summarize, a new series of triazine-containing donor–π-acceptor organic sensitizers with broad absorptions and high molar extinction coefficients have been designed and synthesized based on our previous work. The photovoltaic performances of DSSCs based on these dyes were investigated. Better photovoltaic

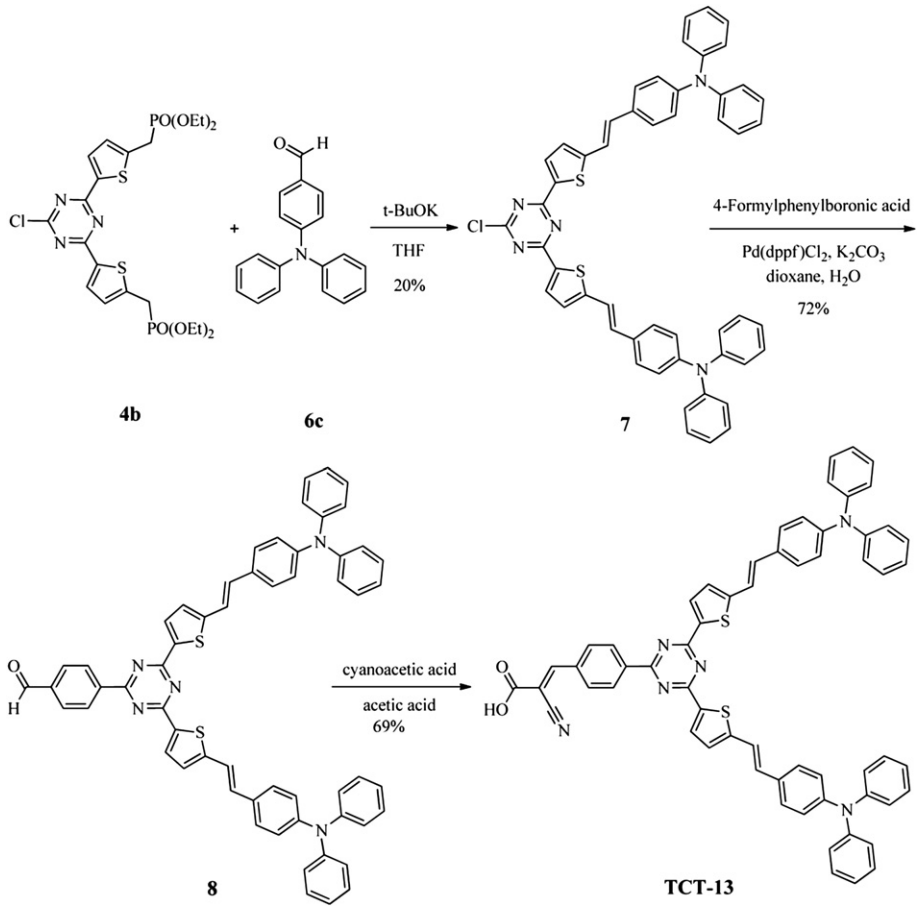


Scheme 1. Synthesis of **TCT-**(**7**–**9**).

performances have been realized through optimizing the chemical structure. The correlations between structure, absorption, and photovoltaic performance were discussed. The new type dyes with terminating hydroxyl group exhibit relatively poor photovoltaic performances due to inefficient electron-injecting from the LUMO orbital of the sensitizers to the conduct band of the TiO_2 through hydroxyl group. However, these dyes show strong and broad absorption in visible region, which are

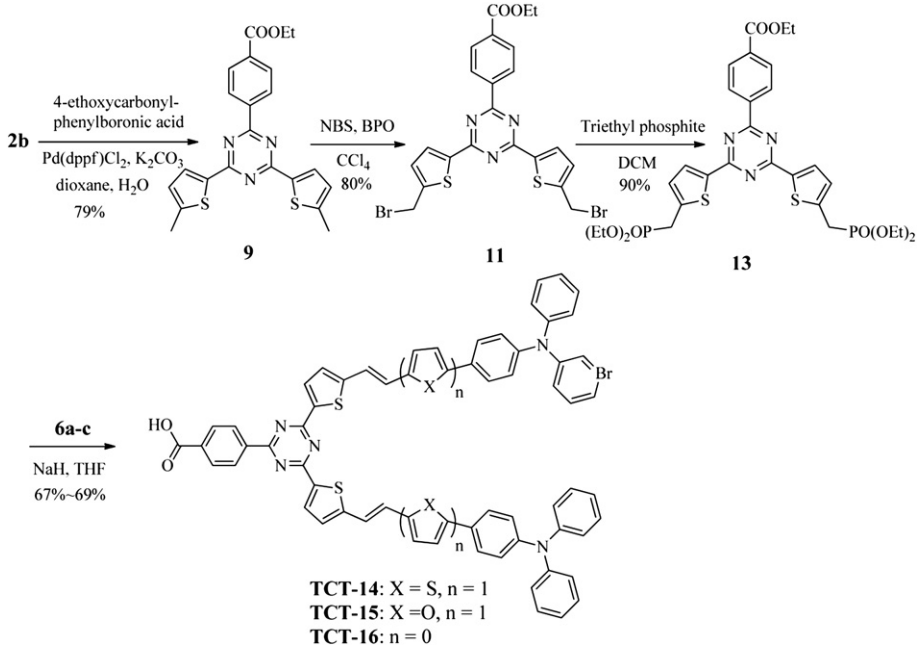


Scheme 2. Synthesis of **TCT-**(**10**–**12**).

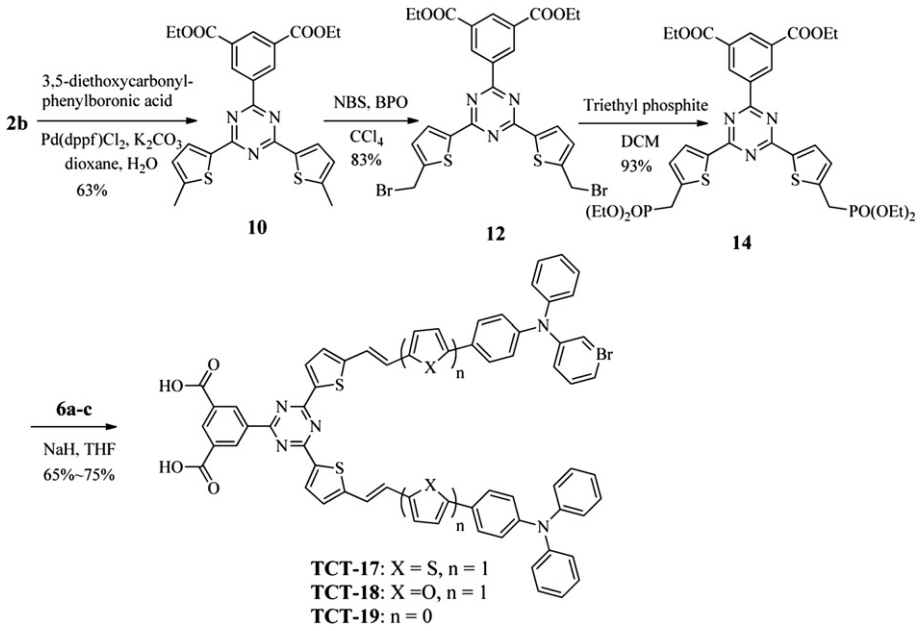


Scheme 3. Synthesis of **TCT-13**.

comparable to the black dye. Di-carboxyl dye exhibits better DSSCs performance than the corresponding mono-carboxyl ones due to their better anchoring on the semiconductor surface. Triazine dyes with cyanoacetic acid as the anchoring groups show good photovoltaic performances owning to their favorable spatial distribution in the LUMO orbital. All these results provide novel insights into the further design of efficient organic sensitizers based on triazine derivate dyes.



Scheme 4. Synthesis of **TCT-**(**14**–**16**).



Scheme 5. Synthesis of **TCT-**(**17**–**19**).

Table 1
Optical properties of **TCT** dyes in DMF and their energy levels of HOMO and LUMO

Dye	$\lambda_{max}/\varepsilon_{max}$ (nm/dm^3 mol^{-1} cm^{-1})	λ_{edge}/E_{0-0}[a] (nm/eV)	E_{HOMO}[b] (V)	E_{LUMO}[b,c] (V)
TCT-7	448/77,035, 306/39,100	614/2.02	1.26	−0.76
TCT-8	455/68,220, 361/55,050, 308/48,315	616/2.01	1.30	−0.71
TCT-9	436/66,580, 310/51,760	574/2.16	1.45	−0.71
TCT-10	493/61,254, 304/34,850	636/1.95	1.27	−0.68
TCT-11	498/63,720, 386/46,525, 305/45,160	639/1.94	1.31	−0.63
TCT-12	477/59,684, 366/34,950, 304/41,460	600/2.07	1.42	−0.65
TCT-13	459/75,840, 338/83,790	562/2.21	1.32	−0.89
TCT-14	465/81,340, 297/47,425	589/2.11	1.23	−0.88
TCT-15	479/79,215, 359/51,090, 299/53,860	590/2.10	1.24	−0.86
TCT-16	451/70,045, 302/58,140	555/2.24	1.34	−0.9
TCT-17	463/79,825, 297/42,240	593/2.09	1.24	−0.85
TCT-18	473/75,840, 357/48,645, 302/49,260	592/2.09	1.26	−0.83
TCT-19	451/72,490, 304/43,465	560/2.21	1.35	−0.86

[a] E_{0-0} was estimated by the absorption edge for the dyes in DMF.
[b] Versus normal hydrogen electrode (NHE).
[c] $E_{LUMO}=E_{ox}-E_{0-0}$.

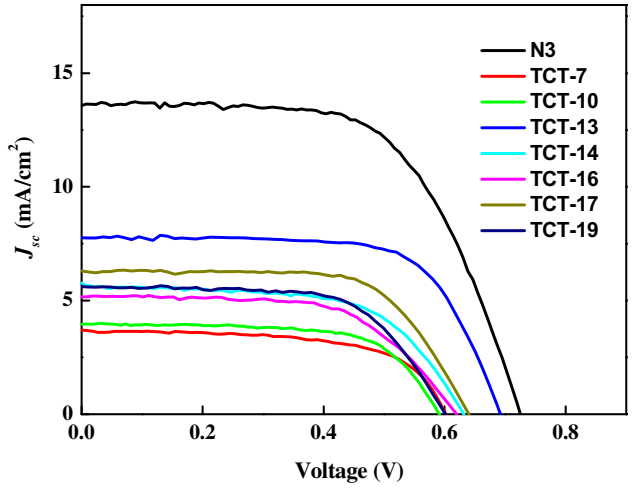


Fig. 4. Photocurrent density–voltage curves of DSSCs based on **TCT** dyes.

4. Experimental section

4.1. Materials and instruments

All reagents were purchased from commercial suppliers and used as received. Tetrahydrofuran (THF) was used after distillation under sodium and benzophenone. Elemental analyses for C, H, and N were performed on a Perkin–Elmer 240C analyzer. H NMR spectra were obtained on a DRX 500 NMR spectrometer. Chemical shifts are reported in parts per million (positive) downfield from TMS. Coupling constants are given in hertz. Mass spectra were acquired on LCQ Fleet ESI Mass Spectrometer.

4.2. Photophysical and electrochemical measurements

The absorption spectra of the triazine dyes either in solution or on the absorbed TiO_2 film were measured by Perkin–Elmer 950

Table 2
Photovoltaic performances of DSSCs based on **TCT** dyes

Dye	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	η (%)
TCT-1	757	3.32	71.8	1.81
TCT-7	602	3.65	62.1	1.37
TCT-8	615	3.72	59.5	1.36
TCT-9	607	3.07	64.4	1.20
TCT-10	591	3.97	66.1	1.55
TCT-11	611	4.16	59.5	1.51
TCT-12	608	3.49	56.3	1.20
TCT-13	691	7.76	68.8	3.69
TCT-14	631	5.65	61.1	2.17
TCT-15	614	6.18	61.1	2.32
TCT-16	619	5.21	60.9	1.97
TCT-17	639	6.29	67.0	2.70
TCT-18	583	6.58	72.2	2.77
TCT-19	601	5.60	64.1	2.15
N3	711	13.59	70.2	6.78

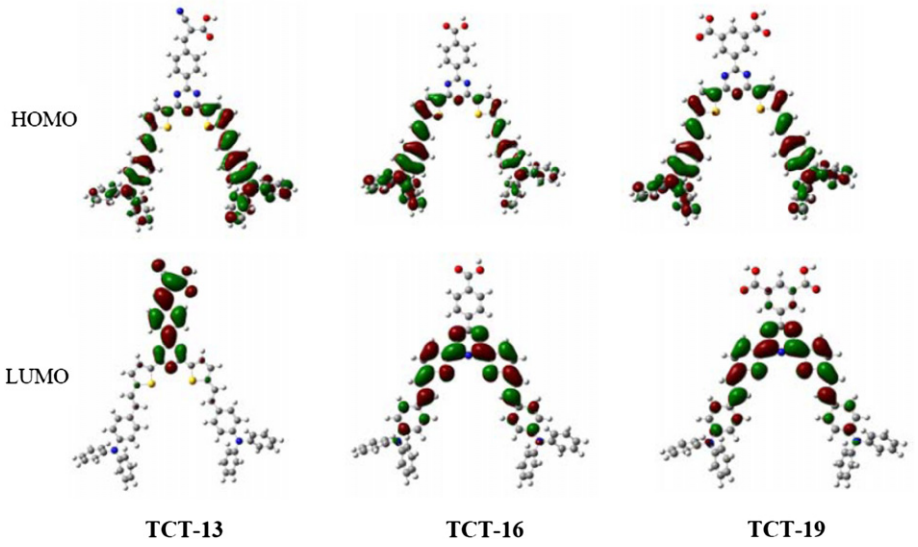


Fig. 5. Schematic representation of the frontier molecular orbitals of the HOMO and LUMO of **TCT** dyes by TDDFT calculations.

spectrophotometer. Absorption of the dye on the TiO_2 surface was done by soaking the TiO_2 electrode in DMF solutions at room temperature for 24 h. Infrared spectra were recorded on a Vector22 Bruker spectrophotometer with KBr pellets in the 400–4000 cm^{-1} region.

Electrochemical measurements were performed at room temperature on an Im6eX electrochemistry working station. All CV measurements were carried out in DMF containing 0.1 M TBAP as a supporting electrolyte, purged with argon prior to conduct the experiment. Platinum electrode, Ag/AgCl in saturated KCl (aq), and a platinum wire were used as working electrode, reference electrode, and counter electrode, respectively. The scan rate was 100 mV/s.

4.3. Fabrication of DSSCs

Photoanodes composed of transparent TiO_2 (20 nm) layer and FTO glass were obtained by following an already reported procedure.[20] The TiO_2 electrodes were immersed into the dye solution (0.5 mM in DMF). The dye-adsorbed TiO_2 electrode and Pt counter electrode were assembled into a sealed sandwich-type cell. A drop of electrolyte was then introduced into the cell, which was composed of 0.05 M iodine, 0.5 M LiI, and 0.05 M *tert*-butylpyridine in acetonitrile and *tert*-butanol (1:1, v/v). It was introduced into the inter-electrode space from the counter electrode side through predrilled holes.

4.4. Characterization of DSSCs

The photocurrent–voltage (I–V) was recorded under the simulated AM 1.5 irradiation (100 mW cm^{-2}) using a Keithley 2400 digital source meter controlled by a computer. The active electrode area was 0.36 cm^2. The IPCE spectra were measured under monochromatic irradiation with a xenon lamp and a monochromator.

4.5. DFT calculations

All calculations were carried out with Gaussian03 programs.[19] The geometries of the organic dyes were fully optimized by B3LYP method without any symmetry constraint. The calculations were carried out using the 6-31g* basis set for all the atoms.

4.6. The detailed experimental procedures and characterization data

*4.6.1. Synthesis of 2-chloro-4,6-di-p-tolyl-1,3,5-triazine (**2a**).* A solution of compound **1a** (17.1 g, 100 mmol) in anhydrous THF (120 mL) was added dropwise to a suspension of iodine-activated magnesium (2.88 g, 120 mmol) in anhydrous THF (20 mL) over 30 min. In the case of a delayed start to the reaction, brief heating was carried out. After complete addition, the reaction mixture was maintained for 3 h at reflux temperature and then cooled to room temperature. The Grignard solution was added dropwise to a solution of cyanuric chloride (6.53 g, 35.7 mmol) in anhydrous THF (50 mL) while the temperature was maintained at 0–10 °C. When the addition was completed, the mixture was stirred for 10 h at 50 °C and then poured into ice water (150 mL). The water suspension was extracted twice with DCM (300 mL). The organic phase was combined, washed with water and brine, dried over anhydrous sodium sulfate, and then concentrated. The residue was purified by flash chromatography on silica gel (hexane/DCM 10:1) to afford **2a** (6.3 g, 60%) as a white solid. IR (KBr, cm^{-1}): 1613, 1518, 1366, 1245, 1183, 802; ^1H NMR (500 MHz, $CDCl_3$): δ 7.62 (d, J=8.5 Hz, 4H), 7.36 (d, J=8.5 Hz, 4H), 2.52 (s, 6H). FABMS (m/z): 295.1 (M^+). Anal. Calcd for $C_{17}H_{14}ClN_3$: C, 69.03; H, 4.77; N, 14.21. Found: C, 68.91; H, 4.72; N, 14.02.

*4.6.2. Synthesis of 2-chloro-4,6-bis(5-methylthiophen-2-yl)-1,3,5-triazine (**2b**).* Compound **2b** was prepared as light yellow solid (6.9 g, 63% yield) from **1b** by using the method established for **2a**. IR (KBr, cm^{-1}): 1645, 1556, 1531, 1455, 789; ^1H NMR (500 MHz, $CDCl_3$): δ 8.06 (d, J=4.0 Hz, 2H), 6.89 (d, J=4.0 Hz, 2H), 2.60 (s, 6H). FABMS (m/z): 307 (M^+). Anal. Calcd for $C_{13}H_{10}ClN_3S_2$: C, 50.72; H, 3.27; N, 13.65. Found: C, 50.63; H, 3.21; N, 13.58.

*4.6.3. Synthesis of 2,4-bis(4-(bromomethyl)phenyl)-6-chloro-1,3,5-triazine (**3a**).* *N*-Bromosuccimide (NBS) (0.79 g, 22 mmol) was added to a stirred solution of compound **2a** (2.95 g, 10 mmol) in CCl_4 (50 mL). The mixture was heated under reflux. AIBN was added in catalytic amounts over a period of 1 h. After being cooled to room temperature, the mixture was filtered. The solid residue was washed with DCM (2×30 mL). The solvent was evaporated under reduced pressure, and the residue was purified by flash chromatograph on silica gel (hexane/DCM 10:1) to afford **3a** (3.83 g, 85%) as a white solid. IR (KBr, cm^{-1}): 1632, 1525, 1493, 1372, 802; ^1H NMR (500 MHz, $CDCl_3$): δ 8.61 (d, J=8.0 Hz, 4H), 7.67 (d, J=8.0 Hz,

4H), 4.58 (s, 4H). FABMS (*m*/*z*): 450.91 (M^+). Anal. Calcd for $C_{17}H_{12}Br_2ClN_3$: C, 45.02; H, 2.67; N, 9.26. Found: C, 44.92; H, 2.61; N, 9.15.

*4.6.4. Synthesis of 2,4-bis(5-(bromomethyl)thiophen-2-yl)-6-chloro-1,3,5-triazine (**3b**).* Compound **3b** was prepared as light yellow solid (5.9 g, 82% yield) from **2b** by using the method established for **3a**. IR (KBr, cm^{-1}): 1645, 1512, 1455, 1264, 1208, 802; ^1H NMR (500 MHz, $CDCl_3$): δ 8.10 (d, *J*=4.0 Hz, 2H), 7.22 (d, *J*=4.0 Hz, 2H), 4.75 (s, 4H). FABMS (*m*/*z*): 462.82 (M^+). Anal. Calcd for $C_{13}H_8Br_2ClN_3S_2$: C, 33.53; H, 1.73; N, 9.02. Found: C, 33.38; H, 1.75; N, 8.96.

*4.6.5. Synthesis of Horner reagent **4a**.* Triethyl phosphate (16.6 g, 100 mmol) was added to a stirred solution of **3a** (4.51 g, 10 mmol) in anhydrous DCM (50 mL), followed by Lewis acid as a catalyst. The resulting mixture was stirred at reflux for 12 h. After being cooled to rt, water (50 mL) was added. The mixture was extracted with DCM. The organic fraction was washed with brine, dried with anhydrous sodium sulfate, and evaporated. The residue was purified by column chromatography (hexane/EA 1:1) to afford **4a** (5.1 g, 90%) as a light yellow solid. IR (KBr, cm^{-1}): 2975, 1613, 1537, 1372, 1245, 1024, 967, 821; ^1H NMR (500 MHz, $CDCl_3$): δ 8.56 (d, *J*=7.5 Hz, 4H), 7.48 (d, *J*=7.5 Hz, 4H), 4.75 (q, *J*=6.5 Hz, 8H), 3.29 (s, 2H), 3.26 (s, 2H), 1.28 (t, *J*=6.5 Hz, 12H). FABMS (*m*/*z*): 567.15 (M^+). Anal. Calcd for $C_{25}H_{32}ClN_3O_6P_2$: C, 52.87; H, 5.68; N, 7.40. Found: C, 52.81; H, 5.61; N, 7.28.

*4.6.6. Synthesis of Horner reagent **4b**.* Compound **4b** was prepared as light yellow solid (5.3 g, 91% yield) from **3b** by using the method established for **4a**. IR (KBr, cm^{-1}): 2982, 1645, 1537, 1455, 1271, 1030, 802; ^1H NMR (500 MHz, $CDCl_3$): δ 8.11 (d, *J*=4.0 Hz, 2H), 7.11 (d, *J*=4.0 Hz, 2H), 4.13 (q, *J*=7.0 Hz, 8H), 3.46 (s, 2H), 3.41 (s, 2H), 1.33 (t, *J*=7.0 Hz, 12H). FABMS (*m*/*z*): 579.06 (M^+). Anal. Calcd for $C_{21}H_{28}ClN_3O_6P_2S_2$: C, 43.49; H, 4.87; N, 7.24. Found: C, 43.36; H, 4.81; N, 7.18.

*4.6.7. Synthesis of 5-(4-(diphenylamino)phenyl)thiophene-2-carbaldehyde (**6a**).* Water of 30 mL was added to a suspension of compound **5a** (2.40 g, 17.11 mmol), 4-bromotriphenylamine (4.62 g, 14.26 mmol), and potassium carbonate (5.9 g, 42.78 mmol) in 1,4-dioxane (120 mL), followed by adding of $PddppfCl_2$ (0.82 g, 1 mmol). The resulting mixture was stirred at 105 °C under argon atmosphere for 5 h. The solvent was evaporated under reduced pressure. The residue was treated with water (50 mL), extracted twice with DCM (80 mL×3). The organic layer was combined and washed twice with water and once with brine, dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the residue was purified by flash chromatography on silica gel column with PE/EA (10/1, v/v) as eluent to give a yellow solid (3.63 g, 75%). IR (KBr, cm^{-1}): 1670, 1588, 1486, 1448, 1284, 1227, 1055, 815, 745, 694; ^1H NMR (500 MHz, $CDCl_3$): δ 9.86 (s, 1H), 7.73 (d, *J*=4.5 Hz, 1H), 7.54 (d, *J*=9.0 Hz, 2H), 7.30–7.34 (m, 5H), 7.15–7.17 (m, 4H), 7.08–7.12 (m, 4H). FABMS (*m*/*z*): 355.1 (M^+). Anal. Calcd for $C_{23}H_{17}NOS$: C, 77.72; H, 4.82; N, 3.94. Found: C, 77.59; H, 4.72; N, 3.77.

*4.6.8. Synthesis of 5-(4-(diphenylamino)phenyl)furan-2-carbaldehyde (**6b**).* Compound **6b** was prepared as light yellow solid (5.4 g, 65% yield) from **5b** by using the method established for **6a**. IR (KBr, cm^{-1}): 1670, 1594, 1480, 1328, 1277, 1024, 751, 701; ^1H NMR (500 MHz, $CDCl_3$): δ 9.66 (s, 1H), 7.69 (d, *J*=4.5 Hz, 2H), 7.31–7.34 (m, 5H), 7.13–7.17 (m, 4H), 7.09–7.12 (m, 4H), 6.73 (d, *J*=3.5 Hz, 1H). FABMS (*m*/*z*): 339.1 (M^+). Anal. Calcd for $C_{23}H_{17}NO_2$: C, 81.40; H, 5.05; N, 4.13. Found: C, 81.29; H, 5.02; N, 4.05.

*4.6.9. Synthesis of N-(4-((1E)-2-(5-(4-(5-(4-(diphenylamino)styryl)thiophen-2-yl)-6-chloro-1,3,5-triazin-2-yl)thiophen-2-yl)vinyl)phenyl)-N-phenylbenzenamine (**7**).* *t*-BuOK (0.774 g, 6.91 mmol) was added to a solution of **4b** (2.0 g, 3.46 mmol) in dry THF (50 mL) at 0 °C. After initial effervescence the suspension was stirred for 1 h at 0 °C under argon. A solution of **6c** (2.08 g, 7.60 mmol) in dry THF (30 mL) was added dropwise. The mixture was stirred at 0 °C for additional 12 h and then quenched with HoAc. All solvents were then removed under reduced pressure. The remaining solid was dissolved in DCM, washed with distilled H_2O, and dried over $MgSO_4$. Evaporation of the solvent under vacuum, the crude product was purified by column chromatography with dichloromethane/hexane (1/1 v/v) as eluant to yield the desired product **7** as a wine-colored powder (0.564 g, 20%). IR (KBr, cm^{-1}): 1581, 1500, 1436, 1277, 758, 694; ^1H NMR (500 MHz, $CDCl_3$): δ 8.20 (d, *J*=4.0 Hz, 2H), 7.36 (d, *J*=8.0 Hz, 4H), 7.31–7.34 (m, 12H), 7.22 (d, *J*=16.0 Hz, 2H), 7.13–7.17 (m, 12H), 7.03 (d, *J*=8.0 Hz, 4H). FABMS (*m*/*z*): 817.2 (M^+). Anal. Calcd for $C_{51}H_{36}ClN_5S_2$: C, 74.84; H, 4.43; N, 8.56. Found: C, 74.76; H, 4.33; N, 8.39.

*4.6.10. Synthesis of 4-(4,6-bis(5-(4-(diphenylamino)styryl)thiophen-2-yl)-1,3,5-triazin-2-yl)benzaldehyde (**8**).* 4-Formylphenylboronic acid (0.112 g, 0.75 mmol), potassium carbonate (0.207 g, 1.5 mmol), and H_2O (10 mL) were added sequentially to a stirred solution of compound **7** (0.408 g, 0.5 mmol) in 1,4-dioxane (40 mL), followed by $PddppfCl_2$ (0.04 g, 0.05 mmol). The resulting mixture was stirred at 90 °C under argon atmosphere for 5 h. The solvent was evaporated under reduced pressure. The residue was treated with water (30 mL), extracted twice with DCM (40 mL×3). The organic layer was combined and washed twice with water and once with brine, dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the residue was loaded onto silica gel column with PE/EA (10:1, v/v) as eluent to give desired aldehyde as a red solid (0.32 g, 72%). IR (KBr, cm^{-1}): 1696, 1588, 1505, 1436, 1277, 758, 701; ^1H NMR (500 MHz, $CDCl_3$): δ 10.14 (s, 1H), 8.80 (d, *J*=8.5 Hz, 2H), 8.20 (d, *J*=3.5 Hz, 2H), 8.04 (d, *J*=8.5 Hz, 2H), 7.40 (d, *J*=8.5 Hz, 4H), 7.31–7.34 (m, 12H), 7.22 (d, *J*=16.0 Hz, 2H), 7.13–7.17 (m, 12H), 7.06 (d, *J*=8.5 Hz, 4H). FABMS (*m*/*z*): 887.3 (M^+). Anal. Calcd for $C_{58}H_{41}N_5OS_2$: C, 78.44; H, 4.65; N, 7.89. Found: C, 78.31; H, 4.58; N, 7.83.

*4.6.11. Synthesis of ethyl 4-(4,6-bis(5-methylthiophen-2-yl)-1,3,5-triazin-2-yl)benzoate (**9**).* Water of 10 mL was added to a suspension of compound **2b** (0.634 g, 2.05 mmol), 4-(ethoxycarbonyl) phenylboronic acid (0.49 g, 2.46 mmol), and potassium carbonate(0.85 g, 7.15 mmol) in 1,4-dioxane (40 mL), followed by $PddppfCl_2$ (0.23 g, 0.2 mmol). The resulting mixture was stirred at 90 °C under argon atmosphere for 8 h. The solvent was evaporated under reduced pressure. The residue was treated with water (40 mL), extracted twice with DCM (40 mL×3). The organic layer was combined and washed twice with water and once with brine, dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the residue was purified by column chromatography (hexane/EA 10:1) to afford **9** as a yellow solid (0.69 g, 79%). IR (KBr, cm^{-1}): 1721, 1581, 1512, 1461, 1366, 1277, 770; ^1H NMR (500 MHz, $CDCl_3$): δ 8.70 (d, *J*=8.5 Hz, 2H), 8.21 (d, *J*=8.5 Hz, 2H), 8.15 (d, *J*=3.5 Hz, 2H), 6.92 (d, *J*=3.5 Hz, 2H), 4.46 (q, *J*=7.0 Hz, 2H), 2.63 (s, 6H), 1.46 (t, *J*=7.0 Hz, 3H). FABMS (*m*/*z*): 421.1 (M^+). Anal. Calcd for $C_{22}H_{19}N_3O_2S_2$: C, 62.68; H, 4.54; N, 9.97. Found: C, 62.56; H, 4.48; N, 9.81.

*4.6.12. Synthesis of diethyl 5-(4,6-bis(5-methylthiophen-2-yl)-1,3,5-triazin-2-yl)benzene-1,3-dioate (**10**).* Water of 15 mL was added to a suspension of compound **2b** (1.29 g, 4.17 mmol), 3,5-di(ethoxycarbonyl)phenylboronic acid (1.36 g, 5.01 mmol), and potassium carbonate (1.8 g, 13.04 mmol) in 1,4-dioxane (60 mL), followed by $PddppfCl_2$ (0.34 g, 0.3 mmol). The resulting mixture was stirred at 90 °C under argon atmosphere for 12 h. The solvent was evaporated under reduced pressure. The residue was treated

with water (60 mL), extracted twice with DCM (50 mL×3). The organic layer was combined and washed twice with water and once with brine, dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the residue was purified by column chromatography (hexane/EA 10:1) to afford **10** as a yellow solid (1.3 g, 63%). IR (KBr, cm^{-1}): 1734, 1601, 1518, 1461, 1360, 1284, 1233, 1030, 758; ^1H NMR (500 MHz, $CDCl_3$): δ 9.42 (s, 2H), 8.80 (s, 1H), 8.17 (d, J=3.5 Hz, 2H), 6.91 (d, J=3.5 Hz, 2H), 4.52 (q, J=7.0 Hz, 4H), 2.62 (s, 6H), 1.51 (t, J=7.0 Hz, 6H). FABMS (m/z): 493.1 (M^+). Anal. Calcd for $C_{25}H_{23}N_3O_4S_2$: C, 60.83; H, 4.70; N, 8.51. Found: C, 60.66; H, 4.58; N, 8.40.

*4.6.13. Synthesis of compound **11**.* *N*-Bromosuccinimide (NBS) (0.59 g, 3.3 mmol) was added to a stirred solution of compound **9** (0.634 g, 1.5 mmol) in CCl_4 (30 mL). The mixture was heated under reflux. AIBN was added in catalytic amounts over a period of 1 h. After being cooled to room temperature, the mixture was filtered, and the solid residue was washed with DCM (2×30 mL). The solvent was evaporated under reduced pressure. The residue was purified by flash chromatograph on silica gel (hexane/EA 10:1) to afford **11** (0.69 g, 80%) as a yellow solid. IR (KBr, cm^{-1}): 1721, 1581, 1518, 1271, 770; ^1H NMR (500 MHz, $CDCl_3$): δ 8.69 (d, J=8.5 Hz, 2H), 8.21 (d, J=8.5 Hz, 2H), 8.15 (d, J=3.5 Hz, 2H), 7.23 (d, J=3.5 Hz, 2H), 4.79 (s, 4H), 4.46 (q, J=7.5 Hz, 2H), 1.46 (t, J=7.5 Hz, 3H). FABMS (m/z): 576.91 (M^+). Anal. Calcd for $C_{22}H_{17}Br_2N_3O_2S_2$: C, 45.61; H, 2.96; N, 7.25. Found: C, 45.46; H, 2.90; N, 7.11.

*4.6.14. Synthesis of compound **12**.* Compound **12** was prepared as light yellow solid (0.813 g, 83% yield) from **10** by using the method established for **11**. IR (KBr, cm^{-1}): 1721, 1518, 1468, 1239, 1018, 802, 758; ^1H NMR (500 MHz, $CDCl_3$): δ 9.41 (s, 2H), 8.89 (s, 1H), 8.18 (d, J=3.5 Hz, 2H), 7.24 (d, J=3.5 Hz, 2H), 4.79 (s, 4H), 4.52 (q, J=7.0 Hz, 4H), 1.52 (t, J=7.0 Hz, 6H). FABMS (m/z): 648.9 (M^+). Anal. Calcd for $C_{25}H_{21}Br_2N_3O_4S_2$: C, 46.10; H, 3.25; N, 6.45. Found: C, 46.02; H, 3.14; N, 6.41.

*4.6.15. Synthesis of compound **13**.* Triethyl phosphate (1.66 g, 10 mmol) was added to a stirred solution of **11** (0.577 g, 1 mmol) in anhydrous DCM (30 mL), followed by Lewis acid as a catalyst. The resulting mixture was stirred at reflux for 12 h. The solvent was evaporated under reduced pressure. The residue was purified by column chromatography (DCM/MeOH 20:1) to afford **13** (0.48 g, 90%) as a light yellow solid. IR (KBr, cm^{-1}): 2982, 1714, 1518, 1461, 1277, 1018, 770; ^1H NMR (500 MHz, $CDCl_3$): δ 8.43 (d, J=8.5 Hz, 2H), 8.06 (d, J=8.5 Hz, 2H), 7.89 (d, J=3.0 Hz, 2H), 7.11 (d, J=3.0 Hz, 2H), 4.43 (q, J=7.0 Hz, 2H), 4.33 (q, J=7.0 Hz, 8H), 3.56 (s, 2H), 3.51 (s, 2H), 1.47 (t, J=7.0 Hz, 3H), 1.38 (t, J=7.0 Hz, 12H). FABMS (m/z): 693.15 (M^+). Anal. Calcd for $C_{30}H_{37}N_3O_8P_2S_2$: C, 51.94; H, 5.38; N, 6.06. Found: C, 51.81; H, 5.22; N, 5.92.

*4.6.16. Synthesis of compound **14**.* Compound **14** was prepared as light yellow solid (1.38 g, 93% yield) from **12** by using the method established for **13**. IR (KBr, cm^{-1}): 2982, 1727, 1518, 1455, 1239, 1030, 758; ^1H NMR (500 MHz, $CDCl_3$): δ 9.13 (s, 2H), 8.69 (s, 1H), 7.95 (d, J=2.5 Hz, 2H), 7.17 (d, J=2.5 Hz, 2H), 4.48 (q, J=7.5 Hz, 4H), 4.33 (q, J=7.0 Hz, 8H), 3.15 (s, 2H), 3.01 (s, 2H), 1.50 (t, J=7.5 Hz, 6H), 1.38 (t, J=7.0 Hz, 12H). FABMS (m/z): 765.2 (M^+). Anal. Calcd for $C_{33}H_{41}N_3O_{10}P_2S_2$: C, 51.76; H, 5.40; N, 5.49. Found: C, 51.71; H, 5.24; N, 5.32.

*4.6.17. Synthesis of **TCT-7**.* NaH (0.06 g, 1.5 mmol, 60% suspension in oil) was added to a solution of **4a** (0.282 g, 0.5 mmol) in dry THF (50 mL) at 0 °C. After initial effervescence the suspension was stirred for 1 h at room temperature under argon. A solution of **6a** (0.373 g, 1.05 mmol) in dry THF (20 mL) was added dropwise. The mixture was heated to 50 °C for 4 h and then cooled and quenched with EtOH. All solvents were then removed under reduced pressure. The residue was purified by column chromatography with DCM/MeOH (30:1 v/v) as eluant to yield the desired product as a wine-colored solid (0.247 g, 52%). IR (KBr, cm^{-1}): 3432, 1645, 1581, 1544, 1500, 745, 691; ^1H NMR (500 MHz, DMSO-d_6): δ 12.86 (brs, 1H), 8.45 (d, J=6.0 Hz, 4H), 7.80 (d, J=6.0 Hz, 4H), 7.62 (d, J=8.0 Hz, 4H), 7.35–7.40 (m, 12H), 7.31 (d, J=15 Hz, 2H), 7.13 (d, J=15 Hz, 2H), 7.05–7.11 (m, 12H), 7.02 (d, J=8.0 Hz, 4H). ESI (m/z): 950.3 (M^-−1). Anal. Calcd for $C_{63}H_{45}N_5OS_2$: C, 79.47; H, 4.76; N, 7.35. Found: C, 79.34; H, 4.68; N, 7.28.

*4.6.18. Synthesis of **TCT-8**.* **TCT-8** was prepared as a wine-colored solid (0.912 g, 55% yield) from **4a** and **6b** by using the method established for **TCT-7**. IR (KBr, cm^{-1}): 3445, 2913, 1664, 1584, 1544, 1486, 1366, 751, 701; ^1H NMR (500 MHz, DMSO-d_6): δ 13.09 (brs, 1H), 8.55 (d, J=6.5 Hz, 4H), 7.80 (d, J=6.5 Hz, 4H), 7.73 (d, J=8.5 Hz, 4H), 7.33–7.37 (m, 12H), 7.18 (d, J=15 Hz, 2H), 7.10 (d, J=15 Hz, 2H), 7.05–7.08 (m, 8H), 7.02 (d, J=8.5 Hz, 4H), 6.94 (d, J=3 Hz, 2H), 6.76 (d, J=3 Hz, 2H). ESI (m/z): 918.3 (M^-−1). Anal. Calcd for $C_{63}H_{45}N_5O_3$: C, 82.24; H, 4.93; N, 7.61. Found: C, 82.13; H, 4.86; N, 7.48.

*4.6.19. Synthesis of **TCT-9**.* **TCT-9** was prepared as a yellow solid (0.756 g, 53% yield) from **4a** and **6c** by using the method established for **TCT-7**. IR (KBr, cm^{-1}): 3439, 1677, 1581, 1537, 1500, 1290, 751, 694; ^1H NMR (500 MHz, DMSO-d_6): δ 12.92 (brs, 1H), 8.44 (d, J=8.0 Hz, 4H), 7.78 (d, J=8.0 Hz, 4H), 7.57 (d, J=8.5 Hz, 4H), 7.43 (d, J=16 Hz, 2H), 7.33–7.36 (m, 8H), 7.10 (d, J=16 Hz, 2H), 7.06–7.11 (m, 12H), 6.97 (d, J=8.5 Hz, 4H). ESI (m/z): 786.3 (M^-−1). Anal. Calcd for $C_{55}H_{41}N_5O$: C, 83.84; H, 5.24; N, 8.89. Found: C, 83.70; H, 5.30; N, 8.81.

*4.6.20. Synthesis of **TCT-10**.* **TCT-10** was prepared as a red solid (1.0 g, 58% yield) from **4b** and **6a** by using the method established for **TCT-7**. IR (KBr, cm^{-1}): 3432, 1664, 1581, 1537, 1493, 1423, 1271, 795, 694; ^1H NMR (500 MHz, DMSO-d_6): δ 12.69 (brs, 1H), 8.01 (d, J=3.5 Hz, 2H), 7.62 (d, J=8.5 Hz, 4H), 7.33–7.37 (m, 12H), 7.22 (d, J=16.0 Hz, 2H), 7.12 (d, J=16.0 Hz, 2H), 7.05–7.08 (m, 14H), 7.00 (d, J=8.5 Hz, 4H). ESI (m/z): 962.2 (M^-−1). Anal. Calcd for $C_{59}H_{41}N_5OS_4$: C, 73.49; H, 4.29; N, 7.26. Found: C, 73.32; H, 4.21; N, 7.17.

*4.6.21. Synthesis of **TCT-11**.* **TCT-11** was prepared as a red solid (0.957 g, 57% yield) from **4b** and **6b** by using the method established for **TCT-7**. IR (KBr, cm^{-1}): 3445, 1664, 1581, 1486, 1423, 1271, 745, 688; ^1H NMR (500 MHz, DMSO-d_6): δ 12.69 (brs, 1H), 8.06 (d, J=3.0 Hz, 2H), 7.69 (d, J=8.5 Hz, 4H), 7.33–7.37 (m, 10H), 7.25 (d, J=15.5 Hz, 2H), 7.08 (d, J=15.5 Hz, 2H), 7.05–7.08 (m, 12H), 7.00 (d, J=8.5 Hz, 4H), 6.91 (d, J=3.0 Hz, 2H), 6.76 (d, J=3.0 Hz, 2H). ESI (m/z): 930.3 (M^-−1). Anal. Calcd for $C_{59}H_{41}N_5O_3S_2$: C, 76.02; H, 4.43; N, 7.51. Found: C, 75.94; H, 4.26; N, 7.48.

*4.6.22. Synthesis of **TCT-12**.* **TCT-12** was prepared as a yellow solid (0.737 g, 51% yield) from **4b** and **6c** by using the method established for **TCT-7**. IR (KBr, cm^{-1}): 3445, 1657, 1588, 1493, 1448, 1271, 751, 688; ^1H NMR (500 MHz, DMSO-d_6): δ 11.89 (brs, 1H), 8.13 (d, J=3.0 Hz, 2H), 7.54 (d, J=8.5 Hz, 4H), 7.33–7.37 (m, 12H), 7.19 (d, J=16.0 Hz, 2H), 7.10 (d, J=16.0 Hz, 2H), 7.05–7.08 (m, 10H), 6.89 (d, J=8.5 Hz, 4H). ESI (m/z): 798.2 (M^-−1). Anal. Calcd for $C_{51}H_{37}N_5OS_2$: C, 76.57; H, 4.66; N, 8.75. Found: C, 76.42; H, 4.56; N, 8.64.

*4.6.23. Synthesis of **TCT-13**.* A mixture of the above aldehyde **8** (0.230 g, 0.26 mmol), cyanoacetic acid (0.085 g, 1 mmol), ammonium acetate (0.077g, 1 mmol), DCM (10 mL), and acetic acid (20 mL) was stirred at reflux for 12 h. The solvent was evaporated under reduced pressure. The residue was treated with 50 mL of water. The precipitate was collected by filtration and washed with ethanol to afford the desired product **TCT-13** as yellow solid

(0.171 g, 69%). IR (KBr, cm^{-1}): 3413, 1682, 1594, 1493, 1436, 1277, 815, 701; ^1H NMR (500 MHz, DMSO-d_6): δ 13.41 (brs, 1H), 8.71 (d, J=9.0 Hz, 2H), 8.36 (s, 1H), 8.11–8.18 (m, 4H), 7.38 (d, J=7.5 Hz, 4H), 7.25–7.31 (m, 12H), 7.12 (d, J=16.0 Hz, 2H), 7.08 (d, J=16.0 Hz, 2H), 6.97–7.06 (m, 14H). ESI (m/z): 953.3 (M^-−1). Anal. Calcd for $C_{61}H_{42}N_6O_2S_2$: C, 76.71; H, 4.43; N, 8.80. Found: C, 76.59; H, 4.41; N, 8.68.

4.6.24. Synthesis of ***TCT-14***. NaH (5 equiv, 60% suspension in oil) was added to a solution of Wittig–Horner reagent **13** (0.16 g, 0.299 mmol) in THF at 0 °C. After initial effervescence the suspension was stirred for 1 h at room temperature the corresponding aldehyde **6a** (0.235 g, 0.658 mmol) was added. The mixture was heated to 50 °C for 12 h and then cooled and quenched with EtOH. All solvents were then removed under reduced pressure. The remaining solid was washed with ethanol, then purified by column chromatography with DCM/MeOH (10:1 v/v) as eluant to yield the desired product **TCT-14** as red solid (0.22 g, 69%). IR (KBr, cm^{-1}): 3425, 1685, 1594, 1500, 1423, 1366, 694; ^1H NMR (500 MHz, DMSO-d_6): δ 8.60 (d, J=8.0 Hz, 2H), 8.23 (d, J=3.5 Hz, 2H), 8.14 (d, J=8.0 Hz, 2H), 7.55 (d, J=8.5 Hz, 4H), 7.37 (d, J=16.0 Hz, 2H), 7.33–7.37 (m, 12H), 7.22 (d, J=16.0 Hz, 2H), 7.05–7.08 (m, 14H), 6.94 (d, J=8.5 Hz, 4H). ESI (m/z): 1066.3 (M^-−1). Anal. Calcd for $C_{66}H_{45}N_5O_2S_4$: C, 74.20; H, 4.25; N, 6.56. Found: C, 74.03; H, 4.16; N, 6.39.

4.6.25. Synthesis of ***TCT-15***. **TCT-15** was prepared as a red solid (0.256 g, 67% yield) from **13** and **6b** by using the method established for **TCT-14**. IR (KBr, cm^{-1}): 3432, 1687, 1588, 1500, 1429, 1271, 701; ^1H NMR (500 MHz, DMSO-d_6): δ 8.50 (d, J=8.5 Hz, 2H), 8.26 (d, J=3.0 Hz, 2H), 8.03 (d, J=8.5 Hz, 2H), 7.74 (d, J=8.5 Hz, 4H), 7.33–7.37 (m, 12H), 7.18 (d, J=16.0 Hz, 2H), 7.05–7.08 (m, 12H), 6.96 (d, J=8.5 Hz, 4H), 6.91 (d, J=3.0 Hz, 2H), 6.80 (d, J=3.0 Hz, 2H). ESI (m/z): 1034.3 (M^-−1). Anal. Calcd for $C_{66}H_{45}N_5O_4S_2$: C, 76.50; H, 4.38; N, 6.76. Found: C, 76.41; H, 4.26; N, 6.63.

4.6.26. Synthesis of ***TCT-16***. **TCT-16** was prepared as a yellow solid (0.205 g, 71% yield) from **13** and **6c** by using the method established for **TCT-14**. IR (KBr, cm^{-1}): 3432, 1689, 1594, 1500, 1436, 1277, 701; ^1H NMR (500 MHz, DMSO-d_6): δ 8.60 (d, J=8.0 Hz, 2H), 8.23 (d, J=3.5 Hz, 2H), 8.13 (d, J=8.0 Hz, 2H), 7.55 (d, J=8.0 Hz, 4H), 7.33–7.37 (m, 10H), 7.22 (d, J=16.0 Hz, 2H), 7.05–7.08 (m, 14H), 6.95 (d, J=8.0 Hz, 4H). ESI (m/z): 902.3 (M^-−1). Anal. Calcd for $C_{58}H_{41}N_5O_2S_2$: C, 77.05; H, 4.57; N, 7.75. Found: C, 77.01; H, 4.38; N, 7.73.

4.6.27. Synthesis of ***TCT-17***. **TCT-17** was prepared as a red solid (0.324 g, 65% yield) from **14** and **6a** by using the method established for **TCT-14**. IR (KBr, cm^{-1}): 3432, 1696, 1594, 1500, 1423, 1277, 694; ^1H NMR (500 MHz, DMSO-d_6): δ 9.14 (s, 2H), 8.74 (s, 1H), 8.19 (d, J=3.5 Hz, 2H), 7.56 (d, J=8.5 Hz, 4H), 7.44 (d, J=15.5 Hz, 2H), 7.33–7.37 (m, 14H), 7.18 (d, J=15.5 Hz, 2H), 7.05–7.08 (m, 12H), 6.96 (d, J=8.5 Hz, 4H). ESI (m/z): 1110.2 (M^-−1). Anal. Calcd for $C_{67}H_{45}N_5O_4S_4$: C, 72.34; H, 4.08; N, 6.30. Found: C, 72.29; H, 3.95; N, 6.18.

4.6.28. Synthesis of ***TCT-18***. **TCT-18** was prepared as a wine-colored solid (0.182 g, 75% yield) from **14** and **6b** by using the method established for **TCT-14**. IR (KBr, cm^{-1}): 3425, 1702, 1594, 1505, 1429, 1284, 694; ^1H NMR (500 MHz, DMSO-d_6): δ 9.18 (s, 2H), 8.72 (s, 1H), 8.20 (d, J=3.0 Hz, 2H), 7.70 (d, J=8.0 Hz, 4H), 7.38–7.42 (m, 10H), 7.34 (d, J=16.0 Hz, 2H), 7.15 (d, J=16.0 Hz, 2H), 7.05–7.09 (m, 12H), 7.01 (d, J=8.0 Hz, 4H), 6.92 (d, J=3.0 Hz, 2H), 6.78 (d, J=3.0 Hz, 2H). ESI (m/z): 1078.3 (M^-−1). Anal. Calcd for $C_{67}H_{45}N_5O_6S_2$: C, 74.49; H, 4.20; N, 6.48. Found: C, 74.29; H, 4.03; N, 6.29.

4.6.29. Synthesis of ***TCT-19***. **TCT-19** was prepared as a yellow solid (0.350 g, 75% yield) from **14** and **6c** by using the method established for **TCT-14**. IR (KBr, cm^{-1}): 3432, 1696, 1588, 1505, 1429, 1271, 701; ^1H NMR (500 MHz, DMSO-d_6): δ 13.51 (brs, 2H), 9.18 (s, 2H), 8.67 (s, 1H), 8.13 (d, J=3.0 Hz, 2H), 7.51 (d, J=8.0 Hz, 4H), 7.38–7.42 (m, 12H), 7.17 (d, J=16.0 Hz, 2H), 7.05–7.09 (m, 12H), 6.85 (d, J=8.0 Hz, 4H). ESI (m/z): 946.3 (M^-−1). Anal. Calcd for $C_{59}H_{41}N_5O_4S_2$: C, 74.74; H, 4.36; N, 7.39. Found: C, 74.57; H, 4.25; N, 7.31.

Acknowledgements

This work was supported by the National Basic Research Program of China (2011CB933303, and 2011CB808704), the National Natural Science Foundation of China (21021062, 91022031 and 21001063), and the funding from Academician Workstation in Changzhou Trina Solar Energy Co. Ltd., Jiangsu Province.

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