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The synthesis and properties of novel diazo chromophores based on thiophene conjugating spacers and tricyanofuran acceptors

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Abstract

Two series of novel diazo chromophores with tricyanofuran as acceptors and 3,4-disubstituted thiophene as bridges were prepared for second-order nonlinear optical applications. The chromophores were fully characterized using FT-IR, UV–vis, NMR and MS; thermal gravimetric analysis and differential scanning calorimetry revealed that the diazo-based chromophores have excellent thermal stability. The electrooptic coefficients (γ_{33}) were measured in the chromophores-doped poly(Bisphenol A Carbonate) films at the fundamental wavelength of 1315 nm, and the highest γ_{33} achieved was 30 pm/V.

Keywords: NLO; EO; Diazo; Chromophore; Thiophene; TCF

1. Introduction

Organic second-order nonlinear optical (NLO) materials have been highlighted due to their tremendous potential in applications including optical data transmission and optical information processing [1]. As the basic element, dipolar push–pull NLO chromophores involve electron-donor and electron-acceptor groups interacting through a π-conjugating spacer [2]. It is generally understood that to obtain large macroscopic NLO activities, large molecular nonlinearities of the chromophores must be achieved while preventing molecular aggregation. In the molecules with large $\mu\beta$ values, the substituted anilines are used the most commonly as the donor systems because of their high stabilities and electron-donating abilities. The tricyanofuran (TCF) series are excellent acceptors for their strong electron-withdrawing ability [3]. The conjugating bridge systems vary from open chain and ring-locked polyenes to various aromatic (heterocyclic) substitutes [4]. Because of high chemical and thermal stability and moderate resonance energy which allow good π-electron delocalization, thiophene-based π-conjugating spacers have been proved effective in improvement of $\mu\beta$ values of NLO chromophores [3–5].

As an efficient segment of π-electron conjugating bridge, diazo (N=N) bond is widely used in the design of NLO chromophores. These diazo-based chromophores have exhibited high stabilities and large NLO activities [6]. In our previous work, a series of diazo chromophores containing TCF acceptors and thiazole or thiophene spacers have been prepared and studied [7]. These materials exhibit large NLO activity and high thermal stability. However, they were found to be low-soluble and easy to aggregate in polymer matrices due to the strong intermolecular electrostatic interactions, which results in the disadvantages in their practical applications. To solve this problem, two series of novel chromophores based on azothiophene conjugating spacer and TCF acceptor were designed and synthesized with improved performances.

In this paper, we report the syntheses and properties of these two series of novel diazo chromophores. The flexible alkyl

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chains were introduced into the thiophene bridges to prevent parallel chromophores' packing and improve the solubility of the materials [3,4a]. The chromophores of the first series (Type **1**) have been built around 3,4-dialkylthiophene spacers while those of the second series (Type **2**) are derived from 3, 4-dialkoxythiophene spacers. All the chromophores were characterized by ^{1}H NMR, MS, FT-IR and UV–vis spectra. The thermal stabilities were studied by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). The nonlinear optical properties were measured in the polymer films by ATR method at the fundamental wavelength of 1315 nm.

2. Results and discussion

2.1. Synthesis

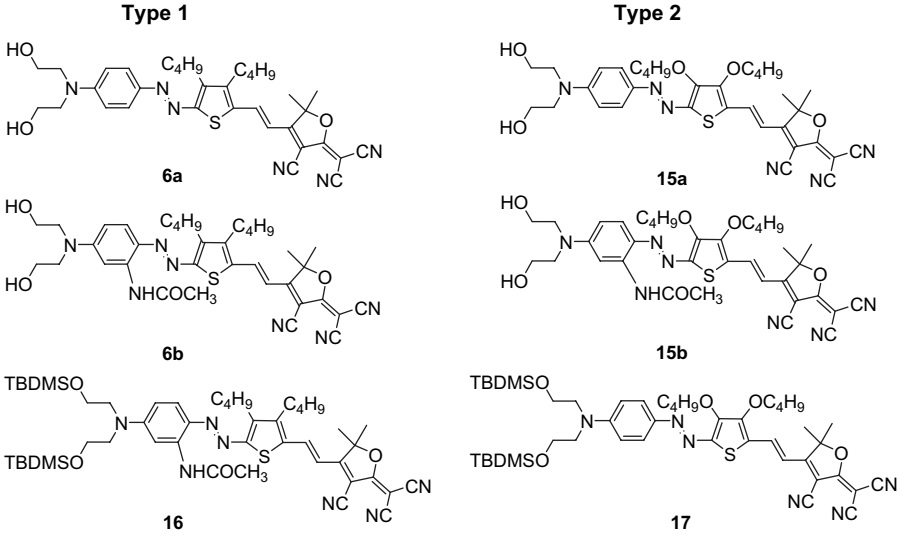
The structures of the push–pull chromophores are shown in Scheme 1. All these materials have been prepared according to a general synthetic methodology as follows: (1) the preparation of 5-nitro-3,4-disubstituted-2-thiophenecarboxyaldehydes (thiophene-based spacers) followed by reduction of nitro groups to yield the amino compounds; (2) the introduction of the donor group by diazo coupling reaction; (3) Knoevenagel condensation between the diazo-based thiophenealdehyde and TCF acceptor; and (4) the protection of the hydroxy-chromophores by *tert*-butyl-dimethylsilane (TBDMS) groups.

The chromophores were synthesized using two different thiophene spacer systems. The Type **1** chromophores contain 3,4-dialkylthiophene-based bridge, which was obtained by the coupling reaction of 3,4-dibromothiophene and butylmagnesium bromide [3d,8]. The reactions were conducted in diethyl ether solution with [1,3-bis(diphenylphosphino)-propane]nickel(II) (dppp) as a catalyst (Scheme 2). The Type **2** compounds possess 3,4-dialkoxythiophene-based bridges. The synthesis of 3,4-dibutyloxythiophene (**11**) was accomplished following the general procedures outlined in the literature (Scheme 3) [9]. Diethyl thiodiglycollate (**8**) was obtained by Williamson ether reaction of sodium sulfide with ethyl chloroacetate [10]. The Hinsberg condensation between compound **8** and diethyl oxalate afforded 2,5-dicarbethoxy-3,4-dihydroxythiophene (**9**) [11]. In our procedures, compound **9**, anhydrous potassium carbonate (K_2CO_3) and 1-bromobutane reacted quantificationally in the solution of *N*,*N*-dimethyl formamide (DMF). After the reaction finished, the mixture was filtrated and the solvent was added to the solution of potassium hydroxide. The solution was refluxed and acidified to afford 3,4-dibutyloxy-2,5-thiophenedicarboxylic acid (**10**). 3,4-Dibutyloxy-thiophene (**11**) was obtained from the decarboxylation reaction by heating compound **10** to 220 °C under N_2 atmosphere for 2 h [12].

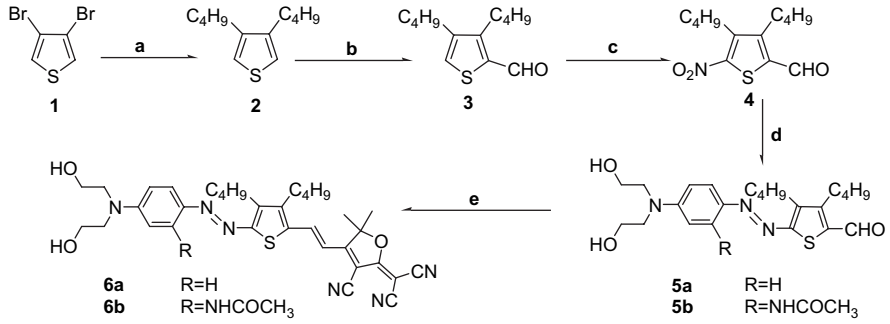
Both of the π-conjugating spacers (**2** and **11**) were subjected to Vilsmeier reactions in the presence of $POCl_3$ and DMF, affording 3,4-disubstituted thiophenealdehydes (**3** and **12**). The subsequent nitration reactions of the thiophenealdehydes by fuming nitric acid in glacial acetic acid gave 5-nitro-3,4-disubstituted-2-thiophenealdehydes (**4** and **13**). Unlike the method in Ref. [13], the thiophenealdehydes were nitrated in glacial acetic system instead of acetic anhydride. The nitration was carried out at 0–5 °C and a few drops of concentrated sulfuric acid were found to accelerate the reaction.

The nitro-compounds **4** and **13** were reduced with stannous chloride ($SnCl_2$) in the solution of tetrahydrofuran (THF) and concentrated hydrochloride (HCl) [14]. Because of the poor stability, the products were not separated and reacted with sodium nitrite ($NaNO_2$) in the solution of acetic acid and propionic acid to form the solution of diazonium salts. The coupling reaction of the diazonium salts with *N*-phenyldiethanol amine or *N*-(3-acetamidophenyl)diethanol amine introduced the electron donors into the thiophene-based bridges. The electron acceptors were conjugately bound to the thiophene spacers by Knoevenagel condensation between the resulting aldehyde compounds and TCF acceptor with active methylene groups (Schemes 2 and 3).

The hydroxy groups of the chromophores (**6b** and **15a**) were protected by *tert*-butyl-dimethylsilane (TBDMS) groups in the solution of anhydrous DMF (Scheme 4). It is noticed that the TBDMS-attached chromophores had excellent



Scheme 1. The chemical structures of the chromophores.



a. C_4H_9MgBr, diethyl ether, $(dppp)NiCl_2$;
b. $POCl_3$, DMF;
c. HNO_3, HAc, H_2SO_4;
d. $SnCl_2 \cdot 2H_2O/H^+$, THF, $NaNO_2$, N-Phenyldiethanolamine or N-(3-acetamido-phenyl)diethanolamine;
e. TCF, EtOH, NH_4Ac, AcOH.

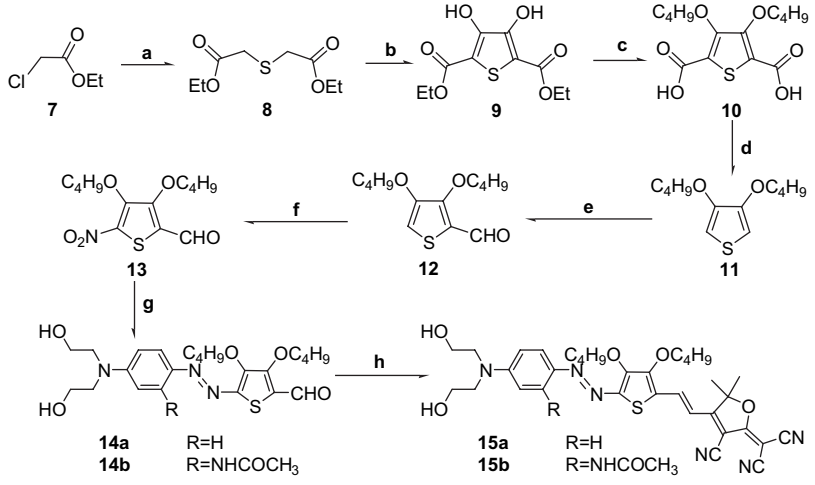
Scheme 2. Synthesis of the chromophores **6a** and **6b**.

solubility compared with the unprotected hydroxy counterparts. This may be attributed to the introduction of the large blocks of TBDMS groups that prevent the molecules from packing tightly. All the chromophores were obtained as dark-blue powder and have been characterized by ^1H NMR, UV–vis, FT-IR and mass spectrometry.

2.2. UV–vis spectra of the chromophores

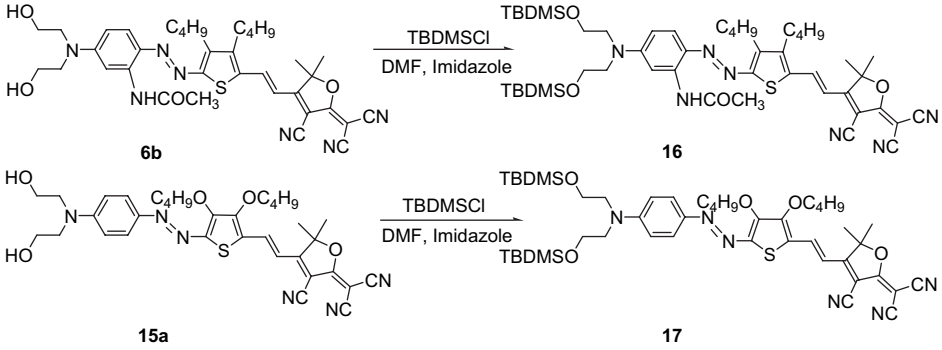
The UV–vis spectra of the synthesized chromophores were determined in chloroform, THF, methanol and DMSO, and the absorption maxima (λ_{max}) are summarized in Table 1.

From the table, all the chromophores exhibit the large λ_{max} values varying from 660 nm to 740 nm in the aforementioned solvents. It has been experimentally and theoretically illustrated that a large λ_{max}, meaning low charge transition energy, is often directly associated with an enhanced second-order NLO response [15]. It can also be seen that the chromophore **6a** exhibits similar λ_{max} in every used solvent to **15a** containing the same electron donor and electron acceptor. Compounds **6b** and **15b** also have similar λ_{max}. The above results indicate that the replacement of the alkyl groups attached to the thiophene bridge by alkoxyl groups does not lead to significant changes of the planarity and aromaticity of the π-conjugated system. On the other hand, compared with **6a** (or **15a**), the chromophore **6b** (or **15b**) show ca. 30–50 nm bathochromic shifts of the maximum absorption wavelengths. This result suggests that the introduction of the $-NHCOCH_3$ group onto the donor end of the chromophore may induce a significant red shift in absorption spectra, which may be attributed to the inductive and hyperconjugative effects of the acetamido group [16]. It is interesting that the introduction of the



a. Na_2S/H_2O, EtOH;
b. diethyl oxalate, NaOEt, H^+;
c. Butylbromide, K_2CO_3, DMF; KOH/EtOH, H^+;
d. 220 °C;
e. $POCl_3$, DMF;
f. HNO_3, HAc, H_2SO_4;
g. $SnCl_2 \cdot 2H_2O/H^+$,THF, $NaNO_2$, N-Phenyldiethanolamine or N-(3-acetamido-phenyl)diethanolamine;
h. TCF, EtOH, NH_4Ac, AcOH.

Scheme 3. Synthesis of the chromophores **15a** and **15b**.



Scheme 4. Synthesis of the chromophores **16** and **17**.

protective group TBDMS results in bathochromic shifts in chloroform and methanol while hypsochromic shifts in DMSO comparing **16** with **6b**, and **17** with **15a**, respectively. It could be explained that the TBDMS substituent probably affects the electronic distribution of the push–pull system and the planarity of the molecules, and thus its linear optical properties.

In addition, the shifts of the absorption maxima in different solvents show the effect of solvent on the energy gap between the ground state and excited state molecules, which reflect different electronic distribution in the molecules. DeMartino et al. have suggested that the high solvatochromic effects are related with a large second-order optical nonlinearity [17]. Several groups have contributed to the studies of solvatochromic effects on the heterocyclic NLO chromophores [18]. For both series of chromophores presented here, large solvatochromic data were obtained implying that all chromophores possess very large molecular nonlinearities. We also noticed that the chromophores **6a**, **6b**, **15a** and **15b** have the largest λ_{max} values in DMSO, while the TBDMS-protected **16** and **17** show largest λ_{max} values in chloroform. This is an interesting phenomenon and further studies are needed for the full interpretation [8,19].

2.3. Thermal stabilities of the chromophores

The thermal stabilities of the chromophores were investigated by DSC and TGA under nitrogen, with a heating rate of 10 °C/min. In DSC thermograms, the peaks corresponded to the changing heat exchanges such as phase transitions (melting) or reactions (decomposition). As shown in Fig. 1, the peaks above the baselines indicate the melting points of the chromophores while the peaks below the baselines are related to the decomposition temperatures of the chromophores. The data from DSC can be confirmed by TGA thermograms (Fig. 2). The melting points and decomposition temperatures of the chromophores are summarized in Table 2.

The results show that all the chromophores are thermally stable with decomposition temperatures higher than 218 °C. Among them, the hydroxyl chromophores (**6a**, **6b**, **15a** and **15b**) exhibit similar decomposition temperatures varying from 218 °C to 230 °C. This result indicates that the aniline-based donors and thiophene-based spacers with different substituents have little impact on overall thermal stabilities of the chromophores. However, the TBDMS-protected chromophores are more stable than the unprotected hydroxy counterparts (about 20 °C higher). This may be due to the TBDMS moieties which prevent hydroxy groups from reacting with acceptor cyano groups when being heated [20].

2.4. The NLO properties of the chromophores

In order to investigate the nonlinear optical properties of the chromophores, guest–host systems were explored. The chromophores were doped into PC (poly (bisphenol A carbonate)) polymer at the same molecular densities (1.35×10^{20}/g, about 15–20 wt%). Solutions of 20% total solids were prepared in cyclopentanone and 2–3 μm thick films were spun-cast onto the substrate coated by indium tin oxide (ITO). The films were vacuum dried at 50 °C overnight, and corona poled at 145 °C for 30 min under the electric field of 3.5 kV/cm. Then, the electric field was removed when the films were cooled to room temperature. The electrooptic

Table 1
UV–vis data of the chromophores

Compound	λ_{max} (nm) ($CHCl_3$)	ε ($CHCl_3$) ($Lmol^{-1}\,cm^{-1}$)	λ_{max} (nm) (THF)	ε (THF) ($Lmol^{-1}\,cm^{-1}$)	λ_{max} (nm) (methanol)	ε (methanol) ($Lmol^{-1}\,cm^{-1}$)	λ_{max} (nm) (DMSO)	ε (DMSO) ($Lmol^{-1}\,cm^{-1}$)
6a	668	53,520	665	57,200	663	55,900	695	52,450
6b	711	58,200	707	53,400	698	56,700	728	53,140
15a	666	52,200	666	55,300	661	54,600	698	51,260
15b	714	55,560	710	54,220	691	54,100	728	54,600
16	741	67,290	701	56,100	705	54,800	718	56,360
17	697	60,620	665	56,300	671	Poor solubility	690	54,800

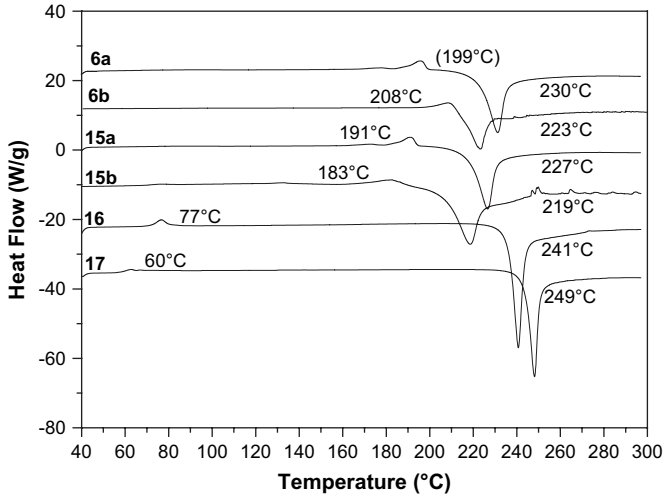


Fig. 1. DSC curves of the chromophores.

(EO) coefficients (γ_{33}) of the films were measured at the fundamental wavelength of 1315 nm by ATR measurements [21].

The EO coefficients (γ_{33}) of the films are also summarized in Table 2. It is found that the TBDMS-protected materials exhibited relatively higher EO activities than the unprotected chromophores. This shows that the TBDMS groups indeed improved the poling efficiencies by minimizing the electrostatic interactions and aggregation among the chromophores [22]. The highest EO coefficient achieved in this study was 30 pm/V for the chromophore **17** doped PC film. Because there are many factors affecting the measurements of EO coefficients, the macroscopic EO activity can be further enhanced by optimizing the system conditions and improving the poling efficiency.

3. Conclusions

Two series of diazo-based nonlinear optical chromophores with TCF as acceptors and 3,4-disubstituted thiophene as spacers have been synthesized and characterized. The moieties attached to the thiophene spacers have little impact on the absorption of the chromophores, while the introduction of $-NHCOCH_3$ and TBDMS groups into the donor ends induce significant shifts of the spectra. The UV–vis data also indicate that the chromophores have large solvatochromic effects. Thermal tests by DSC and TGA indicate that the diazo-based chromophores possess the high decomposition temperatures of 220–250 °C, and especially, the introduction of the TBDMS significantly enhanced the stabilities of the chromophores. The NLO measurements of chromophores doped polymer films indicated the relatively large macroscopic EO activities. Typically, the EO coefficient of 30 pm/V for the TBDMS-protected chromophore **17** doped polymer system was obtained at 1315 nm. In summary, these outstanding properties associated with the chromophores are indicative of very promising candidates for practical applications in the field of electro-optics and photonics.

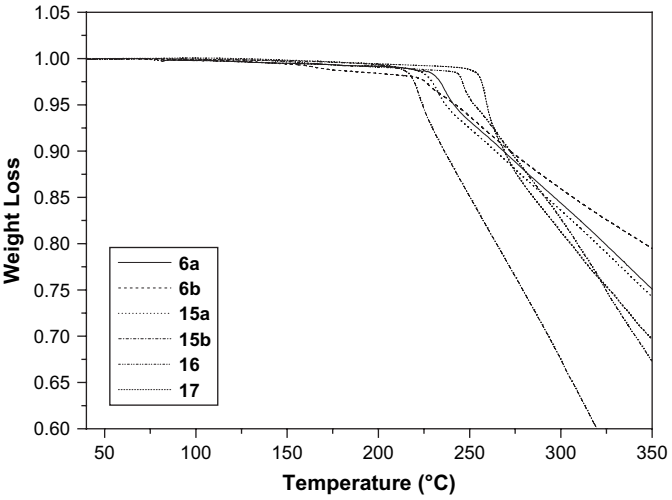


Fig. 2. TGA curves of the chromophores.

Table 2
The properties of the chromophores

Compound	mp. (°C)	T_d (DSC) (°C)	T_d (TGA) (°C)	γ_{33} (pm/V)
6a	199	230	229	13
6b	208	223	223	17
15a	191	227	224	17
15b	183	219	218	19
16	77	241	244	25
17	60	249	256	30

4. Experimental

4.1. Materials and characterization

All the reagents were used as received unless stated. DMF and $POCl_3$ were freshly distilled prior to use; absolute ethanol was purified by standard method. Butylmagnesium bromide was prepared as described in the literature [23]. TCF acceptor was prepared according to the literature [3d].

^{1}H NMR spectra were determined by Varian Gemini 300 (300 MHz) NMR spectrometer (tetramethylsilane as internal reference). FT-IR spectra were recorded on BIO-RAD FTS-165 spectrometer; MS spectra were obtained on TRIO-2000 spectrometer and MALDI-TOF (Matrix Assisted Laser Desorption/Ionization of Flight) on BIFLEX III (Bruker Inc.) spectrometer. UV–vis spectra were performed on Hitachi U2001 photo spectrometer. TGA was determined by TA5000-2950TGA (TA co) and DSC was taken on Perkin–Elmer DSC-7 with a heating rate of 10 °C/min under the protection of nitrogen.

4.2. Syntheses of chromophores

4.2.1. 3,4-dibutylthiophene (*2*) [3d,8]

Under N_2 atmosphere, [1,3-bis(diphenylphosphino)-propane]nickel(II) chloride (dppp) (0.33 g, 0.6 mmol) was added to the solution of 3,4-dibromothiophene (2.5 g, 100 mmol) in

THF (50 ml). The mixture was stirred and butylmagnesium bromide (0.3 mol, in ether solution) was added dropwise. The solution was refluxed overnight and then poured into water with a few drops of hydrochloric acid. The aqueous layer was extracted with ether, and the organic extracts were washed with brine and dried over magnesium sulfate. After filtration and evaporation of the solvent, the product was distilled under reduced pressure (bp. 110 °C/1–2 mmHg) to give 15 g of the compound, 80%. ^{1}H NMR ($CDCl_3$, δ = ppm): 6.76 (s, 2H), 2.56 (t, 4H), 1.70–1.30 (m, 8H), 0.91 (t, 6H).

*4.2.2. 3,4-Dibutyl-2-thiophenecarboxaldehyde (**3**) [3d,24]*

To a mixture of compound **2** (10 g, 51 mmol) and 30 ml DMF, 7.0 ml of $POCl_3$ (76 mmol) was slowly added under nitrogen at 0 °C. After the addition, the temperature of the reaction was allowed to warm up to room temperature for about 1 h, then to 90 °C for 2 h. After cooling to room temperature, the mixture was poured into 200 ml of ice water. The organic layer was collected and the aqueous layer was extracted with diethyl ether. The combined organic layer was washed twice with water, and dried over sodium sulfate. After filtration and evaporation of the solvent, the product was distilled under reduced pressure (bp. 125 °C/1 mmHg) to give 9.0 g of compound **3**, 80%. IR (KBr, ν_{max}, cm^{-1}): 3091, 2958–2870, 1661. ^{1}H NMR ($CDCl_3$, δ = ppm): 10.21 (s, 1H), 7.20 (s, 1H), 2.96 (t, 2H), 2.60 (t, 2H), 1.68–1.34 (m, 8H), 0.91 (t, 6H).

*4.2.3. 5-Nitro-3,4-dibutyl-2-thiophene carboxyaldehyde (**4**) [13]*

To a solution of 20 ml glacial acetic acid, 5.0 ml of fuming nitric acid (0.12 mol) was slowly added. The mixture was stirred at 0 °C and 1.0 ml of concentrated sulfuric acid was added. A solution of compound **3** (10 g, 45 mmol) in acetic acid (15 ml) was added dropwise to the mixture under 0 °C. After the addition, the mixture was stirred at 0–5 °C for 1 h and at room temperature for additional 1 h. Then the mixture was poured into ice water. The organic layer was extracted by ethyl acetate (3 × 100 ml), and washed with brine and the saturated aqueous sodium bicarbonate. The organic phase was dried over sodium sulfate and evaporated. The product was purified by chromatography using petroleum ether as eluent to afford **4** as a light yellow solid (5.4 g, 20 mmol), 45%, mp. 39 °C. IR (KBr, ν_{max}, cm^{-1}): 2960–2858, 1675, 1517, 1333. ^{1}H NMR ($CDCl_3$, δ = ppm): 10.26 (s, 1H), 3.08 (m, 2H), 2.96 (m, 2H), 1.72–1.62 (m, 8H), 1.12 (m, 6H).

*4.2.4. 2-[4-(N,N-di(2-hydroxyethyl)-amino)-phenylazo]-3,4-dibutylthiophene-5-carboxyaldehyde (**5a**) and 2-[4-(N,N-di(2-hydroxyethyl)-amino)-2-acetamino-phenylazo]-3,4-dibutyl-thiophene-5-carboxyaldehyde (**5b**) [14]*

To a solution of 10 ml concentrated hydrochloric acid and 10 ml THF, 6.8 g stannous chloride (30 mmol) was added. The mixture was stirred, and a solution of compound **4** (2.7 g, 10 mmol) was added in one portion. The temperature of the reaction rose to 50 °C and was maintained at the same temperature for 1 h, then gradually cooled to room temperature. A mixture of glacial acetic acid (20 ml) and propionic acid (10 ml) was added and cooled to −5–0 °C. A solution of sodium nitrite (0.69 g, 10 mmol) in minimum amount of water was added cautiously. The reaction mixture was allowed to stir at −5 °C for 2 h to form the diazonium salt.

The diazonium salt solution was slowly added to the solution of *N*-phenyl-diethanol amine (3.0 g, 16 mmol) in the mixture of glacial acetic acid (40 ml), propionic acid (20 ml) and sulfamic acid (1.0 g, 10 mmol) at −5 to 0 °C. After the addition, the red solution was stirred at −5 °C for 12 h and overnight at room temperature. The mixture was into a large amount of water and filtrated. The solid was collected and purified by chromatography by acetone/petroleum ether (v/v = 1/2), to afford compound **5a** as a dark solid, 2.4 g, 50%. IR (KBr, ν_{max}, cm^{-1}): 3420 (OH); 2859, 2956 (CH_2, CH_3); 1650 (CHO); 1596 (C=C). UV–vis ($CHCl_3$): λ_{max} = 507 nm. ^{1}H NMR ($CDCl_3$, δ = ppm): 10.02 (s, 1H), 7.71 (d, 2H), 6.76 (d, 2H), 3.88 (t, 4H), 3.73 (t, 4H), 2.92 (t, 2H), 2.74 (t, 2H), 1.75–1.84 (m, 4H), 1.46–1.56 (m, 4H).

Compound **5b** was prepared according to the procedure of **5a**. IR (KBr, ν_{max}, cm^{-1}): 3369, 3258; 2955, 2931, 2859; 1648, 1608, 1564. UV–vis ($CHCl_3$): λ_{max} = 548 nm. ^{1}H NMR ($CDCl_3$, δ = ppm): 10.02 (s, 1H), 9.40 (1H), 7.90 (d, 1H), 7.40 (d, 1H), 6.42 (m, 1H), 3.96 (t, 4H), 3.72 (t, 4H), 2.86 (t, 2H), 2.74 (t, 2H), 2.20 (s, 3H), 1.70–1.86 (m, 4H), 1.44–1.60 (m, 4H).

*4.2.5. Chromophores **6a** and **6b***

General procedure for the Knoevenagel condensation between the diazo thiophenealdehyde compounds (**5a** and**5b**) and TCF acceptor are as follows.

To a solution of the thiophenealdehyde (2.0 mmol) in 15 ml ethanol, TCF (0.5 g, 2.5 mmol), a little amount of ammonium acetate (NH_4Ac) and a few drops of glacial acetic acid were added. The reaction was refluxed for 2–3 h and petroleum ether was added. After being cooled to room temperature, the solution was filtrated and the product was collected as a dark solid, which was further purified by flash chromatography.

6a UV–vis ($CHCl_3$): λ_{max} = 668 nm. MS (MALDI-TOF, *m/z*): 613.3 (M+). ^{1}H NMR ($CDCl_3$, δ = ppm): 8.41 (d, 1H), 8.08 (d, 2H), 7.3 (2H), 6.77 (d, 1H), 4.14 (s, 4H), 3.95 (s, 4H), 3.15 (t, 4H), 2.93 (t, 4H), 1.87 (s, 6H), 1.81 (m, 4H), 1.73 (m, 4H), 1.62 (m, 8H), 1.13 (m, 6H). Anal. (Calcd.): C 66.50 (66.64), H 6.67 (6.58).

6b UV–vis ($CHCl_3$): λ_{max} = 711 nm. MS (MALDI-TOF, *m/z*): 669.6 (M+). ^{1}H NMR ($CDCl_3$, δ = ppm): 8.32 (s, 1H), 8.12 (d, 1H), 7.75 (d, 1H), 6.97 (s, 1H), 6.62 (d, 1H), 3.99 (d, 4H), 3.80 (s, 4H), 2.96 (t, 2H), 2.75 (t, 2H), 2.61 (m, 3H), 2.32 (s, 3H), 1.82 (m, 2H), 1.74 (s, 6H), 1.46 (m, 2H), 1.26 (m, 4H), 1.05 (q, 6H). Anal. (Calcd.): C 64.43 (64.55), H 6.50 (6.47).

*4.2.6. Diethyl thiodiglycollate (**8**) [10]*

A solution of sodium sulfide ($Na_2S·9H_2O$, 50 g, 0.21 mol) in water (40 ml) was added dropwise to the solution of ethyl chloroacetate (57 g, 50 ml, 0.47 mol) in ethanol (50 ml). The

temperature of the reaction was kept below 40 °C during the addition, and the mixture was stirred at room temperature for additional 10 h. After evaporation of ethanol by rotary evaporation, the organic phase was separated and the water layer was extracted three times with diethyl ether (100 ml). The organic phases were combined and washed by water for three times. After being dried over by anhydrous sodium sulfate, the solution was filtrated and evaporated. The residue was distilled under reduced pressure to give compound **8** as a colorless liquid, 25 g (0.12 mol), 58%, bp. 110 °C/2–3 mmHg. IR (neat, ν_{max}, cm^{-1}): 2984, 2938, 1735, 1276; ^1H NMR ($CDCl_3$, δ = ppm): 4.17 (q, 4H), 3.60 (s, 4H), 1.26 (t, 6H).

4.2.7. 2,5-Dicarbethoxy-3,4-dihydroxythiophene (*9*) [11]

To a solution of sodium ethoxide prepared by adding sodium metal (7.0 g, 0.30 mol) to absolute ethanol (150 ml), a mixture of compound **8** (16 g, 0.13 mol) and diethyl oxalate (19 g, 0.13 mol) was added dropwise over 30 min. After the addition, the mixture was refluxed for additional 2 h, and then cooled to room temperature. The mixture was poured into water (500 ml) and acidified by concentrated hydrochloric acid (30 ml) to afford a yellow precipitate. The solid was collected by filtration and recrystallized from methanol to give compound **9** as a light yellow needle crystal, 20 g, 59%, mp. 135 °C. IR (KBr, ν_{max}, cm^{-1}): 3308, 2989, 1688, 1664, 1513; ^1H NMR ($CDCl_3$, δ = ppm): 1.35 (t, 6H), 4.35 (q, 4H), 9.30 (s, 2H).

4.2.8. 3,4-dibuthoxy-2,5-dithiophenecarboxylic acid (*10*) [9]

Under an atmosphere of nitrogen, a mixture of compound **9** (13 g, 50 mmol), anhydrous potassium carbonate (7.6 g, 55 mmol), 1-bromobutane (15.1 g, 12 ml, 0.11 mol), DMF (30 ml) was vigorously stirred at 90 °C for 6 h. After being cooled to room temperature, the mixture was filtrated and the solvent was added to the solution of potassium hydroxide (17 g, 80%, 0.25 mol) in ethanol (150 ml). The mixture was refluxed for 3 h and a white precipitate was formed. Then the mixture was cooled to room temperature, and poured into water to form a clear solution. After being acidified by concentrated hydrochloric acid (30 ml), the white precipitate formed was collected by filtration. The pure product was obtained as white crystals by recrystallization from methanol, 14 g, 88.6%, mp. 208 °C. IR (KBr, ν_{max}, cm^{-1}): 3500–2300, 1683, 1293. ^1H NMR ($CDCl_3$, δ = ppm): 4.12 (t, 4H), 2.04–1.52 (m, 8H), 0.80 (t, 6H).

4.2.9. 3,4-Dibuthoxythiophene (*11*) [12]

Under an atmosphere of nitrogen, compound **10** (18 g, 57 mmol) was slowly heated to 220–230 °C, and the melt product was vigorously stirred for 2 h. After being cooled to room temperature, the pure product was obtained as a colorless oil by vacuum distillation: bp. 135 °C/1–2 mmHg, 12 g, 90%. IR (KBr, ν_{max}, cm^{-1}): 3112, 2938, 2862, 1500. ^1H NMR ($CDCl_3$, δ = ppm): 6.20 (s, 2H), 4.06 (t, 4H), 1.98–1.42 (m, 8H), 0.90 (t, 6H).

4.2.10. 3, 4-Dibuthoxy-2-thiophenecarboxaldehyde (*12*) [3d,24]

Compound **12** was prepared according to the procedure of compound **3**. IR (neat, ν_{max}, cm^{-1}): 3098, 2961, 2935, 2873, 2773, 1663 (C=O), 1491, 1465. ^1H NMR ($CDCl_3$, δ = ppm): 10.2 (s, 1H), 7.08 (s, 1H), 4.20–4.00 (2t, 4H), 2.00– 0.80 (14H).

4.2.11. 5-Nitro-3,4-dibuthoxy-2-thiophenecarboxyaldehyde (*13*) [13]

Compound **13** was prepared according to the procedure of compound **4**, 50%. IR (neat, ν_{max}, cm^{-1}): 2962, 2936, 2874, 1673 (C=O), 1521, 1326. EI-MS, *m/z* (I%): 301 (M+, 8), 189 (100), 57 (45), 41 (48). ^1H NMR ($CDCl_3$, δ = ppm): 10.40 (s, 1H), 4.40–4.16 (2t, 4H), 2.00–0.70 (14H).

4.2.12. 2-[4-(N,N-di(2-hydroxyethyl)-amino)-phenylazo]-3,4-dibuthoxythiophene-5-carboxyaldehyde (*14a*) and 2-[4-(N,N-di(2-hydroxyethyl)-amino)-2-acetamino-phenylazo]-3,4-dibuthoxy-thiophene-5-carboxyaldehyde (*14b*)

Compound **14a** was prepared according to the procedure of **5a**, 35%, mp. 144 °C. IR (KBr, ν_{max}, cm^{-1}): 3422, 2957, 2871, 1650, 1596, 1510. UV–vis ($CHCl_3$): λ_{max} = 514 nm. ^1H NMR ($CDCl_3$, δ = ppm): 10.03 (s, 1H), 7.73 (d, 2H), 6.82 (d, 2H), 4.64 (t, 2H), 4.37 (t, 2H), 3.93 (t, 4H), 3.72 (t, 4H), 3.33 (s, 2H), 1.87–1.73 (m, 4H), 1.57–1.47 (m, 4H), 1.02–0.96 (m, 6H).

The same procedure and purification afforded compound **14b**. IR (KBr, ν_{max}, cm^{-1}): 3369, 2957, 2871, 1648, 1608, 1510. UV–vis ($CHCl_3$): λ_{max} = 544 nm. ^1H NMR ($CDCl_3$, δ = ppm): 10.02 (s, 1H), 9.35 (1H), 7.98 (d, 1H), 7.56 (d, 1H), 6.47 (m, 1H), 4.57 (t, 2H), 4.34 (t, 2H), 3.96 (t, 4H), 3.72 (t, 4H), 2.23 (s, 3H), 1.75–1.84 (m, 4H), 1.46–1.56 (m, 4H).

4.2.13. Chromophores *15a* and *15b*

Compounds **15a** and **15b** were prepared followed the general procedure of **6a** and **6b**.

15a UV–vis ($CHCl_3$): λ_{max} = 666 nm. MS (MALDI-TOF, *m/z*): 644.4 (M+). ^1H NMR ($CDCl_3$, δ = ppm): 7.93 (d, 1H), 7.77 (d, 2H), 7.05 (m, 2H), 6.61 (d, 1H), 4.73 (t, 2H), 4.36 (t, 2H), 3.97 (t, 4H), 3.79 (t, 4H), 2.63 (s, 2H), 2.00 (m, 8H), 1.73 (s, 6H), 1.01 (m, 6H). Anal. (Calcd.): C 63.30 (63.43), H 6.30 (6.25).

15b UV–vis ($CHCl_3$): λ_{max} = 714 nm. MS (MALDI-TOF, *m/z*): 701.4 (M+). ^1H NMR ($CDCl_3$, δ = ppm): 9.50 (s, 1H), 8.03 (s, 1H), 7.75 (d, 2H), 7.66 (d, 2H), 6.60 (d, 1H), 6.53 (m, 1H), 4.58 (t, 2H), 4.35 (t, 2H), 3.95 (t, 4H), 3.75 (t, 4H), 2.27 (s, 3H), 1.76–1.83 (m, 4H), 1.73 (s, 6H), 1.47–1.54 (m, 4H), 0.98 (m, 6H). Anal. (Calcd.): C 61.50 (61.61), H 6.23 (6.18).

4.2.14. Chromophores *16* and *17*

General procedure for the synthesis of the TBS-chromophores: to a solution of hydroxyl functionalized chromophores in anhydrous DMF, *tert*-butylchlorodimethylsilane (1.1 equiv

to the hydroxy) and imidazole (1.2 equiv to the hydroxy) were added. After stirring at room temperature under N_2 overnight, the mixture was poured into water. Following workup with diethyl ether and water, flash column chromatography was performed to afford the TBDMS-protected chromophores.

16 UV–vis ($CHCl_3$): $\lambda_{max} = 741$ nm. MS (MALDI-TOF, *m/z*): 897.6 (M+). ^{1}H NMR ($CDCl_3$, δ = ppm): 8.16 (d, 1H), 8.12 (s, 1H), 7.68 (d, 1H), 6.60 (d, 1H), 6.53 (d, 1H), 3.87 (t, 4H), 3.72 (t, 4H), 2.92 (t, 2H), 2.74 (t, 2H), 2.29 (s, 3H), 1.72 (s, 6H), 1.53–1.66 (m, 4H), 1.39–1.49 (m, 4H), 0.91–0.99 (m, 6H), 0.87 (s, 18H), 0.03 (s, 12H). Anal. (Calcd.): C 64.07 (64.17), H 8.07 (7.97).

17 UV–vis ($CHCl_3$): $\lambda_{max} = 697$ nm. MS (MALDI-TOF, *m/z*): 872.8 (M+). ^{1}H NMR ($CDCl_3$, δ = ppm): 7.95 (d, 1H), 7.71 (d, 2H), 6.81 (d, 2H), 6.61 (d, 1H), 4.67 (t, 2H), 4.36 (t, 2H), 3.82 (t, 4H), 3.65 (t, 4H), 1.73–1.85 (m, 4H), 1.72 (s, 6H), 1.47–1.57 (m, 4H), 0.97–1.02 (m, 6H), 0.88 (s, 18H), 0.01 (s, 12H). Anal. (Calcd.): C 63.12 (63.26), H 8.00 (7.85).

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