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Novel NLO-phores containing dihexyl amino benzo[b]thiophene exhibiting good transparency and enhanced electro-optical activity

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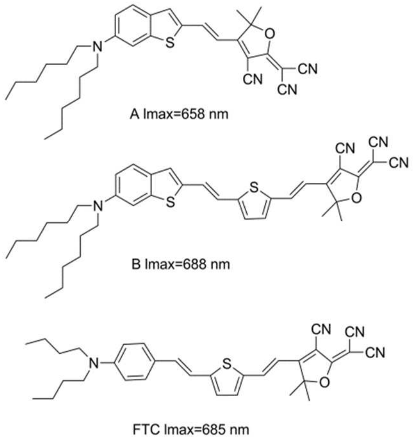
Two new chromophores (A and B) were synthesized, in which a benzo[b]thiophene moiety was first introduced as a donor group. To investigate the macroscopic EO activity of the new chromophores, guest-host doped polymer films were fabricated by doping chromophores A and B into amorphous polycarbonate (APC). The poled films containing A with a loading density of 20 wt% achieved a maximum EO coefficient (r_{33}) of 42pm/V at 1310 nm, while for the poled films containing B, the r_{33} value is 75 pm/V at 1310 nm. UV-vis spectral absorption of new chromophores were studied in solutions and films, and chromophores A and B showed a maximum absorption in chloroform of 658 nm and 688 nm, respectively. Compared to the FTC (r_{33} = 20-50 pm/V at 1310 nm, λ_{max} = 685 nm in chloroform) analogues, they exhibited enhanced electro-optical activity together with high optical gap. This new type of chromophore provided better optimization of the nonlinearity–transparency trade-off

Introduction

Organic electro-optical (EO) materials with large EO activity have potential applications in telecommunication and optical data processing.[1] In such materials, nonlinear optical (NLO) chromophore is the core component, because EO activity is determined by the molecular hyperpolarizability (β) of chromophore. Large β values are essential for large EO activity. To date, chromophores exhibiting large EO activity have been designed.[2] For practical devices applications, molecular nonlinearity is not the only parameters, optical transparency, good thermal and chemical stability are also very important.[3, 4] According to the “two-level model”,[5] the increase in β of such chromophores is usually accompanied by a decrease in optical transparency, leading to the so-called “nonlinearity-transparency trade off”.[6] Therefore, rational design of chromophores to achieve large β values with excellent transparency has been taken up for consideration in the present study. As a consequence, a large number of chromophoes have been designed with high β values and good transparency.[7-11] However, defeating the nonlinearity-transparency trade-off is still a major challenge.

Structure-property relationships that have been established indicate that large β values and other desirable qualities can be achieved by choosing the appropriate pair of strong donor and acceptor moieties with a suitable π-conjugated spacer.[12] Thus, much effort has been focused on the design and synthesis of optimized π-bridge and electron acceptor structures, while the donor groups have remained relatively unchanged. A commonly used donor groups are triarylamines,[13] *N,N*-dialkylaryl/heteroaryl-amines.[14] However, incorporation of these electron donor groups in NLO chromophores was observed saturate molecular nonlinearity and a decrease in optical transparency. To solve such problem, It is necessary to modify the electron donor groups carefully. A successful approach involves introducing electron-rich and electron-deficient heterocycle rings for their special electronic characteristic in designing new chromophores.[15, 16] For instance, with a pyrrole,[17] thiophene,[18] furan[19] and thiazole[20] ring in chromophores can greatly enhanced EO activity.



Scheme 1 Molecular structures of A, B, FTC.

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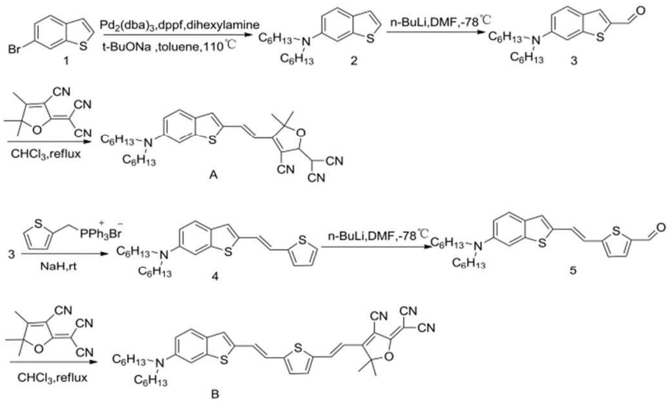
The most studies have focused on five-membered rings. Rare attention has been paid to the benzene fused five-member rings, though they are also important for constructing new chromophores.[21] Among the benzene fused five-membered rings, benzo[b]thiophene attracted our attention. The rigidified polyene conduit of the fused benzo group provides a planar geometry, which allows effective intramolecular charge transfer. Benzo[b]thiophene has been reported in dye-sensitized solar cells (DSSC) and displayed highly energy conversion efficiency.[22] However, to the best of our knowledge, no report about benzo[b]thiophene used as building block in the field of EO materials. In this view, designing a new chromophore with a benzo[b]thiophene unit at the donor end may get a large β.

In this paper, we designed and synthesized two new chromophores A and B containing benzo[b]thiophene ring at the donor end for the first time. These two chromophores contain the same *N,N*-dihexylbenzo[b]thiophen-6-amine donor group and 2-(3-cyano-4,5,5-trimethyl-5H-furan-2-ylidene)-malonitrile (TCF) acceptor group, yet different π-bridges. Chromophore A has the vinylene as the π-bridge. Chromophore B has the thienyl-vinylene as the π-bridge. Their molecular structures are reported in Scheme 1. FTC chromophore[23] was selected as reference for comparison. The photophysical properties, thermal stability, electrochemical properties and nonlinear optical properties of the new chromophores were systematically studied. Compared to the reference chromophore (FTC), the benzo[b]thiophene-containing chromophores A and B showed an enhanced EO activity with a higher optical gap. Our results suggested that benzo[b]thiophene-containing chromophores A and B might represent the new NLO chromophores that could be used for the high-performance EO materials with good optical transparency.

Results and discussion

Synthesis

The chromophores A and B were synthesized as shown in Scheme 2. Compound 2 was prepared by a Hartwig-Buchwald Pd-catalyzed amination reaction[24] of commercially available 1 with dihexylamine. Compound 2 was then treated with butyllithium and anhydrous *N, N*-dimethylformamide to obtain, after aqueous acidic workup, compound 3. Condensation of the aldehyde 3 with thiophene methyl phosphonate gave the intermediate 4. Lithiation of 4 and reaction with DMF provided the aldehyde 5. Finally, chromophores A and B were obtained by Knoevenagel condensation of aldehyde 3, 4 and the 2-(3-cyano-4,5,5-trimethyl-5H-furan-2-ylidene)-malonitrile (TCF) in 60% and 50% yield, respectively



Scheme 2 Synthetic route for chromophores A and B.

The electrochemical properties of chromophores A and B were studied by cyclic voltammetry (CV). As shown in Fig. 1. Chromophore A showed an oxidation reversible wave with half-wave potentials $E_{1/2} = 0.5(E_{ox}+E_{red})$ at about 0.85 V (vs Ag/AgCl), while an irreversible reduction wave with potential at about -0.66 V corresponding to the donor and acceptor group, respectively. One irreversible oxidation wave and two irreversible reduction waves were observed for chromophore B. where the half-wave oxidation potential $E_{1/2}$ of B indicates a highly electron-rich characteristic of the *N,N*-dihexylamino donor, which was determined to be 0.63 V. The first reduction potential was determined to be -0.56 V which was involved the TCF group and the π-bridge. The results are summarized in Table 1. It could be clearly observed that chromophore B (1.19 eV) has a lower energy gap than chromophore A (1.51 eV). This is due to the longer π-bridge of chromophore B. Compared with the FTC chromophore whose energy gap is 1.53 eV.[25] The introduction of benzo[b]thiophene ring at the donor end could effectively reduce the energy gap by 0.34 eV of chromophore B.

Based on the "two level model", chromophore B with lower energy gap indicates the π-electron delocalization efficiency and may get a larger molecular hyperpolarizability (β).

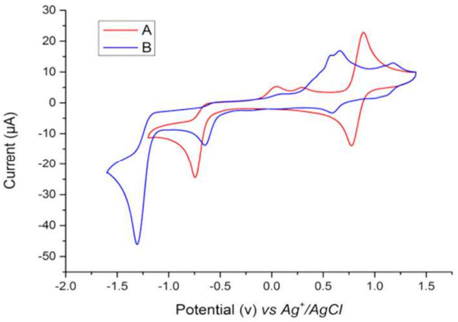


Fig. 1 Cyclic voltammograms of chromophores A and B.

Table 1 Electrochemical properties for A, B and FTC.

chromophore	E_{ox}/V	E_{red}/V	E_{ge}(eV)
A[a]	0.85	-0.66	1.51
B[a]	0.63	-0.56	1.19
FTC[b]	-	-	1.53

[a] 10^{-3} M in CH_2Cl_2 versus Ag/AgCl, glassy carbon working electrode, Pt counter electrode, 20°C, 0.1M Bu_4NPF_6,100 mv s^{-1} scan rate, Ferrocene internal reference E1/2 = +0.43 V.
[b] Reference 25

In order to disclose the role of the benzo[b]thiophene on the properties of these NLO chromophores, DFT calculations have

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been carried out on chromophores A, B and FTC (selected for comparison) using B3LYP/6-311G* geometries by means of Gaussian 03 (G03). All C-C double bonds outside the aromatic rings were set to be in trans configuration. The geometry optimization of A and B indicates that both chromophores are perfectly planar. From the analysis of the electronic structure of A, B and FTC (Fig. 2), it emerges that the electron density is uniformly distributed along the donor and π-bridge moiety at the HOMO state. While at the LUMO state, the electrons are shifted to the π-bridge and acceptor moiety due to the intramolecular charge transfer. The comparison of B and FTC electron distribution at the HOMO and LUMO states indicates the easier delocalization of electrons of B, thus suggesting the excellent charge transfer, in agreement with the cyclic voltammetry. Here, the energy of the HOMO, LUMO levels, Zero-frequency (static) molecular first hyperpolarizability (β_0) and dipole moment (μ) of A, B and FTC are listed in Table 2. From the table we can see that increasing the length of the conjugated bridge resulted in a great improvement of β. The calculated β_0 of B (1330×10^{-30} esu) is about one and a half times larger than FTC (827×10^{-30} esu) and four times larger than A (312×10^{-30} esu).

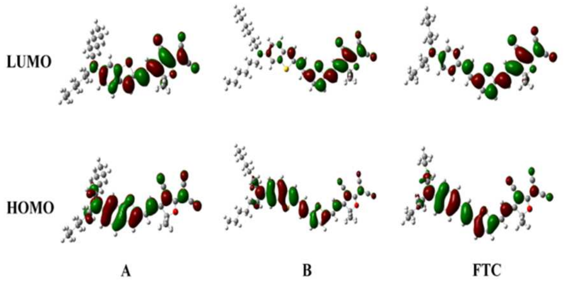

Fig. 2 The frontier HOMO and LUMO orbitals of the A (left), B (middle) and FTC (right) at the B3LYP/6-311G* level

Table 2 Calculated properties of A, B and FTC.

entry	μ/ D	β_0/ 10^{-30} esu	HOMO/ eV	LUMO/ eV	E_{ge}/ eV
A	20.0	312	-5.67	-3.31	2.36
B	20.6	1330	-5.38	-3.46	1.92
FTC	20.9	828	-5.39	-3.34	2.05

DFT calculations at the B3LYP6-311G* level in vacuum.

The UV-vis spectral absorption of the two chromophores were measuered in a series solvents with different dielectric constants and in films, As shown in Fig. 3. The absorption data were collected in Table 3. It could be found that both chromophores exhibit a broad intramolecular charge-transfer (ICT) absorption band and a distinct red-shift of the maximum absorption when gradually increasing solvent dielectric constants from 1, 4-dioxane to chloroform. With a further increase of solvent dielectric constants both chromophores results not only in a hypsochromic effect but also in a leveling off of the λ_{max} values, and slight change of spectral shape. The absorption range of chromophore A in different solvents is from 500 to 750 nm, that of chromophore B is from 500 to 850 nm. The full width at half maximum (FWHM) values of chromophore A lies in the range of 108 to 139 nm, which is smaller than chromophore B (from 168 to 201 nm). Compared with chromophore A, the broader absorption range and larger FWHM of chromophore B suggested B can be polarized more efficiently. The extinction coefficients of chromophores A and B in different solvents follow the similar trend of the λ_{max}. Chromophores A and B with weaker molar absorption coefficients in low or high-polarity solvents suggested that they had a reduction in π conjugation due to the twist, while in moderate-polarity, such as dichloromethane and chloroform, chromophores A and B showed a larger molar extinction coefficients (A: $\varepsilon > 52000$ M^{-1} cm^{-1}, B: $\varepsilon > 40000$ M^{-1} cm^{-1}). The large molar extinction coefficients are indicative of highly π-conjugated systems. The maximum absorption of chromophores A and B in chloroform are 658 nm and 688 nm, respectively. Due to the less polarity environment in films than in chloroform, in solid states, chromophore A and B showed maximum absorption at 636 nm and 665 nm, respectively. Compared with chromophore A, λ_{max} values in chloroform of chromophore B red shifted by 30 nm due to the longer conjugation length, which is in agreement with the results of cyclic voltammetry. However, the maximum absorption of Chromophore B (688 nm) and FTC (685 nm)[25] had little difference, although B has a longer conjugation length and a lower energy gap (confirmed by cyclic voltammetry and theoretical calculations). Given that the sulfur atom in the benzo[b]thiophene ring was linked to the odd-numbered carbon atom of the conjugated chain and a low λ_{max} of chromophore B was reasonable based on the Dewar's rules.[9, 26] Therefore, an important advantage of chromophore B is that the resulting remarkable decrease in energy gap is not accompanied by a large red shift of the absorption band.

Table 3 Photophysical properties of A[a], B[a] and FTC[b].

entry	solvent	λ_{max}/ nm	ε/ 10^4 M^{-1} cm^{-1}	FWHM/ nm
A	Dioxane	602	4.36	116
	Toulene	617	2.92	116
	Dichloromethane	656	5.23	117
	Chloroform	658	5.88	108
	Acetone	628	4.59	133
	DMF	647	2.60	139
	In films	636	47.93	145
B	Dioxane	633	3.95	170
	Toulene	655	4.12	168
	Dichloromethane	671	4.03	193
	Chloroform	688	4.21	192
	Acetone	631	2.75	192
	DMF	646	2.69	201
	In films	665	1.58	231
FTC	Dioxane	624	-	-
	Chloroform	688	-	-

[a] Absorption spectra were measured in 10^{-5} M solutions

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[b] Reference 25

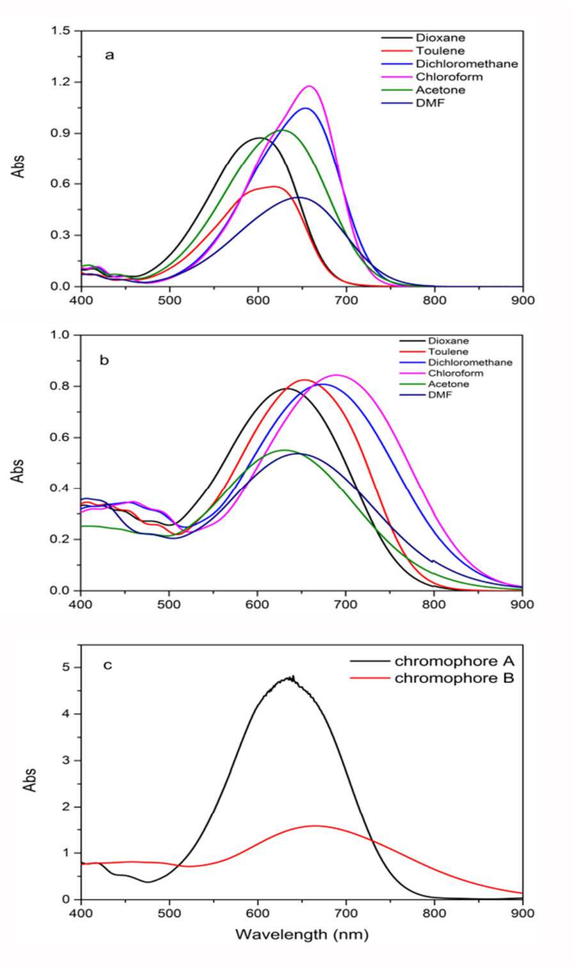
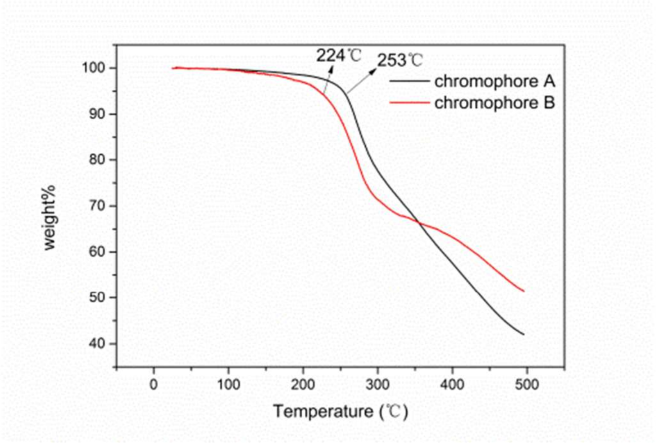


Fig. 3 Photophysical spectral of chromophores A and B in different solvents (a, b), in APC films (c).

The thermal stabilities of chromophores A and B were investigated by thermogravimetric analysis (TGA). The decomposition temperature (T_d, temperature at which 5 % mass loss occurs during heating), as shown in Figure 4, is 253°C for A, 224°C for B. The decomposition temperature of chromophore B was decreased due to its greater degree of π-electron conjugation than A. Both A and B displays good thermal stability enough for materials working and processing. To investigate the macroscopic EO activity of the new chromophores, A and B were doped into amorphous polycarbonate (APC). The films were prepared by spin coating on the indium tin oxide (ITO) glass substrate. The poled films containing A with a loading density of 20 wt%, a maximum EO coefficient (r_{33}) of 42 pm/V at 1310 nm can be achieved, while for the poled films containing B, the r_{33} values is 75 pm/V at 1310 nm. Compared with the previous reported guest-host EO polymers doped with anline-based FTC chromophore analogue (r_{33} = 20-50 pm/V at 1310 nm),[27] the poled films containing B represents at least 50 % improvement in r_{33}, and even for the poled films containing A, a comparable r_{33} values was achieved. Such a great improvement in r_{33} of A and B might be attributed to that fused benzo group provides a planar geometry, which makes an effective intramolecular charge transfer. In addition, the long alkyl chain also provides effective site isolation to decrease the strong electrostatic interactions among chromophores.

Fig. 4 TGA curves of chromophores A and B.



Conclusion

We have designed and synthesized two new chromophores with the benzo[b]thiophene moiety at the electron donor end for the first time. In comparison with FTC analogue, chromophore B just displays a 3 nm bathochromic shift of maximum absorption in chloroform, and more impressively, 50% improvement in EO coefficient. For chromophore A, it shows similar EO coefficient with the benchmark FTC, while a 27 nm blue-shifted maximum absorption in chloroform. So, these molecules present an optical transparency at the telecommunication wavelengths (1300 and 1550 nm). This verifies the important role of benzo[b]thiophene ring in NLO chromophore, thereby providing a simple means for defeating the "nonlinearity-transparency trade-off".

Experimental details

Instruments and materials.

^{1}H NMR and ^{13}C NMR spectra were determined by an Advance Bruker 400M (400MHz) NMR spectrometer (tetramethylsilane as internal-reference). The MS spectra were obtained on MALDI-TOF (Matrix Assisted Laser Desorption/Ionization of Flight) on BIFLEXIII (Broker Inc.) spectrometer. The UV-vis experiments were performed on Cary 5000 photo spectrometer. The TGA was determined by TA5000-2950TGA (TA co) with a heating rate of 10 °C min^{-1} under the protection of nitrogen. Cyclic voltammetry (CV) experiments were performed on a CHI660C electrochemical workstation by a cyclic voltammetry (CV) technique in CH_2Cl_2 solution, using glassy carbon as working electrode, Pt as counter electrode, Ag/AgCl electrode as the reference electrode in the presence of 1 mM n-

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tetrabutylammonium perchlorate as the supporting electrolyte. The DFT calculations using Gaussian 03 were carried out at the hybrid B3LYP level by employing the split valence 6-31 g (d) basis set.[28] All chemicals, commercially available, are used without further purification unless stated. The DMF, toluene and THF were freshly distilled prior to its use. 2-dicyanomethylene-3-cyano-4-methyl-2, 5-dihydrofuran (TCF) acceptor was prepared according to the literature.[29]

Poling and r_{33} measurements.

Guest–host polymers were prepared by formulating chromophores A and B into amorphous polycarbonate (APC) using dibromomethane (CH_2Br_2) as the solvent. The resulting solutions were filtered through a 0.22 μm Teflon membrane filter and spin-coated onto indium tin oxide (ITO) glass substrates. Films of doped polymers were baked in a vacuum oven at 40ºC to remove the residual solvent. The poling process was carried out at a temperature of T_g of the polymer. The r_{33} values were measured using Teng-Man simple reflection technique at the wavelength of 1310 nm.[30]

Synthesis.

Synthesis of compound 2. Under the N_2 atmosphere. A mixture of 6-bromobezo[b]thiophene (2.13 g, 10 mmol), the corresponding secondary amine dihexylamine (1.85 g, 10 mmol), $Pd_2(dba)_3$ (0.11 g, 0.24 mmol), 1,1′-bis-(diphenylphosphino)-ferrocene (0.88 g, 0.16 mmol), and t-BuONa (1.42 g, 12.6 mmol) in toluene (60 mL) was refluxed at 110 °C for 24 h. After the solution cooled to room temperature, the toluene was removed under reduce pressure. The crude product was dissolved in 200 ml water and extracted with ethyl acetate (3×50 ml). The organic layer was removed in vacuum. The residue was purified by column chromatography (eluent Petroleum ether) to give a yellow oil (1.54 g, 4.8 mmol) in 48.5% yield. ^1H NMR (400 MHz, $CDCl_3$, δ ppm) : 7.62 (d, J = 8.7 Hz, 1H), 7.15 (d, J = 5.4 Hz, 1H), 7.08 – 7.01 (m, 2H), 6.81 (d, J = 2.4 Hz, 1H), 3.35 – 3.26 (m, 4H), 1.61 (d, J = 3.9 Hz, 4H), 1.34 (s, 12H), 0.96 – 0.84 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, δ ppm): 146.30, 142.36, 129.99, 123.88, 123.45, 120.86, 112.03, 103.85, 51.73, 31.93, 27.44, 27.06, 22.88, 14.23. MS (EI): m/z 317.2092 ($C_{20}H_{31}NS$, calcd: 317.53).

Synthesis of compound 3. To a solution of prepared 2 (0.88 g, 2.8 mmol) in dry THF (20 ml), n-BuLi (1.8 ml, 4.2 mmol, 2.4 M in hexane) was added dropwise at -78 °C under the N_2 atmosphere. After the solution was stirred at -78 °C for 1 h, DMF (0.41 g, 5.6 mmol) was added and kept at -78 °C for another 4 h. Several drops of water were added to quenching the reaction. The mixture was poured into ice water and extracted with dichloromethane (3×50 ml). The combined organic layer was dried over MgSO4. The pure product was obtained by column chromatography (acetone: Petroleum ether = 1:100, v/v) to give a yellow oil 3 (0.88 g, 2.6 mmol) in 92.8% yield. ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 9.92 (s, 1H), 7.81 (s, 1H), 7.68 (d, J = 9.0 Hz, 1H), 6.92 (d, J = 2.0 Hz, 1H), 6.82 (dd, J = 9.1, 2.3 Hz, 1H), 3.36 (d, J = 7.7 Hz, 4H), 1.64 – 1.61 (m, 4H), 1.34 (s, 12H), 0.92 (d, J = 6.5 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, δ ppm): 183.72, 148.93, 146.74, 137.84, 135.61, 128.51, 127.09, 112.68, 102.46, 51.48, 31.79, 27.36, 26.89, 22.77, 14.13. MS (EI): m/z 345.9403 ($C_{21}H_{31}NOS$, calcd: 345.54).

Synthesis of compound 4. To a solution of 3 (0.36 g, 1 mmol) in dry THF, thiophene methyl phosphonate (0.55 g, 1.2 mmol) and Sodium hydride (0.25 g, 10 mmol) was added. The mixture was stirred at room temperature. After 24 h, the mixture was poured into the ice water and extracted with dichloromethane (3×50 ml). The combined organic layer was dried over $MgSO_4$. The organic layer was removed in vacuum. The residue was purified by column chromatography (acetone: Petroleum ether = 1: 150, v/v) to give a yellow oil 4 (0.33 g, 0.8 mmol) in 77% yield. ^1H NMR (400 MHz, $CDCl_3$, δ ppm) : ^1H NMR (400 MHz, $CDCl_3$): 7.40 (d, J = 8.8 Hz, 1H), 7.09 (d, J = 5.0 Hz, 1H), 7.01 (d, J = 15.7 Hz, 1H), 6.96 (s, 2H), 6.93 – 6.89 (m, 1H), 6.89 – 6.82 (m, 2H), 6.65 (dd, J = 8.9, 2.1 Hz, 1H), 3.28 – 3.18 (m, 4H), 1.52 (s, 4H), 1.26 (s, 12H), 0.84 (t, J = 6.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, δ ppm): 147.43, 143.65, 142.54, 137.74, 130.94, 128.51, 126.48, 124.79, 124.25, 123.57, 121.99, 112.44, 104.19, 52.32, 32.62, 28.19, 27.75, 23.58, 14.94. MS (EI): m/z 425.2211 ($C_{26}H_{35}NS_2$, calcd: 425.69).

Synthesis of compound 5. To a solution of 4 (0.33 g,0.8 mmol) in dry THF (20 ml), n-BuLi (0.6 ml, 1.6 mmol, 2.4 M in hexane) was added dropwise at -78 °C under the N_2 atmosphere. After the solution was stirred at -78 °C for 1 h, DMF (0.11 g, 1.6 mmol) was added and keep at -78 °C for another 2 h. Several drops of water were added to quenching the reaction. The mixture was poured into ice water and extracted with dichloromethane (3× 50 ml). The combined organic layer was dried over MgSO4. The solvents were removed in vacuum. Pure product 5 was purified by column chromatography (acetone: Petroleum ether = 1:30, v/v) to give a yellow oil (0.32 g, 0.7 mmol) in 87.5% yield. ^1H NMR (400 MHz, Acetone, δ ppm): 9.89 (s, 1H), 7.86 (d, J = 3.8 Hz, 1H), 7.57 (d, J = 8.9 Hz, 1H), 7.50 (d, J = 15.8 Hz, 1H), 7.33 (s, 2H), 7.08 (s, 1H), 7.01 (d, J = 15.8 Hz, 1H), 6.85 (d, J = 10.4 Hz, 1H), 3.45 – 3.38 (m, 4H), 1.68 – 1.61 (m, 4H), 1.35 (s, 12H), 0.91 (d, J = 6.7 Hz, 6H).^{13}C NMR (101 MHz, Acetone, δ ppm): 183.29, 152.58, 148.13, 143.31, 142.28, 138.79, 136.44, 130.74, 127.80, 127.54, 127.24, 125.38, 120.34, 112.74, 103.79, 51.78, 32.44, 28.01, 27.38, 23.33, 14.28. MS (EI): m/z 453.2297 ($C_{27}H_{35}NOS_2$, calcd: 453.70).

Synthesis of chromophores A and B.

General Procedure. To a solution of prepared aldehyde (1 equiv) in ethanol, TCF (1 equiv) and several drops of piperidine were added. The mixture was refluxed for 2-4 h. The residue was purified as described below.

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Chromophore A. 3 (0.38 g, 1.1 mmol) in ethanol, TCF (0.22 g, 1.1 mmol), piperidine in ethanol were reacted following the general procedure. The residue was purified by column chromatography (acetone: Petroleum ether = 6: 1, v/v) to give a green solid (0.35 g) in 60 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.93 (d, J = 15.4 Hz, 1H), 7.62 (d, J = 9.1 Hz, 1H), 7.56 (s, 1H), 6.87 (s, 1H), 6.80 (d, J = 9.1 Hz, 1H), 6.42 (d, J = 15.4 Hz, 1H), 3.43 – 3.34 (m, 4H), 1.74 (s, 6H), 1.65 (s, 4H), 1.35 (s, 12H), 0.92 (t, J = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, δ ppm): 146.30, 142.36, 129.99, 123.88, 123.45, 120.86, 112.03, 103.85, 51.73, 31.93, 27.44, 27.06, 22.88, 14.23. MS (MALDI-TOF): m/z 526.971 ($C_{24}H_{20}N_4OS$, calcd: 526.74).

Chromophore B. 5 (0.19 g, 0.4 mmol), TCF (0.08 g, 0.4 mmol), piperidine in ethanol were reacted following the general procedure. The residue was purified by column chromatography (acetone: Petroleum ether = 4: 1, v/v) to give dark solid 3 (0.15 g, 0.2 mmol) in 50 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.68 (d, J = 15.7 Hz, 1H), 7.45 (d, J = 8.9 Hz, 1H), 7.30 (d, J = 4.0 Hz, 1H), 7.22 (d, J = 15.5 Hz, 1H), 7.12 (s, 1H), 6.99 (d, J = 4.0 Hz, 1H), 6.82 (s, 1H), 6.78 (d, J = 15.5 Hz, 1H), 6.67 (dd, J = 9.0, 2.2 Hz, 1H), 6.51 (d, J = 15.7 Hz, 1H), 3.31 – 3.21 (m, 4H), 1.68 (s, 6H), 1.57 – 1.52 (m, 4H), 1.27 (d, J = 3.4 Hz, 12H), 0.84 (t, J = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, δ ppm): 175.65, 172.78, 152.44, 147.34, 142.99, 139.06, 138.29, 137.11, 135.68, 129.73, 128.07, 127.78,127.10, 124.80, 119.32, 112.23, 111.88, 111.40, 110.94, 102.78, 97.02, 96.67, 56.35, 51.42, 31.73, 27.33, 26.85, 26.55, 22.71, 14.07, 1.04. MS (MALDI-TOF): m/z 634.868 ($C_{38}H_{42}N_4OS_2$, cacld: 634.90).

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Notes and references

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