

# Synthesis and Characterization of Indole-Containing Chromophores for Second-Order Nonlinear Optics

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Push–pull indole-containing nonlinear optical chromophores with different acceptor and  $\pi$ -conjugated moieties have been synthesized and characterized. Experimental measurements of the second-order nonlinear optical response demonstrated that the chromophores exhibit similar or superior optical nonlinearity compared with their analogues with an aniline moiety as the donor group, but the indole-based chromophores display blue-shifted absorption, even up to 30 nm.

## Introduction

Organic and polymeric second-order nonlinear optical (NLO) materials have attracted much attention and been extensively studied in the past decades due to their potential applications involving switching or modulation of light.<sup>1</sup> As one of the key points of NLO materials, organic chromophores, which exhibit good properties such as high thermal and chemical stability, high nonlinearity, and transparency as well the capability to be incorporated easily into polymers through covalent bonds, are currently being pursued for the next generation of high-performance photonics devices. And most attempts concentrated on the optimization of the compounds with the “push–pull” structure, in which a  $\pi$ -conjugated bridge is encapped with an electron donor group and an electron acceptor group.<sup>2</sup> However, from the two-level model,<sup>3</sup> the nonlinear property ( $\beta$  value) of this type of chromophore is a strong function of the absorption maximum ( $\lambda_{\text{max}}$ ), leading to the so-called “nonlinearity–transparency tradeoff”. That is to say, the enhancement of the  $\beta$  values of chromophores often accompanies decreased transparency, which results in the primary source of optical loss in NLO materials at the operation wavelength of electrooptical devices (typically 0.8, 1.3, and 1.5  $\mu\text{m}$ ).<sup>4</sup> Thanks to the efforts of scientists, some special NLO chromophores exhibit good transparency and large nonlinearity, even remarkably defeating the nonlinearity–transparency tradeoff in some degree. Mainly, all the attempts could be divided into three kinds: using a combination of different types of conjugated bridge, seeking the best cooperation of donor and acceptor moieties, and designing two or multicharge-transporting molecules (including the octupolar 2-D and 3-D strategy).<sup>5</sup> In the past several years, we have successfully prepared some series of chromophores defeating the tradeoff by using the combined conjugation bridge or special electron acceptors.<sup>6</sup>

On the other hand, while the electron acceptor groups and  $\pi$ -conjugated bridges are widely studied to optimize the comprehensive properties of chromophores,<sup>2,5</sup> the donor moieties have not received much attention, though they are also important

blocks for the construction of chromophores just as the other two. During the exploration of new NLO polymers with good properties, we noted a special compound, indole. All of the polymers containing indole-based chromophores as side chains demonstrate good NLO effects, similar to those polymers possessing aniline analogue pendant moieties, but exhibit much blue-shifted absorption, which was also confirmed in the literature.<sup>7</sup> On the basis of this point, also there are no systemic reports on the indole-containing NLO chromophores, we designed and synthesized a series of indole-containing chromophores with different conjugated bridges and electron acceptors. And all of the chromophores show blue-shifted absorption and large nonlinearities, combined with good thermal stability.

## Experimental Section

**Materials.** Tetrahydrofuran (THF) was dried over and distilled from a K–Na alloy under an atmosphere of dry nitrogen. *N,N*-Dimethylformamide was dried over and distilled from  $\text{CaH}_2$  under an atmosphere of dry nitrogen. 1,2-Dichloroethane was dried over and distilled from phosphorus pentoxide. Phosphorus oxychloride and malononitrile was freshly distilled before use. Tricyanovinylidihydrofuran (TCF) was prepared following the procedure reported in the literature.<sup>8</sup> All other reagents were used as received.

**Instrumentation.** A  $^1\text{H}$  NMR spectroscopy study was conducted with a Varian Mercury300 spectrometer. FT-IR spectra were recorded on a Testscan Shimadzu FT-IR 3000 series in the region of 3000–400  $\text{cm}^{-1}$  on KBr pellets. UV–vis spectra were obtained using a Shimadzu 160A spectrometer. FAB-MS spectra were recorded with a VJ-ZAB-3F-Mass spectrometer. Elemental analyses were performed by a CAR-LOERBA-1106 or VarioEL III microelemental analyzer. Thermal analysis was performed on a NETZSCH STA449C thermal analyzer at a heating rate of 10  $^\circ\text{C}/\text{min}$  in nitrogen at a flow rate of 50  $\text{cm}^3/\text{min}$  for thermogravimetric analysis (TGA). The second-order nonlinear hyperpolarizability of these chromophores was determined by hyper-Rayleigh scattering in chloroform using the fundamental excitation wavelength of 1064 nm, and in the same solvent, the known hyperpolarizability of

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*p*-nitroaniline (*p*-NA) was used as the external reference. The thermometer for measurement of the melting point was uncorrected.

**(2-Furylmethyl)triphenylphosphonium Bromide (3).** To a solution of furan-2-carbaldehyde (**1**) (19.2 g, 0.2 mol), sodium hydroxide (20 mL, 0.25 mol, 12.5 M in H<sub>2</sub>O) was added dropwise under vigorous stirring at 0 °C. Then the addition of a few drops of water led to a clear reaction mixture. The mixture was extracted with Et<sub>2</sub>O and dried over Na<sub>2</sub>SO<sub>4</sub>. Purification by distillation gave the corresponding alcohol (**2**), a yellow oil (5.17 g), which was directly dissolved in anhydrous CHCl<sub>3</sub> (150 mL) in the presence of HPPPh<sub>3</sub>Br (17.2 g, 50 mmol) (prepared from a solution of HBr 40% and PPh<sub>3</sub>). The reaction mixture was refluxed for 3 h, and after cooling, the solvent was evaporated. After recrystallization from EtOH, a red solid was obtained (15.9 g, 75%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ (ppm): 7.76–7.34 (m, 15H), 7.16 (d, 1H), 6.54 (d, 1H), 6.24 (m, 1H), 5.59 (d, *J* = 12.6 Hz, 2H).

***N*-Hexylindole (5).** To a solution of potassium hydroxide (17.2 g, 0.31 mmol) in anhydrous DMF (90 mL), indole (**4**) (7.18 g, 61.2 mmol) was added slowly and stirred for 1 h. After the addition of 1-bromohexane (12.1 g, 73 mmol) in DMF (20 mL), the solution was stirred at 50 °C. The resulting mixture was poured into water and extracted with CHCl<sub>3</sub> and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The crude product was purified by vacuum distillation at 140–142 °C/0.4 mbar to yield a yellow oil (10.2 g, 83%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ (ppm): 7.65 (d, *J* = 8.1 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 2H), 6.50 (d, *J* = 2.1 Hz, 1H), 4.12 (t, *J* = 6.9 Hz, 2H), 1.83 (m, 2H), 1.32 (m, 6H), 0.87 (br, 3H).

**3-Formyl-*N*-Hexylindole (6).** To a solution of **5** (2.01 g, 10 mmol) and DMF (0.95 g, 13.0 mmol) in 1,2-dichloroethane (25 mL) was added POCl<sub>3</sub> (1.16 mL, 12.6 mmol), and the mixture was refluxed for 2 h. After the mixture was cooled, it was poured into an aqueous solution of sodium acetate 1 M (100 mL) and stirred for another 2 h. The solution was extracted with CHCl<sub>3</sub> (50 mL × 3). The organic fractions were gathered, dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated in a vacuum. Purification by chromatography on silica gel (eluent, CHCl<sub>3</sub>) yielded a brown, viscous oil (1.56 g, 68%). IR: 1660 cm<sup>-1</sup> (C=O). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ (ppm): 9.98 (s, 1H), 8.29 (d, *J* = 6.3 Hz, 1H), 7.71 (s, 1H), 7.36–7.28 (m, 3H), 4.17 (t, *J* = 7.2 Hz, 2H), 1.90 (m, 2H), 1.32 (br, 6H), 0.88 (br, 3H).

**(*Z*)/(*E*)-3-[2-(*N*-Hexylindole)vinyl]-2-furan (**7**).** Under the atmosphere of nitrogen, potassium *tert*-butoxide (1.68 g, 15 mmol) was added to the suspension of **3** (4.23 g, 10 mmol) in THF (20 mL) at room temperature, and the solution turned red. Then a solution of **6** (2.40 g, 10 mmol) in THF (20 mL) was added dropwise. The reaction mixture was stirred overnight at room temperature and poured into water (100 mL). The organic product was extracted with CHCl<sub>3</sub> and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After the removal of the solvent, the *cis*–*trans* isomers of **7** were obtained from a silica gel chromatography column (eluent, CHCl<sub>3</sub>/petroleum ether (1:1)) to give a red oil (1.85 g, 69%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ (ppm): 7.93 (d, *J* = 7.8 Hz, 1H), 7.87 (s, 1H), 7.38–7.32 (m, 2H), 7.28–7.14 (m, 3H), 6.89 (d, *J* = 16.5 Hz, 1H), 6.42 (s, 1H), 6.26 (d, *J* = 3.3 Hz, 1H), 4.14 (m, 2H), 1.86 (m, 2H), 1.30–1.25 (m, 6H), 0.88 (br, 3H).

**(*Z*)/(*E*)-3-[2-(*N*-Hexylindole)vinyl]-2-furaldehyde (**8**).** To a solution of **7** (1.60 g, 5 mmol) and DMF (0.88 g, 12 mmol) in 1,2-dichloroethane (25 mL) was added POCl<sub>3</sub> (1.07 g, 12 mmol), and the mixture was refluxed for 2 h. After the mixture was cooled, it was poured into an aqueous solution of sodium acetate (1M, 100 mL) and stirred for another 2 h. The solution was

extracted with CHCl<sub>3</sub> (50 mL × 3). The organic fractions were gathered and dried over Na<sub>2</sub>SO<sub>4</sub>, then evaporated in a vacuum. Purification by chromatography on silica gel (eluent, CHCl<sub>3</sub>) yielded a dark, viscous oil (1.37 g, 86%). The product **8** was obtained as a mixture of *cis* and *trans* isomers (*cis*/*trans* = 1:3). The product was carried over to the next step without further purification. IR: 1664 cm<sup>-1</sup> (C=O). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ (ppm) of the *trans* product: 9.49 (s, 1H), 7.92 (d, *J* = 7.5 Hz, 1H), 7.58 (d, *J* = 16.2 Hz, 1H), 7.38–7.31 (m, 2H), 7.23–7.14 (m, 3H), 6.88 (d, *J* = 16.2 Hz, 1H), 6.42 (d, *J* = 3.6 Hz, 1H), 4.11 (d, *J* = 6.9 Hz, 2H), 1.85 (m, 2H), 1.31 (br, 6H), 0.88 (br, 3H).

**(2-Thiophylmethyl)triphenylphosphonium Bromide (11).**<sup>9</sup> To a solution of 2-methylthiophene (**9**) (5.01 g, 50 mmol) in CCl<sub>4</sub> (150 mL), *N*-bromosuccinimide (NBS) (10.7 g, 60 mmol) and benzoyl peroxide (BPO) (0.1 g mmol) were added. The mixture was refluxed for 2 h and then cooled to room temperature. The organic phase was collected by filtration and evaporated in a vacuum. The residue was dissolved in CHCl<sub>3</sub>, and the solution was washed with water, dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated in a vacuum. Then the resultant yellow oil (**10**), triphenylphosphonium (10.7 g, 50 mmol), and CHCl<sub>3</sub> (100 mL) were mixed and refluxed for 2 h. After the mixture was cooled to room temperature, the precipitate was collected by filtration, washed with CHCl<sub>3</sub>, and dried to give a white powder product (14.0 g, 64%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ (ppm): 7.80–7.60 (m, 15H), 7.12 (m, 2H), 6.84 (m, 1H), 5.73 (d, *J* = 13.2 Hz, 2H).

**(*Z*)/(*E*)-3-[2-(*N*-Hexylindole)vinyl]-2-thiophene (**12**).** Under the atmosphere of nitrogen, potassium *tert*-butoxide (2.20 g, 20 mmol) was added to the suspension of **11** (4.80 g, 11 mmol) in THF (40 mL) at room temperature, and the solution turned red. Then a solution of **6** (2.07 g, 9 mmol) in anhydrous THF (20 mL) was added dropwise. The reaction mixture was stirred overnight at room temperature and poured into water (100 mL). The organic product was extracted with CHCl<sub>3</sub> and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After the removal of the solvent, compound **12** was obtained from a silica gel chromatography column (eluent, CHCl<sub>3</sub>/petroleum ether (1:1)) as a red oil (1.80 g, 65%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ (ppm): 7.94 (d, *J* = 7.5 Hz, 1H), 7.53 (d, *J* = 8.1 Hz, 1H), 7.33 (d, *J* = 3.6 Hz, 1H), 7.25–7.05 (m, 5H), 7.00 (s, 1H), 6.65 (s, 1H), 4.09 (t, *J* = 6.9 Hz, 2H), 1.83 (m, 2H), 1.31 (br, 6H), 0.87 (br, 3H).

**(*Z*)/(*E*)-3-[2-(*N*-Hexylindole)vinyl]-2-thiophenaldehyde (**13**).** Compound **12** (0.92 g, 3 mmol) was dissolved in THF (50 mL). *n*-Butyllithium (1.3 mL, 2.5 M solution in hexane, 3 mmol) was added dropwise at –78 °C. The mixture was warmed to –20 °C and cooled back to –78 °C again. DMF (3 mL) was then added. The resultant mixture was allowed to warm followed by stirring at room-temperature overnight before the THF was removed. The residue was poured into water (100 mL) and extracted with CHCl<sub>3</sub>. The organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. A mixture product **13** of *cis* and *trans* isomers was obtained from a silica gel chromatography column (eluent, CHCl<sub>3</sub>) as a dark solid (0.81 g, 81%). The mixture was carried over to the next step without further purification. IR: 1656 cm<sup>-1</sup> (C=O). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ (ppm) of the *trans* product: 9.71 (s, 1H), 7.84 (s, 1H), 7.72 (d, *J* = 5.7 Hz, 1H), 7.48 (d, *J* = 5.1 Hz, 1H), 7.44–7.23 (m, 5H), 7.20 (t, *J* = 3.9 Hz, 1H), 4.16 (t, *J* = 7.2 Hz, 2H), 1.88 (m, 2H), 1.32–1.24 (m, 6H), 0.87 (br, 3H).

**General Procedure for the Synthesis of Chromophores I(a–d) and II(a–d).** The prepared aldehyde (1 equiv) and the acceptor (1 equiv) were dissolved in absolute ethanol, and then 2–3 drops of piperidine was added as the catalyst. The mixture was refluxed for 2–4 h, then the solvent was removed on a

rotary evaporator. The solid was purified through a silica chromatography column to yield pure product.

**Chromophore Ia.** Aldehyde **8** (161 mg, 0.5 mmol), malononitrile (33 mg, 0.5 mmol), and piperidine (catalyst) were reacted in absolute ethanol (50 mL) following the general procedure. Chromophore **Ia** was obtained from a silica gel chromatography column (eluent,  $\text{CHCl}_3$ ) as a dark red solid (140 mg, 76%). Mp: 95–96 °C. IR: 2218  $\text{cm}^{-1}$  ( $\text{C}\equiv\text{N}$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 7.95 (d,  $J = 8.1$  Hz, 1H), 7.74 (d,  $J = 15.3$  Hz, 1H), 7.44 (s, 1H), 7.40–7.24 (m, 5H), 6.90 (d,  $J = 15.6$  Hz, 1H), 6.52 (d,  $J = 3.0$  Hz, 1H), 4.14 (t,  $J = 7.5$  Hz, 2H), 1.88 (m, 2H), 1.34 (br, 6H), 0.90 (br, 3H). MS (FAB) ( $m/z$ ) [ $\text{M}^+$ ]: 370.0; calcd, 369.2. Anal. Calcd for  $\text{C}_{24}\text{H}_{23}\text{N}_3\text{O}$ : C, 78.02; H, 6.27; N, 11.37. Found: C, 77.63; H, 6.49; N, 11.78.

**Chromophore Ib.** Aldehyde **8** (161 mg, 0.5 mmol), 3-phenyl-5-isoxazolone (80 mg, 0.5 mmol), and piperidine (catalyst) were reacted in absolute ethanol (50 mL) following the general procedure. Chromophore **Ic** was obtained from a silica gel chromatography column (eluent,  $\text{CHCl}_3$ ) as a dark purple solid (167 mg, 72%). Mp: 118–120 °C. IR: 1665  $\text{cm}^{-1}$  ( $\text{C}=\text{O}$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 7.94 (d,  $J = 7.5$  Hz, 1H), 7.63–7.59 (m, 5H), 7.46 (s, 1H), 7.40–7.26 (m, 6H), 6.92 (d,  $J = 16.2$  Hz, 1H), 6.69 (d,  $J = 3.0$  Hz, 1H), 4.15 (t,  $J = 7.5$  Hz, 2H), 1.88 (m, 2H), 1.34 (m, 6H), 0.90 (br, 3H). MS (FAB) ( $m/z$ ) [ $\text{M}^+$ ]: 465.0; calcd, 464.2. Anal. Calcd for  $\text{C}_{30}\text{H}_{28}\text{N}_2\text{O}_3$ : C, 77.56; H, 6.08; N, 6.03. Found: C, 77.43; H, 6.37; N, 5.98.

**Chromophore Ic.** Aldehyde **8** (161 mg, 0.5 mmol), 1,3-diethylthiobarbituric acid (100 mg, 0.5 mmol), and piperidine (catalyst) were reacted in absolute ethanol (50 mL) following the general procedure. Chromophore **Ib** was obtained from a silica gel chromatography column (eluent,  $\text{CHCl}_3$ ) as a dark solid (163 mg, 65%). Mp: 198–200 °C. IR: 1665  $\text{cm}^{-1}$  ( $\text{C}=\text{O}$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 8.91 (br, 1H), 8.40 (s, 1H), 7.97 (d,  $J = 7.2$  Hz, 1H), 7.71 (d,  $J = 15.9$  Hz, 1H), 7.45 (s, 1H), 7.41–7.26 (m, 3H), 6.95 (d,  $J = 16.2$  Hz, 1H), 6.71 (d,  $J = 3.0$  Hz, 1H), 4.62 (q,  $J = 6.6$  Hz, 4H), 4.17 (t,  $J = 7.5$  Hz, 2H), 1.91 (br, 2H), 1.36 (br, 12H), 0.91 (br, 3H). MS (FAB) ( $m/z$ ) [ $\text{M}^+$ ]: 504.1; calcd, 503.2. Anal. Calcd for  $\text{C}_{29}\text{H}_{33}\text{N}_3\text{O}_3\text{S}$ : C, 69.16; H, 6.60; N, 8.34. Found: C, 68.85; H, 6.05; N, 8.51.

**Chromophore Id.** Aldehyde **8** (128 mg, 0.4 mmol), TCF (80 mg, 0.4 mmol), and piperidine (catalyst) were reacted in absolute ethanol (50 mL) following the general procedure. Chromophore **Id** was obtained from a silica gel chromatography column (eluent, ethyl acetate/ $\text{CHCl}_3$  (3:20)) as a dark solid (100 mg, 50%). Mp: 202–204 °C. IR: 2223  $\text{cm}^{-1}$  ( $\text{C}\equiv\text{N}$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 7.98 (d,  $J = 7.5$  Hz, 1H), 7.60 (d,  $J = 16.5$  Hz, 1H), 7.47 (s, 1H), 7.41–7.26 (m, 3H), 7.05 (br, 1H), 6.95 (d,  $J = 16.5$  Hz, 1H), 6.81 (d,  $J = 15.3$  Hz, 1H), 6.57 (br, 1H), 4.15 (t,  $J = 6.9$  Hz, 2H), 1.88 (m, 2H), 1.77 (br, 6H), 1.32–1.25 (m, 6H), 0.88 (br, 3H). MS (FAB) ( $m/z$ ) [ $\text{M}^+$ ]: 502.9; calcd, 502.2. Anal. Calcd for  $\text{C}_{32}\text{H}_{30}\text{N}_4\text{O}_2$ : C, 76.47; H, 6.02; N, 11.15. Found: C, 76.73; H, 6.12; N, 9.52.

**Chromophore IIa.** Aldehyde **13** (130 mg, 0.4 mmol), malononitrile (27 mg, 0.4 mmol), and piperidine (catalyst) were reacted in absolute ethanol (50 mL) following the general procedure. Chromophore **IIa** was obtained from a silica gel chromatography column (eluent,  $\text{CHCl}_3$ ) as a dark red solid (96 mg, 62%). Mp: 115–117 °C. IR: 2218  $\text{cm}^{-1}$  ( $\text{C}\equiv\text{N}$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 7.94 (d,  $J = 7.2$  Hz, 1H), 7.68 (s, 1H), 7.56 (d,  $J = 3.6$  Hz, 1H), 7.46 (d,  $J = 15.3$  Hz, 1H), 7.39–7.26 (m, 3H), 7.21 (d,  $J = 15.6$  Hz, 1H), 7.08 (d,  $J = 3.6$  Hz, 1H), 4.15 (t,  $J = 6.6$  Hz, 2H), 1.89 (m, 2H), 1.34 (br, 6H), 0.91 (br, 3H).

MS (FAB) ( $m/z$ ) [ $\text{M} + 1$ ] $^+$ : 386.5; calcd, 385.2. Anal. Calcd for  $\text{C}_{24}\text{H}_{23}\text{N}_3\text{S}$ : C, 74.77; N, 10.90. Found: C, 74.57; N, 10.54.

**Chromophore IIb.** Aldehyde **13** (130 mg, 0.4 mmol), 3-phenyl-5-isoxazolone (64 mg, 0.4 mmol), and piperidine (catalyst) were reacted in absolute ethanol (50 mL) following the general procedure. Chromophore **IIb** was obtained from a silica gel chromatography column (eluent,  $\text{CHCl}_3$ ) as a dark purple solid (125 mg, 64%). Mp: 139–140 °C. IR: 1733  $\text{cm}^{-1}$  ( $\text{C}=\text{O}$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 7.96 (d,  $J = 7.2$  Hz, 1H), 7.80 (s, 1H), 7.64–7.57 (m, 7H), 7.40–7.22 (m, 4H), 7.15 (d,  $J = 4.5$  Hz, 1H), 4.15 (t,  $J = 6.6$  Hz, 2H), 1.89 (m, 2H), 1.21–1.35 (m, 6H), 0.91 (br, 3H). Anal. Calcd for  $\text{C}_{30}\text{H}_{28}\text{N}_2\text{O}_2\text{S}$ : C, 74.97; N, 5.83. Found: C, 74.90; N, 5.58.

**Chromophore IIc.** Aldehyde **13** (130 mg, 0.4 mmol), 1,3-diethylthiobarbituric acid (80 mg, 0.4 mmol), and piperidine (catalyst) were reacted in absolute ethanol (50 mL) following the general procedure. Chromophore **IIb** was obtained from a silica gel chromatography column (eluent,  $\text{CHCl}_3$ ) as a dark solid (140 mg, 68%). Mp: 191–193 °C. IR: 1653  $\text{cm}^{-1}$  ( $\text{C}=\text{O}$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 8.60 (s, 1H), 7.98 (d,  $J = 7.8$  Hz, 1H), 7.79 (d,  $J = 4.2$  Hz, 1H), 7.67 (d,  $J = 16.5$  Hz, 1H), 7.37–7.23 (m, 5H), 4.61 (m, 4H), 4.14 (t,  $J = 7.2$  Hz, 2H), 1.87 (m, 2H), 1.296–1.391 (m, 12H), 0.88 (t, 3H). MS (FAB) ( $m/z$ ) [ $\text{M}^+$ ]: 520.0; calcd, 519.2. Anal. Calcd for  $\text{C}_{29}\text{H}_{33}\text{N}_3\text{O}_2\text{S}_2$ : C, 67.02; H, 6.40; N, 8.08. Found: C, 66.03; H, 6.87; N, 8.42.

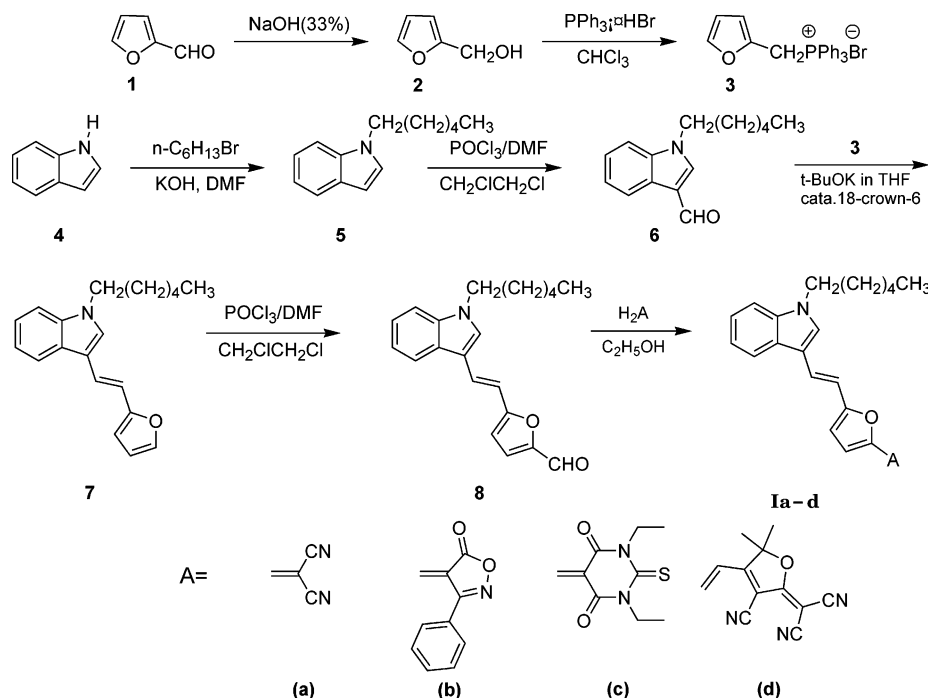
**Chromophore IId.** Aldehyde **13** (130 mg, 0.4 mmol), TCF (80 mg, 0.4 mmol), and piperidine (catalyst) were reacted in absolute ethanol (50 mL) following the general procedure. Chromophore **IId** was obtained from a silica gel chromatography column (eluent, ethyl acetate/ $\text{CHCl}_3$  (3:20)), affording a dark solid (114 mg, 55%). Mp: 178–180 °C. IR: 2225  $\text{cm}^{-1}$  ( $\text{C}\equiv\text{N}$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 7.95 (d,  $J = 7.5$  Hz, 1H), 7.76 (d,  $J = 15.6$  Hz, 1H), 7.39–7.26 (m, 5H), 7.21 (d,  $J = 15.6$  Hz, 1H), 7.05 (d,  $J = 3.6$  Hz, 1H), 6.59 (d,  $J = 15.6$  Hz, 1H), 4.16 (t,  $J = 6.9$  Hz, 2H), 1.90 (m, 2H), 1.79 (s, 6H), 1.35 (m, 6H), 0.91 (br, 3H). MS (FAB) ( $m/z$ ) [ $\text{M}^+$ ]: 518.9; calcd, 518.2. Anal. Calcd for  $\text{C}_{32}\text{H}_{30}\text{N}_4\text{OS}$ : C, 74.10; N, 10.80. Found: C, 73.66; N, 10.42.

## Results and Discussion

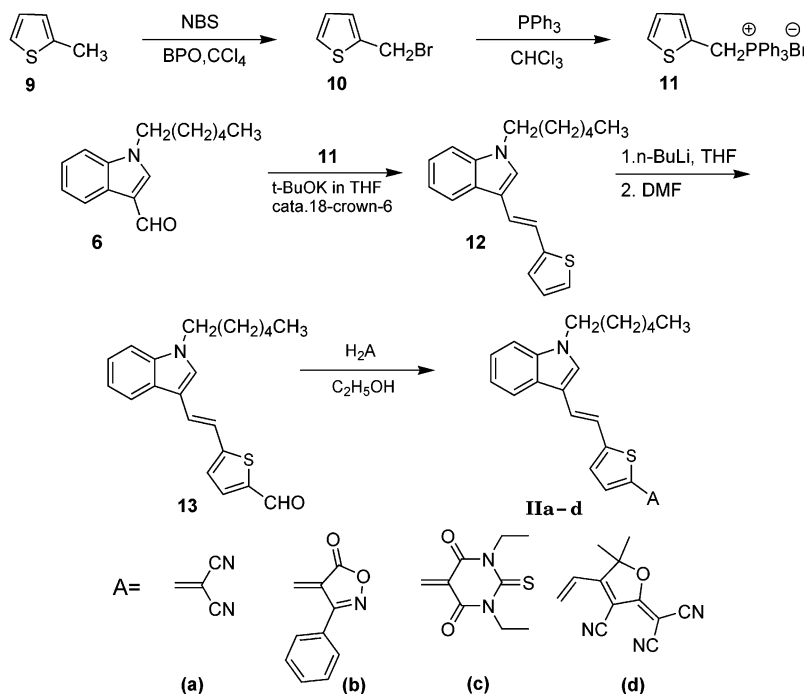
**Synthesis.** The (vinyl furan)-bridged chromophores (**Ia–d**) were prepared according to Scheme 1. (2-Furylmethyl)triphenylphosphonium bromide was synthesized directly from the corresponding alcohol (**2**) and  $\text{HPPH}_3\text{Br}$ , with no need to convert the hydroxy groups to bromine atoms first, and then reacted with triphenylphosphine as reported previously.<sup>10</sup> The yield is dramatically improved as well. The Wittig reaction of the obtained 3-formyl-*N*-hexylindole (**6**) from a Vilsmeier reaction with (2-furylmethyl)triphenylphosphonium bromide gave the corresponding vinyl furan (**7**). Another Vilsmeier reaction of **7** yielded the aldehyde **8**, which was readily converted to chromophores **Ia–d** by Knoevenagel condensations with different acceptor moieties under basic conditions (ethanol with piperidine catalyst). The Wittig reaction gave mixtures of *Z* and *E* isomers, and the aldehyde was also, therefore, obtained as mixture. But after the Knoevenagel condensations, the final obtained chromophores were totally *E* isomers. This should be due to the linkage of the strong acceptors, and similar cases were reported previously.<sup>2c,11</sup> By nearly the same procedure (Scheme 2), vinyl-thiophene (**12**) was prepared. However, this time the formyl group was not introduced by the Vilsmeier reaction but by following the general method as other scientists did: lithiation of the vinyl thiophene, reaction with DMF, and



SCHEME 1



SCHEME 2



subsequent hydrolysis afforded the aldehyde.<sup>12</sup> Similarly, after the Knoevenagel condensations, the obtained chromophores (IIa–d) were no longer mixtures but *E* isomers. All of the compounds were well characterized, and the spectral data are shown in the Experimental Section, with the <sup>1</sup>H NMR and IR spectra demonstrated in the Supporting Information.

As shown in Schemes 1 and 2, indole was first reacted with 1-bromohexane to substitute the active hydrogen atoms on the nitrogen atoms, and this reaction goes easily. Also, some other alkyl groups could be easily introduced to indole following the same procedure, especially those containing the functional groups at the other end of the alkyl groups, such as hydroxyl groups, alkyl groups, and others, which could make the resultant

chromophores easily bonded to the polymeric system.<sup>7a–f</sup> This is another convenient point for the indole-based chromophores. This study is currently under way in our lab.

**Optical Properties.** The UV–vis absorption maxima,  $\lambda_{\text{max}}$ , and the transition energy,  $E_{\text{eg}}$ , for the new chromophores are summarized in Table 1. The values of  $\beta$  were measured in chloroform by hyper-Rayleigh scattering (HRS) using the fundamental excitation wavelength of 1064 nm, and in the same solvent, the known hyperpolarizability of *p*-nitroaniline (*p*-NA) was used as an external reference.<sup>13</sup> The dispersion-corrected  $\beta_0$  values were estimated using an approximate two-level model. For comparison, we listed those data of chromophores III(a–

TABLE 1

Cpd	$\lambda_{\max}/\text{nm}^a$	$\lambda_{\max}/\text{nm}^b$	$E_{\text{eg}}/\text{eV}^c$	$\beta_{\text{HRS}}^d$	$\beta_0^e$	$T_d^f$
Ia	526	525	2.35	1162	20	322
Ib	566	578	2.19	412	39	187
Ic	590	601	2.10	1540	245	244
Id	650	654	1.90	615	190	234
IIa	524	525	2.36	1068	25	337
IIb	561	570	2.21	685	56	204
IIc	586	591	2.11	1108	165	249
IId	638	632	1.94	597	167	260
IIIa		552		77	34	
IIIb		604		300	101	
IIIc		630		254	75	
IVa		554		62	27	

<sup>a</sup> Tested in chloroform. <sup>b</sup> Tested in DMSO. <sup>c</sup> Calculated from their UV-vis spectra tested in chloroform. <sup>d</sup>  $\beta$  values (in unit of  $10^{-30}$  esu) measured by the hyper-Rayleigh scattering (HRS) technique in chloroform using the fundamental excitation wavelength of 1064 nm. <sup>e</sup> Dispersion-corrected  $\beta$  values calculated by using an approximate two-level model. <sup>f</sup> The 5% weight loss temperature (TGA).

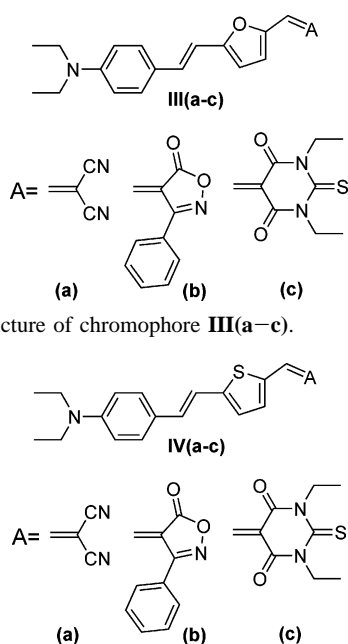


Figure 1. Structure of chromophore III(a–c).

Figure 2. Structure of chromophore IV(a–c).

d) and IV(a–d) reported in the literatures, and their structures are shown in Figures 1 and 2.

It can be seen that the chromophores I(a–d) exhibit similar UV-vis absorption maxima to their corresponding chromophores II(a–d) with the same electron acceptor. With the increasing strength of the acceptor groups in each series, the absorption maxima become longer with the transition energy decreasing correspondingly and their profile curves are shown in Figures 3 and 4. However, both of these two series of chromophores with indole moieties as the donor demonstrated much better transparency (blue shifted more than 25 nm) in comparison with the corresponding analogues (III and IV) with aniline groups as the donor moieties. The phenomena are reasonable if we only consider the conjugation-bridge length of the chromophores: in indole-based chromophores, there is only one vinyl bridge in the five-membered ring between the nitrogen atom and the vinyl furan (or thiophene) moieties, so the conjugation-bridge length of indole-based chromophores is shorter than their analogues, III and IV, in which it can be considered that there are two vinyl bridges in the benzenyl ring between the nitrogen atom and the vinyl furan (or thiophene) moieties. But there may be also contributions due to steric

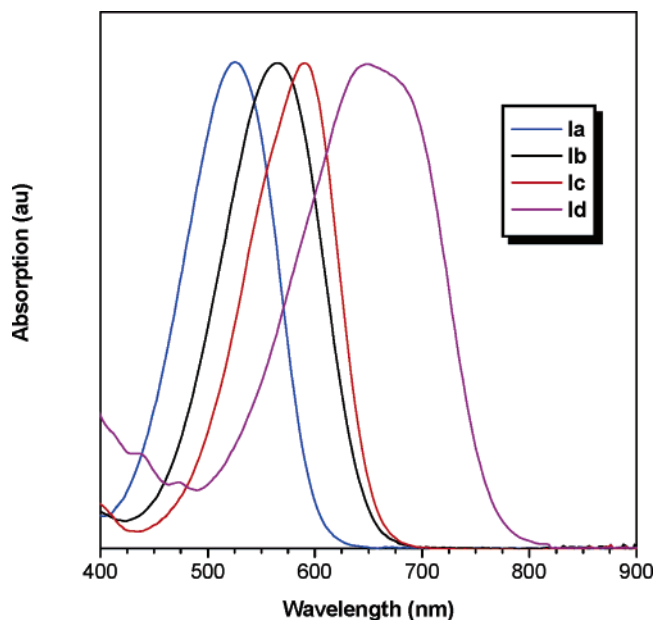


Figure 3. Comparison of the absorption spectra of chromophore I–(a–d) in chloroform.

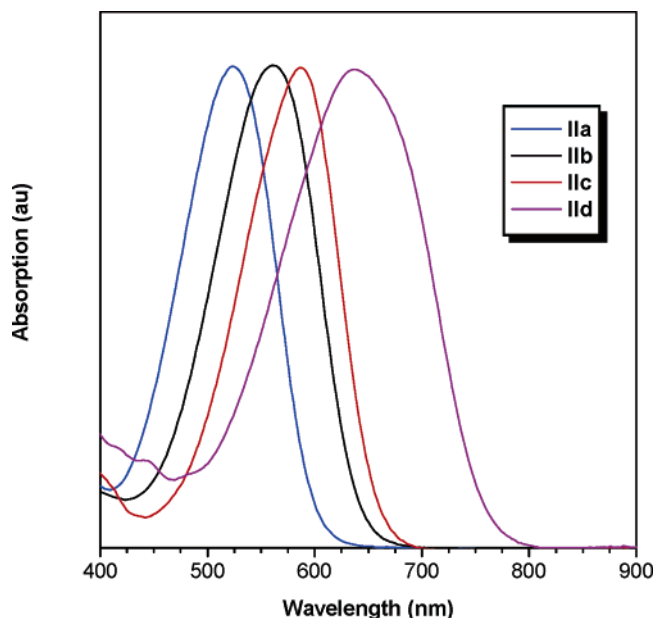


Figure 4. Comparison of the absorption spectra of chromophore II–(a–d) in chloroform.

hindrance between hydrogen atoms on the indole and furan (or thiophene) rings leading to a nonplanar structure and further disrupting ground-state charge transfer.

Although the indole-based chromophores showed much blue-shifted absorption maxima, their tested  $\beta_0$  values are quite competitive with those of their corresponding analogues from the experimental results. Accompanying the absorption red shifting in the series of I and II, the tested  $\beta_0$  values become larger except that of Ic, coinciding well with the increasing strength of the electron acceptor. Ic shows the highest tested  $\beta_0$  values in the prepared eight chromophores, even higher than that of Id. It is reasonable though the TCF group is a much stronger electron acceptor than barbituric acid. It has been well established that the  $\beta$  value increases until it reaches a maximum and then decreases as the bond length alternation (BLA) decreases from a large positive value toward a negative one.<sup>14</sup> Since the BLA should decrease as the strength of the acceptor

increases in the order  $a < b < c$ , the results of **Ia–Ic** could reasonably be attributed to the gradual decrease in the BLA from a large positive value toward the optimum with the same variation of the acceptor. As the electron acceptor becomes even stronger, the BLA value would become more negative, however, deriving from the optimum point this time, so the tested  $\beta_0$  values would not increase but decrease. A similar trend is present in **II(a–d)**, but this time, the tested  $\beta_0$  values of **Ic** and **IId** are similar, indicating that the BLA is still toward the optimum from **Ic** to **IId** or they are at a similar distance from the optimum point, because there are different electron properties between the thiophene and furan moieties.

The prediction by the theoretical calculation and earlier results demonstrated that, for a given acceptor and donor, the  $\beta_0$  values are larger for the chromophores with furan as the conjugation bridge than those for the thiophene derivative.<sup>15</sup> However, there were reported results in contrast to the above idea.<sup>16</sup> In our case, the tested  $\beta_0$  values of **Ia** and **Ib** are smaller than those of **IIa** and **IIb**, respectively. While the electron acceptor groups are barbituric acid and TCF, the things become totally different:

the tested  $\beta_0$  values of **Ic** and **IId** are much larger than those of **IIc** and **IIId** respectively. This might be due to the different combination effects among the donor, acceptor, and conjugation bridge. Also, it should be pointed out that the dipole moments of **IId** and **IIId** might be much larger than other chromophores, according to the reported literatures.<sup>8</sup>

The tested  $\beta_0$  values of **Ia** and **IIa** are less than those of their analogues, respectively, while that of **Ib** is less than that of **IIb**. This perhaps could be explained by the fact that the  $\pi$ -electron delocalization efficiency is somewhat reduced due to the shorter conjugation bridge and possible poorer coplanarity than their analogues, **III** and **IV**, as discussed above concerning their UV–vis absorption maxima. But, the much larger  $\beta_0$  values of **Ic** compared with that of **IIc** may give us abnormal information, reminding us the special point of indole moieties. We also should pay attention to the UV–vis absorption maxima measured in chloroform and dimethyl sulfone (DMSO). There are nearly no differences in the case of **Ia** and **IIa**, relatively big differences in **I(b–c)** and **II(b–c)** but still less than normal chromophores, while strange phenomena occur in chromophore **IIId** with TCF as the electron acceptor: the maximum absorption is blue shifted in DMSO than that in chloroform.

The strange thing should surely have a relationship to the nonlinear optical properties of the chromophore. As we know, there are a total of 10 electrons (eight  $\pi$  electrons and one pair of electrons on the nitrogen atom) in the indole ring to form the big  $\pi$  system, however, the electronic cloud does not distribute equally on the nine atoms and the most active point is the meta position to the nitrogen atom in the five-membered ring, which easily undergoes an electrophilic aromatic substituted reaction and here just this position linking to the vinyl bonds in the resultant chromophores.<sup>17</sup> Therefore, perhaps, we could assume that, in the big  $\pi$  system of indole, there are not only the electronic properties of  $\pi$  electrons but also those of  $n$  electrons to some degree, especially the electron cloud on the five-membered ring, then accordingly there is not only the composition of the  $\pi$ – $\pi^*$  transition but also the composition of the  $n$ – $\pi^*$  transition accounting for the UV–vis absorption in the resultant chromophores. Or we could express it in another way: the  $\pi$ – $\pi^*$  transition of chromophores **I** and **II** contains the property of the  $n$ – $\pi^*$  transition at some degree. So the shorter  $\pi$  conjugation bridge compared with their analogues would result in the blue-shifted absorption maxima, while the abundant electronic cloud at the meta position to nitrogen atom

would benefit the delocalization efficiency of chromophores. Also, when the polarity of the solvents becomes stronger, the component part of the  $n$ – $\pi^*$  transition property would lead to the blue-shifted absorption. However, all of the above guesses still lack experimental proof, and further study is needed for a full interpretation.

**Thermal Stability.** The thermal stabilities of chromophores were evaluated by thermal gravimetric analysis (TGA) under nitrogen, with a heating rate of 10 °C/min. The temperature for 5% weight loss of each chromophore is summarized in Table 1. The chromophores **Ib** and **IIb**, containing the 3-phenyl-5-isoxazolone acceptor, show the lower temperature, which might be due to the instability of the 3-phenyl-5-isoxazolone moieties. Compounds **Ia** and **IIa** with the dicyanovinyl acceptor are more thermally stable than chromophores with other electron acceptors, exhibiting the higher temperature (over 320 °C). These results are not like those chromophores with different electron acceptors reported in the literature, indicating that the thermal behavior is dependent on the whole molecule including its combination of different parts, the electronic structure, and some other factors, not only always on the property of some special part.

## Summary

Two series of indole-based nonlinear optical chromophores with different acceptors and  $\pi$ -conjugated moieties have been synthesized. Compared with the previously reported aniline-donor analogues (**III** and **IV**), all of the compounds display blue-shifted absorption (even up to 30 nm); they exhibit comparable or superior nonlinear optical properties to their analogues. And all the chromophores are thermally stable. The chromophore **Ic** shows a combination of large nonlinearity, high thermal stability, and relatively good transparency among the chromophores. All these verify the important role of the indole moieties in the construction of new NLO chromophores, thereby providing a new method for defeating the “nonlinear–transparency tradeoff”. The design and synthesis of other chromophores containing an indole group and further insight research on the origin of the role of indole moieties are under way in our lab.

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**Supporting Information Available:** Figures of <sup>1</sup>H NMR and FT-IR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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