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Synthesis and nonlinear optical properties of branched pyrroline chromophores

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New tricyanopyrroline (TCP) chromophores with rigid–flexible dendron were prepared for second-order nonlinear optical (NLO) application. The chromophores were fully characterized using ultraviolet-visible spectroscopy, nuclear magnetic resonance spectroscopy and mass spectrometry. Thermal gravimetric analysis (TGA) revealed that the chromophores had excellent thermal stability. Large λ_{max} and high solvate chromic effects revealed that the chromophores had large second-order optical nonlinearity. The electro-optic coefficients (r_{33}) were measured in the chromophores-doped poly(bisphenol A carbonate) films at the fundamental wavelength of 1310 nm, and the highest γ_{33} achieved was 217 pmV^{-1}. Copyright © 2010 John Wiley & Sons, Ltd.

Keywords: chromophore; electro-optic effect; NLO; rigid–flexible dendron; TCP; thiophene

INTRODUCTION

Organic second-order nonlinear optical (NLO) materials have many excellences, for example, large NLO coefficients, ultra-fast response time, large bandwidth, low dielectric constant, small dispersion in the refractive index, structural flexibility, ease of integration, and so on,[1,2] so they have been extensively investigated for potential applications in telecommunications and electro-optic devices in the last decades. But there are still some disadvantages in their practical applications, such as: the strong intermolecular electrostatic interaction, the incompatibility of the chromophores in polymers, and poor solubility in most common organic solvents. Fortunately, controlling the shape, size and conformation of the chromophores has been proved to be an effective approach for minimizing intermolecular electrostatic interaction and enhancing the poling efficiency of electro-optic (EO) materials.[3–5,6–8]

Recently Jen and coworkers have firstly reported the strong potential of tricyanopyrroline (TCP) chromophore and their detailed microscopic analysis data.[9,10,11] The electron-withdrawing properties of TCP unit are considerably stronger than those of tricyanofuran (TCF) and other electron acceptors. In their research, the largest molecular first hyperpolarizability was 8700×10^{-30} esu, which was six times higher than the chromophore with TCF acceptor, but the macroscopic electro-optic coefficients could not increase so obviously.[12,13,14] It is inferred that the chromophores packing is easily formed due to the strong electrostatic interaction.[15,16] From both theoretical and experimental analyses, the Dalton group has shown that the maximum achievable EO activity of a chromophore can be greatly enhanced by modification of its shape. In fact, the derivatization of chromophores with bulky substituents will make them more spherical and hence limit intermolecular electrostatic interactions.[3,17–21] Therefore the rigid–flexible dendron is introduced into the TCP acceptor to prevent parallel chromophores' packing and improve the solubility of the materials in this paper. We report the syntheses and properties of these novel TCP chromophores with rigid–flexible dendron (the dendron containing both rigid group and flexible group). Both of the chromophores are characterized with ^{1}H NMR, MS, and UV–Vis spectra. The thermal stabilities are studied by thermal gravimetric analysis (TGA). The NLO properties are measured in the polymer films by ATR method[22] at the wavelength of 1310 nm.

RESULTS AND DISCUSSION

Synthesis of chromophores

The 3,5-bis(2′-ethylhexyloxy)benzylalcohol (**1**) was prepared from 2-ethylhexyl bromide and 3,5-dihydroxybenzyl alcohol using K_2CO_3 as base, in the solvent of DMF. Then the 3, 5-bis(2′-ethylhexyloxy)benzylalcohol was brominated by carbon tetrabromide using triphenyl phosphorous as the catalyzer.

The synthetic routes to chromophores are sketched in Scheme 1. The chromophores were prepared according to a synthetic methodology as follows: *p*-*N*,*N*-bis(2-hydroxyethyl)-aminobenzaldehyde was synthesized according to a well known method. The thiophene bridge compound was prepared in eight steps to yield the Wittig salt. After the final Wittig condensation of the thiophene ylide with the aldehyde, the desired donor bridges were prepared. Donor bridge was subjected to Vilsmeier reactions in the presence of $POCl_3$ and DMF, affording the desired aldehyde function on the thiophene ring. The donor bridge was then reacted with the acceptor to yield the chromophore.

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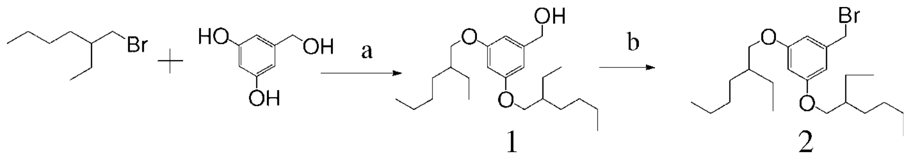


a. K_2CO_3, acetone;
b. PPH_3, CBr_4, THF;

Scheme 1. Syntheses of 3,5-bis(2′-ethylhexyloxy)benzyl bromide.

Physical properties of chromophores

It was found that TCP chromophores have poor solubility in common organic solvents such as ethyl acetate, dichloromethane, tetrahydrofuran, probably due to the existence of strong intermolecular electrostatic interaction. As expected, chromophores reported here exhibit good solubility in the above-mentioned solvents, which is a necessary condition for subsequent preparation of device-quality polymer films. The enhanced solubility may be attributed to the introduction of bulky flexible chain in the bridge and acceptor.

The absorption spectra have been obtained in both THF and DCM, the absorption maxima (λ_{max}) are summarized in Table 1. Absorption peaks in THF were observed in visible region at 782 and 805 nm, respectively for chromophore FTC-z-1 and FTC-z-2. 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.[23] And the absorption peaks in DCM were observed at 869 and 873 nm, respectively, 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,[24,25] which reflects different electronic distribution in the molecules. Demartino *et al*. have suggested that the high solvatechromic effects were related with a large second-order optical nonlinearity.[26] Chromophore FTC-z-1 shows larger shift of absorption (87 nm) than chromophore FTC-z-2 (68 nm). Maybe the first-order hyperpolarizability is reduced, due to the introduction of bulky flexible chain in TCP acceptor.

The thermal stabilities of the chromophores were investigated by TGA under nitrogen, with a heating rate of 10 °Cmin^{-1}. The results are listed in Table 1 and the weight loss diagrams are attached (Fig. 1). This result indicates that both the chromophores are thermally stable with decomposition temperatures higher than 260 °C. From Table 1, we can see that decomposition temperature of the chromophore with dendron in the TCP acceptor is a little higher than the chromophores without dendron.

The NLO properties of the chromophores

In order to investigate the NLO properties of the chromophores, guest-host systems were explored. The chromophores were doped into APC [poly (bisphenol A carbonate)] at the same molecular densities (10 wt%). Solutions of 20% total solids were prepared in dibromomethane 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 (the glass transition temperature is about 138 °C) for 10 min under the electric field of 9 kV. After the films were cooled to room temperature, the electric field was removed. In the process of poling, we also researched the stability of the chromophore in electric field. The highest electric field the chromophore can bear is summarized in Table 1. It is seen that TCP chromophore with dendron shows better stability than the chromophore without dendron.

The UV–Vis absorption spectrum changes of EO films were employed to describe the chromophore alignment, as shown in Fig. 2. After the corona poling, the dipole moments of the chromophore moieties in the polymer were aligned, and the absorption curve decreased due to birefringence. From the absorption change, the order parameter (Φ) for polymer can be calculated according to the following equation:

$$\Phi = 1 - \frac{A_1}{A_0} \qquad (1)$$

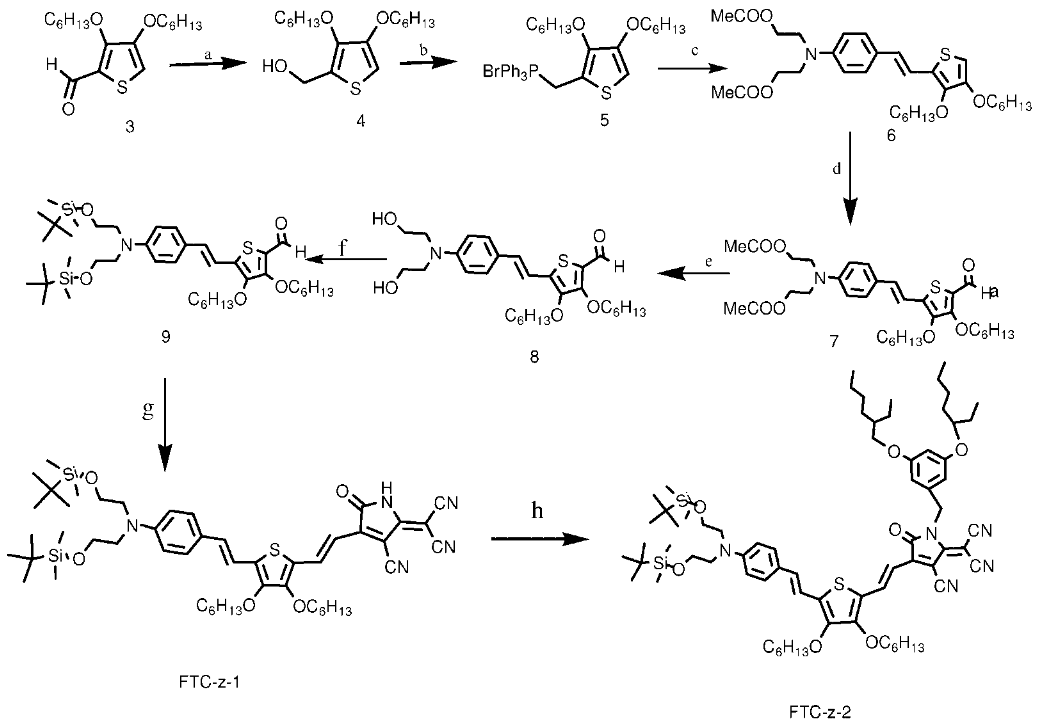
where A_1 and A_0 are the absorbances of the polymer film after and before cornona poling, respectively. The Φ value of the poled film contained chromophore FTC-z-2 is about 24%, but the order parameter of the film contained FTC-z-1 is only 18%. It indicates that the dendritic moieties make the chromophore molecular radius increase largely, the interaction among the dendritic chromophore molecules is less and the material is easier to be polarized.

A reflective EO polymer light modulator was fabricated using the EO material. The EO characterization of the EO film in this modulator was conducted by an improved ATR technique. The

Table 1. Properties of chromophores

Chromophore	λ_{max}(THF) (nm)	ε(THF) (L mol^{-1} cm^{-1})	λ_{max}(DCM) nm	ε(DCM) (L mol^{-1} cm^{-1})	$\Delta\lambda_{max}$ (nm)	pV (V)	γ_{33} (pmV^{-1})	*Td* (°C)
FTC-z-1	782	50702	869	71250	87	11000	147	261
FTC-z-2	805	57425	873	74851	68	12000	217	279

pV is the polarization voltage the chromophore can bear.



a. $NaBH_4$, methanol
b. Triphenyl phosphorous hydrogen bromide,
c. 4-[N,N-Di[2-(acetyloxy)ethyl]amino]benzaldehyde, ether, NaH;
d. $POCl_3$, DMF;
e. methanol, H_2O, K_2CO_3;
f. imidazole, DMF, TBDMSCl;
g. TCP, ethanol;
h. Compound 1,K_2CO_3 , Acetonitrile.

Scheme 2. Syntheses of the chromophores.

ATR spectrum of this multilayer waveguide system for TM-polarized light of $\lambda = 1310$ nm was obtained through angular scanning, which was carried out by a computer-controlled $\theta/2\theta$ goniometer. Several resonance dips correspond to different guide modes. Since the width of the dip is a function of the loss and determines the driving voltage, TM1 mode, which has the narrowest resonance width and means the largest k value in Eqn (2), is used as the working probe. The working angle is chosen at the midst of the fall-off of the reflection dip, where the linearity is fairly good. When applying an electrical field of $V = 40$ V (peak-to-peak) at a frequency of 50 kHz to the electrode across the poled polymer, the polymer refractive index will change due to Pockels effect and the propagation constant of the guided wave will change. So the energy coupling efficiency and

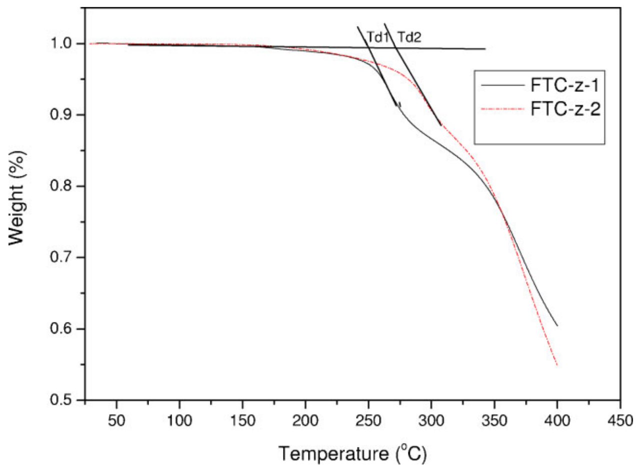


Figure 1. TGA curves of the chromophores.

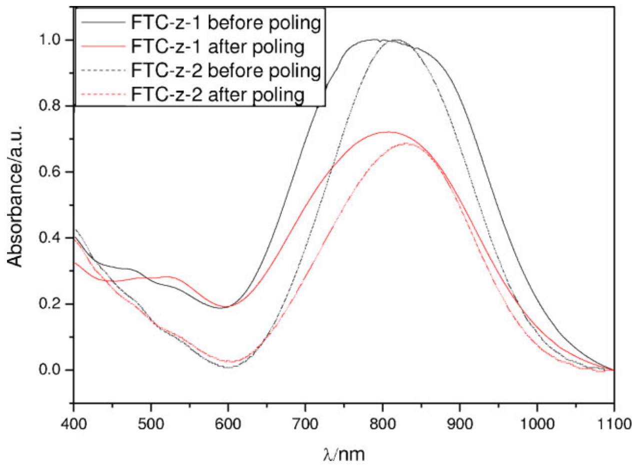


Figure 2. UV–Vis spectra of EO films before and after poling.

light reflectivity can be electrically modulated. The stable traces of the modulation drive voltage and the reflected light intensity were observed through an oscilloscope.

The EO coefficients (r_{33}) of the films are also summarized in Table 1. The poled film shows very high EO coefficient up to 217 pmV^{-1} for chromophore FTC-z-2/APC, this value is exceptionally large compared to the poled film forFTC-z-1/APC (147 pmV^{-1}). Such a great increase in EO activity is attributed to structural features of the chromophore. The rigid–flexible dendron in the end of the chromophore provides effective site isolation to decrease the strong electrostatic interactions among chromophore molecules. The chromophores with similar structure with chromophore FTC-z-1 in literature[6] showed an r_{33} of 51 pmV^{-1}, the difference between the chromophore in literature[6] and chromophore FTC-z-1 was that we instead of the simple thiophene electron bridge with 3,4-dihexyloxy thiophene electron bridge. There were three reasons for such a great increase in EO activity. The first one is that the oxygen atom in the thiophene increased the electron density of the conjugated system, which made the first-order hyperpolarizability larger than the chromophore without oxygen atom in the thiophene electron bridge. The second reason is that the large flexible chain in the thiophene electron bridge decreased the electrostatic interactions among chromophore molecules. The third one is that the wavelength used to measure r_{33} in literature[6] is 1550 nm, we measured it in 1310 nm, the wavelength has a great impact on r_{33}.[27]

CONCLUSIONS

New NLO chromophores with TCP acceptors and rigid–flexible dendron as spacers have been synthesized and characterized. The Uv–Vis data indicate that the chromophores have large solvatachromic effects. Thermal tests by TGA indicate that the TCP chromophores possess the high decomposition temperature. The NLO measurements of chromophores doped polymer films indicated the relatively large macroscopic EO activities. Typically, the EO coefficient of 217 pmV^{-1} for chromophore FTC-z-2 doped polymer system was obtained at 1310 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.

EXPERIMENTAL

Materials and characterization

All the reagents were used as received unless stated. DMF and $POCl_3$ were freshly distilled prior to use; TCP acceptor was prepared according to the literature.[6] ^1H 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 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) with a heating rate of 10 °Cmin^{-1} under the protection of nitrogen.

Syntheses

*1 3,5-Bis(2′-ethylhexyloxy)benzyl bromide (**2**)*

2-Ethylhexyl bromide (9.6 g, 0.050 mol), 3,5-dihydroxybenzyl alcohol (2.9 g, 0.021 mol), anhydrous potassium carbonate (5 g), and dibenzo-18-crown-6 in catalytic amount were dissolved in 50 ml anhydrous DMF, and kept at 70 °C under stirring in N_2 atmosphere for 24 h. The mixture was poured into 100 ml water. The organic phase was then extracted twice with ether (2*100 ml), washed with water, and dried over Na_2SO_4. The solvent was then removed, obtaining a yellow oil, which is 3,5-bis(2′-ethylhexyloxy)benzylalcohol (**1**). Yield: 71%. The crude product was used in the next step directly.

3,5-bis(2′-ethylhexyloxy)benzyl alcohol (1 g, 2.7 mmol) and tetrabromomethane (1.1 g, 3.4 mmol) were dissolved in 20 ml THF, under stirring in N_2 atmosphere at room temperature. After the entire solid dissolved, Triphenyl phosphorous (0.88 g, 3.4 mmol) was added. After half an hour, the mixture was poured into 50 ml water. The organic phase was then extracted twice with dichloromethane (2*50 ml), washed with water and dried over Na_2SO_4. The crude product was purified with short column chromatography. Yield: 75%. IR(KBr), υ_{max}/cm^{-1}: 2929, 2873, 1460, 947, 841, 695; MS, *m/z*: 426(M$^+$); ^1H NMR(300 MHz, CD_3COCD_3), δ: 6.60(s, 2*H*), 6.44(s,1*H*), 4.53(s,2*H*), 3.86(t, 4*H*), 2.04(m, 2*H*), 1.45(m, 8*H*), 1.33(m, 8*H*), 0.91(t, 6*H*), 0.86(t, 6*H*).

*3, 4-Bis (hexyloxy) thiophenmethanol (**4**)*

The solution of 3, 4-bis (hexyloxy)-2-thiophene (2.84 g, 10 mmol) in 5.5 ml DMF and 35 ml 1,2-dichloroethane was stirred and cooled to 0 °C, then 5.4 ml phosphorus oxychloride was added dropwise to the solution. The mixture was refluxed for 2 h, cooled to room temperature and poured to 150 ml solution of sodium carbonate (20%). The water phase was then extracted twice with ether (2*150 ml). The organic phase was dried over magnesium sulfate, and then the ether was removed by evaporation under reduced pressure. The yield of 3,4-bis (hexyloxy)thiophenecarboxaldehyde (**3**) was 2.96 g (95%).

The solution of 3, 4-bis (hexyloxy)thiophenecarboxaldehyde (**3**) (3 g, 9.6 mmol) in 30 ml methanol was cooled to 0 °C, 0.2 g sodium hydride was added. The mixture was stirred for 24 h, and then the methanol was removed. The solution was acidificated by hydrochloric acid and extracted twice with ether, and dried over magnesium sulfate. The yield of compound was 3 g (99%). MS (MALDI-TOF), *m/z*: 314 (M$^+$), ^1H NMR (300 MHz, CD_3COCD_3), δ: 6.1(s, 1*H*), 4.7(s, 2*H*), 4.0(m, 2*H*), 3.9(m, 2*H*), 1.7(m, 4*H*), 1.45(m, 4*H*), 1.3(m, 8*H*), 0.9 (t, 6*H*).

*3, 4-Bis (hexyloxy){4-[N,N-di [2-(acetyloxy) ethyl] amino] styryl} thiophene (**6**)*

The mixture of 3,4-bis(hexyloxy)thiophenmethanol (**4**) (3 g, 9.6 mmol), PPh_3HBr (3 g, 8.7 mmol), and 50 ml chloroform was refluxed for 3 h, and then the chloroform was removed. 50 ml ether was added and filtrated. After the ether was removed, the compound 6 precipitated. The yield was 5 g (82%).

The solution of compound **6** (4 g, 6.4 mmol), NaH (5.5 g) and 4-[*N,N*-bis[2-(acetyloxy)ethyl]amino]benzaldehyde (1.9 g, 6.4 mmol) in 100 ml ether was stirred at room temperature for 24 h under N_2 atmosphere, then poured into 200 ml water. The mixture was then extracted twice with ether (2*200 ml), dried over magnesium sulfate, 3,4-bis (hexyloxy){4-[*N,N*-di [2-(acetyloxy) ethyl] amino] styryl} thiophene (**6**) was purified with short column chromatography. The yield was 1 g (27%). MS (MALDI-TOF), *m/z*: 573(M^+); ^{1}H NMR(300 MHz, CD_3COCD_3), δ: 7.3(d, 2*H*), 7.15(s, 1*H*), 7.0(d, 1*H*), 6.7(d, 2*H*), 6.0(d, 1*H*), 4.2(t, 4*H*), 4.1(t, 2*H*), 3.9(t, 2*H*), 3.6(t, 4*H*), 2.1(s, 6*H*), 1.7(m, 4*H*), 1.45(m, 4*H*), 1.3(m, 8*H*), 0.9 (t, 6*H*).

*3,4-Bis(hexyloxy)-2-{4-[N,N-bis [2-(acetyloxy)ethyl]amino]styryl}thiophenecarboxaldehyde (**7**)*

The solution of 3,4-bis (hexyloxy){4-[*N*,*N*-di [2-(acetyloxy) ethyl] amino] styryl} thiophene (**6**) (1 g, 13.4 mmol) in 40 ml DMF was stirred and cooled to 0 °C. Then phosphorus oxychloride (1.7 ml) was added dropwise to the solution. After the phosphorus oxychloride being added, the temperature was raised to 90 °C slowly, and kept for 3 h, then cooled to room temperature. The mixture was poured into 150 ml solution of sodium carbonate (10%), extracted twice with chloroform (2^*100 ml), washed with water, and dried over magnesium sulfate. 3,4-bis(hexyloxy)-2-{4-[*N*,*N*-bis [2-(acetyloxy)ethyl]amino]styryl} thiophenecarboxaldehyde (**7**) was purified with short column chromatography. The yield was 0.6 g (29%). MS (MALDI-TOF), *m/z*: 601(M^+); ^{1}H NMR(300 MHz, CD_3COCD_3), δ: 10.0(s, 1*H*), 7.3(d, 2*H*), 7.2 (d, 1*H*), 7.0(d, 1*H*), 6.7(d, 2*H*), 4.2(t, 4*H*), 4.1(t, 2*H*), 3.9(t, 2*H*), 3.6(t, 4*H*), 2.1(s, 6*H*), 1.7(m, 4*H*), 1.45(m, 4*H*), 1.3(m, 8*H*), 0.9(t, 6*H*).

*3,4-Bis(hexyloxy)-2-{4-[N,N-di[2-hydroxyethyl] amino]styryl}thiophenecarboxaldehyde (**8**)*

The solution of 3,4-bis(hexyloxy)-2-{4-[*N*,*N*-bis [2-(acetyloxy)-ethyl]amino]styryl}thiophenecarboxaldehyde (**7**) (0.6 g, 1 mmol) in 25 ml methanol was kept for 40 °C, and then 10 ml solution of potassium carbonate (10%) was added. And the temperature was raised to 80 °C, and kept for 6 h. After the methanol and water removed, the solid was dissolved in alcohol, and filtrated. Remove the alcohol of the solution, and 3,4-bis(hexyloxy)-2-{4-[*N*,*N*-di[2-hydroxyethyl]amino]styryl}thiophenecarboxaldehyde (**8**) precipitated. The yield was 0.42 g (94%). M^+: 517; ^{1}H NMR(300 MHz, CD_3COCD_3), δ: 10.0(s, 1*H*), 7.3(d, 2*H*), 7.2 (d, 1*H*), 7.0(d, 1*H*), 6.7(s, 2*H*), 6.0(s, 1*H*), 4.2(t, 4*H*), 4.1(t, 2*H*), 3.9(t, 2*H*), 3.6(t, 4*H*), 1.7(m, 4*H*), 1.45(m, 4*H*), 1.3(m, 8*H*), 0.9(t, 6*H*).

Chromophore FTC-z-1

The solution of 3,4-bis(hexyloxy)-2-{4-[*N*,*N*-di[2-hydroxyethyl]-amino]styryl}thiophenecarboxaldehyde (**8**) (0.52 g, 1 mmol), imidazole (0.8 g, 10 mmol) and *tert*-butyldimethylsilyl chloride (0.75 g, 5 mmol) in 25 ml DMF, was kept in room temperature for 8 h, then poured into 200 ml water, extracted twice with ethyl acetate (2^*50 ml). After removed the ethyl acetate, the crude product was purified with short column chromatography. The yield of compound **9** was 0.46 g (62%).

The solution of compound **9** (0.46 g) and TCP acceptor (0.6 g) in 5 ml alcohol was kept at 70 °C for 2 h. After removed the alcohol, the crude product was purified with short column chromatography using petroleum ether as eluent to afford chromophore FTC-z-1 as a green solid (0.25 g), 79%. UV–Vis(CH_3COCH_3): $\lambda_{max} = 796.5$ nm; MS (MALDI-TOF), *m/z*: 911(M^+); ^{1}H NMR-(300 MHz, CD_3COCD_3), δ: 8.81(d, 1*H*), 8.05(d, 1*H*), 7.41(d, 2*H*), 7.13(d, 1*H*), 7.09(d, 1*H*), 6.81(s, 1*H*), 6.73(d, 2*H*), 4.35(t, 2*H*), 4.02(t, 2*H*), 3.79(t, 4*H*), 3.59(t, 4*H*), 1.78(m, 4*H*), 1.50(m, 4*H*), 1.35(m, 4*H*), 1.25(m, 4*H*), 0.92(t, 6*H*), 0.85 (s, 18*H*), 0.15(s, 12*H*); ^{13}C NMR (100 MHz, CD_3COCD_3): δ (ppm) 167.0, 157.2, 150.6, 147.3, 145.0, 141.4, 136.4, 134.6, 130.7, 123.1, 122.8, 112.6, 112.3, 76.0, 74.8, 62.7, 61.9, 54.4, 48.8, 32.6, 31.4, 26.7, 23.5, 18.8, 14.5, −5.0.

Chromophore FTC-z-2

Potassium carbonate (2.0 mmol) was added by steps to the solution of chromophore FTC-z-1 in 2 ml acetonitrile, the solution was heated to 65 °C for 10 min. Then the 3,5-bis(2′-ethylhexyloxy)benzyl bromide (1.0 mmol) was added slowly. The mixture was refluxed for 2 h. After the solvent was removed, the product was purified with short column chromatography. Yield: 63%, UV–Vis(CH_3COCH_3): $\lambda_{max} = 826.5$ nm, MS (MALDI-TOF), *m/z*: 1260(M^+); ^{1}H NMR(300 MHz, CD_3COCD_3), δ: 7.26(d, 2*H*), 6.52(m, 6*H*), 6.40(s, 3*H*), 4.41(m, 6*H*), 3.81(m, 12*H*), 1.71(m, 6*H*), 1.45(m, 8*H*), 1.32(m, 20*H*), 0.90(m, 36*H*), 0.15(s, 12*H*); ^{13}C NMR (100 MHz, CD_3COCD_3): δ (ppm) 166.7, 163.5, 161.9, 150.8, 147.9, 145.2, 142.4, 138.5, 136.6, 135.4, 130.4, 124.5, 120.3, 114.0, 113.1, 11.2.7, 105.9, 100.9, 75.8, 75.0, 71.1, 61.4, 54.3, 45.2, 40.3, 32.5, 32.4, 31.3, 30.9, 26.3, 24.6, 23.7, 23.4, 18.8, 14.5, 11.7, −5.0.

EO modulator fabrication and NLO properties measurement

An EO ATR modulator, whose cross-section view is shown in Fig. 3, was fabricated using the chromophores doped APC as EO material. The modulator consists of five parts: (1) a high index prism, (2) a thin silver film as the coupling layer and the top electrode, (3) a poled EO film as the guiding layer, (4) a ITO glass as the bottom electrode.[18,20] The silver film was sputtered onto the hypotenuse face of a high index prism served as the top electrode. The EO film was spin-coated onto ITO glass substrate with a thickness of 1.5–3 μm depending on the polymer solution concentration and the spin rate. The corona poling was performed to make the chromophore dipoles aligned along the direction of the electric field. Finally, the ITO glass with EO film was press on the prism with silver film.

The EO coefficient of active polymer layer in the EO modulator can be determined according to the following equation:

$$r_{33} = \frac{2\lambda}{n^3} \times \frac{I_{AC}}{I_{DC}} \times \frac{\partial n}{\partial \theta} \qquad (2)$$

where r_{33} is the EO coefficient of the poled polymer layer; *n* is the refractive indices of the polymer film; I_{AC} is the modulated light

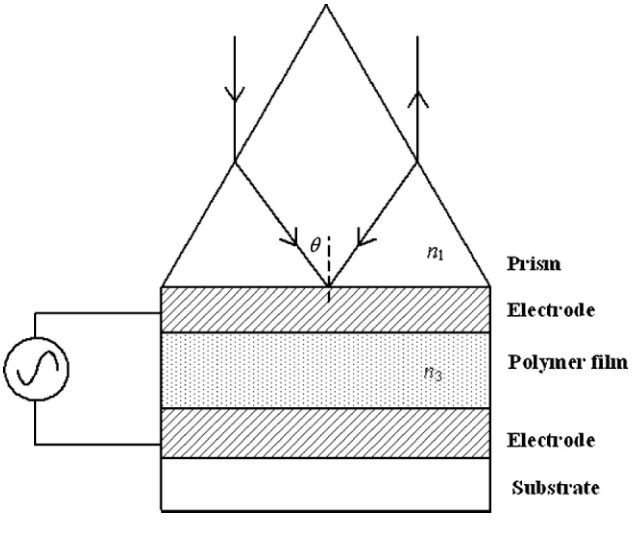


Figure 3. Schematic diagram of the ART modulator.

intensity; I_{DC} is the reflected light intensity; θ is the light incident angle which is defined as the modulator's working interior angle.

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