Molecular Design and Synthesis of Hetero-trichromophore for Enhanced Nonlinear Optical Activity

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ABSTRACT: A new hetero-trichromophore (**HT-1**) was designed and synthesized by linking neutral-ground-state (NGS) chromophore **1** with zwitterionic (ZWI) chromophore **2**, and their molecular structures were confirmed by elemental analysis, UV−vis absorption spectra, ^{1}H NMR, etc. Theoretical calculations show that there is a decrease of molecular dipole moments in gas phase when chromophores **1** and **2** are linked together. The polymer films were fabricated by doping trichromophore **HT-1**, NGS chromophore **1**, and ZWI chromophore **2** into poly(4-vinylphenol) (PVPh). The second harmonic generation coefficients (d_{33}) of the films and the thermal stability of optical nonlinearities were measured by in situ second harmonic generation (SHG) measurement. The results show that almost a 5-fold enhancement in second harmonic coefficients (d_{33}) is realized as the combination of NGS chromophore and ZWI chromophore. The results indicate that NGS and ZWI chromophore combined hetero-trichromophores can efficiently improve the macroscopic optical nonlinearities in poled polymer materials.

Introduction

Organic nonlinear optical (NLO) materials have drawn considerable research interest due to their potential applications in photonic devices, such as electro-optic (EO) modulation, frequency doubling, optical switching, and optical information processing.[1−12] Compared with inorganic NLO materials, these materials have clear advantages such as high NLO coefficients, low dielectric constants, and good processability. In the past several years, chromophores with quite high hyperpolarizabilities (β) values have been developed, such as FTC-type chromophores and TCP-type chromophores.[3,13−19] For practical applications, the most highly studied materials class is the poled guest−host polymer type. To generate macroscopic optical nonlinearities, NLO chromophores in polymers should be poled by means of an electrical field to obtain the noncentrosymmetric arrangement. However, the conversion from quite high β values of chromophores to large macroscopic optical nonlinearities is difficult to realize, mainly due to the very strong interchromophore dipole−dipole interactions that lead to unfavorable antiparallel packing of the chromophores, thus reducing the optical nonlinearities.[20,21] Several approaches have been found to reduce the strong intermolecular electrostatic interactions, such as site isolation of chromophores via addition of bulky substituents to the chromophore backbone,[15,22] designing of chromophores with spherically shaped structures,[20,23] and dendritic chromophores where NLO dipolar chromophores covalently bound to form a dendritic structure.[9,16,24−26] Site isolated NLO materials and multichromophore dendritic NLO materials have proven to be efficient methods for reducing interchromophore electrostatic interactions that are detrimental to the realization of large macroscopic optical nonlinearities.

Recently, researches in the mutual effects of neutral-ground-state (NGS) chromophores and zwitterionic (ZWI) chromophores have attracted attention for the potential adjustment of dipole moments and hyperpolarizabilities in molecular level and application in supramolecular assembly.[27,28] Neutral-ground-state chromophore and zwitterionic chromophore[25,29−33] are two major types of dipolar NLO chromophores. Neutral-ground-state chromophores possess positive hyperpolarizabilities ($+\beta$) along the direction of the dipole moment. Contrarily, zwitterionic chromophores have negative hyperpolarizabilities ($-\beta$) which are in the opposite direction from the ground-state dipole moment. A bichromophore linking a strong neutral-ground-state NLO chromophore with a zwitterionic NLO chromophore in an antiparallel conformation was reported.[28] It was confirmed that an increase in β and decrease of the dipole moment were achieved in the bichromophore. It seems to be an efficient route in the design of chromophores to modulate the dipole moment and thus reduce the aggregation of chromophores in organic materials. A Langmuir−Blodgett NLO film was fabricated containing mixtures of NGS and ZWI chromophores with their β aligned and dipole moments antialigned.[27] The mechanism of aggregates formation was investigated, indicating that electrostatic forces can be applied to optimize chromophore alignment. However, the LB film containing physically mixed NGS and ZWI chromophores led to a 4-fold and 5-fold reduction in the second harmonic generation intensity of pure ZWI film and NGS film. To the best of our knowledge, there have been no reports on the macroscopic optical nonlinearities of organic materials containing neutral-ground-state and zwitterionic chromophores chemically linked hetero-multichromophores.

Here, we describe a method for synthesis of hetero-trichromophore by combination of NGS and ZWI NLO chromophores. Our approach is designed to reduce the strong intermolecular electrostatic interaction, thus improving macroscopic optical nonlinearities of organic NLO materials. In this approach, a ZWI chromophore is linked with two molecules of NGS chromophore to form a hetero-trichromophore, as shown in an somewhat parallel conformation in Figure 1, which is quite different from the literature reported[28] antiparallel conformation in the approach of designing hetero-bichromophore. It showed that a single molecule of trichromophore contains two active molecules of NGS chromophore and one of ZWI chromophore. Since the molecular dipole moments of all the three monochromophores in trichromophore point to the tether group, a decrease of the whole dipole moment of trichromophore may be predicted. In this investigation, a hetero-trichromophore **HT-1** by linking two NGS chromophores **1** with a ZWI chromophore **2** via esterifi-

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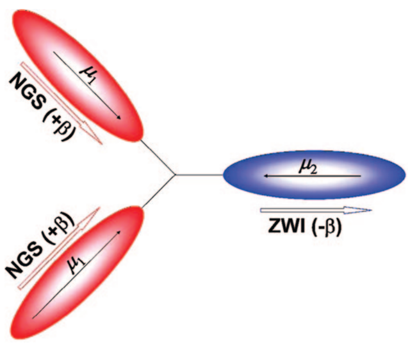


Figure 1. Conceptual diagram of a hetero-trichromophore by combination of neutral-ground-state chromophore and zwitterionic chromophore.

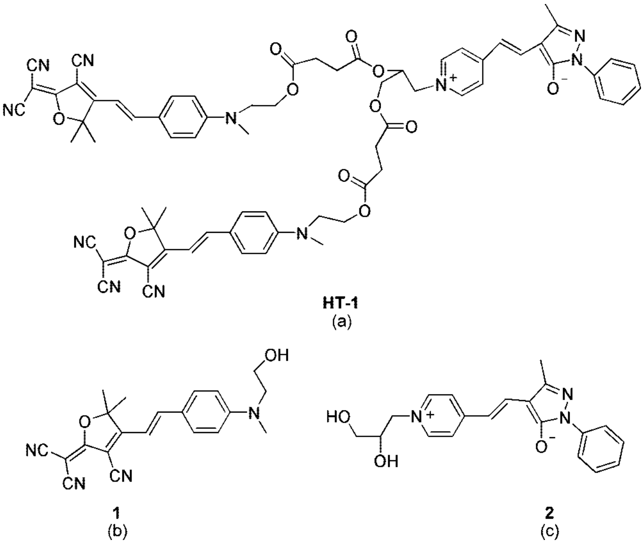


Figure 2. (a) Structure of the trichromophore **HT-1**. (b) Structure of the NGS chromophore **1**. (c) Structure of the ZWI chromophore **2**.

cation was synthesized, as shown in Figure 2. Characterizations of the trichromophore **HT-1** were presented in detail by element analysis, ^{1}H NMR, UV−vis absorption spectra, etc. Quantum chemical calculations (Hartree−Fock method) were performed to evaluate the change of molecular dipole moments. Trichromophore **HT-1**-doped poly(4-vinylphenol) (PVPh) thin films were fabricated, and chromophore **1**-doped PVPh films and chromophore **2**-doped PVPh films were also fabricated for comparison. The second harmonic generation (SHG) experiment[34,35] was used to measure the macroscopic optical nonlinearities and study the thermal stability of the optical nonlinearities. The results indicate that the NGS and ZWI chromophores combined hetero-trichromophore can reduce the strong interchromophore electrostatic interactions and efficiently enhance the optical nonlinearity.

Experimental Section

Materials. All chemicals were purchased from Alfa Aesar and Aldrich and used without further purification. Dichloromethane and *N*, *N*-dimethylformamide (DMF) were distilled over drying agents before used.

Synthesis of (*E*)-2-(3-Cyano-4-(4-((2-hydroxyethyl)(methyl)amino)styryl)-5,5-dimethylfuran-2(5*H*)-ylidene)malononitrile (1). NGS chromophore **1** was prepared according to a literature procedure.[36] To a solution of 4-((2-hydroxyethyl)(methyl)amino)benzaldehyde (0.89 g, 5 mmol) and 2-(3-cyano-4,5,5-trimethylfuran-2(5*H*)-ylidene)malononitrile (1.15 g, 5.5 mmol) in 30 mL of absolute ethanol, 10 drops of piperidine were added. The reaction mixture was refluxed for 6 h with stirring and then cooled to room temperature. The blue solid was filtered and recrystallized from ethanol. Yield: 67%. ^{1}H NMR (500 MHz, DMSO-d_6, δ ppm): 1.75 (s, 6H, $C(CH_3)_2$), 3.12 (s, 3H, $N(CH_3)$), 3.58−3.59 (d, 4H, NCH_2CH_2), 4.78 (s, 1H, OH), 6.85−6.87 (d, 3H, ArH, CH=CH), 7.75−7.77 (d, 2H, ArH), 7.90−7.94 (d, 1H, CH=CH). Anal. Calcd for $C_{21}H_{20}N_4O_2$: C, 69.98; H, 5.59; N, 15.55. Found: C, 69.76; H, 5.55; N, 15.43.

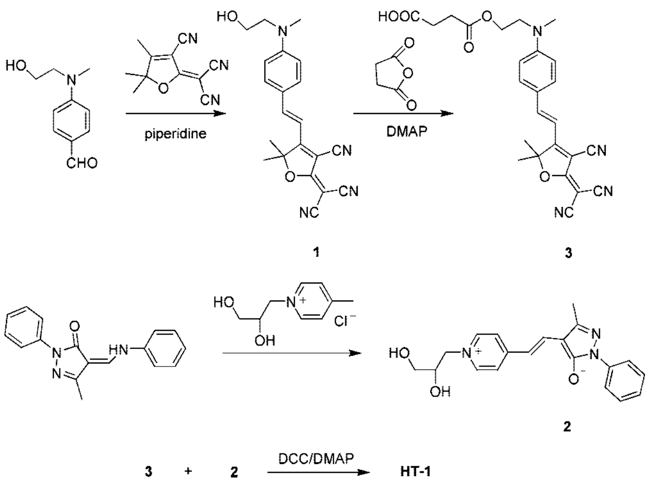
Synthesis of (*E*)-4-(2-((4-(2-(4-Cyano-5-(dicyanomethylene)-2,2-dimethyl-2,5-dihydrofuran-3-yl)vinyl)phenyl)(methyl)amino)ethoxy)-4-oxobutanoic Acid (3). To a solution of **1** (0.29 g, 0.84 mmol) and succinic anhydride (0.09 g, 0.9 mmol) in 30 mL of anhydrous dichloromethane, 0.90 g of DMAP and 0.3 mL of pyridine were added. The reaction mixture was stirred at room temperature overnight. The mixture was then washed with brine and DI water. The organic phase was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was purified by silica column chromatography using 5% ethanol in CH_2Cl_2 as the eluent. Yield: 78%. ^{1}H NMR (500 MHz, DMSO-d_6, δ ppm): 1.76 (s, 6H, $C(CH_3)_2$), 2.34 (d, 2H, $COCH_2$), 2.41 (m, 2H, CH_2COOH), 3.10 (m, 3H, NCH_3), 3.77 (d, 2H, NCH_2), 4.23 (d, 2H, CH_2O), 6.87−6.91 (d, 3H, Ar*H*, C*H*=CH), 7.78 (d, 2H, Ar*H*), 7.91 (d, 1H, CH=C*H*). MS (ESI): exact mass calcd for $C_{25}H_{24}N_4O_5$ $[M-H]^-$, 459.1. Found: 459.1.

Synthesis of (*E*)-4-(2-(1-(2,3-Dhydroxypropyl)pyridinium-4-yl)vinyl)-3-methyl-1-phenyl-1*H*-pyrazol-5-olate (2). ZWI chromophore **2** was prepared according to a literature procedure.[32] A solution of 1-(2,3-dihydroxypropyl)-4-methylpyridinium chloride (0.28 g, 1 mmol) and (*Z*)-3-methyl-1-phenyl-4-((phenylamino)methylene)-1*H*-pyrazol-5(4*H*)-one (0.21 g, 1 mmol) in 5 mL of ethanol was refluxed under a N_2 atmosphere for 5 min. Then, 0.2 mL of piperidine was added, and the resulting solution was refluxed for 12 h. After cooling the solution, the red solid was filtered and washed with a little cold methanol. Yield: 70%. ^{1}H NMR (500 MHz, DMSO-d_6, δ ppm): 2.15 (s, 3H), 3.29 (d, 1H, higher field branch of AB quartet, CH_2OH), 3.44 (d, 1H, lower field branch of AB quartet, CH_2OH), 3.76 (d, 1H, CHO*H*), 3.96 (d, 1H, higher field branch of AB quartet, NCH_2), 4.22 (d, 1H, lower field branch of AB quartet, NCH_2), 4.94 (m, 1H, CH_2OH), 5.29 (m, 1H, CHO*H*), δ 6.97 (m, 1H, C*H*=CH), δ 7.16−7.27 (m, 3H, Ar*H*), δ 7.60 (d, 1H, CH=C*H*), δ 7.92 (d, 2H, Ar*H*), δ 8.04 (d, 2H, Ar*H*). Anal. Calcd for $C_{20}H_{21}N_3O_3$: C, 68.36; H, 6.02; N, 11.96. Found: C, 68.11; H, 6.01; N, 11.87.

Synthesis of Trichromophore HT-1. A solution of chromophore **3** (0.13 g, 0.282 mmol) and **2** (0.047 g, 0.135 mmol) in 10 mL of anhydrous dichloromethane and 0.5 mL of DMF was stirred for 10 min at room temperature. The mixture was then cooled to 0 °C with an ice bath. DMAP (0.016 g, 0.135 mmol) and DCC (0.058 g, 0.28 mmol) were added to the mixture. The ice bath was removed, and the reaction mixture was stirred at room temperature for 12 h. The solvent was evaporated under reduced pressure. The product was obtained by silica column chromatography using 10% ethanol in CH_2Cl_2 as the eluent. Yield: 45%. ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm) 1.70 (d, 12H, $C(CH_3)_2$), 2.18 (s, 3H, CCH_3), 2.60−2.65 (m, 8H, $COCH_2$), 3.04−3.08 (s, 6H, NCH_3), 3.74−3.77 (d, 4H, NCH_2), 4.12(d, 1H, higher field branch of AB quartet, NCH_2), 4.20 (d, 4H, OCH_2), 4.33−4.36 (m, 3H, $CHCH_2O$(2H); lower field branch of AB quartet, NCH_2(1H)), 5.32 (d, 1H, $CHCH_2$), 6.63−6.78(m, 8H, Ar*H*, C*H*=CH), 7.08 (m, 2H, C*H*=CH), 7.33−7.36 (m, 3H, Ar*H*), 7.46−7.56 (m, 7H, Ar*H*), 8.06 (d, 2H, C*H*=CH). Anal. Calcd for $C_{70}H_{65}N_{11}O_{11}$: C, 68.00; H, 5.30; N, 12.46. Found: C, 67.94; H, 5.35; N, 12.38. MS (ESI): exact mass calcd for $C_{70}H_{65}N_{11}O_{11}$ $[M+H]^+$, 1236.5. Found: 1236.5.

Thin Film Fabrication. Each chromophore was mixed with solid PVPh. The solid components were then dissolved into cyclopentanone (8% of total solid weight). The chromophore loading densities of **HT-1** in polymer films were 9, 12.8, 16 and 20 wt %. For polymer films containing **1**, the loading densities were 7.5, 10, 12.8, 16, and 20 wt %. Because of the poor solubility of chromophore **2** in common organic solvents, DMF was used as solvent, and up to 7 wt % loading density was achieved. The

Scheme 1. Synthesis of the Hetero-trichromophore HT-1



solutions were stirred in a vial for 1 h and then filtered through a 0.22 μm Teflon membrane filter and spin-coated on the indium−tin oxide (ITO) glass substrates. The films were then dried in a vacuum oven at 85 °C for 12 h to remove the residual solvent.

Second Harmonic Generation Measurement. The second-order optical nonlinearity of the polymer films was determined by in situ second harmonic generation (SHG) measurement. A closed temperature controlled oven with optical windows and equipped with tungsten needle electrodes was used. The films were kept at 45° to the incident beam and poled inside the oven. The poling condition was as follows: voltage, 6 kV; gap distance, 1 cm. The laser source is a Q-switched Nd:YAG pulse laser with a 1064 nm fundamental beam (500 mJ maximum energy, 3−5 ns pulse width, and 10 Hz repeating rate). The generated second harmonic wave was passed through a monochromator and detected by a photomultiplier. The signal was averaged on a Stanford Research Systems (SRS) model SR-250 gated integrator and boxcar averager module and transferred to a microcomputer through a computer interface module SR-254.

Characterization. ^{1}H NMR spectra were taken on a Bruker Avance DMX500 spectrometer using tetramethysilane (TMS) as an internal standard. UV−vis absorption spectra were obtained using a Perkin-Elmer Lambda 20 spectrophotometer. Elemental analyses were obtained from an EA1112 microelemental analyzer. Differential scanning calorimetry (DSC) was performed using a TA DSC Q100 with a heating rate of 10 °C/min under a nitrogen atmosphere. Thermal gravimetric analysis (TGA) was performed using a TA Instruments SDT Q600 at a heating rate of 10 °C/min in a nitrogen atmosphere. Mass spectrometry was performed on a Bruker Daltonics esquire3000^{plus} mass spectrometer. Film thicknesses were measured using a Zygo NV200HR surface profilometer.

Results and Discussion

Synthesis and Characterization. The overall synthetic route to the trichromophore **HT-1** is shown in Scheme 1. Knoevenagel reaction of TCF acceptor 2-(3-cyano-4,5,5-trimethylfuran-2(5*H*)-ylidene)malononitrile with 4-((2-hydroxyethyl)(methyl)amino)benzaldehyde was performed to yield the NGS chromophore **1**. To create an attachment point, the reaction between succinic anhydride and chromophore **1** produced the carboxylic acid-functionalized chromophore **3**. *N*-Phenylamino acceptor (*Z*)-3-methyl-1-phenyl-4-((phenylamino)methylene)-1*H*-pyrazol-5(4*H*)-one was synthesized by the reaction of 3-methyl-1-phenyl-2-pyrazolin-5-one, aniline, and triethyl orthoformate. Then the reaction of the *N*-phenylamino acceptor with 1-(2,3-dihydroxypropyl)-4-methylpyridinium chloride produced the ZWI chromophore **2**. Two molecules of chromophore **3** were then attached to a molecule of ZWI chromophore **2** via esterification to create hetero-trichromophore **HT-1**. The structure of **HT-1** was confirmed by elemental analysis, ^{1}H NMR, and mass spectrometry. The details of the synthesis and characterizations are provided in the Experimental Section.

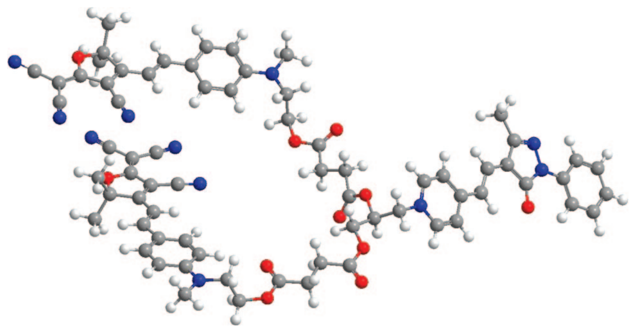


Figure 3. HF/6-31G-optimized structure of **HT-1**.

Table 1. HF/6-31G Calculated Ground-State Dipole Moments of Compounds 1, 2, and HT-1

compound	μ (D)
1	14.94
2	11.93
HT-1	13.84

The self-consistent field method calculation (Hartree−Fock method) was performed to optimize the structure of trichromophore **HT-1** by means of Gaussian03 program,[37] choosing 6-31G as the basis set. The optimized structure of **HT-1** in the gas phase is shown in Figure 3. The trichromophore **HT-1** has a three-dimensional (3D) shape while most of the monochromophores are two-dimensional (2D) shape molecules and has a much larger spatial bulk than chromophores **1** and **2**. The ground-state dipole moments of chromophores **1** and **2** and trichromophore **HT-1** were also calculated by performing the HF/6-31G method after optimization of their structures, as shown in Table 1. The calculated results indicated that the total dipole moment (μ) of trichromophore **HT-1** is larger than that of chromophore **2** but smaller than that of chromophore **1**. As expected, the total dipole moment of trichromophore was reduced by combining NGS and ZWI chromophore together. When dissolved in solvents, the conformation of trichromophore **HT-1** may be changed and thus changing the dipole moment of **HT-1**, due to interaction with solvent molecules.[28,38] With the conformation change of hetero-trichromophore in different polar solvents, the hyperpolarizabilities (+β) of **HT-1** may potentially be changed, which needs to be further systematically researched. In this paper, we mainly concern on the macroscopic nonlinear optical effects of the hetero-trichromophore.

The linear optical properties of the trichromophore **HT-1** were studied by UV−vis absorption spectroscopy. Figure 4 shows the UV−vis spectra of **1**, **2**, and **HT-1** in DMF. It seems that the shape of the absorption spectrum of the trichromophore **HT-1** is similar to the superimposed spectra of **1** and **2**. In the case of molecules held together via a terminal ring, the most significant UV−vis absorption is attributed to the monochromophore antenna, as the literature reported.[39] Therefore, the absorption spectrum of the trichromophore **HT-1** confirmed the successful synthesis of hetero-trichromophore **HT-1** by holding chromophores **1** and **2** together and suggested that there is little orbital overlap among the components.[28,40] Except the maximum absorption at 536 nm, the absorption of **HT-1** in DMF appears a slight shoulder at about 575 nm. This shoulder originates from the charge transfer band of chromophore **1**, the neutral part of hetero-trichromophore **HT-1**. The maximum absorption wavelengths (λ_{max}) of **HT-1** are 539 nm in $CHCl_3$ and 537 nm in DMF, as shown in Figure 5. The λ_{max} shows a blue shift of 3 nm, and the full wave at half-maximum (fwhm) of the peak broadened from 103.5 to 115.5 nm when the polarity of solvents

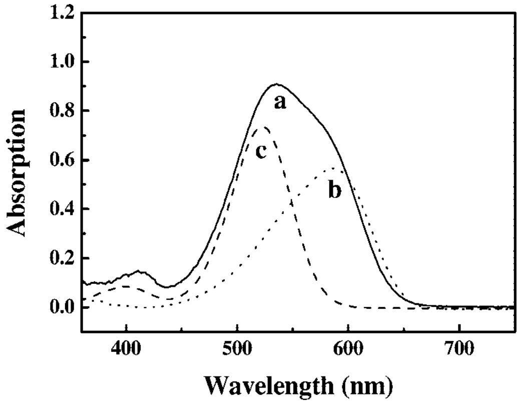


Figure 4. UV−vis absorption spectra of **1**, **2**, and **HT-1** in DMF (10^{-5} mol/L): a, **HT-1**; b, **1**; c, **2**.

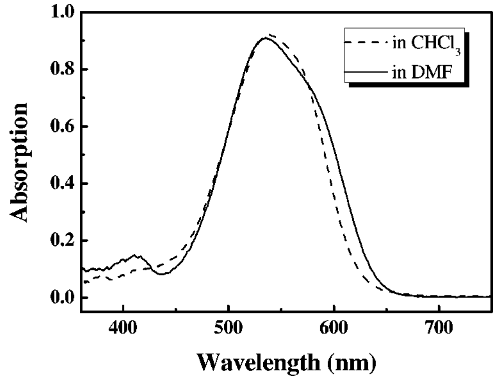


Figure 5. UV−vis absorption spectra of trichromophore **HT-1** in CHCl$_3$ and DMF (10^{-5} mol/L): solid line, **HT-1** in DMF; dashed line, **HT-1** in CHCl$_3$.

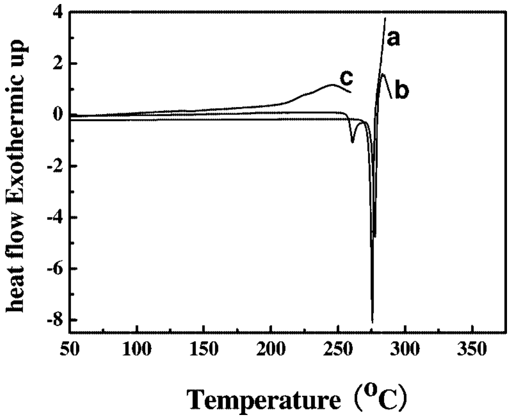


Figure 6. DSC thermograms of compounds **1**, **2**, and **HT-1**: a, **1**; b, **2**; c, **HT-1**.

increased from CHCl$_3$ to DMF. The little shift of the λ_{max} and the broadening about 12 nm of the peak can also be explained by the spectra superimposing of **1** and **2**. With increased polarity of the solvents, the charge-transfer band of the NGS chromophore **1** will red shift, while that of the ZWI chromophore **2** will blue shift. So the overall absorption peak of the trichromophore **HT-1** is broadened from CHCl$_3$ solution to DMF solution while little shift of λ_{max} occurs.

Thermal properties of chromophores **1** and **2** and trichromophore **HT-1** were explored by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA), as shown in Figure 6 and Figure 7. Compounds **1** and **2** have melting temperatures (T_m) of 276 and 278 °C, respectively. Compound **HT-1** shows no melting temperature before decomposition. Chromophore **2** has the highest decomposition temperature (T_d) (282 °C), followed by **1** (281 °C), and **HT-1** has the lowest decomposition temperature (233 °C). The decomposition temperature of **HT-1** is about 50 °C lower than chromophores **1** and **2** due to the introduction of succinic acid ester as the attachment unit, yet it is still quite comparable to many commonly used chromophores.[15,41]

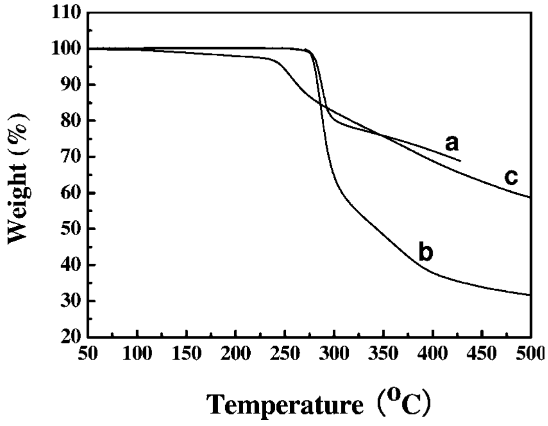


Figure 7. TGA curves of compounds **1**, **2**, and **HT-1**: a, **1**; b, **2**; c, **HT-1**.

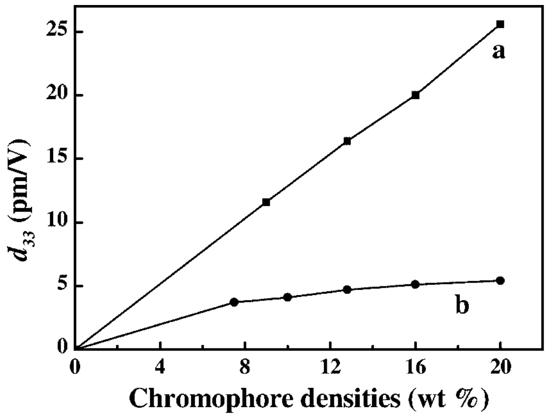


Figure 8. d_{33} values of polymer films as a function of chromophore loading densities: a, **film-HT-1**; b, **film-1**.

Nonlinear Optical Properties. NLO thin films containing trichromophore **HT-1** were prepared by choosing poly(4-vinylphenol) (PVPh)[42,43] as polymer matrix. The chromophore loading densities were up to 20 wt % without phase separation. Chromophore **1**-doped PVPh films (7.5, 10, 12.8, 16, and 20 wt %) were also fabricated. Because of the poor solubility of zwitterionic chromophore **2**, only 7 wt % loading density of **2**-doped polymer films was achieved. The loading density of chromophore **2**-doped polymer films (7 wt %, 2.4×10^{19} molecules in 0.25 g of PVPh) contains the same level of chromophore active molecules with **HT-1**-doped polymer films (20 wt %, 2.4×10^{19} molecules in 0.25 g of PVPh), for 1 mol of molecules of **HT-1** contain 2 mol of molecules of chromophore **1** and 1 mol of molecules of chromophore **2**. The thickness of the films was in the range 500−600 nm.

The second-order NLO properties of the polymer films were characterized by SHG measurement using the Maker fringe technique.[44,45] The second harmonic coefficient (d_{33}) of the film can be calculated by comparison with the SHG intensity of a standard Y-cut quartz crystal plate. The films were poled by applying a 6 kV dc voltage. The d_{33} values of the films are shown in Figure 8. With the increase of chromophore loading densities, the d_{33} values of films containing **1** (**film-1**) appeared to be saturated due to the strong interchromophore electrostatic

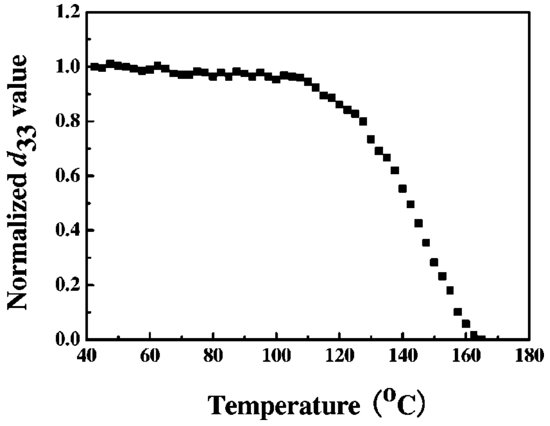


Figure 9. Decay of the normalized d_{33} values as a function of temperature for the **film-HT-1** at a ramp rate of 10 °C/min.

interactions.[2,21,23] Yet, comparing with **film-1** in the same loading densities, the d_{33} values of films containing **HT-1** (**film-HT-1**) were not saturated and showed almost linear improvement with loading densities increasing, indicating that the interchomophore interactions were reduced in **film-HT-1**.[24,46] The largest d_{33} values of **film-HT-1**, **film-1**, and films containing **2** (**film-2**) are 25.6, 5.4, and 3.2 pm/V, respectively. The data indicate that **film-HT-1** has an almost 4 times larger d_{33} values than that of **film-1** and about 7 times larger than that of **film-2**. The hetero-trichromophore **HT-1** is combined by three molecules of monochromophore, and thus it has a three-dimensional shape and possesses much larger spatial size than the 2D-shaped chromophores **1** and **2**. Meanwhile, there is a decrease of dipole moments when chromophores **1** and **2** are linked together. The strong interchromophore dipole−dipole electrostatic interactions are detrimental to the realization of large macroscopic optical nonlinearities, and thus minimizing dipole−dipole interaction could significantly improve the poling efficiency and the resulting macroscopic optical nonlinearities.[22,47,48] The 3D shape and large size could shield from strong intermolecular electrostatic interactions through steric interaction, thus reducing detrimental dipole interactions.[6,23] Moreover, the decrease of dipole moments can also efficiently reduce the intermolecular electrostatic interactions.[28,39] These factors simultaneously induced the efficient improvement of the d_{33} values by almost more than 5-fold.

Thermal dynamic stability of the NLO properties was investigated through a depoling experiment via monitoring normalized d_{33} coefficients as a function of temperatures. The poled film was heated at a ramp rate of 10 °C/min. The results of **film-HT-1** are shown in Figure 9. **Film-HT-1** showed good thermal stability, and the d_{33} value was still stable when heating to 110 °C, which is similar to the thermal stability of multichromophore dendrimer NLO materials.[16]

Conclusion

A new strategy in designing NLO chromophores by combination of neutral-ground-state chromophores and zwitterionic chromophores to form hetero-trichromophore was developed. The macroscopic optical nonlinearities of hetero-multichromophores were reported and studied for the first time. Following the strategy, hetero-trichromophore **HT-1** was synthesized by combination of NGS chromophore **1** and ZWI chromophore **2** via esterification. Hartree−Fock method calculations indicated that the ground-state dipole moment (μ) of trichromophore **HT-1** in gas phase is smaller than that of chromophore **1**. SHG measurement indicated that d_{33} value of the film containing **HT-1** was 25.6 pm/V at 1064 nm, which was about 5 times the value of the film containing NGS chromophore **1** and 8 times the value of the film containing ZWI chromophore **2**. The 3D architecture and large molecular size of the trichromophore **HT-1** which could spatially shield from strong intermolecular electrostatic interactions, as well as the decrease of dipole moments, are the main reasons for the efficient enhancement of d_{33} values. The design and synthesis of hetero-trichromophores by combining NGS chromophores and ZWI chromophores together could be an efficient route to pursue organic NLO materials with large macroscopic optical nonlinearity.

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Supporting Information Available: Full author list of ref 37; the UV−vis absorption spectra of doped polymer films and chromophores **1**, **2**, and **HT-1** at different concentrations in solutions. This material is available free of charge via the Internet at http://pubs.acs.org.

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