

Antiparallel-Aligned Neutral-Ground-State and Zwitterionic Chromophores as a Nonlinear Optical Material

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Abstract: Efficient noncentrosymmetric arrangement of nonlinear optical (NLO) chromophores with high first-order hyperpolarizability (β) for increased electro-optical (EO) efficiency has proven challenging as strong dipolar interactions between the chromophores encourage antiparallel alignment, attenuating the macroscopic EO effect. This work explores a novel approach to simultaneously achieve large β values while providing an adjustable dipole moment by linking a strong neutral-ground-state (NGS) NLO chromophore with positive β to a zwitterionic (ZWI) chromophore with negative β in an antiparallel fashion. It is proposed that the overall β of such a structure will be the sum of the absolute values of the two types of chromophores while the dipole moment will be the difference. Molecules 1–3 were synthesized to test the feasibility of this approach. Molecular dynamics calculations and NMR data supported that the NGS chromophore component and the ZWI chromophore component self-assemble to an antiparallel conformation in chloroform. Calculations showed that the dipole moment of 1 is close to the difference of the two component chromophores. Hyper-Rayleigh scattering (HRS) studies confirmed that the first hyperpolarizability of 1 is close to the sum of the two component chromophores. These results support the idea that an antiparallel-aligned neutral-ground-state chromophore and a zwitterionic chromophore can simultaneously achieve an increase in β and a decrease of the dipole moment.

Introduction

Organic and polymeric nonlinear optical materials have emerged as viable alternatives to conventional inorganic crystalline materials such as lithium niobate in active photonic components.¹ These new materials have many possible advantages: facile processing and reduced production cost, lower dielectric constants, and higher electrooptic coefficients. Katz et al. at Bell Laboratories have demonstrated an organic EO modulator architecture with a bandwidth of 150 GHz and a detectable terabit signal² using a simple nonlinear optical chromophore, DR1, in a polymer host. In 2000, Dalton and co-workers demonstrated modulators with drive voltages V_{π} below 1 V.³

To achieve high EO efficiency, an organic material must be comprised of nonlinear optical (NLO) chromophores with a large first hyperpolarizability (β), arranged noncentrosymmetrically. In recent years, NLO chromophores with large values of β have been developed.⁴ However, efficient arrangement of

NLO chromophores has proven challenging. Organic NLO chromophores, especially those demonstrating high β values, typically have large dipole moments. They tend to align in an antiparallel fashion, diminishing the macroscopic EO effect.⁵ Various approaches, including electric-field poling,⁶ siloxane-based multilayer films,^{7,8} Langmuir–Blodgett techniques,⁹ and vapor phase self-assembly¹⁰ have been employed to induce noncentrosymmetric arrangement of NLO chromophores. In all these approaches, the static interaction between dipoles hinders efficient noncentrosymmetric arrangement.^{5,6}

An ideal solution to this problem would be an NLO chromophore possessing a large β value but a moderate dipole moment for electric poling or zero dipole moment for self-

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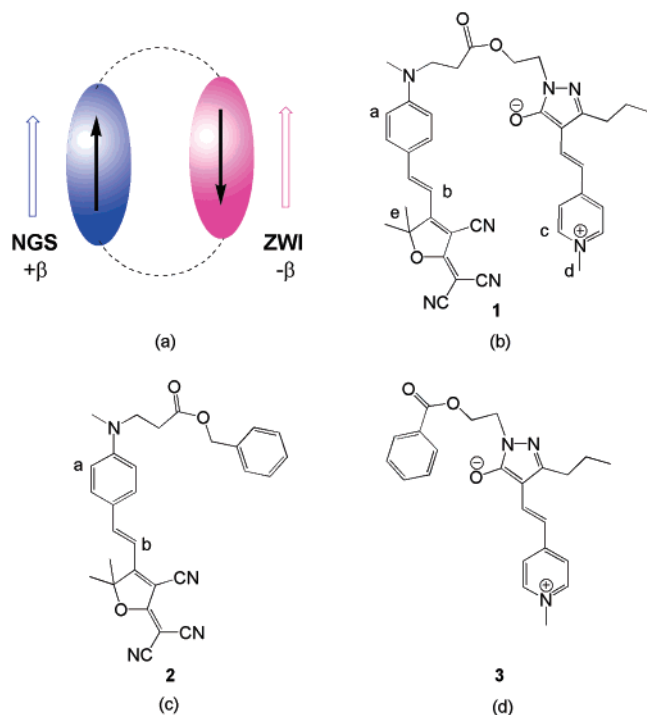


Figure 1. (a) Conceptual diagram of a pair of antiparallel aligned neutral-ground-state chromophore and zwitterionic chromophore; (b) Structure of the bichromophore **1**; (c) Structure of the NGS molecule **2**; (d) Structure of the ZWI chromophore **3**.

assembly. It has been well established that a chromophore, which possesses a large first-hyperpolarizability, generally possesses a strong donor, a strong acceptor, and a long conjugated bridge. This architecture inevitably yields a large dipole moment. Octupolar NLO chromophores¹¹ have been explored as an alternative as they have little or no dipole moment. Unfortunately, octupolar molecules are difficult to arrange noncentrosymmetrically, and thus their potential has yet to be realized.

This work explores a novel approach to simultaneously achieve large β -values while providing an adjustable dipole moment. In this approach, a strong neutral-ground-state (NGS) NLO chromophore is linked with a zwitterionic (ZWI) chromophore, as is shown in an antiparallel conformation in Figure 1a. Assuming that there is not a strong interaction between the two components of the bichromophore, to first order, the dipole moments of the two components should add linearly in this conformation. Thus, the overall dipole moment of the bichromophore should be approximately the difference of the dipole moments of the two chromophores. Neutral-ground-state chromophores have a positive β tensor element along the direction of the dipole moment, typically along the long axis of the molecule, while zwitterionic chromophores have a negative β .¹² The negative β of the ZWI chromophore has been theoretically predicted and experimentally demonstrated.^{12,13} As the dipole moments of the two chromophores are antiparallel, the overall β , to first order, should be the sum of the absolute value of the two chromophores' β values. Thus simultaneous increase of β and decrease of dipole moment may be realized.

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Results and Discussion

To the best of our knowledge, there have been no prior experimental or theoretical studies investigating combined zwitterionic and NGS chromophores. Therefore, bichromophore **1** was synthesized. NGS chromophore **2** and ZWI chromophore **3**^{13b} were also synthesized for experimental comparison. The synthesis of **1–3** followed the route in Scheme 1, and the details as well as the characterizations are provided in the Experimental Section.

The zwitterionic nature of **3** was confirmed by a solvatochromism study. The absorption maximum (λ_{\max}) of **3** decreases with increasing solvent dielectric constants (ϵ) (Table 1), which is expected for zwitterionic ground-state chromophores. In **1**, the donor end (i.e., the partially positively charged end) of the NGS chromophore is linked with the negatively charged end of the ZWI chromophore by a flexible linkage. It is expected that the dipole–dipole interaction between the two components will provide a force for an antiparallel alignment.

The conformation of **1** was modeled with molecular dynamics using the CVFF force field¹⁴ in the MM/MD program Discover¹⁵ from Accelrys. This force field is derived from quantum (Hartree–Fock/6-31g*) calculation of molecular Hessians and subsequent fitting of data to a high quality semiempirical function which includes cross-terms. Selected molecules having functional groups of interest are parametrized, and the derived parameters are transferred to similar functional groups in molecules outside the training set. As implemented,¹⁵ this force field includes generic parameters, which extends its coverage to the “exotic” functional groups found in **1–3**. As expected, face-to-face antiparallel conformations (Figure 2) were obtained regardless of the initial conformation provided. The bonding structure was further optimized using semiempirical AM1 calculations. The dipole moments of **1**, **2**, and **3** were computed by AM1 (see Table 2).¹⁶ Calculations show that the dipole moments for the antiparallel conformation are expected to be nearly subtractive. Similarly, the results show that when the two components are arranged in a higher energy, extended conformation, that the dipoles do effectively add, as expected.

The antiparallel conformation, driven by both dipolar forces and van der Waals forces, is expected to be the most stable conformation from gas-phase calculations. However, **1** may acquire conformations other than antiparallel in solution, due to interactions with solvent molecules. This is particularly likely in polar solvents such as methanol. NMR is widely utilized to study macromolecular conformations in solution. Therefore, **1** was studied by ROESY NMR. Because of the mixing of the zwitterionic ground state and the quinoidal ground state, the peaks of the protons on the ZWI chromophore are broadened.

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Scheme 1

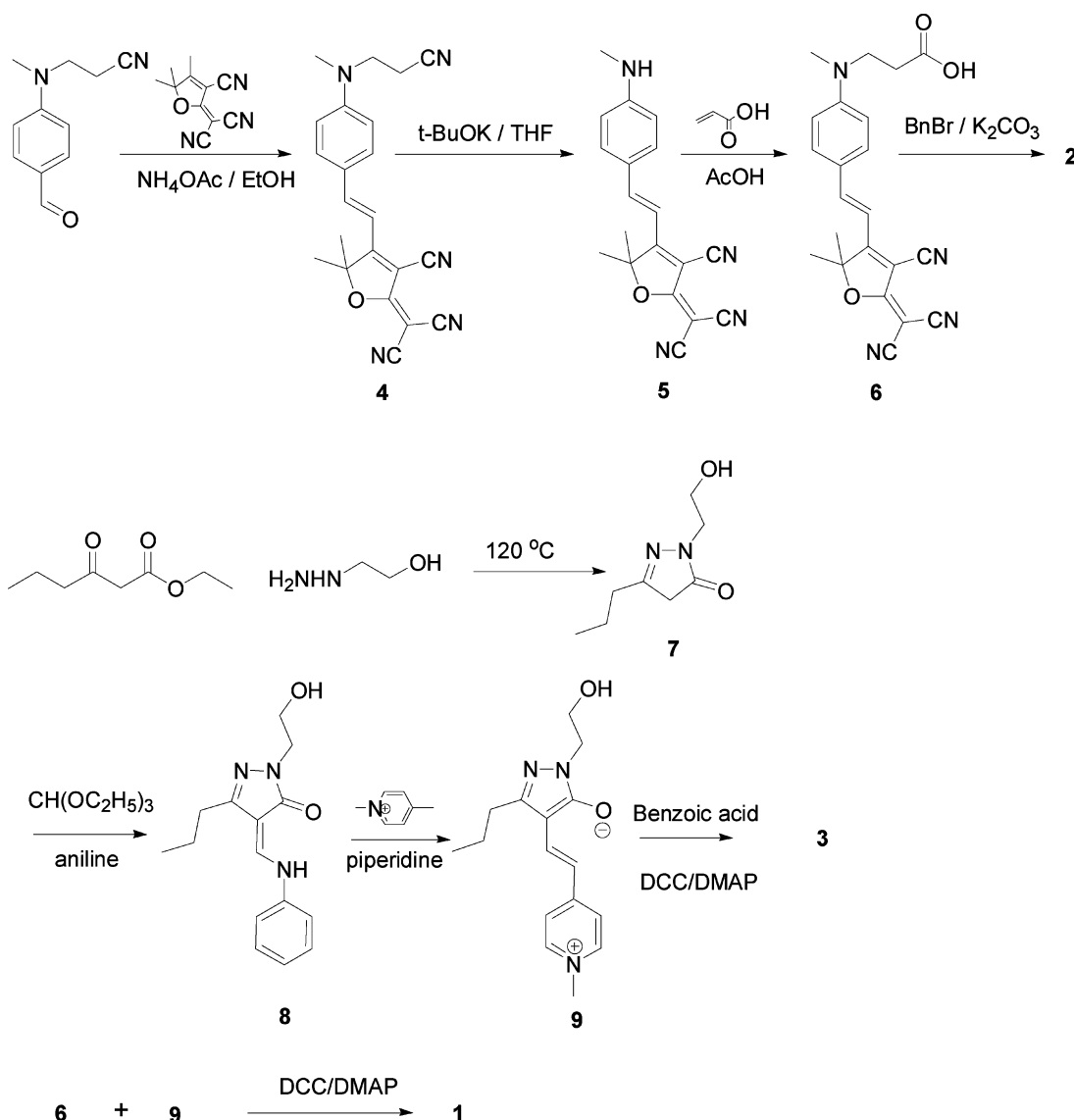


Table 1. Solvatochromism of 3

solvent (ϵ)	chloroform (4.8)	THF (7.6)	acetone (20.7)
λ_{\max} (nm)	536	532	529

Such phenomena have been studied by Abbotto et al.¹⁷ In chloroform, only protons *c* and *d* on the ZWI component show sharp peaks in NMR (Figure 1 and 2). Both *c* and *d* showed throughspace couplings with proton *b* on the NGS component (Figure 1 and 2) in ROESY NMR (Figure 3), which provides supporting evidence of the hairpin conformation. The cross coupling of *b* and *d* and the fact that there is no cross-peak of NGS protons *e* (Figure 1 and 2) with any ZWI proton suggest that, due to the bulky methyl groups *e*, the ZWI plane twists and slides away from the NGS plane to some extent, rather than forming fully antiparallel conformation as in Figure 2.

Additional evidence for the antiparallel conformation can be derived by analyzing one-dimensional ¹H NMR spectra of 1–3 in different solvents.¹⁸ In the antiparallel conformation, each

chromophore perturbs the static field of the other chromophore. In NMR, this perturbation would move the chemical shift of the protons on the positively charged end of one chromophore downfield due to the adjacent negative charge density of the other chromophore, which repels the electron density at the protons. Conversely, the chemical shift of the protons on the negatively charged end will move upfield. The perturbation is small compared with the molecular electrostatic potential. The absolute change of chemical shift is also small. However, because chemical shifts of the protons on different parts of the chromophore move in different directions, the relative displacement of chemical shifts is measurable. The NMR spectra of 1 in chloroform, acetone, and methanol as well as the NMR spectra of the two control molecules 2 and 3 were examined. The predicted chemical shift displacements for the antiparallel conformation of 1 in chloroform were observed. Evidence of this is described below and can be seen in Figure 3. In the NMR spectrum of the NGS chromophore 2, the bridge proton *b* [Figure 1c] has a higher chemical shift than the aniline proton

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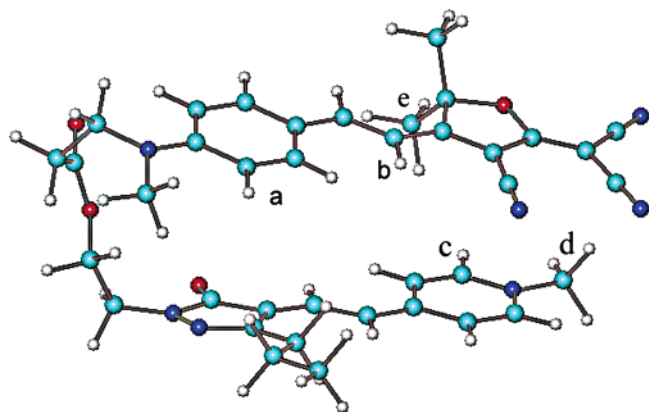


Figure 2. Calculated antiparallel conformation of **1**.

Table 2. Calculated Dipole Moments of **1–3**

molecule	NGS (2)	ZWI (3)	(1) antiparallel	(1) extended
AM1 dipole moment (Debye)	12.6	9.1	4.3	24.5

a on the positively charged end. The same order was observed in the NMR spectra of **1** [Figure 1b] in both methanol and acetone. In chloroform, proton *a* in **1** moves downfield as predicted for the antiparallel conformation. Because the peaks of *a* and *b* are adjacent, this displacement switches the relative position of the peaks of *a* and *b* (Figure 3). In chloroform, proton *a* has a larger chemical shift than proton *b* in the NMR spectrum of **1**. Given that proton *a* is on the ortho-position of the strong amino donor, this phenomenon is pronounced. To show that this effect is not due to intermolecular interactions, the NMR spectrum of a 1:1 mixture of **2** and **3** in chloroform was studied. Proton *a* showed a smaller chemical shift than *b* even when the concentration of each chromophore was 50% higher than the concentration used for the NMR of **1**. Other protons also showed predicted chemical shift displacements, which can be observed by examining the relative distance between the peaks.

The linear and nonlinear optical properties of the bichromophore **1** were studied by UV–visible absorption spectroscopy (Figure 4) and hyper-Rayleigh scattering (HRS) in chloroform. UV–vis absorption spectra of some homo-bichromophores have been studied.^{17,18} For the hetero-bichromophore **1**, the shape of the absorption spectrum is similar to the superimposed spectra of **2** and **3**, which suggests that there is little orbital overlap between the two components, consistent with the molecular modeling. The spectrum of a 1:1 mixture of **2** and **3** is identical to the mathematical sum of **2** and **3**, which indicates that there are no significant intermolecular interactions in the sub-millimolar concentrations used for UV and HRS studies. The extinction coefficient at the absorption maximum of **1** is clearly smaller than the sum of **2** and **3**, while the peak width of **1** is broader than that of the sum of **2** and **3**. The dynamic distribution of the bichromophore conformations and dipolar interactions may be the reasons for peak broadening. Especially in the antiparallel conformation, the existence of one highly dipolar chromophore essentially increases the polarity of the media around the other. With increased media polarity, the charge-transfer band of an NGS chromophore will red shift, while that of a ZWI chromophore will blue shift. Therefore the overall charge-transfer band of **1** will be broadened. Such an effect may also affect the oscillator strength of the charge-transfer bands

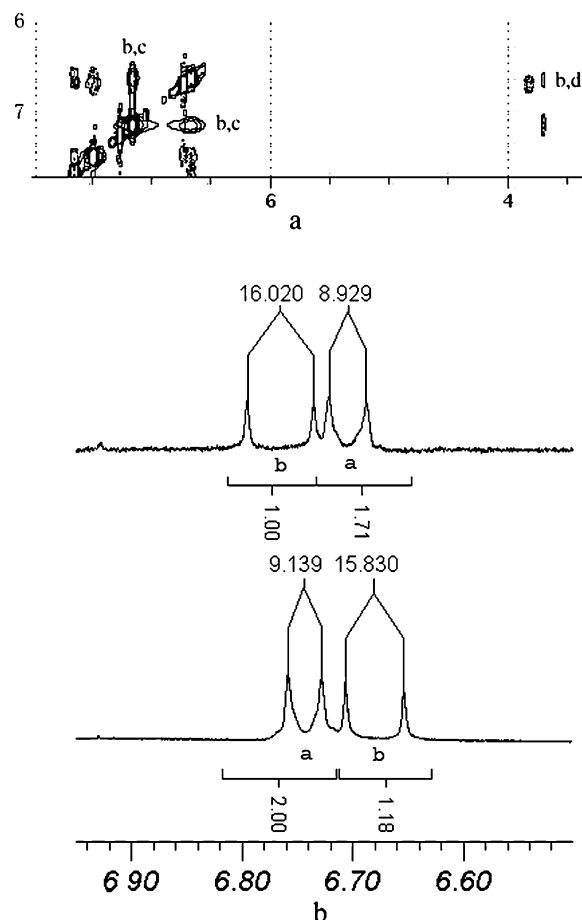


Figure 3. (a) ROSEY NMR (CDCl_3) of **1**. Only the area that contains the coupling peaks (b, c) and (b, d) is shown. (b) ^1H NMR (CDCl_3) of the proton *a* and *b* (Figure 1) of the NGS chromophore **2** (upper spectrum) and the dimer **1** (lower spectrum).

since the apparent oscillator strength is a result of couplings between the transition moment of the chromophore and that of the media molecules. The square of the transition moments that is directly proportional to the oscillator strength of **1–3** were calculated using the equation¹⁹

$$\mu_{\text{trans}}^2 = C \int \frac{\epsilon}{\nu} d\nu$$

$$C = \frac{(6\epsilon_0 \hbar^2) 2303c}{N_A h n}$$

where ϵ is the extinction coefficient from the UV–vis spectra; ν is the frequency; ϵ_0 is the permittivity of free space; h is Planck's constant; c is the speed of light in a vacuum; N_A is Avogadro's constant; and n is the refractive index of the solvent. The μ_{trans}^2 are 18273C, 12026C, and 7897C for **1**, **2**, and **3**, respectively. The transition moment of **1** is slightly smaller than the sum of **2** and **3**. Such hypochromic effects may be due to the shielding effects as discussed above. It may also be partially due to exciton interactions between the two chromophores.^{20,21}

Femtosecond HRS studies were performed on **1**, **2**, and **3** to measure the magnitude of β for each molecule and to provide

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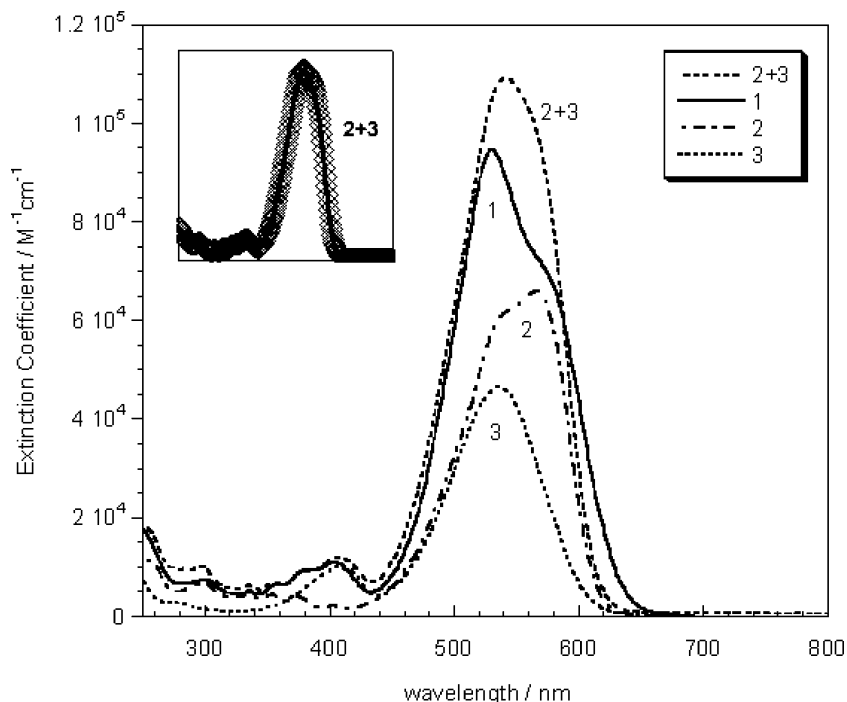


Figure 4. UV-vis spectra of **1**, **2**, **3**, and a 1:1 mixture of **2** and **3** in chloroform; in the inset, diamonds are the experimental data points of a 1:1 mixture of **2** and **3**, while the solid line is the mathematical sum of that of **2** and **3**.

insight into how the NGS and ZWI chromophores act in the bichromophore. HRS measures the orientation average of the square of the β tensor. Therefore the β_{HRS} of **1–3** are

$$\beta_{1\text{HRS}} = \sqrt{\langle \beta_1^2 \rangle} = \sqrt{\langle (\beta_2 + \beta_3)^2 \rangle}$$

$$\beta_{2\text{HRS}} = \sqrt{\langle \beta_2^2 \rangle} \text{ and } \beta_{3\text{HRS}} = \sqrt{\langle \beta_3^2 \rangle}$$

Here we assume that there is no effect on the individual chromophores due to direct molecular interactions. For push-pull NLO chromophores such as **2** and **3**, the β element along the push-pull direction, i.e., β_{zzz} , predominates. If the β tensors of the two components can be replaced by the zzz tensor element,

$$\beta_{1\text{HRS}}^2 \approx \langle (\beta_{2zzz} + \beta_{3zzz})^2 \rangle = \langle \beta_{2zzz}^2 \rangle + 2\langle \beta_{2zzz}\beta_{3zzz} \rangle + \langle \beta_{3zzz}^2 \rangle$$

If the two chromophores are not correlated with each other, we expect

$$0 = \langle \beta_{2zzz}\beta_{3zzz} \rangle$$

$$\beta_{1\text{HRS}}^2 = \langle \beta_{2zzz}^2 \rangle + \langle \beta_{3zzz}^2 \rangle = \langle \beta_{2zzz}^2 \rangle \left\{ 1 + \frac{\langle \beta_{3zzz}^2 \rangle}{\langle \beta_{2zzz}^2 \rangle} \right\}$$

On the other hand if the two are correlated in the antiparallel arrangement, we would expect perfect correlation so that

$$\langle \beta_{2zzz}\beta_{3zzz} \rangle^2 = \langle \beta_{2zzz}^2 \rangle \langle \beta_{3zzz}^2 \rangle$$

The condition of perfect correlation leads to the HRS signal being

$$\beta_{1\text{HRS}}^2 = \langle \beta_{2zzz}^2 \rangle + 2\sqrt{\langle \beta_{2zzz}^2 \rangle \langle \beta_{3zzz}^2 \rangle} + \langle \beta_{3zzz}^2 \rangle$$

$$= \langle \beta_{2zzz}^2 \rangle \left\{ 1 + \sqrt{\frac{\langle \beta_{3zzz}^2 \rangle}{\langle \beta_{2zzz}^2 \rangle}} \right\}^2$$

An excitation wavelength of 880 nm was chosen to reduce the impact of resonant enhancement on the measured values and to minimize self-absorption of the scattered light by the chromophores. As can be seen in Figure 4, the emission at 440 nm is at a minimum in the absorbance spectra of all species and, therefore, is a useful detection frequency for the HRS measurements. Chloroform was used as both the solvent and the internal reference for ascertaining β . Additional procedural details are included in the Experimental Section, and a more thorough discussion of the HRS apparatus is discussed elsewhere.²² The measured β values relative to chloroform ($\beta/\beta_{\text{chloroform}}$) are 2273 ± 74 (**1**), 2043 ± 91 (**2**), and 327 ± 31 (**3**). (Results are provided in relative units to eliminate confusion resulting from disagreement over absolute values of $\beta_{\text{chloroform}}$ in the literature, e.g., $\beta_{\text{chloroform}} = -0.49 \times 10^{-30}$ esu²³ and $\beta_{\text{chloroform}} = 0.16 \times 10^{-30}$ esu.²⁴) Using the above expressions and assuming that

$$\sqrt{\frac{\langle \beta_{3zzz}^2 \rangle}{\langle \beta_{2zzz}^2 \rangle}} = \frac{\beta_{3,\text{HRS}}}{\beta_{2,\text{HRS}}} = \frac{327}{2043} = 0.16 \pm 0.02$$

we expect for the uncorrelated case that

$$\beta_{1,\text{HRS}} = 1.01\beta_{2,\text{HRS}}$$

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and for the perfectly additive correlation

$$\beta_{1,\text{HRS}} = 1.16\beta_{2,\text{HRS}}$$

And for the perfectly subtractive correlation, an analogous analysis yields

$$\beta_{1,\text{HRS}}^2 = \langle \beta_{2,\text{zzz}}^2 \rangle \left\{ 1 - \sqrt{\frac{\langle \beta_{3,\text{zzz}}^2 \rangle}{\langle \beta_{2,\text{zzz}}^2 \rangle}} \right\}^2$$

$$\beta_{1,\text{HRS}} = (0.84 \pm 0.02)\beta_{2,\text{HRS}}$$

Experimental results showed that β of the dimer **1** is 1.11 ± 0.08 times that of **2**, which is closest to the perfectly additive correlation case. The analysis is valid only when a single component of the hyperpolarizability tensor dominates. Moreover, in solution one would expect a large array of conformations about any single conformation, and there are undoubtedly contributions from the other components of the hyperpolarizability tensor included in the averaging. The data indicate that the bichromophore (**1**) has a 10% larger β_{HRS} than the NGS (**2**) chromophore by itself. When coupled with the order of magnitude estimates on possible values, and the errors in the measurements, the measured β_{HRS} values are consistent with the hypothesis that the bichromophore is predominantly in the antiparallel arrangement in solution and that the two components of the bichromophore do not significantly interact with one another.

Conclusion

In summary, model compound **1** was synthesized. UV–vis, HRS, and NMR data support the suggestion that the NGS chromophore component and the ZWI chromophore component form an antiparallel conformation in chloroform. Calculations showed that the dipole moment of **1** is close to the difference of the two component chromophores. The overall first-order hyperpolarizabilities of the bichromophore is close to the sum of the two component chromophores. These results support the idea that a bichromophore with an antiparallel aligned neutral-ground-state chromophore and zwitterionic chromophore can simultaneously achieve an increased hyperpolarizability coupled with a decrease in dipole moment relative to the conventional NGS chromophore. Chromophores of this sort should be a way to optimally tune the dipole moment for acentric order under poling conditions, because they reduce the disruption to acentric order due to intermolecular dipolar interactions. Moreover, such self-assembly techniques may prove useful in constructing chemical adsorption and Langmuir–Blodgett films with a low or zero dipole moment using this design principle.

Experimental Section

General. All commercially available compounds were used as supplied unless mentioned in the procedures. Tetrahydrofuran, dichloromethane, and diethyl ether were distilled over drying agents under nitrogen before used. UV–visible spectra were recorded on a SHIMADZU 1601 UV spectrometer. ^1H NMR spectra were recorded on a Bruker AM 300. Unless indicated the concentration of NMR solution is about 5 mg/mL. The relative molar concentration may be estimated by comparing the intensity of the solvent residue peak with certain peaks of the corresponding compounds. Prevalere Life Sciences, Inc. performed all elemental analyses.

HRS Experiments. Chromophore solutions for HRS measurements were prepared in chloroform (Fisher: ACS Spectranalyzed) in the following concentrations: **1** (1.39 μM), **2** (2.15 μM), **3** (16.0 μM). Excitation was provided by a mode-locked Ti:sapphire oscillator (Spectra-Physics Tsunami: 100-fs, 80 MHz) at 880 nm (~ 20 nm fwhm) with a 1.4 W incident power. The incident light was focused into the middle of a low-volume flow cell equipped with an in-line 0.1- μm PTFE filter. Scattered light was imaged onto the slits of a spectrograph (Acton 300i) equipped with a 700-nm short-pass filter and a piece of blue-green BK7 glass. A 1340 \times 100 pixel, red-edge enhanced, back-thinned, LN₂-cooled CCD camera (Roper Scientific) was used for detection (180 s exposure time). Signal intensity was quadratically dependent on incident power. This, combined with the fact that the spectral-width of the HRS peak was equal to that of the incident field and tracked with changes in excitation wavelength, confirmed HRS. Signal intensity demonstrated no measurable attenuation over consecutive scans, implying that there was no measurable bulk photodegradation. Solution concentrations were carefully selected based on extinction coefficients to minimize self-absorption of the scattered light by the chromophores. No measurable self-absorption effects were observed at the concentrations chosen. HRS peaks were fit to a Gaussian functional form in MATLAB to determine intensities. Low-level multiphoton fluorescence was subtracted via curve-fitting. Intensities were converted to β by comparing spectra of the sample solutions to corresponding spectra of neat chloroform. β -values are expressed relative to $\beta_{\text{chloroform}}$ as determined through the following equation, where I is the signal intensity and N is the number density.

$$\frac{I_{\text{sample}}}{I_{\text{solvent}}} = \frac{N_{\text{sample}} \langle \beta_{\text{sample}}^2 \rangle + N_{\text{solvent}} \langle \beta_{\text{solvent}}^2 \rangle}{N_{\text{solvent}} \langle \beta_{\text{solvent}}^2 \rangle}$$

Synthesis. **2-[3-Cyano-4-(2-{4-[(2-cyanoethyl)methylamino]phenyl}vinyl)-5,5-dimethyl-5H-furan-2-ylidene]malononitrile (4):** 4-[(2-Cyanoethyl)methylamino]benzaldehyde (5 g, 26.6 mmol), 2-dicyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (7.0 g, 35.1 mmol), and ammonium acetate (2 g, 26.0 mmol) were dissolved in a mixture of 5 mL of THF and 25 mL of ethanol. The mixture was stirred for 8 h at room temperature. The products were collected by filtration and washed by ethanol and a little ether. Yield was 9.4 g (96%). ^1H NMR (CDCl_3): 1.79 (6 H, s), 2.97 (2 H, t, $J = 6.7$ Hz), 3.24 (3 H, s), 2.697 (2 H, t, $J = 6.7$ Hz), 6.77 (2H, d, $J = 9.0$ Hz), 6.831 (1 H, d, $J = 16.1$ Hz), 7.60 (2 H, d, 9.0), 7.62 (1 H, 16.1 Hz). HRMS (ESP): 370.1674 (M + H), 392.1492 (M + Na), 408.1231 (M + K).

2-[3-Cyano-5,5-dimethyl-4-[2-(4-methylaminophenyl)vinyl]-5H-furan-2-ylidene]malononitrile (5): A solution of **4** (1.007 g, 2.897 mmol) in anhy. THF (25 mL) was cooled to 0 °C. Potassium *tert*-butoxide (14.5 mL, 14.5 mmol) was added slowly, and the reaction mixture was allowed to stir at room temperature for 2 h. Then the reaction was neutralized by addition of HCl (0.1 M). The aqueous phase was extracted with methylene chloride, the organic layer was dried over sodium sulfate, and the solvent was evaporated. Purple product (450 mg, 52%) was obtained. ^1H NMR (CDCl_3): 1.65 (6 H, s), 2.38 (3 H, s), 6.64 (2 H, d, $J = 8.9$ Hz), 6.78 (1 H, d, $J = 16.0$ Hz), 7.54 (2 H, d, $J = 8.9$ Hz), 7.62 (1 H, d, $J = 16.0$ Hz). HRMS (ESP): 317.1406 (M + H), 339.1225 (M + Na), 355.0965 (M + K).

3-({4-[2-(4-Cyano-5-dicyanomethylene-2,2-dimethyl-2,5-dihydrofuran-3-yl)vinyl]phenyl}methylamino)propionic Acid (6): Acrylic acid (0.7 mL), acetic acid (0.7 mL), and **5** (150 mg, 0.416 mmol) were heated at 80 °C for 12 h. Then the reaction mixture was concentrated and poured into a large excess of water. The product was obtained as the precipitate. The yield is 95 mg (51%). ^1H NMR (acetone- d_6): 1.86, (6H, s), 2.69 (2H, t, $J = 7.2$ Hz), 3.19 (3H, s), 3.86 (2H, t, $J = 7.2$ Hz), 6.93 (2H, d, $J = 8.8$ Hz), 7.02 (1H, d, $J = 16.2$ Hz), 7.80 (2H, d, $J = 8.8$ Hz), 8.00 (2H, d, $J = 16.2$ Hz). HRMS (ESP) m/e : 389.1619 (M + H), 411.1436 (M + Na), 427.1175 (M + K).

3-({4-[2-(4-Cyano-5-dicyanomethylene-2,2-dimethyl-2,5-dihydrofuran-3-yl)vinyl]phenyl}methylamino)propionic Acid Benzyl Ester (2): To a solution of 100 mg (0.26 mmol) of **6** and 0.5 mL of benzyl bromide in 2 mL of acetone were added 35.6 mg of K_2CO_3 . The mixture was stirred and heated at about 70 °C for 4 h and kept at room temperature overnight. The mixture was diluted with methylene chloride and passed through a short plug of silica gel. The resultant solution was concentrated and passed through a silica gel column with 5% ethyl acetate in methylene chloride as the eluant to yield the crude product. The crude product was dissolved in a minimum amount of methylene chloride. The solution was added to 12 mL of hexanes to yield the pure product (104 mg, 84%). 1H NMR: ($CDCl_3$) 300 MHz: 1.77 (6H, s), 2.71 (2H, t, $J = 7.0$ Hz), 3.09 (3H, s), 3.83 (2H, t, $J = 7.2$ Hz), 5.14 (2H, s), 6.73 (2H, d, $J = 8.9$ Hz), 6.79 (1H, d, $J = 15.8$ Hz), 7.37 (5H, m), 7.54 (2H, d, $J = 8.9$ Hz), 7.61 (1H, d, $J = 15.9$ Hz). HRMS (ESP): m/e 501.1880 (M + Na). Anal. Calcd for $C_{29}H_{26}N_4O_3 \cdot 0.15(CH_2Cl_2)$: C, 71.27; H, 5.40; N, 11.40. Found: C, 71.55; H, 4.84; N, 11.39.

2-(2-Hydroxyethyl)-5-propyl-2,4-dihydropyrazol-3-one (7): Ethyl butyryl acetate (2 g, 12.64 mmol) and 2-hydroxyethylhydrazine (962 mg, 12.64 mmol) were heated at 120 °C for 4 h. The crude product was purified using column chromatography with silica gel as the stationary phase and 1:1 ethyl acetate/hexanes as the mobile phase. 1.3 g (60%) of the pure product were obtained. 1H NMR ($CDCl_3$): 0.86 (3H, t, $J = 7.2$ Hz), 1.62 (2H, m), 2.34 (2H, t, $J = 7.2$ Hz), 3.15 (2H, s), 3.84 (5H, m).

2-(2-Hydroxyethyl)-4-phenylaminomethylene-5-propyl-2,4-dihydropyrazol-3-one (8): To **1** (300 mg, 1.76 mmol) in ethanol (12 mL) was added triethyl orthoformate (0.3 mL, 1.76 mmol) and aniline (0.16 mL, 1.76 mmol), and the mixture was refluxed for 12 h. Then the solvent was evaporated, and the crude product was purified on a silica gel column with 7:93 methanol/methylene chloride as the eluant to get bright yellow pure product. 320 mg (67%) of the pure product were obtained. 1H NMR ($CDCl_3$) 300 MHz: 1.02 (3H, t, $J = 7.1$ Hz), 1.71 (2H, m), 2.55 (2H, t, $J = 7.2$ Hz), 3.97 (4H, m), 7.22 (3H, m), 7.43 (2H, d, $J = 7.6$ Hz), 7.93 (1H, s). HRMS (ESP), m/e : 274.1559 (M + H); 569.2860 (2M + Na); 842.4344 (3M + Na).

2-(2-Hydroxyethyl)-4-[2-(1-methyl-1H-pyridin-4-ylidene)ethylidene]-5-propyl-2,4-dihydropyrazol-3-one (9): *N*-Methyl pyridinium iodide (210 mg, 0.950 mmol) and **8** (200 mg, 0.731 mmol) were dissolved in ethanol (2 mL), and pipyridine (0.1 mL) was added. The reaction mixture was heated at 60 °C for 12 h. Then the solvent was evaporated, and the crude product was purified with column chromatography with silica gel as the stationary phase and 12:88 methanol/methylene chloride as the mobile phase to get orange pure product. 190 mg (90%) of the

pure product were obtained. 1H NMR (MeOD): 1.00 (3H, t, $J = 7.5$ Hz), 1.66 (2H, m), 2.59 (2H, t, $J = 7.5$ Hz), 3.79 (2H, t, $J = 5.4$ Hz), 3.91 (2H, t, $J = 5.4$ Hz), 3.99 (3H, s), 6.95 (1H, d, $J = 15.3$ Hz), 7.52 (2H, d, $J = 7.2$ Hz), 7.75 (1H, d, $J = 15.3$ Hz), 8.03 (2H, d, $J = 7.2$ Hz). HRMS (ESP), m/e : 597.3163 (2m + Na), 884.4801 (3m + Na).

Benzoic Acid 2-{4-[2-(1-Methyl-1H-pyridin-4-ylidene)ethylidene]-5-oxo-3-propyl-4,5-dihydropyrazol-1-yl}ethyl Ester (3): **9** (300 mg, 1.04 mmol), benzoic acid (152 mg, 1.25 mmol), DCC (250 mg, 1.20 mmol), and DMAP (14 mg, 0.125 mmol) were dissolved in anhydrous methylene chloride and stirred under N_2 for 12 h. The solvent was evaporated, and the crude product was purified on a silica column with 10:90 methanol/methylene chloride as the mobile phase. 250 mg (61%) of the pure product was obtained. 1H NMR (MeOD): 0.96 (3H, t, $J = 7.4$ Hz), 1.64 (2H, sextet, $J = 7.4$ Hz), 2.59 (2H, t, $J = 7.4$ Hz), 3.99 (3H, s), 4.19 (2H, t, $J = 5.7$ Hz), 4.57 (2H, t, $J = 5.7$ Hz), 6.96 (1H, d, $J = 15.5$ Hz), 7.44 (2H, t, $J = 7.4$ Hz), 7.52 (2H, d, $J = 7.0$ Hz), 7.58 (1H, t, $J = 7.4$ Hz), 7.76 (1H, d, $J = 15.5$ Hz), 8.00–8.05 (4H, m). HRMS (ESP) m/e : 392.1964 (M + H). Anal. Calcd for $C_{23}H_{25}N_3O_3 \cdot 0.25(CH_2Cl_2)$: C, 67.66; H, 6.23; N, 10.18. Found: C, 67.97; H, 5.84; N, 10.20.

Molecule 1. To a mixture of **6** (600 mg, 1.54 mmol) and **9** (404 mg, 1.40 mmol) were added 0.5 mL of DMF and 20 mL of methylene chloride. The mixture was stirred for 10 min at room temperature and then cooled below 0 °C. DCC (433 mg, 2.10 mmol) and DMAP (26 mg, 0.22 mmol) were added to the above mixture. The resultant mixture was stirred at room temperature overnight. About half of the solvent was evaporated under reduced pressure. The product was obtained by passing the resultant mixture through a silica gel column using 10% methanol in methylene chloride as the eluant. 720 mg (78%) of the product were obtained. 1H NMR (MeOD): 0.99 (3H, t, $J = 7.2$ Hz), 1.67 (2H, m), 1.79 (6H, s), 2.59 (2H, t, $J = 7.3$ Hz), 2.64 (2H, t, $J = 7.2$ Hz), 3.07 (3H, s), 3.80 (2H, t, $J = 6.8$ Hz), 3.99 (3H, s), 4.03 (2H, t, $J = 5.5$ Hz), 4.34 (2H, t, $J = 5.4$ Hz), 6.81 (2H, d, $J = 9.0$ Hz), 6.87 (1H, d, $J = 15.7$ Hz), 6.96 (1H, d, $J = 16.0$ Hz), 7.50 (2H, d, $J = 7.1$ Hz), 7.64 (2H, d, $J = 9.0$ Hz), 7.76 (1H, d, $J = 15.5$ Hz), 7.90 (1H, d, $J = 15.9$ Hz), 8.03 (2H, d, $J = 7.2$ Hz). HRMS (ESP) m/e : 658.3134 (M + H). Anal. Calcd for $C_{38}H_{39}N_7O_4 \cdot 0.15(CH_2Cl_2)$: C, 68.34; H, 5.91; N, 14.62. Found: C, 68.53; H, 5.77; N, 14.63.

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