Pyrroline Chromophores for Electro-Optics

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We have synthesized a new class of highly efficient nonlinear optical (NLO) chromophores based on the novel tricyanopyrroline (TCP) electron acceptor. Molecular linear and nonlinear optical properties of the prototypical chromophores were measured and calculated to understand structure−property relationships. One such chromophore showed molecular first hyperpolarizability (β) of (8700 ± 702) × 10^{-30} esu at excitation wavelengths of 1.9 μm, and another showed macroscopic electro-optic (EO) coefficients (r_{33}) of 51 pm/V at 1.55 μm with 20 wt % chromophore loading when poled with 65 V/μm in amorphous polycarbonate film. Synthetic strategies for extending the utility of the acceptor and chromophores are discussed.

Introduction

Polymeric electro-optic (EO) materials with nonlinear optical (NLO) chromophores have shown commercial potential as active media in high-speed broadband waveguides for optical switches, optical sensors, and information processors.[1] Their macroscopic EO response (r_{33}) to an external field is proportional to the scalar product of the dipole moment (μ) and molecular first hyperpolarizability (β) of dipolar NLO chromophores with acentric alignment in polymer matrixes. Efficient translation of large β chromophores into thermally and chemically stable materials with macroscopic EO responses can be achieved by careful modification of the molecular structure of chromophores and host polymers under mild electric-field poling.[2] Nevertheless, further improvements in molecular NLO properties of chromophores are needed to develop polymeric EO materials for many anticipated device applications.

In general, dipolar NLO chromophores used in polymeric EO materials consist of electron-donor and electron-acceptor end groups interacting through a conjugated bridge. It has been well established that β, which characterizes the molecular NLO efficiency, depends on the strength of the donor and acceptor groups, as well as the nature and length of the conjugated bridge.[3] Very large β values can be achieved in NLO chromophores by optimizing the ground-state polarization of the molecules through careful combination of available electron donors, conjugated bridges, and electron acceptors.[4] The strength and efficiency of these groups can be engineered by rational molecular design of modular components of chromophores using guidance provided by quantum mechanical calculations.

A major obstacle in the optimization of dipolar NLO chromophores with high β values is the development of novel electron acceptors. Recently, we reported classes of NLO chromophores based on 2-dicyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (TCF) and 2-dicyanomethylene-3-cyano-4,5-dimethyl-5-trifluoromethyl-2,5-dihydrofuran (CF_3-TCF), acceptor groups with exceptionally large β values.[5]

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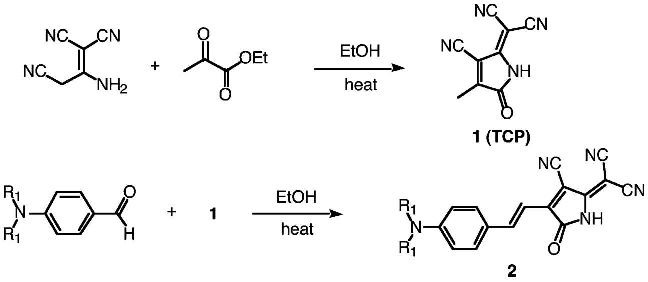
Scheme 1. Synthesis of Acceptors and Styryl TCP Chromophores



During the synthesis of the CF_3-TCF acceptor, we encountered a few synthetic difficulties originating from the dimerizations of α-hydroxy ketone[6] and malononitrile.[7] These dimerizations were found to be the major factors in determining the yield and purity of the acceptor.[8] The malononitrile dimer is the main side product in the conventional one-pot reaction in refluxing ethanol.[9] Related synthesis of the acceptor has been reported in pyridine.[10] Analysis of the reaction mechanisms and products in the synthesis of the CF_3-TCF acceptor, and understanding of the role of functional groups in the electronic structure of the acceptor, led us to the synthesis of TCP (3-methyl-4-cyano-5-dicyanomethylene-2-oxo-3-pyrroline), acceptor **1**. The inductive contribution and potential hyperconjugation of the trifluoromethyl group in the electronic structure of the CF_3-TCF acceptor has been reported.[5d] We expected these effects to be further enhanced by replacing the gem-dialkyl group in the TCF acceptor with a carbonyl group that can participate in the main conjugation path of the chromophores. Here, we report the synthesis of a class of highly efficient NLO chromophores using tricyanopyrroline (TCP) as an acceptor.

Results and Discussion

Synthesis. The TCP acceptor was synthesized from a reaction between the malononitrile dimer and ethyl pyruvate, as shown in Scheme 1.

TCP chromophore **2** can be synthesized by the Knoevenagel condensation of acceptor **1** with a 4-dialkylaminobenzaldehyde in refluxing ethanol.[11] The acceptor can be generated in situ in one pot. Series of styryl TCP chromophores were synthesized using various electron-donor bridges with an aldehyde end group.

One of the major advantages of the TCP chromophores is their flexibility with respect to structural modifications required in the optimization of chemical and optical properties. During the syntheses of styryl TCP chromophores, we found several patents on TCP chromophores.[12] These chromophores were synthesized by electrophilic substitution of electron-rich aromatic substrates with TCP chloride (3-chloro-4-cyano-5-dicyanomethylene-2-oxo-3-pyrroline) in aprotic polar solvents. The reported chromophores were developed for dyeing polyester fibers and synthetic resins and as dyes for optical recording and thermal-transfer printing. To the best of our knowledge, the chromophores have not been used for electro-optic applications previously.[13]

We were encouraged by the desirable thermochemical and photochemical stabilities of the reported chromophores in many practical applications, albeit in the absence of extended conjugation bridges. We were able to develop and extend general synthetic strategies in building TCP chromophores with various functional substituents. For example, chromophore **2c** reacted with diethyl sulfate in the presence of potassium carbonate in refluxing acetonitrile to give **2d** (see Chart 1 for chromophore structures and formulas). The procedures can be used to tune the electronic properties of the chromophores, introduce various cross-linkers, improve solubility, and minimize molecular aggregation in the solid state. Moreover, the procedures can be conveniently applied to other TCP chromophores with conjugated electron-donor bridges.

Single crystals of chromophore **2d** were grown by the slow evaporation of acetone solutions at room temperature. Chromophore **2d** crystallized in the triclinic $P\bar{1}$ space group (No. 2) with crystal parameters of $a = 11.1230(4)$ Å, $b = 13.0450(5)$ Å, $c = 17.9940(7)$ Å, $\alpha = 100.870(2)°$, $\beta = 96.658(2)°$, $\gamma = 102.460(1)°$. As expected, the active dipolar portion of the chromophore is completely coplanar from the donor to acceptor groups, with no significant twisting along

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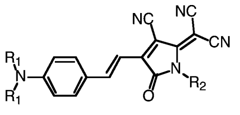
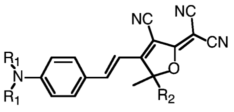
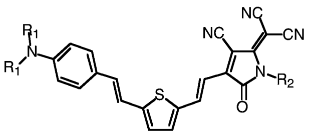
Chart 1



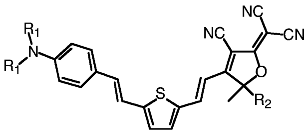
2 a R_1=CH_3, R_2 = H
2 b R_1=CH_2CH_3, R_2 = H
2 c R_1=$(CH_2)_3CH_3$, R_2 = H
2 d R_1=$(CH_2)_3CH_3$, R_2 = CH_2CH_3
2 e R_1=$(CH_2)_3CH_3$, R_2 = CH_2CHCH_2
2 f R_1=$(CH_2)_2OCOCH_3$, R_2 = H
2 g R_1=$(CH_2)_2OSi(CH_3)_2C(CH_3)_3$, R_2 = H



3 a R_1, R_2 = CH_3
3 b R_1=CH_2CH_3, R_2 = CH_3
3 c R_1=CH_3, R_2 = CF_3
3 d R_1=CH_2CH_3, R_2 = CF_3



4 a R_1=CH_3, R_2 = H
4 b R_1=$(CH_2)_3CH_3$, R_2 = H
4 c R_1=$(CH_2)_3CH_3$, R_2 = FD
4 d R_1=$(CH_2)_2OSi(CH_3)_2C(CH_3)_3$, R_2 = H



5 a R_1, R_2 = CH_3
5 b R_1=CH_2CH_3, R_2 = CH_3
5 c R_1=CH_3, R_2 = CF_3
5 d R_1=CH_2CH_3, R_2 = CF_3

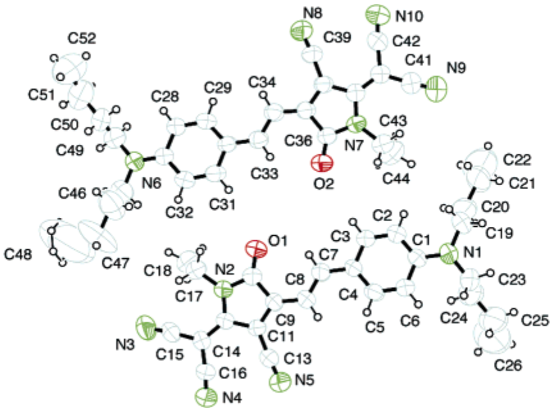


Figure 1. ORTEP representation of a unit cell structure of chromophore **2d**.

the conjugation path with all-trans configuration. All three cyano groups and the carbonyl group are in the same plane of the acceptor structure. There was some disorder in the donor butyl groups, which should not affect electronic properties of the chromophore. Head-to-tail arrangements between chromophores form compact centrosymmetric extended structures. An ORTEP representation of a unit cell structure of chromophore **2d** is shown in Figure 1.

A series of TCP chromophores based on a phenyl vinylene thiophene vinylene (FTC) bridge,[14] such as chromophores **4b** and **4d**, were synthesized by simple addition of the TCP acceptor to the ethanol solution of electron-donor bridges with aldehyde end groups. Excellent yields were obtained under mild reaction conditions. Efforts to increase the yield of the acceptor are ongoing. Acylation of chromophore **4b** with fluorodendronized benzoyl chloride **7** (FD-Cl)[15] in the presence of potassium carbonate gave chromophore **4c** in good yield, see Scheme 2.

Electronic and Optical Properties. On the basis of semiempirical Austin Model 1 (AM1) geometries, we calculated the electronic properties (state and transition dipole moments and transition energies) of simple dimethylamino styryl model chromophores from a semiempirical intermediate neglect of differential overlap (INDO) Hamiltonian in order to understand and compare the electronic structures between chromophores.[16]

The calculated (gas phase) transitions energies for model chromophores show systematic bathochromic shifts in the following order: **3a** (408 nm), **3c** (423 nm),[17,5d] and **2a** (473 nm). The calculated trend is consistent with measured absorption maxima in various solvents, as shown in Table 1 and Figure 2. Moreover, the electronic and optical properties of the model TCP chromophores can be tuned significantly by a simple substitution of the pyrroline nitrogen in the acceptor. For example, addition of an electron-withdrawing group such as an ethyl acetate at the N−H position in chromophore **2c** results in a 20 nm bathochromic shift of the absorption maximum in dioxane. The substituents on the electron-donor end group affect the optical properties more significantly. For example, chromophore **2f** shows a hypsochromic shift of 41 nm compared with **2c** (from 676 to 635 nm), and **2g** shows a hypsochromic shift of 13 nm compared with **2c** (from 676 to 663 nm) in dioxane.

Solvatochromism of the TCP chromophores has been measured to estimate hyperpolarizabilities. These measurements were used to compare β of chromophores qualitatively within closely related structures.[18] TCP chromophores show very strong solvatochromism comparable to the best known TCF chromophores with significantly shorter conjugation lengths. Spectral data for model TCF, CF_3-TCF, and TCP chromophores are shown in Table 1 with solvatochromism data for comparison.

Molecular Hyperpolarizability. The molecular first hyperpolarizabilities of chromophores were calculated using the sum-over-states (SOS) approach.[19] All molecules were assumed to be in trans configurations. In dipolar NLO chromophores, the β is dominated by one diagonal tensor term, say zzz, along the donor−acceptor axis. Therefore, the

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Scheme 2. Synthesis of Chromophores

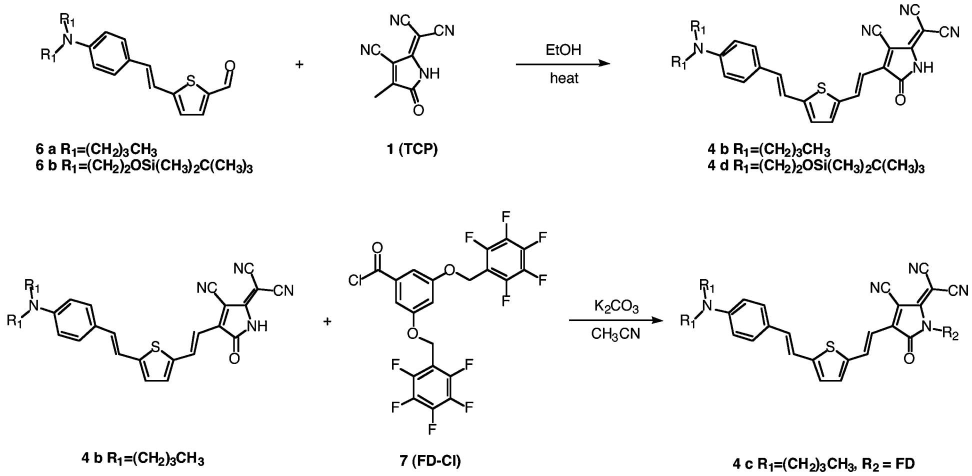

Table 1. UV−Vis Spectra and Solvatochromism Data of Chromophores 3b, 3d, and 2b

	3b	3d	2b
λ_{max} (toluene) (nm)	561	607	691
λ_{max} (chloroform) (nm)	584	628	732
$\Delta\lambda_{max}$ (eV)	0.087	0.069	0.100
$\Delta\lambda_{max}$/mol wt (eV)	2.43×10^{-4}	1.67×10^{-4}	2.91×10^{-4}

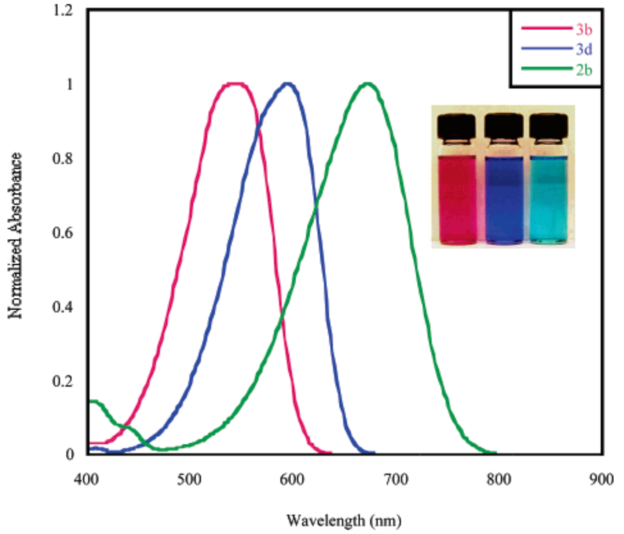

Figure 2. UV−vis spectra of chromophres **3b**, **3d**, and **2b** in dioxane. Inset: photograph of **3b** (pink), **3d** (blue), and **2b** (light green) solutions.

discussion of the properties and trends of β is limited to the β_{zzz} component.

Calculated β_{zzz} values of model chromophores show systematic improvements in the order of **3a** (131×10^{-30} esu), **3c** (176×10^{-30} esu), and **2a** (275×10^{-30} esu). The increase in β_{zzz} between **3a** and **3c** can be understood in terms of the inductive and resonance effect of the trifluoromethyl group relative to that of the methyl group, as noted earlier. A carbonyl group substitution of the methyl group, with a coplanar π system, in the acceptor can enhance the effects further in chromophore **2a**. Interestingly, the β_{zzz} value of **2a** is fully twice that of **3a**.

When increasing conjugated bridge length by adding a thienylene vinylene unit, calculated β_{zzz} values of model chromophores with FTC bridges are still higher: **5a** (320×10^{-30} esu), **5c** (405×10^{-30} esu), and **4a** (581×10^{-30} esu).

β values of chromophores were measured by hyper-Rayleigh scattering measurements at excitation wavelengths of 1.9 μm to validate theoretical predictions.[20] β values of model chromophores show systematic improvements: **3b** ($(452 \pm 5) \times 10^{-30}$ esu), **3d** ($(493 \pm 22) \times 10^{-30}$ esu), and **2b** ($(1290 \pm 179) \times 10^{-30}$ esu). The β of TCP chromophore **2b** is close to being 3 times larger than that of **3b**. Absolute magnitudes of experimentally determined β are expected to exceed those of theoretical calculations because of dispersion and resonance effects. Nevertheless, the experimentally observed trend is consistent with predictions made on the basis of calculations.

The measured β of **4d** ($(8700 \pm 702) \times 10^{-30}$ esu) is dramatically enhanced over that of **5b** ($(1362 \pm 706) \times 10^{-30}$ esu) at excitation wavelengths of 1.9 μm. The 6-fold increase is far greater than the calculated increase of β_{zzz} by a factor of 1.8 in **4a** over **5a**. We expected some resonance contribution in the measured β of **4d** at 1.9 μm, but it is clear from calculated and measured β values that the TCP chromophores with the new pyrroline acceptor show dramatic improvement in β over current chromophores based on TCF acceptors.

Macroscopic EO Properties. In the absence of intermolecular electronic interactions, macroscopic EO activity (r_{33}) of polymeric EO materials is directly proportional to β and the degree of acentric order (order parameter) of NLO chromophores induced by electric-field poling.[21] Thus, it is expected that the higher β values of TCP chromophores compared to those of TCF chromophores should translate directly into changes in electro-optic activity in polymer matrixes. One significant drawback of TCP chromophores for polymeric EO materials may be the formation of strong dipole−dipole dimers and aggregates due to the planar structure of TCP acceptor. Preliminary poling of styryl TCP

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(20) The first-hyperpolarizabilities (β) of chromophores were measured relative to $\beta_{chloroform}$ and reported with conversion. There are two values for the hyperpolarizability of chloroform in the literature. $\beta_{chlorofomr}$ of 0.49×10^{-30} was used for conversion. Comparison of β for all chromophores at a single excitation wavelength, say 1.9 μm, is not useful because of various resonance effects, resulting from the wide range of spectral windows between chromophores.

(21) We thank a reviewer for clarifying that the intermolecular electronic interactions and the poling field on individual molecules cannot be treated independently when we generate an acentric order by applying an external poling field.

chromophores showed that the introduction of several bulky substituents on the acceptor via methylene linkage to the N−H position does not prevent the formation of the electrostatic dipole−dipole dimers between chromophores, resulting in macroscopic EO activities comparable only to those of CF_3-TCF chromophores. These results suggest that even a very bulky substituent on the acceptor may be pushed away from the core of head-to-tail dimers by a simple rotation of the methylene group.

Analysis of the structural differences between TCF, CF3-TCF, and TCP suggests that rather small but effective spacer groups both above and below the conjugation plane of the TCP chromophores are necessary for an efficient electric-field-induced realignment of dipoles, especially at high loading levels. Moreover, careful studies on modes (relative orientation, distance, and degree of overlap between conjugated systems) and strength of the dipole−dipole electrostatic interactions should proceed to guide rational design of chromophores for polymeric EO materials. Recently, related studies on the dimerization of planar merocyanine chromophores have been reported.[22] The spacer groups for each modular component of chromophores should be designed to reduce the dimerization energy between dipolar NLO chromophores for efficient poling. Design and synthesis of TCP chromophores with efficient spacer groups is ongoing.

Acylation of a TCP chromophore at the acceptor end may force insufficient space between chromophores. Nevertheless, a preliminary macroscopic EO activity (r_{33}) measurement of **4c** doped in amorphous polycarbonate film using a simple reflection technique[23] shows a very respectable r_{33} of 51 pm/V at 1.55 μm with 20 wt % chromophore loading density when poled at 65 V/μm. The measurement was limited to 65 V/μm by the high sample conductivity. We are in the process of optimizing the poling conditions with other host polymers. The measurement suggests that macroscopic EO activity of the TCP chromophore with an FTC bridge is comparable to that of CF_3-TCF chromophores with the more-efficient ring-locked tetraene (CLD type)[24] conjugation bridge in guest/host systems.

Thermochemical Properties. Preliminary results have demonstrated that chromophores based on the TCP acceptor are chemically more resistant to dialkylamine nucleophiles compared to TCF and CF_3-TCF chromophores with the activated furano ring structures. In addition, the thermal properties of the chromophores have been studied using isothermal heating and DSC experiments. **2d** (5% decrease in absorbance) was thermally more stable than **3b** (20% decrease) and **3d** (52% decrease) at 170 °C in high T_g polymer matrix (PQ-100).

The large electric fields used in poling polymeric EO materials demand electrochemical stability of chromophores.[25] The redox properties of **3d**, **3b**, and **2d** were studied by cyclic voltammetry in acetonitrile. Voltammograms of **3b** and **3d** showed reversible oxidation and nonreversible reduction couples. **2d** showed a quasireversible reduction couple at reduced potential relative to TCF chromophores, in addition to the reversible oxidation couple. This suggests that the radical anion of chromophore **2d** is electrochemically more stable and easier to reduce than TCF chromophores, even though the differences are small. The half-wave potentials of all voltammograms are consistent with the electronic transition energies evaluated from absorption spectra.

Conclusions

In summary, a new class of highly efficient dipolar nonlinear optical (NLO) chromophores based on a novel pyrroline acceptor (TCP) was discovered. A very large molecular first hyperpolarizability (β) of $(8700 \pm 702) \times 10^{-30}$ esu at an excitation wavelength of 1.9 μm and a macroscopic electro-optic (EO) coefficient (r_{33}) of 51 pm/V at 1.55 μm in an amorphous polycarbonate film have been demonstrated with TCP chromophores. A general design strategy of NLO chromophores using a modified TCP acceptor is proposed.

Experimental Section

General Information. Solvents and reagents were purchased from Aldrich and purified and dried according to standard procedures.[26] Compounds **3a**,[9] **3c**,[14a,5d] **6a**,[14] and **6b**[27,5b] were prepared according to literature procedures. ^{1}H NMR spectra (300 MHz) were recorded on a Bruker AM300 NMR spectrometer at room temperature. UV−vis spectra were obtained on a Perkin−Elmer Lambda-9 spectrophotometer with a 1 cm quartz cell. ESI−MS spectra were recorded on a Bruker Daltonics Esquire ion trap mass spectrometer.

Syntheses of Chromophores 2b and 2c (Method A). To a solution of ethyl pyruvate (2.32 g, 20 mmol) in 10 mL of ethanol was added the malononitrile dimer (1.32 g, 10 mmol), and the mixture was refluxed under argon for 1 h. 4-Diethylamino benzaldehyde (1.24 g, 7 mmol) was added to the reaction mixture and refluxed further under argon for 3 h. The reaction mixture was cooled; 5 mL of the solvent was evaporated, and the precipitated products were filtered. The filtered solid was washed with 20 mL of cold dichloromethane and air-dried overnight to give a green crystalline solid (1.4 g, 58%). Mp: 280 °C (dec). ^{1}H NMR (DMSO): δ 8.38 (1H, d, $J = 15$ Hz), 7.70 (2H, d, $J = 9$ Hz), 6.94 (1H, d, $J = 15$ Hz), 6.83 (2H, d, $J = 9$ Hz), 3.53 (4H, q, $J = 7$ Hz), 1.16 (6H, t, $J = 7$ Hz). UV−vis spectra: $\lambda_{\text{max,dioxane}} = 671$ nm, $\lambda_{\text{max,toluene}} = 691$ nm, $\lambda_{\text{max,chloroform}} = 732$ nm. ESI−MS (m/z): calcd 343.1, found 344.2. Chromophore **2c** was synthesized similarly using 4-butylamino benzaldehyde. Mp: 217−220 °C. ^{1}H NMR (DMSO): δ 8.38 (1H, d, $J = 15$ Hz), 7.70 (2H, d, $J = 9$ Hz), 6.94 (1H, d, $J = 15$ Hz), 6.82 (2H, d, $J = 9$ Hz), 3.53 (4H, m), 1.55 (4H, m), 1.35 (4H, m), 0.92 (6H, t, $J = 15$ Hz). UV−vis spectra: $\lambda_{\text{max,dioxane}} = 676$ nm, $\lambda_{\text{max,toluene}} = 694$ nm, and $\lambda_{\text{max,chloroform}} = 738$ nm. ESI−MS (m/z): calcd 399.2, found 399.6.

Syntheses of TCP Chromophores 2d and 2e. To a solution of chromophore **2c** (399 mg, 1.0 mmol) in 5 mL of acetonitrile was added oven-dried potassium carbonate (410 mg, 3.0 mmol), and

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the mixture was refluxed under argon for 10 min. Diethyl sulfate (244 mg, 2.0 mmol) was added to the refluxing mixture. The reaction mixture was refluxed for one more hour. The resulting reaction mixture was cooled, and the solvent was evaporated using a rotary evaporator. The solid residue was extracted with 10 mL of dichloromethane and purified by column chromatography using the dichloromethane as eluent solvent to give 290 mg (68%) of chromophore **2d**. Mp: 185−187 °C. ^{1}H NMR ($CDCl_3$): δ 8.50 (1H, d, $J = 15$ Hz), 7.58 (2H, d, $J = 9$ Hz), 6.99 (1H, d, $J = 15$ Hz), 6.67 (2H, d, $J = 9$ Hz), 4.01 (2H, q, $J = 7$ Hz), 3.40 (4H, m), 1.60 (4H, m), 1.38 (4H, m), 1.31 (3H, t, $J = 7$ Hz), 0.97 (6H, t, $J = 8$ Hz). UV−vis spectra: $\lambda_{max,dioxane} = 680$ nm, $\lambda_{max,toluene} = 691$ nm, $\lambda_{max,chloroform} = 738$ nm. ESI−MS (*m*/*z*): calcd 427.2, found 428.5. Chromophore **2e** was prepared similarly using allyl bromide in place of diethyl sulfate to give a green solid (75%). Mp: 178−180 °C. ^{1}H NMR ($CDCl_3$): δ 8.49 (1H, d, $J = 15$ Hz), 7.59 (2H, d, $J = 9$ Hz), 7.02 (1H, d, $J = 15$ Hz), 6.69 (2H, d, $J = 9$ Hz), 5.90 (1H, m), 5.30 (1H, d, $J = 10$ Hz), 5.10 (1H, d, $J = 16$ Hz), 4.67 (2H, d, $J = 5$ Hz), 3.41 (4H, t, $J = 16$ Hz), 1.63 (4H, m), 1.35 (4H, m), 1.00 (6H, t, $J = 15$ Hz), UV−vis spectra: $\lambda_{max,dioxane} = 684$ nm, $\lambda_{max,toluene} = 697$ nm, $\lambda_{max,chloroform} = 743$ nm. ESI−MS (*m*/*z*): calcd 439.2.1, found 440.5.

Synthesis of Chromophore 4b (Method A). To a solution of ethyl pyruvate (1.16 g, 10 mmol) in 10 mL of ethanol was added the malononitrile dimer (660 mg, 5 mmol), and the mixture was refluxed under argon for 1 h. Compound **6a** (1.20 g, 3.5 mmol) was added to the reaction mixture and refluxed further under argon for 3 h. The reaction mixture was cooled; the solvent was evaporated, and the solid mixture was purified by column chromatography over silica gel using 30% ethyl acetate in hexane as eluent to give 710 mg (40%) of **4b**. Mp: 220 °C (dec). ^{1}H NMR (DMSO): δ 8.40 (1H, m), 7.70 (1H, m), 7.43 (2H, m), 7.18 (4H, m), 6.65 (2H, d, $J = 8$ Hz), 3.32 (4H, m, under water), 1.50 (4H, m), 1.32 (4H, m), 0.91 (6H, t, $J = 7$ Hz). UV−vis spectra: $\lambda_{max,dioxane} = 764$ nm, $\lambda_{max,toluene} = 807$ nm, $\lambda_{max,chloroform} = 875$ nm. ESI−MS (*m*/*z*): calcd 507.2, found 507.6.

Fluorodendronized benzoic acid[15] (1.0 g, 1.94 mmol) was added to 10 mL of dry dichloromethane, and 2 mL of thionyl chloride was added dropwise. The benzoic acid dissolved gradually. The reaction mixture was allowed to stir under nitrogen at room temperature overnight. The solvent was evaporated to give 1.04 g (∼100%) of fluorodendronized benzoyl chloride **7** (FD-Cl) as white solid.

Chromophore **4b** (100 mg, 0.20 mmol) and potassium carbonate (50 mg, 0.5 mmol) was added to 10 mL of dry acetonitrile. The mixture was heated to reflux for 10 min under nitrogen. Fluorodendronized benzoyl chloride **7** (FD-Cl; 157 mg, 0.296 mmol) was added. The reaction mixture was refluxed further for 30 min. After removal of the solvent using a rotary evaporator, the crude product was purified by flash chromatography over silica gel using 20% ethyl acetate in hexane as eluent to afford 90 mg (45%) of **4c** as black solid. ^{1}H NMR ($CDCl_3$): δ 8.45 (1H, d, $J = 15$ Hz), 7.40−6.60 (12H, m), 5.15 (4H, s), 3.31 (4H, m), 1.55 (4H, m), 1.35 (4H, m), 0.95 (6H, t, $J = 7$ Hz). UV−vis spectra: $\lambda_{max,dioxane} = 816$ nm, $\lambda_{max,toluene} = 856$ nm, $\lambda_{max,chloroform} = 942$ nm. ESI−MS (*m*/*z*): calcd 1003.2, found 1004.4.

Synthesis of TCP Acceptor 1. To a solution of ethyl pyruvate (2.32 g, 20 mmol) in 10 mL of ethanol was added the malononitrile dimer (1.32 g, 10 mmol), and the mixture was refluxed under argon for 1 h. After the evaporation of ethanol, the reaction mixture was extracted with 50 mL of dichloromethane; most of the remaining malononitrile dimer was removed by filteration, and the acceptor was purified with short column chromatography using the dichloromethane as eluent solvent. The first fraction from the column was concentrated to give 184 mg (10%) of pale yellow crystalline TCP acceptor compound. The acceptor compound self-dimerizes in warm ethanol slowly, but it is stable in the solid state at room temperature for normal storage. ^{1}H NMR ($CDCl_3$): δ 2.39 (3H, s), 8.75 (1H, s).

Synthesis of TCP Chromophore 2b (Method B). To a solution of acceptor **1** (184 mg, 1.0 mmol) in 2 mL of ethanol was added 4-diethylamino benzaldehyde (230 mg, 1.3 mmol), and the mixture was heated at 60 °C under argon for 30 min to complete the reaction. The resulting reaction mixture was cooled, filtered, washed with cool ethanol or 2-propanol, and dried to give 310 mg (90%) of pure TCP chromophore **2b**.

Synthesis of Chromophore 4b (Method B). To a solution of acceptor **1** (of 184 mg, 1.0 mmol) in 2 mL of ethanol was added compound **6a** (342 mg, 1.0 mmol), and the mixture was heated at 60 °C under argon for 30 min to complete the reaction. The resulting reaction mixture was cooled, filtered, washed with cool ethanol or 2-propanol, and dried to give 400 mg (79%) of pure TCP chromophore **4b**.

Synthesis of Chromophore 4d (Method B). To a solution of acceptor **1** (of 184 mg, 1.0 mmol) in 2 mL of ethanol was added compound **6b** (546 mg, 1.0 mmol), and the mixture was heated at 60 °C under argon for 30 min to complete the reaction. The resulting reaction mixture is cooled, filtered, washed with cool ethanol or 2-propanol, and dried to give 519 mg (73%) of pure TCP chromophore **4d**. Mp: 266−270 °C. ^{1}H NMR (DMSO): δ 8.49 (1H, m), 7.76 (1H, m), 7.44 (2H, m), 7.24 (4H, m), 6.74 (2H, m), 3.74 (4H, t, $J = 5$ Hz), 3.55 (4H, t, $J = 5$ Hz), 0.82 (18H, s), 0.01 (12H, s). UV−vis spectra: $\lambda_{max,dioxane} = 758$ nm, $\lambda_{max,chloroform} = 849$ nm. ESI−MS (*m*/*z*): calcd 711.3, found 712.1.

Isothermal Heating of 3b, 3d, and 2d. Polymer composites in a host/guest system were prepared by doping 10 wt % chromophore **3d**, **3d**, and **2d** into a commercial polymer (PQ-100). Spin-coated films on glass substrate were heated at 170 °C for 20 min under a nitrogen atmosphere. Decreases in the absorbance of $\pi-\pi^*$ charge-transfer bands were used to monitor and compare the degradation/sublimation of the chromophores in the polymer matrix.

Hyper-Rayleigh Scattering Measurements. The 1907 nm excitation was achieved by equipping a 30 Hz Q-switched Nd:YAG laser (Spectra-Physics Quanta Ray GCR-170) with an H_2−Raman cell (∼15 ATM). The first Stokes line derived from the fundamental of the Nd:YAG laser provided ∼150 mW average power. A 300 mm plano-convex lens was used to focus the 1907 nm light into the middle of the flow cell. The scattered light, passing through a 950 nm interference filter (40 nm full width at half-maximum), was imaged onto the slits of a 0.75 m spectrograph (Acton) and detected by the same CCD camera described above. Data acquisition times ranged from 300 to 360 s.

Samples were prepared in chloroform (Fisher ACS Spectranalyzed) solution. The solutions were flowed continuously through the flow cell and an in-line 0.2 μm PTFE filter to minimize photodestruction and eliminate particulate manner. Observation of the HRS signal intensity over successive measurements made it possible to monitor the onset of bulk photodestruction. No measurable photodestruction was observed for these samples. Solution concentrations were chosen on the basis of extinction coefficients to minimize attenuation of signal intensity by self-absorption of the scattered light by the chromophores. For the 1907 nm wavelength measurements of **4d**, optical transmission was ∼93% at the second harmonic. HRS signal intensity at lower concentrations was insufficient for analysis. Self-absorption is accounted for in the reported error. For all other chromophores at both wavelengths, no affects of self-absorption were observed at the concentrations employed.

The signal intensity scaled quadratically with incident power, consistent with HRS. However, two-photon fluorescence is also expected to increase quadratically with power. Spectral resolution of the scattered light allowed HRS to be distinguished from luminescence through comparison of the line widths of the respective contributions.[28] The narrower line width of the HRS signal was consistent with the bandwidth of the incident field. Additionally, the signal tracked with shifts in excitation wavelength.

Data analysis in the MATLAB environment entailed fitting the broader band of the luminescence to a polynomial function, subtracting it, and fitting the HRS peaks to a Gaussian functional form. For the 1300 nm experiments, each spectrum was compared to a corresponding reference spectrum of neat $CHCl_3$. HRS intensity was converted to β for each spectrum via the internal reference method through the following equation, where I = signal intensity and N = number density

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

At 1907 nm, β values were obtained through external reference to the benchmark chromophore **5b**. As the signal contribution of the neat solvent was insignificant at this wavelength, the following equation was used to ascertain β relative to **5b** (EZ-FTC)

$$\frac{I_{\text{sample}}}{I_{\text{EZ-FTC}}} = \frac{N_{\text{sample}}\langle\beta_{\text{sample}}{}^2\rangle}{N_{\text{EZ-FTC}}\langle\beta_{\text{EZ-FTC}}{}^2\rangle}$$

Film Preparation and Electro-Optic (EO) Measurements. EO measurements were performed in amorphous polycarbonate (Aldrich) doped with chromophore **4c**. The cyclopentanone solution of APC with 20 wt % **4c** was filtered through a 0.2 μm PTFE syringe filter and spin-coated onto half-etched ITO glass substrates at a spread of 500 rpm and spin rate of 1000 rpm. The resulting film showed good optical quality with a thickness of 1.5 μm. The film was soft baked under a vacuum at 85 °C for 12 h to ensure the removal of the residual solvent. A thin layer of gold was sputtered onto the film as the top electrode to perform the electric-field poling. The film was contact-poled at 110 °C for 10 min with a DC electric field of 65 V/μm under a nitrogen atmosphere. The EO coefficient (r_{33}) value was measured using the simple reflection technique at 1.5 μm.

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Supporting Information Available: Experimental details of the X-ray structure determination of chromophore **2d** and crystallographic files in CIF format with the coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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(28) As a reviewer suggested, luminescence is a common issue with HRS measurements. But interference from the luminescence of TCP chromophores is not a complication in these measurements. Because we use a spectrograph to disperse the radiation coming from the sample, we can discern the multiphoton-excited fluorescence background from the HRS signal through analysis of the line width. In these experiments, the HRS intensity was sufficiently intense relative to the luminescence background that it could be readily identified and measured.