Twisted π-Electron System Electrooptic Chromophores. Structural and Electronic Consequences of Relaxing Twist-Inducing Nonbonded Repulsions†

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The synthesis, structural and spectroscopic characterization, and nonlinear optical response properties of a “slightly” twisted zwitterionic 4-quinopyran electrooptic chromophore FMC, 2-{4-[1-(2-propylethyl)-1H-pyridine-4-ylidene]cyclohexa-2,5-dienylidene}malononitrile, are reported. X-ray diffraction data and density functional theory (DFT) minimized geometries confirm that deformation of the four o-, o′-, o″-, and o‴-methyl groups in the parent chromophore TMC-2, 2-{4-[3,5-dimethyl-1-(2-propylethyl)-1H-pyridin-4-ylidene]-3,5-dimethylcyclohexa-2,5-dienylidene}malononitrile, relaxes the arene—arene twist angle from 89.6 to 9.0°. These geometrical changes result in a significantly increased contribution of the quinoidal structure to the molecular ground state of FMC (versus TMC-2), reduced solvatochromic shifts in the optical spectra, and a diminished electric-field-induced second-harmonic (EFISH) generation derived molecular hyperpolarizability (∂β = −2340 × 10⁻⁴⁸ esu of DFMC, the dendrimer derivative of FMC, vs −24000 × 10⁻⁴⁸ esu of TMC-2) in CH₂Cl₂ at 1907 nm. Pulsed field gradient spin–echo (PGSE) NMR spectroscopy and EFISH indicate that the levels of FMC aggregation in solution are comparable to those of TMC-2 (monomers and dimers) in CH₂Cl₂ solution. B3LYP and INDO/S computation of chromophore molecular structure, aggregation, and hyperpolarizability trends are in good agreement with experiment.

Introduction

Substitution of organic electrooptic (EO) materials for their inorganic counterparts (e.g., LiNbO₃) offers great promise in devices for generating, processing, transmitting, detecting, and storing light signals.¹ Further enhancements of molecule-based EO material properties are expected to greatly facilitate advances in technologies such as optical telecommunications, optical data storage, image reconstruction, and optical computing.¹ Given that molecular/multimolecular chromophores are the active components in organic EO materials, the quest for EO devices with greater bandwidths and lower working voltages will require chromophores having very large molecular hyperpolarizabilities (β), thermal stability, and stable macroscopic noncentrosymmetric alignment. These efforts have constituted a very active research front worldwide for 2 decades.¹

When designing chromophores with the aforementioned properties, the conventional approach has been to utilize strong terminal electron donor and acceptor substituents, and a planar intervening conjugated π-network.² To date, theoretical calculations based on the standard “two-level model” have proven qualitatively successful in predicting β as a function of chromophore geometry and substitution.² Here β is determined by three important terms: the difference in dipole moment between the ground and first charge-separated excited electronic state (∆μ̅ = μ̅e − μ̅g), the transition dipole matrix element connecting these states (μ̅ge), and an energy gap (∆E̅ge) term between these states (eq 1). Taking all of these variables into account, β should, a priori, be tunable via appropriate structural manipulations.

\[
\beta \propto \Delta \mu_{ge} \mu_{ge}^2 / (\Delta E_{ge})^2
\]  

(1)

Currently, several proven molecular design strategies are accepted for enhancing molecular hyperpolarizability.⁴ Most commonly employed are those based on extending the π conjugation of planar chromophores, such as “bond length alternation” (BLA)³ and “auxiliary donors and acceptors.”⁶ Here, as a result of structural tuning, the hyperpolarizability is enhanced primarily, but not exclusively, by decreasing the energy gap ∆Ege in eq 1. However, large-response chromophores based on extended planar frameworks typically have elaborated molecular structures, creating multistep synthetic challenges, while incurring potential chemical, thermal, and photochemical instabilities. Another drawback of extending planar π conjugated systems is the bathochromic shifts in optical absorption accompanying such π-system extensions. This tendency decreases transparency in the near-IR region where most working wavelengths for photonic devices are found. Other β enhancement strategies for planar chromophores include multidimensional chromophores and zwitterionic chromophores, which have been shown to provide enhanced near-IR transparency, while to some degree sacrificing optimum hyperpolarizability.⁷

It has been argued that all known organic NLO chromophores exhibit only a small fraction (ca. 10⁻³²) of their potential
maximum hyperpolarizability, leaving considerable room for developing very large \( \beta \) chromophores not accessible by traditional planar \( \pi \)-system approaches. Computational analysis suggested several years ago that chromophores having unconventional twisted \( \pi \)-systems with charge-separated ground-state structures might exhibit very large first-order hyperpolarizabilities. Since this original proposal, considerable synthetic, spectroscopic, and theoretical attention has been devoted not only to maximizing the molecular response but also to understanding twisted intramolecular charge-transfer (TICT) chromophores from a mechanistic standpoint. As an example, chemically and thermally robust chromophores possessing twisted structures, such as chromophore TMC-3 (Chart 1), were synthesized, fully characterized, and shown to exhibit ultralarge hyperpolarizabilities, with \( \mu\beta \) as large as \(-488,000 \times 10^{-48} \) esu at 1907 nm. The TMC-3 figure of merit (\( \mu\beta/M_\text{w} \)) is as large as \( 945 \times 10^{-48} \) esu, about 20 times larger than the highest previously reported (46 \( \mu\beta/M_\text{w} \)).

In the detailed structural, spectroscopic, and theoretical studies on first-generation TICT chromophores, it was found that the twisted zwitterionic chromophores have little or no \( D=\pi-A \) conjugation, thus resulting in charge-localized ground states. The ultralarge hyperpolarizabilities are proposed to arise principally from large dipole moment changes from the molecular zwitterionic ground state to the first excited state, large transition dipole matrix elements, and small ground- to excited-state energetic separations, the latter decreasing markedly in moderately polar solvents such as CH2Cl2. In the past, one powerful means to fully understand NLO mechanisms has been to study the relationship between the experimental response and details of the chromophore molecular geometry. At this point, however, our understanding of the twisted \( \pi \)-system chromophores has been largely based on experimental results for sterically crowded, \( o-, o', o''-, \) and \( o'''\)-methyl substituted chromophores such as TMC-2 and TMC-3 (Chart 1) where the twist angle is varied over only a small range near 85°. These structures do not provide sufficient data to fully understand the distinctive properties of the ultralarge response molecules, nor test theoretical calculations. Here, in an effort to better understand TICT chromophore structural effects, we report a new chromophore series (FMC, DFMC; Chart 1) that is structurally similar to TMC-2, but designed without \( o-, o', o''-, \) and \( o'''\)-methyl substituents, to relax the nonbonded repulsions which impose the large interring twist angle. We report here the synthesis and characterization by X-ray diffraction, solution-phase DC electric-field-induced second-harmonic generation (EFISH), and pulsed field gradient spin–echo (PGSE) NMR spectroscopy of “untwisted” chromophores FMC and DFMC. These physicochemical results are used in combination with computational analysis to understand chromophore molecular structure, solution-phase aggregation effects, and electrooptic response. It will be seen that such chromophores, with small interring twist angles, have significantly diminished \( \mu\beta \) response for reasons that are understandable using quantum chemical models.

### Experimental Section

#### Materials and Methods

All reagents were purchased from Aldrich Chemical Co. and used as received unless otherwise indicated. Tetrahydrofuran (THF) was distilled from sodium/ benzophenone and methylene chloride from CaH2. Toluene was dried by passing through two packed columns of activated alumina and Q2 under N2 pressure and regularly tested with benzophenone ketyl in ether solution. The reagent 2-propyl-1-heptanol was purchased from Narchem Co. Solution NMR spectra were recorded on a Varian P-INOVA 500 MHz spectrometer except for PGSE measurements (see below). Elemental analyses were performed by Midwest Microlabs.

(a) Synthesis of 4-(p-Bromophenyl)pyridine (1). To a solution of 1-bromo-4-iodobenzene (1.69 g, 6.00 mmol) in 50 mL of toluene was added the mixture of 4-pyridineboronic acid (0.615 g, 5.00 mmol) in 15 mL of ethanol, followed by the addition of a solution of Na2CO3 (1.59 g, 15.0 mmol) in 5 mL of water. This solution was degassed using N2 for 10 min, and then tetrakis(triphenylphosphine)palladium(0) (0.289 g, 0.25mmol) was added. The resulting reaction mixture was stirred at 110 °C under N2 overnight. The solvent was then removed using rotary evaporation, and the residue was dissolved in methylene chloride and washed with brine and water. The organic layer was next dried over magnesium sulfate, filtered, concentrated, and purified by silica gel flash column chromatography with an eluent of ethyl acetate:methylene chloride = 1:4 (v/v) to afford 0.957 g of title compound (41.1 mmol, 82% yield) of the title compound as a light yellow solid. 1H NMR (CDCl3): δ 8.67 (d, \( J = 6.0 \) Hz, 2 H), 7.62 (d, \( J = 8.0 \) Hz, 2 H), 7.51 (d, \( J = 8.0 \) Hz, 4 H), 7.47 (d, \( J = 6.0 \) Hz, 2H).

(b) Synthesis of 2-(4-Pyridin-4-ylphenyl)malononitrile, Sodium Salt (2). To an ice-cooled suspension of NaH (60% mineral oil, 6.72 g, 168 mmol) in anhydrous dimethoxyethane (240 mL) in a three-necked flask under N2 was added dropwise via syringe, a solution of malononitrile (5.55 g, 84.0 mmol) in anhydrous dimethoxyethane (60 mL). The mixture was stirred for 1 h at room temperature under N2. Then, I (8.82 g, 37.8 mmol) and tetrakis(triphenylphosphine)palladium(0) (4.35 g, 3.76 mmol) were added to the resulting mixture under an N2 flow. The mixture was then stirred at 85 °C overnight. The solvent was then removed under reduced pressure. The resulting solid was washed with benzene and dried under vacuum, and then was purified via recrystallization from water to afford the title compound as an orange solid (3.40 g, 38% yield). 1H NMR (dimethyl sulfoxide-d6 (DMSO-d6)): δ 8.47 (d, \( J = 6.1 \) Hz, 2 H), 7.57 (d, \( J = 6.5 \) Hz, 2 H), 7.54 (d, \( J = 8.4 \) Hz, 4 H), 6.83 (d, \( J = 7.8 \) Hz, 2H).
(c) **General Procedure for Synthesis of 2-4-(1-alkyl-1H-pyridine-4-ylidene)cyclohexa-2,5-dienylidene]malononitrile.** To a solution of **2** (2.74 g, 11.4 mmol) in 60 mL of anhydrous acetone was added a solution of appropriate alkyl triflate (12.5 mmol) in 60 mL of acetone. The color of the mixture changed from yellow to deep purple immediately. After stirring in the dark at room temperature overnight, the solvent was removed under reduced pressure. The resulting solid was dissolved in methylene chloride and washed with brine and water. The organic layer was then dried over magnesium sulfate, filtered, concentrated, and purified by silica gel flash column chromatography with a gradient eluent of 2–4% (v/v) of methanol in methylene chloride to afford the various title compounds.

(d) **Synthesis of 2-4-[1-(2-propylheptyl)-1H-pyridine-4-ylidene]cyclohexa-2,5-dienylidene]malononitrile (3).** Compound 3 was obtained as a purple solid (53% yield). 1H NMR (CDCl3): δ 7.98 (d, J = 6.8 Hz, 2 H), 7.52 (d, J = 7.0 Hz, 2 H), 7.20 (d, J = 8.8 Hz, 4 H), 6.71 (d, J = 8.8 Hz, 2H), 4.27 (d, J = 7.9 Hz, 2H), 1.93 (m, 1H), 1.2–1.4 (m, 12H), 0.90 (m, 6H). MS (high resolution, EI): m/z 360.2441 [M+H]+; calcd, 360.2439. Anal. Calcd for C24H29N3: C, 80.18; H, 8.13; N, 11.7.

(e) **Synthesis of 2-[4-([2,3,5-Bis(2-ethylhexyloxy)phenyl]ethyl)-1H-pyridine-4-ylidene]cyclohexa-2,5-dienylidene]malononitrile (4).** Compound 4 was obtained as a brown-red solid (60% yield). 1H NMR (CDCl3): δ 7.77 (d, J = 8.1 Hz, 2 H), 7.40 (d, J = 7.7 Hz, 2 H), 7.13 (d, J = 8.8 Hz, 4 H), 6.66 (d, J = 8.8 Hz, 2H), 6.34 (t, J = 1.8 Hz, 1H), 6.11 (d, J = 1.8 Hz, 2H), 4.59 (t, J = 6.9 Hz, 2H), 3.71 (m, 4H), 3.11 (t, J = 6.1 Hz, 2H), 1.64 (m, 2 H), 1.5–1.2 (m, 16 H), 0.88 (m, 12 H). MS (high resolution, EI): m/z 580.3894 [M+H]+; calcd, 580.3903. Anal. Calcd for C35H43N3O2: C, 78.90; H, 8.16; N, 11.69. Found: C, 79.80; H, 7.91; N, 11.47.

(f) **Synthesis of Methyl 2-(3,5-Bis(2-ethylhexyloxy)phenyl)acetate (5).** A mixture of methyl 2-(3,5-dihydroxyphenyl)acetate (911 mg, 5.00 mmol), 2-ethylhexyl bromide (2.10 mL, 11.7 mmol), anhydrous K2CO3 (2.00 g, 14.55 mmol), and 18-crown-6 (300 mg, 1.13 mmol) in acetone (20 mL) was refluxed for 3 days. Acetone was then removed using rotary evaporation, and the residue was extracted with hexanes and washed with water. The organic layer was dried over anhydrous magnesium sulfate, filtered, evaporated, and purified by silica gel flash column chromatography with an eluent of hexanes:dichloromethane = 3:1 (v/v) to afford 1.83 g (90% yield) of colorless viscous oil, 5. 1H NMR (CDCl3): δ 6.41 (s, 2 H), 6.37 (s, 1 H), 3.80 (d, J = 4.4 Hz, 4 H), 3.70 (s, 3 H), 3.54 (s, 2 H), 1.69 (m, 2 H), 1.2–1.6 (m, 16 H), 0.92 (t, J = 6.4 Hz, 12 H).

(g) **Synthesis of 2-(3,5-Bis(2-ethylhexyloxy)phenyl)ethanol (6).** To a suspension of LiAlH4 (270 mg, 7.11 mmol) in anhydrous THF (10 mL) was added dropwise a solution of methyl 2-(3,5-bis(2-ethylhexyloxy)phenyl)acetate (1.92 g, 4.73 mmol) in anhydrous THF (5 mL) at room temperature. The resulting reaction mixture was stirred for another 1.5 h and then carefully quenched with ethyl acetate, followed by water. Dilute HCl(aq) was added to dissolve the aluminum salts, and the product was extracted with ethyl acetate and washed with water. The organic layer was dried over anhydrous magnesium sulfate, filtered, evaporated, and purified by silica gel flash column chromatography with an eluent of methylene chloride to afford 1.78 g (99%) of colorless viscous oil, 6. 1H NMR (CDCl3): δ 6.36 (s, 2 H), 6.35 (s, 1 H), 3.86 (t, J = 6.4 Hz, 2 H), 3.81 (d, J = 5.2 Hz, 4 H), 2.80 (t, J = 6.8 Hz, 2 H), 1.70 (m, 2 H), 1.2–1.6 (m, 16 H), 0.92 (t, J = 6.4 Hz, 12 H).

(h) **Synthesis of 3,5-Bis(2-ethylhexyloxy)phenethyl trifluromethanesulfonate (7).** To a solution of **6** (1.40 g, 3.70 mmol) in anhydrous methylene chloride (30 mL) was added dropwise triflic anhydride (0.820 mL, 4.87 mmol) in anhydrous methylene chloride (7 mL) at room temperature. The solution was stirred for another 2 h and poured into crushed ice. The mixture was then neutralized with saturated aqueous NaHCO3 solution. The product was next extracted with ethyl acetate and washed with water. The organic layer was dried over anhydrous magnesium sulfate, filtered, evaporated, and purified by silica gel flash column chromatography with an eluent of dichloromethane to afford 1.80 g (96% yield) of light brown viscous oil, 7. 1H NMR (CDCl3): δ 6.38 (s, 1 H), 6.33 (s, 2 H), 4.68 (t, J = 7.0 Hz, 2 H), 3.80 (m, 4 H), 3.05 (t, J = 7.0 Hz, 2 H), 1.70 (m, 2 H), 1.2–1.6 (m, 16 H), 0.92 (m, 12 H).

**Optical Spectroscopy.** Optical spectra were recorded on a Cary 5000 spectrophotometer. Dilute solutions (10–5 M) of chromophores in various solvents were prepared to study solvent effects on chromophore optical absorption. Variable-concentration measurements at higher concentrations for intermolecular aggregation studies were not feasible due to the strong extinction coefficients.

**Single-Crystal X-ray Diffraction.** Single crystals of FMC were obtained via slow vapor diffusion. A small vial containing a solution of FMC in methylene chloride was placed in a closed chamber, into which diethyl ether was added. The small vial was sealed with a plastic cap having a small hole to allow the slow diffusion of diethyl ether vapor from the chamber into the vial for single-crystal growth. All diffraction measurements were carried out on a Bruker SMART CCD diffractometer with graphite-monochromated Mo Kα (0.71073 Å) radiation. Data were collected using the Bruker SMART software, processed using the SAINT-NT package from Bruker, and corrected for Lorentz and polarization effects. The structure was solved using direct methods (SHELXTL-90) and expanded using Fourier techniques (SHELXTL-97). The non-hydrogen atoms were refined anisotropically, with the exception of several disordered 2-propylheptyl carbon atoms which were refined with group anisotropic displacement parameters. Hydrogen atoms were included in idealized positions but not refined. All calculations were performed using the Bruker SHELXTL9 crystallographic software package. Crystallographic parameters are summarized in Tables S1–S5 of the Supporting Information.

**Pulsed Field Gradient Spin–Echo NMR Spectroscopy.** Intermolecular aggregation was quantitatively analyzed using PGSE NMR spectroscopy. 1H PGSE NMR measurements were performed at 295.7 K without spinning by using the standard stimulated echo pulse sequence18 on a Bruker AVANCE DRX 400 spectrometer equipped with a GREAT 1/10 gradient unit and a QNP probe with a Z-gradient coil. The shape of the gradients was rectangular, their duration (δ) was 4 ms, and their strength (G) was varied during the experiments. All spectra were acquired using 32K points and a spectral width of 5000 Hz and were processed with a line broadening of 1.0 Hz. Different values of “nt” (number of transients) and numbers of different gradient strengths (G) were used for different samples, depending on solution viscosity and solute concentration. The dependence of the resonance intensity (I) on a constant diffusion time and on a varied G is described by eq 2:

$$\ln I = -(\gamma \delta^2 D (\Delta - \delta^2 / 3)) G^2$$  (2)

where I = intensity of the observed spin–echo, I0 = intensity of the spin–echo without gradients, D = diffusion coefficient, $\Delta$ = delay between the midpoints of the gradients, and $\delta$ =
length of the gradient pulse, and \( \gamma = \text{magnetogyric ratio}. \) The semilogarithmic plots of \( \ln(\|I_0\|) vs G^2 \) were fitted using the standard linear regression algorithm implemented in the Origin 7 software package; the \( R \) factor was always greater than 0.99. For pure solvents, the diffusion coefficient \( D_s \), which is directly proportional to the slope of the regression line obtained by plotting \( \log(\|I_0\|) vs G^2 \) was estimated by measuring the proportionality constant using an HDO sample (0.04%) in \( D_2O \) (known diffusion coefficient in the range of 274–318 K) \(^1\) under the exact same conditions as the sample of interest \( [D_4(\text{CD}_2\text{Cl}_2) = 33.2 \times 10^{-10} \text{m}^2 \text{s}^{-1}, D_d(\text{DMSO-}d_6) = 6.5 \times 10^{-10} \text{m}^2 \text{s}^{-1}] \). Solvents were used as internal standards to account for possible changes in solution viscosity, \(^1\) temperature, and gradient strength. \(^1\) The experimental error in \( D_0 \) was estimated to be 3% for all solutions except those with concentration values smaller than \( 10^{-3} \) M. In such cases, the error can approach 5–8%.

**EFISH Measurements.** Measurements of \( \mu \beta \), the products of the chromophore dipole moment (\( \mu \)) and the projection of \( \beta_{\text{VEC}} \), the vector part of the molecular first-order hyperpolarizability \( \beta \) tensor along the direction of \( \mu \), were performed by the solution-phase DC EFISH generation method. EFISH measurements were carried out in \( \text{CH}_2\text{Cl}_2 \) solutions at a nonresonant fundamental wavelength of 1907 nm using a Q-switched, mode-locked Nd\(^{3+}\)-YAG laser [pulse durations of 15 ns (90 ns) at a 10 Hz repetition rate]. The 1064 nm initial wavelength was shifted to 1907 nm by a Raman shifter with a high-pressure \( \text{H}_2 \) cell. \(^1\) The \( \text{CH}_2\text{Cl}_2 \) was freshly distilled from \( \text{P}_2\text{O}_5 \). The organic base 1,4-diazabicyclo[2.2.2]octane (DABCO; molar ratio DABCO/\text{chromophore} = 0.5:1.0) was added to the solutions to increase chromophore stability.

**Computational Methodology.** (a) **Gas-Phase Electronic Structure.** Three model monomers were used for addressing response-dependent relationships associated with stericly induced modification of the twist angle: \( \text{FMC, HMC, and TMC} \) (Chart 2A). Geometries were obtained at the B3LYP level \(^{16,17} \) in \( \text{Jaguar}^{18} \ v5.00.22 \) using the Maestro Molecular Modeling Interface c5.10.20 and a 6-31G** basis set. In several previous studies of TICT chromophores, this methodology has yielded results in good agreement with experimental data. \(^9,10\) (b) **Gas-Phase Dimerization Analysis.** The quinopyran chromophores \( \text{FMC, HMC, and TMC-2} \) were examined for intermolecular aggregation as density functional theory (DFT)-minimized centrosymmetric eclipsed dimers using the Spartan\(^1\) software package (Chart 2B). Starting with centrosymmetric model structures for \( \text{FMC, HMC, and TMC-2} \), each chromophore pair was separated in a stepwise fashion, starting from the DFT-minimized pair geometry. By adjusting the center-to-center interplanar distance in one direction, single-point energies were computed in finite intervals along the \( z \)-axis, as shown in Chart 2B, at the restricted Hartree–Fock level with a 3-21G* basis set within Spartan. To simplify the calculation further, we assumed that upon increase in interplanar separation, no further molecular structural changes occur. From this analysis we obtained dimer distance-dependent energies (\( E_D \); Figure 7). Using both \( E_D \) and monomer energies (\( E_M \)), the \( \Delta E_D \) was calculated by via eq 3.

\[
\Delta E_D = E_D - 2(E_M)
\]

The difference in the energy associated with the FMC and TMC-2 dimer pairs is then given by eq 4.

\[
\Delta E_{D_{\text{diff}}} = \Delta E_{D_{\text{FMC}}} - \Delta E_{D_{\text{TMC-2}}}
\]

(c) **Solution-Phase Calculations.** To provide a more accurate estimate of solvent effects on monomer and dimer energetics, initial DFT structures were used in single-point RHF continuum-solvation calculations by solving the Poisson–Boltzmann (PB) equation numerically within the Jaguar\(^1\) package (Figure 7).\(^10\) This involves the numerical solution of the PB equation to determine the self-consistent reaction field (SCRF) of the solvent acting on the quantum mechanical solute. In this approach, the solute is either monomeric FMC or TMC-2 or their corresponding dimers immersed in a continuum solvent characterized by four properties: the solvent probe radius \( r_{\text{probe}} = 2.33 \) for \( \text{CH}_3\text{Cl}_2 \), the solvent dielectric constant \( (\varepsilon_{\text{solvent}} = 9.08) \), the solvent molecular weight \( (\text{MW} = 84.93) \), and the solvent density \( (\rho = 1.326) \). \( \text{CH}_3\text{Cl}_2 \) was chosen since it was used extensively in the PGSE and EFISH experiments. PB RHF single-point solvation energies \( (E_{\text{sol}}) \) were then computed for the monomers \( (E_{\text{sol}}^M) \) and dimers \( (E_{\text{sol}}^D) \) of each molecule. This computation gives the dimer pair solvation energy correction term \( (\Delta E_{\text{corr}}) \) as in eq 5.

\[
\Delta E_{\text{corr}} = E_D^D - 2(E_M^D)
\]

With the effect of solvation and/or dimerization \( (\Delta E_{\text{corr}}) \) for each molecule calculated, these values were then used to correct for solvation in the gas-phase evaluations of the equilibrium structure dimers (those having the shortest interplanar separation) to give total environmental stabilization energies versus the nonsolvated monomers \( (\Delta E_{\text{sol}}) \). These were determined from the expression in eq 6.

\[
\Delta E_{\text{sol}} = \Delta E_D + \Delta E_{\text{corr}}
\]

(d) **Semiempirical INDO/S\(^2\) CI Calculations.** Semiempirical calculations employing the INDO/S\(^2\) model developed by Zerner and co-workers were also performed using the CND0\(^2\) program. INDO/S at the monoeexcited CI level provided the linear spectral properties and excitations necessary for the hyperpolarizability calculations. To better understand solvent-dependent response changes associated with \( \text{CH}_3\text{Cl}_2 \) (used in the EFISH and PGSE experiments), additional calculations were implemented in which a simple dipolar field \( (\text{electric constant} = 9.08) \), the solvent molecular weight \( (\text{MW} = 84.93) \), and the solvent density \( (\rho = 1.326) \). \( \text{CH}_3\text{Cl}_2 \) was chosen since it was used extensively in the PGSE and EFISH experiments. PB RHF single-point solvation energies \( (E_{\text{sol}}) \) were then computed for the monomers \( (E_{\text{sol}}^M) \) and dimers \( (E_{\text{sol}}^D) \) of each molecule. This computation gives the dimer pair solvation energy correction term \( (\Delta E_{\text{corr}}) \) as in eq 5.

\[
\Delta E_{\text{corr}} = E_D^D - 2(E_M^D)
\]

With the effect of solvation and/or dimerization \( (\Delta E_{\text{corr}}) \) for each molecule calculated, these values were then used to correct for solvation in the gas-phase evaluations of the equilibrium structure dimers (those having the shortest interplanar separation) to give total environmental stabilization energies versus the nonsolvated monomers \( (\Delta E_{\text{sol}}) \). These were determined from the expression in eq 6.

\[
\Delta E_{\text{sol}} = \Delta E_D + \Delta E_{\text{corr}}
\]
dependence of the molecular induced dipole moment ($\mu_i$) on the applied electric field $F$ experienced by the molecule (eq 7).

$$\mu_i = \mu_i^{(0)} + \sum_i \alpha_i F_i + \frac{1}{2} \sum_{jk} \beta_{jk} F_j F_k$$

(7)

Here $\mu_i^{(0)}$ is the permanent dipole moment of the molecule in direction $i$, $F_i$ is the component of the electromagnetic field in direction $i$, and $\alpha$ and $\beta$ are the static (zero frequency, $\omega = 0.0$ eV) first- and second-order polarizability tensors. We concentrate here on $\beta$. To avoid issues of resonance enhancement, we report only the limiting zero frequency or “static” case ($\omega = 0.0$ eV).

We are interested in the $\beta_{\mu i}$ component of the $\beta$ tensor (eq 8):

$$\beta_{\mu i} = \sum_{jk=x,y,z} \beta_{jk} F_j F_k$$

(8)

As has been discussed elsewhere, the use of simple INDO/S SOS is not extremely accurate for calculating the response properties of TICT chromophores. We use it here only to support and interpret trends in the nonlinear response.

**Results**

In the following discussion, we present physicochemical data combined with theoretical calculations aimed at analyzing and understanding the effects of reduced interring twist angle on zwitterionic TICT chromophore EO response. We begin with a discussion of synthetic strategies for FMC/DFMC chromophore preparation and then focus on solution and solid-state structural characterization, including comparison with the TICT structure of TMC-2. We then discuss solution optical spectra and solvatochromism as revealed by the solvent dependence of the spectra. Chromophore aggregation is then assayed by PGSE NMR spectroscopy and compared to that in TMC-2. Next, EFISH spectroscopy in solution is employed to quantify FMC/DFMC chromophore hyperpolarizability and to compare it with the $\alpha\alpha\alpha\alpha$-tetramethyl-TICT chromophore response. Finally, a computational analysis of interring twist angle effects on hyperpolarizability and chromophore aggregation is carried out, and the results are compared with experiment.

**Chromophore Synthetic Approaches.** The straightforward synthetic pathways to reduced twist angle chromophore FMC and its dendron derivative DFMC (for greater solubility) are summarized in Schemes 1 and 2, respectively. Building block 1 is synthesized via Suzuki coupling of commercially available 4-pyridineboronic acid and 1-bromo-4-iodobenzene in high yield (82%). Pd-catalyzed coupling of 1 with sodium dicyanomethanide then affords sodium salt 2 in acceptable yield (38%). This intermediate is then regioselectively N-alkylated with the appropriate alkyl triflates to afford chromophores FMC and DFMC. The synthesis of the dendrimeric alkyl triflate substituent for DFMC (Scheme 2) begins with commercially available methyl 3,5-dihydroxyphenylacette, which undergoes 18-crown-6-catalyzed alkylation with 1-bromo-2-ethylhexane to afford dialkoxy compound 5, in high yield (90%). Near-quantitative reduction of 5 using LiAlH4 gives alcohol 6, which is then treated with triflic anhydride to afford dendrimenial trifluoro triflate 7 in very high yield (96%).

Chromophores FMC and DFMC are characterized by high-resolution mass spectroscopy, elemental analysis, 1H NMR spectroscopy, and, in the case of FMC, single-crystal X-ray diffraction. Details are compiled in the Experimental Section.

**Solid-State Structure of Chromophore FMC.** Chromophore FMC is found to belong to crystallographic space group P1. Disorder in the 2-propylheptyl substituent prevents optimum structural refinement; however, the metrical parameters were obtained with sufficient accuracy to discern important bond distance and angle trends, which are summarized in Table 1. Metrical data for TMC-2 are also presented here for comparison. The molecular structure of FMC is shown in Figure 1.

Compared to the diffraction-derived arene dihedral twist angle in TMC-2 of 89.6°, FMC exhibits a much smaller twist angle of 9.0°. In addition, the (ring)C−C(ring) distance in FMC (C9−C10 = 1.449(6) Å) is also significantly shorter than in TMC-2 (1.488(5) Å), as is the (ring)C−C(CN2) distance. Furthermore, the internal arene distances C11−C13 = 1.346(6) Å, C12−C14 = 1.360(6) Å, C5−C7 = 1.364(6) Å, and C6−C8 = 1.360(6) Å appear to be significantly shorter than the corresponding distances in TMC-2 of 1.369(5), 1.373(5), 1.390(5), and 1.390(5) Å, respectively.

These differences between the crystal structures of FMC and TMC-2 are doubtless an indication of the change in electronic structures of these TICT chromophores with sterically induced changes in ring–ring twist angle. The relative contributions of two possible resonance hybrids, zwitterionic and quinoidal, to the TICT chromophore ground states explain the observed
The changes in molecular structure are expected to lead to changes in relative fractions of the contributions from the two contributing resonance structures and, concomitantly, to changes in electronic structure. In TMC-2, nonbonded repulsions among the \( \sigma^- \), \( \sigma'^- \), \( \sigma''^- \), and \( \sigma'''^- \)-methyl substituents forces a nearly perpendicular arene—arene twist angle. The result is pronounced reduction in interring conjugation, reduced intramolecular charge transfer, and a dominant ground-state zwitterionic structure. However, in FMC, with minimal \( \sigma^- \), \( \sigma'^- \), and \( \sigma'''^- \) nonbonded repulsions, intramolecular charge transfer is greatly enhanced due to molecular near-planarity and effective interring conjugation. Thus, the contribution from the quinoidal structure is increased in the ground state, as assessed by the greater double bond character in the (ring)C–C(ring), (ring)C–C(CN)\(_2\), and other intraring C–C bond distances. This result is in good accord with other data (see below).

### Optical Spectroscopy.

FMC and DFMC exhibit rather similar optical spectra, both evidencing negative solvatochromic shifts (Figure 2), reminiscent of those for twisted chromophore TMC-2, but with larger extinction coefficients.\(^{10c,d}\) The FMC and DFMC charge-transfer bands exhibit large blue shifts with increased solvent polarity (Table 2), strongly indicating a more polar ground state. Note however from the data in Table 2 that the solvatochromic shift is significantly greater for twisted chromophore TMC-2, indicating smaller changes in the dipole moment from the ground state to the first charge-transfer excited state in the more planar, more quinoidal FMC and DFMC chromophores.

### PGSE NMR Spectroscopic Analysis of Chromophore Aggregation.

PGSE NMR is a powerful tool to provide quantitative information on solution-phase chromophore aggregation. PGSE NMR experiments are used here to estimate the molecular dimensions and level of aggregation of chromophores FMC and DFMC in solution. The procedural precautions, described recently,\(^{23}\) were followed here for treating the diffusion data. Diffusion coefficients \( (D_t) \) as a function of...
The ratio between the radius of the solvent and that of the diffusing particle, $f_a$ is the “shape factor”, and $a$ and $b$ are the major and minor semiaxes of the ellipsoid, respectively. The dependence of $f_a$ on $a$ and $b$ for prolate or oblate ellipsoids is known. Structure parameter $P$ (eq 10) is derived from the known values of $\eta$ and $T$ and the measured $D_t$ values (Table 3).

The aggregation numbers $N$ (the average number of monomer units in an aggregate) were calculated via eq 13 (see below) and are seen to significantly diverge from unity (Table 3), indicating that all three chromophores are to some extent associated in CD$_2$Cl$_2$. Nevertheless, $N$ never approaches 2, which would correspond to the predominance of dimers. Assuming that: (i) self-aggregation is limited to a monomer–dimer equilibrium and (ii) both monomer and dimer have prolate ellipsoidal shapes, the dimerization equilibrium constant ($K_D$) can be estimated by fitting the experimental trends of $P$ vs concentration, $C$, with an appropriate expression (eq 11).

$$P = x_{M} P_{M} + x_{D} P_{D}$$  \hspace{1cm} (11)

Here $x_M$ and $x_D$ are the mole fractions of the monomer and dimer, respectively, which can be expressed as a function of $K_D$ and $C$ (eq 12):

$$x_M = 2 - \frac{2C}{\sqrt{1 + 8K_DC}} - 1$$  \hspace{1cm} (12)

$$x_D = 1 - x_M$$

Parameters $P_M$ and $P_D$ depend on the semiaxes of the ellipsoids ($a_{M}$, $a_{D}$, $b_{M}$, and $b_{D}$) and $\eta_{D}$. The latter can be considered approximately equal to the van der Waals radius of CD$_2$Cl$_2$ ($\eta_{D} = 2.49$ Å). Some structural hypotheses must be made as far as the $a$ and $b$ parameters are concerned. The case of chromophore FMC is examined in detail. FMC is treated as a prolate ellipsoid having the major axis ($2a_{M}$) equal to 21 Å (approximately the distance between the terminal CH$_3$ group and the nitrogen of the CN moiety in the conformer having a fully elongated alkyl chain, Figure 3A). The minor semiaxis ($b_{M}$, 3.5 Å) can be derived (Figure 3A) from the experimentally determined $P_M$ value in DMSO (29.02 Å), reasonably assuming that only monomers are present in such a polar solvent.

Having estimated $a_{M}$ and $b_{M}$, the theoretical value of $P_M$ in CD$_2$Cl$_2$ is derived (29.47 Å). Experimental $P$ data in CD$_2$Cl$_2$ as a function of $C$ are then fitted using eq 11 in which $P_M$ is set equal to 29.47 Å, while $K_D$ and $P_D$ are the parameters to determine (Figure 4, black squares). The best fit gives $K_D = 293 \pm 149$ M$^{-1}$ and $P_D = 43.13 \pm 2.27$ Å.

Reasonably assuming that two monomers stack in an anti-parallel fashion, minimizing the distance between positive and negative charges with an overlap region (L) along the major

### Table 2: Optical Absorption ($\lambda_{\text{max}}$, nm, and Extinction Coefficient $\epsilon$, M$^{-1}$ cm$^{-1}$) Data and Estimated Changes in Dipole Moment ($\Delta \mu$, 10$^{-30}$ C·m) from the Ground to First Excited State for Chromophores FMC and DFMC in Selected Solvents

<table>
<thead>
<tr>
<th>solvent (EC)</th>
<th>FMC</th>
<th>TMC-2 $^a$</th>
<th>DFMC</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>556 (1840)</td>
<td>582 (63900)</td>
<td>585 (62100)</td>
</tr>
<tr>
<td>DMF</td>
<td>520</td>
<td>521</td>
<td></td>
</tr>
<tr>
<td>MeOH</td>
<td>440</td>
<td>503</td>
<td>505</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>$-21.4$</td>
<td>$-6.5$</td>
<td>$-6.5$</td>
</tr>
</tbody>
</table>

$^a$ Assigned to a low-energy inter-subfragment charge-transfer (CT) excitation. From refs 10c and 10d. $^b$ DFT-derived change in dipole moment from ground to excited state.

### Table 3: Diffusion Coefficients ($10^{10}$ m$^2$ s$^{-1}$), Structure Parameters ($P$, Å), and Aggregation Numbers ($N$)* for Chromophores FMC, DFMC, and TMC-2 as a Function of Concentration and Solvent

<table>
<thead>
<tr>
<th>entries</th>
<th>C (mM)</th>
<th>$D_t$</th>
<th>$P$</th>
<th>$N$</th>
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</thead>
<tbody>
<tr>
<td>FMC</td>
<td>CD$_2$Cl$_2$</td>
<td>0.23</td>
<td>10.07</td>
<td>30.34</td>
</tr>
<tr>
<td>DMF</td>
<td>0.76</td>
<td>9.68</td>
<td>31.53</td>
<td>1.14 ± 0.06</td>
</tr>
<tr>
<td>MeOH</td>
<td>2.17</td>
<td>9.16</td>
<td>33.35</td>
<td>1.27 ± 0.09</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>3.57</td>
<td>9.03</td>
<td>33.81</td>
<td>1.34 ± 0.10</td>
</tr>
<tr>
<td>DMSO</td>
<td>7.80</td>
<td>8.55</td>
<td>35.72</td>
<td>1.46 ± 0.11</td>
</tr>
<tr>
<td>CD$_2$Cl$_2$</td>
<td>15.12</td>
<td>8.31</td>
<td>36.75</td>
<td>1.56 ± 0.11</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>18.72</td>
<td>8.06</td>
<td>37.88</td>
<td>1.59 ± 0.10</td>
</tr>
<tr>
<td>DMSO</td>
<td>0.15</td>
<td>2.15</td>
<td>28.21</td>
<td></td>
</tr>
<tr>
<td>DMSO</td>
<td>0.75</td>
<td>2.12</td>
<td>28.74</td>
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</tr>
<tr>
<td>DMSO</td>
<td>4.45</td>
<td>2.06</td>
<td>29.47</td>
<td></td>
</tr>
<tr>
<td>DMSO</td>
<td>12.15</td>
<td>2.05</td>
<td>29.65</td>
<td></td>
</tr>
<tr>
<td>DFMC</td>
<td>CD$_2$Cl$_2$</td>
<td>0.108</td>
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<td>38.24</td>
</tr>
<tr>
<td>CD$_2$Cl$_2$</td>
<td>0.13</td>
<td>7.96</td>
<td>38.35</td>
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</tr>
<tr>
<td>CD$_2$Cl$_2$</td>
<td>0.63</td>
<td>7.68</td>
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<td>1.09 ± 0.01</td>
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<tr>
<td>CD$_2$Cl$_2$</td>
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<td>7.63</td>
<td>39.99</td>
<td>1.12 ± 0.03</td>
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<tr>
<td>CD$_2$Cl$_2$</td>
<td>1.76</td>
<td>7.39</td>
<td>41.33</td>
<td>1.19 ± 0.03</td>
</tr>
<tr>
<td>CD$_2$Cl$_2$</td>
<td>3.18</td>
<td>7.05</td>
<td>43.31</td>
<td>1.26 ± 0.05</td>
</tr>
<tr>
<td>CD$_2$Cl$_2$</td>
<td>5.90</td>
<td>6.76</td>
<td>45.19</td>
<td>1.35 ± 0.06</td>
</tr>
<tr>
<td>CD$_2$Cl$_2$</td>
<td>7.42</td>
<td>6.72</td>
<td>45.42</td>
<td>1.38 ± 0.06</td>
</tr>
<tr>
<td>DMSO</td>
<td>12.16</td>
<td>6.52</td>
<td>46.82</td>
<td>1.46 ± 0.06</td>
</tr>
<tr>
<td>DMSO</td>
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<td>1.62</td>
<td>37.56</td>
<td></td>
</tr>
<tr>
<td>DMSO</td>
<td>1.67</td>
<td>1.60</td>
<td>37.88</td>
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<tr>
<td>DMSO</td>
<td>3.08</td>
<td>1.60</td>
<td>37.70</td>
<td></td>
</tr>
<tr>
<td>TMC-2 $^a$</td>
<td>CD$_2$Cl$_2$</td>
<td>0.006</td>
<td>10.06</td>
<td>30.36</td>
</tr>
<tr>
<td>CD$_2$Cl$_2$</td>
<td>0.07</td>
<td>9.32</td>
<td>32.77</td>
<td>1.01 ± 0.02</td>
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<tr>
<td>CD$_2$Cl$_2$</td>
<td>0.50</td>
<td>9.35</td>
<td>33.72</td>
<td>1.08 ± 0.08</td>
</tr>
<tr>
<td>CD$_2$Cl$_2$</td>
<td>1.50</td>
<td>8.52</td>
<td>35.84</td>
<td>1.18 ± 0.13</td>
</tr>
<tr>
<td>CD$_2$Cl$_2$</td>
<td>4.00</td>
<td>7.77</td>
<td>39.26</td>
<td>1.30 ± 0.15</td>
</tr>
<tr>
<td>CD$_2$Cl$_2$</td>
<td>8.40</td>
<td>7.30</td>
<td>41.81</td>
<td>1.41 ± 0.14</td>
</tr>
<tr>
<td>DMSO</td>
<td>0.05</td>
<td>1.99</td>
<td>30.61</td>
<td></td>
</tr>
<tr>
<td>DMSO</td>
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<td>1.94</td>
<td>31.33</td>
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<tr>
<td>DMSO</td>
<td>4.83</td>
<td>1.95</td>
<td>31.15</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Calculated according to eq 13. The error intervals on $N$ are reported at 95% confidence. From refs 10c and 10d.

Twisted $\pi$-Electron System Electrooptic Chromophores

Figure 3. Monomer (A) and dimer (B) van der Waals surfaces of the FMC chromophore. Ellipsoids used as geometrical models for PGSE NMR data analysis are depicted in red (monomer) and blue (dimer).
Note that better theoretical and experimental agreement (Table 5 and Table 7) is obtained when a dipolar field (CH₂C₁₂, \( F = 0.006 \) au, representing very crudely the effect of solvent polarization) was applied, resulting in a more stable zwitterionic state and enhanced response.

It is also found that increasing twist angle gives rise to a concomitant increase in the computed ipso (ring)C–C(ring) and (ring)C–C(CN)₂ bond distances, in good agreement with the crystal structure data (Table 1 and Table 8). Moreover, with this structural progression and increasing dominance of a diradicaloid or zwitterionic ground state, the hyperpolarizability is found to increase substantially due to the increase in change of dipole moment and the decrease in energy separating the zwitterionic ground state and first excited state, as expected using the two-level model (Table 6).

These trends can be understood more completely by considering the HOMO and LUMO spatial distributions for the three chromophores (Figure 5). The HOMO is seen to be increasingly localized on the dicyano methylene group in the progression from FMC to TMC-2, and the LUMO is found to exhibit the opposite trend with increasing localization on the pyridine cation. Note that the HOMO is destabilized by 0.66 eV in progressing from FMC to TMC-2, while the LUMO is stabilized by –0.31 eV. It is found that planarization of TMC-2 by removing \( \sigma \)-methyl substituents in FMC increases the quinoidal resonance contribution and the HOMO–LUMO gap (3.69 vs 4.65 eV, respectively). Lastly, it is found that not only the computed \( \mu \beta \) values decline at zero frequency with the TMC-2 → FMC progression but \( \mu \beta \) also increases in the presence of a dipole field for all respective chromophores, finding acceptable agreement with experiment.¹⁰

Results for issue 2 are plotted in Figure 6, which examines unsolvated chromophore dimer binding energies as a function of interplanar spacing for chromophores FMC, HMC, and TMC-2. It can be seen that the binding at moderate-to-large intermolecular spacings is, not surprisingly, dominated by electrostatic dipole–dipole interactions. TMC-2, the most twisted and the most sterically encumbered chromophore of the series, is identified as having the greatest equilibrium intermolecular distance of 5.81 Å, with a computed dimer stabilization energy of \( \Delta E₀ = -42.3 \) kcal/mol. Decreased twist angle, smaller dipole moment, and more favorable \( \pi–\pi \) stacking results in an equilibrium packing distance of 4.1 Å for FMC. However, the lower dipole moment results in a reduced dimer stabilization energy of \( \Delta E₀ = -29.8 \) kcal/mol, 30% less than for TMC-2. As the dimers are incrementally separated, there is a dramatic loss of stabilization which finally approaches zero, at which point the molecules no longer “sense” one another. It is important to note that by ~15 Å interplanar separation, the stabilization energies (ΔE₀) reach an asymptote near ~5 kcal/mol (Figure 6). This nonzero asymptote may reflect basis set superposition error (BSSE), arising from artificial lowering of the dimer energy due to basis set incompleteness. Since each of these calculations was carried out in the gas-phase, neglecting solvent stabilization effects, an additional calculation was carried out on TMC-2 and FMC at their closest interplanar distances, to correct for the differential effects that solvation would have on each dimer. This was achieved using solvation/dimerization correction energies (\( \Delta E_{\text{sol}} \); see Table 9).

In the absence of solvation, the TMC-2 and FMC dimers (Table 9 and Figure 6), as explained previously, differ in energy by approximately 30%, with the TMC-2 dimer being more stable. However, using a Poisson–Boltzmann scheme (see Experimental Section for details) in CH₂C₁₂, the TMC-2 dimer
is now found to be less stable ($\Delta E_{\text{tail}}$) with respect to the FMC dimer. Using eq 6, the $\Delta E_{\text{tail}}$ values are now found to be $-31.96$ and $-28.11$ kcal/mol, respectively, with only a 12% difference between the two. This decrease in relative energies suggests that FMC and TMC-2 will undergo aggregation in a similar fashion when solvated in moderately polar media such as CH$_2$Cl$_2$. This is in good agreement with the PGSE NMR data (see above). A qualitative state correlation diagram for these results is summarized in Figure 7.

### Discussion

Compared to the synthesis of TMC-2, a major modification in the synthesis of chromophores FMC and DFMC is that the deprotected form, the sodium salt of 2-(4-pyridin-4-ylphenyl)malononitrile, instead of the protonated form, is used as the precursor for regioselective N-alkylation to afford chromophores FMC, HMC, and TMC-2. This is because of the following: (1) the sodium salts can be readily purified via recrystallization from water instead of using flash column chromatography, and, more importantly, (2) the protonated form of 2-(4-pyridin-4-ylphenyl)malononitrile is almost insoluble in most organic solvents, making it unsuitable for subsequent N-alkylation.

As discussed in Results, the difference between the crystal structures of FMC and TMC-2 reveals a major change in electronic structure with reduced twist angle. Given that the (ring)C−C(ring) distance in TMC-2 (1.488(5) Å) is only slightly...
The reduced twist angle TICT chromophore FMC was designed, synthesized, and characterized. The crystallographic data reveal a much smaller dihedral twist angle in FMC than in the highly twisted analogue, TMC-2. The pronounced shortening of the (ring)C−C(ring) and (ring)C−C(CN)2 distances is in accord with a dramatic change in electronic structure: increased contribution from a quinoidal structure in the ground state of FMC rather than the dominant zwitterionic structure of TMC-2. However, similar to TMC-2, negative solvatochromism is observed in optical absorption spectra, and a negative sign of the μβ value is obtained from the EFISH measurements, indicating a similar NLO response mechanism. In addition, as predicted by theoretical calculations, the less twisted FMC chromophores have much smaller molecular hyperpolarizabilities. All these results not only provide strong support for our previously proposed EO response mechanism of TICT chromophores but also reveal the relationship between molecule hyperpolarizability and the dihedral twist angle. These results provide new insights into how simple optimization of chromophore molecular structure can be used to maximize molecular hyperpolarizability by adjusting keymetrical parameters.

The basically similar solution-phase aggregation behavior observed for chromophores FMC and DFMC versus TMC-2 via concentration-dependent EFISH and PGSE measurements indicates that even though the former have smaller dipole moments than TMC-2, that should in principle disfavor self-aggregation, the structural data reveal that a detuned chromophore structure allows shorter interplanar approaching distances and leads to stable face-to-face stacking.

**Conclusion**

The reduced twist angle TICT chromophore FMC was designed, synthesized, and characterized. The crystallographic data reveal a much smaller dihedral twist angle in FMC than in the highly twisted analogue, TMC-2. The pronounced shortening of the (ring)C−C(ring) and (ring)C−C(CN)2 distances is in accord with a dramatic change in electronic structure: increased contribution from a quinoidal structure in the ground state of FMC rather than the dominant zwitterionic structure of TMC-2. However, similar to TMC-2, negative solvatochromism is observed in optical absorption spectra, and a negative sign of the μβ value is obtained from the EFISH measurements, indicating a similar NLO response mechanism. In addition, as predicted by theoretical calculations, the less twisted FMC chromophores have much smaller molecular hyperpolarizabilities. All these results not only provide strong support for our previously proposed EO response mechanism of TICT chromophores but also reveal the relationship between molecule hyperpolarizability and the dihedral twist angle. These results provide new insights into how simple optimization of chromophore molecular structure can be used to maximize molecular hyperpolarizability by adjusting keymetrical parameters.

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**Supporting Information Available:** Crystallographic data (CIF) and PGSE data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

**References and Notes**
