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Push-pull heptamethines near the cyanine limit exhibiting large quadratic electro-optic effect

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Abstract: Harnessing the quadratic electro-optic (QEO) of near-infrared polymethine chromophores over broad telecom wavelength bands is a subject of immense potential but remains largely under-investigated. Herein we report a series of push-pull heptamethines containing the tricyanofuran (TCF) acceptors and indoline or benzo[*e*]indoline donors. These dipolar chromophores can attain a highly delocalized “cyanine-like” electronic ground state in solvents spanning a wide range of polarities, in some cases even closer to the ideal polymethine state than symmetrical cyanines. We use a transmission-mode electromodulation spectroscopy to study the electric-field-induced changes in optical absorption and refraction of polymer films doped with heptamethine chromophores, and obtain large and thermally stable QEO effect with high efficiency-loss figure-of-merits that compare favorably to those from dipolar polyenes in poled or unpoled polymers and III-V semiconductors. Our study opens a path for developing organic materials based on cyanine-like merocyanines for CMOS-compatible, fast, efficient, and low-loss electro-optic modulation.

Keywords: quadratic electro-optic, push-pull heptamethines, cyanine-like, transmission-mode electromodulation, figure-of-merits

1. Introduction

Polymethine dyes close to the cyanine limit have been an archetypal model for the study of electronic structure and third-order nonlinear optical (NLO) properties of one-dimensional (1D) π -conjugated molecules.^[1-17] The widely studied polymethines for third-order nonlinear optics are symmetrical cyanines consisting of charged, odd-numbered polymethine chain with two identical donor (D) or acceptor (A) end groups (**Figure 1a**). These cyanine dyes are featured by sharp, intense absorption band in the near-infrared (NIR) spectral range and large negative $Re(\gamma_0)$, the static (zero-frequency) real part of the molecular third-order polarizability, which are highly correlated with vanishingly small bond length alternation (BLA) of conjugated polymethine chain at the ideal polymethine state (IPS).^[1-5] However, dipolar merocyanines, an important subclass of polymethines asymmetrically substituted with the D and A groups (**Figure 1b**), have been less well studied and not yet been conclusively identified as an alternative type of chromophores that can attain high degree of IPS for large negative $Re(\gamma_0)$ values.^[2,3,18-20]

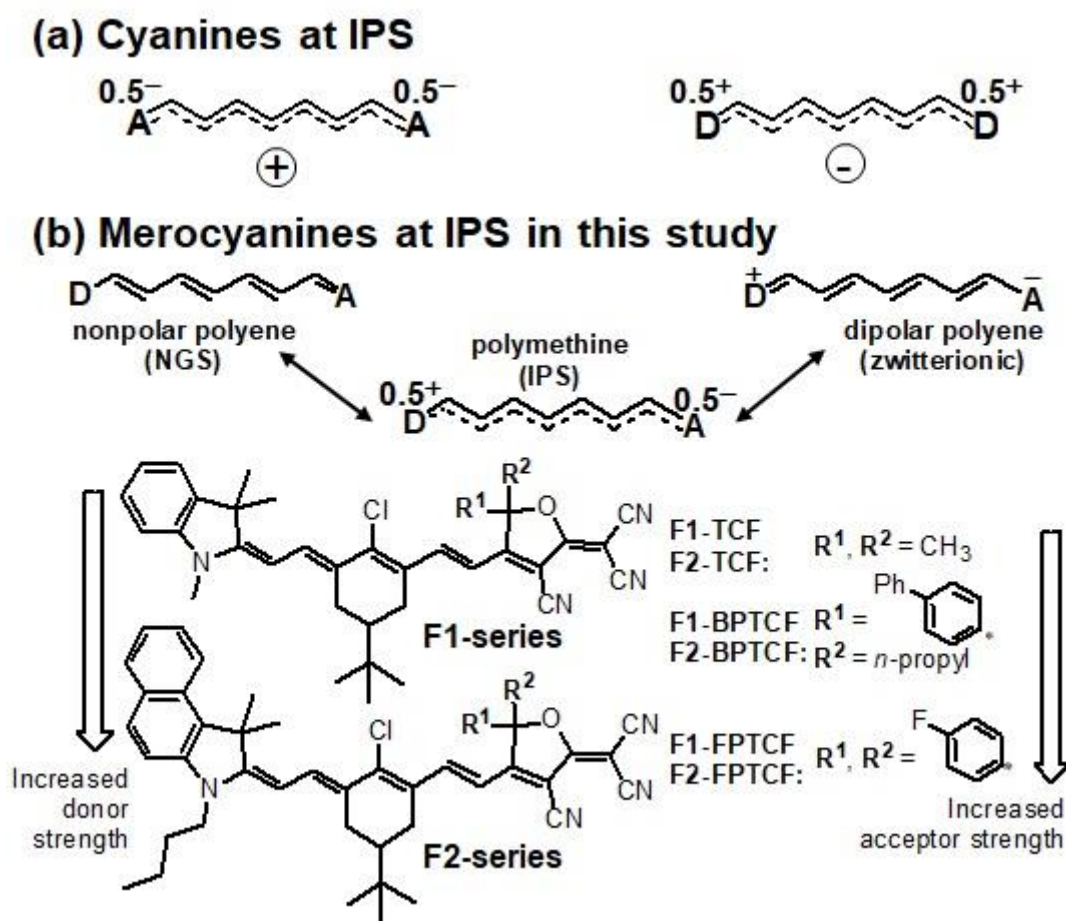


Figure 1. (a) Cationic and anionic cyanine dyes at IPS; (b) Resonance forms of merocyanines and structures of dipolar heptamethines at IPS in this study.

The purpose of this study is to present results from the merocyanine-focused research for electro-optics (EO) ultimately endeavoring to achieve IPS and exceptional third-order NLO properties of materials (**Figure 1b**). The past decade has witnessed considerable research progress in studying the synthesis and structure-NLO property relationships of push-pull heptamethine chromophores.^[21-27] These chromophores contain the tricyanofuran (TCF) acceptor and a variety of donor structures including pyran, thiopyran, selenopyran, indoline, benzindoline, benzothiadiazole, quinolinylidene, and Michler's base derivatives. The concise synthesis, excellent chemical and thermal stability, strong NIR absorption, and highly tunable BLAs make this family of merocyanines very promising for NLO applications. In particular, TCF-based dipolar heptamethines with proper electron donors have been demonstrated to achieve one of the largest molecular second-order polarizabilities (β values) up to $8,437 \times 10^{30}$ esu at 1304 nm in poled polymers.^[27] Furthermore, these research efforts have harvested a variety of push-pull heptamethines exhibiting cyanine-like polymethine properties with sharp, intense NIR absorption band, some of which have been developed as two-photon absorbing (TPA) chromophores active in the short-wavelength infrared (SWIR) spectral range.^[14]

Since the polymethine approach is essential to organic nonlinear optics, we are interested in studying the quadratic EO (QEO) properties of push-pull heptamethines at IPS, in looking for their unique advantages over the cyanine dyes and dipolar polyenes, and in comparing the performance with III-V semiconductor benchmarks. We expect that exploitation of the QEO effect as one of the third-order nonlinear effects from organic materials offers ultra-fast modulation functionalities and opens new possibilities that cannot be otherwise realized with commonly used linear electro-optic (LEO) materials.^[28-32]

The $Re(\gamma_0)$ of NLO-active chromophores is given by

$$Re(\gamma_0) \propto -\left(\frac{\mu_{ge}^4}{E_{ge}^3}\right) + \left(\frac{\mu_{ge}^2 \Delta\mu_{ge}^2}{E_{ge}^3}\right) + \sum_{e'} \left(\frac{\mu_{ge}^2 \mu_{ee'}^2}{E_{ge}^2 E_{ee'}^2}\right) \quad (1)$$

where g labels the ground state, e and e' label the first and high-lying excited states, and μ , $\Delta\mu$, and E are transition dipole moment, changes in dipole moment, and transition energy, respectively, between the labeled states.^[19,20] The polymethines at the cyanine limit generally exhibit large negative $Re(\gamma_0)$ due to large magnitudes of the first term in **Equation 1**, often referred to as a "N" (negative) term that become dominant, and relatively small second term ("D" or dipolar term) and third term ("T" or two-photon term). For the QEO effect, neutral merocyanines would be preferred over the charged cyanines due to negligible ionic conductivities and lower dielectric dissipation factors in the formulated materials.^[33,34] Very importantly, Marder et al have predicted that one can potentially exploit near-resonance

1 enhancement of $Re(\gamma_0)$ without incurring significant optical loss, thanks to the narrow
2 absorption bands of polymethines at IPS.^[12] A big question, however, remains as to what extend
3 the IPS can be obtained in the TCF-based, highly dipolar merocyanines for realizing large
4 $Re(\gamma_0)$, and in what follows, be well-maintained in high-chromophore density films for
5 achieving large real part of third-order susceptibility ($Re(\chi^{(3)})$).
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9 Here we report the synthesis and spectroscopic characterization of several push-pull
10 heptamethines containing the TCF acceptors and indoline (**F1**-series) or benzo[*e*]indoline
11 donors (**F2**-series in **Figure 1b**). Replacing one or two of germinal methyl groups of simple
12 TCF by phenyl derivatives allows a slight increase in electron-withdrawing power of biphenyl-
13 and bis(4-fluorophenyl)-substituted TCF acceptors (hereafter BPTCF and FPTCF,
14 respectively). With **F1** and **F2** donors, the ground-state polarization of chromophores can be
15 attuned from nonpolar polyene-like electronic structure (neutral ground state, NGS), to IPS,
16 and further to zwitterionic resonance structure of dipolar polyene.^[18-20,24-27]
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26 **2. Results and Discussion**

27 **2.1. Material Characterization**

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29 The synthesis of new chromophores followed the protocols of sequential condensation as
30 previously reported.^[21-27] The products were obtained in good yields and characterized by ¹H
31 NMR, ¹³C NMR, HRMS, cyclic voltammetry, UV-vis-NIR spectroscopy, and thermal
32 gravimetric analysis (TGA). Assignments of the protons of the polymethine chain in ¹H NMR
33 spectra of chromophores were supported by the COSY and ROESY spectra and compared with
34 the TCF-based analogs (**Figure S1**). The analysis revealed an all-*trans* configuration of the π -
35 conjugated polymethine bridge in chromophores.
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45 **2.2. Solvatochromism**

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47 The cyanine-like polymethines typically show a sharp, intense long-wavelength
48 absorption band and a shorter wavelength vibronic sub-band. The former is the optical
49 excitation from the electronic ground state (S_0) to excited state (S_1) being largely concentrated
50 in 0-0 vibronic transition, while the latter is attributed to the symmetric C-C valence vibration
51 (such as 0-1 vibronic transition) of the polymethine chain in S_1 .^[35-38] Giant extinction
52 coefficients, relative intensity ratio (RIR) and energy spacing (ES) of 0-1 versus 0-0 sub-bands
53 are the key spectral characteristics to estimate the degree of ground-state polarization of
54 polymethines in approaching the IPS.
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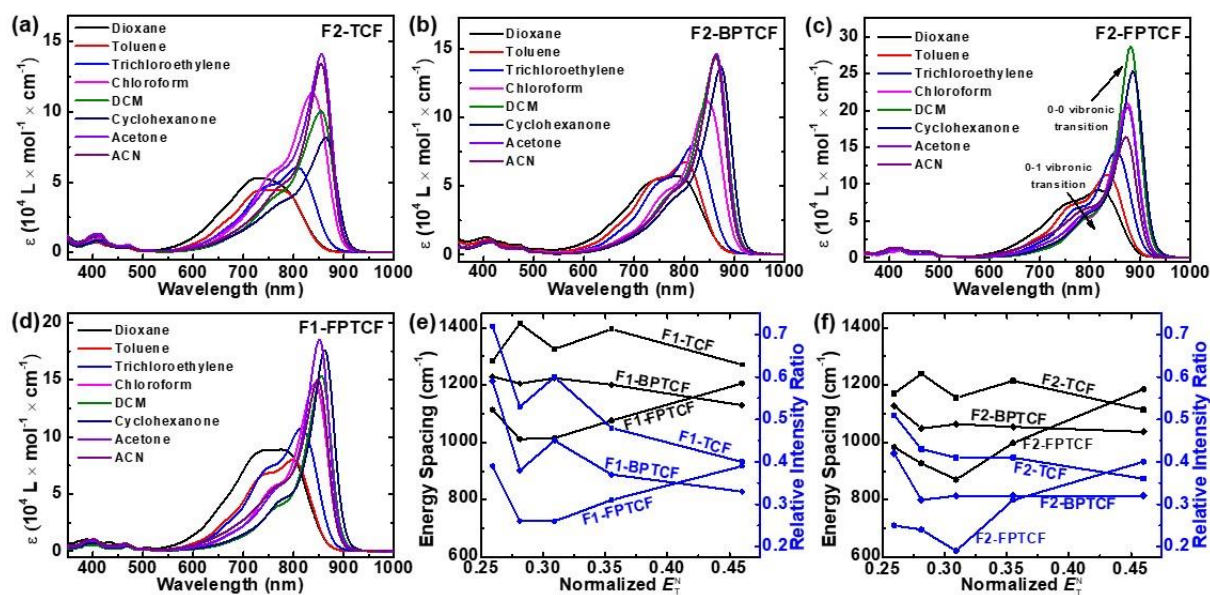


Figure 2. (a-d) UV-vis-NIR absorption spectra of dipolar heptamethine chromophores recorded in solvents spanning a wide range of polarities; (e-f) Effect of solvent polarity on the ES and RIR of 0-1 versus 0-0 sub-bands in the absorption spectra of chromophores. The normalized E_T^N values were used in the plot: 0.259 for chloroform, 0.281 for cyclohexanone, 0.309 for dichloromethane (DCM), 0.355 for acetone, and 0.460 for acetonitrile (ACN).³⁹

The UV-vis-NIR absorption spectra of these chromophores were taken in various solvents with different polarities (**Figure 2a-d and S2**). These TCF-based, highly dipolar heptamethines exhibit weakly solvatochromic, cyanine-like NIR absorption bands in solvents spanning a wide range of polarities from chloroform to acetonitrile. Cyanine-like polymethines usually show an ES of $(1200 \pm 200) \text{ cm}^{-1}$ and RIR less than 0.45 of 0-1 versus 0-0 sub-bands, which have been attained in the spectra of these chromophores in polar solvents. The changes of solvent polarities and donor/acceptor strength of chromophores allow us to acquire the structures close to IPS in the series. In polar solvents ranging from chloroform to acetone, the ES and RIR between two absorption sub-bands show a similar decreasing trend with an increase of acceptor strength in the order of TCF, BPTCF, and FPTCF, and with a slight increase of donor strength from **F1** to **F2**. The plot of ES and RIR versus the normalized E_T^N values of solvent polarity specifies the interplay between the solvent polarity effect and D- π -A structures in stabilizing the merocyanines close to the virtual IPS (**Figure 2e-f**).^[39] Among these, the **F1-FPTCF** and **F2-FPTCF** exhibit ultra-large extinction coefficients (up to $180,000$ - $286,000 \text{ M}^{-1} \cdot \text{cm}^{-1}$), ES of 870 - $1,200 \text{ cm}^{-1}$, and RIR of 0.20 to 0.40. Such ES and RIR values are among the smallest ones of all the reported NIR heptamethines, including the cyanines and merocyanines, based on the same type of donor and/or acceptors (TCF) structures.^[11,17] It indicates that, with a proper combination of donor and acceptor strength, the ground-state polarization of **F1-FPTCF** and **F2-FPTCF** can be kept close to the IPS over a wide range of E_T^N values.

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In nonpolar solvents such as 1,4-dioxane and toluene, the chromophores show positively solvatochromic, broad absorption bands with a substantial decrease in molar extinction. Similar phenomena have been observed in symmetrical cyanines because of symmetry breaking from ion pairing effect.^[37,38] For neutral dipolar merocyanines of this study, it is attributed to an increase of contribution of nonpolar polyene state in low dielectric media.

The NIR absorption bands of chromophores were further analyzed by the method of moments to calculate the mean wavenumber ($\bar{\nu}$) of the photon energy, the oscillator strength (f), and the bandwidth (σ) as the deviation of a spectral band from the band centroid (**Table S1**).^[40] The parameters $\bar{\nu}$ and σ allow quantitatively comparing the relative positions and bandwidths, respectively, of spectral bands of different shapes. The $\bar{\nu}$ corresponds more exactly to the energy of vertical transition than the absorption maximum does and is used to calculate the E_{ge} and μ_{ge} of chromophores as two of key parameter for $Re(\gamma_0)$. We obtained σ value of 1017 cm^{-1} for **F1-FPTCF** and 884 cm^{-1} for **F2-FPTCF** in dichloromethane, which are considerably narrower than those from simple TCF-based heptamethines previously reported.^[11] Also, very large μ_{ge} values, up to 13.8 Debye for **F1-FPTCF** and 15.3 Debye for **F2-FPTCF**, have been determined. In solvatochromism, these chromophores show a slight decrease of $\bar{\nu}$ values in less polar solvents, followed by a small increase in polar solvents. The narrow bandwidth, large oscillator strength, and small scale of inverted solvatochromism further confirm the “cyanine-like” electronic ground state of chromophores in solvents spanning a wide range of polarities.

2.3. Analysis of Bond Length Alternation

We used the $^3J(\text{H,H})$ coupling constants for *trans* vicinal protons in the polymethine chain to estimate the change of BLAs in these chromophores (**Figure 3**). With the increase of donor/acceptor strength and solvent polarity, the $^3J(\text{H}_a, \text{H}_b)$ values decrease from the range of 15.2-15.5 Hz to 14.2-14.5 Hz, and concomitantly the $^3J(\text{H}_c, \text{H}_d)$ values increase from the range of 13.1-13.6 Hz to 13.5-14.2 Hz. The converse change of $^3J(\text{H,H})$ coupling constants indicates a reduced π -bond order of the corresponding C-C bond at the acceptor end, with an increase in the π -bond order of C-C bond at the donor end, suggesting reduced BLAs of chromophores.

As shown in the variable-temperature (VT) ^1H NMR spectra (**Figure S3**), chemical shifts of H_a proton remain essentially unchanged at different temperatures. Below the coalescence temperature, there is no signal splitting occurring, indicating a restricted rotation of FPTCF acceptor. Together with ROESY spectra, the NMR data conclusively rule out the presence of

s-cis conformers that have been observed in TCF-based dipolar polyenes with large BLAs.^[26,27]

The results demonstrate that the all-*trans* configuration of polymethine π -bridge of **F1-FPTCF** and **F1-FPTCF** is rigidified by the diminished BLAs. Furthermore, the coalescence temperature of **F1-FPTCF** is at -22 °C, which is 8 °C lower than that of **F2-FPTCF**. The difference may suggest an increasing inhibition of small degree of axial rotation about the C-C bond linked to the FPTCF acceptor, due to stronger intramolecular charge transfer (ICT) of **F2-FPTCF**.

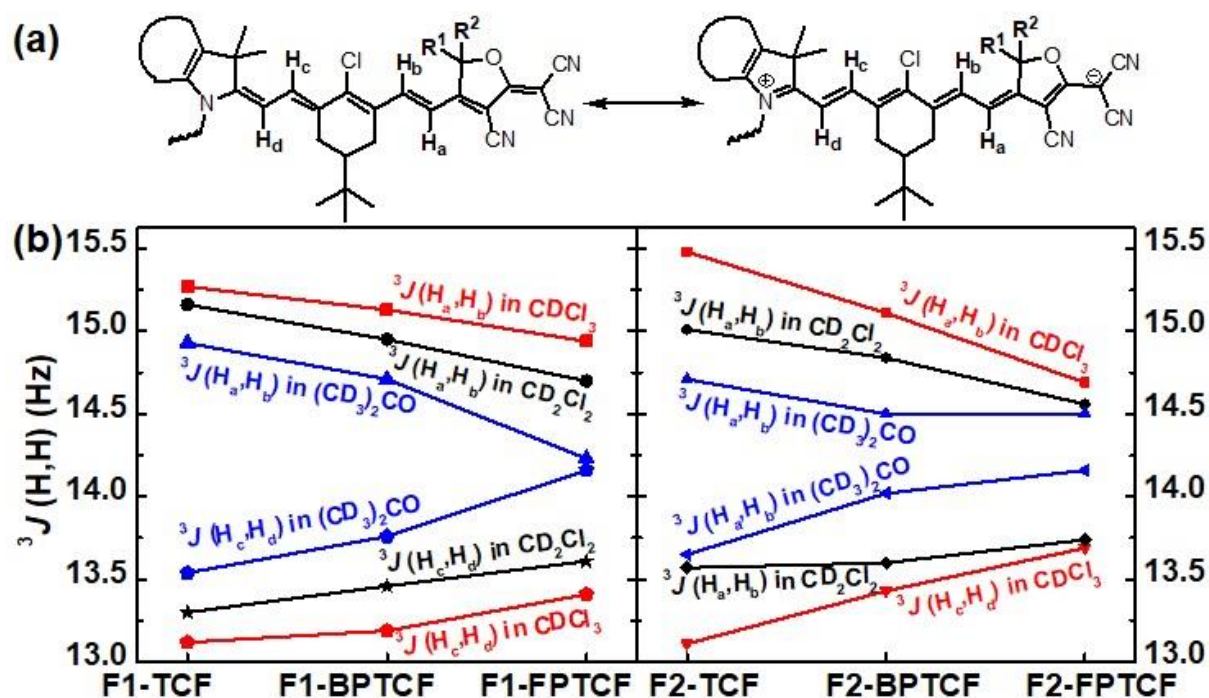


Figure 3. (a) Two resonance forms of dipolar heptamethines with different π -bond order; (b) The $^3J(\text{H,H})$ coupling constants of the H atoms of the polymethine chain in chromophores, recorded in CDCl_3 , CD_2Cl_2 , and acetone- d_6 , respectively.

2.4. Spectroscopic Ellipsometry and Electromodulation of Guest-Host Films

Following the standard formulation and processing protocol of guest-host NLO polymers, we prepared optical quality thin films of materials with high loading density (N) of chromophore **F1-FPTCF** and **F2-FPTCF**. High molecular weight poly(methyl methacrylate) (PMMA) was selected as the host polymer due to its excellent optical and dielectric properties, small birefringence, and good compatibility with TCF-based dipolar chromophores. We prepared three different thin film compositions at ambient conditions, including **F1-FPTCF/PMMA** with N of $2.59 \times 10^{20} \text{ cm}^{-3}$ (hereafter **F1-FPTCF-2.59@PMMA**), **F2-**

FPTCF/PMMA with N of $2.59 \times 10^{20} \text{ cm}^{-3}$ (hereafter **F2-FPTCF-2.59@PMMA**), and **F2-FPTCF/PMMA** with N of $3.24 \times 10^{20} \text{ cm}^{-3}$ (hereafter **F2-FPTCF-3.24@PMMA**).

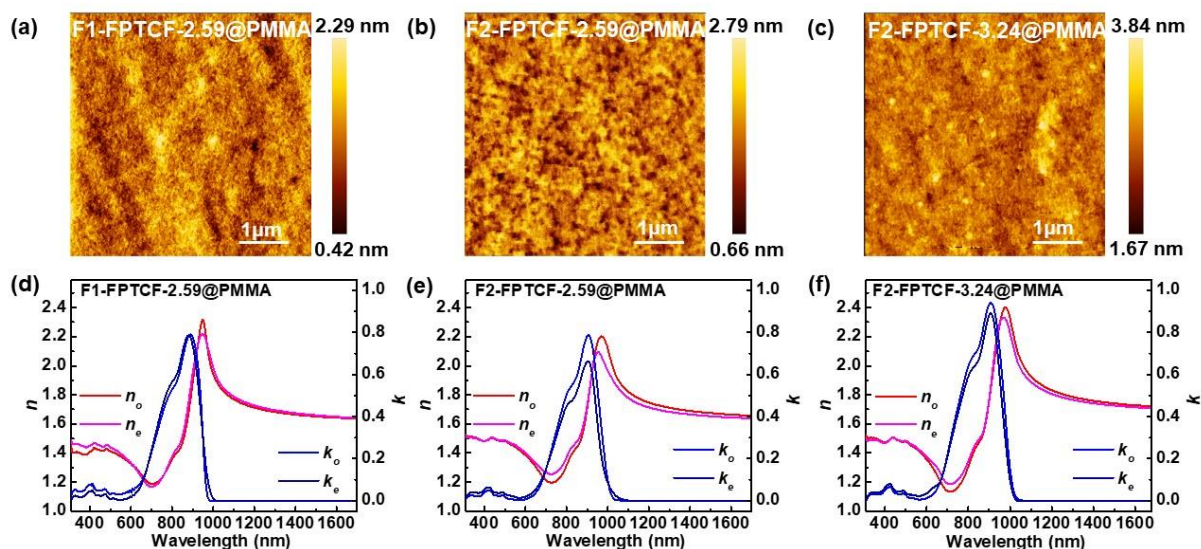


Figure 4. (a-c) AFM height images of **F1-FPTCF/PMMA** and **F2-FPTCF/PMMA** films. The inserted scale bar is at 1 micron; (d-f) Anisotropic optical spectra of **F1-FPTCF/PMMA** and **F2-FPTCF/PMMA** films on glass substrate obtained from the VASE+T data analysis.

Ultra-thin films were prepared on the quartz plates and measured by atomic force microscopy (AFM) to study the nanoscale morphology of guest-host polymers. The films show a homogeneous surface morphology with relatively small roughness, indicative of excellent compatibility of guest-host polymers at high chromophore loading (**Figure 4a-c**). We then used the variable angle spectroscopic ellipsometry (VASE) and transmission (VASE+T) to study the uniaxial optical functions, the refractive index (n) and extinction coefficient (k), of films.^[41-43] Since 1D conjugated dipolar molecules tend to have face-on orientation during the spin coating, the n and k values of guest-host films are expected to show uniaxial anisotropy with in-plane/ordinary (parallel to the sample's surface) component and out-of-plane/extraordinary (perpendicular to the sample's surface) component. Accordingly, a uniaxial model was used to represent the n - k functions. Detailed data analysis of VASE+T can be found in the supporting information (**Figure S4-S12**) and previous publications.^[41-43] The results of the data analysis using B-spline parameterization for the films with uniaxial optical functions respectively are presented in **Figure 4d-f**. The refractive index from the VASE+T data analysis assuming a 1-layer optical model are in good agreement with the prism coupler (PC) results at 1304 nm and 1541 nm, which further demonstrate the consistency of results for these films.

The VASE+T analyses show clearly that **F1-FPTCF** and **F2-FPTCF** can maintain the ground-state polarization close to the IPS in solid thin films with much higher dye concentrations than the dilute solutions. Using the method of moments to quantify the k -spectra of these films, we obtained σ value of 1354 cm^{-1} for **F1-FPTCF-2.59@PMMA**, 1284 cm^{-1} for **F2-FPTCF-2.59@PMMA**, and 1320 cm^{-1} for **F2-FPTCF-3.24@PMMA**, respectively, which are considerably narrower than those from other films doped with symmetrical cyanines and push-pull polyenes.^[11,17,41] Also, very large μ_{ge} values of chromophores in thin films, up to 16.3 Debye for **F1-FPTCF** and 17.9 Debye for **F2-FPTCF**, suggest favorable dipole-dipole interaction in solid states for improved cyanine-like optical properties.

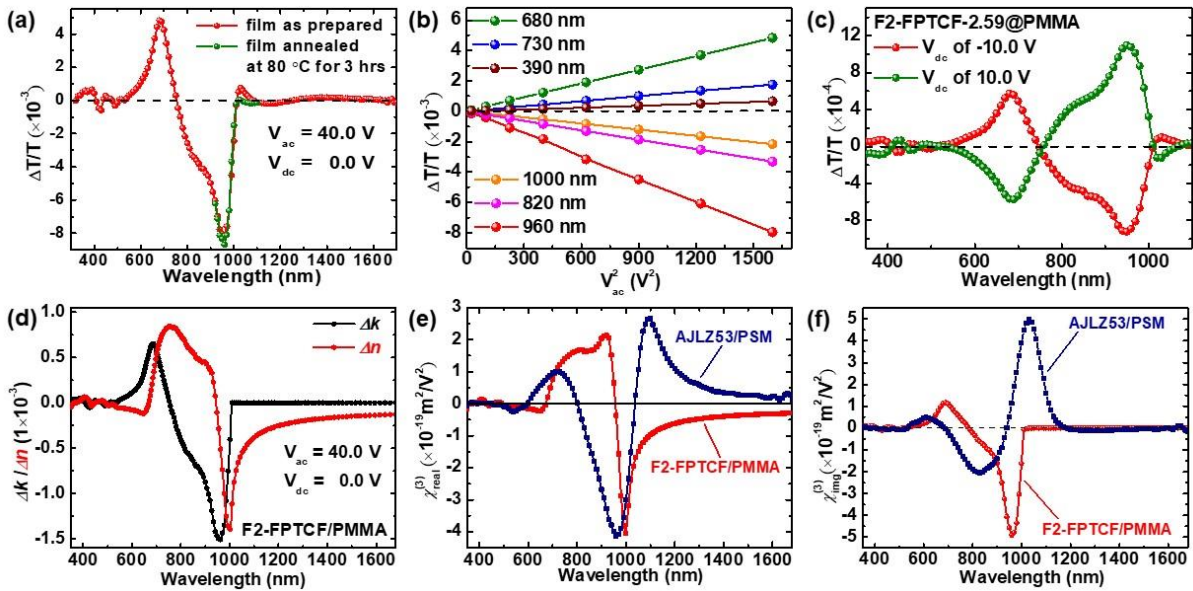


Figure 5. DC and AC response of **F2-FPTCF-2.59@PMMA** with the thickness of 443 nm. (a) EA spectra at the second-harmonic frequency for the film sample as prepared. EA signals at around 1000 nm are re-measured and plotted for the annealed film; (b) Dependence of AC voltage amplitude (V_{ac}) of EA signals at the discrete wavelengths; (c) DC bias dependence of EA spectra of the film at the first harmonic with a fixed V_{ac} at 10.0 V; (d) The second-harmonic EA spectra of the film by plotting the Δk values and Δn results versus wavelengths; (e-f) Dispersion of the real and imaginary parts of $\chi_{1133}^{(3)}(-\omega; \omega, 0, 0)$ derived from the second-harmonic EA spectra of the film. Results of a guest-host polymer containing a push-pull polyene **AJLZ53** are plotted for comparison.

Using a home-made transmission-mode electromodulation (EM) spectroscopy, we study the electric-field-induced changes in optical absorption and refraction of these guest-host films from the visible to near-infrared (NIR) wavelengths (**Figure 5**).^[43,44] The device structure consists of a layer of thin film sandwiched between an indium tin oxide (ITO) glass substrate and a 10-nm semi-transparent gold electrode, and the effective area for optical measurement is

40 mm². The fabricated samples show high optical quality, excellent dielectric strength, and low leak-through currents of 3.3×10^{-6} A/cm² under the applied electric field of 10^5 V/cm, which ensure highly reproducible EA measurements of the study. A Xenon lamp provides a broad spectrum from UV-vis to NIR (320 – 1800 nm). It is monochromatized with minimum resolution of 2 nm per scanning step for the measurement. A beam splitter is used to simultaneously record the electric field modulated signal (ΔT signal) and the chopper modulated one (T signal). During the measurement, an AC voltage is superimposed with a DC voltage to apply to the devices, in which the ITO electrode is connected to the positive lead of the function generator. The modulated light intensity after passing through the devices is recorded by a silicon, or germanium photodetector, connected to a current amplifier and a lock-in amplifier. The first harmonic, i.e. the fundamental frequency component, and the second harmonic of ΔT signal are recorded (**Figure S13**).

The obtained negative $\Delta T/T$ values of **F2-FPTCF-2.59@PMMA** films, up to -0.008 at the wavelength around 950 nm under the applied field strength of 9.0×10^5 V/cm, are one or more orders of magnitude stronger than for other materials such as silicon, perovskites, and organic semiconductors, which all exhibit positive long-wavelength EA bands.^[44-48] Also, the strong near-resonance EA signals of **F2-FPTCF-2.59@PMMA** remained unchanged for the film annealed at the near glass transition temperature (T_g) of 80 °C for 3 hrs (**Figure 5a**). The results indicate large electric-field-induced changes in optical absorption for **F2-FPTCF-2.59@PMMA** as a highly NLO-active, thermally stable polymer. As shown in **Figure 5b-c**, the EA signals scale linearly with the square of AC voltage amplitude (V_{ac}) at the second harmonic, while change linearly with applied DC bias and V_{ac} at the first harmonic. Regardless of the change in applied AC and/or DC voltages and operation frequency, essentially no change in spectral line shape has been observed in the normalized EA spectra. The results support that dipolar chromophore **F2-FPTCF** in the PMMA matrix are weakly interacted with discrete excited energy levels, thus the perturbation of such levels under the applied electric field can be described by the QEO effect as a typical third-order NLO effect.^[43]

2.5. Determination of NLO Properties of Guest-Host Films

The field-induced change in the absorption from the EA spectra can be directly coupled to a change in the refractive index via the Kramers-Kronig (K-K) relation according to

$$\Delta n(E) = 6.3 \times 10^{-6} \text{ cm} \cdot \text{eV} P \int_0^{\infty} \frac{\Delta \alpha(E') dE'}{E'^2 - E^2} \quad (2)$$

where E is the photon energy in electron-volts, α is the absorption coefficient in wavenumber (cm^{-1}), and P denotes the principal value of the integral.^[47,49] Then for the second-harmonic EA spectra, one can use the results of EM spectroscopy and VASE+T to derive the real and imaginary $\chi_{1133}^{(3)}(-\omega; \omega, 0, 0)$ of NLO films as follows

$$\chi_{1133,real}^{(3)} = \frac{4}{3} \frac{(n\Delta n - k\Delta k)}{F^2} \quad (3a)$$

$$\chi_{1133,im}^{(2)} = \frac{4}{3} \frac{(k\Delta n + n\Delta k)}{F^2} \quad (3b)$$

where all in mks units, $\chi_{1133,real}^{(3)}$ and $\chi_{1133,im}^{(3)}$ are the real and imaginary part of third-order susceptibilities of the materials, and F is the applied AC field strength, respectively.^[43,50] Similarly, the $\chi_{1133}^{(3)}$ values can be determined from the first-harmonic EA spectra (**Supplementary Note S1**).

Figure 5e-f show the dispersion of complex $\chi_{1133}^{(3)}$ values of **F2-FPTCF-2.59@PMMA** film from 400 nm to 1600 nm, which were reproducible from both the first- and second-harmonic EA spectra. We obtained the maximal $\chi_{1133,real}^{(3)}$ of $-2.66 \times 10^{-19} \text{ m}^2/\text{V}^2$ and $\chi_{1133,im}^{(3)}$ of $-4.9 \times 10^{-19} \text{ m}^2/\text{V}^2$ at the near-band-edge wavelengths around 1000 nm. These results are among the highest near-resonance negative $\chi_{1133}^{(3)}$ values of organic NLO materials from EM spectroscopy. For comparison, a simple guest-host system was formulated by doping 15 wt% of dipolar polyene **AJLZ53** into a random copolymer poly(styrene-*co*-methyl methacrylate) (PSM) to afford the guest-host polymer with a modest N of $0.94 \times 10^{20} \text{ cm}^{-3}$ (hereafter **AJLZ53-0.94@PSM**) (**Figure S14**). **AJLZ53** is designated as a large first hyperpolarizability chromophore with sizable BLA for LEO application of poled polymers.⁴³ In our recent EA study, at the near-resonance wavelengths around 1050 nm, unpoled **AJLZ53-0.94@PSM** showed maximal positive $\chi_{1133,real}^{(3)}$ of $4.0 \times 10^{-19} \text{ m}^2/\text{V}^2$ and $\chi_{1133,im}^{(3)}$ of $4.97 \times 10^{-19} \text{ m}^2/\text{V}^2$. The comparison indicates that QEO effect of **F2-FPTCF-2.59@PMMA** is contributed by the dominant “N”-term for a large negative $Re(\gamma_0)$ of chromophore, while for **AJLZ53-0.94@PSM**, the “D” and “T” terms become dominant for a large positive $Re(\gamma_0)$.

At higher loading density, **F2-FPTCF-3.24@PMMA** gives higher $\chi_{1133}^{(3)}$ values from the EA spectra, the maximal $\chi_{1133,real}^{(3)}$ of $-6.8 \times 10^{-19} \text{ m}^2/\text{V}^2$ and $\chi_{1133,im}^{(3)}$ of $-8.7 \times 10^{-19} \text{ m}^2/\text{V}^2$ at wavelengths around 1000 nm (**Figure S16**). Here, the improvement of NLO activities, about 1.65 times of the results from **FPTCF-2.59@PMMA**, is considerably higher than what the increase of N can do alone. According to the non-interacting rigid gas model, the $\chi^{(3)}$ value of guest-host NLO polymers is given by

$$\chi_{1133}^{(3)}(-\omega; \omega, 0, 0) = \frac{1}{15} N f_0^2 f_\omega^2 \gamma(-\omega; \omega, 0, 0) \quad (4)$$

where $\gamma(-\omega; \omega, 0, 0)$ is the molecular third-order polarizability, f_0 is the zero-frequency local field factor for the electric field (or Onsager local field correction), and f_ω is the local field factor for lightwave field (or Lorentz-Lorentz local field correction), respectively.^[51] The convention of local field factors gives

$$f_0 = \varepsilon(n^2 + 2)/(n^2 + 2\varepsilon) \quad (5)$$

$$f_\omega = (n^2 + 2)/3 \quad (6)$$

where ε is the dielectric constant of materials. From the analysis, we conclude that higher $\chi^{(3)}$ values of **F2-FPTCF-3.24@PMMA** than those of **F2-FPTCF-2.59@PMMA** are contributed primarily by the enhanced local field factors and higher N . It indicates that exceptional properties of **F2-FPTCF** close to IPS can be well maintained at high loading density in solid states for the improved third-order NLO properties of materials.

The largest tensor component $\chi_{3333}^{(3)}(-\omega; \omega, 0, 0)$ of NLO polymers cannot be directly measured from our normal-incident transmission-mode EM spectroscopy. However, it can be expressed by^[51]

$$\chi_{3333}^{(3)}(-\omega; \omega, 0, 0) = \frac{1}{5} N f_0^2 f_\omega^2 \gamma(-\omega; \omega, 0, 0) \quad (7)$$

According to this convention, **F2-FPTCF-3.24@PMMA** would exhibit extraordinarily large $\chi_{3333}^{(3)}$ values, the maximal $\chi_{3333,real}^{(3)}$ of $-2.0 \times 10^{-18} \text{ m}^2/\text{V}^2$ and $\chi_{3333,im}^{(3)}$ of $-2.6 \times 10^{-18} \text{ m}^2/\text{V}^2$ at the near-resonance wavelengths around 1000 nm.

The change of n_o and n_e of materials by the QEO effect is expressed by

$$\Delta n_o = -\frac{1}{2} \cdot n_o^3 \cdot s_{1133} \cdot F^2 = \frac{1}{n_o} \cdot \frac{3}{2} \cdot \chi_{1133}^{(3)}(-\omega; \omega, 0, 0) \cdot F^2 \quad (8a)$$

$$\Delta n_e = -\frac{1}{2} \cdot n_e^3 \cdot s_{3333} \cdot F^2 = \frac{1}{n_e} \cdot \frac{3}{2} \cdot \chi_{3333}^{(3)}(-\omega; \omega, 0, 0) \cdot F^2 \quad (8b)$$

where s_{1133} and s_{3333} are the QEO coefficients of materials at the ordinary and extraordinary polarization, respectively.^[32] Then we compare the modulation efficiency and figure-of-merit of **F2-FPTCF-3.24@PMMA** in extraordinary polarization to the results from **AJLZ53-0.94@PSM**, GaAs, and InGaAsP. We consider two different wavelengths, 1.3 and 1.55 μm , and at a given field F , the refractive index change is approximately given by

$$\Delta n = K \cdot F^2 \quad (9)$$

where K is the QEO constant for different type of materials. The K values were taken from **Figure S16** and **Equation 8** for doped polymers, and from the literature for GaAs and InGaAsP.^[52] The results are summarized in **Table 1**.

Table 1. Summary of the properties of different materials for QEO effect.

Materials	E_g [eV]	K at 1.3 μm [m^2/V^2]	K at 1.55 μm [m^2/V^2]	$\Delta n/\Delta k$
F2-FPTCF-3.24@PMMA	1.19	1.91×10^{-19}	1.33×10^{-19}	>100
AJLZ53-0.94@PSM	1.09	- ^{a)}	0.68×10^{-19}	>100
GaAs	1.42	1.30×10^{-19}	0.79×10^{-19}	Field-dependent
InGaAsP	1.03	- ^{b)}	5.80×10^{-19}	Field-dependent

E_g , band gap in eV;

^{a)} high optical loss at 1.3 μm ;

^{b)} not far enough below the band gap for QEO effect.

We find that **F2-FPTCF-3.24@PMMA** exhibits excellent QEO properties with relatively large K values and low optical loss around 3.0 dB/cm at 1.3 μm and 1.0 dB/cm at 1.55 μm . In contrast, **AJLZ53-0.94@PSM** gives a high optical loss of 50 dB/cm at 1.3 μm and can only operate at 1.55 μm with a much smaller K value. For achievable optical transparency window, the comparison between **F2-FPTCF/PMMA** and **AJLZ53/PSM** demonstrates the critical advantage of narrow absorption band for **F2-FPTCF** due to its cyanine-like polymethine properties, which is difficult to obtain from **AJLZ53** as a dipolar polyene (**Figure S17**).

Also, the guest-host NLO polymers in this study have demonstrated unique advantages for QEO effect when compared to III-V semiconductors such as GaAs and InGaAsP. For photon energies far below the band gap, the change in the refractive indices of NLO polymers is contributed by pure QEO effect for a wide range of field strengths up to 100 V/ μm , and the K values of **F2-FPTCF-3.24@PMMA** are 1.47 – 1.68 times of the results for GaAs. For GaAs and InGaAsP, the QEO effect can induce the change in refractive index for phase modulation in fact only at lower field strengths, typically less than 10 V/ μm , without undesirable effect of electroabsorption.^[52,53] Here we can use the $\Delta n/\Delta k$ ratio as figure of merit and the phase-dominant modulation should have a ratio $\Delta n/\Delta k$ far great than 1. This can be easily achieved for NLO polymers for photon energies far below or near the band gap. However, for III-V semiconductors, the balance between field-induced Δn and Δk varies dramatically as a function of electric field and relative wavelength, which can leads to smaller $\Delta n/\Delta k$ ratio. It is worthy of note, however, that the QEO activity of **F2-FPTCF-3.24@PMMA** is still at 23% of InGaAsP at 1.55 μm . We expect that materials' QEO performance of push-pull polymethines can be further improved by optimizing the $Re(\gamma_0)$ of chromophores, choosing the operating wavelengths closer to the band gap of materials, and incorporating the chromophore structures to side-chain polymers or supramolecular dendrimers at higher loading densities.^[3,8,17]

3. Conclusion

1
2 In summary, following the general principle of polymethine approach for organic
3 nonlinear optics, our study demonstrates that dipolar merocyanines can ultimately reach the
4 ideal polymethine state in solutions and solid films. Guest-host polymers with these dipolar
5 chromophores exhibit excellent QEO effect with high efficiency-loss figure-of-merits,
6 excellent dielectric properties, and good thermal stability, which compare favorably to those
7 from poled or unpoled guest-host polymers with dipolar polyenes and inorganic semiconductors.
8 We humbly hope that the study can open a new path in developing “cyanine-like” push-pull
9 polymethines with good stability and synthetic scalability for EO applications.
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Supporting Information

20 The Supporting Information is available free of charge on the Wiley Online Library or
21 from the author.
22
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24 Synthetic details, characterizations, NMR and HRMS spectra, additional UV-*vis*-NIR
25 spectra and EA spectra, DFT calculations, and X-ray data collection (PDF).
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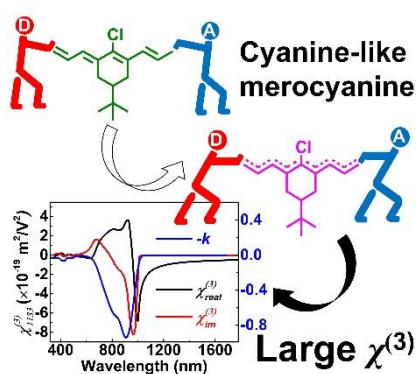
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Push-pull heptamethines near the cyanine limit exhibiting large quadratic electro-optic effect

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We report a series of heptamethines based on the TCF acceptor and the (benzo)indoline donors. These dipolar heptamethines can attain a highly delocalized electronic state, even closer to the ideal “cyanine-limit” than symmetrical cyanines. The study of spectroscopic electromodulation of guest-host polymers containing these heptamethines showed large near-band-edge complex third-order susceptibilities and improved figure-of-merit for modulation.





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