

Site-Isolated Electro-optic Chromophores Based on Substituted 2,2'-Bis(3,4-propylenedioxythiophene) π -Conjugated Bridges

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Application of bis(propylenedioxythiophene) (bis(ProDOT)) π -conjugated bridges bearing alkyl or aryl substituents in electro-optic (EO) chromophores is presented. A series of three bis(ProDOT)-based chromophores and a bithiophene-based control chromophore were prepared and fully characterized with regard to EO applications. The highly planar bis(ProDOT) bridge results in slightly larger ($\sim 10\%$) molecular hyperpolarizability (β) values as compared to the bithiophene bridge, as measured by hyper-Rayleigh scattering at a variety of wavelengths. In amorphous polycarbonate guest–host films, however, the bulky substituents on the bis(ProDOT) bridge result in significantly larger ($\sim 70\%$) poling-induced EO coefficient (r_{33}) values, as measured by simple reflection ellipsometry at 1310 nm. This can be attributed to a roughly 2-fold enhancement in poling efficiency due to reduced intermolecular dipole–dipole interactions. This chromophore architecture also exhibits excellent temporal alignment stability and photochemical stability as compared to benchmark AJL8, FTC, and CLD chromophore systems. Incorporation of the strong CF₃-phenyl-substituted tricyano-furan (TCF) acceptor into a bis(ProDOT)-based chromophore resulted in a $\beta_{zzz}(-2\omega; \omega, \omega)$ value at 1907 nm of $5700 \pm 400 \times 10^{-30}$ esu and an r_{33} value of 69 ± 14 pm/V at 32.8 total chromophore weight %.

Introduction

In the past two decades, organic quadratic nonlinear optical (NLO) chromophores have been heavily investigated for their potential use in photonics-based technology,¹ particularly with regard to electro-optic (EO) applications. The most highly studied materials class in this field is the poled guest–host polymer type in which an EO chromophore is dispersed in a polymer matrix and oriented (poled) by means of an electrical field in order to obtain the noncentrosymmetric arrangement necessary to generate quadratic effects.^{2–4} Although this method allows the facile use of high molecular hyperpolarizability (β) EO chromophores, the material activity is directly dependent on the degree of chromophore ordering obtained during poling. Poling is a low-yield process, however, mainly due to the very strong interchromophore dipole–dipole interactions that lead to unfavorable

antiparallel packing of the chromophoric units.^{5,6} Because the number of truly oriented chromophores after poling is small ($\sim 10\%$), the maximum possible bulk EO activity is never attained. To address this problem, it was found that site isolation of the chromophores, which minimizes the dipole–dipole interactions, significantly improved the poling efficiency and thus the resulting EO coefficient (r_{33}) of materials.⁷ One way to achieve site isolation is via addition of bulky substituents to the chromophore backbone, which reduce dipole–dipole interactions by way of simple steric hindrance. In addition, it has been shown that an ensemble of interacting spherically shaped structures will have greater mobility in the poling field than a similar system composed of typical prolate ellipsoid-shaped molecules.^{8,9}

In this work, we utilized bis(propylenedioxythiophene) (bis(ProDOT)) π -conjugated bridges to produce EO chro-

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mophores with a highly planar conjugated backbone and simultaneously a largely spherical overall shape. EO chromophores based on the related bis(ethylenedioxythiophene) (BEDOT) have been reported in the literature and shown to exhibit significant enhancements in dipole moment–hyperpolarizability product ($\mu\beta$) values compared to bithiophene control molecules.^{10–13} This enhancement was attributed in part to a rigidification and planarization of the conjugated bridge resulting from strong sulfur–oxygen interactions within the BEDOT moiety, as evidenced by the unusually short distance between the sulfur atom of one ring and the oxygen atom of the other ring.^{12–14} These sulfur–oxygen interactions have also resulted in widespread use of poly(EDOT) (PEDOT) for its highly delocalized π -electron structure in a variety of applications such as electrochromic devices,^{15–20} field-effect transistors,^{15,21} and light-emitting diodes.^{15,22} The ProDOT moiety has also been incorporated in highly delocalized polymers,^{15–19} which display properties similar to their EDOT counterparts for these applications.^{16,17} Crystal structures of bis(ProDOT) moieties confirm that they also exhibit the close sulfur–oxygen distances seen in the BEDOT systems, further suggesting similar properties in EO chromophore applications.

Although it is possible to improve the spherical shape of BEDOT-based chromophores through derivatization of the EDOT ring,^{23–25} it is nontrivial. Furthermore, such systems have been limited to a single attachment point, restricting the 3D spherical shape achievable through synthetic modification. Similarly, derivatization of other common bridge structures for EO chromophores, such as the thienylvinylene in FTC and the ring-locked tetraene in CLD systems,^{26–29} is synthetically challenging and generally limited to single attachment points. In contrast, ProDOT moieties are readily derivatized to incorporate a variety of functional groups at the central carbon of the propylene ring. The tetragonal nature of the sp^3 geometry at this tetrasubstituted carbon enhances the 3D spherical shape of the EO chromophores based on bis(ProDOT) derivatives. The enhanced spherical shape should reduce the interchromophore dipole–dipole interactions, thereby enhancing the poling response of the chromophores.

In this paper, we describe the synthesis and EO-relevant characterization of a series of four new EO chromophores (Figure 1). Three of them are based on a substituted bis(ProDOT) core and contain the powerful TCF or CF_3/Ph -TCF acceptor. A fourth chromophore, **OLD-3**, is based on a bithiophene core devoid of side chains and was prepared in order to compare an underivatized and unplanarized structure with the bis(ProDOT) architectures.

Experimental Section

Detailed procedures for the synthesis and spectrometric characterization of compounds reported can be found in the accompanying Supporting Information.

Hyper-Rayleigh Scattering Measurements. Hyper-Rayleigh scattering (HRS) measurements were performed on dilute chloroform (Fisher, ACS Spectranalyzed) solutions of chromophores **OLD-1–4** to evaluate their molecular hyperpolarizability (β)

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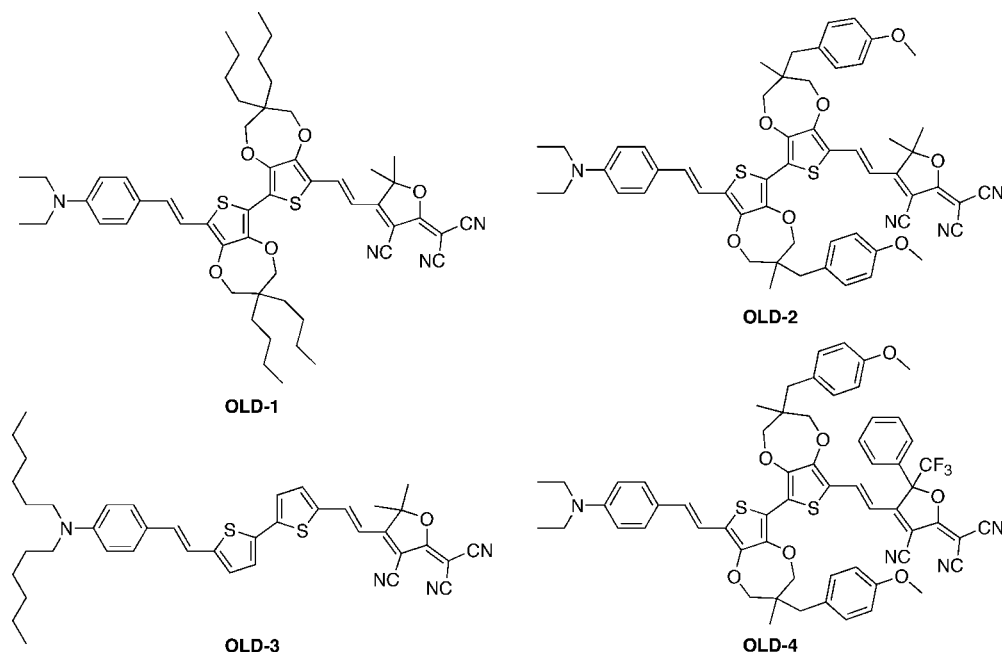


Figure 1. Structures of the OLD Chromophores.

values.^{30,31} Measurements were made at a variety of excitation wavelengths in an attempt to account for the varied ω and 2ω resonance effects arising from the differing absorption characteristics of the chromophores. Excitation at 780 and 1000 nm was obtained from a mode-locked Ti:sapphire (Spectra-Physics Tsunami) with 100 fs pulses (full width at half-maximum, fwhm), at an 80 MHz repetition rate, with an average power of 2 W (780 nm) and ~ 600 mW (1000 nm) and a 3–12 nm spectrum (fwhm). Excitation at 1300 nm was obtained by pumping an optical parametric oscillator (OPO, Spectra-Physics OPAL) with the Ti:sapphire, resulting in pulses with a slightly larger spectrum (~ 20 nm fwhm) and lower power (~ 350 mW) but otherwise identical to the fundamental. Excitation at 1907 nm was obtained from a Q-switched Nd:YAG (Spectra-Physics Quanta-Ray GCR-170) equipped with a H_2 -Raman cell (~ 15 atm), the first Stokes line of which provided 10 ns pulses (fwhm) at a repetition rate of 30 Hz and an average power of ~ 160 mW.

In all cases, the incident light was focused into a small-volume flow cell, pumped with a filtered (in-line 0.2 μ m PTFE) chloroform solution of the chromophore, and the scattered light was imaged onto the slits of a monochromator (Acton 300i) equipped with an appropriate wavelength filter element to remove the excitation signal. A 1340×100 pixel, red-edge enhanced, back-thinned LN₂-cooled CCD camera (Princeton Instruments) was used for detection. The concentration ranges employed for the chromophore solutions were 50–100 nM (780 nm), 206–329 nM (1000 nm), 219–470 nM (1300 nm), and 5–78 μ M (1907 nm), all of which were below the self-absorption limit. In most cases, observation of the HRS signal over multiple scans indicated no photodegradation. In the case of **OLD-1** and **OLD-2**, however, the wavelength of maximum absorption (λ_{\max}) falls close to 780 nm, and HRS signals for these chromophores at this wavelength were seen to degrade at a constant $\sim 7\%$ per spectrum. Consequently, HRS spectra in these circumstances were obtained using fresh solutions for each run, and the data were adjusted for the known degradation rate.

In all cases, the signal intensity scaled quadratically with excitation power, consistent with HRS. Two-photon fluorescence (TPF), however, is also expected to scale quadratically with power. Acquisition of HRS spectra proved critical in deconvolution of TPF and HRS signals as the bis(ProDOT)-based chromophores exhibited vibrationally unrelaxed fluorescence, precluding the use of shifted excitation and time-resolution techniques. The TPF contribution to the HRS signal was removed by fitting the baseline of the raw spectrum to a simple fifth-order polynomial in MATLAB and subtracting, making use of the significantly smaller line width of the HRS (~ 2 –10 nm fwhm) with respect to the TPF (~ 40 nm fwhm). The resulting HRS spectrum is fitted to a Gaussian distribution to provide a corrected sample intensity (I_{sample}). For data at 780, 1000, and 1300 nm, I_{sample} was converted to a β value using the internal reference method (eq 1), where the chloroform solvent acts as the internal standard.

$$\frac{I_{\text{sample}}}{I_{\text{solvent}}} = \frac{N_{\text{sample}} \langle \beta_{\text{sample}}^2 \rangle + N_{\text{solvent}} \langle \beta_{\text{solvent}}^2 \rangle}{N_{\text{solvent}} \langle \beta_{\text{solvent}}^2 \rangle} \quad (1)$$

At 1907 nm, the HRS signal from pure chloroform is negligible, so I_{sample} was converted to a β value using the external reference method (eq 2) using the benchmark chromophore EZ-FTC, which has a known β value.

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

Electro-optic Coefficient Measurements. Samples for EO coefficient (r_{33}) measurements were prepared by mixing the appropriate ratio of chromophore and the polymer (poly[Bisphenol A carbonate-co-4,4'-(3,3,5-trimethylcyclohexylidene)diphenol carbonate] [APC], Aldrich) in cyclopentanone (Aldrich) to produce a solution with 12 wt % solids. The solution was filtered through a 0.2 μ m syringe filter and spin cast onto indium tin oxide (ITO) glass substrates. The films were then baked at 85 $^{\circ}$ C in a vacuum oven overnight to ensure removal of all residual solvent. Gold electrodes were sputtered onto the polymer films (Denton Vacuum Desk II), and the samples were contact poled by heating near the glass-transition temperature (T_g) and applying an electric field under

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a nitrogen atmosphere. The electro-optic coefficients for all chromophores were measured by simple reflection ellipsometry with a 1.31 μm laser³² using the corrected formula.³³ A fresh sample was used for each measurement. Following the guidelines in the literature,³⁴ the film parameters (thickness, refractive index, and absorption of the polymer and ITO layers) were maintained such that error is estimated as $\pm 20\%$.

Photostability Measurements. Samples for photostability measurements were prepared by mixing the chromophore and the APC polymer (Aldrich) to produce a 2.8×10^{-4} mol/g solid solution of chromophore in APC and then dissolving in cyclopentanone (Aldrich) to produce a solution with 12 wt % solids. The solution was filtered through a 0.2 μm syringe filter and dip cast onto freshly cleaved, FC-equipped, SMF-28 single-mode optical fibers (Thor Laboratories). Sample fibers were dried under reduced pressure for 24–48 h to remove residual solvent. The sample fiber was connected via an FC/FC adapter to a 980/1550 nm wavelength division multiplexer (WDM), which permitted continuous irradiation with ~ 200 mW from a 1550 nm (excitation) fiber laser (Keopsys), and intermittent interrogation with a small portion of the unpolarized output from a 635 nm (probe) diode laser (Thor Laboratories). A silicon photodetector was used to measure the transmitted probe beam intensity, which was computer controlled to provide a single 3.5 s exposure every 20 min to reduce probe-induced photodegradation as a function of 1550 nm exposure time. The fiber sample and photodetector were placed in a blackout box to minimize photodegradation induced by ambient light.

The photodegradation rate was determined by monitoring the probe transmittance (or, equivalently, absorbance) as a function of time (I_t or A_t) relative to the initial transmittance value (I_0 or A_0). The data are generally analyzed in the literature with regard to a single-photon absorption model,³⁵ described by a single-exponential decay

$$\frac{N_t}{N_0} = \exp(-t/\tau) \quad (3)$$

where N_t is the chromophore concentration at time t (proportional to A_t), N_0 is the initial chromophore concentration (proportional to A_0), and τ is the effective lifetime. The lifetime depends on the absorption cross-section (σ) at the wavelength of interest (1550 nm) and the quantum yield for photodegradation (B^{-1}) as well as the photon flux (n)

$$\tau = \frac{B}{\sigma n} \quad (4)$$

Thus, B/σ is a figure of merit (FOM) for the photostability of a compound,³⁵ with larger values corresponding to increased stability. In this model, a plot of $\ln(A_t/A_0)$ versus t should be linear,³⁵ with the slope directly related to the FOM. From our experiments, however, it is clear that this model is only valid for the initial decay (~ 300 min) and that the full photodegradation profile is more complicated. It can be adequately fit using a more complex model

that provides two figures of merit (B/σ)₁ and (B/σ)₂,³⁶ one of which corresponds to the fast initial decay and the other to the slower, secondary decay. This suggests there may be two distinct pathways for degradation,³⁶ both of which play important roles in the overall photostability of the chromophore.

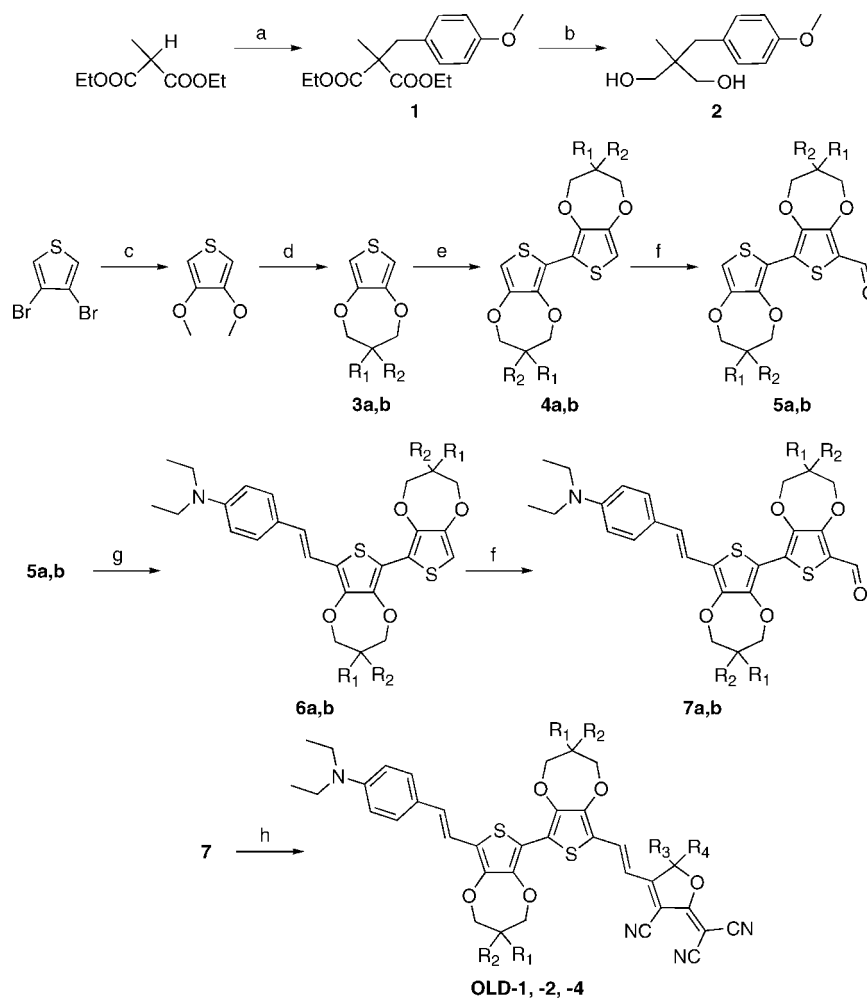
Results and Discussion

Synthesis. The three bis(ProDOT)-based OLD chromophores were synthesized following the general route laid out in Scheme 1. The ProDOT parent rings (**3**) were prepared following a modified literature procedure from 3,4-dimethoxythiophene and the appropriate 1,3-propanediol.¹⁶ For **OLD-1**, the literature procedure using commercially available 2,2-dibutyl-1,3-propanediol was followed.³⁷ For **OLD-2** and **OLD-4**, the 2-methyl-2-(4-methoxybenzyl)propane-1,2-diol (**2**) was synthesized by reducing 2-methyl-2-(4-methoxybenzyl) diethylmalonate (**1**), which was prepared from 2-methyl diethylmalonate and 4-methoxybenzyl chloride using sodium hydride as base. The ProDOT monomers were dimerized via a butyl lithium/ $\text{Fe}(\text{acac})_3$ route described in the literature,³⁸ and the resulting bis(ProDOT)s (**4**) were monoformylated using butyllithium and DMF to yield aldehydes **5**. The diethylaminophenyl donor group was coupled via a Horner–Emmons olefination, and the donor–bridge compounds (**6**) were monoformylated using butyllithium and DMF to give aldehydes **7**. The acceptor, 2-dicyanomethylen-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (TCF) or 2-dicyanomethylen-3-cyano-4-methyl-5-phenyl-5-trifluoromethyl-2,5-dihydrofuran (CF_3/Ph -TCF), was then coupled via a Knoevenagel condensation to yield the final **OLD-1**, **OLD-2**, and **OLD-4** chromophores. **OLD-3** was prepared in a fashion similar to that shown in Scheme 1. 5-Formyl-2,2'-bithiophene (prepared via the literature method)³⁹ was coupled with the dihexylaminophenyl donor phosphonate to maintain comparable solubility with the bis(ProDOT)-based chromophores. The resulting donor–bridge compound (**8**) was monoformylated with butyllithium and DMF to yield aldehyde **9**, which was condensed with the TCF acceptor under Knoevenagel conditions to yield **OLD-3**. All four compounds are soluble in common polar organic solvents and purified by column chromatography followed by recrystallization from a methylene chloride/methanol mixture.

Physical Properties. The physical properties of the OLD series are summarized in Table 1. The UV–vis absorbance spectra of **OLD-1** and **OLD-2** in chloroform (Figure 2) are nearly identical, with the wavelengths of maximum absorp-

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Scheme 1. Synthesis of Bis(ProDOT)-Based Chromophores^a

a, OLD-1: $R_1=R_2=Bu$, $R_3=R_4=Me$; **b, OLD-2:** $R_1=Me$, $R_2=CH_2C_6H_4OMe$, $R_3=R_4=Me$;
OLD-4: $R_1=Me$, $R_2=CH_2C_6H_4OMe$, $R_3=CF_3$, $R_4=Ph$

^a Experimental conditions: (a) (1) NaH, (2) 4-methoxybenzyl chloride, THF; (b) LiAlH₄, methanol, aq. NaOH; (c) NaOMe, CuO, KI, methanol; (d) 2,2-disubstituted-1,3-propanediol, *p*-TSA, toluene; (e) (1) BuLi, THF, (2) Fe(acac)₃, THF; (f) (1) BuLi, THF, (2) DMF, THF; (g) diethyl-[4-(*N,N*-diethyl)aminobenzyl] phosphonate, *t*-BuOK, THF; (h) TCF acceptor, Et₃N, chloroform.

Table 1. Physical Properties of the OLD Chromophores

chromophore	λ_{max} (nm)	T_d (°C) ^a	molecular active wt % ^b
OLD-1	754	238	63
OLD-2	746	227	60
OLD-3	677	210	79
OLD-4	828	155	65

^a DSC, 10 °C/min, sealed pan, under N₂. ^b Ratio of the active core chromophore mass to the total molecular mass.

tion (λ_{max}) of the main charge-transfer band being at 754 and 746 nm, respectively. This is expected as the different ProDOT side chains should have only minimal solvatochromic effects on the charge-transfer backbone. In contrast, the bithiophene-based **OLD-3** exhibits significantly blue-shifted absorption (λ_{max} 677 nm) due to the absence of the electron-donating propylenedioxy substituents. In addition to the extra electron density, the propylenedioxy groups also promote a more planar atomic arrangement as previously mentioned, and both effects likely contribute to the red-shifted absorption in these systems. The UV-vis spectrum of **OLD-4** exhibits a broad absorption band with λ_{max} at 828 nm. This 75 nm red shift with respect to **OLD-2** is consistent with replace-

ment of the TCF moiety with the stronger CF₃/Ph-TCF electron acceptor.⁴⁰

All four chromophores possess sufficient thermal stability for EO device applications, and several exhibit excellent stability as evidenced by their high decomposition temperatures (T_d) presented in Table 1. Notably, **OLD-1** and **OLD-2** display a slight increase in T_d with respect to **OLD-3** (238, 227, and 210 °C, respectively), which indicates that the bulky ProDOT moieties are thermally robust. The lower thermal stability of **OLD-4** (155 °C) can be attributed to the reduced stability of the CF₃/Ph-TCF acceptor moiety as the structure is otherwise identical to that of **OLD-2**. However, the thermal stability of **OLD-4** remains sufficient for EO device fabrication.

The molecular active wt % shown in Table 1 for the **OLD** chromophores is a ratio of the active core chromophore mass

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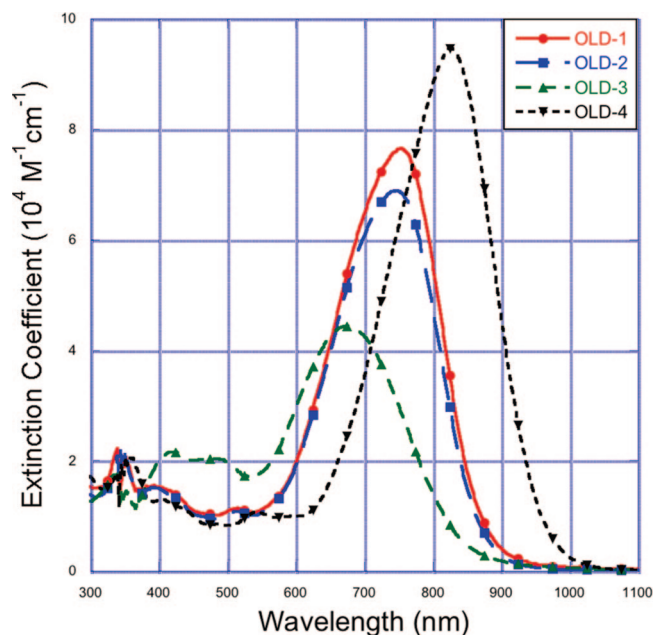


Figure 2. UV-vis absorption spectra of OLD chromophores in chloroform.

to the total molecular mass. The active core is defined as the main charge-transfer backbone, consisting of the donor, bridge, and acceptor, including atoms directly connected to the π -electron system (namely, the methylenes on the donor nitrogen and the hydrogen or oxygen atoms directly connected to the thiophenes), and the entire electron acceptor. This definition was used to incorporate the minimum mass that directly contributes to the hyperpolarizability of the molecule while still maintaining a physically meaningful system. The bis(ProDOT)-based chromophores all exhibit a molecular active wt % of approximately 60%, while **OLD-3** has a higher value (79%) due to the lack of side chains.

Hyper-Rayleigh Scattering Measurements. In order to evaluate the molecular hyperpolarizability (β) values of the OLD chromophores, hyper-Rayleigh scattering (HRS) measurements were performed.^{30,31} HRS provides a direct measure of the tensor-averaged β value of a chromophore with the β_{zzz} component (along the charge-transfer axis) being the most significant contributor in linear systems such as these.⁴¹ As HRS is a second-harmonic generation (SHG) process, the measured $\beta(-2\omega; \omega, \omega)$ value is subject to resonance effects when the excitation wavelength (ω), or the second harmonic (2ω), is near the optical transition(s) of the molecule under study.⁴² The linear EO (Pockels) effect is not a second-harmonic process, however, and it is important to acknowledge that $\beta(-\omega; 0, \omega)$, which is related to the EO coefficient (r_{33}), does not display the same functional dependence as $\beta(-2\omega; \omega, \omega)$ with regard to

Table 2. Experimental and TLM-Derived β Values of the OLD Chromophores

chromophore,	excitation		$\beta_{zzz}(-2\omega; \omega, \omega)^a$	$\beta_{zzz}(0; 0, 0)^b$	$\beta_{zzz}(-\omega; 0, \omega)^c$
	λ_{\max} (nm)	wavelength (nm)			
OLD-1, 754		780	5000 \pm 300	900 \pm 50	1800 \pm 100
		1000	2800 \pm 100	1540 \pm 60	3100 \pm 100
		1000	2800 \pm 100	1540 \pm 60	3100 \pm 100
		1300	6700 \pm 500	1500 \pm 100	3100 \pm 200
		1907	1770 \pm 70	560 \pm 20	1110 \pm 40
OLD-2, 746		780	5600 \pm 700	1300 \pm 200	2500 \pm 300
		1000	2800 \pm 100	1520 \pm 50	3000 \pm 100
		1300	7100 \pm 600	1500 \pm 100	3000 \pm 200
		1907	1900 \pm 200	620 \pm 70	1200 \pm 100
OLD-3, 677		1000	3500 \pm 100	1580 \pm 50	2680 \pm 80
		1300	6700 \pm 300	410 \pm 20	700 \pm 30
		1907	1500 \pm 200	650 \pm 90	1100 \pm 100
OLD-4, 828		1000	5780 \pm 60	3170 \pm 30	7610 \pm 80
		1300	6600 \pm 200	2440 \pm 70	5900 \pm 200
		1907	5700 \pm 400	1140 \pm 80	2700 \pm 200

^a Experimental value in units of $\times 10^{-30}$ esu. ^b TLM-derived wavelength-independent value, in units of $\times 10^{-30}$ esu. ^c TLM-derived value at 1310 nm, in units of $\times 10^{-30}$ esu.

resonance effects. Thus, in order to compare molecular EO activity among chromophores with differing absorption characteristics, care must be taken to account for resonance effects. To illustrate this point, we performed frequency-agile HRS on the OLD chromophores at 780, 1000, 1300, and 1907 nm, the results of which are presented in Table 2.

The experimental technique provides β_{HRS} values relative to the β_{HRS} of chloroform, which is used as an internal standard. We note that the β_{HRS} value of chloroform has historically been and remains to date to be the subject of some debate in the literature.^{43,44} In converting to absolute units, we used Kaatz and Shelton's 0.16×10^{-30} esu value,⁴³ obtained from direct integration of the SHG intensity of pure chloroform. Additionally, we used the Cyvin–Rauch–Decius relationship for a prolate ellipsoid whose β tensor is dominated by the β_{zzz} element, $\beta_{\text{HRS}} \approx 0.414\beta_{zzz}$,⁴¹ to convert to the EO device-relevant β tensor element, β_{zzz} . By employing the two-level model (TLM) approximation to account for resonance effects^{42,45} following the method of Singer et al.,⁴² we converted the $\beta_{zzz}(-2\omega; \omega, \omega)$ values into wavelength-independent $\beta_{zzz}(0; 0, 0)$ values, using eq 5, the excitation wavelength of the HRS experiment (λ_{ex}), and the main charge-transfer transition of the molecule (λ_{max}). Additionally, we further converted the HRS results into EO-relevant $\beta_{zzz}(-\omega; 0, \omega)$ values at the operational wavelength of the simple reflection EO measurement ($\lambda_{\text{op}} = 1310$ nm) using eq 6.⁴²

$$\beta_{zzz}(0; 0, 0) = \beta_{zzz}(-2\omega; \omega, \omega) \left(1 - \left(\frac{\lambda_{\text{max}}}{\lambda_{\text{ex}}} \right)^2 \right) \left(1 - 4 \left(\frac{\lambda_{\text{max}}}{\lambda_{\text{ex}}} \right)^2 \right) \quad (5)$$

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$$\beta_{zzz}(-\omega;0,\omega) = \beta_{zzz}(0;0,0) \frac{\left(3 - \left(\frac{\lambda_{\max}}{\lambda_{\text{op}}}\right)^2\right)}{3\left(1 - \left(\frac{\lambda_{\max}}{\lambda_{\text{op}}}\right)^2\right)^2} \quad (6)$$

The results are presented in Table 2 alongside the experimental $\beta_{zzz}(-2\omega;\omega,\omega)$ values. Note that throughout this paper we examined only the absolute value of β .

At all wavelengths, **OLD-1** and **OLD-2** have nearly identical experimental $\beta_{zzz}(-2\omega;\omega,\omega)$ values, well within experimental error, although **OLD-2** has consistently slightly larger values. This is not always the case for the TLM-derived β values; however, **OLD-1** and **OLD-2** can clearly be considered equivalent in terms of $\beta_{zzz}(0;0,0)$ and $\beta_{zzz}(-\omega;0,\omega)$ as well. This was expected as they have identical active cores with the differences likely arising due to subtle solvatochromic effects from the dissimilar side chains. Comparisons between **OLD-2** and **OLD-3** or **OLD-4**, however, are not as straightforward.

Although the TLM-derived $\beta_{zzz}(0;0,0)$ values are supposed to allow comparison of chromophores with dissimilar absorption characteristic free from resonance effects, it is known that the TLM does not provide accurate results close to resonances.⁴⁶ This is clear from the $\beta_{zzz}(0;0,0)$ values in Table 2 as the values obtained for a given chromophore at different wavelengths should be identical. This makes TLM-derived $\beta_{zzz}(0;0,0)$ and $\beta_{zzz}(-\omega;0,\omega)$ values obtained from experimental data near resonances of questionable accuracy. For example, the $\beta_{zzz}(-\omega;0,\omega)$ value of **OLD-3** ($\lambda_{\max} = 677$ nm) derived from the experimental data at 1300 nm ($2\omega = 650$ nm) is just 0.23 times that of **OLD-2** ($\lambda_{\max} = 746$ nm), while this ratio at 1000 and 1907 nm is 0.89 and 0.92, respectively.

At both 1000 and 1907 nm the contributions to the experimental $\beta_{zzz}(-2\omega;\omega,\omega)$ values from resonance effects are minimized as all chromophores have relatively small molar extinction coefficient (ϵ) values at ω and 2ω (see Figure 2). Although the magnitude of the TLM-derived $\beta_{zzz}(-\omega;0,\omega)$ values at 1000 and 1907 nm does not agree for a given chromophore, the ratios between the chromophores are relatively constant. For example, the ratio of the $\beta_{zzz}(-\omega;0,\omega)$ value of **OLD-4** to that of **OLD-2** is 2.54 and 2.25 at 1000 and 1907 nm, respectively. We have chosen to use the data from 1907 nm for analysis of the EO coefficient as the TLM should be more valid when the operational wavelength (ω) and second harmonic (2ω) are lower energy in energy than the optical transitions of the molecule, as this should limit contributions from high-order excited states.

From the HRS results presented here, using data at select wavelengths away from resonances and using the TLM to convert the data to EO-relevant $\beta_{zzz}(-\omega;0,\omega)$ values, some conclusions are suggested. **OLD-1** and **OLD-2** are around 10% more EO active (at 1310 nm) than **OLD-3**. Although previous research resulted in experimental $\mu\beta(-2\omega;\omega,\omega)$ enhancements (from solution electric-field-induced SHG

experiments) of around 2 times for BEDOT-based chromophores with respect to bithiophene analogs,¹³ there was only a 20% improvement in $\mu\beta(0;0,0)$ values obtained from TLM analysis. Differences in the dipole moments, calculated to be about 8%, based on Gaussian 98 simulations,¹³ further suggest a minimal increase in β for the BEDOT systems. Thus, it is clear that, contrary to the initial hypothesis, the bis(ProDOT)-based systems show only a slight enhancement in EO-relevant β value with respect to their bithiophene analogs. Previous research comparing mono-EDOT- and monothiophene-based EO chromophores implied that the electron-donating effect of the oxygen substituents has a detrimental effect on β .¹³ Together with the HRS data presented here, this suggests that the enhancement in β expected from the increased planarization in bis(ProDOT) and BEDOT systems may be only slightly larger than the decrease due to the electron-donating effect, resulting in slightly larger overall β values. **OLD-4**, however, is 2–2.6 times as EO active as **OLD-1** and **OLD-2**, which is consistent with previous results for the powerful CF₃/Ph-TCF acceptor.⁴⁰ The β values of all the **OLD** chromophores compare favorably with those of the benchmark chromophores EZ-FTC and CLD-5, whose $\beta_{zzz}(-2\omega;\omega,\omega)$ values at 1907 nm are $1100 \pm 600 \times 10^{-30}$ and $1400 \pm 300 \times 10^{-30}$ esu, respectively,⁴⁷ and whose TLM-derived $\beta_{zzz}(0;0,0)$ values are $500 \pm 300 \times 10^{-30}$ and $600 \pm 100 \times 10^{-30}$ esu, respectively.

Electro-optic Coefficient Measurements. In order to evaluate the poling efficiency and EO activity of the **OLD** chromophores, amorphous polycarbonate (APC) guest–host polymer films incorporating these materials were prepared, contact poled, and analyzed via reflection ellipsometry (Teng–Man) at 1310 nm,³² using the corrected formula.³³ Although the Teng–Man technique is subject to significant experimental error, by maintaining sample parameters within the guidelines presented in the literature,³⁴ the error can be limited to $\leq 20\%$. Specifically, the commercial ITO substrates (Abrisa) had complex refractive indices and thicknesses such that $1.4 < n_{\text{ITO}} < 2.0$, $\kappa_{\text{ITO}} < 0.4$, and $d_{\text{ITO}} < 40$ nm, and the polymer films had refractive indices and thicknesses such that $1.5 < n_{\text{film}} < 1.7$ and $d_{\text{film}} > 1.8 \mu\text{m}$ ($> 2.0 \mu\text{m}$ for films with higher chromophore content and refractive index). The measured r_{33} values depend on the chromophore number density (N), $\beta_{zzz}(-\omega;0,\omega)$, and poling efficiency, described by the $\langle \cos^3\theta \rangle$ order parameter, as indicated by²

$$r_{33} \approx \frac{N\beta_{zzz}f\langle \cos^3\theta \rangle}{n^4} \quad (7)$$

where the f term describes electric-field factors and n is the refractive index of the film, both of which remain relatively constant for related chromophores at similar loading densities. In order to facilitate meaningful analysis, the loading densities of the guest–host films are presented in terms of N , assuming the overall density of the films remains that of the APC host (1.15 g/cc, Alridch), which allows normalization of the observed r_{33} values for the chromophore content.

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Table 3. Representative r_{33} Values and Relative Poling Efficiencies of the OLD Chromophores

chromophore	OLD-1	OLD-2	OLD-3	OLD-4
r_{33} (pm/V) ^a	52 ± 10	31 ± 6	17 ± 3	69 ± 14
N^b	2.51	1.59	2.10	2.11
r_{33}/N^c	2.1 ± 0.4	2.0 ± 0.4	0.80 ± 0.1	3.3 ± 0.7
$r_{33}/N\beta_{zzz}(-\omega;0,\omega)^d$	1.9 ± 0.4	1.6 ± 0.3	0.75 ± 0.3	1.2 ± 0.3

^a Experimental value from simple reflection at 1310 nm. ^b Chromophore number density; in units of $\times 10^{20}$ molecules/cc. ^c r_{33} normalized by chromophore number density; in units of $\times 10^{-19}$ pm cc/(V molecules). ^d r_{33} normalized by chromophore number density and TLM-derived $\beta_{zzz}(-\omega;0,\omega)$ at 1310 nm from experimental 1907 nm data; in units of $\times 10^8$ pm cc/(V molecules esu).

The $\beta_{zzz}(-\omega;0,\omega)$ values derived from the experimental $\beta_{zzz}(-2\omega;\omega,\omega)$ values allow further normalization of the r_{33} values for chromophore β , thereby providing an estimation of poling efficiency and allowing comparisons between systems. Thus, the experimental r_{33} values presented in Table 3 are analyzed in this fashion.

Films of **OLD-1** were prepared with 33.3 total chromophore wt %, corresponding to 2.51×10^{20} molecules/cc, and poled between 125 and 140 °C with an electric field of 0.80–1.15 MV/cm for 15 min. The optimized conditions were determined to be 130 °C under an electric field of 1.0 MV/cm, and the resulting r_{33} value was 52 ± 10 pm/V. Dividing the observed r_{33} by N yields a value of $2.1 \pm 0.4 \times 10^{-19}$ pm cc/(V molecules), which effectively normalizes the r_{33} value for the relative chromophore content. Normalizing this adjusted r_{33} value further with the TLM-derived $\beta_{zzz}(-\omega;0,\omega)$ at 1310 nm, from the experimental $\beta_{zzz}(-2\omega;\omega,\omega)$ at 1907 nm, results in a value of $1.9 \pm 0.4 \times 10^8$ pm cc/(V molecules esu), which represents the effective poling efficiency of this chromophore.

Films of **OLD-2** were prepared at 22.1, 35.1, and 52.6 total chromophore wt %, corresponding to 1.59, 2.53, and 3.79×10^{20} molecules/cc, respectively. At 22.1 wt %, the poling conditions were optimized with 15 min of 1.2 MV/cm at 150 °C, resulting in an r_{33} value of 31 ± 6 pm/V. Normalizing this with N yields a value of $2.0 \pm 0.4 \times 10^{-19}$ pm cc/(V molecules), and further normalizing with the TLM-derived $\beta_{zzz}(-\omega;0,\omega)$ at 1310 nm yields a value of $1.6 \pm 0.3 \times 10^8$ pm cc/(V molecules esu). Comparing this value with that of **OLD-1** suggests **OLD-2** has a slightly reduced (~15%) poling efficiency, possibly due to the more rigid nature of the side chain. At 35.1 wt %, poling conditions were not optimized and an r_{33} of just 35 ± 7 pm/V was obtained, yielding a low N -normalized value of $1.4 \pm 0.3 \times 10^{-19}$ pm cc/(V molecules). At 52.6 wt %, the optimized poling conditions of 15 min at 135 °C with 1.0 MV/cm yielded an r_{33} of 62 ± 12 pm/V, corresponding to a N -normalized value of $1.6 \pm 0.3 \times 10^{-19}$ pm cc/(V molecules). This suggests that the optimized poling efficiency of **OLD-2** is somewhat reduced (~20%) at the very high loading density of 52.6 total chromophore wt % relative to that at 21.1 wt %. This may indicate incomplete site isolation from the side functionalization, suggesting further derivatization may be required to eliminate the dipole–dipole interactions. Poling of **OLD-2** was somewhat inconsistent because of electrical shorts that occasionally occurred, particularly at higher loading densities, and attempts to pole

films of 66.6 total chromophore wt % were completely unsuccessful.

Films of **OLD-3** were prepared at 15.0 and 20.0 total chromophore wt %, corresponding to 1.57 and 2.10×10^{20} molecules/cc, respectively, while higher loading densities resulted in poor film quality and electrical shorts. At 15.0 total chromophore wt %, the optimized poling conditions were determined to be 5 min of 1.0 MV/cm at 155 °C and yielded an r_{33} of just 10 ± 2 pm/V, corresponding to a N -normalized value of just $0.65 \pm 0.1 \times 10^{-19}$ pm cc/(V molecules). At 20.0 total chromophore wt %, the optimized conditions of 5 min of 1.0 MV/cm at 145 °C gave an r_{33} of 17 ± 3 pm/V with a N -normalized value of $0.80 \pm 0.1 \times 10^{-19}$ pm cc/(V molecules). Normalizing this latter value further with the TLM-derived $\beta_{zzz}(-\omega;0,\omega)$ at 1310 nm yields a value of $0.75 \pm 0.3 \times 10^8$ pm cc/(V molecules esu). **OLD-2** thus appears to exhibit over twice the poling efficiency of **OLD-3**, at similar total chromophore wt %, in addition to the ~10% improvement in $\beta_{zzz}(-\omega;0,\omega)$.

Films of **OLD-4** were prepared at 32.8 total chromophore wt %, corresponding to 2.11×10^{20} molecules/cc, which were found to have optimized poling conditions of 15 min of 1.15 MV/cm at 130 °C. The resulting r_{33} of 69 ± 14 pm/V can be normalized with N to $3.3 \pm 0.7 \times 10^{-19}$ pm cc/(V molecules) and further normalized with the TLM-derived $\beta_{zzz}(-\omega;0,\omega)$ at 1310 nm to yield a value of $1.2 \pm 0.3 \times 10^8$ pm cc/(V molecules esu). Thus, while the absolute r_{33} of **OLD-4** is larger than that of **OLD-2**, the effective poling efficiency appears to be lower, despite the fact that poling of **OLD-4** was more consistent with lower leakage currents than that of **OLD-2**. One possible explanation for the observed decrease in poling efficiency of **OLD-4** arises from the $\beta_{zzz}(-\omega;0,\omega)$ normalization step; the $\beta_{zzz}(-\omega;0,\omega)$ values derived from the HRS measurements at 1907 suggest that **OLD-4** is 2.3 times as active as **OLD-2**, but the data at other wavelengths suggest that the enhancement may be less. Assuming that **OLD-2** and **OLD-4** have the same poling efficiency as their structures are almost identical, then the ratio of the N -normalized r_{33} values implies the $\beta_{zzz}(-\omega;0,\omega)$ of **OLD-4** is 1.7 times that of **OLD-2**. Alternatively, assuming the $\beta_{zzz}(-\omega;0,\omega)$ of **OLD-4** is twice that of **OLD-2**, as suggested by the average of the HRS results, then the effective poling efficiency value of **OLD-4** becomes $1.4 \pm 0.3 \times 10^8$ pm/(V esu). This suggests the poling efficiencies of the two chromophores may indeed be different. While the small structural differences between **OLD-2** and **OLD-4** likely have little effect on the sterics of poling, it may have a larger influence on the electrostatics of it. **OLD-4** is expected to have a larger dipole moment (μ) than **OLD-2** because of the stronger electron-accepting strength of the CF₃/Ph-TCF acceptor. Although the bis(ProDOT)-based chromophores were designed to minimize intermolecular dipole–dipole interactions, it is possible that the increased μ overcomes the site isolation to some extent in the case of **OLD-4**. In order to conclusively determine the relative contributions of β and poling efficiency to the r_{33} values obtained for **OLD-2** versus **OLD-4**, further investigation is necessary.

The EO coefficient measurements clearly indicate that the bis(ProDOT)-based chromophores show significant improvements in r_{33} as compared to the bithiophene control **OLD-3**. These relatively large r_{33} values for simple guest–host systems clearly indicate the potential of these materials for EO applications. Furthermore, these results suggest that the bis(ProDOT)-based chromophores exhibit significantly enhanced poling efficiencies with respect to **OLD-3**, in support of the 2,2'-substituted bis(ProDOT)-induced site-isolation effect hypothesis. At comparable total chromophore wt %, **OLD-2** exhibits over twice the poling efficiency of **OLD-3** and **OLD-1** exhibits over twice the poling efficiency of **OLD-3** at similar N . It appears, however, that site isolation of the bis(ProDOT)-based chromophores may be incomplete, as films of **OLD-2** with very high loading densities suffer from reduced poling efficiencies. Similarly, the increased μ from the stronger acceptor in **OLD-4** may also result in reduced poling efficiencies due to incomplete site-isolation. This suggests that larger side-chains might be desirable in order to enhance the site isolation for stronger CF₃/Ph-TCF-containing chromophores. It should be noted, however, that the loading densities investigated here, up to 33.3 and 52.6 total chromophore wt %, are extremely large for guest–host systems, which usually show significantly lower r_{33} values at such high loading densities as compared to lower levels of loading.^{1,5,9} Clearly, the side-chains are effective in shielding dipole–dipole interactions and preventing aggregation even with small amounts of polymer host. This further suggests that future bis(ProDOT)-based chromophores with larger side-chains might be able avoid using the polymer host entirely by forming amorphous organic glasses,^{28,48} driving up the ratio of active chromophore mass to total mass of the film while still maintaining excellent poling efficiency due to effective site isolation.

The temporal stability of EO activity in a poled film of **OLD-2** in APC (52.6 total chromophore wt %) was tested at 85 °C, and the results are compared in Figure 3 to literature values for the benchmark chromophore AJL8 at 20 total chromophore wt % in APC.⁴⁹ After 528 h at 85 °C, the **OLD-2**/APC sample retains 94% of the initial r_{33} value, while the AJL8/APC sample retains just 80% over the same time frame. One possible explanation for the excellent thermal stability of **OLD-2** is that the centrally located 3D side chains on the backbone of the chromophore may have strongly entangled with the polymer host upon cooling the film from its poling temperature, which, combined with the effective disruption of dipole–dipole interactions due to site isolation, prevented relaxation of the alignment.

Photostability Measurements. In order to evaluate the potential applicability of these materials to device applications, where the materials must be stable under long-term exposure to IR radiation, we examined the photostability of

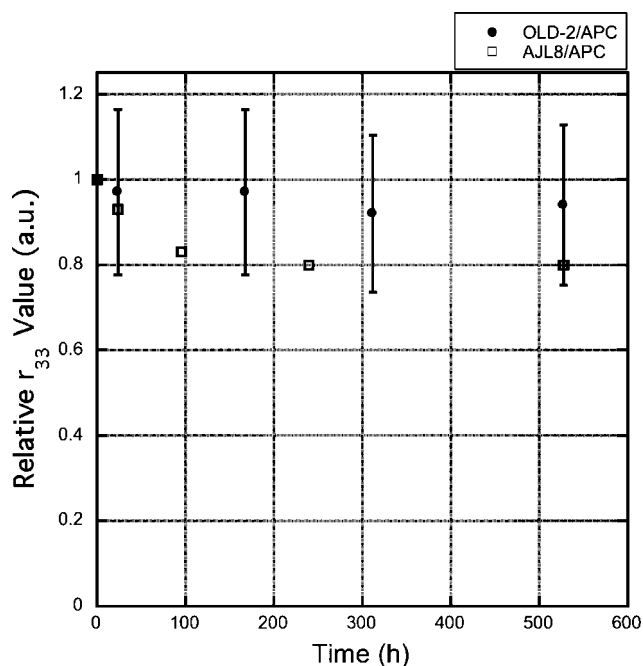


Figure 3. Temporal stability of EO coefficient at 85 °C: **OLD-2**/APC (●), and AJL8/APC (□, unspecified error).⁴⁹

Table 4. Photostability Figures of Merit for **OLD-2** and Benchmark Chromophores

sample	B/σ^a	$(B/\sigma)_1^b$ (% contribution) ^c	$(B/\sigma)_2^d$ (% contribution) ^c
OLD-2 in APC	13 ± 3	2 ± 1 (45%)	22 ± 14 (55%)
CLD-1 in APC ^e	3.2 ± 0.6	0.5 ± 0.4 (58%)	4 ± 3 (42%)
FTC in APC ^e	7.2 ± 0.7	1.0 ± 0.1 (40%)	6 ± 1 (60%)

^a “Linear” photostability FOM; in units of $\times 10^{32} \text{ m}^{-2}$. ^b Fast decay photostability FOM; in units of $\times 10^{32} \text{ m}^{-2}$. ^c Percent contribution of the decay pathway to the overall decay profile. ^d Slow decay photostability FOM; in units of $\times 10^{32} \text{ m}^{-2}$. ^e From refs 36 and 50.

a representative bis(ProDOT)-based chromophore. We chose **OLD-2** as it has one of the largest r_{33} values of the **OLD** series and has similarities to both **OLD-1** and **OLD-4**. The transmission at 635 nm of **OLD-2** in APC films on optical fibers was recorded as a function of exposure time to a 1550 nm fiber laser in order to monitor decomposition of the chromophore. We calculated the B/σ photostability FOM (a combination of B^{1-} , the photodegradation quantum efficiency, and σ , the absorption cross-section, both at 1.55 μm) widely reported in the literature using a single-exponential photodegradation model previously reported.³⁵ We found, however, that the single-exponential decomposition model is only valid for the initial decay (~ 300 min) of the EO film and that the full photodegradation profile is more complicated. It can be adequately fit using a more complex photodegradation model that was recently reported in the literature,³⁶ which produces two FOM values, one for the fast initial and one for the slower long-term decay, and describes the relative contribution of the two pathways to the overall degradation profile. We present the results of both photodegradation models for **OLD-2** in Table 4, along with the values obtained for benchmark chromophores FTC and CLD-1, also in APC.^{36,50} It is clear from both models that **OLD-2** is considerably more stable than the benchmark chromophores. Although the chemical nature of the two

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decay pathways is not well understood,^{36,50} from the complex model we can see that **OLD-2** is only slightly more stable than FTC and CLD-1 with regard to the fast decay pathway. The contribution of the fast pathway to the overall decomposition is slightly greater for **OLD-2** than FTC, however, although it is significantly less than that for CLD-1. In terms of the slow decay pathway, **OLD-2** is significantly more stable than FTC and CLD-1, even accounting for the relative contributions. These results, combined with the excellent temporal alignment stability demonstrated, could translate into reduced long-term drift in the drive voltage of devices.

Conclusions

The bis(ProDOT) bridge is ideally suited to EO applications due to it is highly planar π -conjugated system, inherent 3D architecture, synthetic versatility, and high degree of thermal and photochemical stability. The bis(ProDOT) bridge results in only a modest improvement of $\sim 10\%$ in $\beta_{zzz}(-\omega;0,\omega)$ at 1310 nm over the bithiophene bridge, though modification of chromophore shape and nuclear repulsive (steric) effects results in over twice the poling efficiency in guest–host systems at comparable and even higher film loading densities. Incorporation of the powerful $\text{CF}_3/\text{Ph-TCF}$ acceptor results in a $\beta_{zzz}(-2\omega;\omega,\omega)$ of $5700 \pm 400 \times 10^{-30}$

esu at 1907 nm and a $\beta_{zzz}(-\omega;0,\omega)$ at 1310 nm approximately twice that of comparable TCF-based chromophores. Apparently, incorporation of the $\text{CF}_3/\text{Ph-TCF}$ acceptor also results in a reduced poling efficiency possibly due to increased μ , and further functionalization to enhance the site-isolation effect and allow formation of polymer-free organic glasses presents an attract avenue of future research. Regardless, large r_{33} values (52–69 pm/V) are obtained for the bis(ProDOT)-based chromophores at high loading densities (33.3–52.6 total chromophore wt %), suggesting significant site isolation. The long-term temporal stability of the r_{33} value, 94% after over 500 h at 85 °C, and the excellent photochemical stability as compared to benchmark chromophores suggest these materials have practical application to EO devices.

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Supporting Information Available: Synthetic procedures and spectrometric characterization data for all new compounds prepared in this work. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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