

# Nonlinear optical properties of push-pull polyenes for electro-optics

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Improved nonlinear organic chromophores of varying conjugation length with either thiobarbituric acid or 3-dicyanomethylene-2,3-dihydrobenzothiophene-1,1-dioxide (FORON<sup>®</sup> Blue) acceptors have been synthesized and investigated for their nonlinear optical properties. Very large quadratic hyperpolarizabilities  $\beta(-2\omega; \omega, \omega)$  have been found, up to  $25,700 \times 10^{-48}$  esu at  $\lambda = 1.91 \mu\text{m}$ . In a guest-host polymer very high electro-optic (EO) coefficients, of up to 55 pm/V, have been determined at  $\lambda = 1.31 \mu\text{m}$  with 20-wt % chromophore loading. We find good agreement between molecular parameters evaluated by electric-field-induced second-harmonic generation (EFISH) and the measurements of guest-host solid-solid solutions. The latter method is well suited to the determination of the product of dipole moment  $\mu$  and hyperpolarizability  $\beta$  quickly and reliably at the wavelength of interest for EO applications without the complications associated with EFISH measurements. © 1996 Optical Society of America.

## 1. INTRODUCTION

Recently, rational design criteria and systematic investigations have led to the development of novel nonlinear optical (NLO) chromophores with greatly enhanced molecular hyperpolarizabilities and good thermal stabilities.<sup>1-4</sup> Compared with the de facto standards disperse red and diamino nitro stilbene, the relevant nonlinear parameter  $\mu\beta(-\omega; \omega, 0)$  is increased by up to more than 20-fold. Therefore the novel chromophores have the potential to increase the electro-optic (EO) coefficient of polymeric materials much above the present level of 30 pm/V found in state-of-the-art devices (either polymers or inorganic materials like LiNbO<sub>3</sub>) at the wavelength of interest (1.3 or 1.5  $\mu\text{m}$ ).

A substantial increase of the EO  $r$  values is needed for the design of integrated optical modulators and switches. Besides possessing high nonlinearity, NLO chromophores should be thermally and photochemically stable and have low optical loss at the operating wavelength. In addition, it should be possible to incorporate these molecules as

main-chain or side-chain elements into a polymeric matrix to produce a temporally stable nonlinear system.

In this paper we present results of synthesis as well as optical and NLO characterization of different series of chromophores that have been designed according to criteria outlined by Ref. 1. These push-pull chromophores use electron-donor-substituted aromatic rings connected by a  $\pi$ -electron conjugation bridge (charge-transfer system) to an electron-acceptor group. To enhance the nonlinearity of the molecule, one must optimize the strength of the donor and the acceptor for a given conjugation bridge. In our case an alkylamino donor is used together with either thiobarbituric acid or 3-dicyanomethylene-2,3-dihydrobenzothiophene-1,1-dioxide (FORON<sup>®</sup> Blue<sup>5,6</sup>) acceptors and electron conjugation bridges of varying length. In the following the chromophores will be referred to as TBA if they contain a thiobarbituric acid acceptor and FB if they contain a FORON<sup>®</sup> Blue acceptor.

The NLO molecules are characterized as guest-host systems at  $\lambda = 1.31 \mu\text{m}$  by ellipsometric methods, allowing for the determination of the EO  $r$  coefficient. From

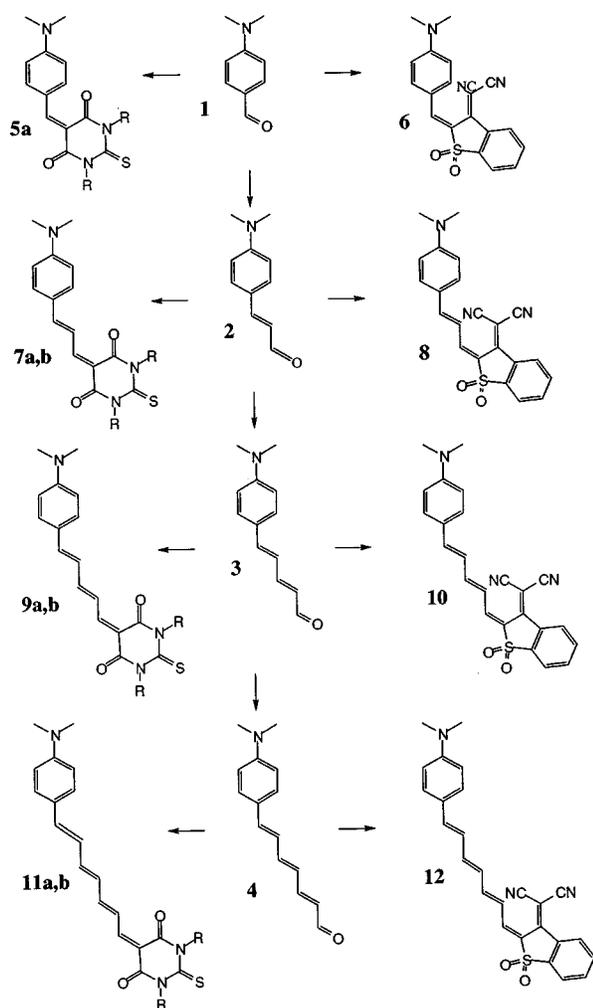


Fig. 1. Structure and route of synthesis of push-pull polyenes with thiobarbituric acid (TBA) and 3-dicyanomethylene-2,3-dihydrobenzothiophene-1,1-dioxide (FB) acceptors. R denotes  $C_2H_5$  (5a),  $C_2H_5$  (7a),  $C_6H_5$  (7b),  $C_2H_5$  (9a),  $C_6H_5$  (9b),  $C_2H_5$  (11a), and  $C_6H_5$  (11b).

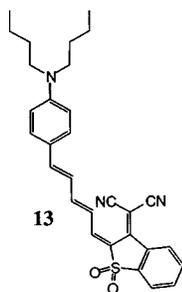


Fig. 2. Highly soluble di-*n*-butyl analog of molecule 10 in Fig. 1.

the  $r$  coefficients we deduce the nonlinear molecular parameters  $\mu\beta(-\omega; \omega, 0)$  and compare them with electric-field-induced second-harmonic generation (EFISH) measurements<sup>7</sup> at the wavelength of  $1.91 \mu\text{m}$ . The agreement between both techniques is good, and we argue that the EO technique is an alternative that is well suited for the characterization of NLO chromophores, alleviating some

of the common problems associated with EFISH. The use of EFISH for the determination of the relevant molecular parameter  $\mu\beta(-\omega; \omega, 0)$  is hampered by several difficulties and drawbacks. First, this method needs a calibration standard (normally  $d_{11}$  of quartz), of which different values from the literature are in use.<sup>8</sup> Second, the EFISH signal has an electronic contribution arising from the second-order hyperpolarizability  $\gamma^e$ . For extended molecules this contribution can be significant, and without an independent measurement of  $\gamma^e$  it is difficult to correct for this effect.<sup>9</sup> Third, the data need to be corrected for dispersion and resonance effects. Finally, when converting to the  $r$  value, one has to deal with several inconsistencies as pointed out by Willetts *et al.*<sup>10</sup> EO measurements of the kind described in this work can circumvent some of these problems. They give the essential quantity, i.e., the relevant EO coefficient at the wavelength of interest. However, possible problems with the use of guest-host systems should be kept in mind, which include insolubility and aggregation problems and possible sublimation during the curing and poling cycles. For thermally sensitive chromophores the method might not be usable at all, as the sample has to be heated up close to the glass transition temperature of the guest-host system.

Compared with the often used Azo chromophore DR1, the chromophores described in this work have nonlinear molecular parameters  $\mu\beta(-\omega; \omega, 0)$  as much as 24 times higher. In a guest-host system with 20-wt % chromophore loading we measured an EO coefficient of  $55 \text{ pm/V}$  at  $\lambda = 1.31 \mu\text{m}$  for one chromophore.

## 2. EXPERIMENT

### A. Structures and Synthesis

The NLO chromophores bearing thiobarbituric acids<sup>1,11</sup> or 3-dicyanomethylene-2,3-dihydrobenzothiophene-1,1-dioxide (FORON<sup>®</sup> Blue) were prepared by standard Knoevenagel reactions from the corresponding aldehydes and diethyl or diphenyl thiobarbituric acid or 3-dicyanomethylene-2,3-dihydrobenzothiophene-1,1-dioxide,<sup>12</sup> as shown in Fig. 1. The extended dimethylaminophenyl-substituted aldehydes 3 and 4 were prepared from dimethylaminocinnamic aldehyde 2 by means of a Wittig homologation reaction as described by Spangler and McCoy.<sup>13</sup> Molecule 13 (Fig. 2) is a highly soluble di-*n*-butyl analog of 10. The detailed synthetic procedures and the characterizing data are left out of this paper.

Initially, EO experiments were performed on solid solutions containing the chromophore Azo 1 and on a side-chain polymer containing the same chromophore at 56

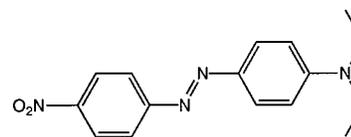


Fig. 3. Structure of the chromophore Azo 1.

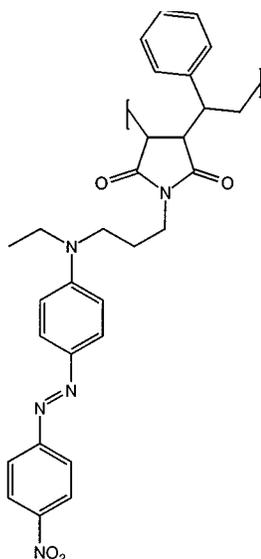


Fig. 4. Structure of the side-chain polymer containing Azo chromophores.

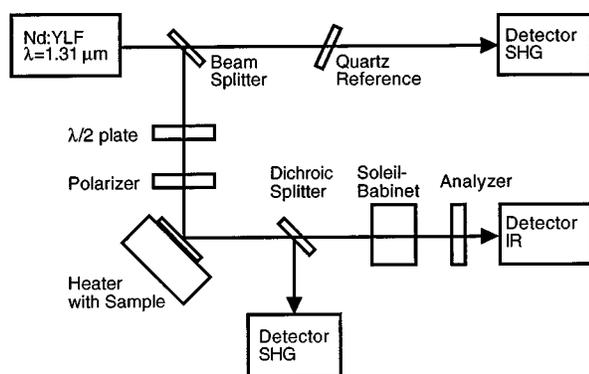


Fig. 5. Experimental setup for the electro-optic (EO) characterization of guest–host films.

wt %. The structures of these two compounds are given in Figs. 3 and 4, respectively. The detailed synthetic procedures of the side-chain polymer are given in Ref. 14.

### B. Electro-Optic Measurements

For the determination of the EO coefficients thin films of chromophore guest–host solid solutions of different concentrations were prepared by spin coating onto glass substrates coated with indium tin oxide from a solution of chromophores dissolved in a mixture of tetrachloroethane and polycarbonate (PC) (Lexan<sup>®</sup> LS1, GE Plastics Corp., Amsterdam, The Netherlands). Before spin coating, the solutions were filtered through 0.1- $\mu\text{m}$  polyamide filters. The samples of typically 2- $\mu\text{m}$  thickness were poled by electrode poling close to or slightly above the glass transition temperature of the film. For optimization of the poling process it was monitored by second-harmonic generation (SHG), as shown in Fig. 5. A diode-pumped Nd:YLF laser ( $\lambda = 1.31 \mu\text{m}$ ) was used as the fundamental source. The sample was mounted at an

angle of  $45^\circ$  with respect to the beam direction. The gold electrode on top of the film was used as a contact for application of the electric field and as a mirror for the laser beam to allow for observation of the SHG signal and the EO measurements. Modulated ellipsometry<sup>15</sup> was used for the determination of the EO coefficients. The dichroic mirror after the sample allows one to observe SHG (pulsed-laser operation) and EO response (cw laser operation) without changing the setup.

For a poling cycle an electric poling field of typically  $100 \text{ V}/\mu\text{m}$  was applied, and the temperature of the film was ramped up until the SHG signal saturated. This took place close to the glass transition temperature  $T_g$  of the polymer.  $T_g$  depends on the host and on the chromophore and its concentration and for the investigated samples was between  $120^\circ\text{C}$  and  $140^\circ\text{C}$ . Then the film was cooled down to room temperature, the electric field was switched off, and the EO measurement was carried out at a modulation frequency of 4 kHz. To minimize possible chromophore degradation and sublimation of the chromophore out of the polymer host, we kept the poling cycles as short as possible (less than 10 min). In order to detect possible degradation and sublimation, we routinely checked the absorption of the films before and after poling and EO measurement. The concentration of the chromophore in the polymer host was calibrated prior to poling by comparison with solution spectra.

### C. Electric-Field-Induced Second-Harmonic Generation Measurements

The quadratic hyperpolarizability of each compound was determined with the EFISH experiment.<sup>16–18</sup> The light source was a  $Q$ -switched Nd:YAG laser operating at  $1.064 \mu\text{m}$ . This initial wavelength was Raman shifted to  $1.9 \mu\text{m}$  with the use of a high-pressure hydrogen cell. The wedge cell technique was used, and the molecules in the solution are partially aligned by a dc electric field for the induction of noncentrosymmetry. The solvent used was dichloromethane ( $\text{CH}_2\text{Cl}_2$ ). The measurements were calibrated relative to a quartz wedge whose quadratic susceptibility was taken equal to  $d_{11} = 1.1 \times 10^{-9} \text{ esu}$  at  $1.9 \mu\text{m}$  (corresponding to  $0.46 \text{ pm/V}$ ).

The mean microscopic hyperpolarizability  $\gamma^0$  can be derived from the EFISH measurements:

$$\gamma^0 = \gamma^e(-2\omega; \omega, \omega, 0) + \frac{\mu\beta(-2\omega; \omega, \omega)}{5kT}, \quad (1)$$

where  $\omega$  is the fundamental pulsation and  $\beta(2\omega)$  [shorthand notation for  $\beta(-2\omega; \omega, \omega)$ ] is the vector part of the  $\beta_{ijk}(2\omega)$  tensor,

$$\beta_i(2\omega) = \sum_j \beta_{ijj}(2\omega). \quad (2)$$

The electronic part  $\gamma^e(-2\omega; \omega, \omega, 0)$  has not been determined experimentally for the series of molecules presented in this study. In a different study<sup>19</sup> this has been done for a series of push–pull polyenes of increasing size with up to eight double bonds by coupling EFISH and third-harmonic generation experiments. Based on these results, we estimate an error of less than 30% by neglect-

**Table 1. Results of Electro-Optical (EO) Measurements on Guest–Host Films Containing the Chromophore Azo 1 and Comparison with EO Measurements on the Azo-Containing Side-Chain Polymer ( $\lambda = 1.31 \mu\text{m}$ )**

Host	Guest–Host Polymer (solid solutions of Azo 1)			pSMA <sup>a</sup> Side-Chain Polymer Containing 56 wt % Azo ( $E = 150 \text{ V}/\mu\text{m}$ )	
	Concentration (wt %)	Poling Field ( $\text{V}/\mu\text{m}$ )	$r_{33}$ Measured ( $\text{pm}/\text{V}$ )	$r_{33}$ Scaled to 56 wt % ( $E = 150 \text{ V}/\mu\text{m}$ ) ( $\text{pm}/\text{V}$ )	$r_{33}$ Measured ( $\text{pm}/\text{V}$ )
pSMA	8.4	95	$1.9 \pm 0.4$	$20 \pm 4$	
pSMA	11.3	190	$4.8 \pm 0.6$	$19 \pm 2$	$20 \pm 1$
pc	9.5	100	$2.4 \pm 0.2$	$21 \pm 2$	

<sup>a</sup>Poly(styrene-alt-maleic anhydride).

ing the electronic part for compounds 11a, 11b, and 12. For the other compounds this error should be less than 10%.

### 3. RESULTS AND DISCUSSION

#### A. Electro-Optic Method for the Characterization of Electro-Optic Chromophores

For the evaluation of chromophores for EO applications we chose EO measurements on solid solutions because this experimental technique is simpler than EFISH in terms of equipment and yields directly the relevant molecular parameter of interest. In order to evaluate the suitability of the EO method, we first tested the chromophore Azo 1 (Fig. 3), which is similar to the well-known dye disperse red DR1. EO measurements of guest–host polymers with Azo 1 dissolved in PC or poly(styrene-alt-maleic anhydride) (pSMA) as host were compared with results obtained earlier from a side-chain polymer containing the same chromophore (Fig. 4). Because of the high chromophore loading (56 wt %), this side-chain polymer exhibits high NLO effects.<sup>14,20,21</sup>

For the polymers the EO response at frequency  $\omega$  is given by<sup>7,20</sup>

$$r_{33} = 2Nf \frac{\mu\beta(-\omega; \omega, \omega, 0)}{5kTn^4} E, \quad (3)$$

where  $N$  is the number density of the dissolved chromophores,  $E$  is the poling field,  $T$  is the poling temperature,  $k$  is the Boltzmann factor, and  $n$  is the index of refraction of the film. The factor  $f$  contains the local-field corrections. In order to compare the guest–host results with the side-chain results, we scaled the  $r_{33}$  values of the guest–host polymers linearly, according to Eq. (3), to the poling field and to the chromophore density (weight percent) of the side-chain polymer. Scaling the  $r_{33}$  values with respect to weight percent has been chosen because it delivers data that are relevant for practical applications. On account of different polymer densities, errors could be introduced. However, the difference among the polymer densities lies within the error limit of the EO experiment ( $\rho_{\text{pSMA}} = 1.45 \pm 0.03 \text{ g}/\text{cm}^3$ ,  $\rho_{\text{PC}} = 1.35 \pm 0.03 \text{ g}/\text{cm}^3$ ,  $\rho_{\text{pSMA side chain}} = 1.40 \pm 0.03 \text{ g}/\text{cm}^3$ ). The results of the

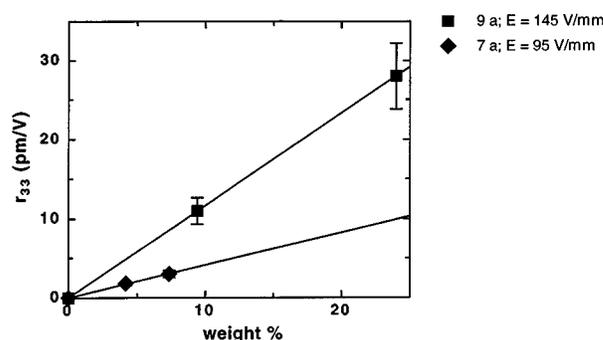


Fig. 6. EO coefficient at  $\lambda = 1.313 \mu\text{m}$  versus chromophore loading of polycarbonate (PC) guest–host polymers.

comparison are given in Table 1. The scaled  $r_{33}$  values of the guest–host systems correspond well with the 20  $\text{pm}/\text{V}$  of the side-chain polymer.

The good correspondence between the  $r_{33}$  values of the guest–host and the side-chain system implies that scaling of the electric field and concentration within the limits employed with the two systems are possible. However, this need not be the case with other guest–host or side-chain systems. In order to validate the EO method for the measurement of molecular parameters, one should check for linearity with the chromophore concentration and the electric field within the measurement range.

Figure 6 shows the EO coefficient  $r_{33}$  versus chromophore concentration for the chromophores 7a ( $\text{TBA}_{n=1}$ ) and 9a ( $\text{TBA}_{n=2}$ ). High chromophore concentrations of up to 24 wt % could be dissolved in PC, resulting in the very high EO values of 28  $\text{pm}/\text{V}$  at a poling field strength of 145  $\text{V}/\mu\text{m}$ . Within the range considered we observe a linear concentration relation of the EO coefficient.

According to Eq. (3), the  $r_{33}$  value depends on the refractive index of the polymer. The variation of the refractive index with the chromophore concentration is relatively weak and varies from 1.65 for the unloaded PC film up to 1.76 for a PC film loaded with 56 wt % of the dye Azo 1 (measured at  $\lambda = 1.31 \mu\text{m}$ ). For chromophore concentrations of up to 24 wt % this change of the refractive index would result in less than a 15% variation of the  $r_{33}$  value, which lies within the error limit of the EO experi-

ment. Thus, for the evaluation of the  $r_{33}$  values, this change of the refractive index has been neglected. Maximum poling field strengths of the order of 150 V/ $\mu\text{m}$  could be applied before dielectric breakdown occurred during contact electrode poling.

Figure 7 demonstrates the good linearity of  $r$  as a function of the applied field for a sample of 11-wt %  $\text{FB}_{n=0}$  dissolved in PC.

These results suggest that it should be possible to use guest–host systems as a simple and straightforward method to assess the EO potential of chromophores. Especially, it is possible to evaluate the relevant molecular parameter  $\mu\beta(-\omega; \omega, 0)$  directly according to Eq. (3).

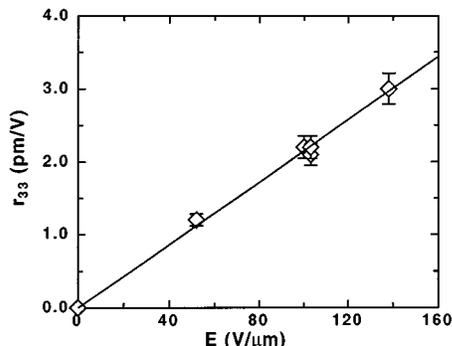


Fig. 7. EO coefficient versus poling field  $E$  of a guest–host polymer (11-wt % of molecule 6 dissolved in PC, with  $\lambda = 1.313 \mu\text{m}$ ).

## B. Optical Properties of Thiobarbituric Acid- and FORON<sup>®</sup> Blue-Substituted Polyenes

In this subsection we detail the results of EO and EFISH measurements. Typically, for a given molecule, several EO measurements have been performed on different concentrations and poling fields. In Table 2 the highest achieved  $r$  values of the guest–host films containing the TBA- and FB-substituted polyenes are given. Chromophore concentrations between 0.76 and 24 wt % in PC have been used at poling fields of up to 151 V/ $\mu\text{m}$ . Because of considerable variation in concentration and applicable poling fields, we obtain  $r$  values between 1 and 55 pm/V. The highest values have been measured for compound 13, which is a  $\text{FB}_{n=2}$  molecule, specifically designed for high solubility. The value of 55 pm/V is remarkably high for a guest–host polymer.

The results of the EO measurements of the TBA series are given in Table 3. In order to compare the results with molecular data, we list in Table 3 the EO data together with molecular nonlinearities determined by EFISH. For consistency of the data the values of the EO measurements have been normalized to a chromophore concentration of 10 wt % and an electric poling field of 100 V/ $\mu\text{m}$ . The normalized  $r$  values given in Table 3 are averaged results of several measurements on different samples with varying guest concentrations.

The  $r_{33}$  values increase from 1.5 to 14 pm/V with increasing conjugation length (double bonds  $n = 0$  through

**Table 2. Measured  $r$ -Values of PC–Guest–Host Thin Films Measured at  $\lambda = 1.31 \mu\text{m}$ <sup>a</sup>**

	Guest–Molecule											
	$\text{FB}_{n=0}$ 6	$\text{FB}_{n=1}$ 8	$\text{FB}_{n=2}$		$\text{FB}_{n=3}$ 12	$\text{TBA}_{n=0}$ 5	$\text{TBA}_{n=1}$		$\text{TBA}_{n=2}$		$\text{TBA}_{n=3}$	
			10	13			7a	7b	9a	9b	11a	11b
Concentration (wt %)	10	1.6	9.3	20	0.76	10	7.4	2.9	24	3.2	9.4	2.4
$E$ (V/ $\mu\text{m}$ )	71	150	151	150	100	71	97	122	147	95	35	87
$r_{33}$ (pm/V)	1.0	1.5	21	55	2.8	1.0	3.0	1.2	28	2.5	4.4	2.4

<sup>a</sup>The values are given for samples with the highest chromophore concentration and the maximum poling fields that could be applied.

**Table 3. Nonlinear Optical Properties of Polyenes with Thiobarbituric Acid (TBA) as Acceptor**

Molecule	Conjugation Length	R	$M$	EO in Guest–Host Polymers (TBA in PC)						EFISH	
				$\lambda_{\text{max}}$ (nm)	No. of Samples	$r_{33}$ <sup>a</sup> Scaled to 10 wt % and $E = 100$ V/ $\mu\text{m}$ (pm/V)	$\mu\beta(-\omega; \omega, 0)$ <sup>b</sup> Relative to Molecule 7a	$\mu\beta(2\omega; \omega, \omega)$ ( $10^{-48}$ esu)	$\lambda_{\text{max}}$ (nm)	$\mu\beta(-\omega; \omega, 0)$ <sup>c</sup> Relative to Molecule 7a	
5a	$n = 0$	$\text{C}_2\text{H}_5$	331	490	2	$1.3 \pm 0.5$	0.28	370 <sup>e</sup>	484	0.22	
7a	$n = 1$	$\text{C}_2\text{H}_5$	357	570	5	$4.4 \pm 0.5$	(1)	1780 <sup>d</sup>	572	(1)	
7b	$n = 1$	$\text{C}_6\text{H}_5$	454	575	2	$3.3 \pm 0.5$	0.95	—	—	—	
9a	$n = 2$	$\text{C}_2\text{H}_5$	384	600	3	$8.8 \pm 2$	2.2	3950 <sup>e</sup>	604	2.1	
9b	$n = 2$	$\text{C}_6\text{H}_5$	480	610	2	$8.3 \pm 2$	2.6	—	—	—	
11a	$n = 3$	$\text{C}_2\text{H}_5$	410	610	3	$14 \pm 2$	3.7	9830 <sup>e</sup>	624	5.1	
11b	$n = 3$	$\text{C}_6\text{H}_5$	506	630	2	$12 \pm 2$	3.9	—	—	—	

<sup>a</sup> Measured at  $\lambda = 1.31 \mu\text{m}$ .

<sup>b</sup> Calculated for  $\lambda = 1.31 \mu\text{m}$  from  $\mu\beta(-2\omega; \omega, \omega)$ .

<sup>c</sup> From Ref. 1; measured at  $\lambda = 1.91 \mu\text{m}$ , solvent is chloroform, reference is  $d_{11}(\text{quartz}) = 0.5 \text{ pm/V}$ .

<sup>d</sup> Measured at  $\lambda = 1.91 \mu\text{m}$ , solvent is  $\text{CH}_2\text{Cl}_2$ , reference is  $d_{11}(\text{quartz}) = 0.46 \text{ pm/V}$ .

**Table 4. Nonlinear Optical Properties of Novel Polyenes with 3-Dicyanomethylene-2,3-Dihydrobenzothiophene-1,1-Dioxide (FB) as Acceptor**

Molecule	Conjugation Length	$M$	EO in Guest-Host Polymers (FB in PC)				EFISH			
			$\lambda_{\max}$ (nm)	No. of Samples	$r_{33}^a$ Scaled to 10 wt % and $E = 100 \text{ V}/\mu\text{m}$ (pm/V)	$\mu\beta(-\omega; \omega, 0)^a$ Relative to Molecule 7a	$\mu\beta(2\omega; \omega, \omega)^b$ ( $10^{-48}$ esu)	$\lambda_{\max}$ (nm)	$\mu\beta(-\omega; \omega, 0)^c$ Relative to Molecule 7a	
6	$n = 0$	361	592	2	$1.5 \pm 0.5$	0.35	1070	585	0.59	
8	$n = 1$	387	680	5	$6.5 \pm 0.5$	1.6	3300	672	1.7	
10	$n = 2$	414	720	4	$14 \pm 2$	3.7	10 500	732	4.6	
13	$n = 2$	497	750	2	$18 \pm 3$	5.7	13 500	772	5.2	
12	$n = 3$	440	750	2	$38 \pm 7$	11	25 700	742	11	

<sup>a</sup> Measured at  $\lambda = 1.31 \mu\text{m}$ .

<sup>b</sup> Measured at  $\lambda = 1.91 \mu\text{m}$ , solvent is  $\text{CH}_2\text{Cl}_2$ , reference is  $d_{11}(\text{quartz}) = 0.46 \text{ pm/V}$ .

<sup>c</sup> Calculated for  $\lambda = 1.31 \mu\text{m}$  from  $\mu\beta(-2\omega; \omega, \omega)$ .

$n = 3$ ). The  $\mu\beta(-\omega; \omega, 0)$  values in Table 3 have been obtained by dividing the  $r$  values by the molecular mass  $M$  and normalizing relative to the value of the  $\text{TBA}_{n=1}$  chromophore (molecule 7a). The nonlinearity parameter  $\mu\beta(-\omega; \omega, 0)$  of the  $\text{TBA}_{n=3}$  chromophore is  $\sim 3.7$  times higher than the  $\text{TBA}_{n=1}$  value. The increase of  $\mu\beta(-\omega; \omega, 0)$  is slightly larger for the diphenyl-substituted form of TBA. Because of the larger molecular mass, however, the EO coefficients are larger for the diethyl TBA. The increase in nonlinearity is accompanied by a shift of the absorption maximum from 500 nm for  $n = 0$  to 610 nm for  $n = 3$ .

The results of the FB series in Table 4 show a further enhancement of the nonlinearity-dipole product. With extended conjugation length the normalized EO coefficient increases to 38 pm/V for  $n = 3$ . Relative to molecule 7a, we observe  $\mu\beta(-\omega; \omega, 0)$  values that are up to 11 times higher. The FB chromophores have a higher absorption red shift than do the TBA chromophores, with absorption maxima between 610 and 750 nm.

The results of both groups of chromophores are summarized in Fig. 8, where the relative  $\mu\beta(-\omega; \omega, 0)$  values are displayed in a log-log plot versus the absorption maximum  $\lambda_{\max}$ . In this figure the  $\mu\beta(-\omega; \omega, 0)$  values are normalized to the value of Azo 1, which was found to be 50% of the value for molecule 7a. For both groups the nonlinearity increases strongly with conjugation length (or wavelength), as is observed for other donor-acceptor-substituted charge-transfer molecules.<sup>9</sup> For a given conjugation length  $n$  the absorption maximum of the FB-substituted chromophores is almost 100 nm shifted toward the infrared, compared with the absorption maximum of their TBA-substituted counterparts. For  $n = 1, 2, 3$  this absorption shift is accompanied with a higher nonlinearity of the FB-substituted chromophores relative to the TBA-substituted ones. This holds even for the static  $\mu\beta(0)$  values, calculated with the two-level model. Thus the higher nonlinearity of the FB chromophores relative to the TBA chromophores for a given conjugation length  $n$  is not due only to resonance enhancement.

In order to compare the EO results with independent measurements and to validate the EO technique, we had performed EFISH measurements as well. The EFISH results for the FB series are listed in Table 4. For the

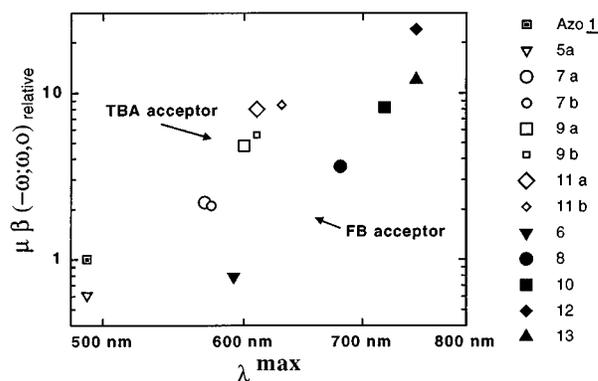


Fig. 8. Log-log plot of  $\mu\beta(-\omega; \omega, 0)$  versus absorption maximum  $\lambda_{\max}$ . All data are from EO measurements at  $\lambda = 1.313 \mu\text{m}$  and normalized to the value of the chromophore Azo 1.

TBA series in Table 3 we give EFISH data from literature. To compare EFISH data with the EO measurements, we corrected for dispersion and calculated the molecular parameter  $\mu\beta(-\omega; \omega, 0)$  relative to molecule 7a with the relation

$$\mu\beta(-\omega; \omega, 0)_{\text{relative}} = \frac{\mu\beta(-2\omega; \omega, \omega)}{(\mu\beta)^{7a}(-2\omega; \omega, \omega)} f_{\text{EO}} f_{\text{EFISH}}. \quad (4)$$

The factors  $f_{\text{EO}}$  and  $f_{\text{EFISH}}$  take into account the dispersion of the EO and EFISH values, respectively, and are for EO given by<sup>7,20</sup>

$$f_{\text{EO}} = \frac{[1 - (\lambda_{\max, \text{PC}}^{7a})^2/\lambda^2]^2}{3 - (\lambda_{\max, \text{PC}}^{7a})^2/\lambda^2} \frac{3 - \lambda_{\max, \text{PC}}^2/\lambda^2}{[1 - (\lambda_{\max, \text{PC}})^2/\lambda^2]^2}. \quad (5)$$

In this equation  $\lambda_{\max, \text{PC}}$  is the absorption maximum of the chromophore in the PC host, and  $\lambda = 1.31 \mu\text{m}$  is the laser wavelength used in the EO experiment.

For EFISH the dispersion correction is given by<sup>22,23</sup>

$$f_{\text{EFISH}} = \frac{1 - (\lambda_{\max, \text{solv}})^2/\lambda^2}{1 - (\lambda_{\max, \text{solv}}^{7a})^2/\lambda^2} \frac{1 - 4(\lambda_{\max, \text{solv}})^2/\lambda^2}{1 - 4(\lambda_{\max, \text{solv}}^{7a})^2/\lambda^2}. \quad (6)$$

Here  $\lambda_{\text{max,solv}}$  is the absorption maximum of the chromophore in the solvent, and  $\lambda = 1.91 \mu\text{m}$  is the laser wavelength used in the EFISH experiment. The dispersion correction factors are valid within the limit of the two-level approximation. In the case of the larger compounds the SHG wavelength is close to  $\lambda_{\text{max}}$ , and the approximation may no longer be sufficient. The results of these calculations are given in the last column of Tables 3 and 4.

The  $\mu\beta(-\omega; \omega, 0)$  values from the EFISH experiment are in reasonable agreement with the  $\mu\beta(-\omega; \omega, 0)$  values from the guest–host measurements. Therefore the EO technique seems to be well suited to evaluate reliably the EO potential of nonlinear optical chromophores.

On account of their high nonlinearity, the chromophores presented here seem to be attractive candidates for incorporation into EO devices. In addition to possessing high nonlinearity, NLO chromophores, for practical applications, also need to be thermally and photochemically stable. We performed initial experiments for the investigation of photochemical stability. Thin films of TBA and FB were exposed to daylight for extended time periods, and the decrease of absorption was noted. For the ethyl-substituted TBA compounds (7a, 8a, 9a) a decrease of  $\approx 20\%$  was observed after 1 d, whereas for the phenyl-substituted TBA compounds (7b, 8b, 9b) the decrease was  $\approx 60\%$ . For the FB chromophores, on the other hand, the decrease was insignificant.

#### 4. CONCLUSION

In summary, we presented EO and EFISH measurements on chromophores, using either thiobarbituric acid or 3-dicyanomethylene-2,3-dihydrobenzothiothiophene-1,1-dioxide (“brilliant blue”) acceptors. These NLO molecules were shown to have large hyperpolarizability–dipole moment products, up to  $\mu\beta_0 = 5000 \times 10^{-48}$  esu and  $\mu\beta_0 = 8700 \times 10^{-48}$  esu in the cases of TBA and FB, respectively, with a conjugation length of three free double bonds. In terms of  $\mu\beta_0$ , these molecules are therefore over 20 times more nonlinear than disperse red molecules. Very high EO coefficients, up to  $r_{33} = 55$  pm/V, have been observed in guest–host systems with  $\text{FB}_{n=2}$  (compound 13) and 20-wt % chromophore concentration. We used an EO characterization technique (modulated ellipsometry) to determine  $\mu\beta(-\omega; \omega, 0)$  at the wavelength of interest. A comparison with the values from the EFISH measurements shows that the method is well suited for the characterization of NLO chromophores. Experiments to attach these chromophores as side-chain elements of high- $T_g$  polyimide polymers are in progress.

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