Bis(1,3-dithiole) Polymethine Dyes for Third-Order Nonlinear Optics – Synthesis, Electronic Structure, Nonlinear Optical Properties, and Structure-Property Relations

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The synthesis of a series of new sulfur-containing polymethine dyes is reported. The linear optical properties of these bis(1,3-dithiole) (mono-, tri-, penta-, and hepta-)methine dyes show intense and narrow optical absorptions typical of cyanine dyes. The absorption maximum is increasingly red-shifted from 489 nm for the monomethine dye to 911 nm for the heptamethine compound. Based on third-harmonic generation measurements at fundamental wavelength between 1064 nm and 1907 nm, γ values were evaluated to lie in the range between $1 \cdot 10^{-33}$ e.s.u. and $14 \cdot 10^{-33}$ e.s.u. showing that the nonlinear response of the bis(1,3-dithiole) polymethine dyes compare well with other organic π-electron systems of similar size. Comparisons of the experimental values of γ to calculated static values obtained by ab initio and semiempirical calculations (AM1, PM3) have been made as well as comparisons to dynamic values estimated from a free-electron model. The computed dynamic values can be described by a power law; $\gamma \approx L^5$ where L denotes the length of the molecules. Our studies confirm the stabilizing effect of a carbocyclic ring in the cyanine backbone making the heptamethine dye an unusually stable and highly nonlinear polymethine chromophore possessing a strong NIR optical transition and very good transparency in the visible region.

Introduction

In the search for materials exhibiting nonlinear optical properties to be exploited in photonic devices stable polyconjugated π-electron systems have attracted considerable attention, as shown in recent reviews[1][2][3][4][5].

A number of experimental and theoretical studies have focused on the relationship between molecular structure and the third-order molecular polarizability (γ). The main results comprise the following: (i) The degree of bond-length alternation in conjugated polyenes has been shown to be a key structural factor determining both sign and magnitude of γ and favoring cyanine dye molecules[6–9]. (ii) The dependence of γ on the total length (L) of the molecule in oligomers or homologous series has been shown to follow power laws ($\gamma \approx L^n$)[10][11][12][13][14][15][16][17][18][19][20][21] where γ vs. effective molecular conjugation length generally yields the highest power ($n \approx 5-10$) for cyanine-like molecules[10][14][18][19] while systems with alternating double bonds follow power laws with $n \approx 3-5$[11][12][16][20][21]. (iii) Saturation phenomena in bond-alternating systems are observed experimentally[12][22][23][24][25][26] and predicted theoretically[27][28][29] as L increases. In cyanine-like systems, which initially have no or little bond-length alternation, a Peierls instability resulting in bond-length alternation is expected to occur for molecules longer than ca. 14 methylene units[4][30]; saturation effects have recently been observed experimentally in symmetric cyanines[31]. (iv) Triple bonds tend to localize electrons compared with double bonds in conjugated systems with bond alternation[11][12], i.e. acetylenic systems have lower values of the third-order polarizability (γ) relative to their vinylenic analogs[11][12]. (v) The

  1434–193X/98/1212–2747 $ 17.50+.50/0

relative positions and oscillator strengths of the excited A_g and B_u states have pronounced effects on the sign and magnitude of γ[6][7][8][32][33][34][35].

In summary, these results indicate that extended cyanine-like molecules of intermediate length are good candidates for the molecular constituents in materials with large third-order nonlinear optical response. Table 1 compares γ values measured by third harmonic generation (THG) for a number of polyenes and cyanines reported in the literature[6][10][12][22][32][36][37][38]; it is clearly seen that the bis(1,3-dithiole) polymethine dyes *reported here* possess very high γ values compared to polyenes of similar length.

The synthetic strategy of the present work has been to identify effective routes to an extended cyanine-type molecule with a high γ value. In a second step, the target molecules can be stabilized as chromophores in polymer films by modifications in the non-cyanine part of the molecule. For this purpose, bis(1,3-dithiole) polymethine dyes are promising since the 4,5-positions offer the possibilities to alter the chemical structure without affecting the delocalized π-electron system significantly (Figure 1). The synthesis of a homologous series of these molecules as well as their linear and nonlinear optical properties measured in thin polymer films is presented in the following and compared to a theoretical model based on free-electron theory as well as ab initio and semiempirical calculations.

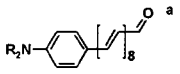
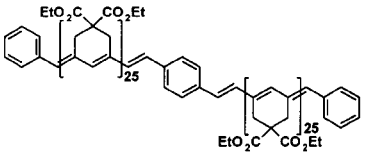
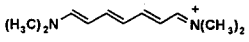
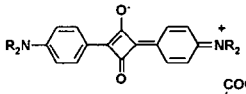
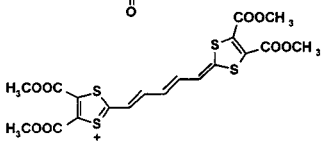
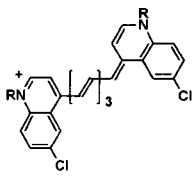
Results and Discussions

Syntheses

Although the synthesis of polymethine dyes has interested synthetic chemists over the last century[39][40], only two reports concerning the small analogous (mono- and trimethines) using 1,3-dithioles as the heterocyclic part have been published[41][42]. This is surprising since previous experiments indicate that incorporation of sulfur atoms into dyes has a favorable effect on the stability of the dye[43].

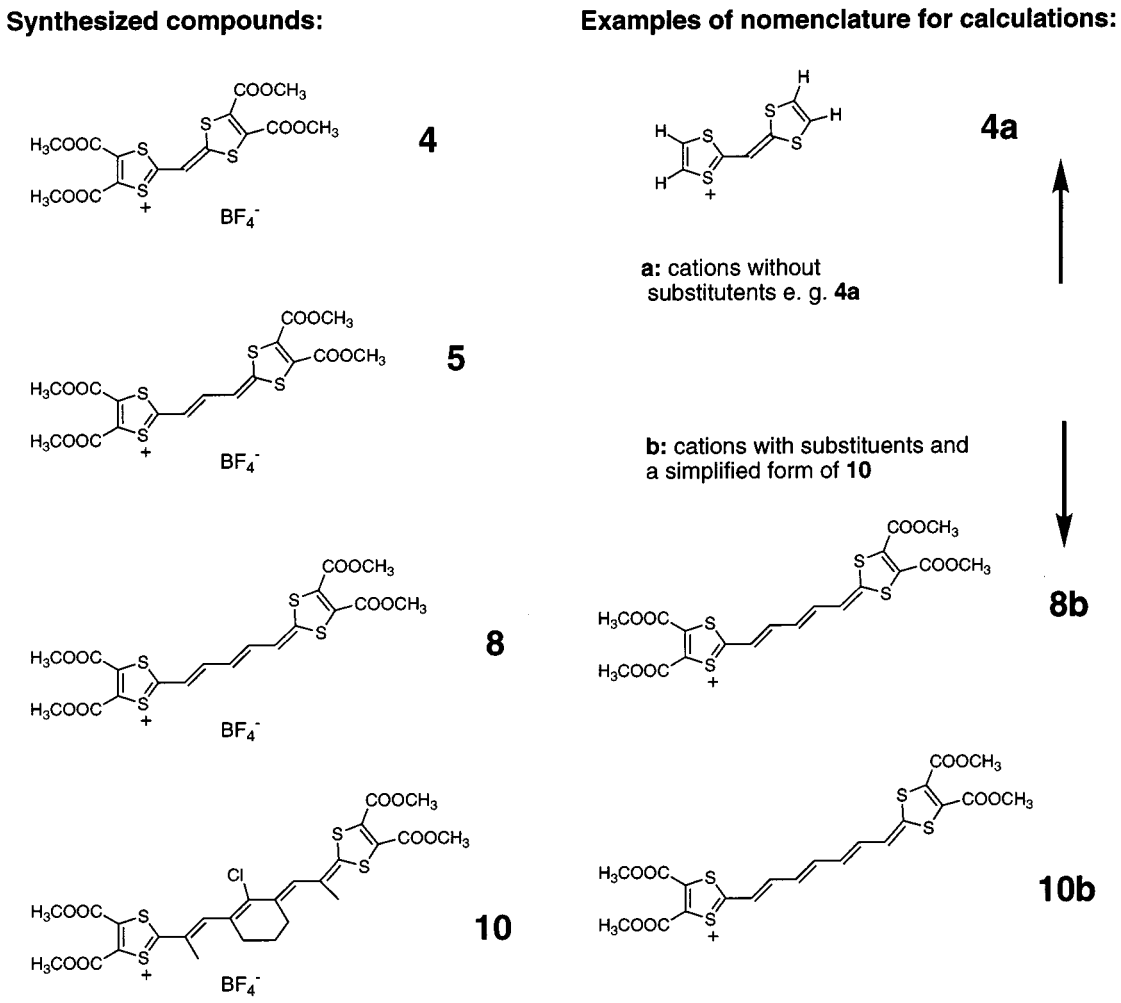
The preparation of the smaller dyes **4** and **5** follows the procedure outlined by Soder et al.[41] using the methylene

Table 1. Comparison of $\gamma(-3\omega;\omega,\omega,\omega)$ measurements by THG on polyenes and cyanine-like dyes; N: number of double bonds

Chemical formula	λ_{max} nm	λ_{laser} nm	$\lvert\gamma(-3\omega;\omega,\omega,\omega)\rvert$ x10^{-36} esu	N	$\lvert\gamma(-3\omega;\omega,\omega,\omega)/N\rvert$ x10^{-36} esu	Ref.
Donor–Accepor	422 500	1907 1907	100 56600	4 10	25 5660	6 21
	498	1907	8000	10	800	12
β-Carotene	452 460	1908 1890	11000 8000	11 11	1000 730	37 36
	516	1907	24700	60	410	22
	519	1908	510	4	128	37
	635	1390	3700	6	617	32
	743	1907	12500	4	3100	this work
	980	1900	100000	7	7150	10
	556	1907	--	--	20000	5,26

[a] Methyl groups on polymer backbone are omitted. – [b] Fully conjugated (n – 50); estimated according to refs.[5][26].

Figure 1. Molecular structures of molecules encountered in the present study

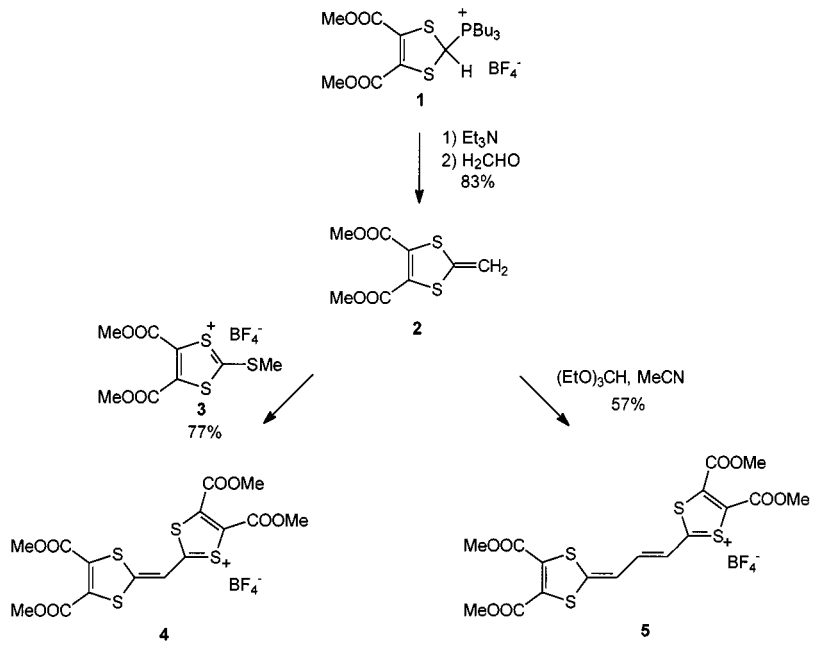


base **2**, prepared from the corresponding Wittig salt[44] **1** and formaldehyde in acetonitrile, as outlined in Scheme 1. Equimolar amounts of **2** (nucleophilic at the exocyclic carbon atom) and the 4,5-bis(methoxycarbonyl)-2-methylthio-1,3-dithiole **3**, which is electrophilic at C-2, in the presence of fluoroboric acid afforded the monomethine **4** in good yield. The condensation on two equivalents of **2** and triethyl orthoformate in refluxing acetonitrile in presence of acid yielded the corresponding trimethine **5** in moderate yields.

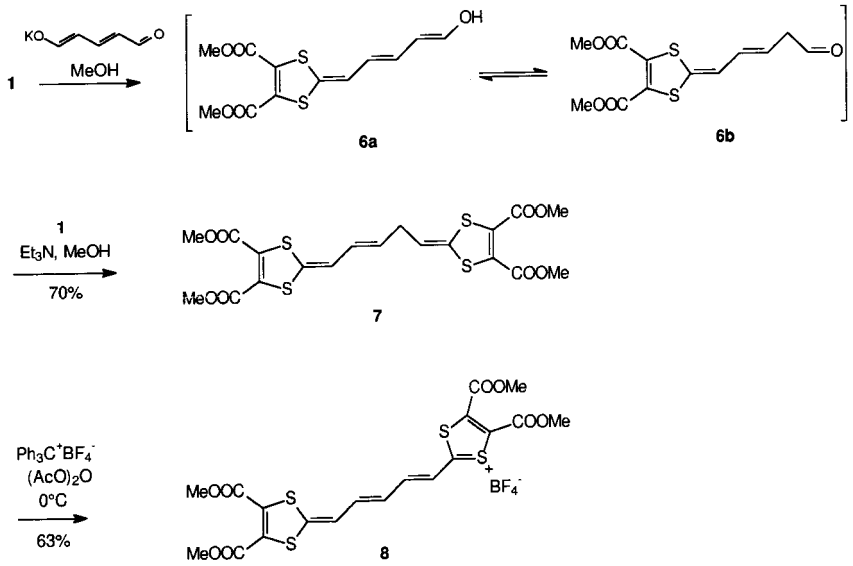
The synthesis of the pentamethine analogue could not be accomplished using standard polymethine strategies, thus the reactions between the methylene base **2** and standard C_3 synthones such as 3,3-diethoxypropyne, 1,3,3-triethoxypropene, and 3-anilinopropa-2-yliden-1-anilinium chloride all failed. We therefore developed a new method for the preparation of the pentamethine **8**, using the readily available Wittig salt **1** in a *one-pot* synthesis, outlined in Scheme 2; thus the reaction of glutaconaldehyde potassium salt[45] with one equiv. of the Wittig salt **1** in MeOH without any base gave the intermediate **6** (indicated on TLC), which was not isolated. After 30 min, another equivalent of Wittig salt **1** and triethylamine (1 ml) were introduced whereupon chromatographic separation afforded **7** in good yield as a mixture of tautomers. The partly reduced pentamethine **7** was easily transformed into the corresponding fully conjugated pentamethine by hydride abstraction using triphenylcarbenium tetrafluoroborate in acetic anhydride. During this oxidation the different tautomers of **7** result in formation of only one pentamethine, namely **8**. The pentamethine **8** is stable in the crystalline form, whereas it is quite unstable in solution and loses the intense color after a few hours.

In order to prepare a stable heptamethine which absorbs in the near infrared we had to adopt the synthetic strategy developed by Reynolds et al.[43]. Reynolds demonstrated that, in the pyrylium series, the stability of the polymethine dyes was greatly improved by incorporating carbocyclic rings in the polymethine chain, making the chain much more rigid. Thus, the reaction between two equiv. of the methylene base **9** (prepared analogously to **2**) and 2-chloro-1-formyl-3-(hydroxymethylene)cyclohexene in the presence of fluoroboric acid in acetic anhydride afforded the corresponding heptamethine **10** as large red-brown needles in fair yield (Scheme 3). In contrast to **8**, compound **10** was stable in solution [CH_2Cl_2, $(AcO)_2O$, MeCN] for several days.

Scheme 1



Scheme 2



Linear Optical Properties

The linear optical properties of dilute solutions of the dyes **4**, **5**, **8**, **10** are displayed in Figure 2A showing progressively red-shifted transitions with increasing length of the molecule. The extinction coefficients at λ_{max} increase with molecular length for the first three members of the series whereas a decrease is observed for the longest member, **10**. Molecular mechanics calculations show that the π-electron system in **10** is lacking planarity due to the steric interactions between the cyclohexene ring and the adjacent methyl groups. The relative decrease in extinction coefficient of **10** may be related to this lack of planarity. All members of the series possess sharp optical transitions characteristic of undistorted polymethines.

The Free Electron Model (FEM)[46][47] has often been used to describe the linear optical properties of such systems and a fit to the model (Figure 3) reveals excellent agreement with the linear optical data also in the present case (see Experimental Section for further details). The good fit to the FEM indicates that the π-electrons are efficiently delocalized in all the molecules under study, including the structurally distorted **10**.

As guests in polymer thin films the longer dyes aggregate as shown for **8** in Figure 2B. The comparison between the

Scheme 3

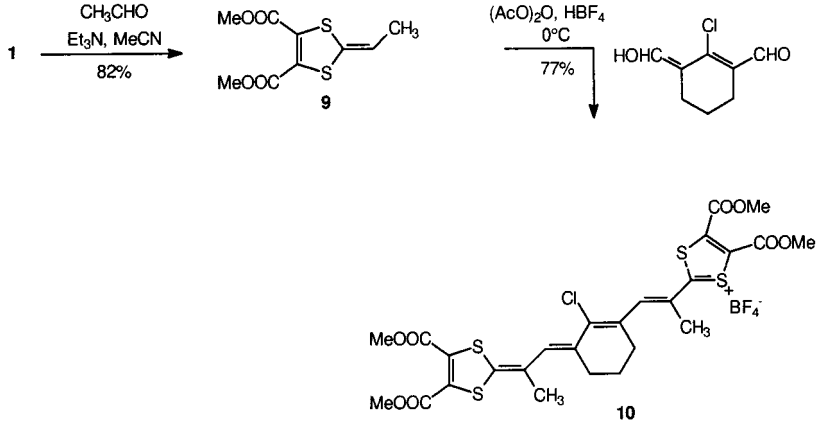
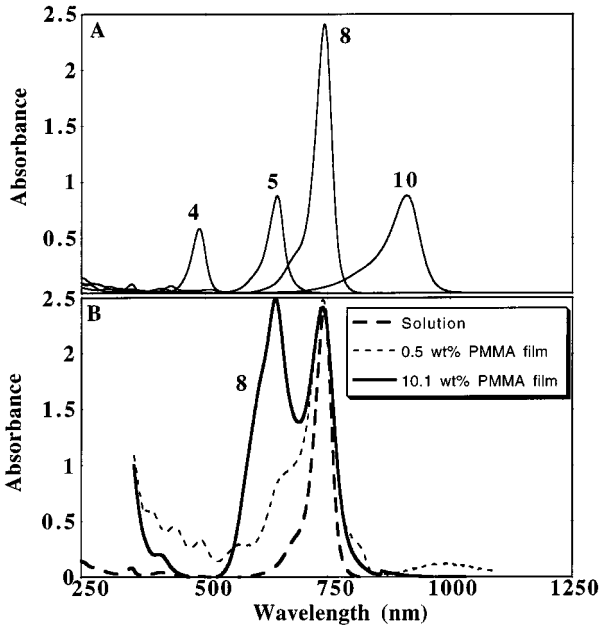
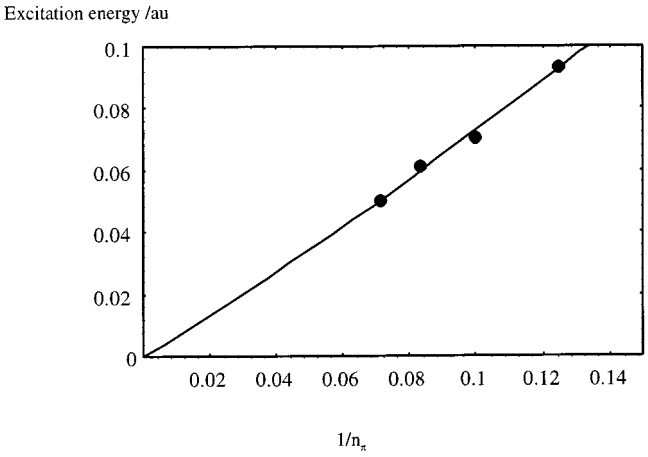


Figure 2. A: Absorption spectra of CH_2Cl_2 solutions (normalized to 10^{-5} M) of **4**, **5**, **8**, **10**; B: Spectrum of **8** in a PMMA films with different loading



absorption spectrum of **8** in solution and as guests in PMMA films reveals the presence of a blue-shifted new peak in the film spectrum indicating the formation of aggregates. The dependence of the relative intensity of the monomer and aggregate absorptions are illustrated in Figure 2B by depicting the spectrum of two PMMA films with different loadings of **8** (0.5 wt-% and 10.1 wt-%, respectively). The spectra have been normalized to the monomer absorption peak. The degree of aggregation is clearly dependent on the concentration of monomer as evidenced by the relative increase in the aggregate absorption with increasing monomer concentration. The number of monomers forming the aggregate was established by describing the equilibrium between n monomers (M) and the aggregate (A) by an equilibrium constant $K = A/M^n$ and plotting the aggregate vs. monomer concentration in a log-log plot. The slope of this plot (not shown) yields $n \approx 2$ indicating that the aggregate of **8** is a dimer molecule.

Figure 3. Calculated and observed first excitation energies; the line is calculated from Eq. 9 using the values of d and n_{extra} given in the text; the number of π electrons is treated as a continuous variable; the observed values are marked at the values of n_ϕ given in the text



Nonlinear Optical Properties

The molecular third-order polarizabilities, <γ>, obtained from Maker fringe patterns measured at λ = 1064 nm and 1907 nm are presented in Table 2. The values are representative for measurements on several films of each compound each having a different film thicknesses, l_f, less than 200 nm and doped with different weight percentages of the dye. A typical pair of Maker fringe patterns is shown in Figure 4 together with curves fitted to the data[48].

The obtained <γ> values were dependent on the concentration of molecules in the thin films. This was very pronounced for the two longer molecules. For example, an increase by a factor of three was observed for **8** when decreasing the weight percent from 5 to 0.5. However, as evidenced from Figure 2B a considerable aggregation takes place in the PMMA films. The results presented in Table 2 are hence the values obtained from films with a low weight percent dye; i.e. aggregation effects are assumed to be negligible. For comparisons with calculated γ values, the γ values from Table 2 are depicted in Figure 5 together with values obtained by the FEM.

Table 2. Linear and nonlinear optical data

	λ_{max}	ε	$\lvert\gamma_{1064}\rvert$	$phase_{1064}$	$\lvert\gamma_{1907}\rvert$	$phase_{1907}$
	nm (eV)	$M^{-1}\ cm^{-1}$	10^{-33} esu	degrees	10^{-33} esu	degrees
4	489 (2.54)	60.000	1.4	±35	1.7	±20
5	647 (1.97)	90.000	2.5	±20	4.2	–
8	743 (1.62)	210.000	14	±20	12.5	±20
10	911 (1.37)	110.000	11	±15	–	–

Figure 4. Maker fringe pattern of PMMA film of dye **8** (0.5 wt-%, 160 nm thick); triangles = THG from film and substrate; full line = fit to THG from film + substrate; squares = THG from substrate; dotted line = fit to THG from substrate

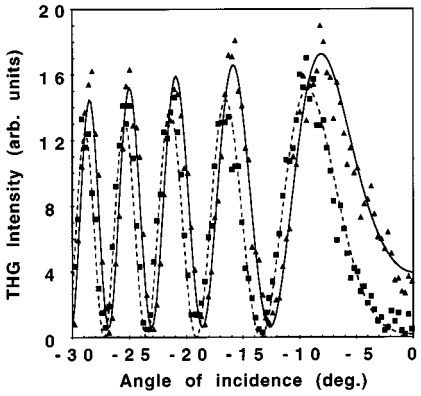
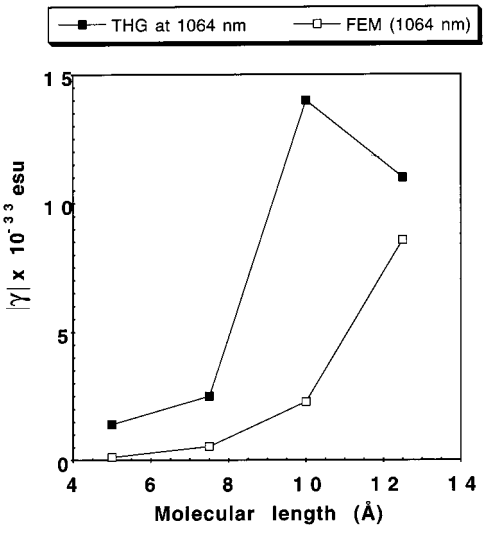


Figure 5. γ vs. effective conjugation length; comparison of experimental data measured at 1064 nm to free electron model



THG measurements in the range 1150−1400 nm on **5** revealed a resonance-induced feature in the dispersion of $<\gamma>$ with a maximum of $5\cdot10^{-33}$ e.s.u. around 0.95 eV (1300 nm).

Calculations

Table 3 provides the evolution of the electronic properties as a function of chain length for the four molecular systems studied. From the ab initio results, we note a nearly linear increase in polarizability $<\alpha>$. This is due to the combination of the different behaviors of the individual components: the yy component increases nonlinearly with chain length, as it is customary for conjugated systems, while the xx and zz components decrease on a relative basis. The values of the second polarizability β remain quite small, in agreement with the behavior of a cyanine-like system[6][7][8][9].

The absolute value of the third polarizability increases in a nonlinear way vs. chain length, and $<\gamma>$ values are negative as expected for cyanine-like molecules. It is interesting to observe that the positive $<\gamma>$ value computed for the smaller system is due to the influence of the components of the tensor other than the yyyy; for this molecule, the computational method gives the same order of magnitude for all the components, and the resulting average values are positive. By increasing the size of the molecule, the contribution of the yyyy component becomes dominant, and the average value becomes negative. The ab initio results presented in Table 3 can be compared with the ab initio CPHF estimates obtained by Hurst et al. for polyenes[49]. The best basis set adopted by Hurst et al. is a 6-31G+pd which is similar to the one used in this work, except for the presence of an additional diffuse p-type function on the carbon atoms; in our case, the lack of diffuse functions on the carbon atoms is compensated by the presence of the d-type functions on the sulfur atoms. The values of $<\gamma>$ reported in ref.[49] for the shortest polyenes are 7.5, 17.7, 41.4, and 89.9 $\times10^{-36}$ e.s.u. for C_4H_6, C_6H_8,C_8H_{10}, and $C_{10}H_{12}$ respectively; these have to be compared with our estimates of 6, −83, −380, and -1103×10^{-36} e.s.u. obtained for molecules **4a**, **5a**, **8a**, and **10a** (see Table 3). Both the sign and the magnitude of our results appear to be consistent with the expected behavior of cyanine-like systems with respect to polyenes[4]: for the shortest molecules, the magnitude of $<\gamma>$ is comparable in the two systems; then the evolution with chain length is much stronger in the case of the bis(dithioles), which is expected for cyanines[15]. The polarizabilities computed at the semiempirical AM1 level are given in the last four columns of Table 3. The latter shows the same qualitative behavior as the ab initio values; however, the absolute AM1 values are systematically larger. In particular, the $<\gamma>$ AM1 values are one order of magnitude larger than the corresponding ab initio ones. This comparison again points to the caution with which the semiempirical results have to be taken for the study of the cubic NLO properties, although here the qualitative trends are reproduced. The same qualitative trends are obtained with

Table 3. Ab initio and AM1 CPHF electric response properties for bis 1,3-dithiole polymethine dyes of increasing chain length[a][b]

		Ab initio 6-31G+d				AM1			
Prop.		**4a**	**5a**	**8a**	**10a**	**4a**	**5a**	**8a**	**10a**
μ(D)	z	1.4	1.4	−1.8	2.0	0.6	1.0	−1.4	1.8
	xx	10	12	14	15	4	4	4	5
$\alpha(10^{-24}$ e.s.u.)	yy	37	72	117	174	51	112	193	302
	zz	19	22	26	29	22	25	28	31
	$<\alpha>$[c]	22	36	52	73	25	47	75	112
	xxz	0	0	0	0	0	0	0	0
$\beta(10^{-30}$ e.s.u.)	yyz	−1	−14	36	71	−7	−18	79	170
	zzz	0	0	1	1	−1	−1	1	1
	xxxx	4	5	7	8	0	0	0	0
	yyyy	−4	−478	−2001	−5677	−333	−4976	−22338	−77140
	zzzz	6	7	9	11	2	4	6	8
$\gamma(10^{-36}$ e.s.u.)	xxyy	4	8	12	17	1	11	20	35
	xxzz	2	2	3	4	1	2	2	2
	yyzz	5	15	28	51	6	8	7	26
	$<\gamma>$[d]	6	−83	−380	−1103	−63	−986	−4453	−15401

[a] Numerical values are consistent with the Taylor series expansion, see Eq. 8. – [b] Dipole moment in Debyes, polarizabilities in e.s.u. Conversion factors: μ: 1 D ≈ 0.3934 a.u. ≈3.3356 Cm. α: 1 e.s.u. ≈ $6.7834\cdot10^{24}$ a.u. ≈ $1.1126\cdot10^{-16}$ Cm^2/V. β: 1 e.s.u. ≈ $1.1575\cdot10^{32}$ a.u. ≈ $3.7114\cdot10^{-21}$ Cm^3/V^2. γ: 1 e.s.u. ≈ $1.9854\cdot10^{39}$ a.u. ≈ $1.2380\cdot10^{-25}$ Cm^4/V^3. – [c] $<\alpha> = 1/3(\alpha_{xx}+\alpha_{yy}+\alpha_{zz})$. – [d] $<\gamma> = 1/5[\gamma_{xxxx}+\gamma_{yyyy}+\gamma_{zzzz}+2(\gamma_{xxyy}+\gamma_{yyzz}+\gamma_{xxzz})]$.

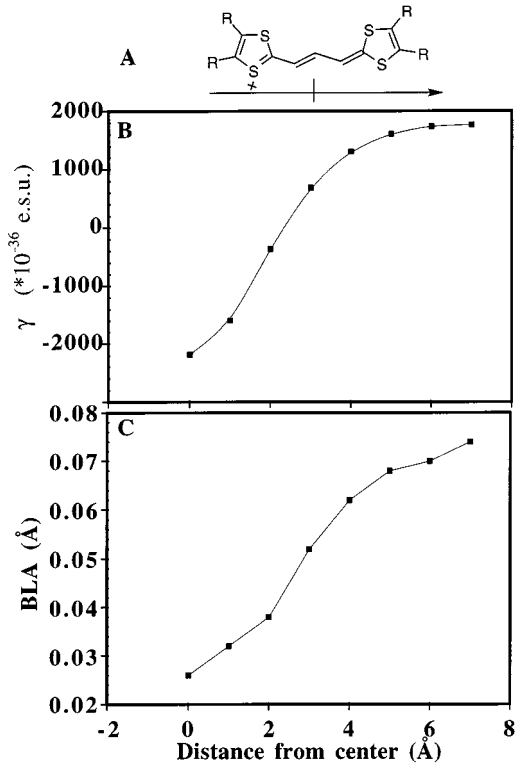
the PM3 method, which gives $<\gamma> = -60, -636, -2286,$ and -5706×10^{-36} e.s.u. for **4a**, **5a**, **8a**, and **10a**; these values are in general slightly increased (−54, −972, −3846, -7782×10^{-36} e.s.u.) when the substituted systems **4b**, **5b**, **8b**, and **10b** are taken into account.

The results of the PM3 calculation, in which we displaced a negative point charge above the molecular backbone, are displayed in Figure 6 for molecule **8b**. The results for the molecules **4b**, **5b** are similar. In Figure 6A it is seen that γ is tuned smoothly from negative to positive values as the point charge is displaced from the center to the end of the molecule. When paying attention to Figure 6B where BLA is plotted against the displacement of the point charge, it is seen that the molecule is going from a cyanine-like structure (BLA = 0) to a polyene-like structure (BLA = 0.1 Å), which is consistent with the change in sign of γ. These results indicate that the value of γ is very sensitive to the position of the anion; they also suggest that it might be possible to influence the sign and magnitude of γ by attachment of an anionic substituent along the polymethine backbone[50].

A sum-over-states calculation based on the free electron model $\gamma_{yyyy}(-3\omega;\omega,\omega,\omega)$ was performed including 16 states; this secured convergence for all four compounds.

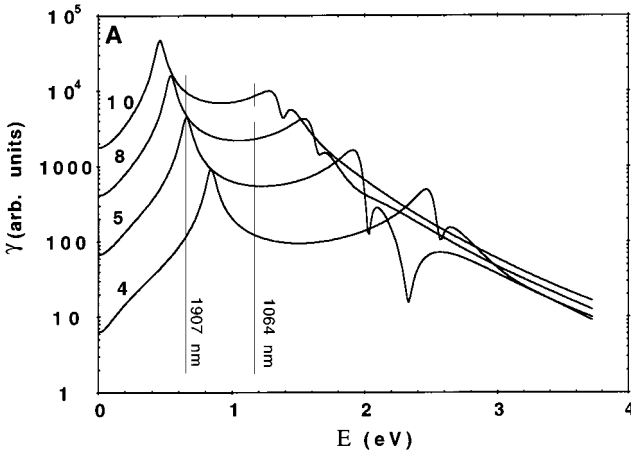
Figure 7 shows the calculated dispersion from the FEM of the absolute value of γ for the four compounds. A pronounced resonance is found at a wavenumber corresponding to one third of the first excitation energy. Close to the excitation itself, a number of resonances is found. For all four compounds, the laser frequency corresponding to λ = 1064 nm used in the experiment lies in a region between resonances. The quantitative results are influenced by the actual choice of line-broadening parameters, whereas the qualitative picture does not change. Also, qualitatively, it is seen that the first excited state has a dominant influence on the dispersion curves.

Figure 6. Influence on γ and BLA as calculated using PM3, of displacing the sparkle (unit negative charge) laterally from 5 Å above the center of the molecule (distance = 0 Å) to 5 Å above the end of the molecule



Included in Figure 5 are the γ values calculated from FEM as well as the measured values. It is seen that the FEM model only shows a fair agreement with the experimental data. In addition the FEM cannot account for the observed dispersion in the THG data measured between 1150 and 1400 nm.

Figure 7. Dispersion of the absolute value of γ as a function of wave number for the four compounds **4**, **5**, **8**, and **10** calculated by the free electron model (A)



Conclusion

A flexible and efficient synthetic scheme for a series of new sulfur-containing polymethine dyes has been presented and the dyes have been characterized by their linear and nonlinear optical properties. The linear optical properties are well represented by a free-electron model indicating efficient delocalization of the π electrons in the dyes. The third-order nonlinear optical properties cannot be accounted for by the simple free-electron model emphasizing the importance of specific excited-state properties for the nonlinear response of the molecules. The 1,3-bis(dithiole) polymethine dyes resemble other cyanine systems studied previously with regard to their stability in solution. Our studies confirm the stabilizing effect of a carbocyclic ring in the cyanine backbone making the heptamethine dye **10** an unusually stable and highly nonlinear polymethine dye possessing a strong NIR optical transition and very good transparancy in the visible region. Finally, it is noted that the bis(dithioles) reported here possess a very sharp linear optical transition at relatively long wavelength compared to the cyanines reported earlier[10][18][38].

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Experimental Section

Synthesis: Solvents and reagents were standard reagent grade and used as received unless otherwise stated. Dry solvents were obtained by standard techniques. Microanalyses were performed at the Microanalytical Laboratory, University of Copenhagen or at the Microanalytical Laboratory, Leo Pharmaceutical Products, Copenhagen.

4,5-Bis(methoxycarbonyl)-2-methylene-1,3-dithiole (**2**): To a solution of tributyl[4,5-bis(methoxycarbonyl)-1,3-dithiol-2-yl]phosphonium tetrafluoroborate[44] (**1**) (2.00 g, 3.9 mmol) in acetonitrile (20 ml) and formaldehyde (36% in methanol, 0.4 ml, 5.0 mmol) in a 100-ml round-bottomed flask was added triethylamine (1 ml) whereupon the solution turned deep yellow, and the mixture was stirred for additional 30 min. Concentration in vacuo followed by filtration through a short column (silica gel, CH_2Cl_2/AcOEt, 95:5) gave **2** as the first yellow fraction. Removal of the solvent in vacuo afforded **2** as an yellow oil (0.76 g, 83%) which was used without further purification (pure by TLC and ^{1}H NMR). **2** was unstable and therefore prepared prior to use. – ^{1}H NMR (250 MHz, $CDCl_3$) δ = 5.10 (s, 2 H), 3.83 (s, 6 H). – MS (EI); *m/z* (%): 232 (69) [M^+], 201 (22), 169 (19), 131 (26), 119 (27), 69 (100).

2-{[4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]methyl}-4,5-bis(methoxycarbonyl)-1,3-dithiolium Tetrafluoroborate (**4**): To a solution of **2** (0.60 g, 2.6 mmol) and 4,5-bis(methoxycarbonyl)-2-methylthio-1,3-dithiolium tetrafluoroborate (easily prepared form the corresponding 1,3-dithiole-2-thione in neat dimethyl sulfate) (**3**) (0.70 g, 2.6 mmol) in glacial AcOH in a 100-ml round-bottomed flask equipped with a reflux condenser was added ethereal fluoroboric acid (54%, 1 ml) and the solution turned dark green. The mixture was refluxed for 1 h. Addition of ether (40 ml) to the cooled solution afforded a dark green oil, which slowly solidified. Recrystallization from AcOH/ether gave **4** as dark red crystals (1.04 g, 77%); mp 231–233 °C. – IR (KBr): $\tilde{\nu}$ = 2958, 1739, 1639, 1435, 1225 cm^{-1}. – ^{1}H NMR (250 MHz, CD_3CN) δ = 8.16 (s, 1 H), 4.04 (s, 12 H). – ^{13}C NMR (CD_3CN) δ = 55.5, 109.7, 118.3, 158.7, 173.9. – PDMS: 449 (M^+). – $C_{15}H_{13}BF_4O_8S_4$: calcd. C 33.59, H 2.44; found C 33.58, H 2.51.

2-{3-[4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]propenyl}-4,5-bis(methoxycarbonyl)-1,3-dithiolium Tetrafluoroborate (**5**): Compound **2** (0.90 g, 3.9 mmol), triethyl orthoformate (0.5 ml, 3.0 mmol), and acetonitrile (20 ml) were mixed in a 100-ml round-bottomed flask equipped with a condenser. The solution turned intense blue after addition of fluoroboric acid (54% etheral solution, 1 ml) and was refluxed for 1 h. The solution was cooled to room temperature and addition of ether (50 ml) gave **5** as dark blue crystals which were filtered and washed with ether. Recrystallization from MeCN/ether (0.61 g, 57%); m.p. 195–196 °C. – ^{1}H NMR (250 MHz, CD_3CN) δ = 7.80 (t, 1 H, *J* = 12.8), 7.00 (d, 2 H, *J* = 12.9), 3.99 (s, 12 H). – IR (KBr): $\tilde{\nu}$ = 2962, 1737, 1533, 1207, 1085 cm^{-1}. – PDMS: 475 (M^+). – $C_{17}H_{15}BF_4O_8S_4$: calcd. C 36.31, H 2.69; found C 36.71, H 2.80.

2,2-(2-Pentene-1,5-diylidene)bis[4,5-bis(methoxycarbonyl)1,3-dithiole] (**7**): Glutaconaldehyde potassium salt[45] (0.75, 5.5 mmol) was dissolved in *dry* MeOH (40 ml) in a 100-ml round-bottomed flask with a nitrogen inlet. 1 equiv. of tributyl[4,5-bis(methoxycarbonyl)-1,3-dithiol-2-yl]phosphonium tetrafluoroborate (**1**) (3.00 g, 5.9 mmol) was added, the solution turned yellow and was stirred for 1 h. Another equiv. of phosphonium salt **1** (3.00 g, 5.9 mmol) was added together with triethylamine (1 ml). The reaction was monitored by TLC. Concentration in vacuo, followed by column chromatography (silica gel, CH_2Cl_2/AcOEt, 95:5) gave **7** as the first red fraction. The solvent was removed in vacuo affording a red oil (1.95 g, 70%) as a mixture of tautomers which was used without further purification (pure by TLC and ^{1}H NMR). – ^{1}H NMR (250 MHz, $CDCl_3$) δ = 5.8 (m, 2 H), 5.4 (m, 1 H), 4.54 (s, 1 H), 3.82 (s, 6 H), 3.80 (s, 6 H), 2.75 (T, 2 H). – IR (KBr) $\tilde{\nu}$ = 3006, 2953, 2843, 1719, 1572, 1435, 1261, 1027 cm^{-1}. – MS (EI): *m/z* (%): 502(100) [M^+], 194 (100), 121 (40).

2-{5-[4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]-1,3-pentadienyl}-4,5-bis(methoxycarbonyl)-1,3-dithiolium Tetrafluoroborate (**8**): To an ice-cooled solution of triphenylcarbenium tetra-

fluoroborate (0.65 g, 32 mmol) in acetic anhydride (30 ml) in a 100-ml round-bottomed flask equipped with a dropping funnel was slowly added a solution of **7** (1.00 g, 2 mmol) in acetic anhydride (20 ml). The reaction mixture turned dark blue/green indicating the oxidation to the polymethine **8**. After the addition was complete (approx. 2 h), the solution was stirred for 1 h. **8** precipitated as green crystals after addition of *dry* ether (50 ml) and was filtered and washed with ether; yield 0.97 g (63%); mp. 188−190°C (dec.). − ^{1}H NMR (250 MHz, CD_3CN) δ = 7.71 (t, 2 H, *J* = 12.8), 7.05 (d, 2 H, *J* = 13.1), 6.68 (t, 1 H, *J* = 12.6), 3.97 (s, 12 H). − IR (KBr): $\tilde{\nu}$ = 2926, 1736, 1634, 1558, 1462, 1435, 1258, 1158, 1085 cm^{-1}. − PDMS: 501 [M^+]. − $C_{19}H_{17}BF_4O_8S_4$: calcd. C 38.78, H 2.91; found C 38.77, H 3.14.

2,3-Bis(methoxycarbonyl)-6-methyl-1,4-dithiafulvene (**9**): To a solution of tributyl[4,5-bis(methoxycarbonyl)-1,3-dithiol-2-yl]phosphonium tetrafluoroborate (**1**) (2.00 g, 3.9 mmol) and acetaldehyde (0.25 ml, 4.4 mmol) in acetonitrile (20 ml) in a 50-ml round-bottomed flask was added triethylamine (0.5 ml) whereupon the solution turned deep yellow, and the mixture was stirred for additional 30 min. Concentration in vacuo followed by filtration through a short column (silica gel, CH_2Cl_2) gave **9** as the first yellow fraction. Removal of the solvent in vacuo afforded **9** as a yellow oil (0.78 g, 82%) which was used without further purification (pure by TLC and ^{1}H NMR). **9** was unstable and therefore prepared prior to use. − ^{1}H NMR (250 MHz, $CDCl_3$) δ = 5.40 (q, 1 H, *J* = 6.8), 3.81 (s, 6 H), 1.13 (t, 3 H, *J* = 6.7). − IR (KBr): $\tilde{\nu}$ = 3004, 2954, 2846, 1728, 1607, 1435, 1378, 1260, 1028 cm^{-1}. − MS (EI) *m/z* (%): 246 (100) [M^+], 245 (77), 219 (20), 215 (16), 71 (38).

2-{7-[4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]-4-chloro-1,7-dimethyl-3,5-trimethylene-1,3,5-heptatrienyl}-4,5-bis(methoxycarbonyl)-1,3-dithiolium Tetrafluoroborate (**10**): The fulvene **9** (1.21 g, 4.9 mmol) and 2-chloro-1-formyl-3-(hydroxymethylene)cyclohexene[43] (0.50 g, 2.8 mmol) were dissolved in acetic anhydride (40 ml) in a 100-ml round-bottomed flask. The mixture was cooled to 0°C and fluoroboric acid (54% ethereal solution, 0.8 ml) was added slowly whereupon the solution became deep purple. The reaction mixture was stirred overnight and addition of ether (50 ml) afforded **10** as dark brown/red needles. The resulting crystals were filtered, washed with ether, and dried to yield 1.35 g (76.7%); mp. 191−192°C. − ^{1}H NMR (250 MHz, CD_3CN): δ = 7.82 (s, 2 H), 3.98 (s, 12 H), 2.86 (t, 4 H, *J* = 5.7), 2.31 (s, 6 H), 2.34 (s, 6 H, acetic anhydride), 1.88 (q, 2 H, *J* = 6.0). − PDMS: 630 [M^+]. − $C_{26}H_{26}BClF_4O_8S_4$: calcd. C 43.55, H 3.66, Cl 4.94; found C 43.11, H 3.82, Cl 4.94.

Film Preparation: Solid films of the studied polymethines **4**, **5**, **8**, and **10** were prepared by combining the polymethine and PMMA (polymethylmethacrylate, Aldrich) in either chlorobenzene (**4**, **5**, and **10**) or tetrachloroethylene (**8**) in the desired mass percent (0.5−20%) at 80°C for 15−30 min. This mixture was transferred to a fused silica substrate by coating one side only and letting the solvent evaporate. The thickness of the films was estimated by measurement of the optical density[51][52] of the films, and most of the films were in the range from 50 to 300 nm.

THG Measurements: The experimental set-up for thin-film THG Maker fringe measurements has previously been described[11][53]. Briefly, the fundamental beam consisted of 10-ns pulses at a repetition rate of 10 Hz from a Q-switched Nd:YAG laser, at 1064 nm or 1907 nm. The latter was obtained by Raman shifting the fundamental laser line at 1064 nm in a 1-m high pressure (30 bar) hydrogen cell. The vertically polarized beam was weakly focused on the sample. The sample was mounted on a rotation stage contained in a vacuum chamber to eliminate the THG contribution from air. The third-harmonic beam was filtered from other wavelengths by a combination of IR filters and a monochromator and detected in a transmission geometry using a photomultiplier in connection with a photon counter.

Maker fringes were recorded in the range from −30° to 30° (−50° to 50°) at 1064 nm (1907 nm) with respect to normal incidence, with the film facing the detector. Both the film and the substrate contribute to the third-harmonic signal. The contribution from the substrate alone is determined by recording Maker fringes of the bare substrate under the same experimental conditions after removal of the thin film, in situ. Figure 4 shows an example of such a pair of Maker fringe patterns. The Maker fringes allow the complex nonlinear susceptibility, $\chi_f^{(3)}(-3\omega;\omega,\omega,\omega)$, of the thin film to be determined relative to that of the substrate[48].

If the film thickness, l_f, is much smaller than the THG coherence length, $l_c = \frac{\lambda}{6|n_\omega - n_{3\omega}|}$, the third-harmonic field generated in the film is a monotonic function of the angle of incidence and proportional to the film thickness, peaking at normal incidence. The magnitude of the nonlinear susceptibility of the thin film can then be determined by Eq. 1[54]

$$\chi_f^{(3)} = 2/\pi \cdot l_{c,s}/l_f \cdot (I_{3\omega,f}/I_{3\omega,s})^{1/2}\, \chi_s^{(3)} \quad (1)$$

where $l_{c,s}$ and $\chi_s^{(3)}$ are the coherence length and the nonlinear susceptibility of the substrate, respectively. $I_{3\omega,s}$ is the TH intensity from the bare substrate obtained from the envelope function at normal incidence. $I_{3\omega,f}$ is the TH intensity from the thin-film sample corrected for the presence of the substrate[11][55].

The THG measurements in the range from 1150 nm to 1400 nm were performed using a tunable source consisting of a three-pass travelling wave optical parametric generator pumped at 527 nm by 1.5 ps pulses from a negative feed-back oscillator/regenerative amplifier Nd:Glass laser system.

Due to a large bandwidth (>50 cm^{-1}) of the pulses it is not possible to resolve Maker fringes from a 1 mm thick substrate. It is, however, also in this case possible to determine the magnitude of the nonlinear susceptibility of the thin films. $I_{3\omega,f}$ and $I_{3\omega,s}$ can be deduced from TH measurements at normal incidence of the thin film sample (substrate + film) and the bare substrate in the following way. From the latter the measured TH intensity, $I_{3\omega,a}$, is according to Eq. 2

$$I_{3\omega,a} = 1/2\, I_{3\omega,s} \quad (2)$$

From the film sample the measured TH intensity, $I_{3\omega,b}$, is according to Eq. 3

$$I_{3\omega,b} = I_{3\omega,f} + 1/2\, I_{3\omega,s} + I_{3\omega,f}^{1/2}\, I_{3\omega,s}^{1/2} \sin\phi \quad (3)$$

where φ is the relative phase between nonlinear susceptibilities of the substrate and the thin film. If we assume that φ is close to 0 (or π), i. e. the nonlinear susceptibility of the film has a real part which is much larger than the imaginary part, then the following approximation can be made (Eq. 4).

$$I_{3\omega,b} = I_{3\omega,f} + 1/2\, I_{3\omega,s} \quad (4)$$

The magnitude of the nonlinear susceptibility of the film can be obtained from the measured TH intensities at normal incidence by Eq. 5.

$$\chi_f^{(3)} = 2/\pi \cdot l_{c,s}/l_f \cdot (I_{3\omega,b}/2I_{3\omega,a} - 1/2)^{1/2}\, \chi_s^{(3)} \quad (5)$$

The last term in Eq. 3 has to be taken into account if the imaginary part of the nonlinear susceptibility is significant. Especially if $I_{3\omega,f}$ is of the same order of magnitude as $I_{3\omega,s}$ knowledge about the relative phase ϕ is necessary. In both of the above-described experimental situations the isotropic orientational average of the molecular hyperpolarizability (Eq. 6)

$$<\gamma> = 1/5\ [\Sigma_i(\gamma_{iiii}) + \Sigma_{i\neq j}(\gamma_{iijj})] \quad (6)$$

is obtained from the nonlinear susceptibility, $\chi_f^{(3)}$, by use of Eq. 7

$$<\gamma> = \chi_f^{(3)}/LN \quad (7)$$

where N is the number density of molecules in the polymer and L is a correction factor due to local-field effects. For the films investigated in the present work a correction factor $L = 4$ obtained from the Lorentz approximation[1] with refractive indices close to 1.5 was used. Due to the moderate loading the refractive indices are close to the ones of PMMA. For long one-dimensional molecules the local field factor approaches 1[21]. We may therefore have overestimated the local field effects for the longer molecules.

Computational Approach

The total energy and the total dipole moment of a molecule perturbed by an external static electric field E_j can be written as Taylor series (Eq. 8)[56]

$$W = W^{[0]} - \mu_i^{(0)}E_i - 1/2\ \alpha_{ij}\ E_iE_j - 1/6\ \beta_{ijk}\ E_iE_jE_k\ ....$$
$$-1/24\ \gamma_{ijkl}\ E_iE_jE_kE_l - \mu = \mu^{(0)} + \alpha_{ij}\ E_i - 1/2\ \beta_{ijk}\ E_iE_k\ ...$$
$$-1/6\ \gamma_{ijkl}\ E_iE_kE_l - ... \quad (8)$$

where $W^{(0)}$ is the unperturbed total energy, and $\mu^{(0)}$ is the permanent dipole moment. The linear and nonlinear molecular electric responses are rationalized by means of the electric polarizability tensor α_{ij} and the second and third electric polarizability tensors β_{ijk} and γ_{ijkl}, respectively. According to their definition, these quantities can be evaluated from derivatives of the total energy or the total dipole moment with respect to the external field.

Molecular electric polarizabilities α, β, and γ have been computed for the four molecular systems **4a**, **5a**, **8a**, and **10a** (Figure. 1). Calculations have been performed at the ab-initio static Coupled Perturbed Hartree-Fock (CPHF) level using the SYSMO computer program package[57]. The SYSMO implementation of the CPHF approach is based on the density matrix formalism, developed by McWeeny, Diercksen and co-workers[58][59][60][61][62], and modified by Lazzeretti and co-workers[63][64]. Within this method, response properties are analytically evaluated from first and second-order perturbative corrections of the Hartree-Fock wavefunction, computed by means of Roothaan-like iterative calculations. Molecular symmetry can be exploited to reduce the computational effort[64].

The basis set adopted for the determination of electric properties is a standard 6−31G split-valence basis set[65] augmented by d-type diffuse functions on carbon and sulfur atoms. The exponents of the diffuse functions (0.05 for carbon and 0.03 for sulfur) have been chosen in order to realize the best compromise between size and quality[66]. The geometries are optimized at the semiempirical Austin Model one (AM1)[67] level; no symmetry constraints have been imposed to the optimization, but the equilibrium geometries obtained all possess the C_{2v} symmetry. For computational purposes, the systems have been chosen to lie in the yz plane, with the z direction in coincidence with the C_2 symmetry axis. A useful structural parameter to describe the geometry and properties of a polymethine system is the degree of Bond-Length Alternation (BLA)[6][7][8][9]. Here, we define BLA as the sum of the numerical deviation of each bond in the chain from the average bond length divided by the number of repetition units. The computed values of BLA are 0, 0.002, 0.004, and −0.01 Å for systems **4a**, **5a**, **8a**, and **10a**, respectively.

Static molecular polarizabilities were also calculated for the isolated cationic molecules **4b**, **5b**, **8b**, and **10b** using the semiempirical PM3 and AM1 models[67][68]; the polarizabilities were calculated using the finite-field method in MOPAC[69]. No symmetry constraints were imposed on the molecules. The optimized geometries were similar to those used in the CPHF calculations, except for the extra substituents in molecules **4b**, **5b**, **8b**, and **10b** relative to molecules **4a**, **5a**, **8a**, and **10a**.

In general, hyperpolarizabilities were calculated for the isolated cationic molecules contrary to the measurements, that were performed on films made from the tetrafluoroborate salt. In order to study the effect of the anions, calculations simulating the presence of the anion were also performed using the PM3 Hamiltonian for molecules **4b**, **5b**, and **8b**. In the finite-field calculations, we used a negative point charge to simulate the effect of the anion, which is similar to the method described by Gorman et al.[9] To examine the relation between molecular topology and NLO properties, we displaced the point charge along the molecular axis. While this procedure simulates the effect of the position of the anion, it also makes predictions of the effect of attaching a charged substituent to different carbon atoms along the polymethine chain. As illustrated in Figure 6 we started out by placing the point charge 5 Å above the center of the molecule in the direction orthogonal to the plane in which the dithiole rings lie, and then displaced laterally towards one end of the molecule.

The measured excitation energies for the compounds **4**, **5**, **8**, and **10** indicate that a free-electron model (FEM) may adequately describe the π-electron properties for this series of compounds. We have fitted the experimental absorption spectra to a free-electron model and calculated the dispersion of $\gamma(-3\omega;\omega,\omega,\omega)$ within this model using the sum-over-states (SOS) expression of Orr and Ward[70][71]. In the FEM model, the electronic properties are modelled by a particle in a one-dimensional box of length d ($n_\phi/2$). The unit cell length is given by d. The number of π electrons is given by $n_\phi = n' + n_{extra}$, where n' is the number of π electrons in the cyanine skeleton and takes the values 2, 4, 6, and 8 for the four compounds; n_{extra} is the "effective" number of π electrons due to the dithiolene groups. The unit cell length and the number of extra π electrons are found by fitting the experimental first excitation energies for the four compounds to the expression derived from the FEM model (Eq. 9)

$$h\nu_{exp} = \frac{h^2}{2m_e d^2}\left(\frac{1}{n'+n_{extra}} + \frac{1}{(n'+n_{extra})^2}\right) \quad (9)$$

where ν_{exp} is the experimental absorption frequency, m_e and h are the electron rest mass and Planck's constant, respectively.

Fitting to the FEM resulted (Figure 3) in a unit cell length of d = 2.9 Å and n_{extra} = 6. (Only integer numbers for n_{extra} were considered in the fitting procedure.) The estimate of n_{extra} is in fair agreement with the number of π electrons available in the dithiole moieties; if every sulfur donated two π electrons, n_{extra} should equal to 8. The accuracy of the fit to the linear optical data is illustrated in Figure 3. Using the fitted values, the excitation energies are cal-

culated from Eq. 9 as a continuous function of n_ϕ. The observed energies for the four compounds are marked at the positions corresponding to n_ϕ = 8, 10, 12, and 14 in Figure 3.

In the SOS calculation, transition dipole moments and excitation energies are calculated within the FEM using the fitted values. The homogeneous and inhomogeneous line broadening is taken into account in an approximative way by choosing a broadening of 700 cm^{-1} for the ground state and 10000 cm^{-1} for all excited states. These values are used for all four compounds. As the model is one-dimensional only $\gamma_{yyyy}(-3\omega;\omega,\omega,\omega)$ is calculated. The average γ is found by dividing by five to take an isotropic distribution of molecules into account.

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